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## Abstract Book

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# 大会报告

## Metal-organic-framework-derived functional nanomaterials

### electrochemical energy storage and conversion

Xiong Wen (David) Lou\*

School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore

Email: [xwlou@ntu.edu.sg](mailto:xwlou@ntu.edu.sg)

We use metal-organic frameworks (MOFs) as a unique platform to synthesize nanostructured functional materials with both controlled composition and structure. Due to the atomically arranged metal ions and organic ligands, as well as the wide variety of compositions and porous structures, MOFs can serve as unique precursors for easy preparation of metal-based materials, carbonaceous materials and nanocomposites with high porosity and tunable composition/structure. It is also possible to introduce designed species during the synthesis of MOFs so that functional nanomaterials can be synthesized. In this talk, I will briefly discuss some recent progress we have made in this area. Specifically, I will mention some examples of designed synthesis of nanostructured metal oxides, sulfides, phosphides and carbides using MOF precursors. These MOF-derived nanomaterials exhibit interesting properties in batteries and photo-/electro-catalysts.

## Nanoscale MOFs-based Electrocatalysts

Zhiyong Tang\*

National Center for Nanoscience and Technology, Beijing, China 100190

\*Corresponding Author's E-mail: zytang@nanoctr.cn

Distinct from classic inorganic nanoparticles of solid cores, nanoscale metal-organic frameworks (NMOFs) are of ordered crystalline pores with tunable composite, size and volume, which provide an ideal platform not only to manipulate the reaction active sites but also to understand the structure-functionality relationship. In this presentation, we will introduce two recent works involving catalytic application of NMOFs.

## Defect electrocatalysis: Coordination of carbon defect and atomic metal species

Xiangdong Yao

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, China; School of Environment and Sciences, and Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan Campus, Queensland 4111, Australia  
Email: x.yao@griffith.edu.au

Electrocatalysis is the key for energy conversion and storage devices such as fuel cells, metal-air batteries and water splitting, but the development of highly efficient and non-precious metal catalyst is extremely important. Recently, we presented a new concept of defect electrocatalysis, in which the topological defects on carbons (or oxygen vacancies in oxides) are the active sites for electrochemical reactions. A series of non-metal catalysts have been developed based on this new theory. Besides, the defects are such characterized points with higher energy, thus provides ideal sites to interact with metal species in various sizes. The strong interactions may provide both high reactivity and stability. When the size of metal species reduces to atomic level, the general configurations are metal atoms trapped into defects according to the minimum energy theory. The coordination of the defect and atomic metal species plays the central role for electrocatalysis as the local electronic structures defined by this coordination determines the interaction of reactant and active sites.

## **From Carbon-Based Nanotubes to Nanocages: Materials Design and Energy Applications**

Wu Qiang, Yang Lijun, Wang Xizhang, Hu Zheng

School of Chemistry and Chemical Engineering. Nanjing University, Nanjing, 210023

With the availability of high specific surface area (SSA), well-balanced pore distribution, high conductivity, and tunable wettability, carbon-based nanomaterials are highly expected as advanced materials for energy conversion and storage to meet the increasing demands for clean and renewable energies. In this context, attention is usually attracted by the star material of graphene in recent years. In this talk, I will overview our studies on carbon-based nanotubes to nanocages for energy conversion and storage, including their synthesis, performances, and related mechanisms.

## **One-pot synthesis of nitrogen doped carbon nanotube structure stabilized Ni single atom electrocatalysts for CO<sub>2</sub> reduction**

San Ping Jiang

E-mail: s.jiang@curtin.edu.au

Single-atom catalysts (SAC) is a class of catalyst consisted of atomically dispersed and supported atoms and is characterized by high catalytic activity, selectivity and high atomic efficiency. Despite the significant advantage and benefit of SAC in electrocatalysis, the practical application of SACs is hindered by the very low atomic loading, 1-2 wt%. Here, we report a new one-pot pyrolysis method for the synthesis of nitrogen doped carbon nanotube structure stabilized nickel single atom catalysts (NiSA-N-CNT) with exceptionally high Ni atomic loading up to 20 wt%. The new NiSA-N-CNT shows an excellent activity and selectivity for the electrochemical reduction of CO<sub>2</sub>, achieving a turnover frequency (TOF) of 11.7 s<sup>-1</sup> at -0.55 V (vs RHE), two orders of magnitude higher than Ni nanoparticles supported on CNTs. NiSA-N-CNT consists of Ni-N-C basic units in the carbon lattice throughout the layers of CNTs, which critically contributes to the high loading of single atom nickel. Detailed microstructure, X-ray absorption near edge structure spectroscopy (XANES) measurement and simulation indicate that NiSA-N-CNT is formed during the condensation of Ni-g-C<sub>3</sub>N<sub>4</sub> with the concomitant formation of Ni-N<sub>4</sub> structure.

## Precious Metal-Free Electrocatalysts for Energy Conversion Reactions

Shi-Zhang Qiao

School of Chemical Engineering, The University of Adelaide, SA 5005, Australia

s.qiao@adelaide.edu.au

Replacement of precious metal catalysts by commercially available alternatives is of great importance among both fundamental and practical catalysis research. Nanostructured carbon-based and transition metal materials have demonstrated promising catalytic properties in a wide range of energy generation/storage applications. Specifically engineering carbon with guest metals/metal-free atoms can improve its catalytic activity for electrochemical oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), thus can be considered as potential substitutes for the expensive Pt/C or IrO<sub>2</sub> catalysts in fuel cells, metal-air batteries and water splitting process. In this presentation, I will talk about the synthesis of nonprecious metal and metal free elements-doped graphene, and their application on electrocatalysis. The excellent ORR, OER and HER performance (high catalytic activity and efficiency) and reliable stability (much better than the commercial Pt/C or IrO<sub>2</sub>) indicate that new materials are promising highly efficient electrocatalysts for clean energy conversion. I will also present some research of CO<sub>2</sub> electrocatalytic reduction conducted in my research group.

## **Functionalization and Engineering of Nanomaterials as Effective Electrocatalysts for Electrochemical Energy Conversion and Storage**

Shaowei Chen

Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

Functional nanomaterials play an important role in the development of effective catalysts for electrochemical energy conversion and storage. In this presentation, recent progress in the Chen lab in the design and engineering of metal nanoparticles and nanocomposites for oxygen reduction reaction (ORR) and hydrogen reduction reaction (HER) will be summarized. For ORR electrocatalysis, the electrocatalytic activity has been found to be markedly enhanced by deliberate functionalization of metal nanoparticles with select organic ligands, as a result of the unique metal-ligand interfacial bonds that manipulate the metal nanoparticle electronic density and hence interactions with oxygen intermediates. Remarkable enhancement of ORR activity has also been observed by depositing metal nanoparticles on graphene quantum dots (GQD), where the structural defects of GQD can be exploited for the regulation of the metal-oxygen bonding interactions. In more recent research, carbon-based nanostructures have also been found to exhibit apparent ORR activity. This is demonstrated in a series of recent studies with heteroatom-doped mesoporous carbons. Both experimental studies and DFT- based theoretical calculation show that in N-doped carbon, graphitic N represents the ORR active sites, and in the presence of metal dopants such as Fe, the ORR activity is mostly ascribed to the formation of FeNx moieties. Formation of select heterostructures is also an effective route to the development of carbon-based electrocatalysts for HER. This is evidenced in some of our recent studies where we observe that ruthenium ion (II) embedded carbon nitride nanosheets exhibit remarkable HER activity, due to the formation of Ru-N coordination bonds such that the Ru, N and adjacent C sites act synergistically in facilitating HER.

## Energy Research & High Impact Publishing in Joule

朱昌荣

In this talk I will offer a unique insight into the publishing process of a high-impact energy journal, from the perspective of a recent energy researcher-turned-editor. I will first introduce Joule, the new high-impact energy journal from Cell Press, and our Editorial team. Next, I will motivate and demonstrate Joule's strong interest in serving the energy research community in China. I will then shed light on the life of a scientific editor, the manuscript life cycle, and the peer review process. Finally, I will give additional detail describing editor considerations when evaluating manuscripts and provide advice to authors from an editor's point of view.

# A Satisfactory Cure for the Painful Unity between Activity and Stability for Oxygen Evolution: Dual-ligand Synergistic Modulation

Lishan Peng, Li Li and Zidong Wei\*

Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization,  
College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044,  
China

E-mail: zdwei@cqu.edu.cn

The sluggish kinetics of the oxygen evolution reaction (OER) is the bottleneck of water electrolysis for hydrogen generation. In developing cost-effective OER materials with a high value of practical application, it is prerequisite to achieve an extreme performance in both activity and stability. Herein, we report a “dual ligand synergistic modulation” strategy to accurately tune the structure of transition-metal materials in atomic level, which finally get a satisfactory cure for the unity between robust stability and high activity. Remarkably, the elaborately designed S and OH dual-ligand NiCo<sub>2</sub>(SOH)<sub>x</sub> catalyst exhibits an excellent OER activity with a very small overpotential at a large current density, and a strong durability even after 30 h accelerated ageing at a larger current density, both of which are superior to most of the state-of-the-art OER catalysts so far. The density functional theory (DFT) calculations disclose that the synergy of OH ligands and S ligands on the surface of NiCo<sub>2</sub>(SOH)<sub>x</sub> can delicately tune the electronic structure of metal active centers and their chemical environment. The OH ligands on the surface of NiCo<sub>2</sub>(SOH)<sub>x</sub> could attracts electrons from the antibonding orbital of M-S bonds to M-O bonds, resulting in a strengthened bond between metal and Sand thus enhancing the stability. Meanwhile, the synergy between S and OH ligands appropriately modulate the electronic structure of NiCo<sub>2</sub>(SOH)<sub>x</sub>, leading to an optimized binding strength of the OER intermediates (\*OH, \*O, and \*OOH), therefore facilitating the oxygen evolution proceedings. Meanwhile, the special non-magnetism of NiCo<sub>2</sub>(SOH)<sub>x</sub> can significantly weaken the resistance of O<sub>2</sub> desorption from the catalyst surface and thus further facilitating the O<sub>2</sub> evolution proceeding

# 主题报告

## Oxygen Electrocatalysis on Transition Metal Spinel Oxides

Zhichuan J. Xu\*

School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore

Solar Fuels Laboratory, Nanyang Technological University, 639798, Singapore

Energy Research Institute@NTU, ERI@N, Nanyang Technological University, 639798, Singapore

\* E-mail: xuzc@ntu.edu.sg

Exploring efficient and low cost oxygen electrocatalysts for ORR and OER is critical for developing renewable energy technologies like fuel cells, metal-air batteries, and water electrolyzers. This presentation will presents a systematic study on oxygen electrocatalysis (ORR and OER) of transition metal spinel oxides.<sup>[1]</sup> Starting with a model system of Mn-Co spinel, the presentation will introduce the correlation of oxygen catalytic activities of these oxides and their intrinsic chemical properties. The catalytic activity was measured by rotating disk technique and the intrinsic chemical properties were probed by synchrotron X-ray absorption techniques. It was found that molecular orbital theory is able to well-explain their activities.<sup>[2]</sup> The attention was further extended from cubic Mn-Co spinels to tetragonal Mn-Co spinels and it was found that the molecular theory is again dominant in determining the catalytic activies. This mechanistic principle is further applied to explain the ORR/OER activities of other spinels containing other transition metals (Fe, Ni, Zn, Li, and etc.).

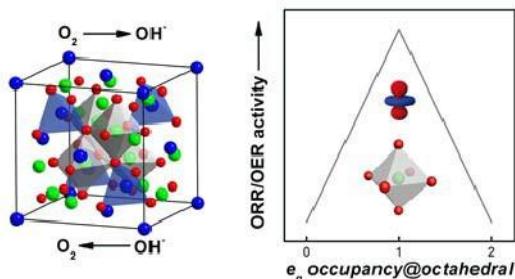


Figure 1. Octahedral site in spinel is influential in determining its oxygen electrocatalysis.

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## Selected Applications of *in situ* ATR-IR Spectroscopy in Electrocatalysis

Wen-Bin Cai\*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, i-ChEM, Department of  
Chemistry, Fudan University, Shanghai 200433, China.  
Email: wbcrai@fudan.edu.cn

In *situ* ATR-IR spectroscopy has been widely applied to study interfacial electrocatalysis, ranging from mechanistic understanding of electrocatalytic oxidation of small organic molecules (SOMs), reduction of CO<sub>2</sub> and O<sub>2</sub> and decomposition of solvent in Li–O<sub>2</sub> batteries to spectral correlation with properties of catalytic materials. Despite its obvious advantage and power. This technique should be often coupled with one or more of other techniques including but not limited to electrochemical methods, DFT calculation, isotope labeling, IRAS and DEMS for comprehensive investigations. More ATR-IR applications should be directed to the reviving hot areas such as CO<sub>2</sub> reduction and SOMs oxidation on efficient electrocatalysts, and the solvent degradation and the structural stability of solid electrolyte interface (SEI) of lithium-air battery. In this talk, I will give a brief overview of the development of *in situ* ATR-IR spectroscopy as well as some selected applications of this technique in the study of electrocatalysis of SOM oxidation and CO<sub>2</sub> reduction.

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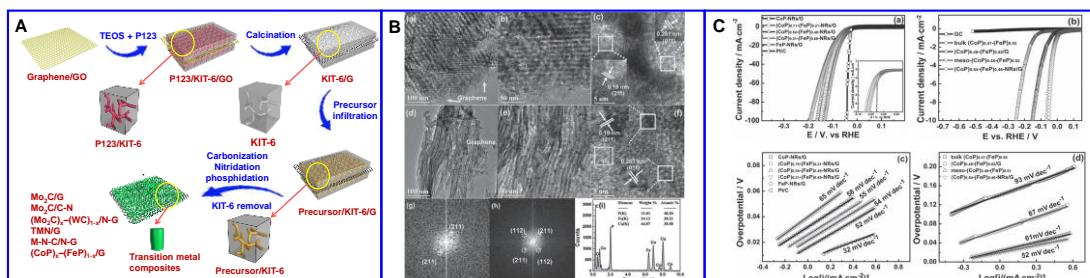
# Highly Active and Durable Two-dimensional Layered Porous Nanocatalysts for Electrocatalytic Applications

Jun Zhang,\* Baocang Liu, and Lili Huo

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, P.R. China

\*Corresponding Author's E-mail: cejzhang@imu.edu.cn

Development of highly efficient electrocatalysts with excellent catalytic activity, long-term stability, high abundance, and low cost is crucial for practical large-scale hydrogen production. Here, we develop a universal strategy to fabricate a series of transition metal hybrid electrocatalysts ( $\text{Mo}_2\text{C}/\text{G}$ ;  $\text{Mo}_2\text{C}/\text{C-N}$ ;  $(\text{Mo}_2\text{C})_{x-(\text{WC})_{1-x}}/\text{N-G}$ ;  $\text{TMN}/\text{G}$ ,  $\text{TM} = \text{Ti}, \text{Cr}, \text{W}, \text{Mo}, \text{TiCr}, \text{TiW}$ , and  $\text{TiMo}$ ;  $(\text{CoP})_{x-(\text{FeP})_{1-x}}/\text{G}$ ;  $\text{M-N-C/N-G}$ ,  $\text{M} = \text{Fe}, \text{Co}$ , and  $\text{Ni}$ ) with a two-dimensional layered structure for electrocatalytic applications.<sup>1-5</sup> The fabrication of these electrocatalysts follows a templating method by filtrating corresponding metal precursors into a mesoporous KIT-6/G template followed by carbonization, nitridation, or phosphidation treatment (Figure 1A). The electrocatalysts possess well-defined 2D mesoporous layered structures with large surface areas, abundant active sites, and strong synergetic interactions of transition metal nanoparticles with heteroatom-doped or undoped graphene (Figure 1B). Due to the structural merits, the electrocatalytic performance of these electrocatalysts show high activity and stability for the oxygen evolution reaction and hydrogen evolution reaction (Figure 1C).



**Figure 1.** (A) Schematic illustration of the synthesis of a series of precious-metal-free mesoporous hybrid electrocatalysts; (B) (a-e) TEM and (c-f) HRTEM images, (g-h) FFT, and (j) EDX spectrum of  $(\text{CoP})_{0.54}-(\text{FeP})_{0.46}-\text{NRs}/\text{G}$  electrocatalyst; (C) (a) Polarization curves for  $(\text{CoP})_{x-(\text{FeP})_{1-x}}-\text{NRs}/\text{G}$  electrocatalysts with different Co/Fe molar rates in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte at 2  $\text{mV s}^{-1}$ , (b) polarization curves for blank GC electrode, bulk  $(\text{CoP})_{0.47}-(\text{FeP})_{0.53}$ ,  $(\text{CoP})_{0.48}-(\text{FeP})_{0.52}/\text{G}$ , meso- $(\text{CoP})_{0.49}-(\text{FeP})_{0.51}$ , and meso- $(\text{CoP})_{0.54}-(\text{FeP})_{0.46}-\text{NRs}/\text{G}$  electrocatalysts in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte at 2  $\text{mV s}^{-1}$ , and (c-d) the corresponding Tafel plots of electrocatalysts in (a) and (b).

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## The Mechanisms of HCOOH/HCOO<sup>-</sup> Oxidation on Pt electrodes, Implication from the pH Effect and H/D Kinetic Isotope Effect

Yan-Xia Chen

Hefei National Laboratory for Physical Science at Microscale and Department of Chemical Physics,  
University of Science and Technology of China, Hefei, 230026, China  
yachen@ustc.edu.cn

The pH effect and the H/D kinetic isotope effect (KIE) for the oxidation of formic acid/formate anions (FOR) on Pt(111) have been studied. The pH-dependent FOR activity displays a volcano shape with a maximum at a pH close to the pK<sub>a</sub> of HCOOH. The H/D KIE factors for HCOOH/DCOOH or HCOO<sup>-</sup>/DCOO<sup>-</sup> are ca. 4, 2, and 1 in solutions with pH=1.1, 3.6, and 13, respectively. These findings reveal that  $\text{HCOOH} \xrightarrow{\text{rds}} \text{COO}_{\text{ad}}^- + 2\text{H}^+ + \text{e}^-$  is the rate-determining step (RDS) for FOR in acid. With increasing pH, the precursor to be discharged changes from HCOOH to HCOO<sup>-</sup>, and the latter goes through  $\text{HCOO}^- \xrightarrow{\text{rds}} \text{HCOO}_{\text{ad}} + \text{e}^-$  as the RDS. The origin of the appearance of the volcano-type pH dependent FOR activity is pH-induced change from excess HCOOH to excess HCOO<sup>-</sup> at pH = pKa and the change in overpotential for the RDS of FOR.

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## 纤维状纳米复合材料的合成与电化学储能应用

陆安慧\*

大连理工大学化工学院，大连，中国，116024

\*Email: anhuilu@dlut.edu.cn

电极材料的微观结构直接影响其电化学储能性能<sup>[1-2]</sup>。因此，定向设计适宜结构以提高电极材料的储锂性能是目前研究的热点。纤维状纳米炭具有孔结构丰富、长径比高、电子导电性好、径向扩散距离短以及嵌/脱锂过程应变小等优点，使其成为优良的储锂材料。我们以纤维状纳米炭基电极材料的结构设计为导向，发展微观结构调控和材料复合新方法，构筑了具有核壳结构及分级结构的纤维状炭基复合材料，并研究材料的微观结构与电化学性能之间的构效关系。(1) 利用溶液化学分子自组装策略，合成了纤维状纳米聚合物。直接热解纤维状聚合物得到实心纤维状纳米炭，采用限域空间热解方法可得到空心结构纤维状炭材料，并且孔结构以介孔为主。研究表明空心纤维状纳米炭展现出优异的储锂容量和倍率性能。(2) 基于氧化硅辅助的动态调孔方法，实现了核壳结构纤维状硫@炭复合材料的制备。以两端封闭、壳壁开放介孔的空心纤维状炭/氧化硅复合物为载体，将单质硫通过开放的介孔浸入空腔内部后，室温下溶液化学去除氧化硅组分，薄的炭壁由于缺少支撑，在表面能作用驱动下，原位收缩并相互搭接，使介孔转变为超微孔。这一动态缩孔过程将活性物质硫巧妙封装在纤维状纳米炭的内部，避免了硫组分与电解液的过度接触和多硫化物的溶出；并且该一维纳米结构可有效缩短电解液扩散路径，提升离子和电子传输速率，并能有效应对充放电过程中硫体积膨胀；微孔炭对多硫化物的强吸附能力，使锂硫电池的循环性能得到了大幅度的提高。当用作锂硫电池正极时，表现出较高的比容量、倍率性能和循环稳定性。<sup>[3]</sup> (3) 针对炭材料元素组成单一、应用功能简单的问题，利用空心纤维状炭/氧化硅复合物的原位转化，合成了多级结构纤维状炭/硅酸镍复合材料。原位生成的硅酸镍纳米片固载于连通的纤维状炭骨架中，赋予材料丰富的孔隙结构，使电极与电解质之间有更大的接触面积。这种内嵌炭与硅酸镍纳米片构建的复合杂化材料具有互连的电子通道和离子通道、丰富的微孔-介孔特性，使材料呈现出优异的储锂性能。这种方法还可以扩展到炭/硅酸锰和炭/硅酸铜复合材料的合成，同样展现出优异的电化学性能。<sup>[4]</sup>

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## 基于 MOF 的光电催化研究

张健\*

结构化学国家重点实验室，中国科学院福建物质结构研究所，福州，中国，350002

\*Email: zhj@fjirsm.ac.cn

近期，我们通过外延负载法制备的均匀分散的 Ce(III)配位化合物负载的钴卟啉 MOF PIZA-1 薄膜孔道中，从而形成客体负载型 MOF 复合薄膜材料。通过调整复合薄膜的厚度和煅烧温度，成功地获得了具有均相分散的  $\text{CeO}_2$  负载型 PIZA-1 衍生物的薄膜（图 1）。然后通过电化学工作站对所得到的薄膜进行电催化实验电化学实验数据表明我们所制备的均一分散的  $\text{CeO}_2$  纳米颗粒能够有效地提高电催化产氧性能(在 10.0 mAc<sup>-2</sup> 下过电位为 370 mV)，并且我们可以有效地优化电催化产氧的活性，为制备其他复合薄膜电催化材料提供了很好的借鉴。

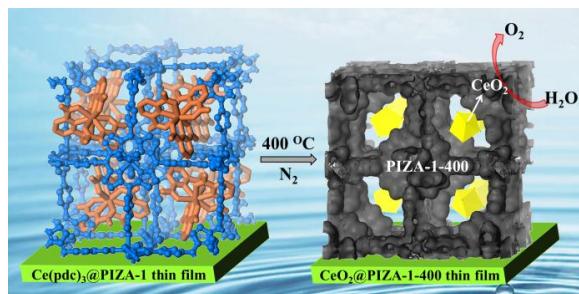


图 1 外延负载法制备的具有电催化性能的了均相分散的  $\text{CeO}_2$  负载型 PIZA-1 衍生物的薄膜

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# 低含量的 Pt 负载的 MoCx/BP 作为稳定且优异的电催化剂在碱性 介质 ORR 中的应用

蔡慧珠, 孟想, 石川\*

大连理工大学 等离子体物理化学实验室, 辽宁大连, 116024

\*Email: chuanshi@dlut.edu.cn

燃料电池(Fuel Cell)是一种将燃料的化学能直接转化为电能的装置, 具有能量转换效率高、污染小、燃料多样化、噪声低等优点, 使世界各国越来越重视对其的研究。阴极的氧还原反应(ORR)由于其缓慢的动力学过程, 是限制燃料电池商业化的主要因素。目前商业催化剂主要以Pt基催化剂为主, 但商业20% Pt/C含Pt量偏多, 成本高昂。实验室前期工作已经表明过渡金属碳化物与Pt存在很强的相互作用, 这种相互作用影响着被分散金属的形貌、粒子大小及电子状态, 从而影响催化体系的活性, 且其具有类Pt性质<sup>[1-3]</sup>。

本研究中, 利用BP-2000具有良好的导电性和大比表面积, 我们将BP-2000作为导电载体, 来负载MoC和Pt纳米粒子, 制备了5%Pt/30%Mo<sub>2</sub>C/65%BP将其用于ORR, 仅以低Pt负载量取得了非常优异的电催化性能。碳化钼充当助剂的作用, 相较于5%Pt/95%BP, 5%Pt/30%Mo<sub>2</sub>C/65%BP催化剂氧还原起始电位逐渐向正向移动, 分别为0.82V和0.86vsRDE, 半波电位也均向正向移动, 极限电流随之增大, 我们将其归因于MoC<sub>x</sub>极易吸附O<sub>2</sub>, 从而促进O原子的活化, 所以在同样Pt担载量时, 活性明显提高, 掺N后, 进一步增大了极限电流密度。经过10000cycles的CV后, 5%Pt/30%Mo<sub>2</sub>C/65%BP在0.1M KOH碱性介质中表现出非常好的稳定性, 是非常稳定且优异的ORR电催化材料。

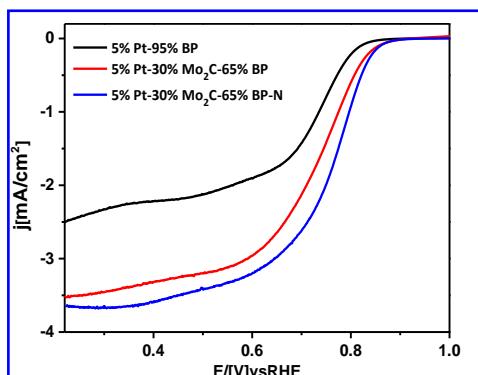
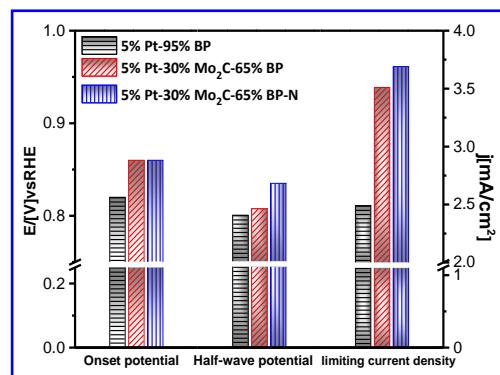


图1 0.1M KOH溶液中催化材料在旋转速度为1600 rpm下的氧还原LSV曲线, 扫描速度为10 mV s<sup>-1</sup>,

图2 催化材料的起始电位、半波电位、极限电流密度比较。催化剂负载量: 51ug/cm<sup>2</sup>



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# Electrochemical reduction of CO<sub>2</sub> into tunable syngas production by regulating crystal facets of earth-abundant Zn catalyst

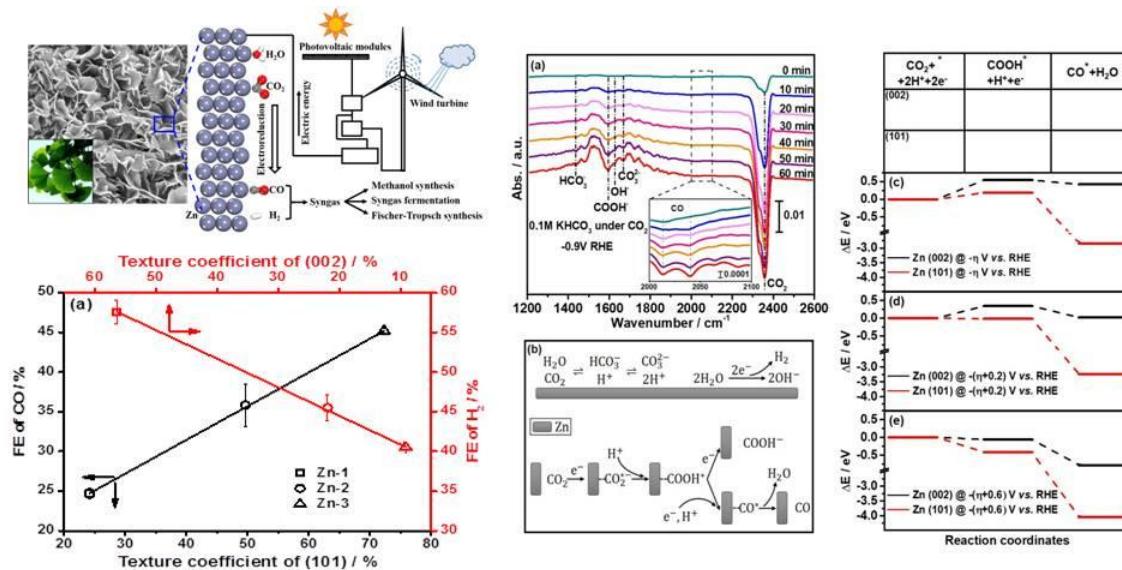
Binshao Qin<sup>a</sup>, Feng Peng<sup>a,b,\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China.

<sup>b</sup> Guangzhou Key Laboratory for New Energy and Green Catalysis, School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou, 510006, China

\* Corresponding author: cefpeng@scut.edu.cn; fpeng@gzhu.edu.cn (F. Peng)

The crystal facets of Zn catalyst have been regulated by a simple method of adding CTAB. Zn-1 catalyst has a preferentially exposed (002) facet, Zn-3 catalyst has a preferentially exposed (101) facet. Electroreduction of CO<sub>2</sub> into syngas (CO and H<sub>2</sub> mixtures) has been achieved on Zn electrodes with different crystal facet ratios of Zn (002) and Zn (101). Faradic efficiencies of syngas are greater than 85% at -0.9 V (vs RHE) in aqueous electrolyte with CO/H<sub>2</sub> ratios between 0.2 and 2.31 which could be used as raw materials for methanol synthesis, syngas fermentation and Fischer-Tropsch synthesis. Zn (101) shows better catalytic activity for CO<sub>2</sub>RR to CO than Zn (002). Moreover, Zn-3 also shows high faradic efficiency and good stability for CO<sub>2</sub>RR to syngas. Meanwhile, the mechanism of electroreduction of CO<sub>2</sub> on Zn electrode has been studied by in-situ infrared absorption spectroscopy and density functional theory calculations. The results show that Zn (101) facet is better than Zn (002) facet for CO<sub>2</sub>RR at lower reduction potential.



## Highly Efficient Electrocatalysts for Electrochemical Energy Storage and Conversion

Haixia Zhong, Zhong-Li Wang, Jun Wang, Ji-Jing Xu, Xinbo Zhang\*

State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry,  
Chinese Academy of Sciences , 5625 Renmin Street, Changchun 130022  
\*E-mail: xbzhang@ciac.ac.cn

Electrochemical energy storage/conversion has been receiving great attentions for potential applications in electric vehicles and renewable energy systems. Our research interests focus on highly efficient electrocatalysts for next-generation lithium-air batteries, fuel cells and electrochemical water splitting devices, with the aim to significantly improve the energy conversion efficiency and energy storage density. By finely tuning the composition, shape, and structure, advanced electrode materials with high capacity, high-rate capability, and long cyclic stability have been successfully obtained. The lithium-air batteries research is focusing on improving the electrochemical performance by mainly regulating the electrolyte, porous structure and conductivity of the air-electrode as well as clarifying the underlying structure-performance relationship, and high performance all-in-one air-electrode has been successfully designed and fabricated.

## 邀请报告

### Synergistic Effects in Electrocatalysis for Enhanced Performance

Jin-Song Hu \*

Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190

\* E-mail: hujss@iccas.ac.cn

The increasing concerns on severe environmental issues and rapid fossil fuel depletion stimulate the intensive interests in renewable and sustainable energy sources. Fuel cells and electrochemical water splitting is considered as one of ideal options to feed energy demand without environmental concerns. The commercialization of these techniques requires the efficient, low-cost and durable electrocatalysts for oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and oxygen evolution reaction (OER).

The catalytic performance of these electrocatalysts are closely related to the intrinsic activity and the number of the accessible catalytic sites in the electrocatalysts. This presentation will focus on the exploration of earth-abundant efficient ORR, HER and OER electrocatalysts with an emphasis on the performance boosting by synergistically electronic and structural engineering. Several reasonable ways will be introduced for rationally engineering the morphological structure, electronic structure, and crystalline structure of electrocatalysts to augment the accessible catalytic sites and synergistically boost their intrinsic activity, thus leading to the significant performance enhancement of these low-cost materials for practical applications.<sup>[1-5]</sup> These results will open opportunities for the rational design and bottom-up synthesis of cost-effective and high-performance electrocatalysts for fuel cells and sustainable hydrogen production through electrochemical water splitting.

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## Bismuth-Based Nanostructures for Electrocatalytic and Solar Conversion of CO<sub>2</sub> to Formate

Yanguang Li\*

Institute of Functional Nano & Soft Materials, Soochow University, Suzhou, Jiangsu 21523, China

\* E-mail: yanguang@suda.edu.cn

High-performance electrocatalysts for CO<sub>2</sub> reduction to valueable chemical fuels are a key component in the design of efficient artificial photosynthetic systems. Formate is a common CO<sub>2</sub> reduction product, and its selective electrochemical production is desirable but challenging. Most current attention focuses on Sn-based materials, which unfortunately exhibit moderate-to-high formate selectivity only within a very narrow and highly cathodic potential region. Bi has a great potential for formate production but remains under-explored. In this presentation, we report several different strategies to prepare unique Bi-based nanostructures with large surface areas. The final product exhibits large cathodic current density, excellent Faradaic efficiency (>90%) over a broad potential window and great stability for CO<sub>2</sub> reduction to formate. Furthmore, we integrate Bi with a p-type Si photocathode and achieve photoelectrochemical CO<sub>2</sub> reduction to formate with high selectivity and stability. We also couple Bi with an oxygen evolution reaction electrocatalyst in full cells, and achieve battery-driven or solar-driven splitting of CO<sub>2</sub>/H<sub>2</sub>O into formate and oxygen at high energy conversion efficiency.

## 界面效应增强电催化活性和选择性

陈煜\*

陕西师范大学大学 材料科学与工程学院，陕西 西安，中国，710000

\*Email: ndyuchen@gmail.com

直接甲醇燃料电池具有比能量高、清洁、结构简单、安全方便等优点，在便携式电子设备和汽车电源等领域具有广泛的应用前景。直接甲醇燃料电池中，Pt 基纳米材料是阴极氧气还原(ORR)首选催化剂。然而，ORR 动力学迟缓、催化剂稳定性差、醇渗透等问题限制直接甲醇燃料电池的商业化进程。通过控制反应温度、pH 等条件成功合成出高度分支的聚丙烯胺(PAA)功能化的具有长针海胆形态的 Pt 纳米结构物(Pt-LSSUs@PAA)(图 1A)，实验结果显示 Pt-LSSUs@PAA 高度分枝的三维结构可有效抑制奥斯特瓦尔德熟化，改进电催化剂的稳定性(图 1B)。PAA 分子中的-NH<sub>2</sub> 官能团质子化显著提高贵金属纳米晶表面质子浓度，从而提高 ORR 动力学。特别地，表面的 PAA 层可充当“分子窗纱”有效地阻止体积较大的醇分子通过，而允许体积较小的氧气分子通过，从而显示出良好的 ORR 选择性(图 1C)。实验结果显示贵金属纳米晶表面化学功能化改变电极/电解液界面结构，进而改变贵金属纳米晶电催化活性，这对于发展新的电催化剂设计理念和新的电催化剂制备方法方面具有很好的理论意义<sup>[1]</sup>。

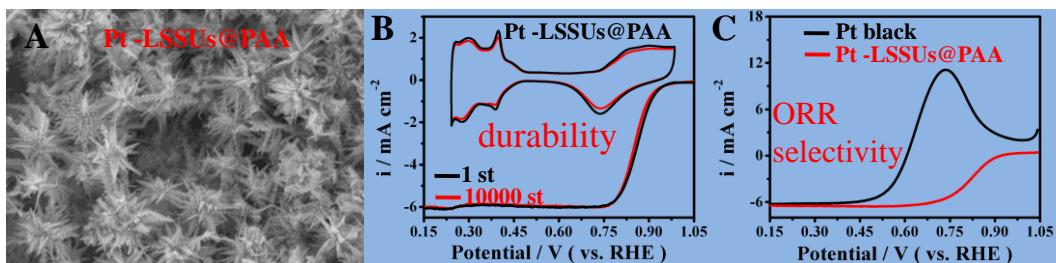


图 1 (A) Pt-LSSUs@PAA 的 SEM 图; (B) Pt-LSSUs@PAA 稳定性; (C) ORR 选择性。

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## 纳米管中的界面结构设计及其电催化性能调控

冯锦先, 叶盛华, 李高仁\*

中山大学, 广州, 510275

\*E-mail: ligaoren@mail.sysu.edu.cn

以氢能、燃料电池等为代表的清洁能源目前已受到了国际社会的广泛关注, 电催化是实现氢能、燃料电池等广泛应用的关键技术之一, 在这些能源转化过程中发挥着极其重要的作用。在小有机分子氧化、氧还原、水分解等过程中, 尽管铂表现出非常好的电催化性能, 但铂催化剂却存在价格昂贵和易中毒等问题。为攻克这些难题, 近年来人们对低铂及非铂复合电催化剂进行了广泛的研究。低铂及非铂复合物纳米管阵列因其许多优异的特性, 已受到了科学家们的广泛关注, 但复合物纳米管阵列的可控合成仍面临着诸多挑战。本研究通过电沉积方法实现了复合纳米管阵列的可控合成, 研究了复合纳米管中金属/合金界面对活性位点的调控、金属/金属羟基氧化物界面对电催化活性的调控、金属/导电高分子界面对催化稳定性的调控等。以低贵金属或非贵金属复合纳米管作为电催化活性结构单元, 以有序化组装和构建协同增效为突破口, 结合纳米管阵列的表面效应、电子效应等, 实现了电催化活性位点的高效调控, 显著提升了催化剂的电催化活性及稳定性<sup>[1-5]</sup>。

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## 电催化材料表面原子结构调控和性能研究

凌涛\*

天津大学材料科学与工程学院, 天津, 中国, 邮编 300072

\* E-mail: lingt04@tju.edu.cn

控制催化剂表面原子结构是提高催化剂性能的有效途径。对于金属氧化物, 表面电子结构可控制备及原子尺度结构与催化性能关系研究仍然具有巨大挑战。我们采用动力学控制的气相离子交换策略, 在高导电碳纤维基底上可控制备了 CoO 纳米线阵列。原子分辨率球差电镜及 X 射线近边吸收表明 CoO 纳米线表面暴露织构化的金子塔结构, 由氧空位富集的{111}面组成。这些具有特殊表面原子结构的 CoO 纳米线阵列获得了优异的 ORR/OER 催化活性。理论计算表明, 在{111}表面引入氧空位后能实现有效的反应物活化, 适合的反应中间体吸附及快速的电荷转移。

## 设计三维陷光电极在光电催化制氢的应用

丘勇才\*

华南理工大学环境与能源学院

\*E-mail: ycqiu@scut.edu.cn

三维电极因其具有超强的陷光效果和改善的电荷收集能力被应用于光电化学电池领域。基于此特性，我们设计和制备了几类三维电极（如纳米钉、纳米锥和倒置的纳米锥等），当这些电极被装饰上纳米结构的光活性材料后（如  $\text{Fe}_2\text{O}_3$  薄膜、多孔  $\text{BiVO}_4$  薄膜等），显著提升了光电化学电池性能。为了更进一步提升太阳能制氢性能，我们也结合可调带宽的钙钛矿电池来构建自驱动的光电化学电池，使光能到氢能的转换效率超过了 7%。<sup>[1-5]</sup>

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## 核壳结构光电催化材料设计、制备与性能研究

邵明飞

化工资源有效利用国家重点实验室；北京化工大学，北京 100029

\* E-mail: shaomf@mail.buct.edu.cn

光电化学（Photoelectrochemical, PEC）制氢技术是指直接利用太阳能作为能量源来驱动，结合电化学氧化还原反应过程催化目标反应物分解制备氢气的过程，它已成为当前洁净能源生产开发和环境污染治理的重要手段。其中，为了克服光阳极/阴极材料的固有缺陷，实现光电化学分解水制氢效率的不断提高与功能强化，借助新型的纳米技术和材料可控制备方法对光阳极/阴极材料的组成与微纳结构进行精细调控具有重要的意义。除了对电极材料的结构进行调变，探索新型的光阳极材料对于该领域的发展也至关重要。我们以层状双金属氢氧化物（LDHs）为基础，通过构筑光催化剂/水分解电催化剂核壳式异质结构，优化光电催化材料的结构、组成、形貌调控等特征，发展了一类高效的光电化学催化材料，并实现了材料的性能强化。

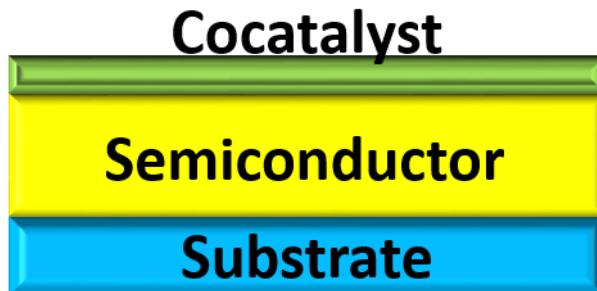


图1. 光催化剂/水分解助催化剂核壳结构光电材料

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## 利用电化学中和能降低制氢能耗

温珍海\*, 李燕, 王根香

中国科学院福建物质结构研究所, 福州, 350002

\* E-mail: Wen@fjirsm.ac.cn

化石能源的过度消耗引起的能源危机和环境污染问题时刻在困扰着我们, 这也极大地促进了可持续能源的发展繁荣。因其高能量效率, 大燃烧热值和无污染等有点, 氢能被认为有望代替化石能源。但是, 氢气的制备通常需要很大的能耗, 如何降低制氢能耗成为了巨大的挑战。另一方面, 酸碱中和反应中, 其化学反应能量通常以热能的形式释放出来, 这些能量很难收集利用。所以, 如何将化学能转换为电能并将其应用于电化学制氢体系中具有重要意义。<sup>[1,2]</sup>基于此, 我们开展了以下几个体系:

- (1) 发展了析氢和析氧双功能催化剂, 能够有效降低水分解电压, 再利用不同 pH 下的反应, 使得水分解电压再降一个台阶。
- (2) 开发出尿素氧化催化剂, 用尿素氧化代替水的氧化, 再加上充分利用电化学中和能, 能够有效降低电催化制氢的电压。

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## 基于晶格扭曲修饰耦合原子界面结构的 CuS/NiS<sub>2</sub> 柔性锌空电池

安丽，席聘贤\*

兰州大学，甘肃省兰州市城关区天水南路 222 号，730000

\*E-mail: xipx@lzu.edu.cn

社会文明水平的快速提升促进人们对柔性与便携式电子设备的迫切需求，其中柔性锌空电池应运而生。该技术得到进一步发展的核心问题是降低过电位对其电压的消极损耗。受限于贵金属高成本的缺陷，绿色环保的新型非贵金属能源成功进入人们的视野。启发于“表界面”在催化界的特殊性能，我们采用“相似半径金属离子掺杂”的制备新方法对硫属化合物进行修饰改性，成功构造得到两相原子界面结构CuS/NiS<sub>2</sub>。根据“软硬酸碱理论”，硫化铜作为“路易斯酸”可促进界面处另一区域NiS<sub>2</sub>向“路易斯碱”的转变，加速电子在微观耦合界面处的流动；二价铜离子作为典型的八面体配位原子，可诱导配位八面体发生“姜泰勒效应”导致分子的几何构型发生畸变，引起晶格扭曲，诱发大量的空位缺陷，作为催化反应的活性点。<sup>[1]</sup>该工作揭示了“离子掺杂-晶格畸变-空位缺陷”之间的物性关系，实现了对材料功能调控的目标，为柔性电子设备性能的提升提供了新的途径。

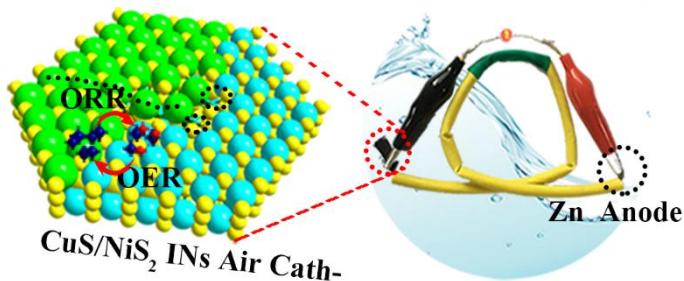


Fig. 1 Schematic illustration of flexible Zn-air batteries.

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# Nanoconfinement-synthesis of highly efficient electrocatalysts basing on covalent organic polymers

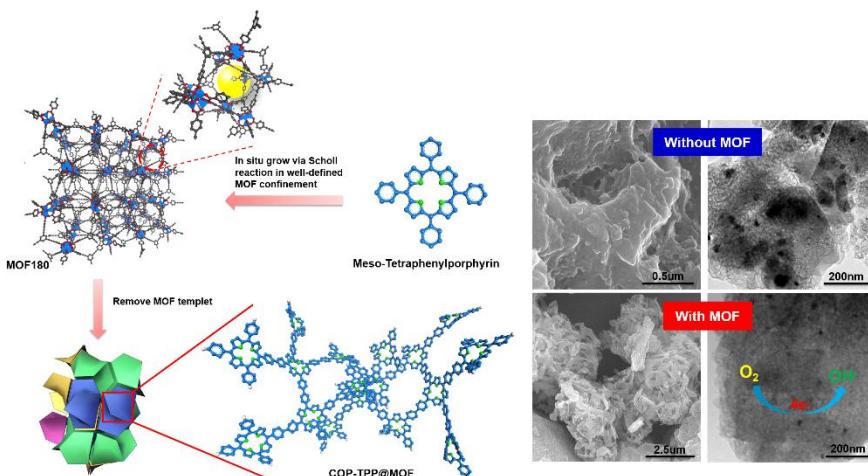
Zhonghua Xiang\*

State Key Lab of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing

100029 (P.R. China)

\*E-mail: xiangzh@mail.buct.edu.cn

Highly efficient electrocatalysts are vital to meet the energy and environmental challenges. Although numerous nonprecious-metal or metal-free carbon-based catalysts have been demonstrated to entirely or partially replace noble-metal-based electrocatalysis, the absence of precise design and predictable process hindered the development. Well-defined 2D Covalent Organic Polymers(COPs)<sup>1-6</sup> as a new exciting type of electrocatalyst presented superior potentials with precisely controllable capacities, such as robust tailoring heteroatom incorporation and location of active sites. Here we demonstrate the possibilities and potential of the well-defined 2D COPs used as highly efficient energy electrocatalysts for clean and renewable energy technologies. Furthermore, we discuss the possible future directions on designed synthesis of intrinsic COPs without carbonization to modulate active sites and the density of active sites at the molecular level. COP materials as a new family of electrocatalysts offer practical possibilities to study the structure, mechanism and kinetics of energy electrocatalysis and may lead to a better solution for energy and environmental issues.



**Fig. 1** Hypothetic network fragments for colorful 2D COPs show the potential for oxygen reduction.

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## Rational Synthesis of Noble Metal-based Nanostructures toward High-Performance Electrocatalysis

Lin Xu\*

Schcool of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, China

\* E-mail: njuxulin@gmail.com

Electrocatalysis plays vital roles in energy conversion and storage devices, such as fuel cells, metal-air batteries, CO<sub>2</sub> reduction and water splitting, etc. The overall efficiency of an electrocatalytic reaction is highly dependent on the electocatalyst. However, the current commercial electrocatalysts still rely on precious metals, such as Pt nanostructures, which usually suffer from high-cost, sluggish kinetics, and poor durability. To address these issues, nanostructure engineering and compositional tuning provide two promising strategies to optimize the electrocatalysis performances. Herein, we demonstrate several approaches to synthesize a series of nanocatalysts with shape and composition-control, including ultrathin 1D alloyed nanowires, 2D porous nanosheets, porous nanoframes and so on. Due to the unique structural features and compositional synergy, the synthesized electrocatalysts exhibit improved electrocatalytic performances toward electro-oxidation of liquid fuels (methanol and formic acid) and oxygen reduction reaction (ORR) in terms of activity and stability.

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## 几种经济实用的电化学还原催化体系

徐维林\*

中科院长春应用化学研究所，吉林长春，130022

\* E-mail: weilinxu@ciac.ac.cn

在本报告中，主要介绍本课题组针对能源化学过程中的几种经济适用型电化学还原催化体系的研究进展<sup>[1]</sup>。针对电化学析氢、氧还原和二氧化碳还原这三个经济实用的重要电催化体系过程，基于廉价的超低铂或非铂（铁氮（图 1），锌氮等）体系<sup>[2]</sup>，我们得到了一系列高效、高稳定性的具有高的性价比的催化材料，结合量子化学计算，进一步详细揭示了这些廉价高效催化体系的活性中心结构及其高活性反应机制。由于这些体系的高活性、高稳定性和低成本，它们有望在将来的能源电化学转化过程中得到大规模的应用。

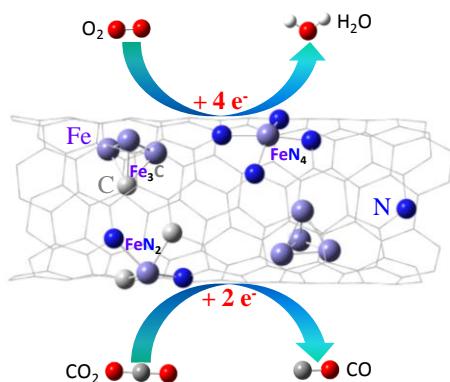


图 1 基于铁氮共掺杂的廉价高性能双功能催化体系。

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## A general polymer-assisted strategy enables unexpected efficient metal-free oxygen-evolution catalysis on pure carbon nanotubes

You Zhang,<sup>a,§</sup> Xuliang Fan,<sup>a,§</sup> Junhua Jian,<sup>a,§</sup> Dingshan Yu,<sup>a,\*</sup> Zishou Zhang,<sup>a,\*</sup> and Liming Dai<sup>b,\*</sup>

<sup>a</sup>School of Chemistry Sun Yat-Sen University, Guangzhou, 510275, China.

E-mail: yudings@mail.sysu.edu.cn, zhzhish@mail.sysu.edu.cn

<sup>b</sup> Department of Macromolecule Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, USA.

E-mail: liming.dai@case.edu

A conceptually-new and general strategy was, for the first time, proposed to significantly boost the electrocatalytic activity of metal-free pure carbon nanotubes (CNTs) towards oxygen evolution reaction (OER) by simple polymer wrapping without introducing any heteroatom dopants, functional groups or edge defects into the graphitic structure. Our strategy is straightforward, efficient, green, and easy to be scaled up. After wrapping pure CNTs with a certain class of electrochemically inert polymers (i.e. poly (ethylene-alt-maleic acid), poly (vinyl alcohol), poly (vinyl acetate), poly (ethylene glycol)) with polar oxygen-containing groups (i.e. -COOH, -OH, -COOCH<sub>3</sub>, -O-) through noncovalent interactions, a series of advanced metal-free composite membrane catalysts were easily achieved, which yielding unexpected, surprisingly high OER activity—on par with the commercial noble RuO<sub>2</sub> catalyst, though pure CNTs have rather poor OER activity. Combined experimental and computational studies revealed that the observed superb OER activity could be attributed to a synergistic effect of intrinsic topological defects in CNTs as active centres and the coated polymer layer as a co-catalyst to optimize adsorption energies of intermediates for improving the OER energetics.

