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会议摘要集

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多孔单晶与表界面化学

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摘要正文：

多孔单晶兼具长程有序晶格结构和无序连通孔道结构，结构清晰且组分精准，表面终止原子层确定，对构筑表界面精细结构具有独特的优势。然而，晶格结构长程有序与多孔微结构是相互矛盾的问题，晶体中难以容忍连通孔缺陷，晶体定向生长的特点也限制了多孔微结构的生长。因此，多孔人工晶体尚属于国际空白。本文将介绍多孔单晶生长方法学，阐述单晶结构和多孔结构协同生长的晶格重构机制，简要介绍多孔单晶生长的普适性方法及生长出的系列化多孔单晶40余种；这些多孔单晶的宏观尺寸在~2-4cm可调，孔径在~5nm-2 μ m可调，比表面积在~5-150m²/g可调，孔隙率在~30-70%可调。^[1-5] 通过生长多孔单晶构筑表界面精细结构，明确了催化反应中的表界面结构演化及催化机制与性能。此外，也简要介绍多孔单晶在核废料处置、同位素电池、同位素分离的应用。

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碳材料支撑的过渡金属化合物的构筑及在可充式锌空电池中的应用研究

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摘要正文:

可充式锌-空气电池具有转换效率高、环境友好、可重复循环使用等优点, 可广泛应用于电动汽车、便携式电源及发电厂等领域。可充式锌-空气电池的性能取决于阴极氧还原反应 (ORR) 和氧析出反应 (OER) 动力学。当前, 可充式锌-空气电池主要采用Pt、Pd、Au等贵金属材料为阴极ORR催化剂、RuO₂和IrO₂材料为阴极OER催化剂。这些贵金属催化剂材料存在资源稀缺、反应动力学缓慢、稳定性差等问题, 严重阻碍了可充式锌-空气电池的发展。因此, 开发新型价格低廉、催化性能高的双功能催化剂对促进阴极ORR和OER动力学、提高可充式锌-空气电池的性能具有重要意义。过渡金属资源丰富, 且具有电催化性能, 被认为是ORR和OER催化剂的可选择材料。但过渡金属基催化剂普遍存在着催化性能低、稳定性差等问题, 因此, 要将过渡金属基催化剂直接用于可充式锌-空气电池中, 必须通过改性提高其ORR和OER催化性能和稳定性。本论文以发展价格低廉、高性能过渡金属基催化剂材料为目标, 主要设计与制备了碳材料支撑的过渡金属基化合物电催化剂材料, 研究了其在锌-空气电池中的应用, 并详细讨论了电催化剂的形貌、结构和组成等与ORR/OER电催化性能之间的关系^[1-4]。

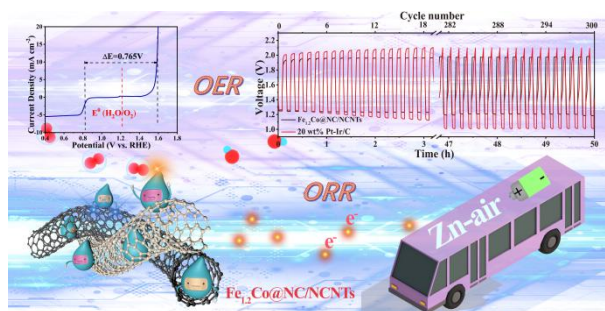


Fig. 1 FeCo alloy nanoparticles coated by ultrathin N-doped carbon layer and encapsulated in carbon nanotubes as highly efficient bifunctional air electrode for rechargeable Zn-air batteries.