## 廉价过渡金属纳米材料与结构的电催化水氧化研究

张伟

陕西师范大学，化学化工学院

E-mail: zw@snnu.edu.cn

人工模拟光合反应将太阳能转化为化学能并储存起来是一种行之有效解决人类能源环境危机的手段。光合反应的初始为水的氧化过程，这一过程的动力学极其缓慢，因此其效率大大限制了人工模拟光合反应研究的进程。为了使人工模拟光合反应进入实际应用阶段，我们必须开发高效可靠的水氧化催化体系。由于其良好的催化活性，基于廉价过渡金属的纳米材料在电催化水氧化研究方面受到了广泛的重视。

在膜电极研究中，通过分步电镀成膜法制备了多孔交联状的超薄 NiFe 膜材料。该方法首先通过阴极还原电镀负载 Ni 催化剂，进而在另一电解质体系中通过循环伏安法掺入 Fe 物种。制备的膜材料具有良好的表面空隙，利于催化反应中的高效传质，同时交联状的材料特性有利于电催化过程中的电荷迁移。值得提出的是，制备的膜材料由于其超薄性能而具有优异的透光性能，具有在光伏器件表面作为催化剂的潜在应用。

在多级纳米材料研究中，于近期成功合成了新颖的  $\text{Co(OH)F}$  等级维度结构材料。该材料是一种新奇的多级组装体系。其基本结构单元为单晶纳米棒，其次级结构为由纳米棒编织而成的多孔纳米片层结构，其高级结构为由纳米片层结构搭建而成的独立微球聚集体超级结构。这种新颖的材料组装形式导致最终结构中同时包含了一维、二维和三维材料特性，这些多维特性在催化过程中均起到明显的积极作用。一维基本单元的各向异性特性带来快速的电荷转移能力、高比例的低能晶面和超高表面积体积比率；一维结构编织的二维单元带来催化过程中快速的传质与传荷；三维超级结构的高孔隙率可以极大提升底物扩散效率。同时， $\text{Co(OH)F}$  也是首次被报导为电催化水氧化催化剂。惰性氟配体的引入不仅形成了新颖的组装结构并很好的稳定了催化剂表面结构。电化学及理论计算表明在催化水氧化前表面二价钴被逐步氧化成高价态活性钴中心。

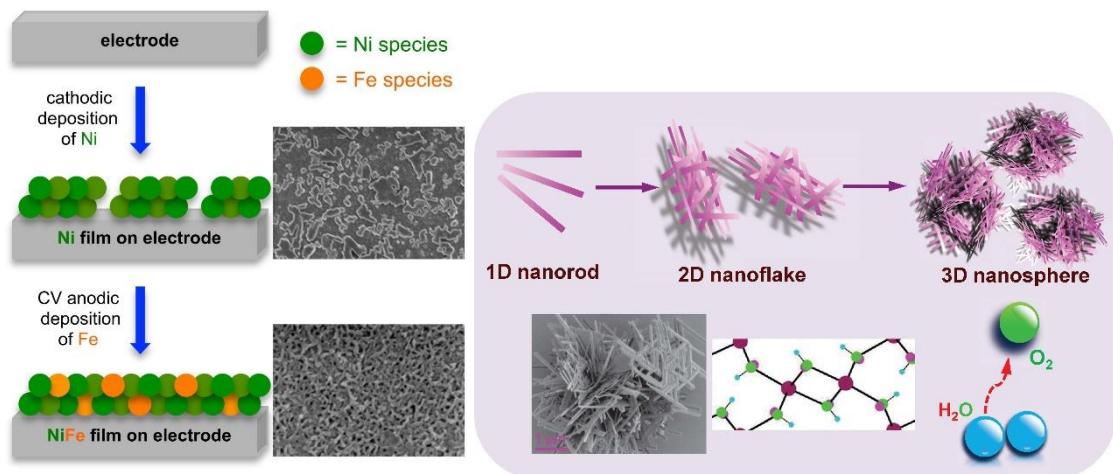


图 1. (左) 有限原子层的超薄 NiFe 膜与 (右) 具有等级维度的  $\text{Co(OH)F}$  纳米材料用于电催化水氧化研究

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## 纳米电催化剂与界面调控

郑耿峰\*

复旦大学化学系、先进材料实验室，上海市，200438

\* E-mail: gfzheng@fudan.edu.cn

近半世纪来，人类社会对于化石能源的使用急剧增加，造成了大量二氧化碳气体的排放<sup>[1,2]</sup>，对生态环境造成一系列难以逆转的严重影响。控制 CO<sub>2</sub> 等气体的排放已成为人类社会持续和发展所面临的一大挑战。近年来，科学家们在太阳能电池和分解水催化剂的领域已取得众多重要进展，大大提高了光电转化效率及其分解水的效率。相比之下，虽然 CO<sub>2</sub> 电催化剂的研究已有很长时间，然而 CO<sub>2</sub> 的还原反应复杂，包括多步多电子-质子耦合的反应过程，产物种类众多，且溶液中的水分子会强力竞争 CO<sub>2</sub> 电催化还原反应所需要的电子，直接导致溶液的产氢气过程，降低 CO<sub>2</sub> 还原的法拉第效率。本报告将汇报我们课题组近年在常温水溶液中 CO<sub>2</sub> 电催化还原领域的研究<sup>[3,4]</sup>，主要围绕着基于金属及其氧化物作为电催化剂的结构、掺杂、与界面的调控，可实现对多种 CO<sub>2</sub> 的深度还原产物，包括甲烷、乙烯、乙醇等，进行高活性、高选择性的电催化制备，并对其催化原理进行较为深入的研究。

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## 柔性有机太阳能电池的器件稳定性研究

郑世昭<sup>1,2,\*</sup>, 苏彤彤<sup>1</sup>, 周竹欣<sup>1</sup>, 谢宗良<sup>1</sup>, 王文慧<sup>1</sup>, 李文朗<sup>1</sup>, Naveed Ur Rahman<sup>1</sup>, 蒋星<sup>1</sup>, 杨志涌<sup>1</sup>, 于涛<sup>1</sup>, 赵娟<sup>1</sup>, 刘四委<sup>1</sup>, 张艺<sup>1</sup>, 黄景扬<sup>2</sup>, 池振国<sup>1</sup>, 许家瑞<sup>1</sup>

1.中山大学化学学院,聚合物复合材料及功能材料教育部重点实验室,广东省有机聚合物光电功能薄膜工程技术研究中心,广州,510275,中国 2.香港中文大学物理系,香港,中国

\* E-mail: zshizhao@mail.sysu.edu.cn

有机太阳能电池能量转换效率已经达到 14%，目前迫切需要进一步提高器件效率和环境稳定性。从有机材料分子设计工程、器件界面工程和新型柔性衬底三个方面努力，可以进一步推进柔性太阳能电池的商业化发展。

我们通过氯化 ITO 阳极界面，显著提高界面的功函数，可以将 PCDTBT: PCBM 体系的开路电压从 PEDOT: PSS 界面上的 0.80 V，提高到 0.90 V，从而将器件整体效率提高 29%，进而我们发现不同给体材料的正极化态对于器件效率的提升起到重要作用。我们不使用传统的热退火工艺，仅通过溶液静置效应可以将 P3HT: PCBM 体系的能量转化效率提高 19%，而且这种溶液静置效应针对不同的界面具有一定的选择性。我们探讨了有机太阳能电池 P3HT: PCBM 体系界面退化的机理，发现金属氧化物界面层可以有效提高器件的环境稳定性。

我们设计合成了高透明、耐高温、耐辐照的功能化聚酰亚胺作为新型柔性器件衬底，这种功能化聚酰亚胺薄膜可以将太阳光中的紫外光部分转换为可见光，被太阳能电池器件吸收利用。这种新型的柔性衬底对于克服紫外光对于太阳能电池的不利影响具有重要的实际应用价值。

# 水裂解电催化材料的合成化学

邹晓新\*

吉林大学 无机合成与制备化学国家重点实验室，长春，中国，130012

\* E-mail: xxzou@jlu.edu.cn

以发展高效的水裂解催化材料为目标，开展新型催化材料结构化学、合成化学等方面的研究，尤其强调催化活性位点的预测、识别与精准构筑。<sup>[1-5]</sup>在搜寻、筛选具有应用潜力的新型（指新组成和新晶体结构）水裂解电催化材料的基础上，利用不同组元间的强耦合杂化作用和纳米结构效应，对材料的催化活性位点进行调控，以实现增加活性位点数量、提高活性位点活性及增强活性位点稳定性的目的。利用“自下而上”的无机材料制备技术，从原子、分子或纳米晶簇的水平对材料的组成、结构和形貌等微结构参数进行优化，实现材料能带结构和表面结构的精准调控，制备具有高催化活性和稳定性等特点的水裂解催化材料。利用理论建模和实验相结合的方法，探究材料表、界面原子结构和电子结构对催化活性的影响，研究材料在催化过程中微结构的变化，研究反应物或反应中间体与材料催化位点的化学相互作用，揭示内在催化机制。

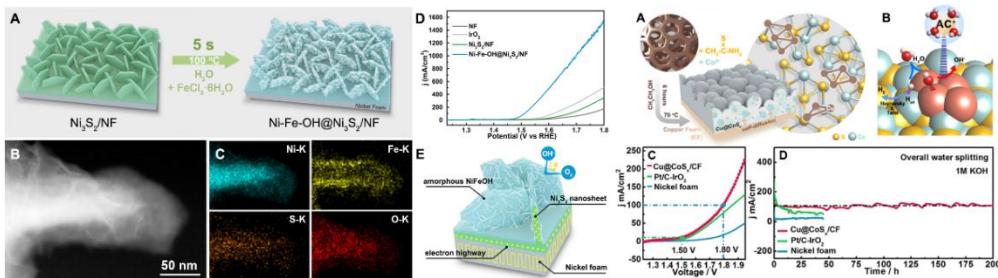


图1 (左) Ni-Fe-OH复合的Ni<sub>3</sub>S<sub>2</sub>水裂解催化材料 (Adv. Mater. 2017, 29, 1700404)；(右) 亚纳米铜簇复合的Co<sub>9</sub>S<sub>8</sub>薄膜催化材料 (Adv. Mater. 2017, 29, 1606200)。

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## 锂-氧电池中的关键科学问题和技术挑战

彭章泉\*

中国科学院长春应用化学研究所，电分析化学国家重点实验室

\*E-mail: zqpeng@ciac.ac.cn

锂-氧电池与传统的锂-离子电池相比，具有更高的能量密度，近年来倍受关注<sup>[1]</sup>。该电池的典型结构为：金属锂负极/锂盐有机电解液/多孔碳正极。正极中的活性物质来自空气中的氧气。目前的锂-氧电池普遍表现为循环寿命有限、能量效率低下，其能量损失主要来自氧气电极反应的过电势。深入研究锂-氧电池反应原理有利于解决该电池体系中的技术难题。报告人利用现场电化学研究方法结合第一性原理计算，对锂-氧电池中的氧气电极反应过程，包括基元反应、中间产物、反应位点和受限因子等进行了系统研究，对氧气电极反应过电势的起源进行了探讨，并提出了解决这一关键科学问题的可行方案<sup>[2-10]</sup>。

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## Functional Carbon-based Smart Hybrids for High-efficiency hydrogen production

Chang Yu (于畅), Jieshan Qiu (邱介山) \*

Liaoning Key Lab for Energy Materials and Chemical Engineering, Dalian University of Technology,

Dalian 116024 (P.R. China)

chang.yu@dlut.edu.cn; jqiu@dlut.edu.cn

Water splitting assisted by electricity has been regarded as a potential path for the production of clean, renewable H<sub>2</sub> fuel to power human civilization. Nevertheless, the efficiency and practical application of this process is often limited by the noble electrocatalysts adopted for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The two dimensional transition metal-based materials as one of the promising electrocatalysts have exhibited unique charms, while the efficiency is usually sacrificed by the limited accessible active sites and low conductivity. Herein, a series of carbon-integrated smart hybrids containing transition metal oxides, hydroxides, and their derivatives (oxyhydroxides and phosphides), were designed and configured for highly efficient OER and HER. The relationship between electrocatalytic activities and the intrinsic structure of the catalysts was discussed in terms of intrinsic microstructure and component of materials, and reaction process intensification. Benefiting from the highly exposed active sites and the modulated electrical structure, the as-made hybrids can deliver outstanding electrocatalytic activity and stability, which represents a novel class of electrocatalysts with low-cost and high electrochemical stability for water splitting.

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## 抗催化剂疲劳的流动电催化

周一歌<sup>\*1</sup>, Jiaxing Huang<sup>2</sup>, 康毅进<sup>3</sup>

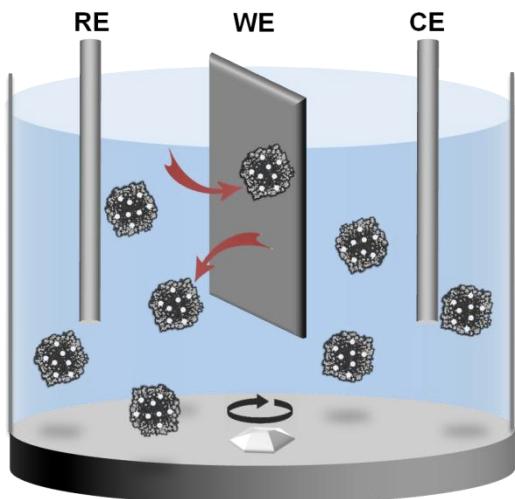
1.湖南大学化学化工学院; 湖南大学化学生物学与纳米医学研究所

2.美国西北大学材料与工程学院

3.成都电子科技大学基础与前沿研究院

yigezhou@hnu.edu.cn

在电催化中，催化剂无一例外都被固定在一个惰性电极上，如玻碳电极，而持续经受电化学压力。催化剂疲劳(催化性能衰减)是在电催化中的一个常见问题，表现为催化剂在电化学压力下的一系列退化机制。此项目拟采用流动电催化策略，以实现电催化剂的抗疲劳性能。在流动电催化中，催化剂不是固定在电极上，而是在电解液中流动。催化反应在每个单催化粒子与电极发生碰撞时发生，而多个粒子的碰撞集合将产生连续的、高度稳定的电化学电流。由于催化粒子现在是轮流工作的，所以它们避免了电化学压力的逐渐积累，这有助于抑制各种机制的催化剂退化。另外，流动催化剂也将促进更快的反应动力学和催化剂更有效的利用。甲醇氧化、氧析出和氢析出是三个重要的电催化反应，并具有不同的催化剂退化机制，本工作采用商业 Pt/C 催化剂验证了流动电催化确实对此三个反应均具有抗催化剂疲劳性能，可作为一种抗催化剂疲劳的普适方法。



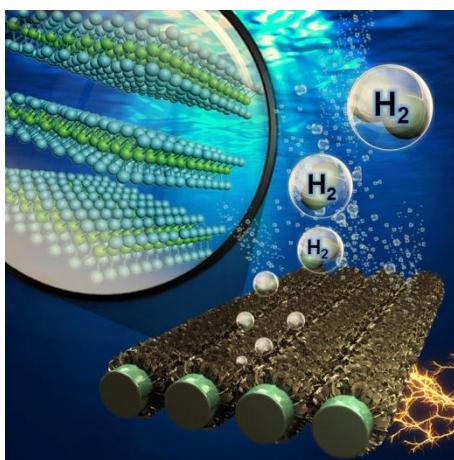
# 硫-硒基核壳纳米阵列的构建及其电催化应用

夏新辉

浙江大学，浙江省杭州市浙大路 38 号，310058

\*Email: helloxxh@zju.edu.cn

电催化产氢是一种极其有效的产氢技术，然而目前的贵金属Pt及Pt基合金催化剂因其低自然丰度和高昂价格限制了其工业化应用。硫硒化物（硒化钼和硫化镍、八硫化九钴等）是一种优良的非贵金属催化剂，但是上述块状粉末催化剂颗粒电导率偏低，且催化活性中心少导致电催化产氢效率低下。针对这些问题，我们通过无粘结剂核壳阵列化设计构建成分和形态可调的硫-硒基核壳纳米阵列如垂直石墨烯/硒化钼， $TiO_2/Co_9S_8$ 等。与通常的粉末材料，自支多元核壳纳米阵列催化材料具有无添加剂和粘结剂、更优异的一体化导电网络、可集成、高活性等优点，并可通过可控技术实现规模化生产。这些新型多元核壳阵列材料可望带来新的催化电极设计理念和高性能电化学器件构建。



**Fig. 1** Multiscale nanocarbon based arrays

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## 纳米结构电催化剂构建和性能研究

陈 卫\*

电分析化学国家重点实验室，中国科学院长春应用化学研究所，长春，中国，130022

Email: weichen@ciac.ac.cn

氧还原反应是燃料电池的阴极反应，与阳极上氢及其它燃料分子的氧化反应相比，由于氧还原反应动力学缓慢，严重降低了燃料电池能量转换效率。因此，近年来在燃料电池电催化领域，人们把更多的研究兴趣集中于阴极氧还原反应。迄今为止，人们设计了各种纳米结构电催化剂，包括零维纳米粒子，单原子催化剂，一维纳米线、纳米棒，二维纳米片，以及三维组装体及多孔材料等。催化剂材料包括贵金属，过渡金属氧化物、碳化物等，以及非金属材料，例如杂原子掺杂的碳材料。材料设计主要是基于提高催化剂的活性、稳定性以及降低贵金属负载量。虽然通过新型结构设计使得电催化剂的性能得到了很大提高，但是尚未达到商业化电催化剂的要求。在电催化材料领域，人们通过结构合理设计和可控制备，从而降低贵金属负载量及提高电化学活性。同时，如何提高稳定性也是电催化剂设计中需要考虑的一个重要因素。基于此，我们通过设计特定尺寸和晶面的电化学界面材料，研究界面结构对电催化性能的影响，一方面通过对原子排列结构明确金属团簇的可控合成和表面修饰，提高其电化学活性，探索和推动了金属团簇在电催化领域的应用；另一方面，利用基底对催化剂电子结构的调控作用，提高催化剂对小分子的电化学活性，从而提高其电催化性能。最近，我们通过表面结构设计，可有效提高纳米晶体的电化学稳定性及降低贵金属的负载量。

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## 钴基纳米催化剂的设计及其在锂-氧电池和电解水中的应用

张立学\*

青岛大学化学化工学院，青岛，266071

\*zhanglx@qdu.edu.cn

从基础研究和应用研究两个视角来看，设计并制备出具有低成本、高活性和高稳定性的电催化剂均是能源电催化研究的重要任务[1-2]。针对锂-氧电池阴极上缓慢的氧气还原反应(ORR)和氧气析出反应(OER)动力学过程，开发了 $\text{Co}_3\text{Mo}_3\text{N}$ 、 $\text{NiCo}_2\text{O}_4$ 纳米片等纳米结构催化剂，用作锂-氧电池的阴极催化剂后，都有效降低了电池的充放电极化、提高了循环稳定性；为深入研究该类催化剂的工作机制，利用电化学微分质谱技术，原位研究了基于 $\text{NiCo}_2\text{O}_4$ 纳米片催化剂的锂-氧电池的实时充放电过程。针对全水电解的OER及氢气析出反应(HER)，从结构调控及电子状态调控出发，设计并制备了 $\text{NiCo}_2\text{S}_4$ 纳米片和P掺杂 $\text{Co}_3\text{O}_4$ 纳米线阵列等钴基双功能催化剂，均表现出了较为优异的催化活性和稳定性。

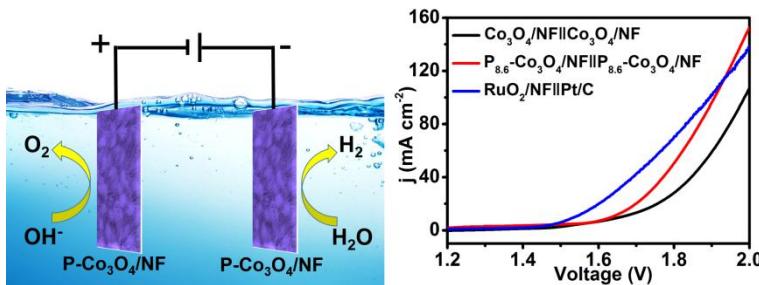


图 1. P 掺杂  $\text{Co}_3\text{O}_4$  纳米线阵列用作全水电解双功能催化剂

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## Rational design electrocatalysts of transition-metal based selenides toward low energy consumption

Chundong Wang\*

School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074 P.R.  
China

\*Corresponding Author's E-mail: apcdwang@hust.edu.cn

Exploring active, stable, earth-abundant, low-cost, and high-efficiency electrocatalysts is highly desired for large-scale industrial applications toward the low-carbon economy. In this talk, I will introduce versatile selenizing technology to synthesize Se-enriched  $\text{Co}_{1-x}\text{Fe}_x\text{Se}_2$ , “Cuju”-Structured  $\text{FeSe}_2$ , Ni-Fe diselenide hollow nanochains catalysts for oxygen evolution reactions (OERs) and disclose the relationship between the electronic structures of the precursor selenides catalysts and their OER performance. Besides, I will also talk a little bit about non-metal elements doping of electrocatalysts and interface engineering in boosting the catalytic performance.

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## 锂空气电池双效电催化剂的设计、表界面调控及构效关系研究

刘向峰\*

中国科学院大学，北京，中国，100049

\*liuxf@ucas.ac.cn

可充放的锂空气二次电池因具有高比容量（其理论比容量最大可达3828mAh/g）和高能量密度（800~1000 W h/kg）而受到了很大关注。但是，其缓慢的氧还原/氧析出（ORR/OER）反应动力学以及由此导致的严重极化、效率低、循环性能及倍率性能差等问题限制了锂空气电池的实际应用。因此，设计、开发具有氧还原/氧析出双重催化功能的高效电催化剂体系以促进ORR/OER进程，减小电极极化，提高循环稳定性和寿命，是目前锂空气电池亟待解决的关键问题之一。本报告将重点介绍课题组在锂空电池高效催化剂设计、表界面结构调控以及构效关系研究方面的最新进展，主要包括：晶面调控、氧缺陷、界面协同等材料设计策略及同步辐射原位X射线衍射、吸收谱、正电子湮灭、原位拉曼光谱等催化剂或产物结构分析手段的应用。此外，还将介绍基于非晶态超氧化锂转换反应的具有超低过电位和高倍率特性的新型锂-氧电池体系。

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# Structure Engineering Carbon Atomic-Scaled Metal-Nitrogen-Carbon Catalysts for Efficient Oxygen Electrocatalysis

Jianan Zhang\* Yingying Guo, Shiyu Guo

College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China. Emails:  
zjn@zzu.edu.cn (J. N. Zhang)

Single-atom catalysts (SACs) with monodispersed single atoms supported on solid substrates are recently emerging as an exciting class of catalysts that combine the merits of both homogeneous and heterogeneous catalysts. Herein, we introduce phosphorus (P) and boron (B) into the Co-N-C atomic active sites, which can achieve remarkable enhanced ORR, OER, and Zn-air battery. Significantly, the introduced B and P elements play an exciting role on improve electrocatalytic performance, that can active the electron transfer around the Co-N-C sites, strength the interaction with oxygenated species, and thus accelerate reaction kinetics in the 4e<sup>-</sup> processed ORR and OER. Theoretical calculations and controlled experiments further demonstrated that the coupling of Co-N<sub>x</sub> active sites with B and P atoms prefers to adsorb O<sub>2</sub> molecule in side-on mode and accelerates ORR kinetics.

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## 基于多孔配位聚合物的纳米复合材料制备与电催化性能研究

李光琴\*

中山大学，广州，中国，邮编：510275

liguangqin@mail.sysu.edu.cn

多孔配位聚合物(PCPs)又称金属有机骨架(MOFs)，与传统无机多孔材料相比，具有结构多样性、可设计性、孔径尺寸可控以及超大的比表面积等优点，其高度不饱和金属活性位点和较大的孔隙率使其可以应用于气体存储、催化、分离等。再者，由 MOFs 衍生的多孔碳材料不仅具有高的化学/热稳定性、良好的导电性、较高的比表面积，而且价格低廉。当向碳骨架中引入一些 N、P 等杂原子后，可以有效调节碳材料的电子结构和导电性，进一步优化性能，大大拓展了 MOFs 衍生材料在电催化领域的应用。近期，本课题组已制备部分 MOFs 与金属纳米颗粒的复合材料，并研究了其在常温常压下化学与物理性质。结果表明，与钯纳米颗粒相比，MOF(HKUST-1)与钯纳米颗粒的复合材料在室温下储氢性能大大提高<sup>1</sup>。我们以 MOFs 为前体制备非贵金属纳米多孔材料，该材料保留了 MOFs 固有的配位金属和杂原子，是潜在的高效、低成本的电解水电催化剂<sup>2</sup>。

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# 能源存储与转化电极材料的原子尺度及原位机制研究

王熙\*, 徐永

北京交通大学理学院, 北京市海淀区上园村 3 号, 100044

天津大学分子+研究院, 天津市南开区卫津路 92 号, 300072

\*Email: xiwang@bjtu.edu.cn

电化学能源存储与转化器件, 比如锂离子电池与燃料电池, 正越来越广泛的应用在当今生产生活的各个地方。然而, 电极材料中的存储与运输的微观机制不明晰, 是制约电化学器件性能改进的一个重要因素。原位透射电子显微镜测量技术, 是研究动态的微观过程最直接有效的手段。我们课题组采用原位电镜技术, 在高分辨透射电镜中原位构造锂离子电池的原型, 并对原型电池进行电化学充放电, 用高分辨电子显微术结合能谱分析技术实时地表征充放电过程中正负极电极材料的结构演变, 深入研究锂离子电池的微观工作机制, 对新型锂离子电池电极材料的探索提供实验上的指导<sup>[1-2]</sup>。此外, 鲜有对燃料电池电极机制的原子层面进行研究。因此, 我们在原位电镜中搭建 HER 以及 OER 单根纳米器件, 在原子层面上研究其电催化过程的机制, 为高性能的电化学能源存储与转化材料的设计提供指导。

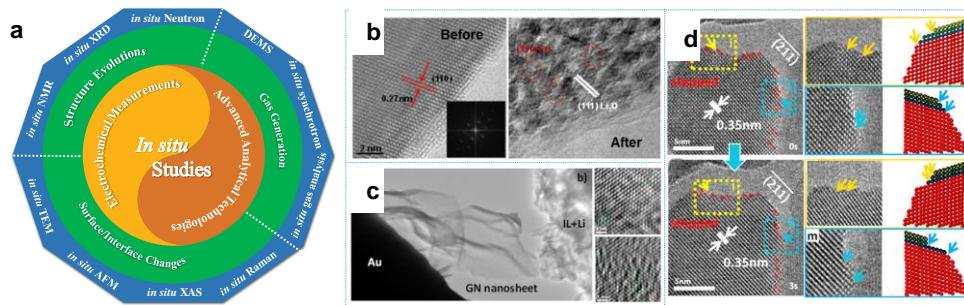


图 1 a) Various *in situ* techniques used in an *in situ* electrochemistry and b-d) unveiling the atomic-scale ion storage/release mechanisms by *in-situ* TEM.

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## 高效光电催化水分解系统

张兴旺\*, 金松, 雷乐成

浙江大学化学工程与生物工程学院, 浙江杭州, 310027

威斯康星大学麦迪逊分校化学系, 麦迪逊, 美国

Email: xwzhang@zju.edu.cn

光电催化由于较少使用有机溶剂、条件温和, 被认为是绿色催化技术, 是很有前景的水分解制氢技术。高效光电催化电极是提高光电催化效率的关键, 主要有两个关键科学问题: 如何构建高效异质结构光电催化电极, 实现光生载流子的有效分离? 如何制备非贵金属高效电催化剂, 实现光生载流子的高效催化利用? 申请人针对上述关键科学问题, 从材料的设计和制备入手, 系统开展了高效半导体异质结和高效电催化剂的研究: 通过电催化剂合成方法学的创新, 开发了一系列高效非贵金属电催化剂(如金属硫族化合物、氧化物), 极大提高了电催化的效率, 特别是水分解制氢、释氧的效率; 利用电沉积等温和方法, 构建了高效半导体-催化剂系统, 改善半导体表面催化反应动力学, 而且有效减少了界面缺陷。上述成果不仅提高了光电催化水分解制氢的效率, 而且对于构建半导体-催化剂界面提供了新的策略。

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## 基于电池电极的分步法电解水

陈龙, 候孟研, 董晓丽, 夏永姚, 王永刚\*

复旦大学化学系, 能源材料化学协同创新中心, 上海 200438

\*Email: ygwang@fudan.edu.cn

采用可再生能源, 如太阳能、风能等来电解水制氢则被认为是最有效、最可靠的制氢方法之一。然而, 传统的电解水制氢的工作原理是基于阴极析氢反应(HER)和阳极析氧反应(OER), 离子交换膜(或多孔膜)则需要用来分隔两极, 避免氢/氧混合, 这大大限制电解水的灵活性, 同时限制了间歇且不稳定的可再生能源在电解水制氢的直接利用。近期, 我们课题组首次采用商业化的  $\text{Ni}(\text{OH})_2$  电池电极作为固体氧化还原电对 (即固体的电子-耦合-质子缓存体), 将碱性电解水分隔成连续的制  $\text{H}_2$  步骤和制  $\text{O}_2$  步骤, 实现了无膜条件下的分步电解水制氢<sup>[1]</sup>。由于,  $\text{Ni}(\text{OH})_2$  电极具有良好的可逆性和充放稳定性, 制  $\text{H}_2$  和制  $\text{O}_2$  可以分时循环交替进行。此外, 由于  $\text{NiOOH}$  电极良好的自放电稳定性, 该体系还有望实现  $\text{H}_2$  和  $\text{O}_2$  的分地制备。最近, 我们课题组采用  $\text{Na}_{0.44}\text{MnO}_2$  电极的可逆钠离子嵌入脱出反应作为氧化还原对, 成功实现了常规氯碱工艺的分步法电解, 即产氢和产氯分步进行<sup>[2]</sup>。此外, 课题组还首次采用固体有机物电极的 p-型掺杂/脱掺杂反应, 实现了酸性条件下的无膜分步法电解制  $\text{H}_2$ <sup>[3]</sup>。本文将详细总结课题组在分步法电解水方面所取得的研究进展。

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## 设计合成纳米多孔碳球及在能量转换和储存中的应用

刘健\*

中国科学院大连化学物理研究所，辽宁省大连市沙河口区中山路 457 号，邮编 116023

\* Email: jianliu@dicp.ac.cn

在本报告中，我将介绍我们最近在先进多孔碳球合成与应用方面所取得的进展。我们开发并合成了具有高分散的、规则孔径和方向、可控比表面积及表面结构特性的纳米孔结构碳球（包括新型微孔碳球，介孔碳球，核壳和蛋黄壳碳球等多孔结构<sup>[1]</sup>）。（1）我们发展了制备单分散聚合物球的策略，包括酚醛（RF）树脂和“Stöber”碳<sup>[2]</sup>。（2）通过使用不同的功能化前体及后修饰方法，通过自下而上的自组装策略制备了改性的碳球<sup>[3,4]</sup>。利用这种方法，我们合成了尺寸均一，壳层厚度可调的碳@金属，碳@二氧化硅，金属@碳，二氧化硅@碳或金属氧化物@碳材料材料。（3）将介孔二氧化硅纳米球的合成方法拓展到有序介孔间苯二酚纳米球的制备<sup>[7]</sup>。（4）构建了一系列金属纳米粒子（Au, Pt, Rh, Ru, Ag, Pd, Ir, Fe and Cu）负载或限域的炭球基纳米反应器，在苯甲醛氢化反应中表现出极好的活性、选择性及稳定性。

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## The Electrocatalysis Activity of Metal Coordination Polymer toward Hydrogen Evolution Reaction: A DFT Study

Huiying Yao<sup>1</sup>, Xing Huang<sup>2</sup>, Wei Hao<sup>3</sup>, Shuzhou Li<sup>3</sup>, Jia Zhu<sup>1,\*</sup>, Wei Xu<sup>2,\*</sup>

1 Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry,  
Beijing Normal University, Beijing 100875

2Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190

3School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798

\* E-mail: zhu.jia@bnu.edu.cn, wxu@iccas.ac.cn

A family of coordination complexes based on MX<sub>4</sub> (M=Fe, Co, Ni, Cu, *et al.*, X=S, N, Se, *et al.*) structure exhibits satisfied electrocatalysis activities toward hydrogen evolution reaction (HER). It has been shown that the introduction of MX<sub>4</sub> structure into the coordination polymer catalyst with rigidity framework can promote the electrochemical activities. Among them, the ligand benzenehexathiol (BHT) and transition metal Cu<sup>1</sup>, Co<sup>2</sup> and Ni<sup>3</sup> formed different coordination polymers: Metal-BHTs, which have attracted our interests. We investigated the effect of metal and coordination structure of Metal-BHTs on their electrocatalysis activity toward HER by DFT. We found that Metal-BHT with porous structure possess higher activity than that with a dense topological structure without obvious pores and Ni-BHT is of the highest activity. The relationship between electrocatalysis activity and M-BHTs structures have been studied through exploring the Gibbs free energy change of hydrogen adsorption<sup>4</sup> and their electronic structures.

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## 反尖晶石结构 $\text{Co}(\text{Co}_{2-x}\text{Fe}_x)\text{O}_4/\text{NCNTs}$ 复合电极的制备及应用

刘兆清\*, 王孝通, 黄灿, 肖抗

广州大学, 广州, 中国, 510006

lzqgzu@gzhu.edu.cn

锌空气电池的理论能量密度高( $1218 \text{ Wh/kg}^{-1}$ )、电极材料来源低廉、安全性高，在可再生资源能源储存及下一代储能领域中具有巨大的应用潜力。<sup>[1-4]</sup>然而，目前缺乏高效的空气正极材料。其关键问题在于正极缓慢的氧还原反应(ORR)动力学过程，该过程涉及到了固、液、气三相界面反应。与其它大多数只需要考虑两相的电极相比，研究和开发中面临着更大的挑战。贵金属材料作为空气扩散电极，有着较好的 ORR 活性，电阻小等优势，但成本较高且稳定性较差。尖晶石氧化物虽然具有较好的 ORR 活性，但因为电阻较高， $\text{OH}^-$ 脱附速度慢传质过程缓慢。在这项工作中，我们从传质与传荷两个过程出发，设计了一种反尖晶石结构的  $\text{Co}(\text{Co}_{2-x}\text{Fe}_x)\text{O}_4/\text{CNTs}$  复合材料，制备过程如图 1 所示。反尖晶石结构的  $\text{Co}(\text{Co}_{2-x}\text{Fe}_x)\text{O}_4$  氧化物有着低的电化学传荷电阻和高的氧还原活性；一维的空心结构的纳米管基底有利于提高电极材料的利用率和电导率以及  $\text{OH}^-$  脱附速率。电化学测试结果显示，该复合电极材料组成锌空电池测试最大功率密度可达  $91.6 \text{ mW cm}^{-2}$ ，经过 100 次充放电循环之后，库伦效率仍有 65%。

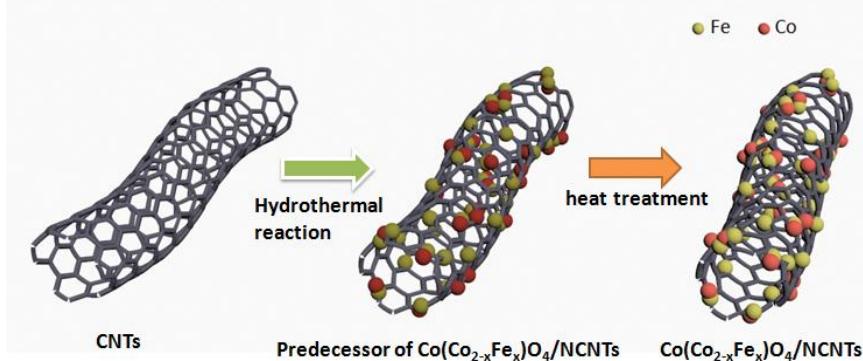


图 1  $\text{Co}(\text{Co}_{2-x}\text{Fe}_x)\text{O}_4/\text{NCNTs}$  复合材料的合成示意图

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## 碳基电催化材料的设计构建及原位球差电镜研究

林岳 1\*, 韩敏 2, 熊胜林 3

1 中国科学技术大学, 合肥微尺度物质科学国科学家研究中心, 230026;

2 南京师范大学, 化学与材料科学学院, 210023;

3 山东大学, 化学与化工学院, 250100;

\*通讯作者: 林岳, Emial: linyue@ustc.edu.cn

球差电镜技术作为表征纳米材料的原子结构、电子结构、元素分布和三维构型的重要利器, 尤其是其空间分辨率能够达到亚埃尺度的优势, 在表征催化剂的结构、理解结构与性能的关联性上, 具有越来越重要的应用。我们通过对碳基底和负载物的构型调控, 制备了基于二维、三维碳框架的复合材料。在二维碳体系中, 我们将双原子 Pt 和富缺陷的 Ni<sub>3</sub>FeN 纳米颗粒分别生长在二维石墨烯上<sup>(1, 2)</sup>, 发现双原子 Pt 的构型和 Ni<sub>3</sub>FeN 纳米颗粒中的缺陷结构对于催化活性的提高具有重要作用。在三维碳体系中, 我们制备了三维氮掺杂碳框架包裹的 MnO@Mn<sub>3</sub>O<sub>4</sub> 的核壳结构和掺氮石墨烯包裹的层状 TiO<sub>2</sub> 结构<sup>(3, 4)</sup>, 利用原子分辨高角环形暗场像 (HAADF-STEM) 和电子能量损失谱 (EELS) 等技术表征了该样品。两种材料用于锂离子和钠离子电池正极材料, 分别达到了 1500 mA h g<sup>-1</sup> 和 0.2 A g<sup>-1</sup> 下循环超过 270 次和 146 mA h g<sup>-1</sup> 和 5 C 条件下工作 8000 个循环, 116 mA h g<sup>-1</sup> 和 20 C 条件下循环超过 10000 次。此外, 我们利用球差校正电镜在原子尺度下研究了 Cu 纳米颗粒在石墨烯上的原位生长过程, 观察到了从 Cu 原子到单晶 Cu 和孪晶 Cu 的成核和生长过程。发现生长过程中, 优先生长面随着生长阶段发生改变, 例如{111} 和 {100} 面是初期生长面, 后期则是{011} 和 {100} 面优先生长。除此之外, Cu 纳米颗粒的表面生长伴随着瞬态的表面结构变化, FCC 结构的{111} 面会瞬时变为 HCP 结构。原位过程的观察, 从原子尺度揭示了纳米材料的生长过程, 提高了对人们对生长过程的认识。

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## IrMn/Fe<sub>3</sub>Mo<sub>3</sub>C 作为高性能的 ORR/OER 双功能催化剂

崔志明\*, 杜丽, 章本天

广东省燃料电池技术重点实验室, 华南理工大学化学与化工学院, 广州天河区五山路 381 号 邮编: 510641

\*Email: zmcui@scut.edu.cn

可充电金属-空气电池具有超高的能量密度被认为是最有发展前景的能源存储与转换装置之一, 例如锌-空气电池和锂-空气电池。空气电极中氧还原/析出 (ORR/OER) 反应动力学缓慢, 过电位高是影响金属-空气电池充放电速率、能量效率和循环寿命的关键因素。目前, 制备双功能 (ORR/OER) 催化剂的策略主要有两种, 一种是碳负载贵金属基催化剂; 另一种是碳/过渡金属氧化物复合材料。这两类材料均用碳作为载体和导电材料, 但是, 碳材料在高电位和碱性环境中易发生电化学氧化腐蚀结果导致催化性能的衰减。在本研究中, 我们设计发展了以双金属碳化物 (Fe<sub>3</sub>Mo<sub>3</sub>C) 作为基体, 负载纳米IrMn合金的复合材料作为新型双功能催化剂。Fe<sub>3</sub>Mo<sub>3</sub>C不仅仅可以作为稳定的导电支撑材料, 还具有良好的ORR催化活性, 超小粒径的IrMn合金具有优异的OER活性。以IrMn/Fe<sub>3</sub>Mo<sub>3</sub>C为双功能催化剂的锌空电池展示了极好的循环稳定性, 100小时的充放电测试, 过电位仅增加9.7%, 远低于以Pt/C+Ir/C为催化剂的锌空电池 (42.6%)。

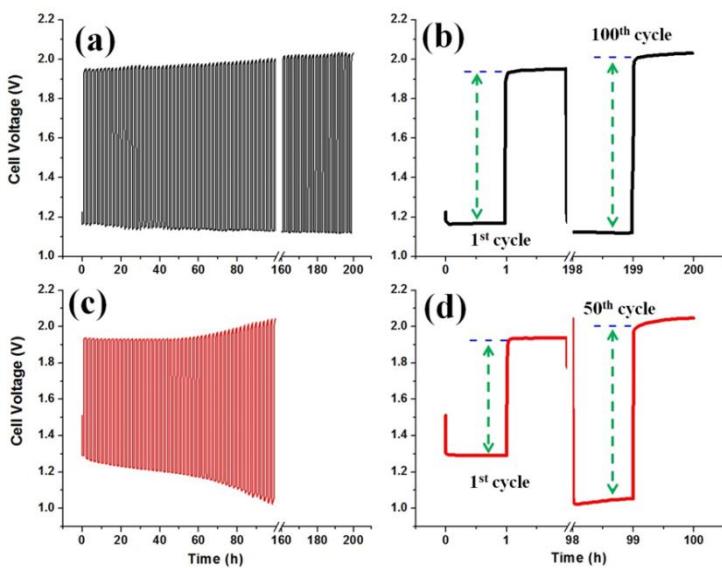


图1 (a, b) 以IrMn/Fe<sub>3</sub>Mo<sub>3</sub>C为催化剂的锌空电池充放电曲线; (c, d) 以常规Pt/C + Ir/C为催化剂的锌空电池充放电曲线。

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## 电输运谱在电化学表界面原位表征中的应用

丁梦宁<sup>1,2\*</sup>

1 南京大学化学化工学院, 江苏省南京市栖霞区仙林大道 163 号, 210023

2 介观化学教育部重点实验室, 江苏省南京市栖霞区仙林大道 163 号, 210023

\*mding@nju.edu.cn

新型原位表征技术的发展和在此基础上对于催化表界面现象的深入理解和研究, 对认识催化过程中界面原子间相互作用的微观细节, 从而提出新的反应机理和对催化过程的调节机制, 进一步提高催化材料的活性和性能, 有着极其重要的意义。结合微纳电子器件制备及测量手段, 我们在芯片反应平台的基础上实现了一种基于纳米材料电学性质测量的新型原位化学信号获取技术, 即电输运谱 (Electrical Transport Spectroscopy, ETS)。由于在介观尺度上载流子的量子限域作用, 纳米催化材料的导电性质对其表面化学状态表现出超高的灵敏性和特异性。催化剂表面吸附/成键所带来的载流子 (如自由电子等) 表面散射的改变, 可以显著地影响材料本身的电学性质。电输运谱借助这一原理, 在 (原位获得的) 电学测量信号与催化过程中的表界面化学信息之间建立了定量联系, 从而实现了对催化表界面进行原位表征和研究的目的。这种全新原位测量技术在机理上不同于所有传统光谱表征技术, 从本质上避免了这些技术的共性缺陷。基于微纳电子器件测量的特点, 电输运谱 (ETS) 具有取样量小, 实验设备简单, 仪器成本低, 测量精度高, 匹配电化学测量体系并易于原位测量等优点, 其信号具有高度的表面灵敏性和选择性, 从根本上解决了传统光谱表征技术中常见的技术难题。我们在此展示运用电输运谱 (ETS) 对纳米金属 (铂) 催化剂在催化重要电化学反应 (包括过氧化氢的氧化还原, 甲醇氧化和甲酸氧化反应) 过程的表界面化学研究。通过电输运谱 (ETS) 的原位表征和机理研究, 成功的获取了新的原位表界面化学信息, 为燃料电池相关的电催化反应的机理研究, 和未来清洁能源催化剂的进一步发展, 提供了新的理解、研究思路和表征工具。此外, 电输运谱 (ETS) 技术也被初步应用于其他研究领域, 包括金属材料传感器的优化, 二维材料物理性质的电化学调控及电催化研究, 以及表征和探索生物燃料电池中微生物细胞模型的工作原理。

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# A Universal Descriptor for Large-Scale Screening of High Performance MXene-based Materials for Energy Storage and Conversion

Jia Lia\*, Wei Jiang<sup>a</sup> Xiaolong Zou<sup>b</sup>

<sup>a</sup> Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, People's Republic of China

<sup>b</sup> Tsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, Shenzhen 518055, People's Republic of China

Density functional theory calculations are employed to systematically investigate the trend of hydrogen evolution reaction (HER) performance of oxygen-terminated MXenes. By studying 30 transition-metal carbides and 30 transition-metal nitrides,  $M_{n+1}C_nO_2$  and  $M_{n+1}N_nO_2$  ( $M = Sc, Cr, Hf, Mo, Nb, Ta, Ti, V, W, Zr; n = 1, 2, 3$ ), the tendency of oxygen desorption after hydrogen adsorption is elucidated to play a key role in HER performance of oxygen-terminated MXenes. Based on these observations, we propose a suitable HER descriptor, oxygen vacancy formation energy ( $E_f$ ), which scales linearly with the adsorption free energy of hydrogen,  $\Delta G_H$ . In addition, this new descriptor is linearly correlated with the lithium binding strength on oxygen-terminated MXenes. Therefore,  $E_f$  is a universal descriptor for identifying the trend of adsorption processes where adsorbed species donate electrons to oxygen-terminated MXenes. This work provides a general guideline for large-scale screening of promising MXene-based materials for energy storage and conversion.

# 非晶 NiFe 氧化物中的局域短程结构及在电催化产氧反应中的动态行为

干林\*

清华大学深圳研究生院，能源环境学部，深圳，中国，518055

\*Email: lgan@sz.tsinghua.edu.cn

过渡金属氧化物，尤其是Ni-Fe（羟基）氧化物、钙钛矿以及尖晶石等，在碱性或中性条件下表现出优异的析氧催化性能，作为非贵金属催化剂引起人们的广泛兴趣。近年来，非晶氧化物因表现出比晶态氧化物更好的产氧催化性能而逐渐得到关注。<sup>1,2</sup>同时，原位谱学电化学研究报道，一些晶态氧化物催化剂<sup>3</sup>在OER反应过程中其表面转变成非晶，这种非晶结构才是OER真正的活性结构。非晶材料具有长程无序和短程有序的特点，但目前对结构上的认识仅局限于衍射实验（如X射线、电子衍射等）中表现出的长程无序结构，对短程结构的认识很少；此外，由于非晶在热力学实际上是一种亚稳相，非晶氧化物本身在OER过程中是否存在动态结构变化也不得而知。

本文，我们报道一种简单、高效合成双金属非晶氧化物的微波溶剂热法，采用此法合成了具有可控成分的Ni-Fe非晶氧化物，显示出很高的OER催化活性和稳定性。利用X射线衍射、拉曼光谱和高分辨透射电子显微镜，我们发现这种非晶氧化物具有长程无序而短程类尖晶石结构的特点，且Fe的含量对短程有序结构有显著影响。利用原位拉曼光谱分析，进一步研究了非晶的短程结构在析氧反应过程中的动态结构变化，表明不同成分的Ni-Fe非晶氧化物表现出完全不同的结构变化行为。这些结果有助于深入认识非晶氧化物中局域短程结构及其对产氧电催化性能的影响。

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# Graphene and Other Two-Dimensional Nanosheets: Exfoliation, Dispersion and Application in Electrocatalysis

Zhenyu Sun\*

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029,

China

[zhenyus@mail.buct.edu.cn](mailto:zhenyus@mail.buct.edu.cn)

Nanosheets are materials that have a quasi-two-dimensional (2D) nanostructure composed of less than ~ 10 stacked monolayers.<sup>[1]</sup> Remarkable changes in electronic and optical properties occur when the thickness of such layered materials is reduced to a single layer or few layers. This provides new opportunities to engineer 2D nanosheets for energy conversion, electronics, and catalysis.<sup>[2,3]</sup> Another important feature is the specific surface area created when bulk material is thinned to few layers. To fulfill their potential applications, production of high-quality 2D nanosheets in a cost effective industrial scale needs to be achieved. Direct exfoliation of layered materials (interlayer cohesive energies  $\leq 200$  meV per atom) in an appropriate liquid appears to be a promising route.<sup>[4,5]</sup> Such top-down approaches have a number of advantages in that they are versatile, facile to operate, insensitive to environmental conditions, and easily scalable. The colloidally stable sheets obtained typically comprise a small number of stacked layers ( $\leq 10$ ) that can be sorted and separated to yield desirable sizes and thicknesses. The cartoon in Fig. 1 illustrates the essence of physical exfoliation.

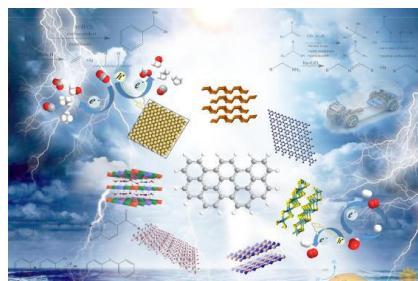


Figure 1. Schematic of two-dimensional nanosheets for applications in catalysis.

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# Phosphonate-based Metal-Organic Frameworks for Oxygen Reactions

Tianhua Zhou\*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter

Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

\*Corresponding Author's E-mail: thzhou@fjirsm.ac.cn

Oxygen reactions, including the oxygen evolution reaction (OER) and oxygen reduction reaction, are critical reactions for electrochemical renewable energy conversion and storage such as fuel cells and water electrolysis. Both reactions are kinetically sluggish, leading to the requirement of highly active catalysts to achieve high efficiency. Currently, various low-cost catalysts have been developed as alternatives to noble metal catalysts for the OER and ORR; however, the nature of the activity for oxygen reactions still remains as a daunting challenge. Recently, we systematically investigate phosphonate-based metal-organic frameworks (MOFs) and their derived hybrids as highly efficient catalysts for the OER and ORR. Our observations unveil that the flexible phosphate group not only serves as proton management but also adopts diverse structures, which tune the catalytic active sites and change the reaction pathway during catalysis. These studies not only demonstrate the potential of the low-cost OER catalysts derived from phosphonate-based MOF but also open a promising avenue into the exploration of highly active and stable catalysts toward replacing noble metals as oxygen electrocatalysts.

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## Heavy Oil Based Carbon Nanomaterials for Electrocatalysis

Hui Liu, Jingyan Liu, Zhongtao Li, Mingbo Wu\*

State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum,  
Qingdao 266580, China.

\*Corresponding Author's Email: wumb@upc.edu.cn

Environmentally friendly and renewable energy technologies, such as fuel cells, batteries, and water splitting, hold great promise for solving current energy and environmental challenges. The three seemingly simple reactions-the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER)-pose great scientific challenges for the development of efficient catalysts for clean and renewable energy technologies. Here, we demonstrated our recent progresses on the catalysts derived from heavy oil for the ORR, OER and HER.

A novel supramolecular polymerization-mediated N/S co-doped porous graphene networks (N,S-PGN) was synthesized from petroleum coke. Benefiting from compositional and structural advantages, N,S-PGN offers a remarkable ORR performance with an extremely positive onset potential, high limiting current density and excellent long-term durability in alkaline environments. Nitrogen-doped carbon dots (N-CDs) was synthesized by a simple electrochemical approach from petroleum coke. The N-CDs was then introduced into the in-situ growth of Ni<sub>3</sub>S<sub>2</sub>, and the self-standing NCDs/Ni<sub>3</sub>S<sub>2</sub>/NF electrode showed superior performance for overall water splitting. A novel nitrogen-doped carbon dots/graphene (NCDs-NG) composite was also constructed for ORR. The synergistic effects, i.e. CDs as pillars for graphene and catalytic sites for ORR, the high conductivity of graphene, the quick O<sub>2</sub> adsorption on doped pyridinic nitrogen endow NCDs-NG composites with superior ORR catalytic performance.

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## 自支撑纳米多孔金属的制备及其电催化性能研究

李晓克, 刘静, 杜芳林, 姜鲁华\*

青岛科技大学, 材料科学与工程学院

山东省青岛市郑州路 53 号, 266042

Email: luhujiang@qust.edu.cn; homepage: jiang.qust.edu.cn

自支撑纳米多孔金属由于其具有连续孔道、良好的导电性和较高的比表面积, 作为电极在电池和催化领域应用前景广阔。本报告将报导课题组近年来在自支撑纳米多孔金属的制备及应用方面的进展。主要包括: 发展了一种电化学制备自支撑多孔纳米金属的绿色、原子经济的方法, 制备的纳米多孔 Ag、Cu 等对燃料电池氧还原反应、甲醛电氧化、CO<sub>2</sub>电还原等反应均具有良好的催化活性, 通过分析制备条件对产物形貌等的影响探讨了多孔结构形成的机理, 结合 DFT 理论计算研究了催化作用机制<sup>[1]</sup>; 在上述电化学法制备纳米多孔金属的基础上, 通过调变溶液中阳离子种类, 发展了利用微电池原理自发反应制备纳米多孔金属的方法, 该方法降低了能耗, 提高了效率<sup>[2]</sup>。上述工作为制备自支撑纳米多孔金属提供了思路。

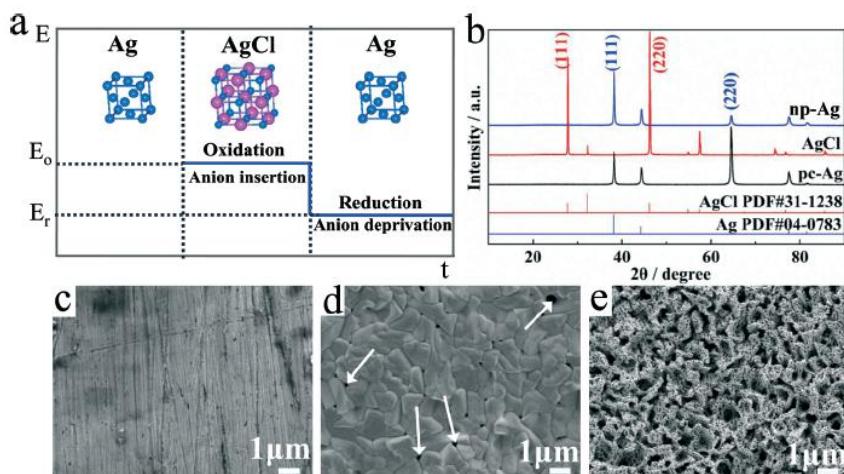


Fig. 1 (a) Scheme of electrochemical preparation of nanoporous metals. (b) The XRD patterns of the starting material: silver sheet (Ag), silver sheet after electro-oxidation (AgCl) and further electro-reduction (np-Ag). (c–e) SEM images of Ag (c), AgCl (d) and np-Ag (e).

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## 异原子掺杂碳作为锌空气电池电催化剂的研究

郑祥俊, 吴娇, 曹学成, 孙志辉, 陈鑫, Peter Strasser, 杨瑞枝\*

苏州大学, 苏州, 215006

\*yangrz@suda.edu.cn

可充电锌-空气电池作为一种新型的二次电池具有能量密度高、成本低和环境友好等特点，在便携式电子产品、通讯设备和电动汽车等领域具有广泛的应用前景；然而，空气电极缓慢的电化学动力学性能限制了其实际应用。催化剂的使用能够有效解决以上问题，通过纳米材料的合理设计，制备高效、环保和低成本的氧气还原（ORR）和氧气析出(OER) 反应的双功能催化剂成为锌-空气电池研究与发展的核心。

我们采用具有不同键合环境的含 P 离子液体和含 S、N 离子液体合成了 N, P, S 掺杂石墨烯，研究了掺杂石墨烯的结构、表面积、导电性和掺杂种类等对 ORR 和 OER 催化性能以及锌空气电池性能的影响。尤其对 N, P 和 S 的键合环境对材料电化学性能的影响进行了深入讨论。X-射线光电子能谱（XPS）和密度泛函理论（DFT）研究表明，高催化活性位的暴露、O<sup>\*</sup>、OOH<sup>\*</sup>和 OH<sup>\*</sup>的化学吸附、降低的电荷转移阻抗以及 2D 结构是其活性提高的重要原因。

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# 口头报告

## 金属有机框架材料直接作为电极阴极材料催化氧化水

廖培钦\*, 张杰鹏\*, 陈小明

中山大学化学学院, 广东省广州市, 中国, 510275

\* E-mail: liaopq3@mail.sysu.edu.cn, zhangjp7@mail.sysu.edu.cn

电化学氧气析出反应 (OER) 是许多可再生能源系统如水分解和金属-空气电池的核心过程。要提高目前 OER 效率, 即降低 OER 过电位, 需要高效的催化剂和强酸碱性环境。传统的 OER 催化剂集中于金属或者金属氧化物。由于大多数 MOF 材料的导电性和化学稳定性都比较差, 因此不被认为是一种具有前景的 OER 催化剂。我们基于氯离子  $\text{Cl}^-$ , 过渡金属 M(II), 和苯并双三氮唑阴离子构筑了一类化学稳定性很高的结构 MAF-X25/MAF-X27。例如, 暴露在孔表面的 M(II)可以被氧化成 M(III)-OH, 用于高效催化氧化烷烃芳基或湿润条件捕获  $\text{CO}_2$ 。最近申报人发现含有 Co(II)的这种 MOF 可以在 pH=14 的条件下作为 OER 电化学催化剂。有趣的是, 申报人发现该  $\text{OH}^-$ 配体可以在碱性条件下将 MOF 中的  $\text{Cl}^-$ 离子配体完全交换, 提供了能垒较低的框架内耦合路径, 极大提高了 OER 电催化活性, 在 pH=14 水溶液中  $10 \text{ mA cm}^{-2}$  对应的过电位可以低至 292 mV, OER 性能远高于绝大多数的传统无机催化材料, 证明了金属-有机框架在该研究领域具有应用前景。

上述工作启发我们 MOF 的金属离子配位环境对其 OER 性能具有很重要的影响作用。钴离子的配位环境通常有四面体配位、三角双锥五配位以及八面体的六配位。而平面四边形配位钴离子则仅在 MOF 中发现。双核钴簇中的钴离子的配位方式为平面四边形配位, 其配位轴向位置天生喜欢配位小分子的习性说明其具有非常好的催化活性, 不过其稳定性比较差, 极难获得。最近我们通过模块构筑策略成功将双核钴簇固定到 MOF 中, 获得一例目前电催化析氧活性最好的催化剂, 在 pH=13 水溶液中  $10 \text{ mA cm}^{-2}$  对应的过电位可以低至 225 mV, 其性能远高于作为标杆的贵金属催化剂。

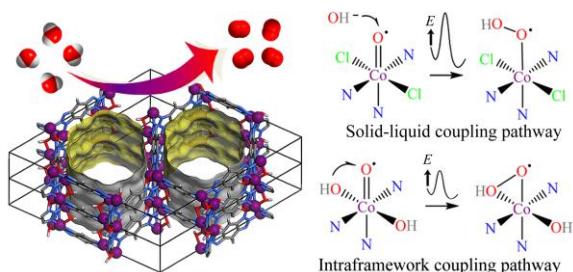


图 1. MAF-X27-OH 作为电极阴极材料催化氧化水

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# 锌-空电池氧气电极反应碳基非贵金属催化剂

刘希恩\*, 李平, 王帅

青岛科技大学化学与分子工程学院, 青岛市郑州路 53 号, 266042

\*E-mail: liuxien@qust.edu.cn

锌-空电池的能量密度高及安全性强, 使其成为化学电池一个热门分支。研究人员已经制备和研究了大量的非贵金属或无金属氧还原电催化剂<sup>[1]</sup>, 本文归纳了几种改进氧气还原性能的方法, 包括利用合金<sup>[2]</sup>, 混合金属氧化物以及一种富磷酸碳基底支持的多孔 FePON 中空球新型催化剂, 催化剂的形貌和结构见 SEM 和 TEM in Figure 1。在碱性介质中显示了优异的电催化氧还原性能, 半波电势相对于可逆氢电极为 0.91 V。该催化剂用于催化锌-空电池正极氧还原反应, 电池比电容达到 640 mAh g<sup>-1</sup> (Figure 2), 该研究提供一种新的非贵金属催化剂制备方法, 具有潜在应用前景

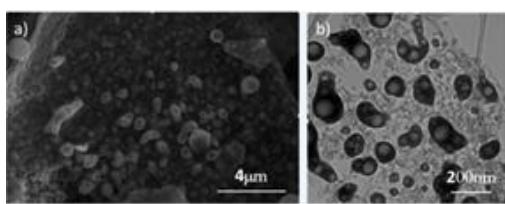


Fig. 1 a) SEM images of FePON/C. b) TEM image of FePON/C.

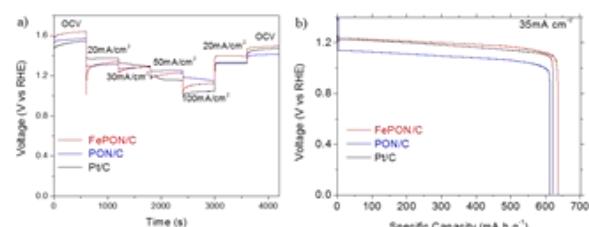


Fig. 2 a) Discharge curves of Zn-air batteries assembled from the FePON/C, PON/C and Pt/C catalysts at 35 mA cm<sup>-2</sup> discharging rate in 6 M KOH b) Rate discharge curves of zinc-air batteries using FePON/C, PON/C and Pt/C as cathode catalysts

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## 氧化亚铜催化二氧化碳还原的理论与实验探究

赵志坚\*, 杨漂萍, 常晓侠, 巩金龙\*

天津大学化工学院 天津化学化工协同创新中心 天津 300072

\* E-mail: zjzhao@tju.edu.cn, jlgong@tju.edu.cn

利用可再生能源在水溶液中将二氧化碳转化为化石燃料是解决全球能源危机与环境问题的有效手段之一。在铜基催化剂中, 氧化亚铜催化剂不仅可以将  $\text{CO}_2$  转化为更具价值的碳氢的产物, 并且能够抑制析氢副反应, 从而提高含碳产物的选择性。但由于  $\text{Cu}_2\text{O}$  在水溶液中的自腐蚀比较严重, 导致其表面结构复杂, 活性位点性质难以预测。因此缺乏对  $\text{Cu}_2\text{O}$  催化剂的理论指导与理性设计。将  $\text{Cu}_2\text{O}$  催化剂作为暗阴极, 可以获得稳定的  $\text{CO}_2$  还原的活性与选择性。为了深入理解  $\text{Cu}_2\text{O}$  催化性能的本质, 本文利用密度泛函理论探究了部分还原的  $\text{Cu}_2\text{O}(111)$  表面上  $\text{CO}_2$  还原反应。通过建立不同羟基覆盖度的表面, 发现较高的羟基覆盖度可以抑制析氢副反应, 但是  $\text{CO}_2$  还原活性较低; 当羟基覆盖度较低时, 析氢副反应将成为主要的反应, 从而降低了含碳产物的选择性。具有适中的羟基覆盖度的  $\text{Cu}_2\text{O}$  催化剂则可以既可以抑制析氢副反应又能获得较高的  $\text{CO}_2$  还原活性。在实验上制备了不同还原程度的氧化亚铜并测试其二氧化碳还原的活性与选择性, 表现出的趋势与理论预测的结果一致。

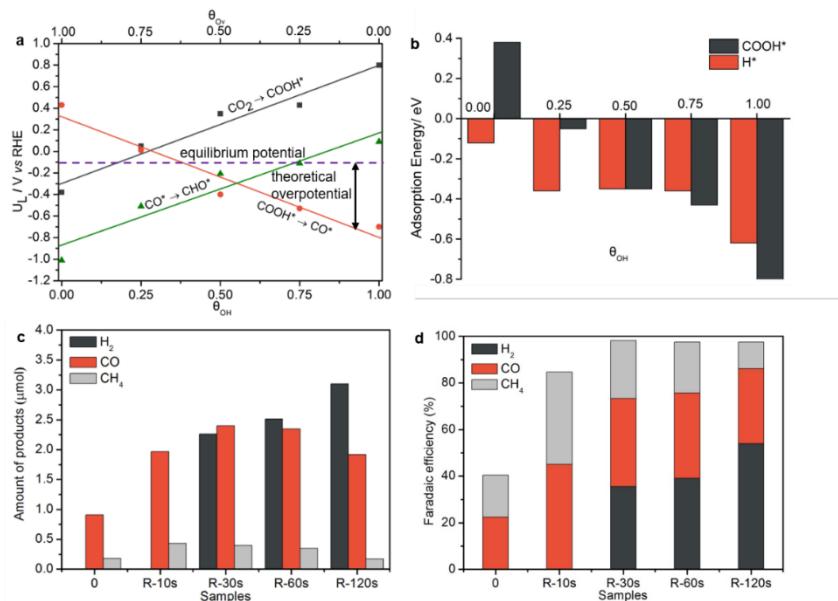


图 1 (a) 随羟基覆盖度变化的活性趋势 (b)随羟基变化的选择性趋势 (c) 不同还原程度的氧化亚铜上各产物的物质的量 (d) 不同还原程度的氧化亚铜上个产物的法拉第效率

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## Pt、Pd 和 Au 催化剂上低元醇的电催化氧化行为研究

周春梅\*（报告作者），王贝，杨艳辉

南京工业大学先进化学制造研究院，南京，中国，510000

\*ias\_cmzhou@njtech.edu.cn

本工作主要选择了甲醇、乙醇、正丙醇（正一元醇）以及乙二醇、甘油（满多元醇）在单金属 Pt、Pd、Au 电极上的电催化氧化活性规律进行研究。

图 1 左，除甲醇在 Au 电极表面无氧化峰外，各种醇类底物均能在 Pt、Pd、Au 电极表面发生氧化并产生氧化峰。Pd 和 Au 氧化各种醇类的峰电流相近，而 Pt 产生的峰电流略高于 Pd 和 Au，表明 Pt 有更高的醇类催化活性。而正丙醇的峰电流异常减小，一方面由于 C-C 键比 C-H 和 C-O 键的断裂更困难，另一方面过长的烷基链容易位阻作用，底物与催化剂活性位点的碰撞变得困难。

图 1 右，Pt 催化的起始电位：甲醇 < 乙醇 < 正丙醇，甲醇更容易被氧化；Au 催化的起始电位：甲醇 > 乙二醇 > 甘油，甘油更容易被氧化。Pd 催化剂规律与 Pt 相反。分析原因，Pt 在碱性介质中，醇类优先脱去质子生成醛类；烷基为给电子基团，随着链的增长，质子的脱去更为困难；而羟甲基是吸电子基团，所以甘油的羟甲基比甲醇和乙二醇更易脱去质子而被氧化。Pd 在碱性介质中氧化醇类的反应路径与 Pt 不同，醇类主要选择性地被氧化成对应的羧酸盐，因而 Pd 与 Pt 规律正好相反。

在 Pt 和 Pd 电极上，几种正一元醇的碳数越大，越容易发生氧化，但在几种满多元醇上的规律并不明显；而在 Au 电极上，不管是对正一元醇还是满多元醇，都是碳数越大，越难发生氧化。

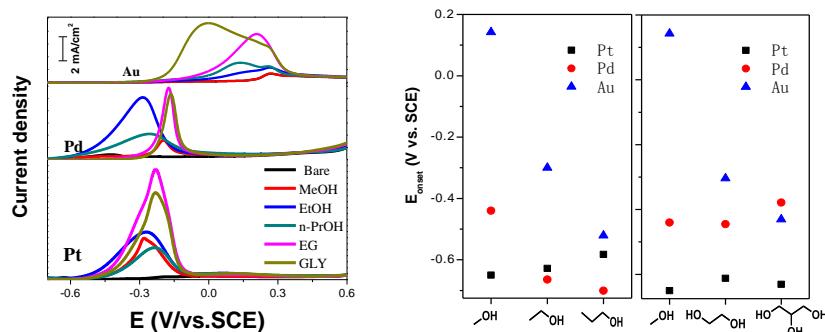


图 1. 不同醇类底物在铂、钯、金电极上催化氧化的 CV 曲线图（左）及其氧化起始电位（右）

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## 金属磷化物的电催化析氢

张星, 王瑞虎\*

中国科学院福建物质结构研究所, 福州, 350002

\*ruihu@fjirsm.ac.cn

氢气是理想的化学能源载体和许多重要化工产品的原材料。开发廉价、高活性、可循环使用的催化剂是电催化分解水制氢的关键。金属磷化物是一种有应用前景的氢气析出催化剂材料, 构筑特殊纳米结构和形貌的磷化物纳米结构以增加暴露表面催化活性位点、提高反应过程中的电荷转移及传质速率是提升催化性能一种重要的手段。我们致力于发展新型的合成方法构筑多孔、高结晶度和高稳定性的磷化物纳米催化材料, 发展在酸性、中性和碱性等电解质中高效稳定的电催化体系。

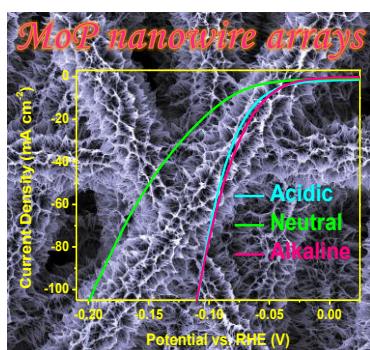


图 1 碳纤维纸负载有序 MoP 纳米线阵列的电催析氢性能

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## 基于超分子金属水凝胶的杂合气凝胶催化剂

何庭, 吴慧琼, 谭敏力, 马静, 张翼\*

中南大学化学化工学院

E-mail: yzhangcsu@csu.edu.cn

在前期研究基础上, 将已知的几种响应单一过渡金属离子的小分子金属凝胶进一步与不同的过渡金属依次配位, 制备了一系列双金属水凝胶。将双金属水凝胶本身作为自支撑模板, 氮源及碳源, 经过原位水热处理后得到了具有良好导电性的杂合气凝胶。此类气凝胶由于均匀复合了 C-M-N 核心的单簇结构 (2 nm-5 nm), 表现出来了优异的氧还原 (C-Co-Fe-N)、二氧化碳 (C-Co-Cu-N) 还原及良好的固氮性能 (C-Ru-Co-N)。这种超分子双金属凝胶作为模板原位合成双金属杂合气凝胶的方法无需外加模板, 而且配位基团可以有效防止活性位点聚集。由于不同金属离子之间的距离和摩尔比例可调, 因此能够较好地形成  $1+1>2$  的协同效应。制备方法简单, 符合绿色化学的要求, 可以大规模制备, 成本较低廉。

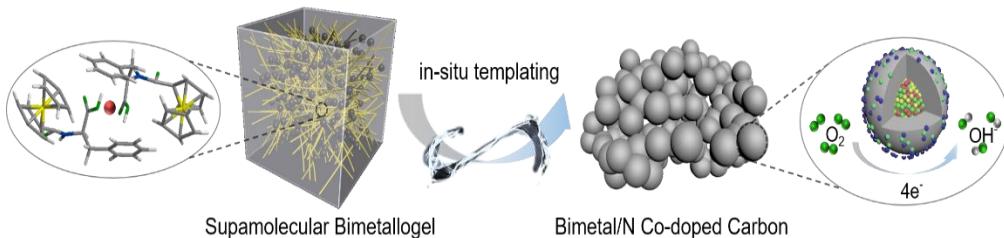


图 1. 杂合水凝胶的制备示意图

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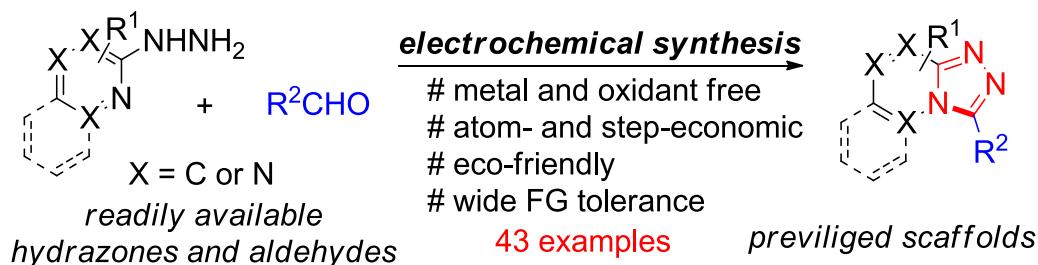
## Electrochemical Synthesis of 1,2,4-Triazole-Fused Heterocycles

Zenghui Ye, Mingruo Ding, Yanqi Wu, Yong Li, Wenkai Hua and Fengzhi Zhang\*

Zhejiang University of Technology, Hangzhou, P. R. China, 310014

\*Corresponding Author's E-mail: zhangfengzhi@zjut.edu.cn

A reagent-free intramolecular dehydrogenative C–N cross-coupling reaction has been developed under mild electrolytic conditions.<sup>1</sup> In this atom- and step-economic one-pot process,<sup>2</sup> valuable 1,2,4-triazolo[4,3-a]pyridines and related heterocyclic compounds could be synthesized efficiently from commercially available aliphatic or (hetero)aromatic aldehydes and 2-hydrazinopyridines.<sup>2</sup> Various functional groups are compatible with this metal- and oxidant-free protocol which can be carried out on gram scale easily. This novel method was applied to the synthesis of one of the top selling drugs Xanax and late stage functionalization for generating chemical diversity of biologically relevant lead molecules.



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## N掺杂石墨烯量子点的制备及C、N对ORR的不同催化作用

赵红<sup>1\*</sup>（报告作者），何晓寒<sup>1</sup>，丁伟元<sup>1</sup>

<sup>1</sup> 大连交通大学，大连，中国，116028

Email: zhaohong@djtu.edu.cn

采用Hummers法制备氧化石墨烯(GO)，再利用尿素水热反应制备N掺杂石墨烯，表示为N-G(X)，其中X=15、25、35、50，依次代表GO与尿素的质量比。最后通过酸化氧化、透析等手段得到N掺杂石墨烯量子点(N-GQDs)<sup>[1,2]</sup>。GO和N-G都是单层薄纱状，GO平整无褶皱，N-G边缘卷曲褶皱可能由于氮原子掺杂进所致。N-GQDs粒径范围在5~8 nm，分散均匀不易团聚。N-G出现了明显的C、N双键和单键的振动峰，且以吡啶N，吡咯N和石墨化N的方式与二维石墨烯网结合。N-G和N-GQDs都对ORR有催化活性，其中N-GQDs(35)表现出较好的催化活性，还原反应为3.45电子过程，即四电子过程占主导地位。随着N量的增加，出峰位置右移；而电流密度则正比例于C的含量。

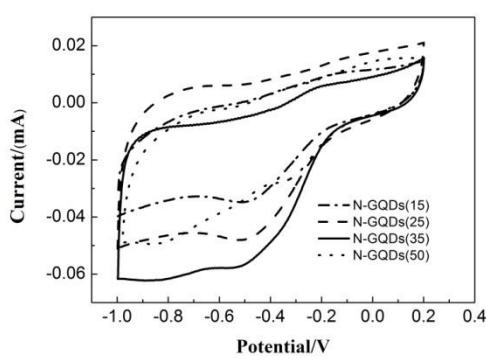


图1 N-GQDs(15)、N-GQDs(25)、N-GQDs(35)、N-GQDs(50)的CV表征结果

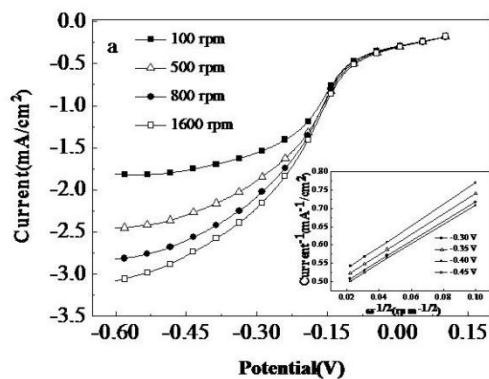


图2 不同转数下N-GQDs(35)的线性扫描结果（在O<sub>2</sub>饱和的0.1 M KOH介质中）。其中插图是K-L拟合结果

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## 非贵金属 Co 基催化剂的原位合成及其电化学应用研究

尹振<sup>1\*</sup>, 高建<sup>1</sup>, 郑玉梅<sup>1</sup>

天津工业大学环境与化工学院, 天津, 中国, 300387

\*yinzheng@tjpu.edu.cn

以钛基膜作为膜电极, 开发出一维金属氧化物可控原位负载方法, 将一维Co<sub>3</sub>O<sub>4</sub>纳米线均匀负载于钛基膜, 制备高效的钛基电催化膜电极, 并以此为基础构建电催化膜反应器(图1左)。与钛基膜和负载Co<sub>3</sub>O<sub>4</sub>纳米颗粒的钛基膜相比, 负载Co<sub>3</sub>O<sub>4</sub>纳米线的钛基膜电极的催化性能和稳定性都大幅提高, 而且在醇类选择性氧化反应中显示出优异的催化活性和选择性。

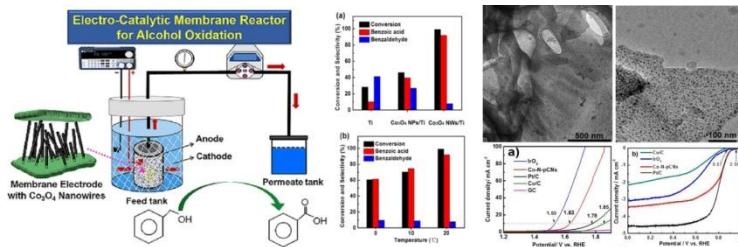


图 1. 双功能碳纳米片负载 Co 基催化剂(左); Co<sub>3</sub>O<sub>4</sub> 纳米线负载钛基膜电极及其催化醇类氧化反应(右)

通过设计和合成具有特定官能团的离子液体, 以此作为前驱体, 成功地制备出一系列 N掺杂的碳基负载 Co 基催化剂, 在 ORR 反应中显示出优异的催化性能。其中 N 掺杂的多孔碳纳米片, 不但具有类石墨烯的片层结构, 而且 Co 基纳米粒子负载量高且分散均匀, 在 ORR 和 OER 反应中均显示出优异的催化性能, 如图 1 (右) 所示。

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## 4-羟基-3-氯苯甲酸甲酯的电合成研究

李媛，李国华\*

浙江工业大学化学工程学院，浙江杭州，中国 310032；

\*E-mail: nanozjut@zjut.edu.cn

4-羟基-3-氯苯甲酸甲酯是重要的化工中间体，常用于制备医药、防腐等领域的卤代芳香衍生物。传统化学方法通过添加二氯亚砜或盐酸/双氧水来制备目标产物<sup>[1-2]</sup>，但存在反应时间长，“三废”污染严重等问题。本文以尼泊金甲酯为原料，铂为工作电极，铜为辅助电极，盐酸为支持电解质，在H型双室电解槽中采用恒电流电解法成功制备了4-羟基-3-氯苯甲酸甲酯，系统探讨了有机溶剂种类，反应温度和电流密度对电氯化效果的影响。结果表明，尼泊金甲酯在恒温30℃和恒电流密度0.11 A cm<sup>-2</sup>的甲醇-盐酸混合液中反应，产率高达83.2%，电流效率为26.8%，产物选择性良好。这为4-羟基-3-氯苯甲酸甲酯的合成指明了可行的技术途径。

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# 一种基于磷化钼量子点双功能催化剂的锂-空气电池

魏明会，金超\*，杨瑞枝

苏州大学能源学院/能源与材料创新研究院，江苏苏州，中国，215006

\*E-mail: jinchao@suda.edu.cn

在二次电池中，锂-空气电池（LABs）是最有希望替代锂离子电池的储能元件。锂-空气电池具有可与汽油相媲美的理论比能量，作为未来电动汽车的理想动力电源，受到广泛关注。一直以来，LABs 中较低的 ORR 和 OER 反应动力学限制了 LABs 的充放电比容量、倍率性和长期稳定性。因此，开发具有高比容量和循环寿命长的 LABs 的 ORR 和 OER 双功能催化剂对促进优化相关电池技术及其商业化发展至关重要<sup>[1]</sup>。

本研究我们选用 PPy 空心纳米纤维作为前驱体，经过水热反应和高温磷化退火，在 N,P 共掺杂空心碳纤维上均匀原位生长 MoP 量子点催化剂，并制作无粘结型 MoP QD@HCF 膜电极，探讨其对 LABs 性能的影响。

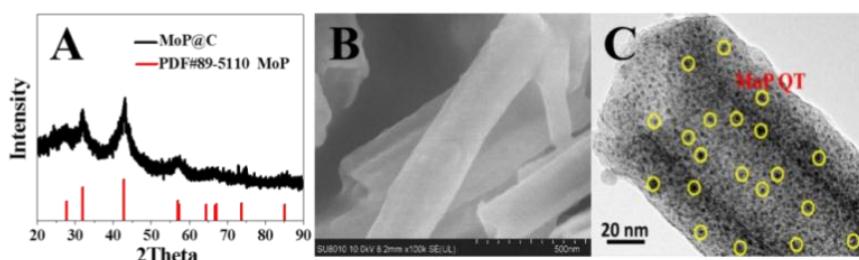


图 1 MoP QD@HCF 的 XRD 图 (A)；SEM 图 (B)；TEM 图 (C)

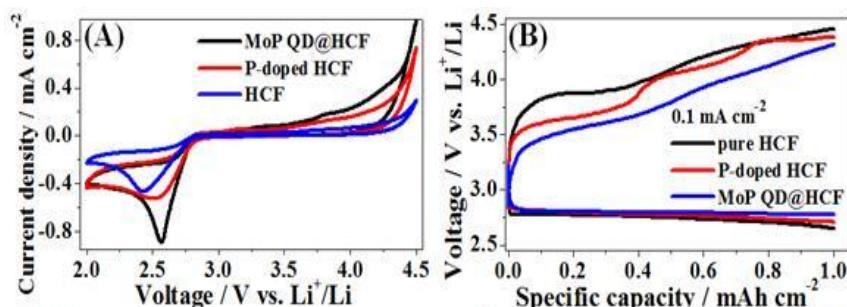


图 2 HCF、P-doped HCF 和 MoP QD@HCF 三种空气电极组装 LOBs 的电化学性能

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# Selective electrochemical reduction of CO<sub>2</sub> by binder-free and flexible nitrogen-doped carbon catalysts with remarkable efficiency and reusability

Chuanxin He

Shenzhen University

During the last few decades, atmospheric CO<sub>2</sub> amount has reached the highest level of the last 20 million years, causing a series of unpredictable climate changes. Converting CO<sub>2</sub> to useful products is an attractive proposal to mitigate these issues and simultaneously obtain useful chemical products. Nitrogen-doped carbon materials have great potential in electrochemical reduction of CO<sub>2</sub>. Unfortunately, these materials are almost entirely powder-based, which always involve the utilization of polymer binders, causing mechanically weakness and recycling difficulty in electrolysis.

This report is based on the direct electrospinning of N-doped carbon nanofibers, embedding with metal nanoparticles, onto flexible substrate (like copper foil or carbon cloth). The as-synthesized composite could be named as Pt-NPs@NCNFs@Cu-foil or Pt-NPs@NCNFs@CC. Importantly, these flexible substrates were used as the conductive collecting substrate in the electrospinning process and mechanical support for the fragile nanofibers. Pt-NPs@NCNFs@Cu-foil could be directly used as cathode for electrochemical reduction of CO<sub>2</sub> in aqueous solution, without any binder or extra carrier. Formate with 96% Faradaic efficiency or alcohols with 35% Faradaic efficiency could be obtained at -0.5 V<sub>RHE</sub> or -0.9 V<sub>RHE</sub> using the same Pt-NPs@NCNFs@Cu-foil cathode, respectively. Pt-NPs@NCNFs@CC could catalyze CO<sub>2</sub> direct reduction into formate with 91% Faradaic efficiency and CO<sub>2</sub> carboxylation with halides into 2-phenylpropionic acid with 99% yield. What's more, these catalysts also have excellent recyclability and reusability, which might have practical applications in the future.

## Identification of Active Sites in 1T'-MoS<sub>2</sub> for HER

Yifu Yu\*, Yuting Wang, Bin Zhang

Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China.

\*Corresponding Author's E-mail: yyu@tju.edu.cn

MoS<sub>2</sub> has been proved as efficient HER electrocatalysts, but the further progress in performance is hampered by the challenges how to clearly identify the function of different factors during catalysis process. Previously experimental and computational studies have proved that the active sites locate along the edge of 2H-phase MoS<sub>2</sub>, so numerous follow-up works are focused on increasing the density of active edge sites over the inert basal planes in semiconducting 2H-phase MoS<sub>2</sub>.<sup>1</sup> Recent studies have shown that the introduction of metallic phase can efficiently improve the electrocatalysis activities of MoS<sub>2</sub>, nevertheless, interpretations of the enhanced performance still remain controversially. Herein, we prepare metallic-phase 1T'-MoS<sub>2</sub> bulk crystals, which are designed and processed to different electrocatalytic devices based on individual MoS<sub>2</sub> nanosheet. We find that the basal planes of 1T'-MoS<sub>2</sub> are catalytically active for HER, even superior to edge sites of 2H-MoS<sub>2</sub>. Moreover, the ohmic junction between 1T'-MoS<sub>2</sub> and metal electrode does enhance the catalytic performance through promoting the charge transport to the active sites. Importantly, the active basal planes make more contribution than low-resistance contact to improved electrocatalysis activities in 1T'-MoS<sub>2</sub>.<sup>2</sup> We anticipate that our design strategy will open up a new avenue for development of high efficient electrocatalysts for important yet challenging reactions, especially once the mechanism of catalysis reaction is contentious.

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## Direct synthesis of Porphyrin Covalent Organic Framework for Efficient Oxygen Electrocatalysis

Bo-Quan Li, Shu-Yuan Zhang, Xiang Chen, Chen-Yu Chen, Zi-Jing Xia, and Qiang Zhang\*

Department of Chemical Engineering, Tsinghua University, Beijing, China, 100084

\*Corresponding Author's E-mail: zhang-qiang@mails.tsinghua.edu.cn

The discovery and application of new energy materials impulse the development of sustainable energy for the modern society. Controllable synthesis of the rationally designed energy materials at *the atomic level* has always been the holy grail in regards of both science and practical application. Covalent organic frameworks (COFs) constructed by infinite repulsion of organic structural units connected by covalent bonds serve as desired molecular materials for energy storage and conversion.

Herein, we designed and synthesized a porphyrin covalent organic framework (POF) to demonstrate its advances in chemistry and electrocatalysis. A direct synthesis methodology is proposed as a guidance for bulk synthesis of COF by using simple and low cost feedstocks, employing simple operations, and producing materials with high quality, output, and yield. POF was one-pot synthesized under the direct synthesis methodology, with an output of 2.17 g and a yield as high as 95%. The as-synthesized POF exhibits unique two-dimension (2D) layered structure and further demonstrates versatility in composition, structure, and morphology, affording nanocarbon POF hybrids, and transition metal coordinated POFs.

The cobalt coordinated graphene-POF hybrid (named as G@POG-Co) serves as an excellent electrocatalyst for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline electrolyte. The ORR reactivity of G@POF-Co is super high with an half-wave potential being 0.81 V vs RHE, close to the state-of-art Pt/C electrocatalyst. The overpotential at 10.0 mA cm<sup>-2</sup> for OER is only 430 mV for G@POF-Co. The bifunctional performance of G@POF-Co is excellent with the potential gap being 0.85 V and among the best noble-metal-free bifunctional electrocatalysts. POF presents the ability to synthesis and control materials *at the atomic level* for advanced sustainable energy. More molecular materials are coming from the POF family to serve as emerging platform for the future sustainable world.

# Regulating p-block metals in perovskite nanodots for efficient electrocatalytic water oxidation

Bo-Quan Li<sup>1</sup>, Zi-Jing Xia<sup>1</sup>, Bingsen Zhang<sup>2</sup>, Cheng Tang<sup>1</sup>, Hao-Fan Wang<sup>1</sup>, and Qiang Zhang<sup>1,\*</sup>

<sup>1</sup>Department of Chemical Engineering, Tsinghua University, Beijing, China, 100084

<sup>2</sup>Shenyang National Laboratory for Material Science, Institute of Material Research, Chinese Academy of Sciences, Shenyang, China, 110016

\*Corresponding Author's E-mail: zhang-qiang@mails.tsinghua.edu.cn

Water oxidation represents the core process of many sustainable energy systems, such as fuel cells, rechargeable metal-air batteries, and water splitting. Material surface defects with high-energy hanging bonds possess superb intrinsic reactivity, whose actual performance is limited by the dimension and conductivity of the electrocatalyst. Perovskites are a family of defect-abundant materials and exhibit excellent oxygen evolution reaction (OER) reactivity. However, the perovskite defects are in body phase dominantly, which cannot function during practical OER process.

Herein, we proposed a surface defect-rich perovskite electrocatalyst through a *p*-block metal regulation concept to achieve high performance for OER. *P*-block metals possess a dual nature of metallicity and non-metallicity that can dissociate as soluble coordination complexes under certain conditions. As a typical *p*-metal, Sn<sup>4+</sup> dissolves from solid model SnNiFe perovskite nanodots during electrochemical activation, resulting in abundant surface defects and superior water oxidation performance. The activated perovskite electrocatalyst exhibits the overpotential required for 10.0 mA cm<sup>-2</sup> to be 350 mV in alkaline electrolyte, which is comparable to the state-of-art IrO<sub>2</sub> electrocatalyst. An oxygen pool model is therefore proposed that the amorphous oxygen surface after electrochemical activation is more inclined to reactant fusion and product evolution. Therefore, the strategy of *p*-block metal regulation reported herein not only proves to be effective and rational for constructing surface defect-rich highly active electrocatalysts, but also helps to tackle critical issues in multi-electron oxygen electrocatalysis.

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## Tuning selectivity of oxygen reduction by isolated active site

Yizhong Lu\*, Yuanyuan Jiang, Pengjuan Ni, Chuanxia Chen

School of Materials Science and Engineering, University of Jinan, Jinan 250022, China

\*Corresponding Author's E-mail: mse\_luyz@ujn.edu.cn

The isolated active sites can be effectively tune the activity and selectivity for electrochemical reactions<sup>[1]</sup>. Here, by using the single-Pd atom doped Au<sub>25</sub> nanoclusters as catalysts (Pd<sub>1</sub>Au<sub>24</sub>), surprising high selectivity (95% at 0.5 V vs RHE) toward hydrogen dioxide production from oxygen reduction and excellent activity and stability were achieved.<sup>[2]</sup> The present study not only provide a new strategy to design single-atom catalysts but also help us to understand the interaction between the structure and observed properties of catalysts.

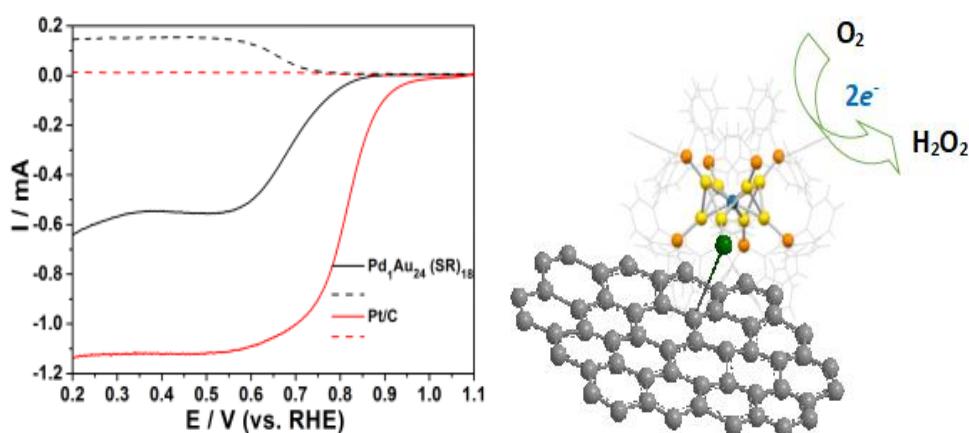


Figure 1. left) RRDE voltammograms at 1600 rpm in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$ . Ring potential: 1.2 V vs RHE. right) Mechanism illustration of  $\text{H}_2\text{O}_2$  production from selective two-electron oxygen reduction.

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# Electrochemical production of lactic acid from glycerol oxidation catalyzed by AuPt nanoparticles

Chencheng Dai<sup>1,2</sup>, Adrian C. Fisher<sup>2,5</sup>, Zhichuan J. Xu<sup>1,2,3,4\*</sup>

1. School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

2. The Cambridge Centre for Advanced Research and Education in Singapore, 1 CREATE way, Singapore 138602, Singapore

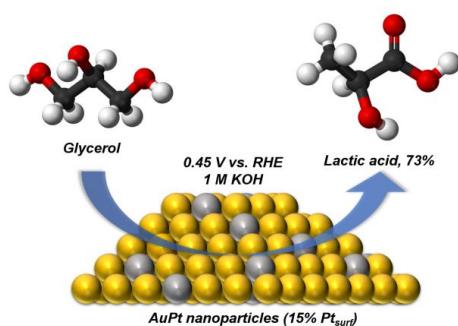
3. Solar Fuels Laboratory, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

4. Energy Research Institute @ Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

5. Department of Chemical Engineering and Biotechnology, University of Cambridge, New Museum Site, Pembroke Street, Cambridge CB2 3RA, UK

\*Corresponding Author's E-mail: [xuzc@ntu.edu.sg](mailto:xuzc@ntu.edu.sg)

The production of valuable chemicals from relatively inexpensive feedstocks utilizing electrochemical methods has been attracting widespread attention in recent years since it is highly efficient, decentralized, environmental-friendly and can operate in room temperature and pressure. Currently, the industrial production of lactic acid is mainly based on bio-fermentation, leading to drawbacks including severe conditions, unfriendliness to environment, low efficiency and requirement of expensive equipment, which can potentially overcome by electrochemical methods. Herein, we report the electrochemical production of lactic acid from glycerol at room temperature and pressure. The selectivity for lactic acid can be achieved > 70% on AuPt nanoparticles with a controlled surface composition. Lower oxidation potentials promoted the formation of lactic acid, and the Au-enriched AuPt bimetallic catalyst showed an optimal performance, with the highest lactic acid selectivity and glycerol conversion. Additionally, the glycerol conversion was found to be tunable by varying the electrolyte pH, glycerol concentration, and reaction time, in addition to the applied potential and catalyst surface composition.



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# 墙报

## Fe掺杂NiSe<sub>2</sub>多孔纳米片的电催化析氢性能

高大强\*, 王彤彤

兰州大学, 兰州市, 730000

\* E-mail: gaodq@lzu.edu.cn

寻找低成本、高效能、性能稳定的析氢反应电催化剂一直以来都是广大研究者工作的焦点。过渡金属硒化物是一类很有前景的析氢反应电催化剂, 研究者们也提出了通过掺杂和调节形貌等方法来提高其电催化效率。因此, 我们通过两步水热法在碳布上生长了多孔的Fe掺杂的NiSe<sub>2</sub>纳米片, 对该样品的电化学测试结果表明, 与无掺杂NiSe<sub>2</sub>纳米片相比, Fe元素的掺杂大大提高了样品的析氢反应电催化效率。具体来说, 在较低的过电位(64 mV)下, Ni<sub>0.8</sub>Fe<sub>0.2</sub>Se<sub>2</sub>电催化剂可以实现 10 mA cm<sup>-2</sup>的电流密度, 并且具有长期稳定性。另外, 第一原理计算显示, 掺杂的Fe原子不但可以激发掺杂位点周围Ni和Se原子的电催化活性, 而且可以增强NiSe<sub>2</sub>的导电性, 因此能够有效地提高材料的电催化析氢性能。此外, 我们进一步的计算结果预测了其他过渡金属掺杂的NiSe<sub>2</sub>的电催化活性。通过过渡金属掺杂来提高NiSe<sub>2</sub>的电催化析氢性能的策略为设计和合成其他低成本、大规模电化学能源应用开辟了道路。

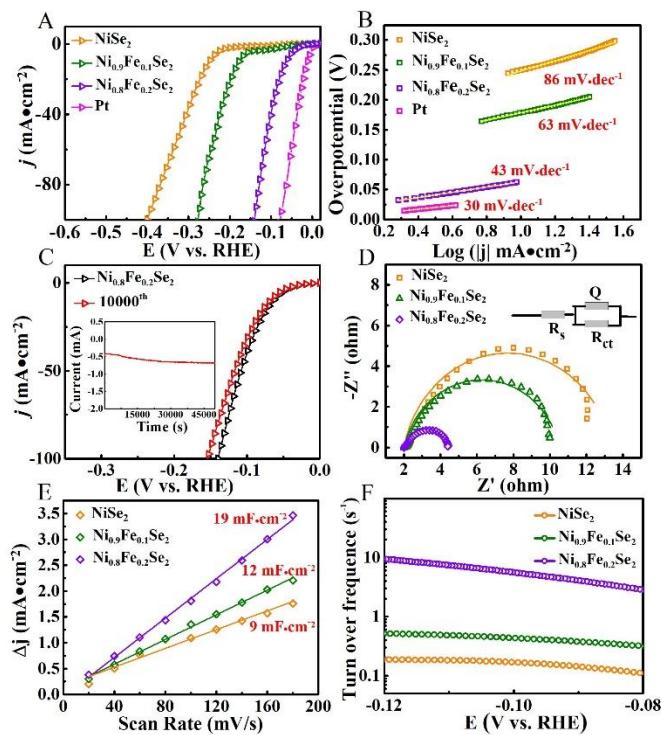


图 1. Ni<sub>x</sub>Fe<sub>1-x</sub>Se<sub>2</sub>/CFC 样品的电催化析氢性能

## 凤眼莲 ORR 生物碳电极的制备和性能研究

梁珈祥, 汤迪勇, 黄丽, 陈伊妃, 孙杰\*

中南民族大学资源与环境学院 武汉 430074

\* E-mail: jetsun@mail.scuec.edu.cn

本实验通过使用凤眼莲生物质经过氯化锌熔盐碳化后制成电极, 与商用的石墨粉进行对比, 研究其 ORR 产过氧化氢和电芬顿降解内分泌干扰物 DMP 性能。通过 BET 测试可知经过熔盐碳化之后其比表面积是石墨粉的 30.1 倍。从高分辨 N 1s XPS 分析结果可知, 凤眼莲生物质碳材料拥有丰富的 ORR 反应活性位点吡啶氮和石墨氮。从 Warburg 常数计算可得知其拥有最强的离子传输效率, 从 LSV 测试结果可知其有最佳的 ORR 电催化活性。过氧化氢浓度反应 30 min 后达到  $5.09 \text{ mmol L}^{-1}$ , 是石墨粉的 5.0 倍。DMP 反应 10 min 的降解率达 95.84%, 反应动力学常数为  $0.318 \text{ min}^{-1}$ 。

# 聚多巴胺纳米管衍生一维铁-氮-碳高效氧还原催化剂的制备与性能研

## 究

唐峰, 金朝霞\*

中国人民大学化学系, 北京, 100872

\* E-mail: jinzx@ruc.edu.cn

燃料电池被视为可替代传统化石燃料的高效且可再生的能源储存器件, 在近些年受到科学界越来越多的关注。氧气还原反应(ORR)是燃料电池负极的重要反应, 其高效催化剂的研究对于推动燃料电池的发展起到至关重要的作用<sup>[1]</sup>。氧还原催化剂的形貌及组成对其催化性质有着极大的影响。一维多孔碳材料有着独特的形貌优势, 如较大的比表面积, 易形成导电网络, 较高的活性位点密度, 快速质量传递等, 有利于提高氧气还原催化活性。而在组成方面, 氮原子掺杂将会进一步增强碳材料的催化活性: 一方面通过加强氧还原过程中的电子传递和质量传递; 另一方面, 所形成的金属-氮-碳被视为高效的催化活性中心位点, 有利于催化反应的动力学过程。因此, 作为氮杂碳材料的前驱体, 聚多巴胺纳米涂层在氧还原催化剂中有着广泛应用。<sup>[2]</sup>

在本研究中, 我们使用多孔聚多巴胺纳米管-铁离子复合物作为前驱体, 通过高温热解大量制备了一维 Fe-N-C 氧还原催化剂<sup>[3]</sup>。多孔聚多巴胺纳米管不仅可以作为良好的氮源与碳源, 而且由于其与 Fe<sup>3+</sup>的配位作用, 在高温烧结后 Fe-N 活性位点有着均匀的分布, 同时在 Fe/Fe<sub>3</sub>C 颗粒表面形成了厚度合适的石墨碳层有效防止了颗粒的聚集。催化剂良好的一维多孔形貌和杂化组成使其在碱性条件下展现出与商业活性炭负载铂催化剂相当的氧还原催化效果, 同时还具有优异的稳定性和抗甲醇性质。这种基于聚多巴胺纳米管的氧还原催化剂有望在燃料电池中得到广泛应用。

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# A strongly coupled CoS<sub>2</sub>/ reduced graphene oxide nanostructure as an anode material for efficient sodium-ion batteries

Kongyan Xie<sup>a</sup>, Wei Zhou<sup>a\*</sup>, Zongping Shao<sup>b,c\*</sup>

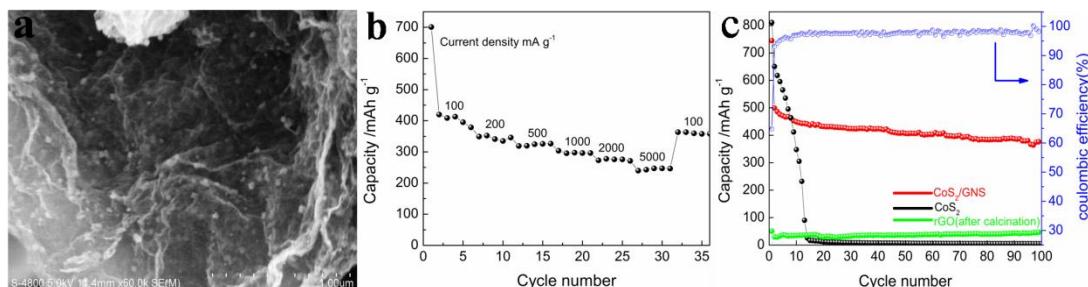
<sup>a</sup>Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, China

<sup>b</sup>School of Energy Science and Engineering, Nanjing Tech University, Nanjing 210009, China

<sup>c</sup>Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia

E-mail: shaozp@njtech.edu.cn

Sodium-ion batteries (SIBs) are highly attractive electrochemical devices for massive energy storage because of their low cost and abundance of sodium, but insufficient anode performance remains a key challenge for the commercialization of this attractive technology. In this study, a hierarchically porous CoS<sub>2</sub>/graphene composite with an architecture of CoS<sub>2</sub> nanoparticles embedded in reduced graphene oxide (rGO) is synthesized through a one-step hydrothermal route allowing the growth of the CoS<sub>2</sub> phase and the reduction of the graphene oxide simultaneously. This composite is applied as an anode material for SIBs, delivering favorable performance. The CoS<sub>2</sub> phase consists of nanoparticles of ~10 nm that are uniformly anchored on the rGO, forming a CoS<sub>2</sub>/rGO hybrid with strong phase interaction. As a conversion-type anode for SIBs, the electrochemical testing results show significantly enhanced sodium-storage properties for the CoS<sub>2</sub>/rGO composite compared with that of bare CoS<sub>2</sub>. Impressively, the CoS<sub>2</sub>/rGO nanostructure exhibits a high discharge capacity of approximately 400 mAh g<sup>-1</sup> after 100 cycles at specific current of 100 mA g<sup>-1</sup>, corresponding to approximately 80% of the discharge capacity in the second cycle.



**Fig. 1** (a) An SEM image of the CoS<sub>2</sub>/rGO composite; (b) rate performance of the CoS<sub>2</sub>/rGO electrode at current densities of 100, 200, 500, 1000, 2000, and 5000 mA g<sup>-1</sup> in a potential window of 0.01–3.0 V.; (c) Cycling performance (left y-axis) and coulombic efficiency (right y-axis) of the bare CoS<sub>2</sub>, rGO and CoS<sub>2</sub>/rGO composite at a current density of 100 mA g<sup>-1</sup>.

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## 双金属磷化物的构型演变与催化性能:从非晶、面心立方到多晶

赵明\*, 康子楠, 仲宁

中国矿业大学, 江苏省徐州市大学路 1 号, 221116

\* E-mail: ming815zhao@163.com

双金属磷化物同时具有双金属效应和金属-磷电子交互作用, 在能源和催化等领域应用广泛<sup>[1-2]</sup>。众所周知, 钯基金属(合金)催化剂在乙醇和多元醇等的电化学氧化反应中表现出色, 但相较铂而言, 其甲醇氧化(MOR)性能一直处于劣势。本工作通过晶态控制, 合成了一种新型的卵壳形貌的双金属磷化物(Yolk-Shell Pd-Ni-P)。与此前报道的非晶态和面心立方晶型(Fcc)的双金属磷化物不同, 本文中的卵壳催化剂呈现出了多晶纳米构型(图 1a, 1b 中嵌入图), 且在甲醇氧化中表现出超高活性和稳定性。其比表面活性值高达  $3 \text{ mA/cm}^2$ , 分别是商业钯碳的 4 倍和商业铂钌碳的 2.5 倍(图 1b)。在多次的循环伏安(CV)测试中, 卵壳催化剂更表现出优异的稳定性。在 800 圈 CV 之后, 商业钯碳和商业铂钌碳的活性已降至初始活性的 10% 以下, 而 Yolk-Shell Pd-Ni-P/C 仍然保持了高达 96% 的活性(图 1c)。

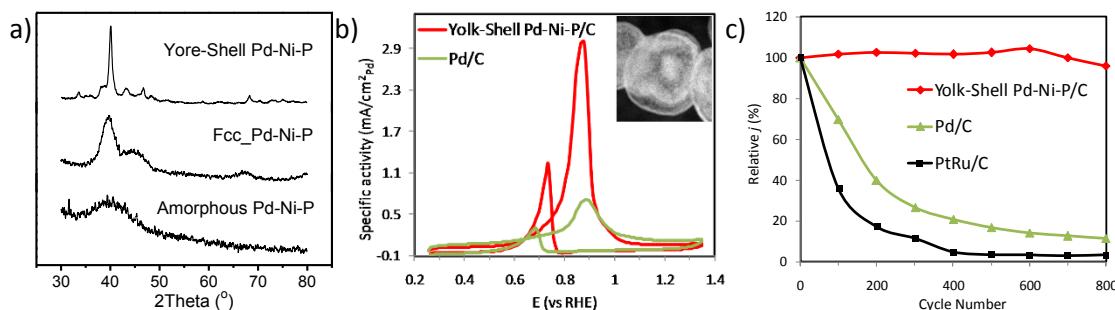


图 1 a) X-ray diffraction of Pd-Ni-P/C with different crystalline. b) Comparison of specific activities of Yolk-Shell Pd-Ni-P/C with Pd/C in MOR; inset shows the scanning transmission microscopy of Yolk-Shell NPs. c) Comparison of the durability of different catalysts during various CV cycles in MOR.

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## Two orders of magnitude enhancement in oxygen evolution reactivity on amorphous $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ nanofilms with tunable oxidation state

Gao Chen,<sup>1</sup> Wei Zhou,<sup>1,\*</sup> Daqin Guan,<sup>1</sup> Jaka Sunarso,<sup>2</sup> Yanping Zhu,<sup>1</sup> Xuefeng Hu,<sup>1</sup> Wei Zhang,<sup>1</sup> Zongping Shao<sup>3,4\*</sup>

<sup>1</sup>Jiangsu National Synergetic Innovation Center for Advanced Materials, State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No.5 Xin Mofan Road, Nanjing 210009, P. R. China.

<sup>2</sup>Faculty of Engineering, Computing and Science, Swinburne University of Technology, Jalan Simpang Tiga, 93350 Kuching, Sarawak, Malaysia.

<sup>3</sup>Jiangsu National Synergetic Innovation Center for Advanced Materials, State Key Laboratory of Materials-Oriented Chemical Engineering, College of Energy, Nanjing Tech University, No.5 Xin Mofan Road, Nanjing 210009, P. R. China.

<sup>4</sup>Department of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia.

\*Corresponding author. Email: zhouwei1982@njtech.edu.cn (W. Zhou); shaozp@njtech.edu.cn (Z.S.)

Perovskite oxides exhibit potential for use as electrocatalysts in the oxygen evolution reaction (OER). However, their low specific surface area is the main obstacle to realizing a high mass-specific activity that is required to be competitive against the state-of-the-art precious metal-based catalysts. We report the enhanced performance of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) for the OER with intrinsic activity that is significantly higher than that of the benchmark  $\text{IrO}_2$ , and this result was achieved via fabrication of an amorphous BSCF nanofilm on a surface-oxidized nickel substrate by magnetron sputtering. The surface nickel oxide layer of the Ni substrate and the thickness of the BSCF film were further used to tune the intrinsic OER activity and stability of the BSCF catalyst by optimizing the electronic configuration of the transition metal cations in BSCF via the interaction between the nanofilm and the surface nickel oxide, which enables up to 315-fold enhanced mass-specific activity compared to the crystalline BSCF bulk phase. Moreover, the amorphous BSCF-Ni foam anode coupled with the Pt-Ni foam cathode demonstrated an attractive small overpotential of 0.34 V at 10 mA cm<sup>-2</sup> for water electrolysis, with a BSCF loading as low as 154.8  $\mu\text{g cm}^{-2}$ .

## Multiscale Principles to Boost Reactivity in Gas-Involving Energy Electrocatalysis

Cheng Tang, Hao-Fan Wang, Qiang Zhang\*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering,  
Tsinghua University, Beijing 100084, China

\*zhang-qiang@mails.tsinghua.edu.cn

Various gas-involving energy electrocatalysis, including oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), have witnessed increasing concerns recently for the sake of clean, renewable, and efficient energy technologies. However, these heterogeneous reactions exhibit sluggish kinetics due to multi-step electron transfer and only occur at triple-phase boundary regions. Insightful principles and effective strategies for a comprehensive optimization, ranging from active sites to electrochemical interface, are necessary to fully enhance the electrocatalytic performance aiming at practical device applications. Herein, we will present our recent attempts under multiscale principles,<sup>[1]</sup> including: 1) regulation of the intrinsic electronic structure for accelerated surface reaction; 2) tailor of the extrinsic hierarchical morphology to ensure high utilization efficiency and smooth electron transfer; and 3) engineering of the working electrode interface with favorable mass diffusion and interface conditions. Such multiscale principles stemmed from the in-depth insights on the structure-activity relationship and heterogeneous reaction characteristics will no doubt pave the way for the future development of gas-involving energy electrocatalysis, and also afford constructive inspirations in a broad range of research including CO<sub>2</sub> reduction reaction, nitrogen reduction reaction, etc.

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# Rh 电极表面 CO 吸附及氧化的原位表面增强红外光谱研究

阳耀月\*, 朱婵

西南民族大学, 成都, 中国, 610041

\*E-mail: yaoyueyoung@swun.edu.cn

目前, 乙醇电氧化 C1 路径的选择性仍需要大幅提升, 而电催化材料研究表明 Rh 可能是有效断裂乙醇 C-C 键的关键组分<sup>[1]</sup>. 为更好地指导开发高活性、高选择性的乙醇电氧化的催化剂, 亟需从分子水平厘清 Rh 表面燃料分子的吸附和反应动力学. 于是, 我们以 CO 为模型分子(同时也是乙醇氧化的重要中间体), 以电化学表面增强红外光谱 (SEIRAS) 为主要手段, 初步研究了 Rh 膜电极表面 CO 吸附构型和电氧化机制. 结果表明, 随着溶液 pH 增大, Rh 电极表面 CO 从以线式吸附为主向以桥式吸附为主转换, 并且在 0.1 M NaOH 溶液中 CO 的起始氧化电位比在 0.1 M H<sub>2</sub>SO<sub>4</sub> 溶液中的提前了约 100 mV, 这都说明表面吸附 CO 与界面 OH<sup>-</sup>存在直接的强交联作用, 其氧化过程可能同时遵循所谓的 Langmuir-Hinshelwood 机理和 Eley-Rideal 机理<sup>[2]</sup>.

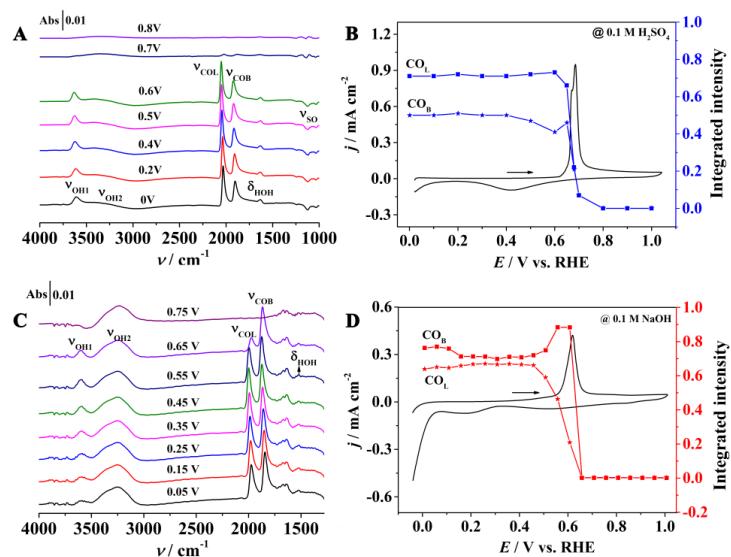


图 1 在 0.1 M H<sub>2</sub>SO<sub>4</sub> (A) 和 0.1 M NaOH (C) 溶液中, Rh 表面单层吸附 CO 氧化的表面增强红外光谱. (B) 和 (D) 为 Rh 表面 CO 谱峰强度随电极电位的变化曲线, 而黑实线为 CO 氧化的伏安曲线, 扫描速率为 5 mV s<sup>-1</sup>.