关键词: 过渡金属化合物; 氧还原反应; 氧析出反应; 可充式锌-空气电池;

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Cyber Hierarchy and Interactional Network Enabling Digital Solution for Battery Full-Lifespan Management

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Lithium ion batteries, as the most successfully customized energy storage, have been widely developed to satisfy the ever-growing demands in the electrical vehicles, 3C devices and other related functions. Unfortunately, the battery safety, reliability and longevity remain challenges for practical applications because of the limited precision in battery detection, fault prognosis and diagnosis in electric drives. Designer energy materials, optimizing micro-structure and manufacturing are highly desired to address these issues coupled with batteries pack design and battery management system (BMS) applying a cloud control based digital solution. The cloud control platform is to decompose complex systems into several interdependent layers, each of which has its own functions, thus can store information and use it in new situations with deep learning ability, organic integration of virtual models and real entities, and iterative evolution in the cloud management platform. Therefore, it is considered as a multi-factor and multi-discipline digital solution for battery full-lifespan management. The presentation will outline the recent status of methodologies, the current research opportunities, challenges and future perspectives of the batteries based on cloud control and intelligent communication technology.

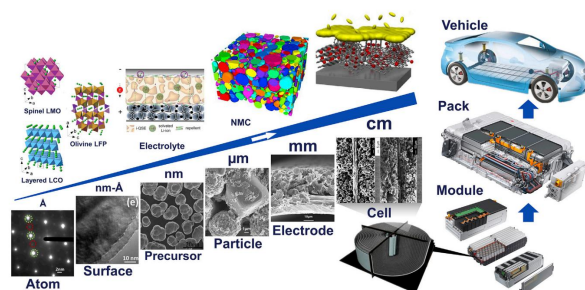


Fig. 1 CHAIN: Multi-scale Processing from Battery Materials to System Control

Keywords: Lithium ion battery, electric vehicle, battery management system, Cyber Hierarchy and Interactional Network (CHAIN)

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碱金属-硫(硒)电池材料的设计以及性能优化

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摘要正文:

硫/硒 (S/Se) 基电极材料由于具有高的理论容量, 已经在锂/钠离子电池中受到了广泛的研究和关注。但是, 该类材料在钾离子电池中的应用却鲜有报道, 主要原因是钾硫/硒电池面临着更严峻的挑战, 比如在充放电过程中材料的中间产物溶解损失严重, 电极体积变化巨大及金属钾活性高易发生副反应等, 这些问题会导致电池的可逆容量低, 循环稳定性差, 难以满足实际应用的需求。因此, 我们课题组近期通过明晰硫/硒电极的储钾机理, 设计材料的组成和构筑特殊微纳结构, 开发出了高比容量, 长循环寿命和高倍率性能的钾硫/硒电池系统。首先, 我们通过简单的抽滤法制备了一种氮氧共掺杂的三维连通的多孔碳薄膜, 然后采用熔融扩散法, 将硒限域在薄膜的微孔中, 成功制备出了一种柔性自支撑的硒/碳复合薄膜电极。将薄膜硒电极应用于钾离子电池中, 在 0.8 A g⁻¹ 电流密度下, 循环 700 圈仍具有高达 335 mAh g⁻¹ 的可逆容量, 该性能优于迄今为止文献报道的数值。该电极材料优异的电化学性能, 一方面得益于对材料孔结构的精细调控, 可以有效增强电极的导电性, 同时提高硒的负载量; 另一方面源于杂原子的掺杂, 加强了对硒及其还原产物的吸附作用, 从而提高了硒的利用率和电极的稳定性。在近期研究中, 我们发现二硫化硒 (SeS₂: 1123 mAh g⁻¹) 相比于硒 (Se: 675 mAh g⁻¹) 具有更高的理论容量, 因此, 使用二硫化硒电极有望进一步提高钾离子电池的能量密度。我们通过构筑一种高氮元素掺杂的多孔碳, 将熔融的二硫化硒封装在孔内, 同时利用碳基体中掺杂的氮 (尤其是吡啶氮和吡咯氮) 对反应中间产物的强化学吸附效果, 提高了活性材料的利用率, 缓解了体积膨胀, 保证了电极结构的稳定性。相对于复合硫电极 (335 Wh kg⁻¹) 和硒电极 (337 Wh kg⁻¹), 我们设计的二硫化硒复合材料可以提供高达 533 Wh kg⁻¹ 的能量密度, 表明二硫化硒材料在钾离子电池中具有极佳的应用前景。

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Well-defined Functional Mesoporous Silica/Polymer Hybrids Prepared by Integrating ICAR ATRP Technique with Mussel-inspired Polydopamine Chemistry