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# In situ prepared perovskite oxides/carbon nanotubes composites as efficient electrocatalysts for oxygen evolution reaction

Xinhao Wu<sup>a</sup>, Wei Zhou<sup>a\*</sup>, Zongping Shao<sup>a,b,c\*</sup>

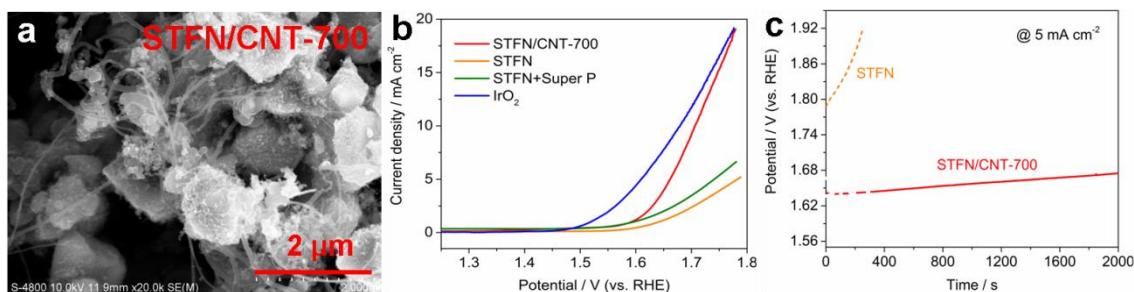
<sup>a</sup>Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, China

<sup>b</sup>School of Energy Science and Engineering, Nanjing Tech University, Nanjing 210009, China

<sup>c</sup>Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia

1150639842@qq.com

Perovskite oxides have recently emerged as efficient electrocatalysts for oxygen evolution reaction (OER) in an alkaline solution. However, most of perovskite materials have poor electrical conductivity at room temperature. Here, to enhance the activity and stability toward OER, we in situ introduced carbon nanotubes (CNTs) on perovskite ( $\text{SrTi}_{0.1}\text{Fe}_{0.85}\text{Ni}_{0.05}\text{O}_{3-\delta}$ ) surface via a simple chemical vapor deposition (CVD) method at an optimized temperature of 700 °C (The obtained composite was denoted as STFN/CNT-700). STFN/CNT-700 exhibited higher OER activities than the bare perovskite, with an onset potential of 1.59 V vs. RHE, overpotential of 0.48 V at 10 mA cm<sup>-2</sup> current density, and Tafel slope of 98 mV dec<sup>-1</sup>. What's more, the long-term stability was also dramatically improved.



**Figure 1.** **a)** SEM image of STFN/CNT-700. **b)** OER polarization curves of STFN/CNT-700 and other catalysts. **c)** Chronopotentiometry curves of STFN/CNT-700 and STFN catalysts at a constant current density of 5 mA cm<sup>-2</sup>

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## Active Sites Engineering towards Superior Carbon-Based Oxygen

### Reduction Catalysts via Confinement Pyrolysis

王思迪, 何群, 江宏亮, 宋礼

中国科学技术大学国家同步辐射实验室, 合肥, 中国, 230026

E-mail: wsd135@mail.ustc.edu.cn

Developing efficient and low-cost defective carbon-based catalysts for oxygen reduction reaction (ORR) is essential to metal-air batteries and fuel cells. Active sites engineering towards these catalysts is highly desirable but challenging to realize boosted catalytic performance. Herein, we report a sandwich-like confinement route to achieve the controllable regulation of active sites for carbon-based catalysts. In particular, three distinct catalysts including metal-free N-doped carbon (NC), single Co atoms dispersed NC (Co-N-C) and Co nanoparticles-contained Co-N-C (Co/Co-N-C) are controllably realized and clearly identified by synchrotron radiation-based X-ray spectroscopy. Electrochemical measurements suggest that the Co/Co-N-C catalyst delivers optimized ORR performance due to the rich  $\text{Co-N}_x$  active sites and their synergistic effect with metallic Co nanoparticles. This work provides deep insight for rationally designing efficient ORR catalyst based on active sites engineering.

# Atomic Identification of Nickel Vacancy in Nickel Hydroxide: the Correlation between Vacancy Structure and Electrochemical Reconstruction

何群, 江宏亮, 宋礼

中国科学技术大学国家同步辐射实验室, 合肥, 中国, 230026

E-mail: hqun@mail.ustc.edu.cn

Anodic oxidation reactions play vital roles in water electrolysis and fuel cells. Recently, the surface self-reconstruction capacity during oxidation reactions is considered as the key of highly active catalysts. Despite that many efforts have been made to obtain efficient catalysts for activating oxygen reactions, the correlation understanding between surface reconstruction and intrinsic structure is highly desirable to unravel the catalytic mechanisms. In this work, we report  $\alpha$ -Ni(OH)<sub>2</sub> catalysts with controllable nickel vacancies ( $V_{Ni}$ ) concentrations via rational synthetic strategy. Electrochemical measurements demonstrate that the  $V_{Ni}$  in  $\alpha$ -Ni(OH)<sub>2</sub> can efficiently mediate the surface reconstruction and thus promote active components generation, leading to remarkably boosted reaction activity. Density functional theory (DFT) calculations reveal that the presence of  $V_{Ni}$  induces the appearance of new defect levels and the increase of hole densities near the Fermi level, which can largely benefit to charge transfer for facilitating the formation of active components. Meanwhile, the high  $V_{Ni}$  concentrations can efficiently decrease the formation energies of the active components from  $\alpha$ -Ni(OH)<sub>2</sub> catalysts. This work not only broadens the fundamental understanding of true catalytically active sites in the typical anodic reactions, but also provides significant guidance for the design of efficient electrocatalysts.

## Bifunctional transition metal hydroxysulfides: room-temperature sulfurization and their applications in Zn-air batteries

Hao-Fan Wang, Cheng Tang, Bin Wang, Bo-Quan Li, Qiang Zhang\*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

\* E-mail: zhang-qiang@mails.tsinghua.edu.cn

The electrocatalysis of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) remains a key problem for various sustainable energy systems. Transition metal sulfides are promising candidates in electrochemical applications for their high electrical conductivity, and have shown much potential in OER/ORR bifunctional electrocatalysis. The traditional hydrothermal method for sulfide synthesis has the shortcomings of high energy cost, poor safety, and the easily agglomerating feature of the as-prepared sulfides. In this contribution, we proposed a mild, safe and facile way to synthesize transition metal sulfides, by simply immersing the precursor into sodium sulfide solution at room temperature. This method was verified to be highly efficient in converting the precursor to sulfide, and enhancing the catalytic activity. Furthermore, the morphology of the precursor can be well maintained. Based on this method, a cobalt-iron sulfide catalyst converted from the corresponding hydroxide was obtained, and exhibited excellent OER/ORR bifunctional activity. The potential for 10 mA cm<sup>-2</sup> OER current density is 1.588 V vs RHE, and the ORR half-wave potential is 0.721 V vs RHE, with a potential gap of 0.867 V. The application in rechargeable Zn-air battery also showed outstanding performance with high power density, capacity and stability.

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## 半导体光阳极材料设计及其光电性能

姜曼, 牛腾娇, 和继娟, 王其召\*

西北师范大学化学化工学院, 兰州, 中国, 730070

\*wangqizhao@163.com; qizhaosjtu@gmail.com

近年来, 光电化学水分解作为一种高效、环保、可持续的技术, 已经引起广泛关注。在光电分解水制氢中, 至关重要的是提高光电极材料的光吸收和光转化效率。由于 $\text{BiVO}_4$ 禁带宽度( $E_g = 2.4\text{--}2.5\text{ eV}$ )小, 具有很好的可见光响应能力, 因此 $\text{BiVO}_4$ 光电极材料引起了广泛关注。但是, 当 $\text{BiVO}_4$ 单独作为光阳极材料时, 电子-空穴对分离弱、载流子传输慢, 从而使 $\text{BiVO}_4$ 不能很好地在光电化学水分解中发挥作用。近年来, 我们课题组针对上述问题开展了一系列的研究工作。基于半金属Bi单质, 通过光还原法、水热法、电化学沉积法合成了Bi单质及其化合物 $\text{NiFe}_2\text{O}_4$ 、 $\text{CoFe}_2\text{O}_4$ 、 $\text{FeF}_2$ 并将其负载于 $\text{BiVO}_4$ 电极表面形成异质结结构, 光电催化分解水实验表明其产氢效率得到大幅度提高。另外, 利用Bi的等离子体共振效应成功制备出Bi/ $\text{BiVO}_4$ 光电极, 利用NiFe-双氢纳米粒子的优点制备出NiFe-LDH/ $\text{BiVO}_4$ 复合电极, 这些措施都有效的提高了光生电子空穴对的分离效率。

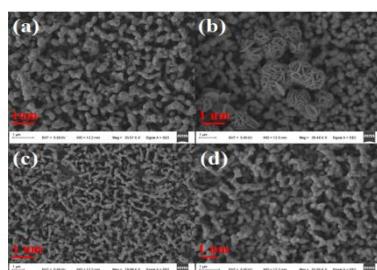


图 1 NiFe 相关材料/ $\text{BiVO}_4$  扫描电镜图

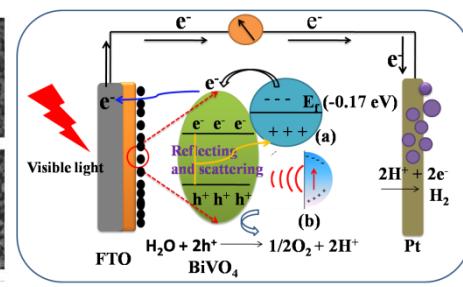


图 2 Bi/ $\text{BiVO}_4$  光阳极分解水反应机理

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## Microfluidic Devices for the Detection of L-cysteine Using a Ferrocene-based Mediator

宋苑

北京工业大学,北京,中国, 100022

sopily@hotmail.com

The development of microengineered techniques which seek to probe electrochemical process coupled with homogeneous chemical reactions was demonstrated. A microfluidic device integrated with the boron doped diamond electrode was designed and fabricated via photolithographic technique to study electrocatalytic (EC') mechanism under both stagnant and flow conditions. Parameters including flow rate, scan rate and substrate concentration were varied to illustrate how the microfluidics influenced the profile of voltammograms. Modified Levich equation was employed to calculate cell depth electrochemically. An increase of limiting current was achieved with the increase of substrate concentration under both stagnant and flow conditions. An enhancement of oxidative current (4.98 times) was observed at a flow rate of  $0.03 \text{ mL min}^{-1}$  while this enhancement was lifted to 5.76 times at the flow rate of  $0.15 \text{ mL min}^{-1}$ . Also, a negative shift of oxidative peak was observed due to the electrocatalytic mechanism. Numerical simulations were carried out to support the corresponding experimental data.

## bisphenol A over TiO<sub>2</sub>-graphene hydrogel with 3D network structure

崔文权

华北理工大学化学工程学院，河北，唐山

Email: wkcui@163.com

We successfully fabricated the three-dimensional (3D) hydrogel of titanium dioxide (TiO<sub>2</sub>)-graphene using a simple one-pot method and exhibited enriched adsorption-photoelectrocatalytic degradation ability of low-concentration bisphenol A (BPA). Combined with the unique adsorption of graphene hydrogel and the effective photoelectrocatalytic performance of TiO<sub>2</sub>, we rapidly enriched the organic pollutants and conducted efficient in situ degradation. The low-concentration BPA (20 mg/L) was degraded completely by the TiO<sub>2</sub>-rGH electrode in 5 h through the synergistic effect of adsorption-photoelectrocatalytic. The photogenerated charge on the surface of TiO<sub>2</sub> is rapidly separated by the action of the applied electric field and the graphene sheet. The high conductivity of the graphene makes the TiO<sub>2</sub>-graphene hydrogel rapidly conducting the charge and solves the problem of poor conductivity of the semiconductor electrode. On the basis of these advantages, the TiO<sub>2</sub>-rGH has a cross-porous network structure that favors the anchor of more TiO<sub>2</sub> nanocrystals, the specific surface area and reactive sites are greater than the thin film electrode, and the structure is conducive to significantly improving the BPA removal efficiency. By contrast, the BPA degradation of TiO<sub>2</sub>-rGO thin film electrode was 40% after 4 h of ultraviolet irradiation, whereas the removal rate of BPA over the same mass of TiO<sub>2</sub>-rGH electrode rate was up to 96%. At the same time, the TiO<sub>2</sub>-rGH electrode without filtering can be achieved quickly separated from the recovery due to its special macro-3D network structure. Its removal ability still maintains above 90% after 10 times cyclic experiments with self-regeneration characteristics. It can be achieved rapid separation and recovery without filtering.

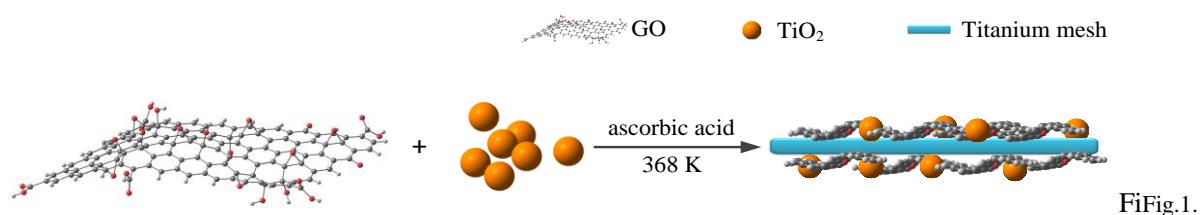


Fig.1.

Schematic of the preparation process of TiO<sub>2</sub>-rGH electrode.

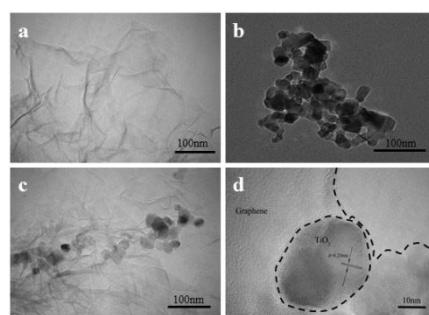


Fig. 2. TEM images of (a) rGH, (b) TiO<sub>2</sub>, and (c) TiO<sub>2</sub>-rGH; HRTEM image of (d) TiO<sub>2</sub>-rGH.

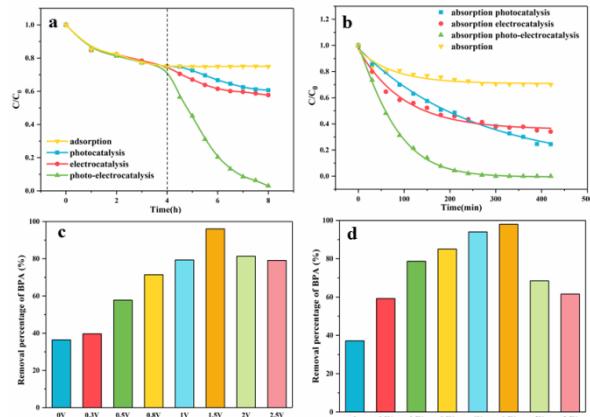


Figure 3. (a) Comparison of PC, EC, and PEC activity of the  $\text{TiO}_2\text{-rGH}$  electrode decomposition of BPA. (b) Adsorption, adsorption-photocatalysis, adsorption-electrocatalysis, and adsorption-photoelectrocatalysis of BPA via  $\text{TiO}_2\text{-rGH}$  electrode. (c) The removal percentage of BPA under different bias conditions after adsorption equilibrium. (d) Adsorption-PEC degradation of BPA under different bias.

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# 空心分级结构 $\text{Co}_{0.85}\text{Se}$ 催化 $\text{I}_3^-/\text{I}^-$ 增强 DSSCs 光电转化性能

赵荣芳, 刁国旺, 陈铭\*

扬州大学化学化工学院, 江苏, 扬州, 225000\*

E-mail: chenming@yzu.edu.cn

随着化石能源的不断消耗, 能源危机和环境问题以成为人类生存亟待解决的重大问题, 须寻求新能源来代替常规能源。太阳能作为一种清洁可再生能源, 且取之不尽、用之不竭, 不受地理位置的影响, 因此合理利用太阳能是解决人类面临的环境问题的首选方案。染料敏化太阳能电池(DSSCs)作为新一代太阳能电池, 因其制备工艺简单, 成本低, 光电转换效率高, 从而引起国内外研究者的广泛关注。DSSCs 通常采用贵金属 Pt 作为对电极。Pt 电极导电性能好, 电催化活性高, 但是价格昂贵, 地球储量有限, 限制了 DSSCs 的大面积使用。本文设计并合成空心分级结构的  $\text{Co}_{0.85}\text{Se}$  作为非铂对电极材料应用到 DSSCs 中, 并探索了该电极材料在染料敏化太阳能电池体系中对电解质溶液中  $\text{I}_3^-/\text{I}^-$  的电催化性能。该材料因其特殊结构, 具有较大的比表面积, 因而与电解质具有较大的接触面积。图 A 为不同对电极材料 DSSCs 的 J-V 特性曲线, 从该图可以看出,  $\text{Co}_{0.85}\text{Se}$  作为对电极时, DSSCs 的光电转换效率为 7.5%, 略高于采用 Pt 作为对电极的 DSSCs。图 B 为不同电极材料的 CV 曲线,  $\text{Co}_{0.85}\text{Se}$  对电极材料  $E_{\text{pp}}$  为 0.097V, 小于 Pt, 同时, 由  $\text{Co}_{0.85}\text{Se}$  作为对电极材料组装成的对称薄层电池的电荷转移阻抗  $R_{\text{ct}}$  小于 Pt 对电极(图 C), 塔菲尔曲线所呈现出的交换电流密度  $J_0$  略大于 Pt 对电极。通过电化学和光电性能测试, 可知这种空心分级结构的  $\text{Co}_{0.85}\text{Se}$  具有较好的电催化活性。该研究结果对非 Pt 对电极材料推动 DSSCs 进一步向商业化发展具有重要意义。

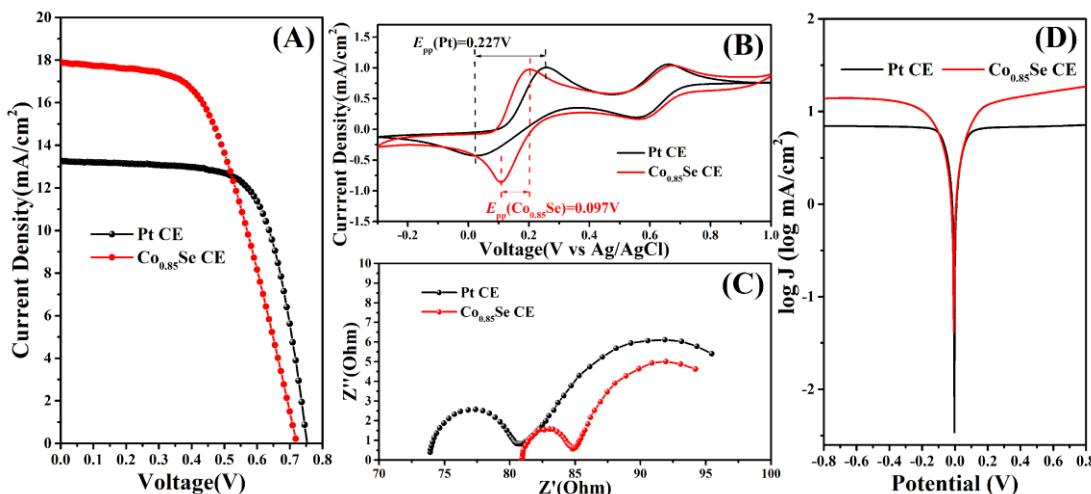


图 1 不同对电极材料 DSSCs 的 (A) I-V 曲线, (B) 循环伏安 (CV) 图, (C) 电化学阻抗图和 (D) 塔菲尔极化曲线

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## Visible-light-induced plasmonic metal nanostructures enhance liquid fuel electrocatalysis

Hui Xu and Yukou Du\*

College of Chemistry, Chemical Engineering and Materials Science, Soochow University,  
Suzhou 215123, PR China

\* Corresponding author: Tel: 86-512-65880089, Fax: 86-512-65880089;  
E-mail: duyk@suda.edu.cn (Y. Du).

The production and conversion of solar energy is a sublime target and the pursuit of appropriate materials as photocatalysts can not only adsorb the broad wavelength sun light, but also lead to the highly efficient photocatalysis performances is also one of the tough challenges. Although most of the photocatalysts are semiconductors, it has also been well demonstrated that plasmonic nanostructures of noble metals such as gold and silver also serve as efficient photocatalysts. Plasmonic metallic nanostructures are featured with their strong interactions with resonant photons *via* exciting the SPR. In addition, the SPR can be characterized by the collective oscillation of valence electrons induced by resonance photons. The investigation of SPR induced photoelectrocatalytic effect based on plasmonic metallic nanostructures is of vital significance for exploring highly efficient photoelectrocatalysts for electrocatalytic oxidation reactions. Therefore, we focus on the SPR enhanced liquid fuel electrocatalysis employing different photocatalysts to develop various plasmonic metal nanostructures with well-defined shape, high-index facet, and high surface active areas. Impressively, the SPR effect also induces the plasmonic metal nanocatalysts under visible light irradiation conditions to display great enhancement in photoelectrocatalytic activity compared to that under dark conditions. More importantly, we also introduce a promising approach towards the designing of a plasmonic metal nanocatalyst with ideal nanostructures for liquid fuel oxidations, presenting a feasible strategy for designing outstanding photocatalysts for fuel cells.

# Carbon Nanosheet Containing Atomic-Scaled M-N-C Catalysts for Efficient Oxygen Electrocatalysis and Rechargeable Zn-Air Batteries

Yingying Guo, Xin Wang, Jianan Zhang\*

College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China. Emails:  
zjn@zzu.edu.cn (J. N. Zhang)

Structural and compositional engineering atomic-scaled metal-N-C catalysts is important yet challenging in boosting their performance for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Here, a boron (B)-doped Co-N-C active sites confined in hierarchical porous carbon sheets (denoted as Co-N<sub>x</sub>B-CSs) were obtained by soft template self-assembly pyrolysis method. Significantly, the introduced B element gives an electron deficient site, that can active the electron transfer around the Co-N-C sites, strength the interaction with oxygenated species, and thus accelerate reaction kinetics in the 4e<sup>-</sup> processed ORR and OER. As a result, the catalyst showed Pt-like ORR performance with a half-wave potential ( $E_{1/2}$ ) of 0.83 V *versus* (vs.) RHE, the limiting current density is about 5.66 mA cm<sup>-2</sup>, and high durability (almost no decay after 5000 cycles) than Pt/C catalyst. Moreover, a rechargeable Zn-air battery device comprising this Co-N<sub>x</sub>B-CSs catalyst shows superior performance, open-circuit potential of ~1.4 V, a peak power density of ~100.4 mW cm<sup>-2</sup>, as well as excellent durability (128 cycles for 14h of operation). DFT calculations further demonstrated that the coupling of Co-N<sub>x</sub> active sites with B atoms prefers to adsorb O<sub>2</sub> molecule in side-on mode and accelerates ORR kinetics.

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## Zn-MoSe<sub>2</sub> 纳米片的电催化析氢反应性能

高大强\*, 钱进梅

兰州大学, 兰州市, 730000

gaodq@lzu.edu.cn

随着环境的急剧恶化和能源的枯竭, 清洁能源的开发利用已成为当务之急。而氢燃料是当下及未来最具有前景的新型能源之一。析氢反应是获得氢燃料最有效地途径, 所以寻找高效且低成本的可替代贵金属的析氢反应催化剂是至关重要的。过渡金属硫化物被认为是目前最有前景的可供为选择的催化剂。在本文中, 通过水热法合成了 Zn-MoSe<sub>2</sub> 纳米片, 并分析讨论了 Zn-MoSe<sub>2</sub> 纳米片的电催化活性, 发现掺杂后的 MoSe<sub>2</sub> 纳米片的电催化活性大有提高, 并讨论了在 Zn 原子不同掺杂量下, 对电催化活性的影响, 发现当掺杂到一定量时其催化活性会有所降低。所以在本文工作中, 当 Zn 原子比为 2.9% 时(Zn-2), MoSe<sub>2</sub> 纳米片的电催化活性最好。在电流密度  $j=10\text{mA}/\text{cm}^2$  时, 可逆氢电极的过电位为 0.230V, Tafel 斜率为 58mV/dec。并通过计算研究证实了 Zn 原子掺杂后可以有效地提高 MoSe<sub>2</sub> 的电催化活性。

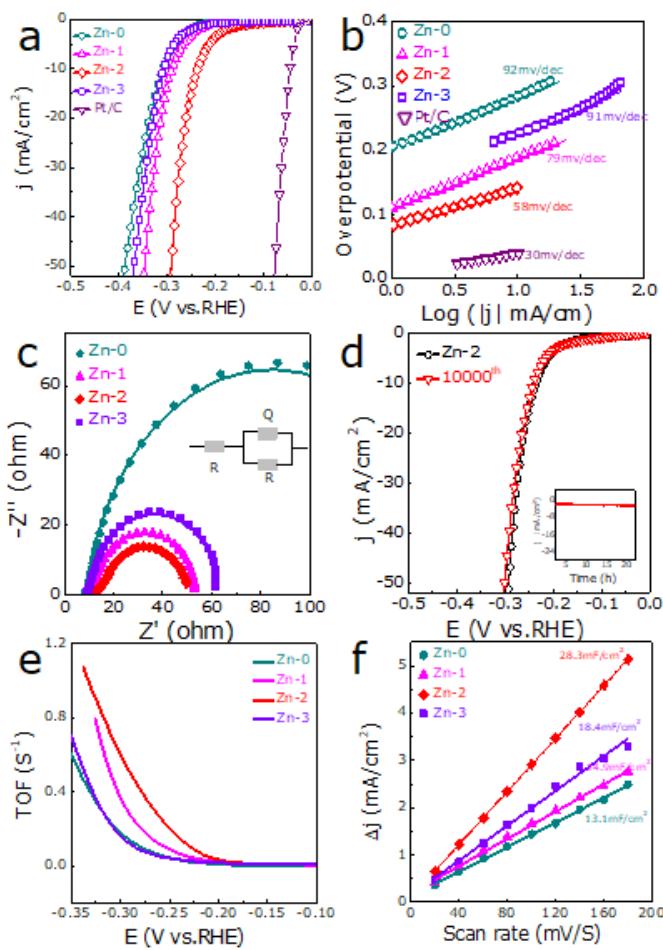


图 1.Zn-MoSe<sub>2</sub>(MoSe<sub>2</sub>)样品的电催化活性分析

# Copper Nanowires as a Robust and Flexible Electrocatalyst for CO<sub>2</sub>

## Reduction

Wei Zhang, Ying Yu \*

College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China

\* yuying01@mail.ccnu.edu.cn

Electrocatalytic CO<sub>2</sub> conversion to value-added products offers a promising route to mitigate the growing energy demand, dwindling fossil fuel reserves and increasing atmospheric CO<sub>2</sub> concentration, during which the electricity can be generated from renewable energy sources, such as solar, wind and biomass.<sup>[1-2]</sup> Over the past decades, researchers have evaluated lots of materials as electrodes for CO<sub>2</sub> electroreduction, such as metals, transition metal oxides, transition metal chalcogenides, carbon-based materials and metal–organic frameworks (MOFs).<sup>[3]</sup> Among various electrocatalysts investigated to date, copper(Cu) has been identified to be promising because of its low cost, and in particular its potential of catalyzing the formation of high quantity of hydrocarbons. Here, we explore the Cu nanowires for CO<sub>2</sub> electroreduction activity through a facile and low-cost synthesis method.

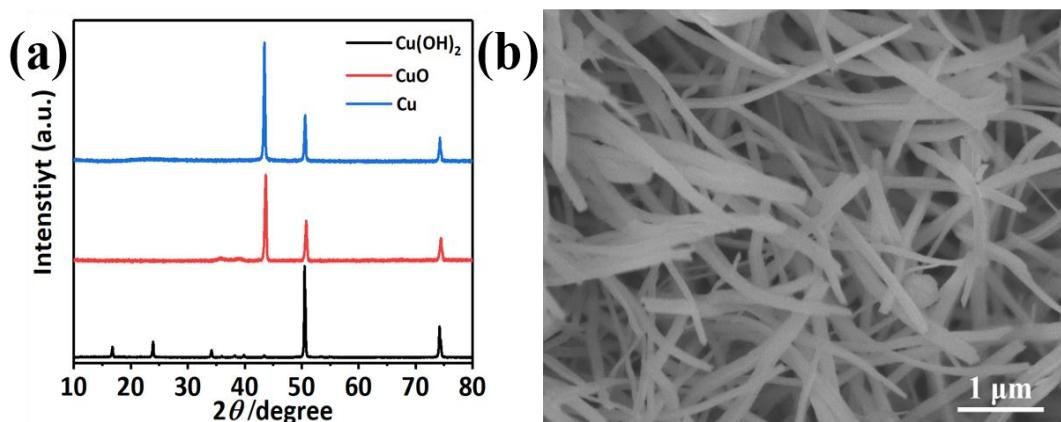


Figure 1 (a) XRD patterns of Cu foam, Cu(OH)<sub>2</sub>/Cu foam and CuO/Cu foam; (b) SEM images of CuO nanowires on Cu foam

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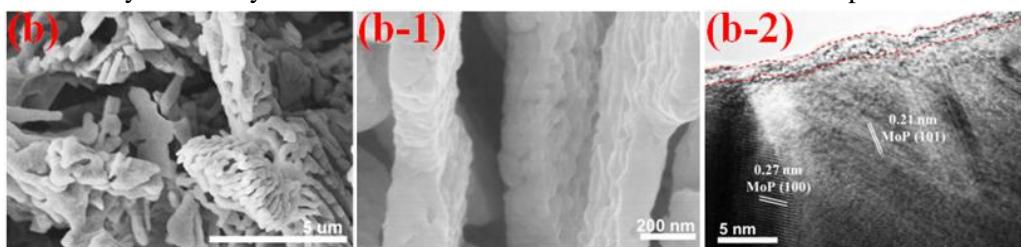
## MoP nanoflakes as efficient catalysts for Li-O<sub>2</sub> batteries

魏明会, 金超\*, 杨瑞枝

苏州大学能源学院/能源与材料创新研究院, 江苏苏州, 中国, 215006

\*E-mail: jinchao@suda.edu.cn

Herein, we firstly report a binder-free electrode with *in-situ* synthesized MoP nanoflakes on the surface of carbon cloth and its application in non-aqueous Li-O<sub>2</sub> batteries (LOBs). The assembled LOBs exhibit improved discharge/charge capability (achieving actual 4.15 mAh at a current of 0.1 mA and cycle stability (400 cycles without capacity fading), which should be attributed to the superior electrocatalytic activity of MoP nanoflakes towards the formation/decomposition of Li<sub>2</sub>O<sub>2</sub>.



[3] 图 1 MoP nanoflakes 的 SEM 图 (b, b-1) 和 TEM 图 (b-2)

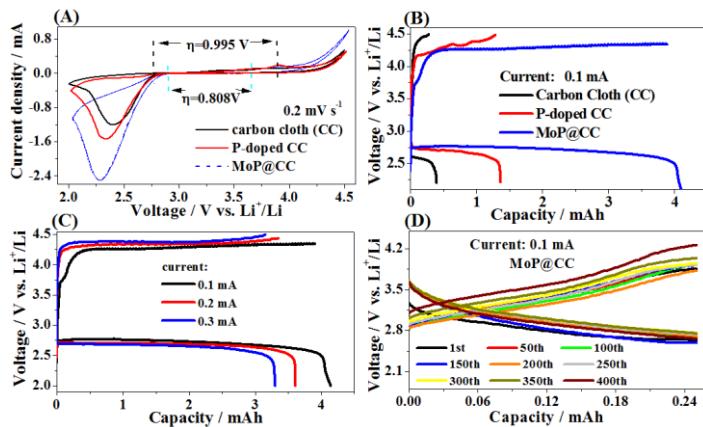


图 2 CC、P-doped CC 和 MoP@CC 三种空气电极组装 LOBs 的电化学性能

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## Electrochemical Synthesis of 1,2,4-Triazole-Fused Heterocycles

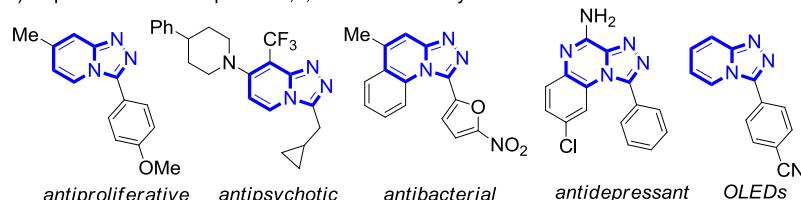
Zenghui Ye, Mingruo Ding, Yanqi Wu, Yong Li, Wenkai Hua and Fengzhi Zhang\*

Zhejiang University of Technology, Hangzhou, P. R. China, 310014

\*Corresponding Author's E-mail: zhangfengzhi@zjut.edu.cn.

A reagent-free intramolecular dehydrogenative C–N cross-coupling reaction has been developed under mild electrolytic conditions. In this atom- and step-economic one-pot process, valuable 1,2,4-triazolo[4,3-a]pyridines and related heterocyclic compounds could be synthesized efficiently from commercially available aliphatic or (hetero)aromatic aldehydes and 2-hydrazinopyridines. Various functional groups are compatible with this metal- and oxidant-free protocol which can be carried out on gram scale easily. This novel method was applied to the synthesis of one of the top selling drugs Xanax and late stage functionalization for generating chemical diversity of biologically relevant lead molecules.

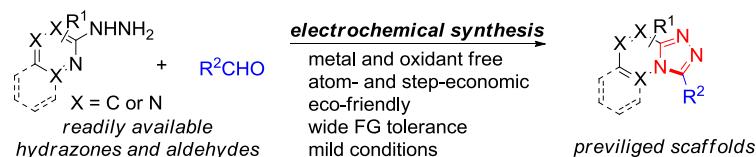
a) Representative examples of 1,2,4-triazoloheterocycles:



b) Previous synthesis of 1,2,4-triazolopyridines:



c) Our one-pot electrochemical synthesis of 1,2,4-triazole-fused heterocycles:



**Scheme 1.** Functionalized 1,2,4-triazolo[4,3-a]heterocycles and their synthesis.

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## 硅基光电化学阳极及其光电化学性能研究

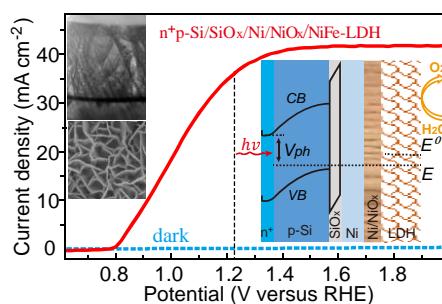
郭北斗<sup>1,2</sup>, Aisha Batool<sup>1,2</sup>, 谢关才<sup>1,2</sup>, Rajender Boddula<sup>1</sup>, 田凉秋<sup>1,2</sup>, Saad Ullah Jan<sup>1,2</sup>, 宫建茹<sup>1\*</sup>

<sup>1</sup> 国家纳米科学中心, 北京市中关村北一条 11 号, 100190

<sup>2</sup> 中国科学院大学, 北京市石景山区玉泉路 19 号(甲), 100049

\*Email: gongjr@nanoctr.cn

设计和制备高性能的界面对光电化学分解水器件至关重要[1]。我们利用表面活化的镍(Ni/NiOx)作为连接层, 实现了光吸收层非晶硅异质结(n+p-Si)和催化剂层NiFe-LDH的集成, 制备出了高性能的光电化学析氧阳极<sup>[2]</sup>。热蒸镀的镍连接层不但可以保护Si不被腐蚀、作为空穴存储层, 由于活化的镍层(包括Ni(OH)<sub>2</sub>和NiOOH)具有与电沉积的NiFe-LDH相似的结构可以形成良好的接触, 进而促进镍连接层存储的空穴向具有高催化活性的NiFe-LDH传输, 在表面氧化水生成氧气。另外, 光电极的背照方式使得NiFe-LDH可以具有足够的厚度, 获得更多的活性位点, 但又不会影响光的吸收。这一全廉价材料集成的光阳极实现了优异的光电性能, 起始电位达到0.78 VRHE, 1.23 VRHE的光电流密度达到37 mA cm<sup>-2</sup>, 是目前晶硅光阳极所报道的最好值。



**Fig. 1** Photoanode structure and PEC property

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# Enhancing electrode performance of cathode material with *in situ* exsolved nanoparticles for low temperature SOFC

Liusheng Zhou,<sup>1</sup> Guangming Yang,<sup>1</sup> Wei Zhou,<sup>1</sup> Zongping Shao<sup>1,2\*</sup>

<sup>1</sup>Jiangsu National Synergetic Innovation Center for Advanced Materials, State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No.5 Xin Mofan Road, Nanjing 210009, P. R. China.

<sup>2</sup>Department of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia

\*Corresponding author. Email: shaozp@njtech.edu.cn (Z.S.)

A material with a heterostructure may significantly extend the length of three-phase boundary (TPB), which is proved critical to oxygen reduction reaction (ORR)<sup>[1]</sup>. Our previous studies have proved that heterostructured composite cathodes with exsolved nanoparticles enhance ORR activity and/or stability, including Ag decorated  $\text{Sr}_{0.95}\text{Ag}_{0.05}\text{Nb}_{0.1}\text{Co}_{0.9}\text{O}_{3-\delta}$  (SANC)<sup>[1]</sup>, NiO decorated  $\text{SrFe}_{0.85}\text{Ti}_{0.1}\text{Ni}_{0.05}\text{O}_{3-\delta}$ <sup>[2]</sup>. In this paper,  $\text{Ba}(\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1})_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$  (BCFZYN) cathode powders were synthesized using a previously developed sol-gel method. The active nanoparticles were introduced by an *in situ* growth technique based on the exsolution of ion from the bulk of the perovskite phase. The nanoparticles are uniformly distributed on and well bonded to the surface of parent electrodes. By means of X-ray diffraction, H<sub>2</sub>-TPR, FE-SEM and electrochemical impedance spectra (EIS) measurements, it is found that the polarization resistance of BCFZYN cathode material at 500 °C decreased to 0.113 Ω cm<sup>2</sup> from 0.135 Ω cm<sup>2</sup> after 10 % H<sub>2</sub>-Ar treatment, which means nanoparticles on the surface of BCFZYN perovskite oxide significantly enhance the ORR kinetics. As a general approach, this exsolution-dissolution of electrocatalytically active nanoparticles on an electrode surface may be applicable to the development of other high-performance cathodes for fuel cells and other electrochemical systems.

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# In situ self-propagating formation of amorphous tungsten phosphide for Highly Efficient Hydrogen Evolution

Xiangyong Zhang\*

School of Materials Science and Engineering, Central South University, Changsha, China, 410083

\*Corresponding Author's E-mail: XYZhang@csu.edu.cn

The urgent need of clean and renewable energy drives the exploration of effective strategies for hydrogen production. With the assistance of highly active non-noble metal electrocatalysts, electrolysis of water is becoming a promising candidate to generate pure hydrogen with low cost and high efficiency. In this work, an active and stable amorphous tungsten phosphide (A-WP) catalyst, as a potential replacement for Pt-based noble metal catalysts, is synthesized via a novel and facile self-propagating reaction. Moreover, there are a lot of defects can be find in the surface of the as-prepared WP catalyst, which can provide more active sites for HER. As a result, the as-prepared catalyst exhibits an excellent activity with a small Tafel slope of  $53 \text{ mV dec}^{-1}$ , among the best records for WP-based catalysts, and excellent stability.

## 过渡金属化合物的表界面调控与碱性电解水催化性能研究

周敏<sup>1\*</sup>（报告作者），翁群红<sup>2</sup>，张秀云<sup>1</sup>，王熙<sup>3</sup>，曾祥华<sup>1</sup>

<sup>1</sup> 扬州大学物理科学与技术学院，江苏省扬州市四望亭路 180 号，225002

<sup>2</sup> National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, 305-0044, Japan

<sup>3</sup> 北京交通大学理学院，北京，100044

\*minzhou@yzu.edu.cn

碱性溶液中电催化析氢反应是工业电解水制氢的关键步骤，也是氯碱工业中的一个重要反应。现有的催化材料中，由于铂基材料的有限储量和昂贵价格，非贵金属材料的催化性能因而受到广泛关注。碱性溶液 HER 过程包含水分解的 Volmer 步骤和析氢的 Tafel/Heyrovsky 步骤，相应分步反应的催化效率决定了催化剂的整体性能。本报告将首先汇报本课题组在基于过渡金属的碱性 HER 催化剂方面的研究进展。一方面，通过构建 NiS<sub>2</sub>/MoS<sub>2</sub> 异质结构，利用异质界面的协同效应获得了碱性 HER 性能的大幅度提高；另一方面，针对 Volmer 步骤的反应速率进行优化，对 Ni<sub>3</sub>N 催化剂进行表面调控，通过提高材料的水分解能力来获得增强的碱性 HER 性能。此外，针对碱性电解水的析氧反应，我们通过电化学原位氧化的方法构筑了 Ni(Fe)S<sub>2</sub>@Ni(Fe)OOH 异质结构。这种结构集成了高催化活性的 Ni(Fe)OOH 表面和高导电性的 Ni(Fe)S<sub>2</sub> 电荷传输通道，而且通过原位合成的方法实现了异质界面充分接触，从而展现出极其优异的电催化析氧性能。

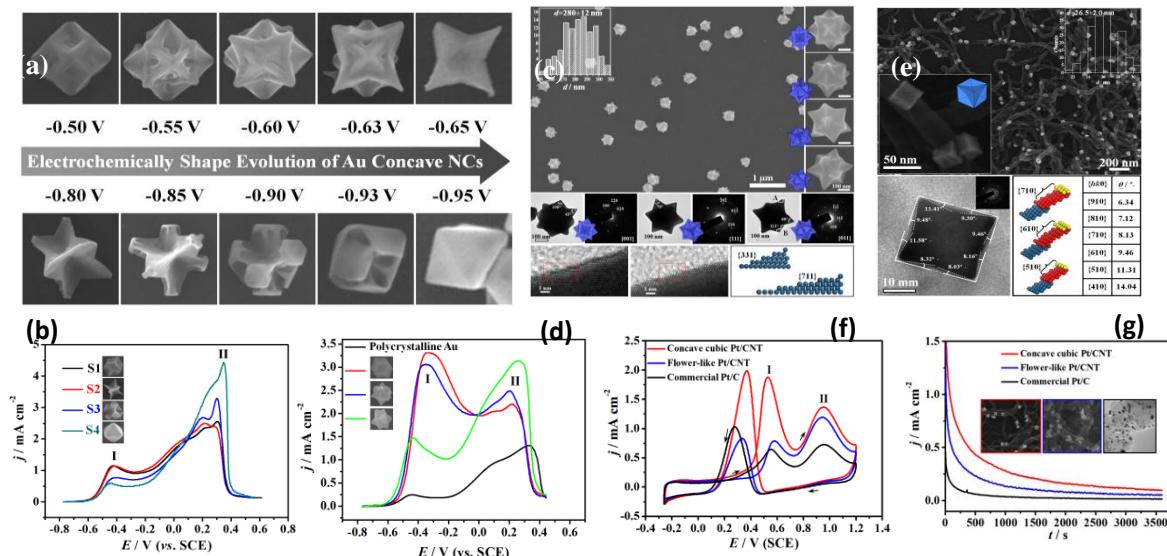
# Electrochemically Shape-Controlled Synthesis of High-Index Faceted Noble Metal Nanocrystals with Enhanced Electrocatalytic Activities

Lu Wei, Yu-Jie Mao, Xin-Sheng Zhao\*

Hydrogen Research Lab for Energy Storage and Application, School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou, 221000

\*Corresponding Author's E-mail: xinshengzhao@jsnu.edu.cn

Shape-controlled synthesis of noble-metallic nanocrystals (NCs) enclosed by high-index facets has attracted intense interest due to their fascinating properties and potential applications such as in catalysis, surface-enhanced Raman scattering (SERS), and fuel-cell technology. High-index facets always expose a high density of low-coordinated atoms on steps, ledges, and kinks, which constitute active sites of catalyst, and have generally a high surface energy, which is always a big challenge for shape-controlled synthesis. In our work the shape-controlled synthesis of high-index faceted noble-metallic NCs was achieved by electrochemical method in deep eutectic solvents (DESs), such as a set of various morphologies of concave Au NCs, high-index {711} and {331} faceted stellated Au NCs, high-index {hk0} faceted concave Pt nanocubes on multi-walled carbon nanotubes (CNTs).<sup>1-3</sup> Thanks to the high density of surface atomic steps, the as-prepared noble-metallic NCs exhibit high electrocatalytic properties.



**Figure:** (a) SEM images of Au NCs electrodeposited at a series of potentials. (b) LSV curves of D-glucose oxidation on Au NCs. (c) SEM, TEM, HRTEM images, SAED patterns of stellated Au NCs and atomic models of Au(771),(331) planes. (d) LSV curves of D-glucose oxidation on stellated, concave TOH, concave HOH Au NCs and polycrystalline Au. (e) SEM, TEM images of concave cubic Pt NCs/CNT and atomic models of Pt {710}, {610} and {510} planes. (f-g) CV and CA curves of ethanol oxidation on concave cubic Pt/CNT (red line), flower-like Pt/CNT (blue line) and commercial Pt/C (black line).

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## Atomic Iridium Incorporated in Cobalt Hydroxide for Efficient Oxygen Evolution Catalysis in Neutral Electrolyte

Youkui Zhang, Hongliang Jiang\*, Li Song\*

University of Science and Technology of China, Hefei, China, 230029

\*Corresponding Author's E-mail: jhlworld@ustc.edu.cn (H.J.); song2012@ustc.edu.cn (L.S.)

Electrochemical water splitting is expected to be a promising chemical process as the solution to the increasing fossil fuel depletion. Herein, a facile one-step approach is developed to synthesize a new type of well-dispersed Ir incorporated cobalt-based hydroxide nanosheets (nominated as CoIr) for OER. The Ir species as clusters and single atoms are incorporated into the defect-rich hydroxide nanosheets through the formation of rich Co-Ir species, as revealed by X-ray spectroscopic characterizations combining with HAADF-STEM measurement. The optimized CoIr displays highly efficient OER catalytic performance with an overpotential of 373 mV to achieve the current density of  $10 \text{ mA cm}^{-2}$  in 1.0 M PBS, significantly outperforming the commercial  $\text{IrO}_2$  catalysts. Further characterizations towards the catalyst after undergoing OER process indicate that unique Co oxyhydroxide ( $\text{CoOOH}$ ) and high valence Ir species with low-coordination structure are formed due to the high oxidation potentials, which authentically contributes to superior OER performance. This work not only provides a state-of-the-art OER catalyst in neutral media, but also unravels the root of the excellent performance based on efficient structural identifications.

## 单一 TiO<sub>2</sub> 纳米粒子中的多种异质结实现高效太阳能制氢

刘家利, 邹倩倩, 张侃<sup>1\*</sup>, 张胜利<sup>2\*</sup>

南京理工大学, 南京, 中国, 210094

\*zhangkan112255@hotmail.com, zhangslvip@njust.edu.cn

由于在异质结界面处具有能量型的 II 型谱带排列, 因此锐钛矿和金红石组成的 TiO<sub>2</sub> 多晶型异质结优于单个异质结。除了传统的多晶型界面之外, 表面无序 TiO<sub>2</sub> 已经引起人们的兴趣, 并被认为是显着提高光催化活性的一种有效的方法。然而, 传统的二氧化钛纳米颗粒与异质结的无序层的引入和定位仍然是一个巨大的挑战。

在这里, 我们报告了一种选择性定位的不同厚度范围的锐钛矿和金红石相之间的概念不同的合成路线高效新型无金属光催化制氢的方法(表示为 DE-P25)。采用两步无序工艺: 在相变温度以下进行金红石相选择性无序化和热退火工艺, 可以合成具有 2~3 nm 无序层的 DE-P25 单纳米粒子中的多异质结, 并通过高分辨率-TEM, 电子能量损失谱(EELS) 和首次在线电子全息测绘。DE-P25 的 EELS Ti-L2,3 光谱几何结构表明两种晶体之间有明显的缺氧变化, 这与由于局部不成对电子导致的无序层内的电势和负电荷密度的急剧下降相对应。DE-P25 的超快电荷迁移的 PL 衰变曲线表明掺入 TiO<sub>2</sub> 纳米颗粒中的无序层的金红石相诱导主导的直接激发形成并减少电荷载体的自陷, 从而抑制电子/空穴复合, 这完全符合全息映射分析。

这种由结晶锐钛矿/无序金红石/有序金红石组成的单个 TiO<sub>2</sub> 纳米颗粒中的这种多重异质结表现出不仅优异的界面电荷分离效率, 而且还具有新型金属自由表面反应性, 其协同产生的 H<sub>2</sub>, 约是传统的锐钛矿和金红石单异质结系统 140 倍的。

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## Defect-Induced Epitaxial Growth for Efficient Solar Hydrogen Production

QianQian Zou, Kan Zhang\*,and ShengLi Zhang\*

Nanjing University of Science and Technology,Nanjing 210094,People's Republic of China

\*Corresponding Author's E-mail:zhangkan12255@hotmail.com;zhangslvip@njust.edu.cn

Hydrogen evolution from water splitting has been considered as a clean, green and efficient strategy to solve the energy shortage and ameliorate environmental pollution. Therefore, exploiting hydrogen evolution reaction cocatalysts. with earth-abundant materials instead of precious platinum group metals has been actively encouraged.

Epitaxial growth suffers from the mismatches in lattice and dangling bonds arising from different crystal structures or unit cell parameters. Here,we demonstrate the epitaxial growth of 2D MoS<sub>2</sub> ribbon on 1D CdS nanowires (NWs) via surface and subsurface defects. The interstitial Cd<sup>0</sup> in the (12̄10) crystal plane of the [0001]-oriented CdS. NWs are found to serve as nucleation sites for interatomically bonded [001]-oriented MoS<sub>2</sub>,where the perfect lattice match (~99.7%) between the(10̄1) plane of CdS and the (002)-faceted in-plane MoS<sub>2</sub> result in coaxial MoS<sub>2</sub> ribbon/Cd S NWs heterojunction. The coaxial but heterotropic epitaxial MoS<sub>2</sub> ribbon on the surface of CdS NWs induces delocalized interface states that facilitate charge transport and the reduced surface state.A less than 5-fold ribbon width of MoS<sub>2</sub> as hydrogen evolution cocatalyst exhibits a~10-fold H<sub>2</sub> evolution enhancement than state of the art Pt in an acidic electrolyte, and apparent quantum yields of 79.7% at 420 nm,53.1% at 450 nm, and 9.67% at 520 nm, respectively.

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# Biomass Derived Transition Metal -N-C catalyst as a Bifunctional Catalyst for Zn-air Battery

Li Xu\*, Yuhui Tian

Institute for Energy Research, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang P. R. China,  
212013

\*Corresponding Author's E-mail: xulichem@ujs.edu.cn

Rational design of low-cost, highly activity and stable bifunctional electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) has been a great significant for metal-air batteries. In this work, we design a cost-effective approach to synthesize transition metal oxides nanoparticles embedded in nitrogen-doped carbon nanosheets for ORR and OER. In view of the components of carbon, oxygen and hydrogen without other heteroatoms, The peach gum was employed as carbon precursor for producing conductive carbon matrix to host transition metal oxide nanoparticles and M-N-C sites by hydrothermal treatment and further pyrolysis. The M-N-C catalyst presents high ORR catalytic activity with excellent four-electron selectivity and a low OER overpotential in alkaline condition. Moreover, the primary Zn-air battery assembled with M-N-C catalyst exhibits a low discharge/charge overpotential and outstanding stability, which has a bright potential for practical application on rechargeable Zn-air batteries.

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## 不同形貌碳化硅薄膜的光电析氢性能

童希立\*, 韩秀秀, 刘畅, 郭向云

中国科学院山西煤炭化学研究所, 太原, 030001

\*tongxili@sxicc.ac.cn

光电催化可通过选择半导体光电极来加速光电化学反应的作用[1]。纳米碳化硅薄膜具有可吸收利用可见光, 导电性好, 化学性质稳定性好等优点, 是一种非常有潜力的光电催化材料[2]。本工作中, 我们通过调控化学沉积碳化硅薄膜的工艺参数, 获得了微粒碳化硅, 纳米碳化硅和外延碳化硅三种薄膜。在此基础上, 我们详细研究了三种碳化硅薄膜中因缺陷, 导电性以及暴露晶面不同导致光电析氢性能的原因, 为发展先进的光电析氢催化薄膜材料提供理论基础。

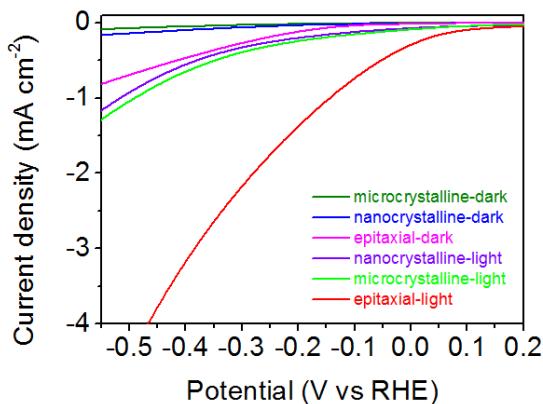


图 1. 不同形貌碳化硅薄膜的光电析氢性能测试

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## High Energy Density Redox Flow Batteries for Large Scale Energy Storage

Mei Ding, Chuankun Jia\*

College of Materials Science and Engineering, Changsha University of Science & Technology, Changsha, 410114, China

\*Corresponding Author's E-mail: jack2012ding@gamil.com

Redox flow batteries (RFBs) are considered as one of the most promising electrochemical energy storage technologies due to the decoupled energy storage and power output, flexible design and long cycle life [1]. Many kinds of RFBs have been reported. Among them vanadium redox flow battery (VRB) is the most successful system and there are many demonstrated VRB systems with energy capacity of kWh even of MWh all over the world. However, the fully commercialized of it is still hindered by its high cost and low energy density [2]. Therefore, the development of a RFB system that is shown to be compatible for both high energy and low cost are highly desired.

Here we report our results on high energy density redox targeting based systems. These systems employed high energy storage solid materials in catholyte and anolyte, respectively. A cation ion exchange polymeric membrane was used in the cell to separate the anolyte and catholyte, and prevent the permeability of active materials. The solubility of active material can reach as high as 4 M in both catholyte and anolyte, Therefore, the energy density of these RFBs are as high as 500 Wh/L, which is 5-10 time higher than that of traditional VRB. These RFB cells shown 95% Coulombic efficiency and 80% energy efficiency. The capacity retention is more than 90% even after 300 cycles. Therefore, with above merits, these redox targeting based RFBs is expected to have excellent commercial prospects as a large-scale energy storage technology.

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## 核壳结构碳化钨复合微球催化剂对甲醇电催化性能

周阳<sup>1</sup>（报告作者），俞园<sup>2</sup>，余长林<sup>1</sup>，胡仙超<sup>3,\*</sup>

<sup>1</sup>江西理工大学 工程研究院，赣州 341000；<sup>2</sup> 江西省动力电池及其材料重点实验室，赣州 341000；

<sup>3</sup>浙江工业大学 分析测试中心，杭州 310032

\*huxc@zjut.edu.cn

以偏钨酸铵微球为前驱体，在不同反应时间和 CO/CO<sub>2</sub> 气氛条件下，通过原位还原碳化反应制备了具有核壳结构碳化钨复合微球。采用 X 射线粉末衍射（XRD）、X 射线光电子能谱（XPS）和扫描电镜（SEM）等对催化剂的形貌和结构进行了表征分析。硼氢化钠还原法将平均粒径为 4.6 nm 的 Pt 纳米粒子均匀分布在其表面，得到核壳结构碳化钨复合催化剂。采用循环伏安和计时电流法研究了在酸性溶液中催化剂对甲醇的电催化氧化性能，结果表明与 Pt/WC-15h 和 JM Pt/C 催化剂的电化学性能相比而言，Pt/WC-6h 催化剂对甲醇呈现出更高的电催化氧化活性和稳定性。碳化钨复合微球表面少量 WO<sub>2</sub> 成分的存在有利于甲醇在其表面的电催化氧化过程的发生。

## 改性制备氧化铁光阳极及其光电性能的研究

张志杰（报告作者），梁彭花，黄有国，王红强，李庆余\*

广西师范大学，广西桂林，中国，541004

\* liqingyu62@126.com

氢能作为能量密度最高的燃料，加之其燃烧产物无污染，是非常高效绿色的可再生能源。因此利用太阳能将水分解为氢气和氧气，实现了太阳能的有效利用，成为目前的研究热点。光电化学的原理主要是当光照时，半导体价带中的少量电子可以被激发而进入导带，同时在价带中留下等量的空穴。半导体受激发后产生的空穴或电子若能顺利迁移至半导体表面，即可与吸附的分子进行氧化或还原反应。 $\alpha\text{-Fe}_2\text{O}_3$  性质稳定无毒无害，含量丰富，是室温下存在的最稳定的铁的氧化物。其结构为典型的六方晶系刚玉结构， $\text{O}^{2-}$  在晶体中以六方紧密堆积， $\text{Fe}^{3+}$  位氧原子的八面体空穴中，但仍然有  $1/3$  的空穴未被  $\text{Fe}^{3+}$  占据。 $\alpha\text{-Fe}_2\text{O}_3$ （带隙宽度  $2.0\text{~}2.2\text{eV}$ ）半导体的价带的能级位置比  $\text{O}_2/\text{H}_2\text{O}$  的氧化还原电位正，则在光阳极上发生水的氧化反应，其具有 n 型半导体特征。

本研究以改性基础氧化铁性能为目的，采用简单的水热法修饰氧化铁光阳极以形成复合氧化铁材料。通过水热法制备得到纯氧化铁。配制乙酸镍水溶液，将基础氧化铁放入反应釜中，在  $60^\circ\text{C}$  温度下反应不同时间。图 1 为复合 MOF 不同时间的氧化铁的光电流-电位图，从图中可以看出复合 Ni-MOF10h 的氧化铁不仅可以有效降低氧化铁的开启电势，还可以提高氧化铁光阳极的光电性能。

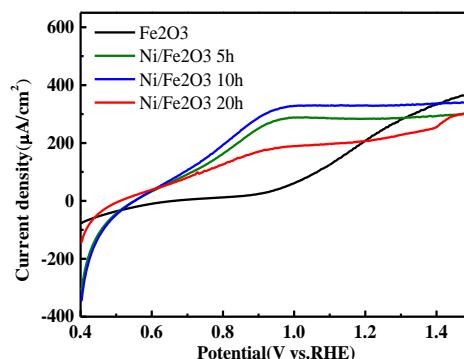


图 1 复合 MOF 不同时间的氧化铁的光电流-电位图

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# Nanocomposites Based on FeCo-based compounds as Oxygen Evolution Reaction Electrocatalysts

Guoxing Zhu,\* Xulan Xie

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China, E-mail:  
zhuguoxing@ujs.edu.cn

FeCo-based materials are promising candidates as efficient, affordable, and sustainable electrocatalysts for oxygen evolution reaction (OER). In our study, some composites containing Fe compounds and Co compounds was successfully prepared as OER catalyst. In the catalysts, there are amounts of exposed heterointerfaces between Fe compounds and Co compounds. It is believed that the exposed heterointerfaces act as catalytic active sites for OER via a two-site mechanism. It was shown that there is strong charge interaction between Co and Fe sites in the catalyst, causing acidic iron sites. The catalysts were then loaded on a  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode, the photocurrent density was increased by three times. These results may provide some hint for the design and engineering of highly active and durable catalysts.

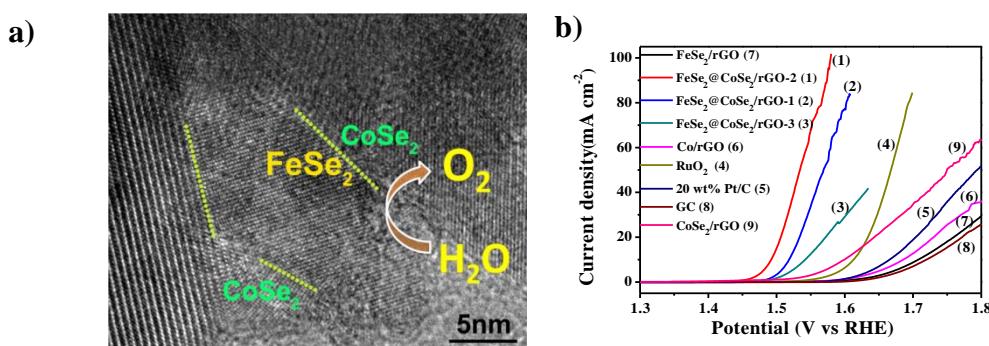


Figure 1. a) HRTEM image suggesting the formation of separated phases of composite catalysts. b) Linear sweep voltammetry curves (after  $iR$ -compensated) obtained with various catalysts.

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## 电还原二氧化碳反应催化剂合成与性能研究

陈志鹏, 牟楷文, 刘立成\*

中国科学院青岛生物能源与过程研究所, 青岛, 中国, 266101

\*E-mail: liulc@qibebt.ac.cn

本文主要研究报道了三维立体多孔碳气凝胶负载金属 Sn 催化剂的合成、表征, 及其在电催化还原二氧化碳制备甲酸反应中催化反应性能。所制备的复合电极在-0.96 V (RHE) 下, 产甲酸的法拉第效率最高达到 82.7%, 过电位降低到 361 mV, 以及电流密度高达  $32.9 \text{ mA cm}^{-2}$ 。

Sn/CNT-Aerogel (碳纳米管气凝胶) 催化剂制备过程如图 1 所示。首先将 CNTs, CS 和  $\text{SnCl}_4$  混合形成均匀的悬浮液 (a), 通过物理交联和冷冻干燥得到  $\text{Sn(OH)}_x/\text{CNT-Agls}$  (b), 所得材料再进一步通过气相氢气还原得到 Sn/CNT-Agls(c)。所得催化剂具有多级孔结构, 密度仅为  $16.2 \text{ mg cm}^{-3}$ 。

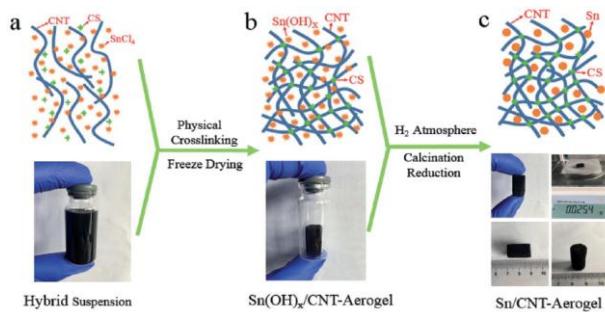


图 1 3D Sn/CNT-Agls 制备过程示意图。

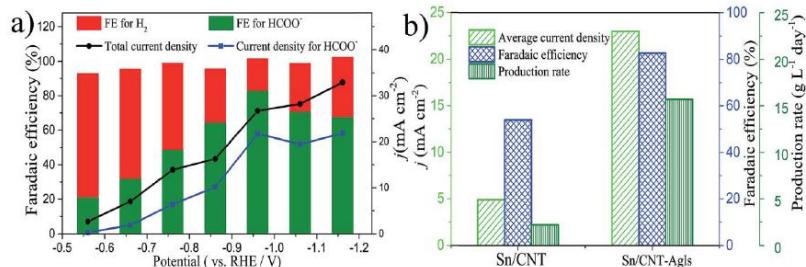


图 2 3D Sn/CNT-Agls 电催化二氧化碳反应性能。

所制备的 3D Sn/CNT-Agls 催化剂在电催化二氧化碳反应结果如图 2 所示, 随施加电压的变化, 甲酸法拉第效率在-0.96 V 有最大值, 其余产物主要是氢气, 平均电流密度随电位增加而增大 (a)。相比普通碳纳米管 (CNT) 负载 Sn 催化剂, 在相同反应条件下, 3D Sn/CNT-Agls 催化剂展现更高的反应活性, 甲酸产率达到  $15 \text{ g L}^{-1} \text{ day}^{-1}$  以上。

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# Atomic regulating Mo doped Ni<sub>5</sub>P<sub>4</sub> with rich active site for wide-pH electrocatalysis

Xianbin Liu\*, Changgan Lai, Ziping Wu, Tongxiang Liang\*

School of Materials Science and Engineering, Jiangxi University of Science and Technology, 86 Hongqi Road, Ganzhou 34100, China,

\*Corresponding Author's E-mail: Xianbin, xianbin\_liu@jxust.edu.cn;  
Tongxiang, liang\_tx@126.com

It is of essential importance to design an electrocatalyst with excellent performance for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water splitting. Ni<sub>5</sub>P<sub>4</sub> has been developed as idea HER and OER electrocatalysts. However, the catalytic efficiency and stability are unable to meet application requirements. In this work, we regulated the atomic structure via Mo doping Ni<sub>5</sub>P<sub>4</sub> via hydrothermal and calcination treatment (Figure 1). The resulted Mo-Ni<sub>5</sub>P<sub>4</sub> exhibits urchin structure with rich active sites and excellent structural stability. And then Mo-Ni<sub>5</sub>P<sub>4</sub> presents outstanding HER and OER performances (Figure 2).



Figure 1 the synthetic process and structural characteristics of Mo-Ni<sub>5</sub>P<sub>4</sub>

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## 基于静电纺丝的多级纳米结构的构筑及其电催化行为

朱罕，刘臣，潘星星，刘文杰，张玲玲，张志力，杜明亮\*

江南大学 化学与材料工程学院，合成与生物胶体教育部重点实验室，中国，无锡，214122

\*Email: du@jiangnan.edu.cn

如何设计和制备具有高活性和稳定性，同时适合规模化使用的非贵金属电催化材料依然是制约电解水制氢和氢燃料电池发展的核心和关键。将静电纺丝纤维作为反应器，在其碳化为 CNFs 过程中，孕育 LDNCs 并对其形貌和电子结构进行调控，得到低维纳米晶体 (LDNCs)/碳纳米纤维 (CNFs) 纳米结构；同时，LDNCs 可以作为催化剂将 CNFs 部分转化为碳纳米管 (CNTs)，在 CNFs 表面形成装载有 LDNCs 的 CNTs 阵列，进而得到 LDNCs@CNTs/CNFs 多级纳米结构材料，该多级纳米结构材料整合了如上所述的制备高效电催化材料的三种方法，实现了高效协同催化，同时解决了电催化材料制备中微观形貌与电子结构的调控、催化剂负载以及规模化制备等诸多问题。

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## N doped carbon dots modified WO<sub>3</sub> for efficient photoelectrochemical water oxidation

Weiqian Kong, Xiaofan Zhang\*, Binbin Chang, Shouren Zhang, Baocheng Yang

Henan Provincial Key Laboratory of Nanocomposite and Applications, Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou, Henan, 450006, China.

\*Corresponding Author's E-mail: xiaofanzhang@aliyun.com

Photoelectrochemical (PEC) solar energy conversion using nanostructure semiconductor oxide electrode is very important for developing of clean and renewable power sources.<sup>[1]</sup> So far, WO<sub>3</sub> has attracted tremendous interests due to its narrow band gap (2.5~2.8 eV), a moderate hole diffusion length (~150 nm) and high electron mobility.<sup>[2]</sup> However, WO<sub>3</sub> still has a poor PEC properties because of its slow charge transfer at the semiconductor/electrolyte interface and rapid electron-hole recombination.<sup>[3]</sup> Some strategies have been used for improving the PEC performance including element doping, coupling with other semiconductor oxides and carbon materials.<sup>[4]</sup> The N doped carbon dots (NCDs) with advantages of stability, unique electron reservoir, photo-induced electron transfer property have been widely applied in photocatalysis.<sup>[5]</sup> In the present work, we fabricate NCDs modified the WO<sub>3</sub> nanoflakes (NCDs/WO<sub>3</sub>) for water splitting. The photocurrent current density of NCDs/WO<sub>3</sub> is 1.45 mA cm<sup>-2</sup> at 1.0 V vs. SCE, which is 2.5 times than that of bare WO<sub>3</sub> photoanode in 1 M H<sub>2</sub>SO<sub>4</sub> solution. In addition, the onset potential of NCDs/WO<sub>3</sub> exhibits a cathodic shift of 70 mV. These results demonstrated NCDs can inhibit the recombination of photogenerated carries and improve the charge transfer process.

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# An one-pot Electrochemical Synthesis of Aryl Nitriles from Methyl Arenes in Aqueous ILs Solution

Zhi-Cheng Cao, Jian-Chao Liu, Ying-Hong Zhu\*

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, China, 310014

Email: yhzuchem@zjut.edu.cn

Nitriles are widely used as synthetic intermediates for pharmaceuticals, pesticides, dyes and material sciences<sup>[1]</sup>. Traditionally, there are two strategies in the synthesis of nitriles: (1) C–C bonds formation, including the Sandmeyer reaction and Rosenmund–von Braun Reaction; (2) C–N bonds formation, including the oxidation of amines, dehydration of amides, aldoximes, and Schmidt reaction. Under the demand of environmental friendliness, the electro-activated transformation of simple hydrocarbon via C–H bonds to corresponding functional group has been established under mild conditions<sup>[2]</sup>. Here, we presented an one-pot electrochemical synthesis of 4-methoxy -benzonitrile(4-MBN) from 4-methoxy toluene(4-MT) with hydroxylamine in aqueous ionic liquid solution<sup>[3]</sup>.

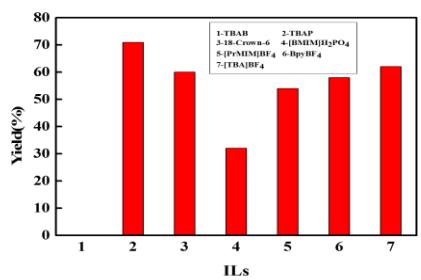
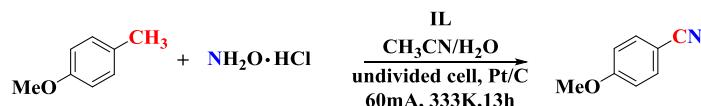


Fig. 1. The constant current electrolysis yields of 4-MBN in different ILs

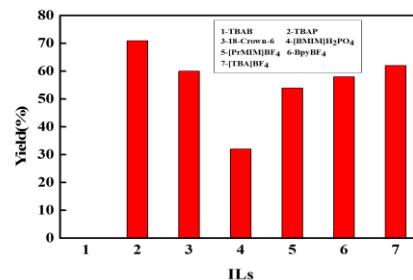


Fig. 1. The constant current electrolysis yields of 4-MBN in different ILs

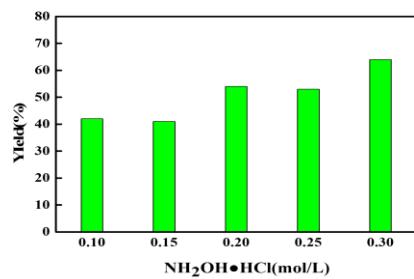


Fig. 3. The yields of 4-MBN under different NH<sub>2</sub>OH·HCl concentration

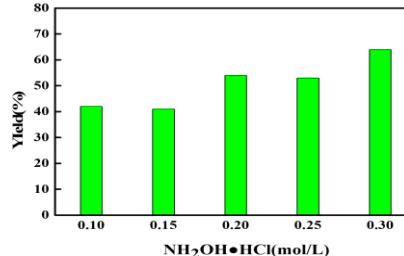


Fig. 3. The yields of 4-MBN under different NH<sub>2</sub>OH·HCl concentration

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# 金属相富缺陷 MoS<sub>2</sub> 纳米卷高效电催化制氢

王龙禄（报告作者），鲁兵安

湖南大学物理与微电子科学学院，湖南省长沙市岳麓区湖南大学，410082

\*Wanglonglu@hnu.edu.cn

近年,非贵金属基复合材料作为一种新型的析氢反应活性催化剂,由于其低廉的成本、高效的催化活性备受人们关注<sup>[1-3]</sup>。二硫化钼(MoS<sub>2</sub>)是一种具有类石墨烯结构的新型层状材料,拥有极高的析氢催化活性,是人们研究的一大热点。MoS<sub>2</sub> 的催化效果主要与其活性位点的活性、数量及其导电性有关, 我们创造性的设计了高密度活性位点的 MoS<sub>2</sub> 纳米卷。研究结果表明,一维材料独特的几何外形克服了二维片层材料易团聚堆叠的现象, 其表面丰富的缺陷为电催化制氢提供了丰富的活性位点。尺寸均一的 MoS<sub>2</sub> 纳米卷在电极表面交错排列,为二硫化钼催化活性位点的暴露提供了高比表面的形貌基础。该材料的催化析氢过电位为-0.11 V,塔菲尔斜率为 38 mV/decade,是一种理想的电催化析氢材料。

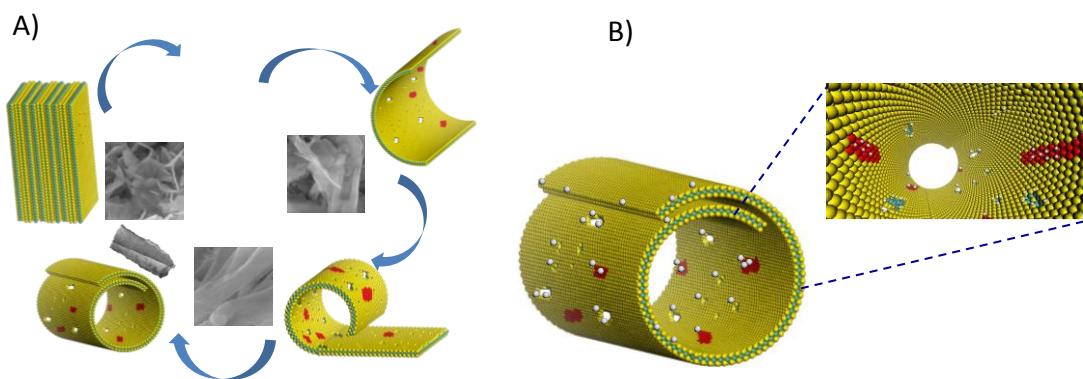


图 1: A)MoS<sub>2</sub> 纳米片蜷曲成纳米卷, B) 多相富缺陷 MoS<sub>2</sub> 纳米卷高效电催化制氢机

图1A)展示了MoS<sub>2</sub>纳米卷的形成过程,首先我们通过水热法合成了一定厚度的MoS<sub>2</sub>纳米片。然后对其进行超声剥离,层数逐渐减少,表面缺陷逐渐增加,同时由于片层两面的缺陷数量不一致,而使得其表面能失衡,为了保持其结构的自身稳定性,片层自然卷曲成纳米卷。从图中可以清晰的看出纳米卷上的缝隙,这种卷曲方式,保持了活性边缘的暴露,并通过缺陷位点的产生而营造出了更多的活性位点。更令人惊奇的是,在纳米卷形成的过程中所产生的应力及表面缺陷存在的情况下,MoS<sub>2</sub>的晶体结构也发生了变化,有半导体性质的2H结构转变成了金属性质的1T相结构。这种1T相结构的引入不仅能够增强材料的导电性,同时也改进了活性位点的活性和数量,甚至改变了电催化制氢的析氢机制(图B)。

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# Atomic-scale Core/Shell Structure Engineering Induces Precise Tensile Strain to Boost Hydrogen Evolution Catalysis

Han Zhu\*, Chen Liu, MingLiang Du

College of Chemistry and Materials Engineering, Jiangnan University, Wuxi, 214122

E-mail:du@jiangnan.edu.cn

The production of hydrogen and oxygen through water splitting are promising and appealing solution for developing clean-energy technologies.<sup>[1,2]</sup> To optimize and enhance electrocatalysts performance and durability for the hydrogen and oxygen evolution reactions through electrolysis, we describe a new class of Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub> core-shell structures formed on carbon nanofibers with cubic Co<sub>9</sub>S<sub>8</sub> as cores and layered layered MoS<sub>2</sub> as shells. The core-shell design of these nanostructures allows us to combine the advantages of MoS<sub>2</sub> and Co<sub>9</sub>S<sub>8</sub>, serving as switchable electrocatalyst for H<sub>2</sub> and O<sub>2</sub> evolutions. The unique Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub> demonstrates low onset potentials and overpotentials at  $j=10\text{ mA/cm}^2$  of 64 and 190 mV for HER and 350 and 430 mV for OER, respectively, when compared with individual MoS<sub>2</sub> and Co<sub>9</sub>S<sub>8</sub> phase. The high hydrogen and oxygen evolution activities of the Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub> is due to the electrocatalytic synergistic effects of nano-interfaces generated by directly contact regions between the Co<sub>9</sub>S<sub>8</sub> and MoS<sub>2</sub> shell. These advantages can generate strong electron transfer between Co and Mo through the intermediate sulfur atoms bonded to both metals, leading to the promising promoted electrocatalytic activity.<sup>[3,4]</sup>

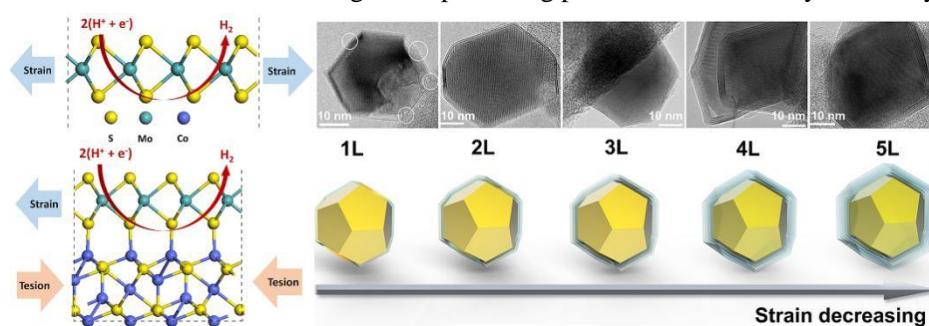


Figure 1 Synthetic process for Co<sub>9</sub>S<sub>8</sub>/MoS<sub>2</sub> core/shell nanocrystals with precisely controlled shell numbers supported on CNFs

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# Anionic Regulated NiFe (Oxy)Sulfide electrocatalysts for Water Oxidation

Shu-Yuan Zhang, Bo-Quan Li, Qiang Zhang\*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, China, 100084

\* E-mail: zhang-qiang@mails.tsinghua.edu.cn

Constructing active sites with intrinsic oxygen evolution reaction (OER) reactivity is of great significance to improve the efficiency of abundant sustainable energy devices. Electronic structure of electrocatalysts is highly considered toward superb OER performance by affording favorable active sites for reactant adsorption, electron transfer, and product desorption. The electronic structure of typical inorganic electrocatalysts is highly dependent on the coordinated anions, which serve as electron donors and interact through ionic polarization. An anion regulation methodology is herein proposed to optimize the electronic structure by regulating the species and content of anions with different polarized degrees for superb OER electrocatalysts. The resultant (oxy)sulfides exhibit the OER reactivity highly dependent on the anion composition with the optimized NiFeS-2 electrocatalyst even better than noble metal  $\text{IrO}_2$  electrocatalyst. The anionic regulation methodology enlightens a new point of view for the in-depth understanding of electrocatalysis at the electronic and atomic level.

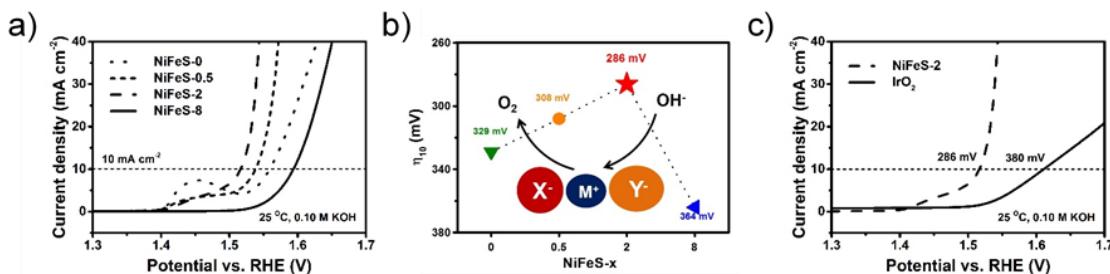


Figure 1. (a) Oxygen evolution reaction (OER) linear sweep voltammetry (LSV) profiles of NiFeS-x ( $x = 0, 0.5, 2, 8$ ) electrocatalysts. (b) Volcano plot of OER reactivity characterized by the overpotential at  $10.0 \text{ mA cm}^{-2}$  against the vulcanization degree under anionic regulation, inset: scheme illustration of the anionic regulation strategy. (c) OER LSV profiles of NiFeS-2 and  $\text{IrO}_2$ .

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## 过渡金属硫化物的催化氧还原性能研究

黄太仲（报告作者），房恒义，梁栋，孙玥，于洁玫，张昭良

济南大学化学化工学院，济南，中国，250022

\* chm\_huangtz@ujn.edu.cn

贵金属氧还原催化剂价格昂贵、资源有限以及还需要进一步提高寿命等缺点已经越来越成为燃料电池的发展障碍，因此开发低成本、资源丰富、高性能的氧还原催化剂就成为燃料电池发展的关键技术<sup>[1]</sup>。在已开发的各种非贵金属催化剂中金属碳化物、氮化物、氧化物以及各种纳米结构的碳材料等都显示出良好的催化性能，但是到目前为止，这类催化剂的研究距离实际应用还有一定距离<sup>[2-4]</sup>。在各种催化剂不断发展的过程中，金属硫化物催化剂也受到了人们的关注<sup>[5]</sup>，本实验室重点研究了  $\text{NiS}_x$ ， $\text{CoS}_x$ ， $\text{FeS}_x$  等金属硫化物的制备和催化氧还原性能，图 1 为  $\text{NiS}$  和  $\text{NiS}_2$  催化氧还原的反应机理以及 RDE 测试结果。

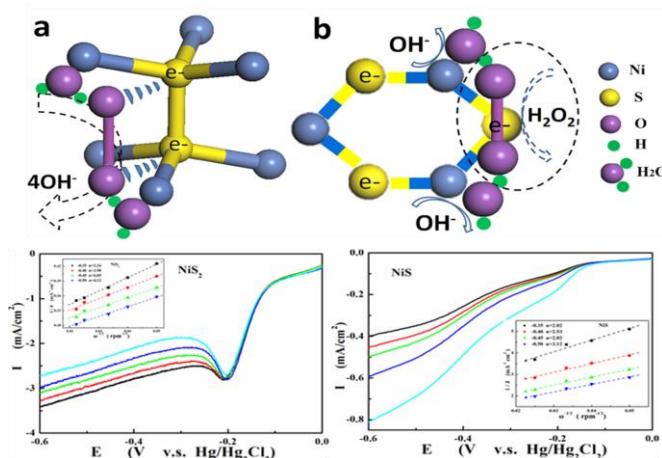


图 1 (a) $\text{NiS}_2$  的反应机理，ORR 主要通过 4 电子反应途径发生；(b) 是  $\text{NiS}$  的反应机制，其 ORR 过程主要通过 2 电子反应途径发生。

在 Fe、Co 基硫化物的研究中，我们得到了类似的结论。金属的二硫化物具有比一硫化物更高的催化氧还原起始电势和峰值电势和电流，石墨烯等导电剂的添加可以改善催化剂的催化性能，这可能是由于催化剂的协同效应以及导电性的改善所引起的，金属硫化物氧还原催化剂在碱性电解液中具有良好的催化氧还原性能，其部分性能甚至超过了传统的 Pt/C 催化剂，具有良好的应用前景。

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## 纳米尺度钯铂合金的结构调控及其电催化性能

陈青松（报告作者），唐敬毅，白冰，赵秀慧，郭国聪\*

结构化学国家重点实验室，中科院福建物质结构研究所，福建，福州，350002

\* gcuo@fjirsm.ac.cn

直接醇燃料电池（DAFCs）因其具有清洁、便捷、能量密度高、环境友好等优点，而引起广泛的研究兴趣。虽然经过几十年的研究，DAFCs 已经有很大的进展，但离商业应用还有很长的一段路要走。主要是因为燃料电池所用的催化剂为贵金属铂，其储量少、价格昂贵，大大限制了其实际应用；另外铂催化剂易中毒，大大降低了其催化效率。钯对有机小分子氧化也有很好的催化活性，且与铂相比具有价格相对低廉的优点，因此钯基催化剂成为近年 DAFCs 研究的热点。催化剂的性能与表面结构和组成密切相关，高指数晶面具有较高的表面能，含有高密度的台阶、扭结等活性位而表现出优异的催化性能，已成为近年纳米材料控制合成、催化研究领域的焦点。我们采用电化学法首次可控合成出八面体、凹-立方体及螺旋状纳米线 PdPt 合金纳米材料，并研究了它们对甲醇、乙醇、乙二醇和丙三醇的电催化氧化性能。研究表明 PdPt 合金纳米材料具有比商业 Pt/C 催化剂更好的催化性能。PdPt 合金的催化性能高度依赖其表面组成和结构。具有高指数晶面的 PdPt 凹立方体和螺旋状纳米线表现出对甲醇、乙醇和乙二醇更好的电催化活性。而表面裸露{111}基础晶面的 PdPt 八面体对丙三醇催化活性更好。

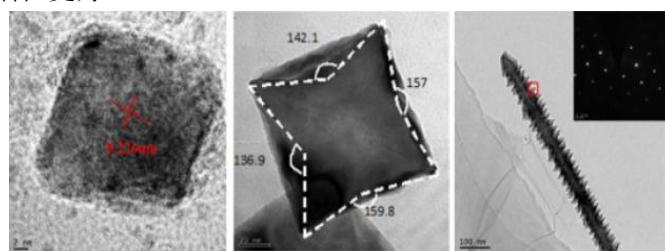


图 1 八面体、凹立方体和螺旋状纳米线 PdPt 合金

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# Facile synthesis of Ni:FeOOH@BiVO<sub>4</sub> photoanode for efficient water oxidation

Xiaofan Zhang\*, Weiqian Kong, Baocheng Yang

Henan Provincial Key Laboratory of Nanocomposite and Applications, Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou, Henan, China, 450006.

\*Corresponding Author's E-mail: xiaofanzhang@aliyun.com

Developing efficient co-catalysts is significantly challenging for the BiVO<sub>4</sub> which suffers from fast electron-hole recombination and slow kinetics during photoelectrochemical (PEC) water splitting [1-2]. Herein, amorphous co-catalyst Ni doped FeOOH (Ni:FeOOH) is loaded onto 3D nanoporous BiVO<sub>4</sub> (BiVO<sub>4</sub>@Ni:FeOOH) by facile electro-deposition method. The BiVO<sub>4</sub>/Ni:FeOOH exhibits a photocurrent density of 2.86 mA cm<sup>-2</sup> at 1.23 V vs. RHE under AM 1.5 G irradiation and a much lower onset potential of 0.25 V vs. RHE. The detailed optical and electrochemical studies reveal the improved electron lifetime and the hetero-junction formed in BiVO<sub>4</sub>/Ni:FeOOH, as well as the excellent optical property of Ni:FeOOH, contributed to the high PEC performance. Therefore, the charge transfer and separation efficiency are both higher than the pristine BiVO<sub>4</sub>. Furthermore, the light absorption is extended to 600 nm attributed to the narrow band gap of Ni:FeOOH, and the IPCE value significantly increases within 380-600 nm. This study provides a facile method to synthesize Ni:FeOOH, which can be widely integrated with various photoanodes to improve PEC water oxidation.

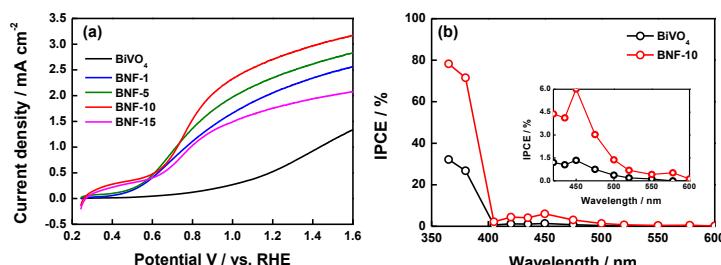


Figure 1. (a) LSV curves and (b) IPCE plots (inset: magnified IPCE spectra within 420-600 nm) of all prepared photoanodes.

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## 铜基镀镓电极用于电解回收镓的研究

段国义（报告作者），张景，乔玲玲，唐阳，孙艳芝，陈咏梅\*，万平玉

北京化工大学理学院应用电化学研究所，北京，100029

\*chenym@mail.buct.edu.cn

将氧化铝生产母液中的镓富集浓缩为高浓度含镓碱液，再通过电沉积使镓以金属形式析出是工业上生产粗镓的主要方法<sup>[1-3]</sup>。受阴极表面析氢副反应的影响，电沉积镓过程中的电流效率往往低于50%。

本研究以高析氢过电位金属镓作为活性物质<sup>[4]</sup>，在铜基电极表面形成镓镀层，并以该铜基镓(Cu/Ga)电极作为阴极电解回收镓。通过对Cu/Ga电极的析氢、析镓电化学行为进行系统研究，表明该电极具有较高的析氢过电位，增加了阴极表面镓沉积电位与析氢电位的差别，从而提高了电沉积镓的电流效率。通过对电解条件的优化表明，在温度低于镓熔点(29.78 °C)时，小电流密度条件下更利于镓的析出。在20 °C温度下，以100 A m<sup>-2</sup>电流密度对镓浓度为40 g L<sup>-1</sup>的电解液进行30 h持续恒流电解，电流效率高达95.45%，远高于工业生产中使用不锈钢电极常见的电流效率45%。

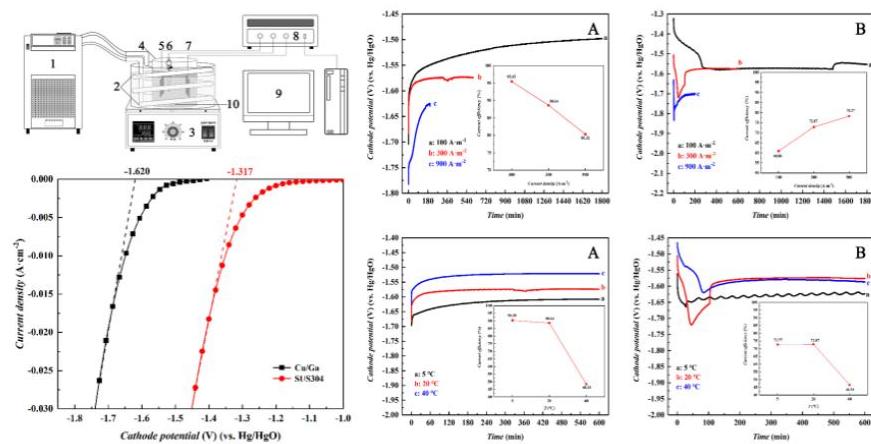


图1 实验装置示意图及主要实验数据

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## Oxygen functionalized $\text{Ti}_3\text{C}_2$ MXene with enhanced electrocatalytic activity for hydrogen evolution

Yanan Jiang, Bingbing Tian\*

Shenzhen University, Shenzhen, China, 518060

\*Corresponding Author's E-mail: tianbb2011@szu.edu.cn

MXenes, a new family of two-dimensional materials, have been predicted to be new catalysts in hydrogen evolution reaction (HER), based on theoretical calculations about -O terminated MXenes. However, fully oxygen terminated MXenes are hard to obtain, for the coexist of -F and -OH terminals. In this context, a designed method to significantly enhance the HER performance of  $\text{Ti}_3\text{C}_2$  MXene by O functionalized terminal groups is reported. O terminated  $\text{Ti}_3\text{C}_2$  ( $\text{Ti}_3\text{C}_2\text{O}_x$ ) obtained by post-processing of -OH terminated groups was found to exhibit far higher HER activity than  $\text{Ti}_3\text{C}_2\text{T}_x$  ( $\text{T}=\text{F}, \text{OH}$  and  $\text{O}$ ). Specifically,  $\text{Ti}_3\text{C}_2\text{O}_x$  afford a low overpotential of 198 mV at the current density of 10 mA cm<sup>-2</sup>. Remarkably, long-term of 20 h with almost no change for the current density indicated the good stability. We propose that O atoms located on the basal planes of  $\text{Ti}_3\text{C}_2$  MXene are active sites for HER, unlike  $\text{MoS}_2$ , whose active sites are located at the edges. This work paves the way for the development of MXene materials applied in HER.

## 二维金属有机框架电催化还原 CO<sub>2</sub>性能研究

侯淑贞（报告作者），古志远\*

南京师范大学，南京，中国，210023

\* E-mail: guzhiyuan@njnu.edu.cn

金属有机多孔骨架材料 (Metal-Organic Frameworks, MOFs) 亦称为配位聚合物 (Coordination Polymers)，是一类由金属离子或金属簇与刚性有机分子形成的一维、二维或三维的多孔材料。这类材料具有高孔隙率、超大的比表面积、孔道结构与性质可调控等优良性能，因此金属-有机骨架材料在分离、气体储存、光电催化[1-2]等领域具有广泛应用前景。本论文利用含 Co 等的二维金属有机框架材料作为催化剂，利用其金属活性位点将二氧化碳 CO<sub>2</sub>电化学还原生成高附加值的化学品或燃料[3-4]，在-0.564V (vs. RHE) 时，CO 的法拉第效率 FE<sub>(CO)</sub>达 69.4%，总电流密度为 1.8mA/cm<sup>2</sup>，将可再生能源转变为高能量密度的燃料储存，具有重要的现实意义。

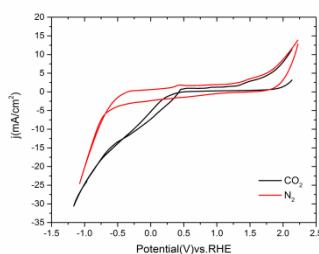


图 1 二维金属有机框架在 N<sub>2</sub> (红色) 或 CO<sub>2</sub> (黑色) 饱和的 0.5M 的 KHCO<sub>3</sub> 电解液中的 CV 曲线

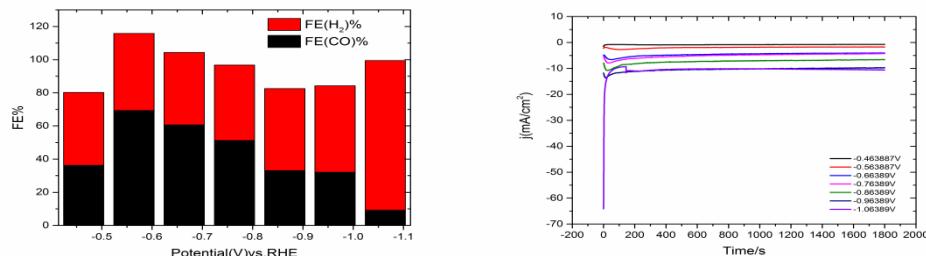


图 2 CO<sub>2</sub>饱和的 0.5M 的 KHCO<sub>3</sub> 电解液中不同电位下的法拉第效率 FE(左)和 i-t 曲线(右)

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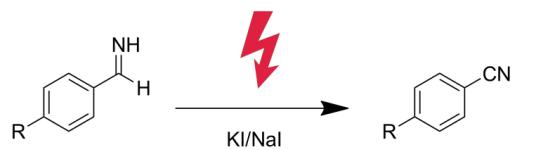
## 有机氰化物的电解合成

袁孟珂, 康红卫\*

黄河科技学院, 郑州, 中国, 450000

\*hongweikang@infm.hhstu.edu.cn

芳香氰基化合物是一类非常重要的有机化合物, 广泛应用在药物合成/材料制备等领域。传统的合成路线是有两种, 其一是使用氰化钠/钾, 氰化亚铜等毒性超强的氰基盐来制备<sup>[1]</sup>; 其二是通过亚胺或者肟的氧化脱氢/脱水制备。在亚胺的脱氢反应中, 普遍使用化学计量的单质碘来反应, 由于碘单质的毒性和高昂的价格, 这就意味着该类反应比较重的污染及高的成本。我们采用电解碘盐的方式, 可再生的产生碘单质, 并循环参与亚胺的脱氢反应。绿色高效的制备了芳香氰基化合物, 探索了制备有机氰化物的一条可持续路线。



10 examples yield: >70%

图 1 电解催化氰基反应示意图

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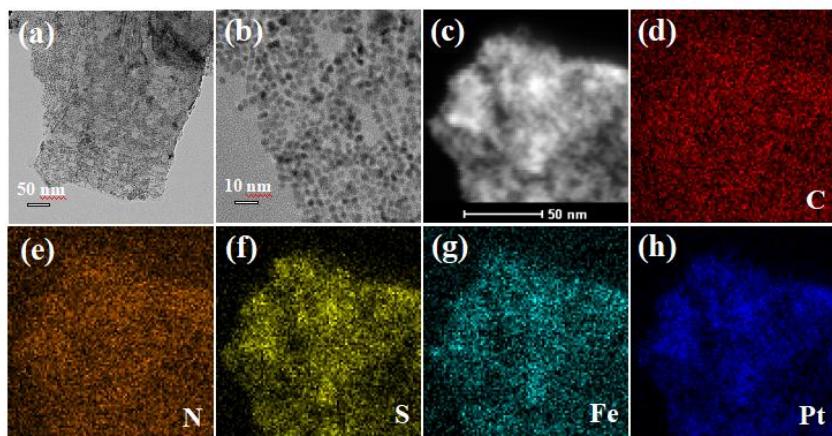
# Fe-S-N 共掺杂石墨烯载 Pt 催化剂的制备及其对甲醇氧化和氧还原反应的性能

钟静萍（报告作者），唐华果，项胜，孙悦，李佳，樊友军\*

广西低碳能源材料重点实验室，广西师范大学化学与药学学院，桂林，中国，541004

\*youjunfan@mailbox.gxnu.edu.cn

近年来的研究发现，在石墨烯表面上引入外来掺杂原子是增强其表面沉积金属纳米颗粒活性的一种有效途径<sup>[1]</sup>。本文通过热处理酞菁铁四磺酸钠功能化石墨烯制得 Fe-S-N 共掺杂的石墨烯（Fe-S-N-GR），然后负载 Pt 纳米颗粒制备了一种新的 Pt/Fe-S-N-GR 催化剂。为了比较其对甲醇氧化和氧还原反应的性能，还在相同条件下制备了未掺杂氧化石墨烯载 Pt 催化剂（Pt/GO）。图 1 给出了 Pt/Fe-S-N-GR 催化剂的 TEM 和 STEM 图，由图 1a 和 b 可知，Pt 纳米粒子均匀地沉积在 Fe-S-N-GR 表面，粒径统计得到该催化剂中 Pt 纳米粒子的平均尺寸为 2.77 nm。STEM 结果表明，Pt, Fe, S, N 等元素在催化剂中分布均匀（图 1c-h）。电化学测试显示，所制备的 Pt/Fe-S-N-GR 具有比 Pt/GO 和商业 Pt/C 催化剂更高的甲醇氧化和氧还原反应电催化性能。



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## C-H 键选择性电氧化合成芳香腈类化合物

曹志成, 刘建超, 廖艳梅, 朱英红\*

浙江工业大学, 杭州, 中国, 310014

Email: yhzuchem@zjut.edu.cn

腈类化合物是一种重要的有机合成中间体, 在农药、医药、功能材料、香料等领域具有广泛的应用<sup>[1]</sup>。传统方法以 Sandmeyer 反应、Rosenmund-von 反应、过渡金属催化卤代芳烃与氰化试剂偶联反应为主。通常会使用剧毒的的氰化试剂, 反应条件比较苛刻, 三废污染严重。近年来通过建立 C-H 键活化方式, 在温和的条件下实现甲基芳烃的氰基化逐渐成热点<sup>[2]</sup>。然而过程以昂贵的过渡金属催化, 氧化剂氧化的方式实现, 反应成本高, 条件苛刻。通过电化学手段活化 C-H 键的方式, 过程只涉及电子得失, 避免催化剂的消耗和氧化剂的浪费, 同时可以通过控制电位、电流等方式提高反应的选择性。根据课题组前期对芳烃类化合物直接电氧化成芳香醛的研究<sup>[3-4]</sup>, 本文设计了以 4-甲氧基甲苯(*p*-MT)为底物, 盐酸羟胺(HAM)为氮源, 四丁基高氯酸盐(TBAP)为支持电解质, 直接电解合成 4-甲氧基苯腈(4-MBN)的绿色合成路线。讨论了电解质、电极材料、溶剂及电流密度对反应收率和选择性的影响。

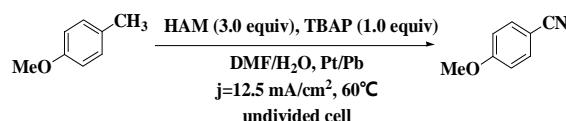


表 1 支持电解质、溶剂、电极材料、电流密度对收率和选择性的影响

Table 1 Effect of supporting electrolyte, solvent, electrode and current density on the yield and selectivity

Entry	Electrolyte (equiv)	Electrode	J(mA/cm <sup>2</sup> )	Solvent	Yield <sup>b</sup> (%)	C(%)	S(%)
1	TBAP(1.6)	Pt-C	15.0	CH <sub>3</sub> CN/H <sub>2</sub> O	71	92	77
2	18-Crown-6(3.3)	Pt-C	15.0	CH <sub>3</sub> CN/H <sub>2</sub> O	60	99	61
3	[TBA]BF <sub>4</sub> (1.6)	Pt-C	15.0	CH <sub>3</sub> CN/H <sub>2</sub> O	62	93	67
4	[PrMIM]BF <sub>4</sub> (3.3)	Pt-C	15.0	CH <sub>3</sub> CN/H <sub>2</sub> O	54	86	63
5	[BMIM]H <sub>2</sub> PO <sub>4</sub> (3.3)	Pt-C	15.0	CH <sub>3</sub> CN/H <sub>2</sub> O	46	98	47
6	TBAP(0.5)	Pt-Pb	12.5	CH <sub>3</sub> CN/H <sub>2</sub> O	79	97	81
7	TBAP(0.5)	Pt-Pb	12.5	DMF/H <sub>2</sub> O	85	99	86

a: Electrolytic conditions: *p*-MT (3mmol), solvent (30 mL), T (60°C), 19h, undivided cell.

b: yields were determined by GC.

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## 仿生催化产生 NO 的级联催化组装体的构建研究

韦天祎

湖南大学

一氧化氮具有扩张血管、调节血压、抑制血小板粘附等作用，补充供给内外源性一氧化氮，提高血液一氧化氮浓度是血栓、高血压等心血管疾病预防和治疗的一种重要措施。目前，内外源性 NO 的供给主要依赖于 NO 供体化合物的补充或者血管内皮细胞的一氧化氮合酶转基因表达。但是 NO 供体药物存在药物作用时间短、生物稳定性差、人体毒副作用大、缺乏靶向性和组织特异性等不足。一氧化氮合酶转基因技术存在表达量难以控制、存在表达滞后的药物见效慢等不足。

针对该问题，该项目拟将生成  $H_2O_2$  的氧化还原酶与  $Fe_3O_4$  纳米颗粒级联，发展 NO 仿生催化酶体系模拟一氧化氮合酶功能，以及体内的精氨酸等内源物质作为反应底物，实现 NO 的持续、稳定、可控的催化生成，将为 NO 的生物供给和利用提供一种新的模式，在心血管疾病预防与治疗方面具有潜在的医学应用前景。

## 彩色 TiO<sub>2</sub> 的合成及其光电催化性能研究

周苇<sup>1,\*</sup>（报告作者），刘春雷<sup>2</sup>，刘会娟<sup>2,\*</sup>，郭林<sup>1</sup>

<sup>1</sup> 北京航空航天大学 化学学院，北京，100191

<sup>2</sup> 中国科学院生态环境研究中心 环境水质学国家重点实验室，北京，100085

\*zhouwei@buaa.edu.cn; hliu@rcees.ac.cn

通过纳米结构微调控，利用简单水热法在泡沫钛基板上生长出一系列彩色的 TiO<sub>2</sub> 纳米阵列，考察一维楔形结构的纳米尺寸对阵列光学性能的影响规律。通过模拟计算发现，纳米阵列的长度对色彩基本没有影响，而每根楔形线的厚度影响材料对紫外和可见光的吸收，其宽度则影响光谱中近红外的吸收。由于这一特殊结构对光子具有极好的局囿作用，以红色 TiO<sub>2</sub> 为光电极，在 0.5 V vs SCE 电压下，其具有 1.5 mA cm<sup>-2</sup> 的光电流，为白色阵列的 3 倍。利用光电联合降解金属络合物 0.1 mM 的 Ni-EDTA，降解效率高达 100%，并且在负极对 Ni(II) 的回收高达 94%，远远超过白色 TiO<sub>2</sub> 阵列（62% 降解率和 58% 的回收率）。其优异的光电催化效果，可以归于红色 TiO<sub>2</sub> 优异的光学特性，近乎 100% 的紫外光吸收特性以及对可见光的在阵列结构上的局囿效应<sup>[1]</sup>。此工作为设计合成高性能光电催化剂提供借鉴，我们也合成了具有 6-nm 光电子传输单通道的 TiO<sub>2</sub> 多级结构，同样具有优异的光电催化特性<sup>[2]</sup>。

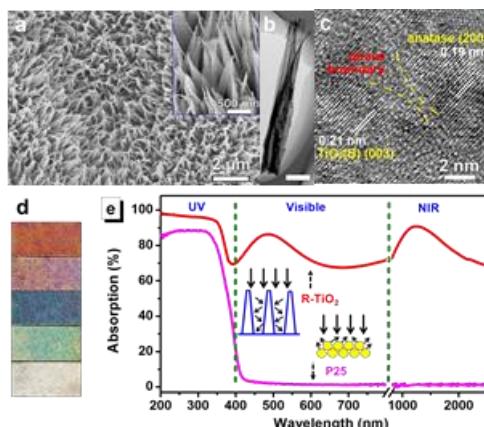


图 1. 合成的红色 TiO<sub>2</sub> 的(a)扫描图及内插放大图；(b)透射图及对应的高分辨图；(c)生长在泡沫钛片上的系列彩色的 TiO<sub>2</sub> 阵列的宏观图；(e)红色 TiO<sub>2</sub> 和 P25 的紫外-可见-近红外谱图

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# Confined Bimetallic Phosphide within P, N Co-doped Carbon Layers towards Boosted Bifunctional Oxygen Catalysis

Shuang Yang, Qun He, Changda Wang, Hongliang Jiang,\* Chuanqiang Wu, Yuikui Zhang, Yu Zhou, Li Song\*

National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience,  
University of Science and Technology of China  
Hefei, 230029, China

\* jhlworld@ustc.edu.cn (H. J.); song2012@ustc.edu.cn (L. S.).

S.Y. and Q.H. contributed equally to this work.

Rational design of bifunctional oxygen electrocatalysts with high efficiency and low cost is crucial but still challenging for the development of rechargeable energy storage devices. In this work, a novel electrocatalyst possessing the structure that P, N co-doped defective carbon shells coated well-defined bimetallic phosphide nanoparticles and sandwiched between another P, N co-doped defective two-dimension (2D) carbon layers, is achieved through a space-confinement phosphorization strategy. Our electrochemical measurements demonstrate that the obtained CoMnP<sub>4</sub> nanoparticles-containing hybrids can serve as a highly efficient bifunctional oxygen reduction and evolution reaction (ORR/OER) catalyst. It delivers a small potential difference of 0.75 V in 0.1 M KOH solution along with long-term catalytic durability, superior to the most non-precious metal catalysts reported to date. This work opens up a facile way to design effective and durable bifunctional oxygen electrocatalysts for practical applications in renewable energy production.

## Synthesis of Bifunctional Electrocatalyst for Oxygen Reactions Using Earth-Abundant Coal as The Raw Material

Xingxing Chen<sup>1,\*</sup>, Huimin Liu<sup>1</sup>, Haoran Pan<sup>1</sup>, Zhenjie Lu<sup>1</sup>, Tao Wang<sup>2</sup>, Justus Masa<sup>3</sup>

<sup>1</sup> Research Group of Functional Materials for New Energy, School of Chemical Engineering, University of Science and Technology Liaoning, 114051 Anshan, China

<sup>2</sup> Key Laboratory of Energy Materials Chemistry, Institute of Applied Chemistry, Xinjiang University, 830046 Urumqi, China

<sup>3</sup> Analytical Chemistry - Center for Electrochemistry, Ruhr-University Bochum, 44801 Bochum, Germany

\*Corresponding author's E-mail: xingchenstar79@163.com

The heteratom-doped carbon has been widely used as potential electrocatalytic materials for many renewable energy conversion and storage systems, such as rechargeable metal air batteries and regenerative fuel cells. On the other hand, the earth-abundant coal, essentially consists of carbon, hydrogen, oxygen, nitrogen and sulfur, together with other trace elements in the ash, such as iron, manganese, alumina, calcium, silica, potassium, sodium, is one of the important family members of carbon. Herein, we report the simple conversion of earth-abundant coal to highly active and stable oxygen electrocatalysts. The mesoporous graphitic coal-derived carbon demonstrated a very good electrocatalytic performance towards both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) in 0.1 M NaOH, thus providing a unique opportunity to directly transform traditional energy resource i.e. coal into a valuable oxygen electrocatalyst.