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Mesoporous silica/polymer hybrids with well-preserved mesoporosity were prepared by integrating the initiators for continuous activator regeneration (ICAR) atom transfer radical polymerization (ATRP) technique with the bio-inspired polydopamine (PDA) chemistry. By manipulating the auto-oxidative polymerization of dopamine, uniform PDA layers were deposited on the surfaces and pore walls of ordered mesoporous silicas (OMSs), thereby promoting the immobilization of ATRP initiators. Poly(glycidyl methacrylate) (PGMA) brushes were then grown from the OMSs by using ICAR ATRP technique. Evolution of the mesoporous silica/polymer hybrids during the synthesis, in terms of morphology, structure, surface and porous properties, was detailed. And, parameters influencing the controlled growth of polymer chains in ICAR ATRP system were studied. More importantly, due to the versatility of the ICAR ATRP technique, combined with the non-surface specific PDA chemistry, the methodology established in this work would provide new opportunities for preparation of advanced organic-inorganic porous hybrids for broadened applications.

论文编号：18-006

插层法制备三聚氰胺/g-C₃N₄复合材料

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摘要正文：

本文利用三聚氰胺丰富的官能团结构作为一种适用性强的插层剂，同时通过化学手段打开g-C₃N₄层间距作为插层基体，采用直接插层法和间接插层法制备了一种三聚氰胺/g-C₃N₄复合材料。试验结果表明：通过蒸发溶剂拓展g-C₃N₄层间距的直接插层法可通过三聚氰胺分子与g-C₃N₄的 π - π 相互作用及化学键合共同作用完成插层；借助Cu²⁺率先插层g-C₃N₄复合结构以拓展层间距，再利用Cu²⁺与三嗪环络合反应的间接插层法也可以完成插层。通过SEM可以观察到插层后三聚氰胺与g-C₃N₄二者紧密堆叠；通过TEM可以观察到插g-C₃N₄片层卷曲程度降低；XRD表明插层后g-C₃N₄的层间距增大，从而实现插层。

关键词：三聚氰胺；g-C₃N₄；插层法；层间距

多功能化聚合物的合成及其对二次电池材料颗粒表面的处理

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摘要正文:

聚合物高分子材料具有一定的柔韧性、粘接性、形状适应性和缓冲应力的能力, 同时还具有电子导电或者离子导电等功能, 在能量存储和转化器件尤其是高能量密度二次电池的设计上具有广泛应用。例如, 新型的锂离子导体聚合物材料Poly(acrylonitrile-co-butadiene) 和 poly(ethyl cyanoacrylate)具有优异的化学和电化学稳定性, 能够在电极颗粒界面上形成稳定的离子传导通道。聚噻吩Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)具有高电子导电率 10^3 S cm^{-1} , 但离子导电率较低、室温下只有 $10^{-7} \text{ S cm}^{-1}$ 。在本研究中, 以本团队开发的锂化聚乙烯醇缩醛单离子导体聚合物(lithiated polyvinyl formal-derived Li^+ single-ion conductor, LiPVFM)为基础, 设计了具有锂离子-电子双电导的聚合物体系(Electronic and Ionic Dual Conductive Polymer, DCP)。聚合物大分子通过官能团之间的相互作用, DCP的柔性显著提高, 呈现高杨氏模量6.8 GPa, 电子导电率达到 68.9 S cm^{-1} 、锂离子电导率 $2.76 \times 10^{-4} \text{ S cm}^{-1}$, 电化学稳定窗口6 V。对二次固态电池复合正极的活性材料颗粒的表面处理, 只需在正极制浆过程中引入DCP, DCP在正极活性材料颗粒的表面形成 $\sim 30\text{nm}$ 的聚合物层, 成功构建了短程-长程离子和电子导电通道, 同时有效保持了循环过程中活性材料、界面和电极的稳定性。应用在高电压 LiCoO_2 固态电池中, 活性物质在极片中的占比提高到89%, 正极载量达到 6.7 mg cm^{-2} , 正极极片的能量密度提升至 552 Wh kg^{-1} 。