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# Porous Polymeric Metallocporphyrin and Exfoliated MnO<sub>2</sub> Layer Composites for Catalytic Water Oxidation

Liming Wang, Yong Gao, YingYing Li, Weijun Yang\*

College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082 Hunan, China

\* wjyang@hnu.edu.cn

Hydrogen energy is widely used due to its high energy density. Of numerous hydrogen production technologies, water splitting using solar energy has been highlighted<sup>[1]</sup>. Water oxidation is the critical step for hydrogen production technology. However, it is thermodynamically uphill and requires high energy input without a catalyst<sup>[2]</sup>. Therefore, the development of efficient and cheap catalyst is essential. Easy to prepare, inexpensive layered manganese oxides (birnessite, etc.) are a new kind of OER catalysts<sup>[3]</sup>, but they also have some shortcomings. On the one hand, poor conductivity at room temperature limits its charge transport properties; on the other hand the layered structure is unstable and its large particle size and particle thickness also inhibit its electrocatalytic activity<sup>[4]</sup>.

Metallocporphyrins have high conjugated structure and good electron transfer properties and are widely used in the study of catalytic oxidation of hydrocarbons. Because the porous conjugated metallocporphyrin polymers have higher conjugated structure, they exhibit higher catalytic activity and electron-delocalization than monomeric metallocporphyrins, so they have good electrochemical performance<sup>[5]</sup>.

In this study, birnessite was exfoliated, finally a thin layer of only 1-2 nm thickness is obtained. And then it was combined with Mn(III) meso-tetra(4-aminophenyl)porphyrin (MTAP). Coupling of MTAP by paradibromobenzene on the surface of the birnessite layer. Finally, a reticulate porous polymeric manganese porphyrin/MnO<sub>2</sub> composite catalyst was obtained. The structural features and chemical compositions were characterized by IR, SEM/TEM,XPS, BET. The electrocatalytic properties of birnesssite particle, birnesssite sheet, birnesssite sheet with MTAP on the surface, and composites of porous polymeric MTAP with birnessite sheet were compared. According to LSV curve and CV curve test, composites of porous polymeric MTAP with birnessite sheet exhibited the highest activity and most stable performance.

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# Design of multidimensional nanocomposite material to realize the application both in energy storage and electrocatalysis

Qiancheng Zhu, Ying Yu\*

Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China

\* E-mail: yuying01@mail.ccnu.edu.cn.

We provide an ideology of multidimensional nanocomposite material design, which is universal both in energy storage and electrocatalysis. The structure design idea provides three main points for the composite material: a strong substrate, an active material and a performance improver, which may lead us to design the composite materials used in other areas. Additionally, we provide an in-situ Raman method to investigate the chemical change in OER process. Especially, the in-situ Raman mapping can reflect the chemical change at a large area, which is more accurate and intuitive than a single point. Thus, this technique can be expected to have a wide application in more and more research areas.

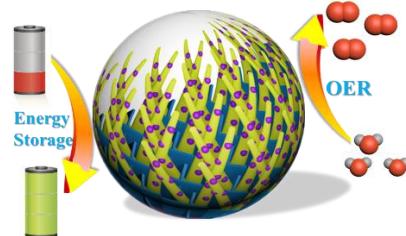


Figure 1. Schematic of the designed TNC with three kinds of dimensions used as energy storage material and OER catalyst simultaneously.

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## 自由交流

### Synthesis of Sub-2 nm Iron-Doped NiSe<sub>2</sub> Nanowires and Their Surface-Confining Oxidation for Oxygen Evolution Catalysis

Chao Gu, Shu-Hong Yu\*

Division of Nanomaterials & Chemistry, Hefei National Research Centre for Physical Sciences

at the Microscale, University of Science and Technology of China, Hefei 230026, China

E-mail: shyu@ustc.edu.cn

Ultrathin nanostructures are attractive for diverse applications owing to their unique properties compared to their bulk materials.<sup>[1,2]</sup> Transition-metal chalcogenides are promising electrocatalysts, yet it remains difficult to make ultrathin structures (sub-2 nm),<sup>[3]</sup> and the realization of their chemical doping is even more challenging.<sup>[4]</sup> Herein we describe a soft template mediated colloidal synthesis of iron-doped NiSe<sub>2</sub> ultrathin nanowires (UNWs) with diameter down to 1.7 nm. The synergistic interplay between oleylamine (OAm) and 1-dodecanethiol (DDT) is crucial to yield these UNWs. The in situ formed amorphous hydroxide layer that is confined to the surface of the ultrathin scaffolds enables efficient oxygen evolution electrocatalysis. The UNWs exhibit a very low overpotential of 268 mV at 10 mA cm<sup>-2</sup> in 0.1 M KOH, as well as remarkable long-term stability, representing one of the most efficient noble-metal-free catalysts.<sup>[5,6]</sup>

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## 甲醇燃料电池中毒化中间体 CO 的有效调控

连小兵, 陈文杰, 黄妙龄, 吴启辉\*

泉州师范学院化学化工学院, 泉州, 中国, 362000

\* E-mail: qhwu@qztc.edu.cn

燃料电池具有高能量利用率和环境友好的优点, 是最有发展前途的一种能量利用方式, 其中催化剂是燃料电池商业化的主要瓶颈, 有机小分子中间产物 (CO) 导致催化剂中毒一直是困扰燃料电池阳极催化剂的重要问题。本小组建立了可控电位高效更换溶液的电解池体系<sup>[1]</sup>, 以此研究了甲醇 ( $\text{CH}_3\text{OH}$ ) 在不同电位下的 Pt 电极上解离 CO 的过程, 。实验结果表明, 如图 1 所示, 随着电位正移,  $\text{CH}_3\text{OH}$  在 Pt 上产生的 CO 覆盖度由-0.1 V 的 11% 逐渐升高到 0.25 V 的 55% 后急剧下降到 0.5V 的 0%, CO 覆盖度随电位变化图呈拱形。这预示着我们可以利用甲醇在不同电位下解离 CO 覆盖度的区别, 在采用高氧化性金属形成合金氧化 CO 的方法<sup>[2]</sup>之外, 可以用降低 Pt 表面电极电势的方式减少 CO 的生成, 从而减轻 CO 毒化的影响。如图 2 所示, 在断路情况下, Pt 电极的状态与所处环境相关, 可通过  $\text{ocp} \sim t$  监测电极表面状态。我们在电极状态改变到-0.1V, 0 V 和 0.2V 时分别加入甲醇, 解离 200s 后去除甲醇, 用 CV 检测表面吸附的 CO 的量, 发现-0.1 V 时加入甲醇产生的 CO 量最少。在燃料电池工作前还原 Pt 催化剂, 例如控制负电位、加入还原剂或者掺杂具有较高还原性的金属, 可有效降低 CO 的毒化作用。

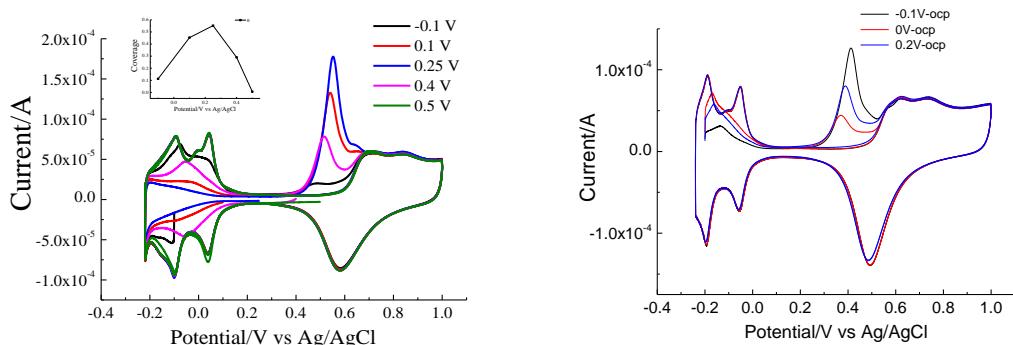


图 1. 0.1 M  $\text{CH}_3\text{OH}$  溶液在不同电位的 Pt 电极上解离并吸附的 CO 在 0.5M  $\text{H}_2\text{SO}_4$  的 CV 曲线, 扫描速度 50mV/s。(内图为甲醇在 Pt 上解离的 CO 覆盖度随解离电位变化图)

图 2. 0.1 M  $\text{CH}_3\text{OH}$  溶液在不同开路电位(ocp)的 Pt 电极上解离 200s 产生的 CO 在 0.5M  $\text{H}_2\text{SO}_4$  的 CV 曲线, 扫描速度 50mV/s。

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## Preparation of polypyrrole modified Pd-Ag cathode for ECH

Xuefeng Wei\*, Xiaoyang Wan, Weiwei Lu

College of Chemical Engineering & Pharmaceutics, Henan University of Science and Technology, Luoyang,  
471023, P.R. China

\*Corresponding Author's E-mail: xfwei@haust.edu.cn

The pollution of chlorophenols (CPs) is of great concern because of their high toxicity, recalcitrance, bioaccumulation, persistence in the environment. CPs have been listed as priority pollutants by USEPA<sup>[1]</sup>. Electrocatalytic hydrodechlorination (ECH), an efficient method, has been employed due to its rapid reaction rate, low apparatus cost, mild reaction conditions, and absence of secondary contaminants<sup>[2,3]</sup>. Polypyrrole (PPy), as electric conductivity polymers, has been developed rapidly, which can be used as proper host matrices to obtain highly dispersed metallic particles<sup>[4]</sup>. Pd-M<sub>IB</sub> bimetallic electrodes exhibit superior catalytic properties in electrocatalysis. Therefore, the PPy modified Pd-Ag bimetallic catalytic electrodes were prepared for ECH. The prepared nano cube Ag@Pd/PPy/Ti composite electrode (shown in Fig.1) showed high catalytic activity for ECH of CPs.

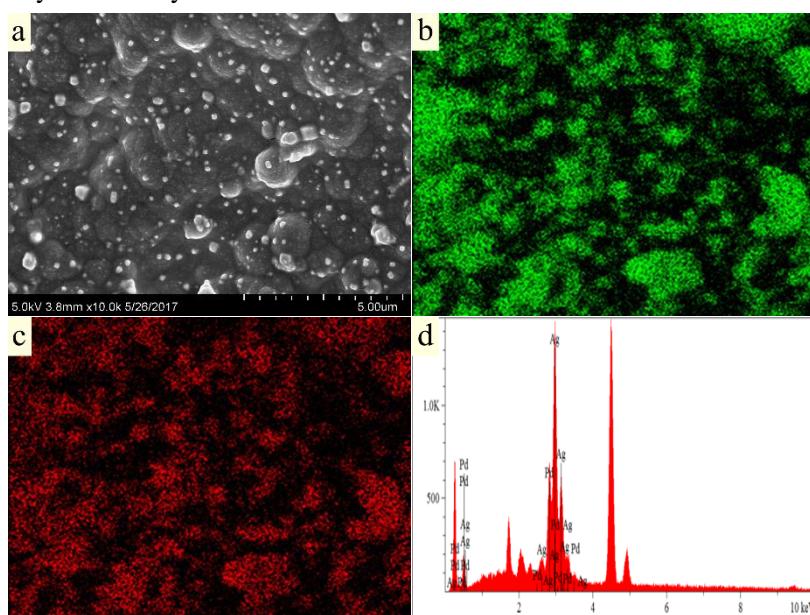


Figure 1. The characterization of prepared nano cube Ag@Pd/PPy/Ti composite electrode

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## 三维有序多级孔道电催化材料的制备与性能研究

徐联宾\*

北京化工大学有机无机复合材料国家重点实验室，北京，中国，100029

\* xulb@mail.buct.edu.cn

三维有序大孔/介孔多级孔道电催化材料结合了大孔材料的优良传质性能、介孔材料的高比表面积，以及互相连通的大孔/介孔网络骨架的增强材料导电性和稳定性的优点，在实际电催化应用上具有独特的优势。本文采用模板法制备了三维有序大孔/介孔（3DOM/m）金属、有序介孔金属微球阵列、3DOM/m 碳负载金属纳米颗粒，以及双掺杂的 3DOM/m 碳等材料，并研究了其电催化甲醇氧化反应（MOR）、氧气还原反应（ORR）、析氢反应（HER）和析氧反应（OER）性能。和非多级孔道的同类催化剂相比，制备的有序大孔/介孔多级孔道电催化剂具有更高的催化活性和稳定性。

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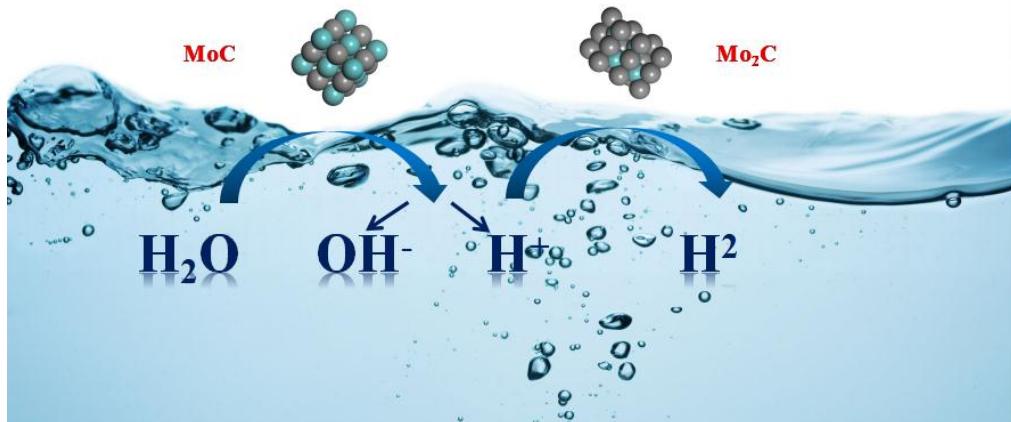
# MoC-Mo<sub>2</sub>C/Co composites as efficient electrocatalysts for hydrogen evolution

author: Hao Zhang, Yuqi Yang, Fanfei Sun, Yang Liu, Zheng Jiang\*

Chinese Academy of Science, Shanghai Institute of Applied Physics, Shanghai, China, 201204

\*Corresponding Author's E-mail: Jiangzheng@sinap.ac

Composites of transition metal carbides present an intriguing opportunity toward enhanced activity in hydrogen evolution reaction (HER). Herein, the dual-phase molybdenum carbide composites were found as highly effective catalysts for HER in alkaline media. Investigation of the catalysts using X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM) and X-ray absorption fine structure (XAFS) spectroscopy uncovered the synergistic effect between  $\alpha$ -MoC and  $\beta$ -Mo<sub>2</sub>C. A series of MoC<sub>x</sub>-Co composites were simply achieved by controlling the Co/Mo ratio of the precursors in the same synthesis condition. The MoC<sub>x</sub>-Co<sub>0.53</sub> catalysts consisting of  $\beta$ -Mo<sub>2</sub>C and  $\alpha$ -MoC was created due to the incorporation of metallic Co. The high activity of the catalyst in alkaline media was possibly attributed to the synergistic effect between  $\alpha$ -MoC and  $\beta$ -Mo<sub>2</sub>C, where  $\alpha$ -MoC site is beneficial for water dissociation and hydrogen prefers to release on  $\beta$ -Mo<sub>2</sub>C sites. Next, we are going to perform density functional theory (DFT) calculations to supply complementary evidence.



## **Electrochemical and XAFS study of mono- and bis-nuclear iron phthalocyanine for oxygen reduction reaction**

刘洋

上海物理研究所

Exploring the efficient non-noble catalysts for oxygen reduction reaction(ORR) is still a major challenge for large-scale commercialization of proton exchange membrane fuel cell(PEMFC). Iron phthalocyanine(FePc), as a similarity to the main struction of Heme a3 in cytochrome c oxidase(CcO), is considered as one of the most promising catalysts, especially the bis-nuclear iron phthalocyanine(bi-FePc). In this work, rotating disk electrode(RDE) experiment was carried out to study the catalytic activity of FePc and bi-FePc, followed by X-ray absorption fine struction(XAFS) in order to study the origin of the catalysis difference between them. EXAFS fitting results show that the structures around the active site Fe-N4 of FePc and Bi-FePc are almost the same, the better catalytic activity for Bi-FePc may result from the capacity to bind the two oxygen atoms simultaneously during ORR.

# MOF衍生纳米碳基高效氧还原电催化剂

来庆学，梁彦瑜\*

南京航空航天大学材料科学与技术学院，江苏省能量转换材料与技术重点实验室，南京，中国，邮编 210016

\*liangyy403@126.com

燃料电池和金属空气电池等作为清洁可持续电化学储能与转换技术均涉及多电子参与的、动力学缓慢的氧还原反应(ORR)，导致器件过电位过高、稳定性差以及贵金属催化剂使用带来的生产成本高昂等问题。因此，迫切需要开发廉价高效的ORR电催化剂材料，降低其生产成本，提高整体器件性能，从而加速其大规模商业化应用历程。

为此，我们利用ZIF-8为前驱物，(1)开发了原位限域热解转换策略，利用聚合物与ZIF-8的界面作用，结合静电纺丝技术和石墨烯复合策略，实现了从一维到三维结构的全方位调控(图1A)，为活性中心的充分利用和快速传质过程提供了可靠的保障；(2)开发了金属掺杂诱导法(图1B)，在碳骨架上成功构筑了高催化活性的复合螯合结构N-Cu<sup>2+</sup>-Cu<sup>0</sup>；(3)利用MOF间的主客体化学作用(图1C)，成功合成了不同配位数的Fe-N活性中心，并结合密度泛函理论计算揭示了5配位的Fe-N中心具有最优的电催化活性，为高效铁基催化剂的设计提供了新的思路。

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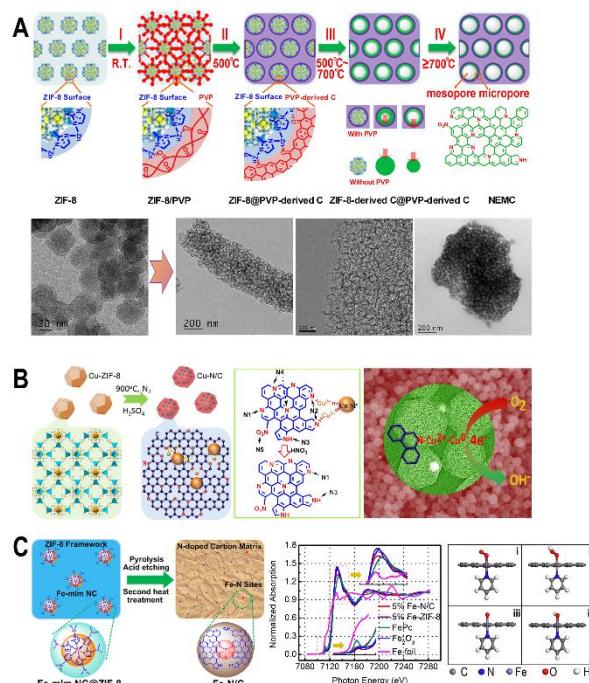


图1 A)原位限域热解策略、B)金属掺杂诱导法以及C) 主客体化学策略制备纳米碳基氧还原催化剂

## 活性氯催化的电化学聚合制备聚三聚氰胺薄膜

陈述\*, 刘思远, 温傲立, 张杰, 聂会东, 陈建, 曾荣今, 龙云飞

湖南科技大学化学化工学院, 湘潭, 中国, 411201

\* chenshumail@gmail.com, chenshu@hnust.edu.cn

聚三聚氰胺是一种新型电活性聚合物, 在电化学和生物传感中已备受关注<sup>[1,2]</sup>。但其电化学聚合机理研究较少, 之前的报道认为三聚氰胺的电化学聚合只能在强酸溶液中发生<sup>[3,4]</sup>。我们首次发现其电聚合过程可以在不同 pH 值的水溶液中进行, 前提是聚合液中须有微量的氯离子存在。实验详细研究了氯离子、聚合电位和 pH 值在电化学聚合过程中的作用, 微量氯离子能有效促进聚三聚氰胺薄膜的生产(即使 5 mM), 电聚合过程中原位阳极氧化生成的活性氯能有效促进聚三聚氰胺薄膜在不同 pH 值溶液中的生长。基于电聚合过程中发生的系列相关反应, 我们给出了可能的电聚合机理<sup>[5]</sup>。由此, 通过澄清三聚氰胺的电聚合新机理, 可以在不同 pH 条件下制备聚三聚氰胺薄膜, 为有效控制导电聚合物薄膜提供依据。

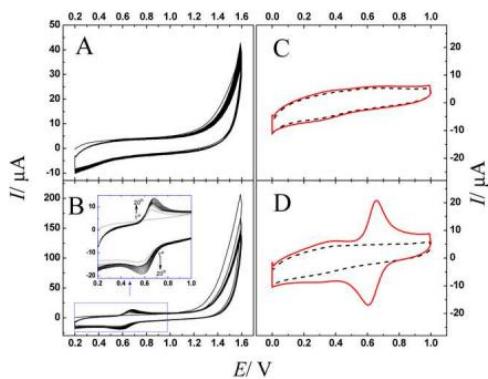


图 1 有无氯离子存在下三聚氰胺的电化学聚合过程

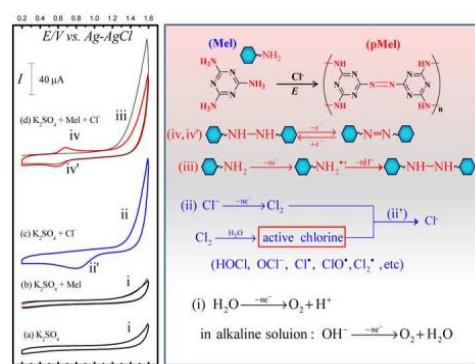


图 2 氯离子催化电化学聚合的机理示意图

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# 功能化 CMK-3 用于电羧化反应的研究

蒙王军, 张志霞, 秦森, 王欢\*, 陆嘉星\*

华东师范大学, 化学与分子工程学院, 上海市绿色化学与化工过程绿色化实验室, 上海, 中国, 200062

\* E-mail: hwang@chem.ecnu.edu.cn; jxlu@chem.ecnu.edu.cn

有序介孔碳的功能化可以将性能优良的介孔碳赋予特定的功能, 使其在应用中发挥更大的作用<sup>1</sup>。电羧化芳香卤代物不仅能降解难以自然分解的有毒物质, 还能固定二氧化碳在一定程度上缓解温室效应<sup>2</sup>。本论文采用二维六方介孔碳 CMK-3 的复合功能化掺杂含氮官能团制备用于芳香卤代物电羧化的工作电极, 优化条件下氯苯电羧化产率可达 79%。

## 1. 复合功能化 CMK-3 材料的制备及表征

以 SBA-15 为模板, 蔗糖为碳源, 硝酸银为金属前驱体, 通过水热法合成金属功能化材料 Ag@CMK-3。在此基础上通过重氮反应向 Ag@CMK-3 引入含氮官能团, 得到复合功能化材料 N-Ag@CMK-3。

如图 1a 所示, 银纳米颗粒均匀的分散在介孔碳当中, 平均粒径大约为 10 nm。由图 1b 可知通过氮杂功能化的样品在 1500 cm<sup>-1</sup> 和 1610 cm<sup>-1</sup> 有明显的特征峰, 分别为-NH<sub>2</sub> 与 C-N 的吸收峰。图 1c 中 N-Ag@CMK-3 材料在 200–450°C 的失重行为与 Ag@CMK-3 的有所区别说明该区间的失重为有机官能团分子。由图 1d 可知表面掺氮功能化课提升材料的二氧化碳吸附性能, 这将有助于电羧化进行。

## 2. 复合功能化 CMK-3 材料的电羧化应用

通过将样品材料制备成工作电极, 使用恒电位电解法电解氯苯可得到表 1 的电羧化结果。通过考察两种工作电极在相同电位电解的结果可知, N-Ag@CMK-3 电羧化催化性能优于单纯金属功能化的 Ag@CMK-3。通过优化 N-Ag@CMK-3 材料的不同电解电位, 可得最优条件下氯苯的电羧化产率可达 79%。

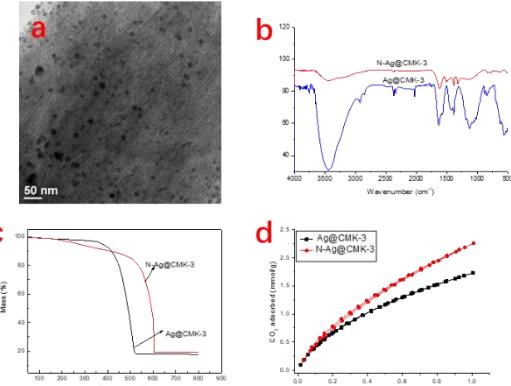


图 1 N-Ag@CMK-3 的 TEM (a)、IR (b)、TGA (c) 和 CO<sub>2</sub> 吸附性能(d)

表 1 氯苯在复合功能化 CMK-3 电极上的电羧化

Entry	Cathode	Potential (V)	Yield (%)
1	Ag@CMK-3	-1.5	58
2	N-Ag@CMK-3	-1.5	67
3	N-Ag@CMK-3	-1.4	79
4	N-Ag@CMK-3	-1.3	53

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# 铜基 MOFs 材料电极的制备及电催化还原二氧化碳研究

刘丽, 杨满平, 智文雅, 王欢\*, 陆嘉星\*

华东师范大学, 化学与分子工程学院, 上海市绿色化学与化工过程绿色化实验室, 上海 200062

\* E-mail: hwang@chem.ecnu.edu.cn; jxlu@chem.ecnu.edu.cn

化石燃料资源的加速消耗导致大气中二氧化碳含量的上升, 进而导致能源危机和全球变暖<sup>[1]</sup>。将二氧化碳转换为高能量密度的燃料和化学原料已经得到较大的关注。电催还原二氧化碳, 由于其温和的反应条件、可控的选择性, 被广泛探索<sup>[2]</sup>。高效催化剂的开发仍然是一个巨大的挑战。本论文中, 我们初步探索铜基 MOFs 材料在水溶液中电还原 CO<sub>2</sub>气体制备醇类化合物的能力。

## 1. 材料的制备及表征

以 Cu(NO<sub>3</sub>)<sub>2</sub> 与 H<sub>3</sub>BTC 为原料制备 Cu-MOF 材料。

材料 XRD 图(图 1a)中的衍射峰通过 Jade 软件分析, 可以知道制备的材料是铜基 MOFs 材料。由 SEM 图(图 2)可以看到实验制备的铜基 MOFs 材料呈粒状, 颗粒规整。

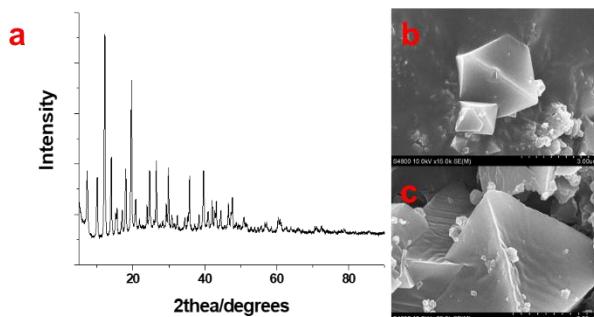


图 1 铜基 MOFs 的 XRD (a) 和 SEM (b, c) 图

## 2. 材料的电催化性能研究

将制备好的材料应用于电还原二氧化碳反应, 产物乙醇电流效率见表 1。看到随着电解电量的增加, 乙醇的电流效率是呈现下降趋势的。

表 1 不同电解电量下的 CO<sub>2</sub> 的电流效率

序号	电解电量/C	乙醇的电流效率/%
1	120	33.3
2	140	28.8
3	160	17.5

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# NiCo<sub>2</sub>O<sub>4</sub> nanowires@MnO<sub>x</sub> nanoflakes supported on stainless steel mesh with superior electrocatalytic performance for anion exchange membrane water splitting

L. Zeng

HKUST Jockey Club Institute for Advanced Study, The Hong Kong University of Science and Technology,  
Clear Water Bay, Kowloon, Hong Kong SAR, China

\*Corresponding Author's E-mail: [melzengan@ust.hk](mailto:melzengan@ust.hk)

Recently, anion exchange membrane (AEM) water splitting has been developed to address the cost issue related to its counterpart, proton exchange membrane water splitting [1-3]. In this talk, a core-shell structured catalyst with NiCo<sub>2</sub>O<sub>4</sub> nanowires as the core and MnO<sub>x</sub> nanoflakes as the shell is synthesized and deposited on a stainless steel mesh, and applied in AEM water splitting. This unique structured catalyst allows the core material, NiCo<sub>2</sub>O<sub>4</sub> nanowires, to serve as the electrically conductive skeleton, and the shell material, MnO<sub>x</sub> nanoflakes, to be the electroactive sites. As a result, the catalyst exhibits a superior electrocatalytic activity ( $\eta=342$  mV @10 mA cm<sup>-2</sup>) toward the oxygen evolution reaction. The water splitting cell with the catalyst can be operated at 200 mA cm<sup>-2</sup> with an overpotential of about 500 mV and stably run for 100 hours without significant degradation. The results demonstrated here shows that the NiCo<sub>2</sub>O<sub>4</sub>@MnO<sub>x</sub> is a promising candidate for the oxygen evolution reaction in the alkaline media. (The work described in this paper was supported by a grant from the Research Grant Council of the Hong Kong Special Administrative Region, China. Project No. T23-601/17-R)

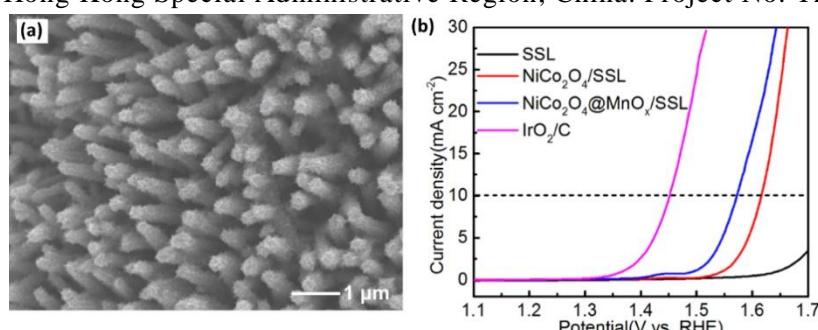


Figure 1: The morphology and catalytic activity of the NiCo<sub>2</sub>O<sub>4</sub> nanowires@MnO<sub>x</sub> nanoflakes

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# High-Stability Pd/Carbon Hetero-Quantum Dots for Efficient Electrochemical and Photoelectrochemical Hydrogen Generation

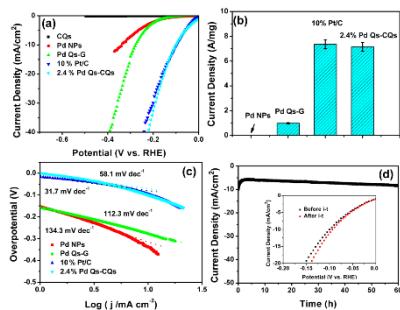
Zhihua Xiang, Xinwen Peng\*

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology,

Guangzhou, China, 510640

\*Email: fexwpeng@scut.edu.cn

A high-quality heterojunction between the semiconductor and the carefully selected high-performance electrocatalyst is crucial for the improved efficiency of photoelectrochemical water splitting for hydrogen generation. Herein, we report an active system of Pd-decorated carbon hetero-quantum dots (2.4%) for the hydrogen evolution reaction (HER). The synergistic effect of the CQs can facilitate electron–hole separation, leading to 1191.2 times and 7.24 times larger catalytic current density than those of Pd NPs and Pd Qs/G. We also demonstrate its enhanced PEC performance with a high photocurrent density of 37.5 mA cm<sup>-2</sup> at 0 V (vs. RHE) under simulated 100 mW cm<sup>-2</sup> (1 Sun) irradiation. The synergistic effects of the excellent light harvesting of the carbon quantum dots, as well as the excellent electrocatalytic activity of the Pd, boost the production and utilization of photogenerated electrons. The design of Pd-decorated carbon quantum dots offers a new strategy for preparing highly efficient photoelectrochemical solar energy conversion devices.



**Fig. 1** (a) Polarization curves (normalized to the geometric electrode area), (b) the catalytic activity (normalized to the content of noble metal) and (c) corresponding Tafel plots of CQs, Pd NPs, Pd Qs/G, 2.4% Pd Qs/CQs and 10% Pt/C. (d) Current-time plots with an overpotential of 100 mV. Inset is HER polarization curves for 2.4% Pd Qs/CQs before and after i-t testing.

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# Co-Fe LDH catalysts for electrochemical synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub>O under ambient pressure

Lingling Qiao, Guoyi Duan, Sheng Zhang, Yongmei Chen\*

School of Science, Beijing University of Chemical Technology, Beijing, Chaoyang District, 100000

\*Corresponding Author's E-mail: chenym@mail.buct.edu.cn

Co-Fe LDH nanowall array was grown on the surface of foamed nickel in hydrothermal conditions (as shown in Fig.1). These modified foamed nickel electrodes were used as cathode and the nickel wire as anode in a non-membrane and hermetically sealed cell with 25 mol kg<sup>-1</sup> KOH as the electrolyte. The electrolysis was performed by constant-potential method at 80 °C with the flow rate of N<sub>2</sub> gas was set in 10-60 mL min<sup>-1</sup>. The concentration of NH<sub>4</sub><sup>+</sup> in 0.01 M H<sub>2</sub>SO<sub>4</sub> (as the absorption solution for the produced NH<sub>3</sub> escaped from the cell) was determined by Nessler's reagent.

The results shown that the rate of ammonia formation in this study is up to 1.1×10<sup>-9</sup> mol s<sup>-1</sup> cm<sup>-2</sup>, comparing with 3.59×10<sup>-12</sup> mol s<sup>-1</sup> cm<sup>-2</sup> in reported study using Fe<sub>2</sub>O<sub>3</sub>-CNT as electrochemical catalyst under ambient pressure and temperature (see the listed data in Tab.1).

**Table 1** The electrocatalytic ammonia formation rates in the reported work and this study

Catalyst	T( °C)	Raw materials	Ammonia formatin rate ( mol s <sup>-1</sup> cm <sup>-2</sup> )	Reference
Ru	90	N <sub>2</sub> and H <sub>2</sub> O	2.12×10 <sup>-11</sup>	[1]
Fe-based Catalyst	250	N <sub>2</sub> and H <sub>2</sub> O	8.27×10 <sup>-9</sup>	[2]
La <sub>0.8</sub> Cs <sub>0.2</sub> Fe <sub>0.8</sub> Ni <sub>0.2</sub> O <sub>3-δ</sub>	600	N <sub>2</sub> and H <sub>2</sub> O	1.23×10 <sup>-10</sup>	[3]
Fe <sub>2</sub> O <sub>3</sub> -CNT	room temperature	N <sub>2</sub> and H <sub>2</sub> O	3.59×10 <sup>-12</sup>	[4]
This work	80	N <sub>2</sub> and H <sub>2</sub> O	1.10×10 <sup>-9</sup>	-

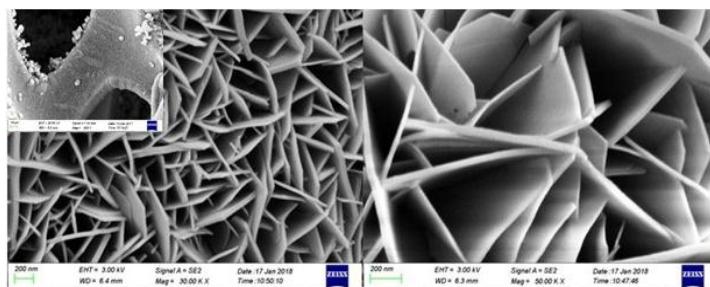


Fig.1 Co -Fe LDH nanowall arrays on the surface of foamed nickel

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## 一种 2, 3, 5, 6 四氯吡啶电催化选择性氢化脱氯的方法

刘建超, 曹志成, 朱英红\*

浙江工业大学, 杭州, 310014

E-mail: yhzuchem@zjut.edu.com

吡啶氯化物的合成研究一直是化工行业的一个热点, 含吡啶结构的化合物已成为近年新农药合成的主要方向。因此含吡啶结构的化合物的电还原有重要的研究价值, 本文以电化学还原 2,3,5,6-四氯吡啶作为底物, 研究不同活化条件电极的催化活性及不同位置氯的还原脱氯电位。

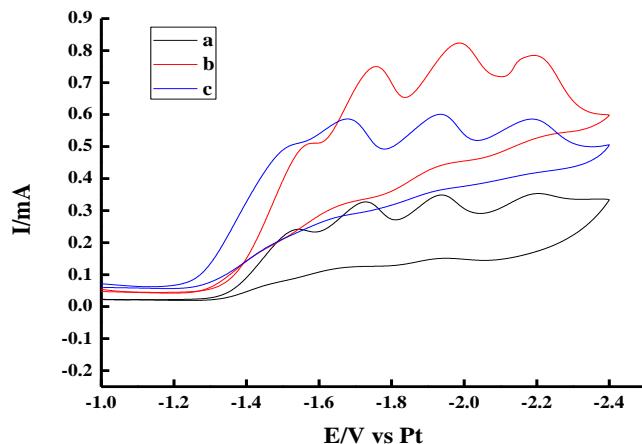


Fig.1 Cyclic Voltammetric Curve of Activation Conditions in 0.1MTBAP Acetonitrile Solution

a: 未活化; b: 计时电位法活化; c: 循环伏安法活化

图 1 是在不同活化条件下 2,3,5,6-四氯吡啶在 0.1M 四丁基高氯酸铵 (TBAP) 乙腈溶液中的循环伏安曲线, 比较 a, b, c 可知, 不同活化条件电极还原脱氯的电催化性差异较大, 经计时电位法活化和循环伏安法活化, 电极表现出更强的催化活性。2,3,5,6-四氯吡啶在计时电位法、循环伏安法活化条件都有较好的电化学响应, 据此可推测对于未经活化的银电极表面结构比较致密, 经活化后电极其表面发生了重整, 重整后电极具有更高的孔隙率和比表面积。同时从图中可以看出, 2,3,5,6-四氯吡啶在该体系下连续出现了 4 个不可逆还原峰, 对应的峰电位为 -1.55V, -1.75V, -2.0V, -2.2V。可以在这些电位下对 2,3,5,6-四氯吡啶进行恒电位电解实验。

# 氮掺杂碳/过渡金属复合材料的制备及其电催化还原二氧化碳性能

苗智超, 刘伟琪, 周晋\*

山东理工大学, 淄博 中国, 255049

\*zhoujin820514@163.com

经济发展和世界人口的不断增加, 加大了对能源的消耗, 从而导致大气中的二氧化碳含量逐年增长, 温室效应产生的影响越来越严重。电化学还原二氧化碳可以利用非高峰电力或间歇性可再生能源, 将二氧化碳转化为具有附加值的液体燃料和化工原料, 是一种绿色能源储存和碳循环的好方法。

## 1.1 Co@CN<sub>x</sub>复合材料电催化还原二氧化碳

金属有机骨架材料(MOFs)是近年来发现的一类新型多孔材料, 它具有高孔隙率、低密度、孔道规则、多活性位点等优点, 目前的研究多数集中在把 MOFs 高温热解合成的材料用于气体吸附、液相催化等方面。受限于其较差的稳定性(在较大电压下易分解), MOFs 材料在电化学催化方面的还不是很多。在本研究中, 我们采用 MOFs 模板法制备氮掺杂碳/过渡金属复合材料用于电催化还原二氧化碳。通过调节 ZIF-67 的热解温度以得到不同结晶程度的 Co@CN<sub>x</sub> 复合材料, 并测试电化学性能。我们以金属钴活性中心, 保持催化还原二氧化碳性能; 以碳为支撑, 增加材料稳定性; 以氮为桥梁, 提高其与二氧化碳结合力。在长时间连续电解下该反应依然能够稳定的进行。其中 Co@CN<sub>x</sub>-800 在-1.3V(vs.Ag/AgCl) 时 CO 的产率最大, 达到 13.3 μmol/g h, 此时 CO 和 H<sub>2</sub> 的法拉第效率分别为 25% 和 50%, 两者比率为 0.5, 产物可直接用于合成气。

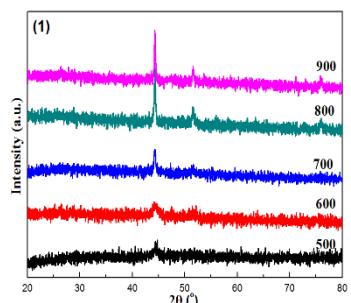


图 1、Co@CN<sub>x</sub>复合材料 XRD 谱图

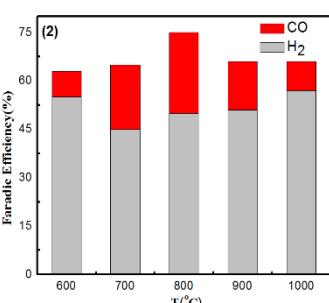


图 2、不同热解温度 Co@CN<sub>x</sub> 复合材料在-0.67V(vs.RHE)法拉第效率

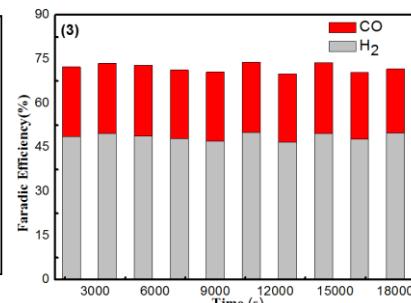


图 3、Co@CN<sub>x</sub>-800 在-0.67V(vs.RHE)法拉第效率

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## CeO<sub>2</sub>-ZrO<sub>2</sub>复合氧化物修饰的Pt/C催化剂的电化学性能研究

王青春，王子豪，蔡长琨，刘媛媛，安胜利\*

内蒙古科技大学，包头，中国，014010

qingchun0221@126.com; shengli\_an@126.com

直接甲醇燃料电池(DMFC)具有能量转换效率高、甲醇来源丰富、价格便宜、运行便捷和噪声低等优点。但其催化剂的活性低、成本高、寿命短已经成为其实用化的主要障碍。CeO<sub>2</sub>由于其储氧性能及协同效应等对Pt/C催化剂具有明显的助催化效应。而在CeO<sub>2</sub>中掺入Zr<sup>4+</sup>易形成铈锆固溶体(Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>)，在Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>固溶体中，中心离子半径的不同及电荷差所导致的晶格畸变和补偿效应可能会引起氧空位浓度的变化<sup>[1]</sup>，氧空位是提高氧的流动性及储氧性能(OSC)的关键因素<sup>[2,3]</sup>，常被应用于汽车尾气三效催化剂中。因而我们推测，同单纯的CeO<sub>2</sub>相比，Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>固溶体由于其较好的储放氧性能及电子效应，其作为助催化剂用于修饰Pt/C催化剂可显著提高Pt的抗CO中毒能力，使其具有更好的甲醇电氧化性能。

在这项工作中，我们设计用微波辅助乙二醇还原法与共沉淀法结合制得Pt-MO<sub>x</sub>/C(M= Ce,Zr)催化剂，以期获得活性和抗毒稳定性都比较好的甲醇电氧化催化剂。研究发现CeO<sub>2</sub>-ZrO<sub>2</sub>形成了固溶体(图1B中可间接看出)，在元素分布图中Pt主要分布在有CeO<sub>2</sub>-ZrO<sub>2</sub>的部位，少量直接与碳结合。催化剂中CeO<sub>2</sub>-ZrO<sub>2</sub>和Pt相接并且存在相互作用，Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>固溶体与纯的CeO<sub>2</sub>相比，ZrO<sub>2</sub>的加入使得CeO<sub>2</sub>产生晶格畸变，氧空位数增加，使得Pt-CO之间所形成的σ-π键的电子组态更容易被破坏，减少了CO脱附和氧化所需的能量，从而使Pt-MO<sub>x</sub>/C(M= Ce, Zr)催化剂的电氧化甲醇性能远远高于Pt-CeO<sub>2</sub>/C。催化剂中随着氧化锆含量的添加，电氧化甲醇峰电流呈现出先增加后减小的趋势。铈锆物质量比为1:2及1:1两组表现出对甲醇较高的电催化氧化性能(图1c可部分说明)。同时通过控制条件，我们合成出了针片状及颗粒状的CeO<sub>2</sub>-ZrO<sub>2</sub>复合氧化物，发现针片状CeO<sub>2</sub>-ZrO<sub>2</sub>表面很难吸附Pt粒子，不利于其助催化效果的发挥。而纳米颗粒状CeO<sub>2</sub>-ZrO<sub>2</sub>由于其较大的比表面积及容易吸附Pt的特点使其助催化效果得到改善。

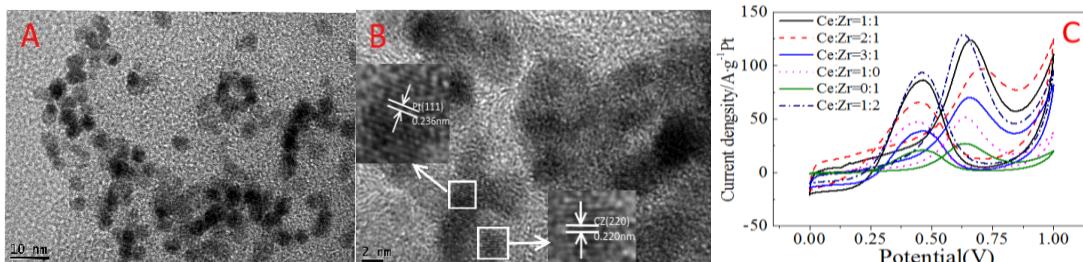


图1 催化剂的TEM图(A)与HRTEM图(B)(Ce:Zr=1:1)及Pt-MO<sub>x</sub>/C(M= Ce,Zr)在0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>+1.0 mol·L<sup>-1</sup> CH<sub>3</sub>OH溶液中的循环伏安(C)曲线图

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# The Structural Integrity of Amorphous Metallic Bulk to Improve the Electrochemical Water Splitting Performance

Fei Hu, Xiaowei Yang

School of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China

Electrochemical water splitting that reserves electrical energy from chemical bonds is a promising technology for future alternative energy production. Designing criterion should not only be focused on the intrinsic electrocatalytic activity, but also the scale-up relationship between electrocatalyst geometry and performance. Unfortunately, it draws forth a large resistance among electrocatalyst particles due to the agglomeration or in-situ oxidation, and consequently deteriorates the catalytic performance. In this work, we introduce a kind of structural-integral material that combines excellent macro-conductivity, abundant micro-porosity, as well as densely active sites that rooted by the amorphous metallic characterization. Benefiting from the synergistic effects, the resultant, for instance NiFeP, achieves an extraordinary electroactivity towards water splitting for both HER and OER, with negligible to the catalyst geometry. Specifically, the electrocatalytic performance for OER in 1.0 M KOH affords an overpotential as low as 210 mV at a current density of 10 mA/cm<sup>2</sup> and a small Tafel slope of 38 mV/dec. And meanwhile, the HER catalytic activity in the same condition is 100 mV and 84 mV/dec, respectively. The overall water splitting potential on such catalyst is lower than 1.54 V at a current density of 10 mA/cm<sup>2</sup>, which surpasses most reported transition metal catalysts and noble metal catalysts. This work sheds a light to the direct application of catalysts into a high-performance electrolysis device.

# Controllable Synthesis and Electrocatalytic Activity of Hierarchical Pd-based Nano-catalysts

白正宇

河南师范大学

Noble metal nanomaterials with hierarchical structures are considered to be promising catalysts owing to its controlling crystal morphology, good chemical stability and environmental-friendly. In order to improve the electrocatalytic activity of catalysts and maximize the utilization of noble metal, Pd-based catalysts with hierarchically ordered structures were successfully synthesized in the presence of different organic additives at ordinary temperature. And the influence of the component and morphology on the electrocatalytic properties of catalysts was also studied. Firstly, a series of Pd hollow nanospheres and nanoparticles with different particle size were prepared in the presence of conducting polymers or different organic additives. Compared with the solid nanoparticles, Pd hollow nanospheres show a very high electrochemically-active surface area and significant increase in electrocatalytic activity ( $160 \text{ mA cm}^{-2}$ ) towards formic acid oxidation, which make them the preferable catalysts for direct formic acid fuel cells (DFAFC). Secondly, a series of Pd-based (PdCu, PdCo, PdRh et al.) bimetallic alloyed hollow nanospheres composed with nanoparticles were successfully synthesized by a novel one-pot template-free strategy. According to cyclic voltammograms, the maximal peak current density of hollow PdCu alloyed nanocubes is  $190 \text{ mA cm}^{-2}$ , greater than those of PdCu alloy catalyst ( $143.1 \text{ mA cm}^{-2}$ ) and Pd nanoparticles ( $106.8 \text{ mA cm}^{-2}$ ). The results reveal that the alloy hollow nanostructures have high electrochemical activity, good stability and excellent anti-CO toxic ability during the process of formic acid oxidation. At the same time, it is one of the effective approaches to reduce the loading of noble metals and lower the cost of the catalysts. Thirdly, a series of Pd-MeO<sub>x</sub> (Pd-Fe<sub>2</sub>O<sub>3</sub>, Pd-CeO<sub>2</sub>, Pd-SnO<sub>2</sub> et al.) hybrid nanostructured electrocatalysts were successfully prepared in the presence of different organic additives at ordinary temperature. On the surface of such metal oxides, hydroxyl species (OH<sup>-</sup>) could form easily and assist oxidization of the adsorbed intermediate species during the electrooxidation. In short, the Pd-MeO<sub>x</sub> catalyst not only lowers the cost by means of less Pd dosage but also shows good performance for electrooxidation with the assistance of oxide additives. Overall, the component and morphology are key factors to the excellent performance of the catalysts. The results reveal that hollow nanostructures composed with nanoparticles represent a new class of powerful catalysts because of the increased surface area, low density and surface permeability. As a result, the catalyst with bimetallic alloy is an effective approach to enhance the catalytic activity, and reduce the cost of catalysts. Obviously, design and synthesis of hollow bimetallic nanosphere catalysts represent a promising way to effectively improve the performance and utilization of catalysts, while the cost can be further decreased.

# 原位光电化学还原法制备 Bi/BiOCl 光电阴极以及光电化学分解水性能研究

白红叶, 葛懿林, 管鹏, 崔伟成, 白亚杰, 高杨, 范伟强\*

江苏大学化学化工学院, 镇江, 中国, 邮编: 212013

\*fwq4993329@yahoo.com

$\text{TiO}_2$  被认为是最早用于太阳能水分解制氢的半导体材料, 是太阳能分解水制氢的一类理想材料。 $\text{TiO}_2$  光电极有个致命缺点是其仅具有紫外光响应能力, 但紫外光仅占太阳光总能量的 5%, 这严重影响  $\text{TiO}_2$  对太阳光的利用率。因此, 如何进一步提高单一  $\text{TiO}_2$  光电极对太阳光吸收范围已经成为该领域的一个关键性问题。以  $\text{TiO}_2$  纳米棒为光阳极和 Bi 修饰  $\text{BiOCl}$  ( $\text{Bi/BiOCl}$ ) 纳米片为光阴极构建了一新型 PEC 体系, 该体系可实现了无偏压辅助 PEC 水分解制氢。 $\text{Bi/BiOCl}$  纳米片通过快速原位光还原  $\text{BiOCl}$  来制备。在紫外和可见光照射下, 系统调控  $\text{Bi/BiOCl}$  光电阴极结构和组成以实现 PEC 分解水制氢性能的优化。系列表征证明了  $\text{Bi/BiOCl}$  纳米片光电阴极与 Pt 相比可有效促进电荷转移并展现出优异的 PEC 产氢性能, 因此  $\text{Bi/BiOCl}$  异质结半导体材料基于其独特性能将有望成为实现 PEC 产氢实际应用的候选材料之一。

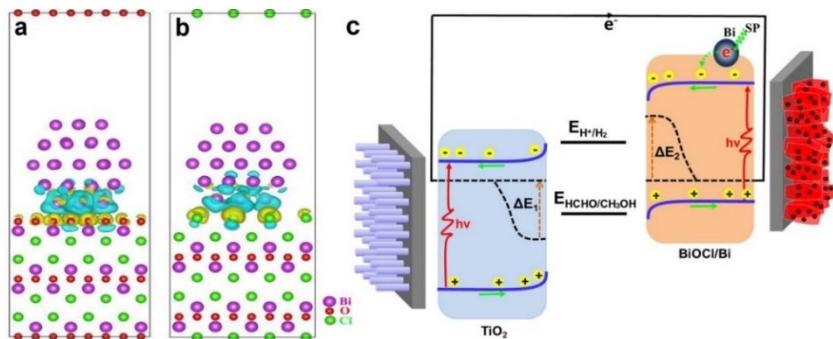


图 1. 沿 (010)面所观察的  $\text{BiOCl}$  (001)面上的 Bi 簇的电荷密度差的轮廓图。O 端表面(a), Cl 端表面(b)。能带和电荷流动的示意图(c)。

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## 氧化镍@镍修饰的二硫化钨纳米片阵列用于全电解水

王德文, 邢志财, 杨秀荣\*

中国科学院长春应用化学研究所, 吉林省长春市, 130022

\*xryang@ciac.ac.cn

开发清洁的可再生资源对于缓解当前的能源危机和环境污染有着至关重要的作用。作为具有高能量密度的清洁燃料, 氢气已经引起广泛的关注。电化学水分解被认为是有效制备氢气并进一步实现其工业化的重要手段, 不仅可以大规模生产高纯的氢气, 而且还可以将多余的能源(风能、核能、潮汐能等)储存在氢气中[1-3]。电化学水分解包括两个过程既析氢和析氧, 目前来说, 析氢性能最好的是基于铂的催化剂, 析氧性能最好的是基于钌和铱的催化剂, 但是贵金属的稀缺和昂贵限制了它们的大规模应用, 所以开发高效低成本电催化剂是当务之急。虽然近年来已经有很多高效电催化剂被开发出来, 但大多数都忽略了同时提高催化剂的析氢和析氧性能。同时进行析氢和析氧的双功能催化剂有很大的实际应用价值, 因为它可以避免使用不同的材料和设备, 从而大大的降低成本。过渡金属二硫化物如二硫化钼和二硫化钨, 早已被研究应用于电化学析氢, 它们类似石墨烯的层状结构对析氢具有良好的作用[1]。与此同时, 镍和氧化镍也被证明具有良好的析氢和析氧性能[2]。考虑到将两者的优势相结合, 我们利用电沉积技术构建了氧化镍@镍修饰二硫化钨纳米片阵列电极作为双功能催化剂用于水分解, 该催化剂在碱性电解液中展示出与商业化铂碳相媲美析氢性能和超越氧化钌的析氧性能及优异的长期稳定性, 值得一提的是, 在全电解性能方面, 仅需要电池电压1.42伏达到10毫安/厘米<sup>2</sup>电流密度, 是目前已知所需电压中最小的[3]。我们相信该工作将为开发新型高效的双功能催化剂用于水电解及相关领域提供新的思路。

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# 非金属含氮介孔碳高效电催化 $\text{CO}_2$ 还原生成乙醇

宋艳芳, 陈为,\* 李圣刚, 魏伟, 孙予罕\*

中国科学院上海高等研究院, 中国科学院低碳转化科学与工程重点实验室

\*Corresponding author. Email: chenw@sari.ac.cn; sunyh@sari.ac.cn

电催化  $\text{CO}_2$  还原在实现可再生能源储存和负碳循环方面是一项很有前景的技术。然而, 将  $\text{CO}_2$  高效且高选择性地电催化转变为 C2 产品仍存在挑战<sup>[1]</sup>。因此, 我们开发了一种圆柱形介孔结构的含氮有序介孔碳材料, 用作电催化  $\text{CO}_2$  还原的非金属催化剂, 能够高效且高选择性地电催化  $\text{CO}_2$  还原为乙醇<sup>[2]</sup>。在 -0.54 V vs. RHE 电解电位下, 其选择性几乎达到 100%, 法拉第效率为 77%。通过对圆柱形以及反相介孔结构的含氮介孔碳催化剂电催化  $\text{CO}_2$  还原性能对比(如图 1 所示), 我们发现圆柱形介孔结构在非金属含氮碳电催化  $\text{CO}_2$  还原的法拉第效率和选择性方面有着举足轻重的作用。电化学分析和密度泛函理论计算表明, 氮杂原子(吡啶型氮和吡咯型氮)和圆柱形孔道结构的协同作用有利于中间产物  $\text{CO}^*$  的二聚, 从而高效且高选择性地生成乙醇。这项工作为开发碳基非金属催化剂电催化  $\text{CO}_2$  转化生成 C2 产物的高效催化体系提供基本科学依据。这对于拓展  $\text{CO}_2$  资源化转化利用的新途径, 具有重要的科学价值和现实意义。

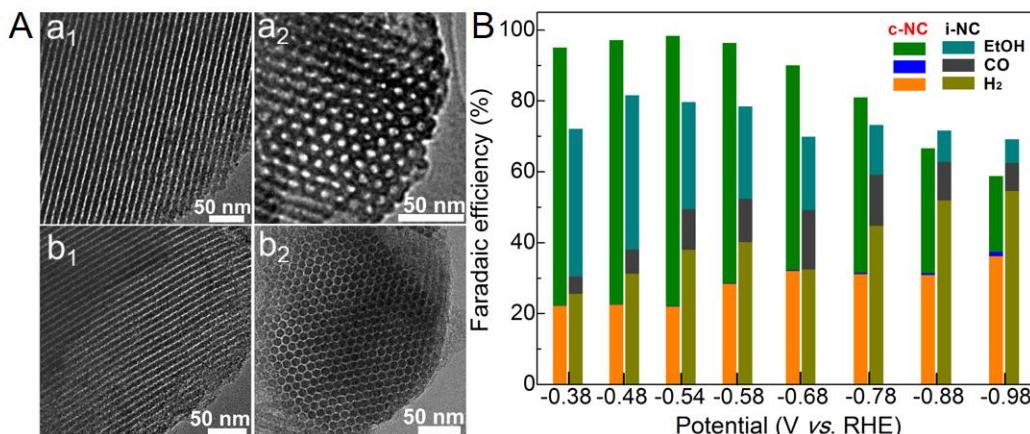


图 1. (A) 圆柱形介孔结构的含氮有序介孔碳 c-NC (a1, a2) 和反相介孔结构的含氮有序介孔碳 i-NC (b1, b2) 沿着[110] (a1, b1) 和 [100] (a2, b2) 方向的 TEM 图; (B) 圆柱形介孔结构的含氮有序介孔碳 c-NC 和反相介孔结构的含氮有序介孔碳 i-NC 在各个电解电位下电催化  $\text{CO}_2$  还原产物的法拉第效率<sup>[2]</sup>。

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# Biomass Based Porous Carbon Nanosheets as Superior Electrocatalyst for Oxygen Reduction

Lei Zhang<sup>1</sup>, Xinwen Peng<sup>1,\*</sup>, Linxin Zhong<sup>1</sup>, Rncang Sun<sup>2</sup>

<sup>1</sup>State Key Laboratory of Pulp and Paper, South China University of Technology, Guangdong, Guangzhou, 510641. <sup>2</sup>Beijing Forestry University, Beijing, 100083.

\*Corresponding Author's E-mail: fexwpeng@scut.edu.cn.

Hierarchically porous carbons derived from low-value biomass as efficient catalysts towards oxygen reduction reaction (ORR) without entailing the conventional template methods is of special interest for implementing the wide spread application of fuel cell technology<sup>[1,2]</sup>. Herein, a high performance doped carbon catalyst with 2D hierarchical porous structure was prepared through a non-template pyrolyzing approach using hydrochar nanosheet derived from hemicellulose and GO. The as obtained catalyst (Fe-NCS-800) showed favorable features for ORR reaction such as ultrahigh surface area ( $1436\text{ m}^2/\text{g}$ ), special nanosheet structure, rich N-doping (3.71%) and trace Fe species remaining., contributing to its excellent ORR performance. The catalyst showed a more positive onset potential (0.996 V vs RHE) and its diffusion limiting current is  $5.32\text{ mA}\cdot\text{cm}^{-2}$  at 0.3 V (vs. RHE), comparable number of electron transfer (3.93 at +0.75 V vs RHE), much higher stability, and stronger tolerance against methanol crossover than commercial Pt/C catalysts in a 0.1 M KOH solution. The remarkable ORR performance was attributed to the high surface area and sufficient exposure of electrocatalytically active sites that arose from the unique N-doped carbon nanosheet architecture.

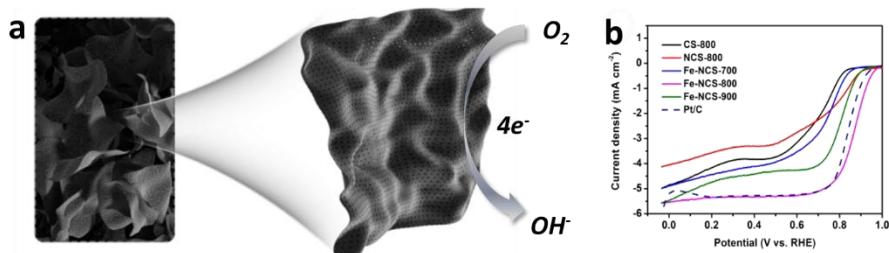


Figure 1. Sketch for Fe-NCS preparation from hemicellulose and GO, and (b) LSV curves of different catalysts.

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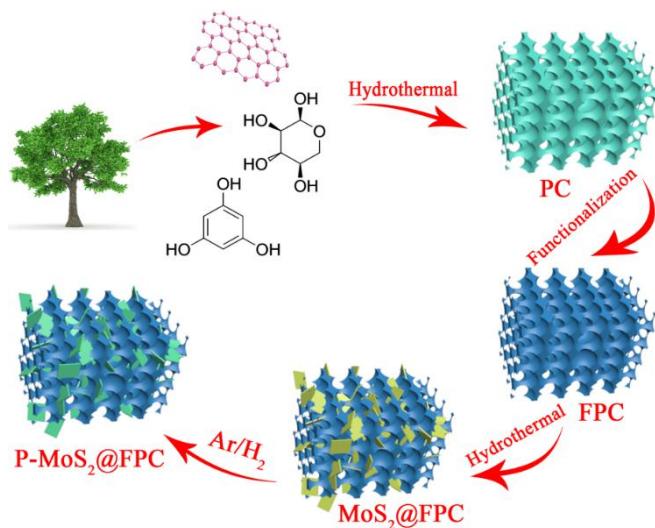
# Defect Engineered MoS<sub>2</sub> anchored on Porous Carbon As Efficient Bifunctional Electrocatalysts

Qiusheng Zhou<sup>1</sup>, Linxin Zhong<sup>1</sup>, Fan Du<sup>1</sup>, Xinwen Peng<sup>1,\*</sup>, Runcang Sun<sup>2</sup>

<sup>1</sup>State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640

<sup>2</sup>Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, 100083

A novel hybrid catalyst consisting of defect engineered MoS<sub>2</sub> and porous carbon is fabricated through simple pyrolysis. Remarkable features of the porous carbon structure, construction of defect engineered MoS<sub>2</sub> and good contact of MoS<sub>2</sub> nanosheets and porous carbon result in a high catalytic activity. The hybrid shows excellent electrocatalytic activity for hydrogen evolution reaction, offering a low overpotential of 144 mV at the current density of 10 mA cm<sup>-2</sup> and a small Tafel slope of 41 mV dec<sup>-1</sup> in acid media, as well as good stability. The hybrid also displays superior performance for oxygen reduction reaction, where its durability and resistance to methanol crossover are superior to those of commercial Pt/C catalyst. Apart from the active nature of the hybrid, the synergistic effect between defect engineered MoS<sub>2</sub> and porous carbon is responsible for its excellent performance.



Scheme1. A schematic of the fabrication process of phosphorus-doped MoS<sub>2</sub> anchored on functional porous carbon

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# Polyvinyl Alcohol-Assisted Electrochemical Reduction of CO<sub>2</sub> to CO on Supported Gold Nanoparticles with Excellent Activity and Selectivity

Lushan Ma, Hui Yang\*

Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai, 201210

E-mail: yangh@sari.ac.cn

Electrochemical reduction of CO<sub>2</sub> to valuable chemicals using renewable energy is a promising route to realize carbon cycle economy. However, the technological and economical availability of this way is severely limited by the development of high-performance and robust catalysts for CO<sub>2</sub> reduction. In this paper, carbon supported gold nanoparticles (Au NPs) prepared by the sol-immobilization method achieve ultrahigh geometric current density of 110 mA/cm<sup>2</sup> and excellent Faradaic efficiency (95.4%) for CO at the -0.8 V versus reversible hydrogen electrode. Through combining the removal of capping agent (polyvinyl alcohol, PVA) on the surface of catalysts and the controllable modification of surfactant-free Au NPs, we find that PVA plays a significant role in the electrochemical reduction of CO<sub>2</sub> to CO. Tafel plots of PVA-modified catalysts (62 mV/decade) versus surfactant-free catalysts (100 mV/decade) further reveal that the capping agent influences mechanistic pathways for CO<sub>2</sub> reduction. Similarly supported Au NPs modified by other soluble polymers also show enhanced performances for CO<sub>2</sub> reduction. The results confirm that polymers that can be introduced in or after the synthetic procedure act as positive roles in the catalytic reduction of CO<sub>2</sub> and provide valuable ideas for developing more efficient catalysts for practical application.

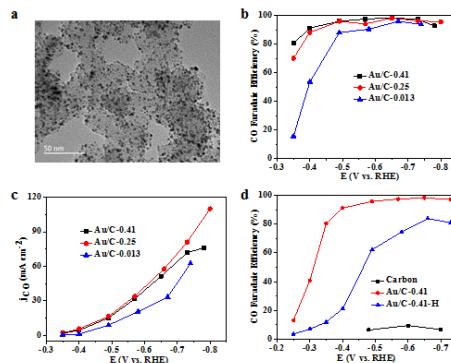


Figure 1 (a) TEM image of Au/C-0.41 catalyst prepared by the sol-immobilization method and applied potential dependence of (b) Faradaic efficiencies and (c) current densities over Au/C catalysts prepared with different amounts of PVA and (d) Faradaic efficiencies for CO production over Au/C-0.41 and Au/C-0.41-H (after heat treatment) in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution.

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# Photoelectrochemical Reduction of CO<sub>2</sub> with Aqueous Ionic Liquids as Electrolyte Solution

Weiwei Lu\*

School of Chemical Engineering & Pharmaceutics, Henan University of Science and Technology Luoyang, China 471023

\*luweiwei@haust.edu.cn

CO<sub>2</sub> is known as the main greenhouse gas that can induce the undesirable environmental changes. Therefore, great efforts have been devoted to the research and development of CO<sub>2</sub> capture and utilization in recent decades.<sup>[1]</sup> In various methods of conversion of CO<sub>2</sub>, photoelectrochemical (PEC) reduction that introduces renewable solar energy is one of the prospective and potential ways to produce solar fuels and chemicals.<sup>[2]</sup> Parallelly, recent years, ionic liquids (ILs) and functionalized ionic liquids have demonstrated their superior absorption capacity of CO<sub>2</sub>, and furthermore their unique activation effect on CO<sub>2</sub>.<sup>[3]</sup>

In this work, we reported CO<sub>2</sub> valorization within a IL-assisted PEC system. PEC reduction of CO<sub>2</sub> was carried out by using BiVO<sub>4</sub>/WO<sub>3</sub> composite film as photoanode and aqueous IL (1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM]BF<sub>4</sub>) as electrolyte solution in the two-electrode proton exchange membrane reaction system (Figure 1). The incident photon-to-current measurement shows that the photocurrent density of BiVO<sub>4</sub>/WO<sub>3</sub> photoelectrode can reach as high as 4.445 mA/cm<sup>2</sup> under the applied potential of 1.23 V (vs RHE). The PEC reduction results show that in this IL-assisted PEC reduction system for CO<sub>2</sub>, the Faradaic efficiency of CO was as high as 92.5% at the applied voltage of 1.7 V, and the photon-to-chemical efficiency was 0.12% at the applied voltage as low as 1.1 V.

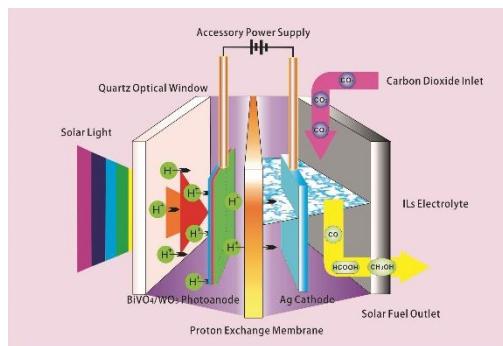


Figure 1. the PEC two-electrode proton exchange membrane reaction system

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# Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Stepped Edged MoS<sub>2</sub> Sheet Stacks

Jue Hu<sup>a,b\*</sup> Bolong Huang,<sup>c</sup> Chengxu Zhang,<sup>a,d</sup> Shihe Yang<sup>b</sup>

a Faculty of Science & Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology,  
Kunming, China.

b Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong,  
China.

c Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong, Kowloon,  
Hong Kong, China.

d Ability R&D Energy Research Centre, School of Energy and Environment, City University of Hong Kong, Hong Kong,  
China.

Two-dimensional molybdenum sulfide (MoS<sub>2</sub>) is an attractive noble-metal-free electrocatalyst for the hydrogen evolution reaction (HER). The number of the exposed edge sites of MoS<sub>2</sub> is crucial for the HER activity [1]. However, engineering the edge surface structures of MoS<sub>2</sub> sheet stacks to promote the HER kinetics haven't been developed [2]. Herein we report the first demonstration of significantly enhanced HER kinetics by tailoring a stepped edge surface structure of MoS<sub>2</sub> multilayers with respect to a flat edge surface. We provide an unambiguous interpretation on the HER performance difference in terms of the different H bonding on the stepped edge surface (se-MoS<sub>2</sub>) and on the flat edge surface (fe-MoS<sub>2</sub>). Vertical arrays of MoS<sub>2</sub> sheets terminated with such a stepped surface structure have proved to be an outstanding HER electrocatalyst with overpotential of 104 mV at 10 mA/cm<sup>2</sup>, exchange current density of 0.2 mA/cm<sup>2</sup> and high stability (Figure 1). DFT calculations suggest a more optimal  $\Delta G_H$  of the active se-MoS<sub>2</sub> edge surface than that of the fe-MoS<sub>2</sub> edge surface, and thereby a faster HER kinetics (Figure 1a). A perfectly designed stepped edge surface terminated MoS<sub>2</sub> sheet array is schematically depicted in Figure 1d, in which the unique vertically terminated, stepped surface structure ensures an optimal hydrogen adsorption energy ( $\Delta G_H$  is ~0.02 eV); the vertical array would permit ultrafast electron transport and promote HER performance [3]. This approach presented here provides a new insight that we tailor the edge active sites to modulate the performance of HER and should be applicable to generalized transition-metal-dichalcogenide catalysts, by engineering their surface structures. We expect that the stepped-edge engineering strategy will prove more generally effective for creating catalysts from abundant noble-metal-free layered materials for hydrogen evolution.

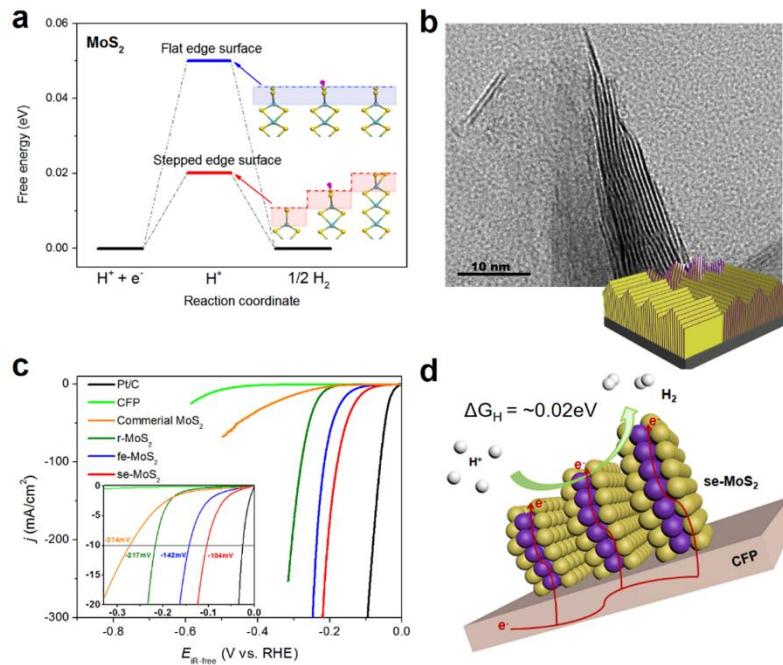


Figure 1. (a) Free energy diagram for hydrogen adsorption at the stepped and flat MoS<sub>2</sub> edges with one-quarter hydrogen coverage on one of the MoS<sub>2</sub> layers. The molecular structures depicted at the top and bottom of (a) show H adsorption on the fe-MoS<sub>2</sub> and se-MoS<sub>2</sub> edges, respectively. The yellow, dark cyan and violet spheres represent S, Mo and H atoms, respectively. (b) HRTEM image and schematic illustration of the se-MoS<sub>2</sub> layers, which clearly shows that crystal fringes of the S-Mo-S layers along the edge are stepped. (c) Polarization curves of the commercial MoS<sub>2</sub>, r-MoS<sub>2</sub>, fe-MoS<sub>2</sub> and se-MoS<sub>2</sub>, and commercial Pt/C catalysts in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. (d) Schematic illustration of the designed stepped edge surface terminated MoS<sub>2</sub> sheet array, in which the unique vertically terminated, stepped surface structure ensures optimal hydrogen adsorption energy ( $\Delta G_H$  is  $\sim 0.02$  eV) and ultrafast electron transport to the stepped MoS<sub>2</sub> edge surface.

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## In-Situ Surface-Derivation of NiMoS Nanosheets Layer on Co<sub>3</sub>O<sub>4</sub>

### Nanoarrays for Highly Efficient Electrocatalytic Overall Water Splitting

熊婷, 张树聪, 黄钦, 胡飞龙, 米艳\*, 尹显洪\*

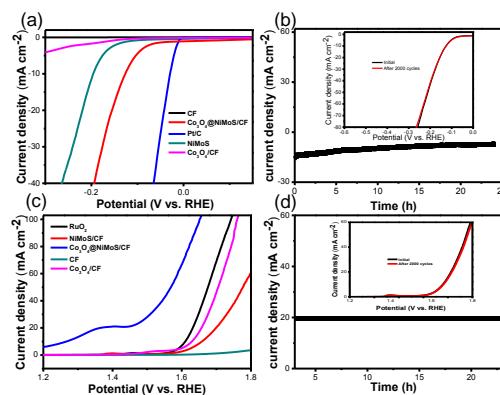
广西民族大学化学化工学院, 南宁, 530006

广西林产化学与工程重点实验室, 南宁, 530006

\*Email: miyan@163.com

Prof. Yin's email

Developing high performance overall water splitting electrocatalysts working under both acid and alkaline conditions is highly desirable. Although numerous efforts have been done, it still remains many challenges. In this communication, we report the in-situ surface-derivation of NiMoS nanosheets layer on Co<sub>3</sub>O<sub>4</sub> nanoarrays which supported on carbon fiber (Co<sub>3</sub>O<sub>4</sub>@NiMoS/CF). It was adopted to efficiently balance both HER and OER performance by improving the kinetics. The heterostructures synergistically favoured the subsequent H adsorption/desorption for NiMoS in acid HER. In addition, the adsorption of oxygen intermediates on Co<sub>3</sub>O<sub>4</sub> also could be enhanced during the OER process. As a result, the Co<sub>3</sub>O<sub>4</sub>@NiMoS/CF heterostructure shows excellent overall water splitting performance with low overpotential and long-term stability, which resulting from outstanding structure design. Thus, such in-situ surface-derivation strategy provides a promising alternative to design efficient overall water splitting catalysts.



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## 锰系氧化物电极材料与锌空气电池

陈祥, 严振华, 孙洪明, 程方益\*, 陈军

南开大学化学学院, 天津, 中国, 300071

\*fycheng@nankai.edu.cn

锌空气电池具有能量密度高（理论能量密度高达  $1086 \text{ Wh kg}^{-1}$ ）、原料资源丰富成本低、安全环保等优点，是电化学能高效转换和储存的重要技术之一。空气电极氧催化反应是锌空气电池性能的主要制约因素，需要使用高效催化剂。锰系氧化物具有资源丰富、价格低廉等优点，作为氧还原和氧析出电催化剂吸引了广泛研究兴趣，但仍存在导电性差、过电位高、构效关系不明确等问题，还需要可控制备、结构优化并提升电极性能。

我们围绕单金属和双金属锰系氧化物电催化材料开展了系列研究工作。在特定气氛中 ( $\text{H}_2$  或  $\text{Ar}$ ) 热处理，使  $\text{MnO}_2$  材料氢化或引入氧缺陷，促进氧气与含氧物种在催化剂表面的吸附，提高电催化活性<sup>[1,2]</sup>。发展了氧化沉淀-嵌入晶化法<sup>[3]</sup>在温和条件下实现了系列尖晶石型锰系氧化物的组成、晶相、形貌的精准调控。在制备基础上的构效关系研究表明，立方相钴锰氧尖晶石氧还原性能最佳，这归因于其高导电性、 $\text{Mn}$  混合价态以及适宜的表面氧吸附能。我们采用热注入快速成核-升温慢速晶化的方法<sup>[4]</sup>，通过调控反应温度制备尺寸可调的单分散超细尖晶石纳米晶。研究了尖晶石钴锰氧化物尺寸与电催化性能之间的关系。结果显示，颗粒尺寸约  $4\text{ nm}$  的尖晶石具有适中的表面吸附氧强度和高载流子浓度，其氧还原和氧析出催化活性分别与商品化  $\text{Pt/C}$  和  $\text{RuO}_2$  相近，且催化稳定性更高。

为提高锰氧化物导电性，最近，我们采用硝酸盐自燃烧法<sup>[5]</sup>在温和条件下快速原位制备钙钛矿型  $\text{La}_x\text{MO}_{3\pm\delta}/\text{C}$  复合材料，得益于其尺寸小、活性位点丰富、合适的  $\text{Mn}$  元素 d 轨道 eg 电子填充，其电催化氧还原活性与商业  $\text{Pt/C}$  催化剂接近，且稳定性更优。组装的一次锌空气电池能量密度为  $837 \text{ Wh kg}_{\text{Zn}}^{-1}$ ，持续运行 340 小时性能无明显衰退。我们还对比了 CNTs、Ox-CNTs、r-GO、Vulcan C 等不同碳载体负载尖晶石氧化物的电催化性能差异，研究催化剂的载体效应<sup>[6]</sup>。结果表明，未经氧化的碳纳米管负载尖晶石具有更高导电性、是优异的氧还原/氧析出双功能电催化剂，组装的锌空气电池循环 200 圈后仍具有较低过电位，在可充锌空气电池方面展现出潜在的应用价值。

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# Oxygen-incorporated defect-rich MoP for highly efficient hydrogen production in both acidic and alkaline media

Zhuangzhi Wu\*

School of Materials Science and Engineering, Central South University, Changsha, China, 410083

\*Corresponding Author's E-mail: [zwu2012@csu.edu.cn](mailto:zwu2012@csu.edu.cn)

Molybdenum phosphide (MoP) has attracted a lot of attentions as a potential electrocatalyst for the hydrogen evolution reaction (HER). Although great efforts have been made to improve the HER activity of MoP, the rational design of MoP catalysts with either more active sites or higher conductivity is still challenging. Herein, a defect-rich structure is synthesized via a novel and facile low-temperature calcination strategy as a HER catalyst (DR-MoP). Moreover, the DR-MoP is also proved to be incorporated with oxygen. The defect-rich structures could provide more active sites, and the incorporation of oxygen could further enhance the intrinsic conductivity. Thus, the DR-MoP catalyst shows outstanding HER activity and stability in both acidic and alkaline media, making it a good alternative to replace the precious-metal catalysts. Besides, the formation mechanism of DR-MoP has been discussed by controlling different annealing temperatures. This work paves a novel and effective way for improving the HER performance of transition metal phosphides by defect engineering.

## 金属磷化物电催化水氧化

陈倩倩, 侯春朝, 陈勇\*

中国科学院理化技术研究所, 北京市, 100190

\*Email: chenyong@mail.ipc.ac.cn

过渡金属磷化物具有半金属特性, 在酸碱环境中较稳定, 同时还具有很好的光、热稳定性, 是继过渡金属碳化物和过渡金属氮化物之后出现的一类新型催化材料。近年来, 过渡金属磷化物在光/电催化分解水产氢、催化加氢和脱氢等反应中表现出与贵金属铂媲美的催化活性, 被誉为“准铂催化剂”。我们的研究结果表明, 过渡金属磷化物在氧化条件下, 可以原位地生成一种表面为过渡金属氧化物/氢氧化物, 内部是过渡金属磷化物的核壳结构。其中, 表面的过渡金属氧化物/氢氧化物层可以作为水氧化的活性中心, 内部的磷化物提高了材料的导电性, 因而表现出高效的电催化水氧化活性。

我们利用水热合成法将超小的  $\text{Co}_3\text{O}_4$  负载在氧化碳纳米管 (CNT) 上, 然后通过低温磷化的方法得到以碳纳米管为载体的超细 CoP (1.5~2 nm) 纳米粒子。CNT 的使用不仅获得了超细的纳米材料, 同时提高了材料的导电性。在 0.1 M NaOH 溶液中, 电催化水氧化的起始电位仅有 290 mV。深度溅射 XPS 表征表明 CoP 纳米粒子表面原位生成了金属氧化物/氢氧化物, 而内部仍保留着 CoP 的结构。<sup>[1]</sup> 我们也利用三维的铜泡沫作为载体, 直接在铜泡沫上制备自支撑的  $\text{Cu}_3\text{P}$  纳米材料, 也具有较高的电催化水氧化活性, 在 0.1 M KOH 溶液中, 电流密度达到 50 mA cm<sup>-2</sup> 时, 水氧化过电位仅为 412 mV。<sup>[2]</sup>

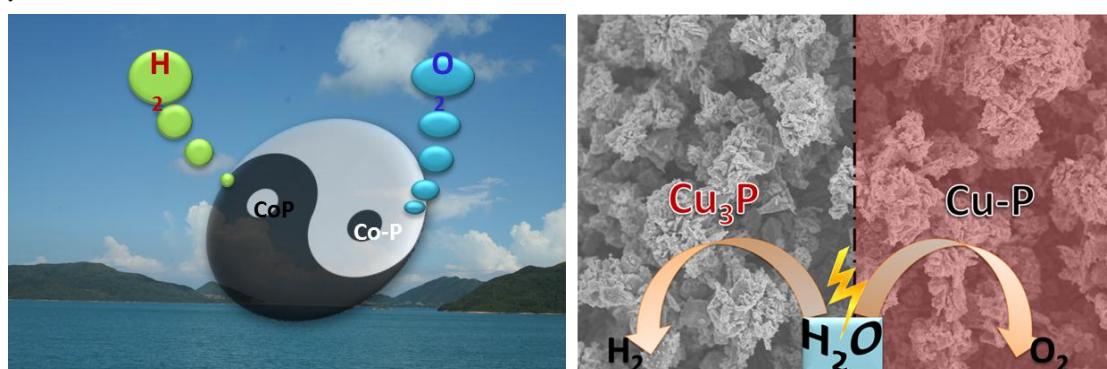


图 1: 金属磷化物电催化水氧化示意图

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# 纳米 $\text{TiO}_2$ 负载炭基电催化膜反应器处理

## 垃圾填埋场生化出水研究

惠洪森<sup>1</sup>, 王虹<sup>1\*</sup>, 莫颖慧<sup>1</sup>, 梁小平<sup>1</sup>, 李建新<sup>1\*</sup>

1.天津工业大学分离膜与膜过程国家重点实验室, 天津, 中国, 300387

\* Email: waho7808@163.com or jxli@tjpu.edu.cn

城市生活垃圾渗滤液由于其有机物浓度高、氨氮含量高、重金属离子含量高等, 处理难度大, 已经成为水处理领域世界性难题。本文采用纳米  $\text{TiO}_2$  负载炭基电催化膜为阳极、不锈钢网作为阴极构建三级固定床电催化膜反应器 (FBER) 处理某垃圾填埋场生化后超滤出水 (COD 为 389 mg/L,  $\text{NH}_3\text{-N}$  69.6 mg/L, 总氮 109.5 mg/L, pH 值 7.60, 电导率 8030  $\mu\text{s}/\text{cm}$ )。结果表明: 在 FBER 操作条件为停留时间 12.0 min, 电压 2.0 V 时, FBER 对于 CODcr 去除率为 82.0%,  $\text{NH}_3\text{-N}$  去除率为 86.5%, 总氮去除率为 76.3%, 能耗仅为 4.81 kWh/kg COD。此外, FBER 出水色度 (8)、重金属离子 ( $\text{Pd}$ 、 $\text{Cr}$ 、 $\text{Cd}$ 、 $\text{As}$ 、 $\text{Hg}$ )、总磷、悬浮物等所有控制污染物都符合国家排放标准 GB16887-2008。

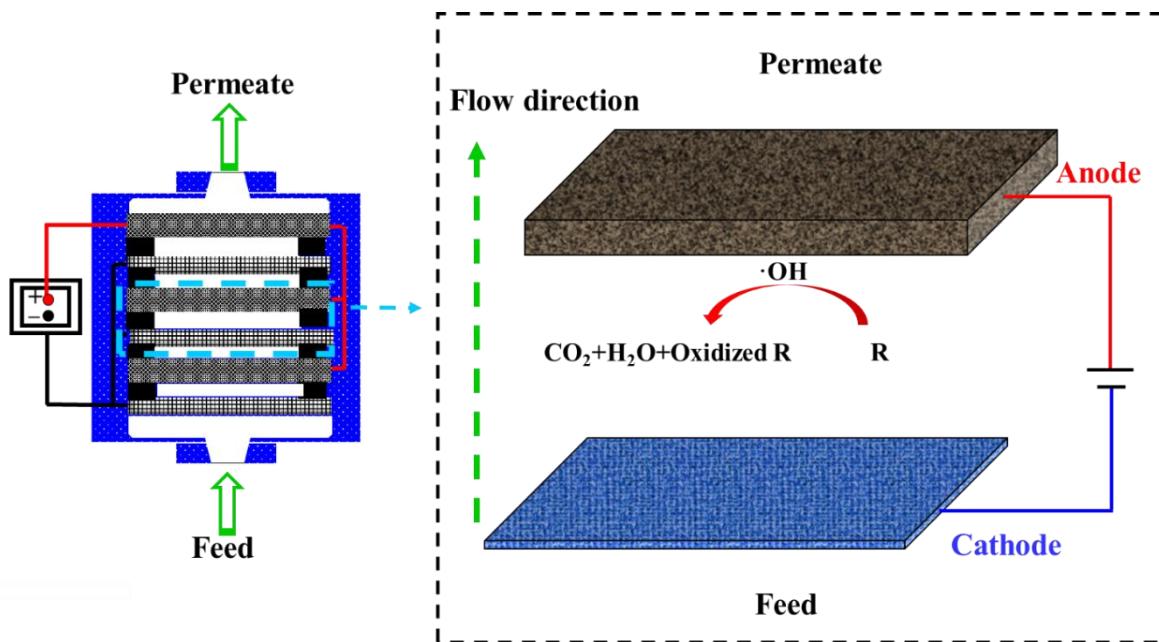


图 1 摘要图

## 3D $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ 介孔纳米片-宽 pH 范围适用析氢电催化剂

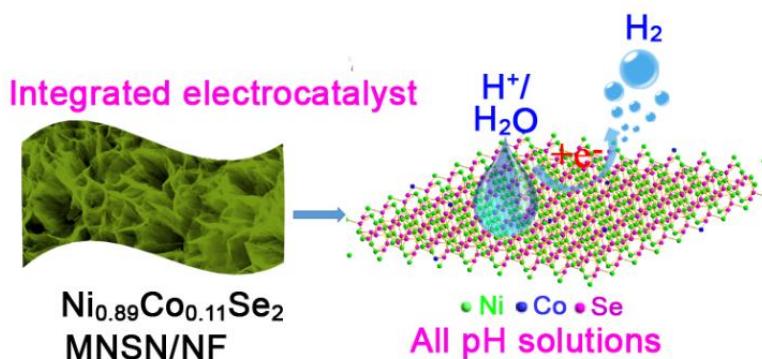
刘宾<sup>a,b</sup>, 张文军<sup>a,b\*</sup>

<sup>a</sup>香港城市大学超金刚石及先进薄膜研究中心, 香港, 中国

<sup>b</sup>香港城市大学材料科学及工程系, 香港, 中国

Email: apwjzh@cityu.edu.hk

随着能源危机以及环境污染的日益加剧, 开发新能源已经迫在眉睫, 氢气以其清洁无污染、高效、可储存和运输等优点, 被视为最为理想的能源载体。电解水析氢反应是制备氢气的高效途径之一, 然而催化性能最好的铂族贵金属催化剂由于储量稀少、价格昂贵而难以广泛利用。因次, 开发成本低廉、性能高效的电催化析氢催化剂是该领域的重要研究方向。基于此, 我们通过简单的水热及酸处理方法制备了一系列泡沫镍负载的 3D  $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$  ( $x: 0 \sim 0.35$ ) 介孔纳米片催化剂, 并研究了其电催化析氢性能。研究发现不同 Co 掺杂量对材料的析氢催化性能有明显影响, 其中  $\text{Ni}_{0.89}\text{Co}_{0.11}\text{Se}_2/\text{NF}$  具有最优的析氢催化性能。在碱性, 中性和酸性电解质溶液中,  $\text{Ni}_{0.89}\text{Co}_{0.11}\text{Se}_2/\text{NF}$  催化  $10 \text{ mA cm}^{-2}$  电流密度所需过电位分别为  $85 \text{ mV}$ ,  $82 \text{ mV}$  和  $52 \text{ mV}$ , 并表现出优异的稳定性。DFT 计算表明催化剂优异的催化性能源于 Co 掺杂调控了其电子结构, 使其对质子和水的吸附能力大大增强。该工作为制备廉价、高效、pH 适用范围广的析氢催化剂提供了思路。



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# 锂氧电池阴极催化剂聚 N-(二茂铁甲酰)咔唑的预掺杂制备 及其电催化性能

徐呈旸, 胡诗帆, 谢婵媚, 张雅迪, 张校刚\*

南京航空航天大学，南京，210016。

E-mail: azhangxg@163.com

锂锂电池因其极高的理论比能量( $3500 \text{ Wh kg}^{-1}$ )得到广泛关注，但由于放电产物 $\text{Li}_2\text{O}_2$ 在电极表面惰性堆积，且充电过程难以分解，令其实际电化学性能受到严重限制<sup>[1]</sup>。有机电极材料虽具有丰富的氧化还原活性位点，可有效分解惰性产物 $\text{Li}_2\text{O}_2$ ，但其在较高的电势下易发生过氧化分解，带来的稳定性问题使其发展受限<sup>[2]</sup>。然而，导电聚合物材料可通过阴离子预掺杂，来实现氧化还原过程中的稳定性提升，并被报道于锂离子电池和太阳能电池等领域，为锂锂电池催化剂材料提供更多可能性<sup>[3]</sup>。本研究中我们通过掺杂复合方式解决了有机电极材料导电性不高、稳定性较差等问题，并充分利用有机分子氧化还原位点丰富的优势，有效分解产物 $\text{Li}_2\text{O}_2$ ，降低反应过电势。

我们采用空穴传导能力强的咔唑，与电活性分子二茂铁甲酰氯形成复合单体 N- (二茂铁甲酰) 咪唑 (如图 1a)，将复合单体在碳纳米管薄膜上原位电聚合 (如图 1b)，对聚合后的自支撑材料进行阴离子 ( $\text{PO}_4^{3-}$ :  $\text{Fe}(\text{CN})_6^{4-} = 10: 1$ ) 预掺杂后，用作锂氧电池空气电极。通过首圈充放电测试发现，聚 N- (二茂铁甲酰) 咪唑材料的丰富电活性位点可有效降低充电过电势 (3.7V，如图 1c)，碳纳米管对于整体材料的导电性提升可维持稳定的放电平台 (2.75V)，且预掺杂的大阴离子可有效改善有机材料的稳定性，在 500 mAh/g 限容条件下循环超过 150 圈 (如图 1d)。

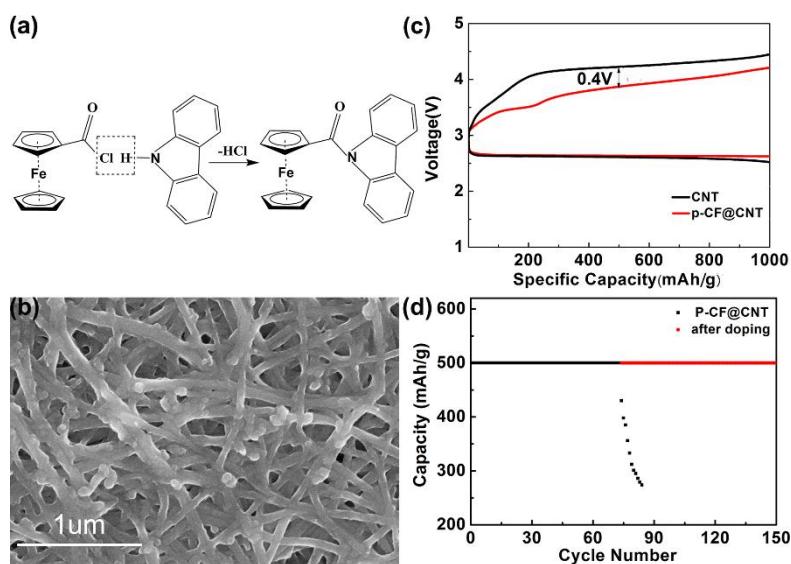


图 1 (a) N- (二茂铁甲酰) 呋唑复合单体制备示意图; (b) 碳纳米管负载 N- (二茂铁甲酰) 呋唑聚合物材料的 SEM  
图; (c) 1000 mAh g<sup>-1</sup> 容量下的首圈充放电曲线; (d) 500 mAh g<sup>-1</sup> 限容下掺杂前后循环圈数对比图

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## 单分散钯硫纳米颗粒在氧还原反应中的应用

杜成

黄冈师范学院

氧还原反应(ORR)在可再生能源技术(例如燃料电池和金属-空气电池)中发挥着关键作用[1-3]。寻找高效的催化剂来克服氧还原过程中缓慢的动力学仍然是清洁能源的关键所在[4]。我们通过简单的一步溶胶方法在油胺溶液中合成硫化钯纳米颗粒(包括Pd<sub>16</sub>S<sub>7</sub>, Pd<sub>4</sub>S和PdS)。在不同类型的钯硫化物中,单分散的Pd<sub>4</sub>S纳米颗粒在0.1 M KOH溶液中显示出对ORR优异的电催化活性,它的半波电位为0.877 V,比商业Pt/C的半波电位高出大约47 mV。与商业Pt/C催化剂相比,所制备的Pd<sub>4</sub>S催化剂还表现出对甲醇更强的耐受性,在稳定性方面也有显著的提高。此外,当把Pd<sub>4</sub>S催化剂用作实验室组装的锌-空气电池的阴极材料时,与商业Pt/C相比表现出更好的催化性能和充放电稳定性,展现出良好的应用前景。密度泛函理论(DFT)计算表明Pd<sub>4</sub>S表面存在氧的吸附位点,能够适当地捕获原子氧并且也很容易解离吸附的O<sub>2</sub>,解释了其优异的ORR催化活性的原因。

# 基于对称双阴极结构 SOFC 的直接电解 CO<sub>2</sub> 研究

官万兵\*, 吴傲路

中国科学院宁波材料技术与工程研究所, 宁波市镇海区中官西路 1219 号, 315201

E-mail: wbguan@nimte.ac.cn

固体氧化物电解池 (SOEC) 在高温下转化 CO<sub>2</sub> 为燃料具有较大的优越性与挑战性。本文在基于作者前期提出的对称双阴极结构电池的基础上, 利用其高温抗氧化还原特性强的特点, 直接对纯 CO<sub>2</sub> 进行电解并进行还原循环研究。结果显示, 这种结构电池可以在纯 CO<sub>2</sub> 环境下稳定运行, 具有较强的抗氧化还原特性, 电解效率有待进一步提升。

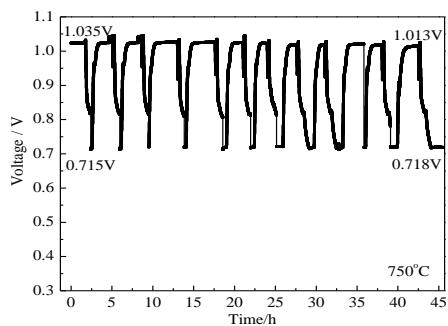


图 1 SOEC 电解 CO<sub>2</sub> 循环过程中 OCV 变化情况

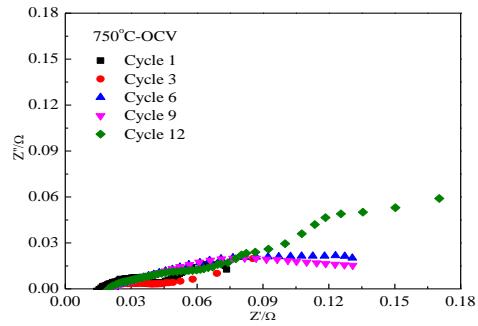


图 2 不同循环次数下的阻抗图

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# 金属铝空气电池催化剂及电池器件研究

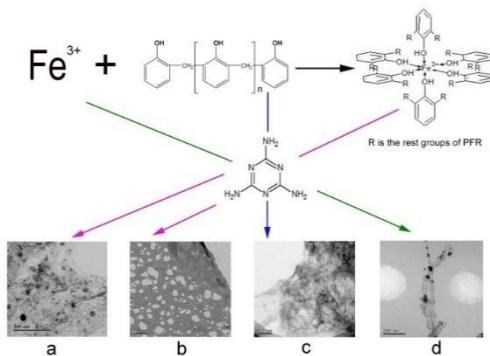
李静莎, 唐有根, 王海燕\*

化学电源湖南省重点实验室, 中南大学化学化工学院, 湖南长沙, 410083

\*wanghy419@csu.edu.cn

铝空电池是用铝代替氢而构建的一种金属燃料电池, 具有能量密度高、安全、成本低、无污染、放电电压平稳等优点, 且铝资源丰富, 能再生利用, 可更换铝电极进行机械充电, 是很有发展前景的电池技术<sup>[1]</sup>。2014年, 美铝公司与以色列 Phinergy 联合开发的铝空电池电动汽车, 续驶里程达到1600公里, 引起了全世界的关注。近年来, 我国铝产能严重过剩, 且新能源汽车产业面临充电难, 国家电网负荷严重不足的困境, 开发铝空动力电池是重要的解决途径。高效空气电极是构建高性能金属空电池的关键技术之一。开发高催化活性、高稳定性、价格低廉的氧还原催化剂是金属和氢氧燃料电池研究的主要方向。

本课题组在多元铝合金、非贵金属氧还原催化剂、电解液缓蚀剂和电堆结构设计等方面相继开展了一系列创新工作, 取得了一些重要的研究成果。课题组与云南美的汽车合作开发电动大巴用铝空电池组, 装载了该电池组的电动大巴成功进行了试运行。本报告将重点介绍近年来我们在低成本、高活性非铂氧还原催化剂的研究进展, 此外, 报告将简单介绍一下课题组在铝空气电池组开发及应用上的进展。



**Fig. 1** Synthesis of ORR catalysts with four different kinds of typical morphologies

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# 异质结电催化材料的设计合成与应用研究

宰建陶\*, 马对, 何凯, 钱雪峰

上海交通大学化学化工学院和金属基复合材料国家重点实验室, 上海电化学能源器件工程技术研究中心, 上海市东川路 800 号, 200240

\*E-mail: zaijiatnao@sjtu.edu.cn

异质结是指两种不同的半导体相接触所形成的具有非线性阻抗特性(整流特性)的界面区域, 通常将具有异质结结构和特性的复合材料称为异质结复合材料。异质结不仅可以构建新的能带结构, 其自建场还能促使光生电子和空穴对在界面处的注入或者转移、提高载流子的分离效率、延长载流子的寿命, 进而提高催化性能。如, 我们通过构建 n-n 型  $\text{Bi}_2\text{S}_3$ - $\text{Bi}_2\text{O}_2\text{CO}_3$ 、 $\text{ZnWO}_4$ - $\text{CdS}$  和 p-n 型  $\text{Ag}_2\text{O}$ - $\text{Bi}_2\text{O}_2\text{CO}_3$  异质结<sup>1-3</sup> 提高催化剂的光降解和光解水制氢能力。这些异质结催化活性的提高源于其整流特性。

那么异质结对于电催化性能的提高是否有效呢? 我们针对  $\text{I}_3^-$  的电催化还原反应, 设计了  $\text{Ag}-\text{Ag}_8\text{SnS}_6$  和  $\text{Cu}_2\text{ZnGeS}_4$ - $\text{PtCo}$  肖特基结<sup>4,5</sup>, 发现可以有效提高电催化活性和染料敏化太阳能电池的转换效率。初步研究表明异质结界面处载流子的定向流动使电子和空穴分别在界面两侧的半导体上富集, 有利于氧化还原反应的进行; 同时金属侧富集的电子可增强金属的抗腐蚀性, 提高电极和器件的稳定性。在此基础上, 我们设计了 n-n 型  $\text{CoS}_2$ - $\text{CoS}$  异质结, 进一步提高了材料的电催化活性和稳定性, 并将其成功的应用与多硫/碘液流电池体系。

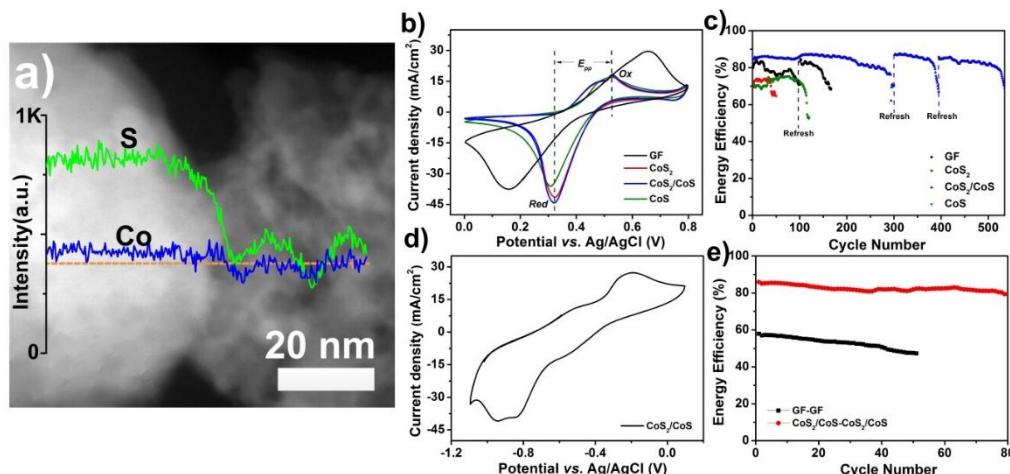


图 1 n-n 型  $\text{CoS}_2$ - $\text{CoS}$  异质结的结构及其电催化活性和液流电池性能。

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# Electrocatalytic artificial nitrogen fixation using a perovskite-type iron complex

Sheng Zhang, Guoyi Duan, Lingling Qiao, Yongmei Chen\*

Beijing University of Chemical Technology, Beijing, China, 100020

\*chenym@mail.buct.edu.cn

Artificial nitrogen fixation has a significant impact on agriculture and industry. Industrial synthesis for ammonia, well known as Haber process, requires high pressures (around 20-40 Mpa) and high temperatures (at least 400 °C), which nowadays hardly meet the high demands for environment protection, energy conservation and sustainable development. Electrocatalytic nitrogen fixation is expected to be performed at lower pressure or lower temperature.

In this study, an iron complex,  $\text{La}_{0.8}\text{Cs}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$  (LCFN), was prepared and its cubic perovskite structure confirmed by XRD and SEM. LCFN powder was fixed onto carbon paper and treated as the cathode for electrochemical ammonia synthesis in 2M KOH solution under atmospheric pressure at 80-100 °C. Ammonia was detected by Nessler's reagent and the rate of ammonia production was found to be  $5.68 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$  at cell voltage of 3.8 V.

The oxygen vacancies in LCFN is confirmed to play an essential role in electrocatalytic ammonia synthesis, although the detailed mechanism still unclear. The catalysts with more oxygen vacancies and their catalytic activity for the synthesis of ammonia are investigated.

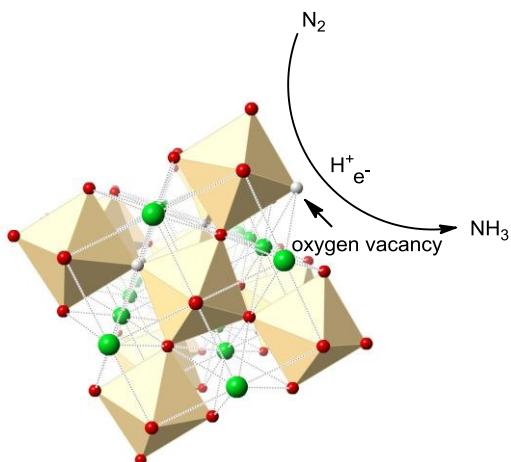


Figure 1. The proposed process for ammonia production with the existence of oxygen vacancy in LCFN.

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## NiTe<sub>2</sub> 纳米片阵列：高效的氧气析出反应电催化剂

王志超，张立学\*

青岛大学化学化工学院，青岛，266071

\*zhanglx@qdu.edu.cn

设计和开发高效、低成本且稳定的过渡金属基氧气析出反应（OER）电催化剂对于电解水制备氢(H<sub>2</sub>)能源至关重要<sup>[1-2]</sup>。在本文中，我们报道了一种通过简单的阴离子交换反应将负载在 Ti 网上的 Ni(OH)<sub>2</sub> 纳米阵列转化为 NiTe<sub>2</sub> 纳米片阵列 (NiTe<sub>2</sub>/TM) 的水热制备方法。作为一种新型的非贵金属基碱性 OER 电催化剂电极，NiTe<sub>2</sub>/TM 表现出优异的电催化性能（仅需要 315 mV 的过电势以达到 10 mA cm<sup>-2</sup> 的电流密度），且此催化剂电极具有优良的电化学稳定性。

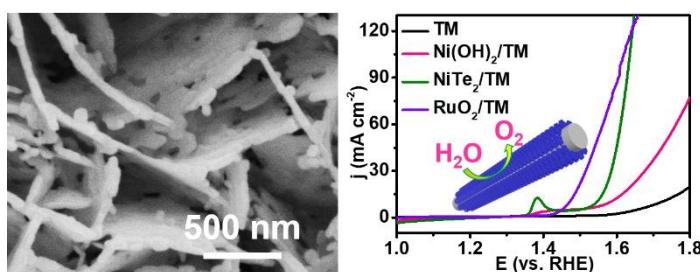


图 1. NiTe<sub>2</sub> 纳米片阵列用作高效氧气析出反应电催化剂

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## ZnO whiskers for dye-sensitized solar cells

Guo Gao

Department of Instrument Science and Engineering, School of Electronic Information and Electrical Engineering, Shanghai

Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China.

E-mail: guogao@sjtu.edu.cn (G. Gao)

With the dramatic rise in world energy demand, reliable cleaner resources must be developed in order to replace the conventional energy derived from fossil fuels and nuclear power. The promising alternative energy resource available for us is the solar energy. If all of the solar radiant energy reaching the surface of earth could be effectively harnessed and utilized, the human's energy problems would be resolved.

Among the reported references, the hybrid ZnO/TiO<sub>2</sub> hierarchical nanostructures has attracted much attention due to the wide-band-gap ZnO ( $E_g=3.37$  eV at 300 K) components are favorable for electron transport, and reduced the recombination loss when used in dye-sensitized solar cells (DSCs). It has been demonstrated that the hybrid hierarchical nanostructures of ZnO and TiO<sub>2</sub> could greatly enhance the DCS's electrochemical performance. First, the TiO<sub>2</sub> can load a large amount of dye that will generate electrons by absorbing visible solar light. Second, the TiO<sub>2</sub> should be sufficiently large in size with excellent mutual connectivity for the efficient diffusion of electrolyte. Finally, the defect level and the number of grain boundaries should be decreased to inhibit the electrons loss by recombination or back reaction. When the synthesized ZnO whiskers (Fig. 1a-d) were mixed with commercial TiO<sub>2</sub> and used in solar cells, the current density increases significantly from 13.68 mA cm<sup>-2</sup> (commercial TiO<sub>2</sub>) to 16.81 mA cm<sup>-2</sup> (TiO<sub>2</sub>-ZnO hybrid materials), endowing the DSCs exhibited a superior conversion efficiency of 7.95 % in comparison with that of commercial TiO<sub>2</sub> (5.87 %), as shown in Fig. 1e. Our study sheds light on the possibility of preparing ultra-long hierarchical ZnO whiskers (>100 μm) with hydrothermal approaches and their potential application for DSCs.

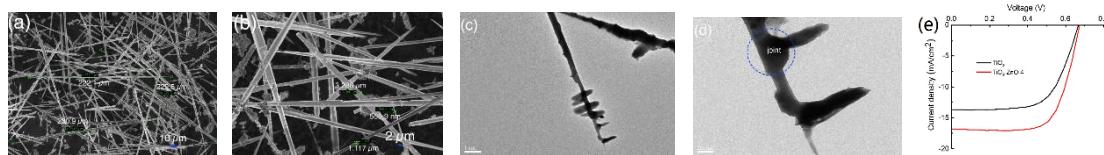


Figure 1 SEM (a-b), TEM (c-d) of synthesized ZnO whiskers, I-V curves of the ZnO/TiO<sub>2</sub> hybrid composites.