同时, 具有优异特性的聚合物高分子材料也通常应用在高能量密度金属锂负极表面, 缓解和抑制严重的界面反应和锂枝晶的问题。在本研究中, 我们提出了采用简单的方法在锂金属表面构建聚合物-无机颗粒原位复合的界面层: 将金属锂漂浮于 γ -缩水甘油醚氧丙基三甲氧基硅烷(GPTMS)的混合溶液中, 金属锂的表面形成聚合物致密层; 进而, 在金属锂负极首次锂剥落过程中无机颗粒 $\text{Li}_6(\text{Si}_2\text{O}_7)$ 自适应分相产生, 与Si-O-Si构建的空间网络基体形成稳定的复合膜(简称 SC-Li membrane)。由无机颗粒与聚合物基质的原位结合形成的复合膜使界面具有高表面能和低锂离子扩散势垒, 实现了锂在电极表面的均匀沉积。同时, 该复合膜具有出色机械和化学稳定性, 致密而且坚固, 提高了金属锂负极和高能量密度二次电池的循环寿命。

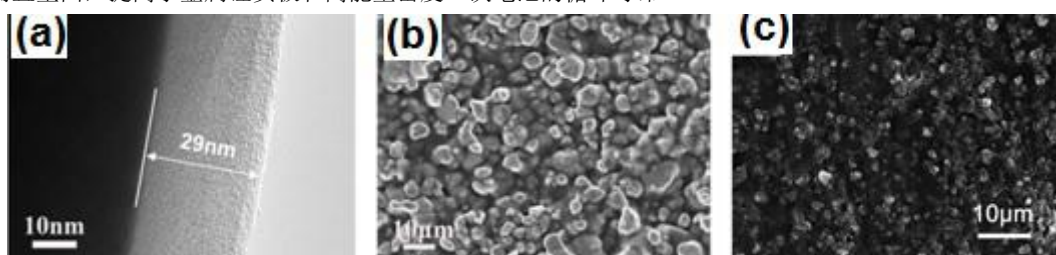


Fig. 1 Surface microstructure of (a) LiCoO_2 particle with DCP, (d) cathode and (c) lithium metal anode with SC-Li membrane

关键词: 聚合物; 功能化; 二次电池; 正极颗粒; 金属锂

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无机碳复合材料的表面调控及储钠性能研究

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摘要正文：

低成本大规模储能技术日益增长需求促使与锂离子电池类似的室温钠离子电池引起了广泛关注，室温钠离子电池由于其资源丰富、分布广泛、成本低廉、循环寿命长、穿刺安全等优点满足未来大规模的电化学储能需求。但是，较大的钠离子半径导致传统石墨负极不能有效脱嵌及存储Na⁺，因此，研究开发高效存储并可逆脱嵌Na⁺的负极材料是钠离子发展的关键。课题组通过无机合成可控构筑出分级碳复合结构、3D氮掺杂碳纳米纤维(NCF)，研究详细表征对其微纳分级结构表面结构与储钠电化学性能之间构效关系进行研究，获得了高储钠电化学性能负极材料，实现高效钠离子存储。

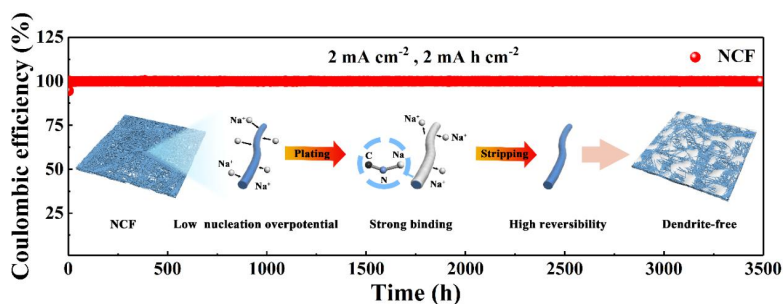


Fig. 1 Schematic illustration of the mechanism of high reversibility of sodium metal on NCF and The coulombic efficiency of sodium plating/stripping on NCF at 2 mA/cm² and 2 mAh/cm²