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# Highly selective electroreduction of CO<sub>2</sub> to CO derived from iron nitride encapsulated in single iron and nitrogen co-doped carbon nanofiber

Qingqing Cheng, Chi Chen, Hui Yang\*

Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai, 201210

\*yangh@sari.ac.cn

The conversion of carbon dioxide (CO<sub>2</sub>) into valuable chemicals has captured extensive attentions for its significance in energy storage and greenhouse alleviation<sup>[1]</sup>, but development of efficient, high selectivity and inexpensive electrocatalyst reaches the bottleneck<sup>[2]</sup>. Nitrogen doped porous carbon material have emerged as an attractive electrocatalyst for the CO<sub>2</sub>RR considering their low cost, tunable surface areas and electrochemical activity. More importantly, the hydrogen evolution on carbon materials is sluggish and kinetically negligible under aqueous media<sup>[3]</sup>. Herein, we firstly introduced a Fe-N-C porous nanofiber (Fe-N/CNF) featured by the iron nitride (FexN) nanoparticles encapsulated in single atom Fe and N co-doped carbon layer, as the electrocatalyst for the CO<sub>2</sub>RR via electrospinning, carbonization and nitridation in pure-NH<sub>3</sub> procedures. Through appropriate nitridation, the homo-dispersed Fe atoms within the CNF are partially nitrided to the Fe2N or Fe4N nanoparticles. Simultaneously, the vapor carbon species etched by NH<sub>3</sub> are *in-situ* chemically deposited near the fresh FexN particles to finally form the core-shell structure. Experimental results indicate that such Fe-N-C architecture exhibit efficient electroreduction of CO<sub>2</sub> to CO with high Faradaic efficiency (FE) of 95% and large current density of 4.41 mAcm<sup>-2</sup> at an overpotential of 420 mV. Theoretical calculations further reveal that the encapsulated FexN particles weaken the adsorption of CO\* intermediate and lower the binding energy of H\* on the outer FeN4C site, thus resulting in the rather facile production of CO with high selectivity. This work suggests a new perspective to design a M-N-C material with core-shell structure as highly efficient and durable electrocatalyst for CO<sub>2</sub>RR.

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# Enhanced CO<sub>2</sub> Reduction Catalysts via Field-Induced Reagent Concentration

Min Liu<sup>1</sup>, and Ted Sargent\*

<sup>1</sup>School of Physical Science and Electronics, Central South University, China

minliu@csu.edu.cn

## INTRODUCTION

Electrochemical reduction of carbon dioxide (CO<sub>2</sub>) to carbon monoxide (CO) offers a renewable-electricity-powered path to value-added carbon-based fuels and feedstocks<sup>1,2</sup>. Unfortunately, because of the low local concentration of CO<sub>2</sub> surrounding typical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) catalysts, this reaction suffers from slow kinetics<sup>2,3</sup>. The competing off-pathway reduction of water to hydrogen produces poor selectivity as a result<sup>3</sup>.

## RESULTS AND DISCUSSION

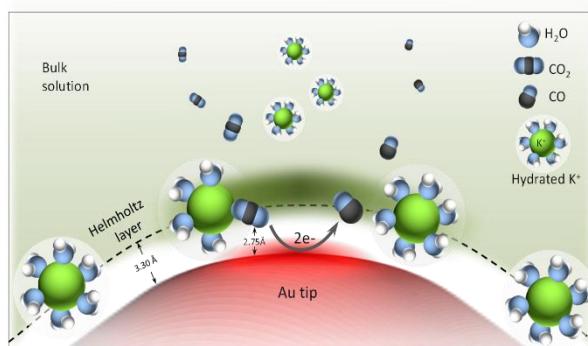


Figure 1. A schematic showing the field-induced reagent concentration (FIRC) process.

Here we report field-induced reagent concentration (FIRC), wherein a nanostructured electrode produces a local high electric field at low applied overpotential. The high field concentrates electrolyte cations, and the cations bring with them a high local concentration of CO<sub>2</sub> proximate the active CO<sub>2</sub>RR surface. Simulations reveal that nanometrically sharp tips on metallic electrodes achieve 10-fold higher electric fields compared to quasi-planar regions. We then use bottom-up nanomaterials chemistry to synthesize gold nanoneedle electrodes that provide a CO<sub>2</sub>RR with record-low onset potential ( $\eta_{CO} = 0.07$  V) and record-high geometric current density ( $j_{CO}$ ) of 22 mA cm<sup>-2</sup> at the low potential of -0.35 V ( $\eta_{CO} = 0.24$  V) with nearly quantitative (>95%) Faradaic efficiency for CO<sub>2</sub> to CO production. We prove robust continuous reactions over 8 hours in an inorganic aqueous electrolyte. The geometric density surpasses by an order of magnitude the performance of the best gold nanorods, nanoparticles, and oxide-derived noble metal catalysts. Furthermore, we have leveraged the FIRC concept to build palladium nanoneedles that also exhibit record breaking geometric current density ( $j_{formate}$ ) of 10 mA cm<sup>-2</sup> at a low potential of -0.2 V over 20 h with >91% Faradaic efficiency for CO<sub>2</sub> to formate production, proving the wider application of the FIRC concept.

## CONCLUSION

This work offers a new strategy to increase the electrosynthesis of carbon-based fuels, including when the precursor molecules are both neutral and highly stable. The sharp-tip-enhancement effect may have contributed to previous successful studies of CO<sub>2</sub>RR on active sites at corners<sup>3</sup> and ridges<sup>4</sup>, since such sites are locally-high-curvature regions. The tip-enhanced field phenomenon can be extended to provide local concentration of reagents for other electrochemical reactions and suggests design principles for efficient electrodes for catalysis.

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# Fe-N Decorated 3D Ordered Mesoporous Carbon Wrapped with CNTs as Bifunctional Catalyst for ORR and OER

Lei Zhao, Xinqi Zhang, Cheng Deng, Hongbin Liu, Mengfu Zhu\*

Institute of Medical Equipment, Academy of Military Medical Sciences, Tianjin, 300161.

\*E-mail: zmf323@163.com

Rational design and development of the highly efficient and robust non-precious metal electrocatalysts with well-defined nanostructure and rich active species are particularly crucial to improve the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). [1] The ordered mesoporous carbon (OMC) shows great potential in oxygen electrocatalysts owing to its unique advantages. [2] Herein, we report the facile, one-step *in situ* encapsulated Fe/Fe<sub>3</sub>C@C nanoparticles in N-doped bamboo-like CNTs on OMC via a solid pyrolysis strategy. [3] The influence of pore size and component has been investigated. The optimized sample shows excellent ORR activity with a half-potential of 0.85 V (vs. RHE) and an overpotential of 420 mV to achieve 10 mA cm<sup>-2</sup> for OER in alkaline (potential difference, 0.80 V). We attribute this high activity to uniform mesopores of 3.2 nm, large S<sub>BET</sub> of 504.4 m<sup>2</sup> g<sup>-1</sup>, distinctive dual-site of Fe-N<sub>x</sub> and Fe@C nanoparticles, etc. Meanwhile, it further displays superior long-term durability comparable to Pt/C under the same condition, exhibiting promising potential in noble-metal-based electrocatalysts for energy conversion and storage, etc.

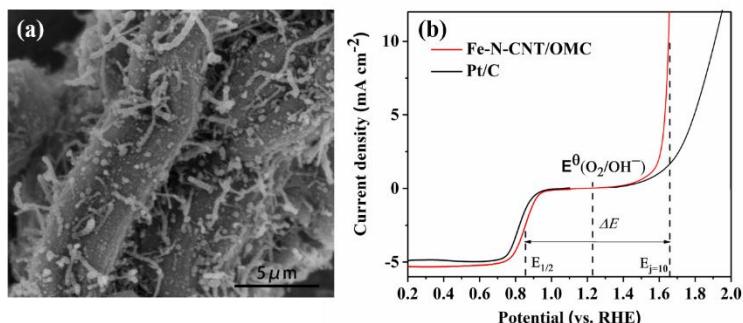


Fig. 1 (a) TEM image of Fe-N-CNT/OMC. (b) The overall polarization curves of Fe-N-CNT/OMC and Pt/C.

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## 稀土氧化物对贵金属电催化氧化醇性能的增强作用

褚海斌\*, 李振宇, 唐龙树, 杨洋

内蒙古大学化学化工学院, 呼和浩特, 010021

\*Email:chuhb@imu.edu.cn

贵金属纳米颗粒在直接醇燃料电池阳极催化剂中发挥着重要的作用, 但是仍面临如何降低 Pt 使用量、提高电催化活性、提高抗 CO 能力等诸多挑战[1]。研究表明, 稀土氧化物如 CeO<sub>2</sub> 拥有丰富的氧空位, 在甲醇电氧化过程中 CeO<sub>2</sub> 表面可以吸附水分子并解离产生羟基, 可用于脱除反应中产生的 CO, 从而提高甲醇电氧化的活性和稳定性。我们利用胺分子将大量羟基稳定在氧化铈的表面, 然后将这种富含羟基的 CeO<sub>2</sub> xH<sub>2</sub>O 与 Pt/CNT 结合。发现 CeO<sub>2</sub> xH<sub>2</sub>O 对甲醇电氧化促进作用远超过氧化铈, 质量活性提高 4 倍左右, 电催化稳定性也显著提高[2]。对于乙二醇和丙三醇电氧化反应, CeO<sub>2</sub> xH<sub>2</sub>O 也能大幅提高 Pt/CNT 的质量活性与电催化稳定性。此外, CeO<sub>2</sub> xH<sub>2</sub>O 还能提高商业催化剂 Pt/C、Pd/C、PtPu/C 的醇电氧化活性与稳定性。因此, 这种方法具有一定的普适性。此外, 二元催化剂 Pd/CeO<sub>2</sub> xH<sub>2</sub>O 对乙醇电氧化的质量活性也远超过 Pd/CeO<sub>2</sub>。这可能与 CeO<sub>2</sub> xH<sub>2</sub>O 表面含有大量的羟基有关, 它能促进贵金属表面吸附的中间有毒物质的快速脱除, 从而大幅度提高它们的电催化活性和稳定性。

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## 铜掺杂二氧化钛纳米片的合成及其在光催化还原二氧化碳中的应用

兰阳春<sup>1</sup>, 张航, 邓丹丹, 崔德虎\*

南方科技大学, 深圳, 中国, 518055

\*cuidh@sustc.edu.cn

传统化石能源燃烧产生二氧化碳引起的地球变暖和能源短缺已经成为一个严重的全球性问题, 利用太阳光和光催化材料将二氧化碳还原为碳氢燃料, 不仅可以减少空气中二氧化碳浓度, 降低温室效应的影响, 还可以提供碳氢燃料, 缓解能源短缺问题, 因此日益受到各国科学家的高度关注。光催化还原二氧化碳的研究核心是光催化材料, 它是决定光催化还原二氧化碳过程得以实际应用的重要因素之一, 因此, 探索和开发各种潜在的高效光催化材料是当今重要的研究方向。

20世纪70年代日本学者Fujishima和Honda等<sup>[1]</sup>人研究发现了二氧化钛在光照射条件下的特殊性质, 自此以后其在光催化领域中逐渐活跃。但是因为二氧化钛禁带宽度大(3.2 eV), 只能利用太阳光中的紫外线部分(仅占太阳光能3~4%), 这大大限制了二氧化钛作为光催化剂的广泛应用。近年来, 二维纳米材料因其独特的物理结构以及电子结构被广泛的应用到光电催化领域中。这是因为二维纳米材料维度的降低使电子更容易集中在二维材料的比表面, 提升了材料本身的导电性。此外, 二维纳米材料的原子级尺度的厚度使其有别于传统块材, 大大提高本身的比表面积, 为催化反应提供了更多的活性位点。另外, 因为二维纳米材料的超薄厚度, 它们的表观结构以及电子结构均可以通过缺陷工程、元素掺杂、结构扭曲等措施进行有效调控, 为光电催化性能的优化提供了有效方法。基于此本工作采用化学合成的方法获得二氧化钛纳米片的二维材料<sup>[2]</sup>, 接着使用掺杂改性的方法来拓展二氧化钛的光谱响应范围, 并将其应用到光催化还原二氧化碳的反应中。通过光催化反应3小时左右, 可以得到0.236~0.36 μmol/g·h的甲酸, 以及少量的一氧化碳和甲烷。

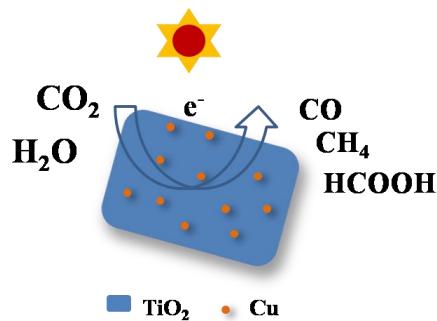


图1 铜掺杂二氧化钛纳米片光催化还原二氧化碳的反应路径。

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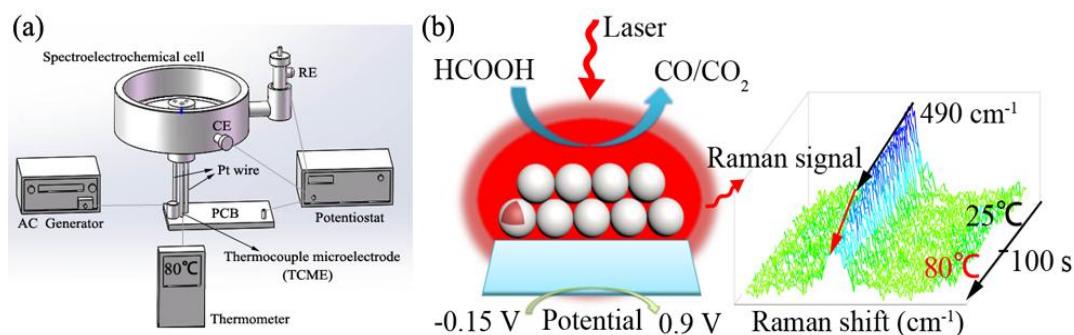
# 高频升温电化学表面增强拉曼光谱对甲酸升温电氧化的研究

谢文昌<sup>1</sup>, 凌云<sup>1</sup>, 张亚真<sup>1</sup>, 刘国坤<sup>2\*</sup>, 汤微<sup>1\*</sup>

1 福州大学化学学院, 福州, 350108 2 厦门大学翔安校区环境与生态学院, 厦门, 361000

\*jingtang@fzu.edu.cn, \*guokunliu@xmu.edu.cn

针对一般液体燃料电池实际工作温度大于室温的情况<sup>[1]</sup>, 本文介绍了一种结合高频交流电加热技术<sup>[2,3]</sup>和 EC-SERS 技术的检测系统, 用以研究升温条件下甲酸的 EC-SERS 行为。



(a) 高频升温电化学表面增强拉曼光谱检测系统示意图, (b)实验原理示意图和升温前后 Pt-C 峰强变化趋势

如图(a)所示是高频升温电化学表面增强拉曼光谱检测系统示意图, 该系统通过高频升温技术在热电偶微电极上施加高频交流电, 使电极表面附近的溶液微区产生大量的焦耳热, 从而实现加热升温的目的, 通过连接热电偶数显温度计实现温度的实时监测, 通过电化学技术改变电极的电势, 同时通过共聚焦拉曼光谱仪对研究体系进行光谱研究。图(b)所示是甲酸升温 EC-SERS 的原理示意图, 将合成的 Au@Pt 纳米粒子负载在热电偶微电极上, 通过高频交流电加热电极附近的溶液, 控制电位变化并进行原位的 SERS 监测。由 SERS 谱可知, 当电位控制在 0.3 V 的时, 室温下 Pt-C 峰强随着时间的推移缓慢下降, 100 s 后升温至 80℃, 谱峰明显骤降, 表明升温可能有利于 CO 的脱附。该系统集合了升温、测温、电化学和拉曼技术于一体, 可以用于升温条件下体系的 EC-SERS 研究, 对研究和理解升温条件下的反应机理具有潜在的应用价值。

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## 界面型光电催化材料的光生电荷行为调控与水裂解性能研究

侯阳\*, 杨建, 雷超君, 杨彬, 雷乐成

浙江大学化学工程与生物工程学院, 杭州, 中国, 邮编 310027

\*yhou@zju.edu.cn

利用太阳能光电催化水裂解制备氢气和氧气被认为是有望解决能源危机与环境问题的理想途径, 也是当今学术界的研究热点和难点。整个光电催化水裂解反应涉及三个关键步骤: (I) 光激发半导体产生光生电子 - 空穴对; (II) 光生电荷载流子分离并迁移至半导体表面; (III) 积累在半导体表面的光生电荷载流子参与水的氧化还原反应。要实现高效地光电催化水裂解制备氢气和氧气反应, 光生电荷在半导体内部和界面的高效分离和输运以及表面催化性能就成为亟需解决的关键科学问题。针对上述问题, 申请者开展了一系列创新性的研究工作, 包括较早地提出了制备纳米阵列光电极“电子输运高速公路”的新思路; 引入基于窗口效应的带隙结构设计新原理, 进而构建具有合理能带区间的半导体异质结构; 建立了一整套新颖的基于“异质结”和“助催化剂”的有效构筑方法、尤其是表界面结构的调控方法、异质结与助催化剂引入对光电极的太阳能吸收、光生电荷输运、电子-空穴再复合的影响机制、以及表面催化调变原理。开发出若干种具有鲜明结构特色的氧化铁、氮化碳、氧化钨和硅基光电极复合材料, 显著提高光电催化水裂解制氢气和氧气的活性(如在模拟太阳光照条件下, 钴掺杂氧化铁/铁酸镁纳米棒异质结阵列光阳极的光电流密度达到  $3.34 \text{ mA cm}^{-2}$ , 高于当时文献中报道的最大值)。现场谱学等手段的研究揭示了异质结和助催化剂的有效构筑促进光生电荷分离和传输以及加速催化反应动力学的本质, 该成果为发展高效光电催化太阳能转化体系提供重要的理论支撑。

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# Chemical vapor deposition synthesis of carbon fibers for immobilization of glucose oxidase in glucose biosensors and glucose/O<sub>2</sub> biofuel cells

Zongqian Hu<sup>1,\*</sup>, Gangyong Li<sup>2</sup>, Yuanlin An<sup>1</sup>, Xiaochen Bo<sup>1</sup>, Shuqiang Jiao<sup>2</sup>

<sup>1</sup>Beijing Institute of Radiation Medicine, Beijing, 100850, P.R. China.

<sup>2</sup>State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083, P.R. China.

\*Corresponding Author's E-mail: [huzongqian@hotmail.com](mailto:huzongqian@hotmail.com)

We report a chemical vapor deposition (CVD) procedure for synthesizing a novel hydrophilic carbon fiber with spiral structure for immobilization of glucose oxidase in glucose biosensor and glucose/O<sub>2</sub> biofuel cell application. Electron microscopy reveals that the as-synthesized carbon fibers present helical structure with a diameter range of 200 ~ 500 nm and a length range from a few microns to dozens of microns. This unique structure is beneficial to immobilize three-dimensional conformation of the enzyme molecule. Contact angle measurements reveal their hydrophilic property even after thermal treatment at 1600 °C. A single glucose/ O<sub>2</sub> biofuel cell (GBFC) fabricated by the as-synthesized carbon fiber modified bioanode and biocathode is able to generate a high open circuit potential of 0.86 V and achieves a maximum power density of 0.79 mW cm<sup>-2</sup> at 0.72 V. Furthermore, two as-assembled GBFCs arranged in series can power a red light-emitting diode lamp (turn-on voltage 1.5 V).

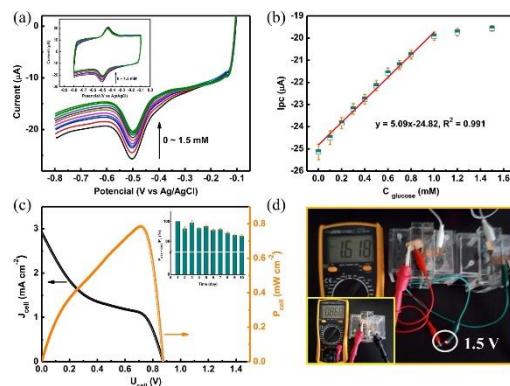


Fig. 1 (a) Half CVs of GOx/CFs-1600 in air-saturated 0.1 M PBS (pH 7.2) with different concentrations of glucose at 50 mV s<sup>-1</sup>, inset is the full CVs; (b) I<sub>pc</sub> vs. C<sub>glucose</sub>; (c) Power output characteristics of the assembled GBFC measured at 20 mV s<sup>-1</sup>. Inset shows the stability test of the GBFC for 10 days; (d) Digital photograph shows the two as-assembled GBFCs arranged in series powering a red LED lamp. Inset presents that a single GBFC can create a high open circuit voltage of 0.86 V.

## 石墨烯负载 Pd-Cu 催化剂的水热法制备

李晨雪<sup>1</sup>, 石晓蜜<sup>1</sup>, 韩静玮<sup>1</sup>, 高晓静<sup>1</sup>, 王辉<sup>2</sup>, 窦红敏<sup>2</sup>, 丁克强<sup>1, 2\*</sup>

河北师范大学化学与材料科学学院, 河北省石家庄市, 050024

河北零点新能源科技有限公司, 河北唐山遵化市, 064204

E-mail: dkeqiang@263.net

以石墨烯、氧化钯和硝酸铜为反应物, 采用水热方法制备了钯铜摩尔比不同的 4 种催化剂。电化学测试结果表明: 在碱性环境下, 当钯铜摩尔比为 1: 1 时, 在循环伏安图中显示出最高的乙醇电氧化峰电流。

### 实验:

按钯铜摩尔比为 1: 0, 1: 0.5, 1: 1 和 1: 2 分别称取 PdO 和 Cu(NO<sub>3</sub>)<sub>2</sub> 为前驱体, 置于四个容器中后, 在分别加入一定质量的石墨烯和二次蒸馏水, 超声混合均匀后, 在一定温度下水热 3h, 冷却至室温, 得到石墨烯负载的 Pd-Cu 催化剂。测试中, 辅助电极为 Pt 电极, 参比电极为饱和甘汞电极(SCE), 修饰有石墨烯(GR)负载的 Pd-Cu 催化剂的玻碳(GC)作为工作电极。

### 结果与讨论

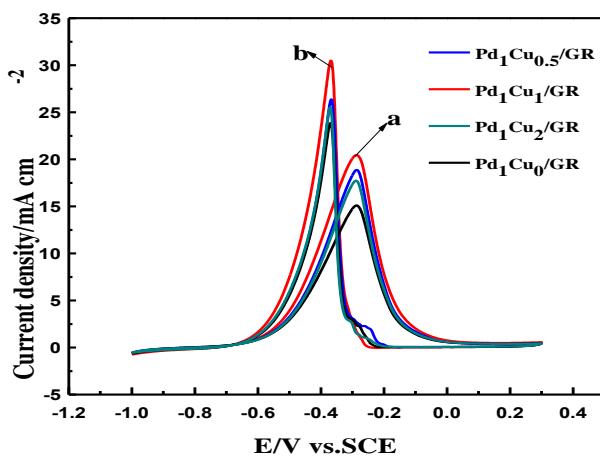


Fig 1.CVs obtained on various graphene supported Pd-Cu catalyst coated GC electrodes in 1M KOH+1M CH<sub>3</sub>CH<sub>2</sub>OH.

图 1 为热解 3h 得到的 4 种催化剂修饰的 GC 电极在 1KOH+1MCH<sub>3</sub>CH<sub>2</sub>OH 中以 50 mV s<sup>-1</sup> 测得的循环伏安曲线。由图可知, Pd<sub>1</sub>Cu<sub>1</sub>/ GR (即钯铜摩尔比为 1:1) 催化剂对乙醇的催化性能最好。

### 结论:

采用水热的方法, 以 PdO 和 Cu(NO<sub>3</sub>)<sub>2</sub> 为前驱体, 合成了石墨烯负载的 Pd-Cu 催化剂, 其中 Pd-Cu 摩尔为 1:1 时, 所制备的催化剂对乙醇的催化性能最好。本工作为开发新型的乙醇燃料电池催化剂具有一定的参考价值。

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# 氧化钯与电解制备的镍锡共热解产物对乙醇电氧化的催化研究

李晨雪<sup>1</sup>, 石晓蜜<sup>1</sup>, 韩静玮<sup>1</sup>, 高晓静<sup>1</sup>, 王辉<sup>2</sup>, 窦红敏<sup>2</sup>, 丁克强<sup>1, 2\*</sup>

河北师范大学化学与材料科学学院, 河北省石家庄市, 050024

河北零点新能源科技有限公司, 河北唐山遵化市, 064204

E-mail: dkeqiang@263.net

## 摘要:

以碳纳米管、电解制备的锡镍、氧化钯为反应物, 采用热解的方法制备了不同质量比的热解产物。电化学性能测试结果表明: 当氧化钯和电解制备的锡镍的质量比为 1: 1 时, 热解产物对乙醇电氧化的催化效果最好。

## 实验:

按氧化钯和电解制备的锡镍的质量比分别为 1: 0、1: 0.5、1: 1、1: 2, 称取 PdO 和电解制备的锡镍, 然后在一定量多壁碳纳米管和二次蒸馏水存在下, 一定温度下热解 3h, 冷却得到产物。在循环伏安电化学测试中, 以饱和甘汞 ( $Hg/Hg_2Cl_2$ ) 电极为参比电极, Pt 片为对电极, 修饰产物的玻碳 (GC) 电极作为工作电极。

## 结果与讨论

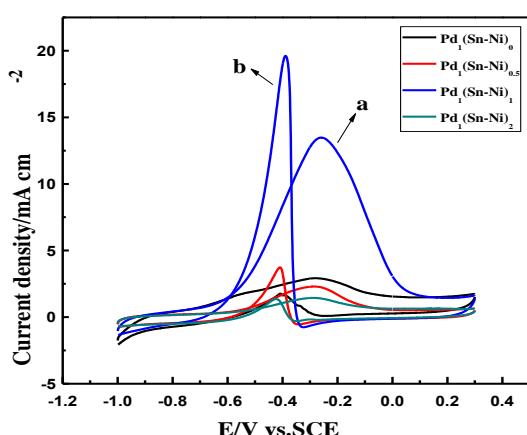


Fig 1.CVs obtained on various Pd-based catalyst coated GC electrode in 1M KOH+1M  $CH_3CH_2OH$  aqueous solution

图 1 为 4 种热解产物修饰的 GC 电极在 1M KOH+1M  $CH_3CH_2OH$  中在 50 mV s<sup>-1</sup> 下测得的循环伏安曲线。由图可知四种产物对乙醇电氧化都有催化性, 且当氧化钯和电解制备的锡镍的质量比为 1: 1 时, 氧化峰最高, 具有最好的催化性能。

## 结论:

本文采用热解的方法, 成功合成了多壁碳纳米管负载的含锡镍的 Pd 基催化剂, 其中氧化钯与锡镍质量比为 1:1 时, 热解制备的产物对乙醇的催化性能最好。本工作对开发新型的乙醇燃料电池催化剂具有一定的借鉴作用。

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# Facile Synthesis of ultrathin 2D Co(OH)<sub>2</sub> for efficient electrochemical oxidation reaction

Lisong Chen\*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, P.R. China, 200062,

\*Corresponding Author's E-mail: lschen@chem.ecnu.edu.cn

Oxygen evolution reaction (OER) and electrochemical methanol oxidation reaction (MOR) are both important energy conversion process, and it is important to development efficient non-precious metal catalysts. We report herein the facile synthesis of cobalt hydroxide nano-sheets with a uniform ultrathin structure under a mild condition. By doping heteroatoms such as Cu, the nanosheets' morphology and dimension can be well-modulated. The prepared heteroatoms-doped cobalt hydroxide nano-sheets exhibit excellent catalytic activity and durability toward the OER and MOR. Specially, Cu-doped cobalt hydroxide (Cu-Co(OH)<sub>2</sub>) shows an electrocatalytic current density of 10 mA cm<sup>-2</sup> and a mass activity of 46 A g<sup>-1</sup> at overpotential of 300 mV, and a Tafel slope of 47 mV dec<sup>-1</sup>, which are markedly higher than those of the state-of-the-art IrO<sub>2</sub>. It also shows high mass activity (764 A g<sup>-1</sup>) and area specific activity (159 mA cm<sup>-2</sup>) as well as good stability and CO tolerance. Importantly, X-ray photoelectron spectroscopy (XPS) suggests the modulated electronic structure by the heteroatoms doping, which results in elevated Co ion valence and is thus in favor of OER and MOR performance. This work presents a green and facile strategy for the synthesis of heteroatoms *in situ* doped ultrathin hydroxides which are of excellent performance for OER and MOR. Possible OER and MOR mechanism for heteroatoms doped samples has also been proposed.

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## Co<sub>3</sub>S<sub>4</sub>/Gr 氧还原催化剂的制备与性能

赵东江\*, 迟彩霞, 田喜强, 马松艳

绥化学院食品与制药工程学院, 绥化, 152061

\*zhaodongjiang1965@163.com

Co<sub>3</sub>S<sub>4</sub> 是较早发现对氧还原反应 (ORR) 有良好催化性能的一种 Co-S 化合物。1975 年, Behret 等<sup>[1]</sup>发现尖晶石结构的 Co<sub>3</sub>S<sub>4</sub> 化合物在酸性电解液中对 ORR 催化活性高, OCP 达到 0.80V (vs. NHE)。2013 年, Mahmood 等<sup>[2]</sup>采用水热法将 Co<sub>3</sub>S<sub>4</sub> 纳米管生长在石墨烯片上制备出具有立方结构的 Co<sub>3</sub>S<sub>4</sub>/Gr 复合物, 在碱性和酸性电解液中, Co<sub>3</sub>S<sub>4</sub>/Gr 均表现出良好的氧还原催化活性, 较强的耐甲醇毒化能力。本研究利用低温回流法, 以乙二醇为溶剂, 采用硫脲为还原剂制备出 Co<sub>3</sub>S<sub>4</sub>/Gr 复合物, Co<sub>3</sub>S<sub>4</sub>/Gr 具有立方结构, 如图 1 所示。纳米级 Co<sub>3</sub>S<sub>4</sub> 在 Gr 上生长形成杂化物, 分散性较好, 如图 2 所示。在酸性介质中, Co<sub>3</sub>S<sub>4</sub>/Gr 具有较高的氧还原催化活性。在 Co<sub>3</sub>S<sub>4</sub>/Gr 上, O<sub>2</sub> 分子主要通过 4 电子转移过程直接还原生成水。

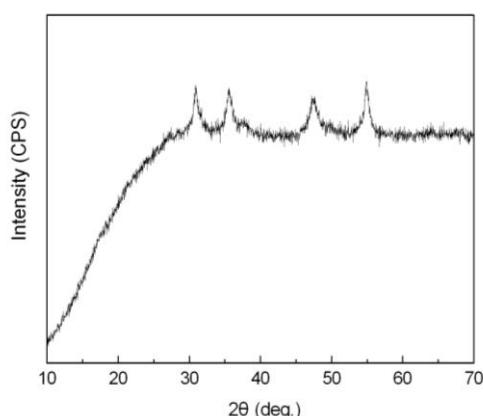


图 1 Co<sub>3</sub>S<sub>4</sub>/Gr 复合物的 XRD 图谱

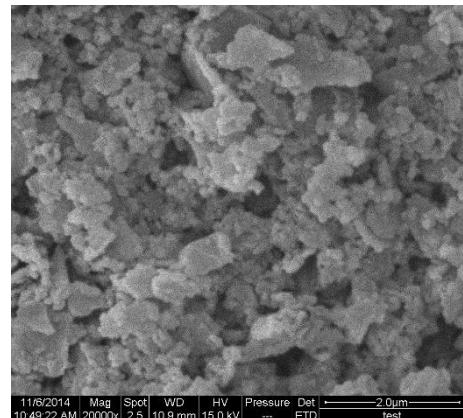


图 2 Co<sub>3</sub>S<sub>4</sub>/Gr 复合物的 SEM 照片

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# The preparation of spherical nano Mn<sub>3</sub>O<sub>4</sub>/MnO catalyst by vacuum DC arc method and its electrochemical performance in lithium-air battery

蔡克迪<sup>1</sup>, 葛芳<sup>1</sup>, 郎笑石<sup>2\*</sup>

1 渤海大学化学化工学院, 辽宁省锦州市松山新区科技路 19 号, 121013

2 渤海大学新能源学院, 锦州滨海新区金山大街 20 号, 121007

\*Email: caikedihit@tsinghua.edu.cn

The lithium-air battery because of its high energy density has been attracted great attention by researchers all over the world. However, the influence of catalytic material on its performance is particularly important. In this paper, a kind of nano catalytic material Mn<sub>3</sub>O<sub>4</sub>/MnO is prepared by vacuum DC arc method. Through XRD、SEM and PL test, it shows that the material has nano structure and the particle size can be controlled between 40-60 nm. The catalyst particle can be evenly distributed in the positive carbon material and it has better electronic conductivity and catalytic activity due to some defects in the crystal structure. The electrochemical performances of air electrode prepared by Mn<sub>3</sub>O<sub>4</sub>/MnO are tested by cyclic voltammetry and AC impedance. The cyclic voltammetry results indicate that it is a bifunctional catalytic material and with the increase of sweep rate, there are obvious oxygen reduction and oxygen evolution peaks and the potential difference has no obvious change. This means that the electrode has good reversibility. The AC impedance results display that the charge transfer resistance of Mn<sub>3</sub>O<sub>4</sub>/MnO catalyst is smaller and the ion diffusion speed is faster. These suggest that Mn<sub>3</sub>O<sub>4</sub>/MnO can improve the electronic conductivity and catalytic activity.

## Graphical Abstract

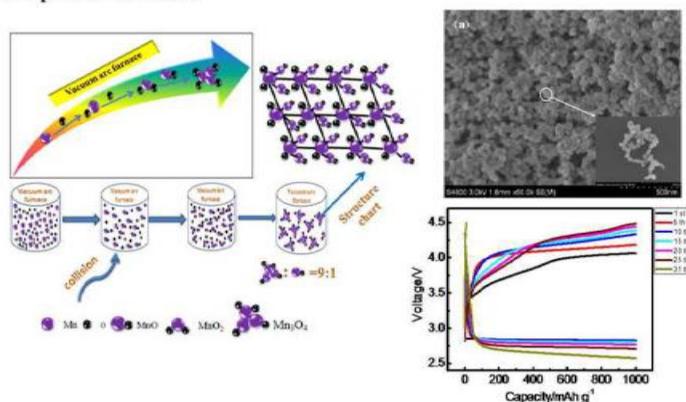


Fig. 1 Graphical Abstract

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## 钨基电极界面的构筑及电化学能源分析

邢志财, 王德文, 李群, 杨秀荣\*

中国科学院长春应用化学研究所, 吉林省长春市, 130022

\*xryang@ciac.ac.cn

创造一个全球可持续能源系统来保护人类赖以生存的环境是当今人类面临的最严峻挑战之一。鉴于传统化石能源的过度消耗并引起气候变使人们对能源供应提出了重大关切。因此, 开发基于非化石燃料 (fossil-free) 的可持续发展途径来实现燃料和化学品的生产不仅为日常生活必需品提供原料, 而且势必在减少二氧化碳排放过程中发挥重大作用。电化学水分解被认为是有效制备氢气并进一步实现其工业化的重要手段, 进而为解决日益严重的能源危机和环境污染能问题发挥关键作用 [1-5]。近年来, 基于第六族过渡金属钨的催化剂由于其蕴藏丰富、低成本和内在活性位点高等优势受到了科研工作者的研究[2,4,5]。我们课题组针对钨基催化剂开展了系列工作: 通过调节前驱体中柠檬酸加入量来调控催化剂形貌制备出具有高比表面积和纳米孔的磷化钨, 而磷化钨中钨和磷分别作为氢受体活性中心和质子受体中心来促进钨-氢氧化物的形成进而通过电化学脱附实现酸性、中性和碱性析氢[2]; 利用 NH<sub>4</sub>Br 为 Br 源和 N 源制备了溴氮共掺杂钨纳米阵列薄膜, 该薄膜作为析氢催化剂测试了其在酸性、中性和碱性条件下的析氢性能[4]; 制备了镍金属单质修饰过渡金属氮化物的异支节纳米线阵列, 该阵列作为高效三维析氢催化剂在碱性条件下展示了超越大部分非贵金属催化剂的催化性能; 利用电沉积技术构建了氧化镍@镍修饰硫化钨的三元阵列电极作为双面催化剂用于水分解, 该催化剂在碱性电解液中展示出与商业化铂碳相媲美析氢性能和超越氧化钌的析氧性能及优异的长期稳定性[5]。我们相信相关工作将为开发设计低价、稳定和高效电极材料并用于水电解及相关领域开辟新途径。

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# 多孔棒状 FeVO<sub>4</sub> 的制备及可见光催化性能研究

蒋海燕, 张帆, 师进生\*

青岛农业大学化学与药学院, 山东青岛, 中国, 266109

\*jsshiqn@qau.edu.cn

在不添加表面活性剂条件下, 采用水热法制备了多种形貌三斜相的多孔 FeVO<sub>4</sub>。采用 X 射线衍射、N<sub>2</sub> 吸附和紫外可见漫反射等技术表征了这些样品的物理性质, 并考察了在可见光照射下这些 FeVO<sub>4</sub> 样品在少量 H<sub>2</sub>O<sub>2</sub> 存在的条件下光催化降解 MO 的催化活性。结果表明, 以具有最高比表面的多孔棒状 FeVO<sub>4</sub> 可见光催化降解 MO 的光催化活性最好。

FeVO<sub>4</sub> 能响应可见光, 采用水热法可有效控制其形貌和尺寸<sup>[1]</sup>。本文采用水热法合成了多孔三斜相 FeVO<sub>4</sub> 纳米棒, 并发现它在光催化降解甲基橙的反应中体现出优良的光催化活性。

## 1.1 实验部分

将 10 mmol Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O 和 10 mmol NH<sub>4</sub>VO<sub>3</sub> 溶于 50 mL HNO<sub>3</sub> (2 mol/L) 溶液中, 以氨水 (14 wt%) 调节反应液 pH 值分别为 4、7 或 10, 再于 120 °C、180 °C 或 240 °C 水热处理 6 h, 再洗涤干燥并于 450 °C 焙烧 6 h 即可制得 FeVO<sub>4</sub> 材料。为表述方便, 将制备的样品命名为 FeVO<sub>4-x-y</sub> (x: 水热温度; y: 反应液的 pH 值)。利用 XRD、SEM、TEM 和 UV-Vis 等技术表征样品的物理性质。在催化剂用量为 0.1 g, H<sub>2</sub>O<sub>2</sub> 溶液(30 wt%)加入量为 0.3 mL; MO 溶液(100 mL)初始浓度为 1.0 × 10<sup>-5</sup> mol/L 并以 300 W Xe 灯为光源的条件下, 在石英反应器中评价样品的光催化活性, 用 UV-Vis 仪确定反应液中的 MO 浓度( $\lambda = 464$  nm)。

## 1.2 结果与讨论

XRD 和 TGA/DSC 测试结果表明, 在 450 °C 焙烧可制得 FeVO<sub>4</sub>-180-4、FeVO<sub>4</sub>-180-7 和 FeVO<sub>4</sub>-120-4 样品均为三斜相 FeVO<sub>4</sub>, BET 比表面积分别为 10.4 m<sup>2</sup>/g、4.7 m<sup>2</sup>/g 和 2.2 m<sup>2</sup>/g, 带隙能分别为 2.00 eV、2.09 eV 和 2.10 eV。由图 1 可知, FeVO<sub>4</sub>-180-4、FeVO<sub>4</sub>-180-7 和 FeVO<sub>4</sub>-120-4 样品粒子分别呈多孔棒状、短棒状和片状。由图 2 可知, FeVO<sub>4</sub>-180-4 样品的光催化活性最好。

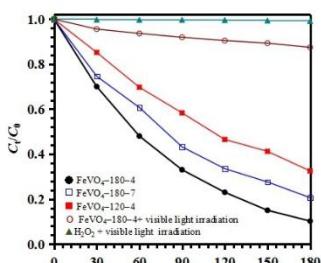


图 1 样品降解 MO 的光催化活性

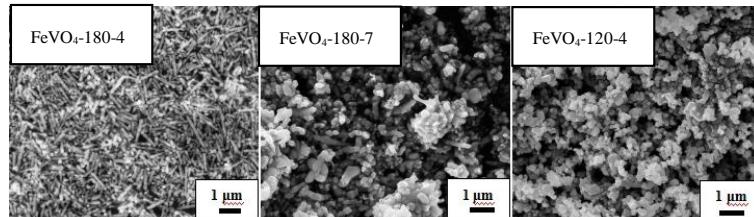


图 2 样品的 SEM 照片

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## 硫属化合物敏化的新型光电阴极

董玉明\*, 王光丽, 蒋平平

江南大学化学与材料工程学院, 光响应功能分子材料国际联合研究中心, 江苏无锡, 214122;

\*dongym@jiangnan.edu.cn

光电化学(photoelectrochemical, PEC)分解水以其便于实际应用而被认为是太阳能储存技术走向工业化的可行路径之一, 受到国际社会高度关注<sup>[1]</sup>。近年来, p型半导体为基础的光电阴极研究相对滞后, 无法兼顾电流密度高、稳定性好、原料丰富的基本要求, 成为限制 PEC 分解水的瓶颈。目前, 硫属化合物作为一类吸光半导体, 具有对太阳光谱吸光系数高、光生电荷分离效率高、光生电子还原能力强的特点, 满足 PEC 光电阴极中对吸光材料需求。将硫属化合物组装到空穴传导层上, 从而构建新型的 PEC 光电阴极是很有意义的研究方向, 。基于这个设想, 本课题组 2015 年以来先后报道了以 NiS/CdTe QDs/NiO、MoS<sub>2</sub>/CdSe layer/NiO 光电阴极并用于 PEC 分解水<sup>[2,3]</sup>, 通过以上的研究发现硫属化合物的优异性能并没有充分体现, 主要是因为目前该类电极空穴传导层都是参照太阳能电池中传统方法制备的 NiO, 空穴传导速率要比光阴极中电子传输速率低约 2 个数量级, 限制硫属化合物敏化光电阴极的性能。因此, 高效的空穴传导层, 对于提高光生电荷的分离效率(导走空穴、减少空穴电子复合)、保持光吸收材料的稳定性(降低空穴积累、阻止氧化光吸收材料)也非常关键。通过查阅文献, 我们发现氧化铟锡(ITO)是一个有潜力的高性能的空穴层材料<sup>[4]</sup>, 根据能级匹配原则, 我们利用硫化铅作为吸光物质敏化氧化铟锡成功构建新型光电阴极, 本实验制备的 FTO/ITO/PbS 光电阴极, 在可见光下产生-75  $\mu\text{A}/\text{cm}^2$  的光电流密度值, 在饱和空气的硫酸钠电解液中经过长时间稳定性测试, 展现出优越的光稳定性<sup>[5]</sup>, 为光电化学分解水的光电阴极寻找新型的空穴传导层提供了一个可能的思路。

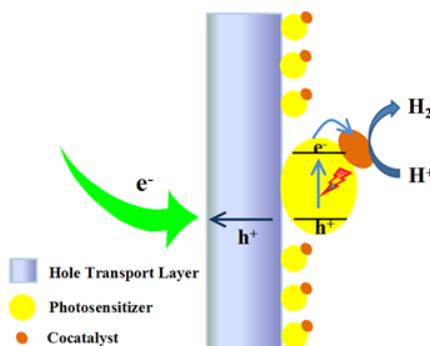


图 1 基于光吸收材料组装的 PEC 分解水新型光电阴极示意图

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## 絮凝与电絮凝低浓度含铀废水处理对比研究

高旭<sup>1</sup>, 李鹏<sup>1,2</sup>, 王学刚<sup>1,2,\*</sup>

1. 东华理工大学水资源与环境工程学院, 南昌, 中国, 330013

2. 东华理工大学核资源与环境国家重点实验室培育基地, 南昌, 中国, 330013

\*wxgecut@163.com

采用絮凝法与电絮凝法对低浓度放射性含铀废水的处理进行了对比研究。结果表明, 絮凝法除铀的主要影响因素是 pH 值和絮凝剂投加量, 在 pH 值为 7.0、PAC 投加量为  $300 \text{ mg L}^{-1}$ 、搅拌速度为  $45 \text{ r min}^{-1}$  的条件下, 铀去除率达 97.94%。电絮凝法除铀的主要影响因素是初始 pH、电流密度、电解质浓度、初始铀浓度等, 初始浊度对电絮凝除 U(VI) 及浊度效果影响较小。在当初始 pH 为 6.5、电流密度  $1.2 \text{ mA cm}^{-2}$ 、电解质浓度为  $0.025 \text{ mol L}^{-1}$  条件下, 反应时间 24 min, 初始铀浓度为  $4.993 \text{ mg L}^{-1}$  的模拟废水铀去除率达 97.37%, 残余铀浓度为  $0.132 \text{ mg L}^{-1}$ 。电絮凝除铀符合二级动力学模型, 在不同 pH 条件下的线性相关系数大于 0.9501。絮凝与电絮凝吨水处理成本分别为 0.61 元  $\text{t}^{-1}$  和 0.45 元  $\text{t}^{-1}$ , 絮体产生量分别为  $258 \text{ g t}^{-1}$  和  $195.6 \text{ g t}^{-1}$ 。投加多羧基的乙二胺四乙酸(EDTA)与铀酰离子 ( $\text{UO}_2^{2+}$ ) 进行螯合形成较为稳定 EDTA-U(VI) 融合物, 易被电絮凝过程阳极产生的  $\text{Fe(OH)}_3$  胶体所捕获, 能够提高直接电絮凝法除 U(VI) 效果。在初始 pH 为 6.5、电流密度  $1.2 \text{ mA cm}^{-2}$ 、电解质浓度  $0.025 \text{ mol L}^{-1}$ 、EDTA 与  $\text{UO}_2^{2+}$  摩尔比为 3:1 最优条件下, 反应时间 24 min, 初始铀浓度为  $4.466 \text{ mg L}^{-1}$ 、浊度 24.85 NTU 的废水 U(VI) 去除率达 99.14%, 浊度去除率 88.93%, 残余 U(VI) 浓度为  $0.039 \text{ mg L}^{-1}$ 、浊度 2.75 NTU, 达到了铀矿冶辐射防护和环境保护规定 (GB 23727—2009) 中排放废水铀含量环境受纳值 ( $<0.05 \text{ mg/L}$ )。絮凝与电絮凝法均可实现铀的高效去除, 但电絮凝工艺较传统絮凝法具有易自动化控制, 处理成本低, 絯体产生量低的特点, 具有较好的推广应用前景。

## 空间限域合成钴@氮掺杂碳双功能结构化电极用于整体水分解

唐彦群, 罗兰, 项项\*

北京化工大学, 化工资源有效利用国家重点实验室, 北京, 100029

\*Email: xiangxu@mail.buct.edu.cn

设计高性能电极、使其兼具优异的水分解析氧与析氢性能是实现电化学能源转化的重要途径之一。层状双金属氢氧化物(LDHs)具有优异的水氧化性质,已经被广泛研究作为析氧电催化剂。LDHs能生长形成纳米片状结构,在一定条件下,纳米片垂直于基底生长还能形成阵列结构。我们提出利用LDHs纳米片阵列形成的三维空间限域生长MOF结构,经过热转化,得到氧化钴嵌入氮掺杂碳结构化电极(Co@N-doped Carbon)。由于LDHs的空间限域作用,Co@N-doped Carbon牢固锚定于电极上,氧化钴高度分散在碳基体里。该电极在碱性溶液里的析氧过电位是320 mV vs RHE ( $10 \text{ mA cm}^{-2}$ ),析氢过电位是-68 mV vs RHE ( $-10 \text{ mA cm}^{-2}$ ),兼具优异的水分解析氧和析氢性能。同时作为阳极/阴极用于整体水分解的电势仅1.59 V ( $10 \text{ mA cm}^{-2}$ ),优于Pt/C // RuO<sub>2</sub>催化体系。研究发现钴氧化物组分对于水氧化起主要作用,钴氧化物与氮掺杂碳的协同增强了析氢性能。该工作为钴基结构化、双功能催化电极设计提供了一条途径。

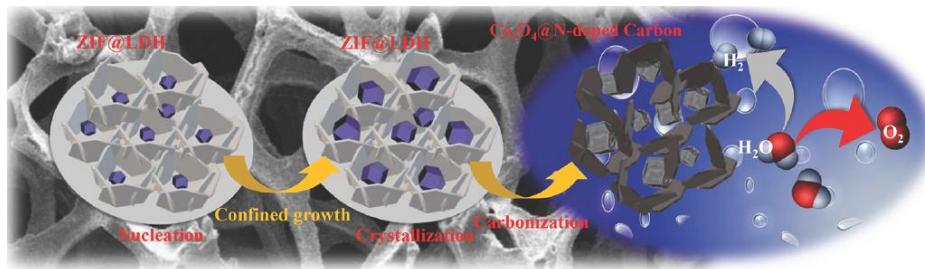


图 1 LDHs三维空间限域合成钴@氮掺杂碳双功能结构化电极

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## MoP 纳米材料的可控合成及电催化性能研究

吴则星\*, 宋敏, 秦清, 王帅, 刘希恩\*

青岛科技大学化学与分子工程学院, 生态化工国家重点实验室培育基地, 青岛, 中国, 266042

\*splswzx@126.com; liuxien@qust.edu.cn

电解水制备氢气相对于传统方法具有高效、绿色和可持续的优势, 而催化剂对于电催化反应的进行起到至关重要的作用。目前, Pt 基纳米材料具有最佳的催化析氢反应性能, 但是价格昂贵、资源有限限制了其大规模应用<sup>[1]</sup>。磷化一钼 (MoP) 具有良好的导电性、催化性能和稳定性而受到广泛的关注<sup>[2]</sup>。我们利用水热和高温磷化的方法得到了石墨烯负载 MoP 的电催化, 纳米材料表现出了优异的电催化析氢反应活性。利用同样的合成方法系统研究了目前研究比较广泛的三种钼基纳米材料, 包括 MoP、Mo<sub>2</sub>C 和 MoS<sub>2</sub>, 实验发现 MoP 纳米材料在酸性和碱性电解液中都具有优异的催化性能和稳定性。我们进一步简化了 MoP 的合成方法, 利用导电高分子为碳基合成了氮掺杂碳负载 MoP 的纳米材料, 研究发现 MoP 经过 S 修饰之后催化性能明显的提升。

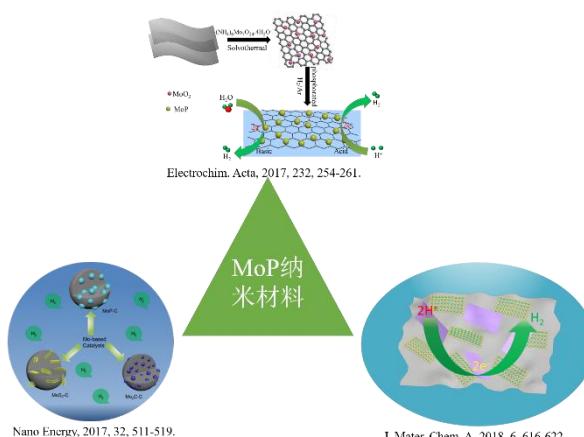
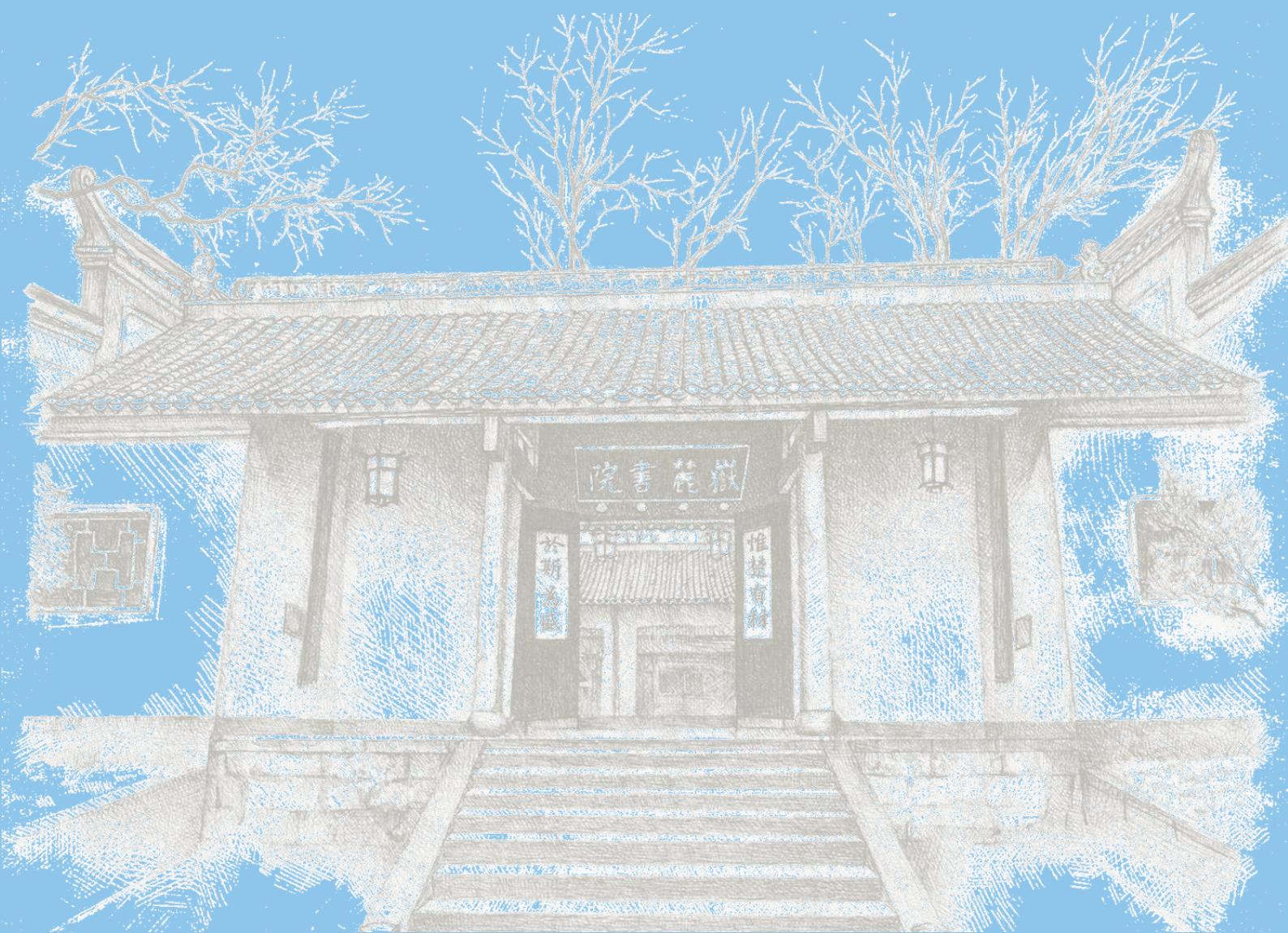


图 1 MoP 纳米材料的可控制备示意图。

### 参考文献

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**Address:** Lushan Road (S), Yuelu District, Changsha, Hunan Province

**Zip Code:** 410082

**Tel:** 0731-88822286