关键词：复合材料；表面与界面；储钠

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论文编号：18-009

pH/Redox Dual-Responsive Polyplex with Effective Endosomal Escape for Codelivery of siRNA and Doxorubicin against Drug Resistant Cancer Cells

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The enhanced endo-lysosomal sequestration of multidrug resistance (MDR) cell makes siRNA delivery much tougher. Herein, a dual-responsive polyplex with effective endo-lysosomal escape based on mPEG-b-PLA-PHis-ssOEI was developed for co-delivering MDR1-siRNA and doxorubicin. The polyplex showed good encapsulation capacity, accelerated release of payloads and enhanced endo-lysosomal escape. In specific, polyplex at N/P of 7 demonstrated much higher payload delivery efficiency, MDR1 gene silence efficiency, cytotoxicity against MCF-7/ADR cell, and stronger MCF-7/ADR tumor growth inhibition than those at higher N/P, which was attributed to the stronger electrostatic attraction between siRNA and OEIs as N/P went higher that suppressed the dissociation. Consistently, hemolysis test, propidium iodide uptake test and confocal laser scanning microscopy result all indicated the OEI-induced membrane permeabilization effect played a dominant role in endo-lysosomal escape. Consequently, the polyplex with effective endo-lysosomal escape provides a rational approach for codelivery of siRNAs and chemotherapy agents for MDR reversal.

Keywords: endo-lysosomal escape, multidrug resistance, siRNA delivery, dual-response

静电喷涂多孔镍锰氧化物薄膜作为锂离子电池负极材料

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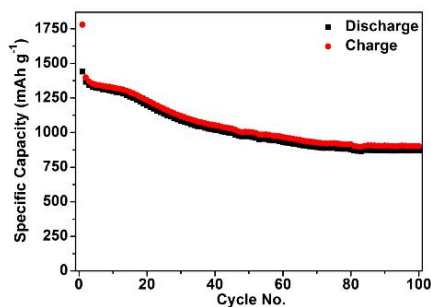
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摘要正文:

本研究通过静电喷涂 (ESD) 的方法, 在氩气气氛下煅烧, 制备得到了一种基于泡沫镍上的多孔镍锰氧化物膜。该多孔Ni-Mn-氧化物结构由 Mn_2O_3 和 $NiMnO_3$ 复合结构^[1]组成。当作为锂离子电池 (LIB) 负极时, Ni-Mn-氧化物电极显示出优异的循环能力 (在 400 mA g^{-1} 下100次循环后为 902 mAh g^{-1}) 和良好的倍率容量。泡沫Ni上的多孔Ni-Mn-氧化物膜的优异电化学性能可以与独特的体系结构相关联, 该体系结构可以提供足够的空隙空间来缓冲充放电过程中的体积变化, 并在电化学反应中提供更多的反应性位点。



关键词: Ni-Mn-氧化物膜; 负极; 锂离子电池; 静电喷涂 (ESD)

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Insight into the Effects of Nitrogen-Doping Structure on the Growth of MoS_{2+x} Nanosheets and Hydrogen Evolution Reaction

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MoS₂, a layered transition metal dichalcogenide (TMDs), with the two-dimensional layered structure has been widely investigated for HER in the past few years.¹ Except for the inert basal plane sites, the intrinsically low conductivity of MoS₂ also hinders electron transfer process, which adversely affects its efficiency towards HER. Therefore, how to expose more edge active sites and improve the conductivity of MoS₂ at the same, either intrinsically or with the aid of highly conducting substrates, is the key matter to improve the HER performance of MoS₂.²⁻³ Herein, the polystyrene (PS) nanospheres are used not only as an intercalation agent of graphene carbon sheets, but also as a spherical template for the preparation of 3D structure of graphene. Different nitrogen precursors and nitrogen doping methods were used to prepare the spherical graphene substrate materials with different nitrogen-doping structure, such as amine N, pyrrolic N, pyridinic N or quaternary N. The investigation results show that the structure of doped nitrogen atom has a great influence on the loading of molybdenum disulfide. Among them, amine N was the most favorable for the loading of molybdenum disulfide, followed by pyrrole N, quaternary N and pyridine N. In addition to the structure of doped N active sites, different preparation methods can also affect the uniform distribution of molybdenum disulfide on spherical porous graphene. The results show that, using ammonia as nitrogen source and PS microspheres as template, the prepared molybdenum disulfide loaded spherical porous graphene electrode material has the best HER performance, which should be attributed to the uniform distribution of the molybdenum disulfide and its close combination with the substrate, as well as the 3D porous structure. Moreover, the amorphous structure of molybdenum disulfide formed in the hydrothermal process at high temperature can also improve the activity of HER.

Keywords: MoS₂; hydrogen evolution reaction; spherical graphene; amine N

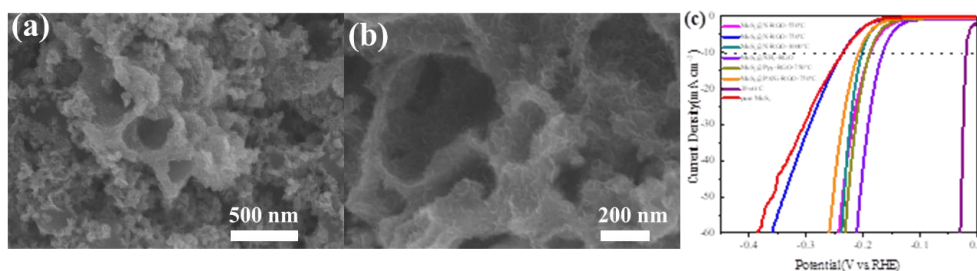


Fig. 1 (a-b) SEM images of MoS₂@NH₂-RGO, (c) HER polarization curves.

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The effect of plasma-assisted phosphating on the hydrogen evolution performance and stability of the ternary NiMoP nanorod array

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For large-scale water electrolysis, it is attractive and challenging to develop high-efficiency non-noble metal electrocatalysts for hydrogen evolution reaction (HER) in alkaline media with high current density.^[1-3] Here, we developed a N₂ plasma-assisted phosphating strategy to prepare the ternary NiMoP nanorod array (P-NiMoP) with more oxygen vacancies. SEM and TEM results show that due to the etching effect caused by the sputtering effect of high-energy particles in the plasma, the particle size formed on the surface of the P-NiMoP catalyst is smaller than that of conventional chemical phosphated NiMoP. XRD and EPR results show that the P-NiMoP catalyst has undergone lattice shrinkage, which is due to the defects formed in the crystal lattice by the bombardment of high energy particles in the plasma, especially the oxygen vacancies. The electrochemical results show that P-NiMoP has high HER performance and excellent stability at high current densities. When driving current densities of 10 and 100 mA cm⁻², only 3 and 98 mV overpotentials are required, respectively, and they exhibit excellent stability in 1M KOH electrolyte. At current densities higher than 100 mA cm⁻², the HER performance surpassed the commercial 40% Pt/C catalyst. The optimized P-NiMoP used as highly active and stable catalyst in the overall water splitting with 1 M KOH electrolyte at room temperature, the required water splitting voltage is only 1.58 V to reach the current density of 50 mA cm⁻², and it can maintain the overall water splitting performance for 60 h without degradation.

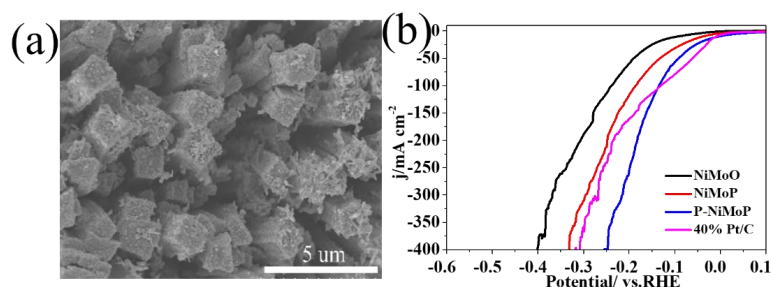


Fig. 1 (a) SEM image, **(b)** HER polarization curves.

Keywords: Plasma; hydrogen evolution reaction; plasma-assisted phosphating; Water splitting

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