Research Highlights in 2019


Abstract: Designing atomically dispersed metal catalysts for oxygen reduction reaction (ORR) is a promising approach to achieve efficient energy conversion. Herein, we develop a template-assisted method to synthesize a series of single metal atoms anchored on porous N,S-codoped carbon (NSC) matrix as highly efficient ORR catalysts to investigate the correlation between the structure and their catalytic performance. The structure analysis indicates that an identical synthesis method results in distinguished structural differences between Fe-centered single-atom catalyst (Fe-SAs/NSC) and Co-centered/Ni-centered single-atom catalysts (Co-SAs/NSC and Ni-SAs/NSC) because of the different trends of each metal ion in forming a complex with the N,S-containing precursor during the initial synthesis process. The Fe-SAs/NSC mainly consists of a well-dispersed FeN₄S₂ center site where S atoms form bonds with the N atoms. The S atoms in Co-SAs/NSC and Ni-SAs/NSC, on the other hand, form metal–S bonds, resulting in CoN₃S₁ and NiN₃S₁ center sites. Density functional theory (DFT) reveals that the FeN₄S₂ center site is more active than the CoN₃S₁ and NiN₃S₁ sites, due to the higher charge density, lower energy barriers of the intermediates, and products involved. The experimental results indicate that all three single-atom catalysts could contribute high ORR electrochemical performances, while Fe-SAs/NSC exhibits the highest of all, which is even better than commercial Pt/C. Furthermore, Fe-SAs/NSC also displays high methanol tolerance as compared to commercial Pt/C and high stability up to 5000 cycles. This work provides insights into the rational design of the definitive structure of single-atom catalysts with tunable electrocatalytic activities for efficient energy conversion.

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**Abstract:** The design of highly efficient non-noble metal electrocatalysts for large-scale hydrogen production remains an ongoing challenge. We report here a Ni$_2$P nanoarray catalyst grown on a commercial Ni foam substrate, which demonstrates an outstanding electrocatalytic activity and stability in basic electrolyte. The high catalytic activity can be attributed to the favourable electron transfer, superior intrinsic activity and the intimate connection between the nanoarrays and their substrate. Moreover, the unique “superaerophobic” surface feature of the Ni$_2$P nanoarrays enables a remarkable capability to withstand internal and external forces and release the in-situ generated H$_2$ bubbles in a timely manner at large current densities (such as > 1000 mA cm$^{-2}$) where the hydrogen evolution becomes vigorous. Our results highlight that an aerophobic structure is essential to catalyze gas evolution for large-scale practical applications.

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Abstract: Sodium-based batteries have attracted considerable attention and are recognized as ideal candidates for large-scale and low-cost energy storage. Sodium (Na) metal anodes are considered as one of the most promising anodes for next-generation, high-energy, Na-based batteries owing to their high theoretical specific capacity (1166 mA h g⁻¹) and low standard electrode potential. Herein, an overview of the recent developments in Na metal anodes for high-energy batteries is provided. The high reactivity and large volume expansion of Na metal anodes during charge and discharge make the electrode/electrolyte interphase unstable, leading to the formation of Na dendrites, short cycle life, and safety issues. Design strategies to enable the efficient use of Na metal anodes are elucidated, including liquid electrolyte engineering, electrode/electrolyte interface optimization, sophisticated electrode construction, and solid electrolyte engineering. Finally, the remaining challenges and future research directions are identified. It is hoped that this progress report will shape a consistent view of this field and provide inspiration for future research to improve Na metal anodes and enable the development of high-energy sodium batteries.

Abstract: 2D genuine unilamellar nanosheets, that are, the elementary building blocks of their layered parent crystals, have gained increasing attention, owing to their unique physical and chemical properties, and 2D features. In parallel with the great efforts to isolate these atomic-thin crystals, a unique strategy to integrate them into 2D vertically stacked heterostructures has enabled many functional applications. In particular, such 2D heterostructures have recently exhibited numerous exciting electrochemical performances for energy storage and conversion, especially the molecular-scale heteroassembled superlattices using diverse 2D unilamellar nanosheets as building blocks. Herein, the research progress in scalable synthesis of 2D superlattices with an emphasis on a facile solution-phase flocculation method is summarized. A particular focus is brought to the advantages of these 2D superlattices in applications of supercapacitors, rechargeable batteries, and water-splitting catalysis. The challenges and perspectives on this promising field are also outlined.


**Abstract:** Potassium metal batteries are considered as attractive alternatives beyond lithium-ion batteries. However, the uncontrollable dendrite growth on the potassium metal anode has restrained their practical applications. Herein, we report a high-performance potassium anode achieved by confining potassium metal into a titanium-deficient nitrogen-containing MXene/carbon nanotube free-standing scaffold. The high electronic transport and fast potassium diffusion in this scaffold enable reduced local current density and homogeneous ionic flux during plating/stripping process. Furthermore, as verified by theoretical calculations and experimental investigations, such “potassium-philic” MXene sheets can induce the nucleation of potassium, and guide potassium to uniformly distribute in the scaffold upon cycling. Consequently, the as-developed potassium metal anodes exhibit a dendrite-free morphology with high Coulombic efficiency and long cycle life during plating/stripping process. Such anodes also deliver significantly improved electrochemical performances in potassium-sulfur batteries compared with bare potassium metal anodes. This work can provide a new avenue for developing potassium metal-based batteries.

Abstract: The synthesis of low-dimensional transition metal nitride (TMN) nanomaterials is developing rapidly, as their fundamental properties, such as high electrical conductivity, lead to many important applications. However, TMN nanostructures synthesized by traditional strategies do not allow for maximum conductivity and accessibility of active sites simultaneously, which is a crucial factor for many applications in plasmonics, energy storage, sensing, and so on. Unique interconnected two-dimensional (2D) arrays of few-nanometer TMN nanocrystals not only having electronic conductivity in-plane, but also allowing transport of ions and electrolyte through the porous nanosheets, which are obtained by topochemical synthesis on the surface of a salt template, are reported. As a demonstration of their application in a lithium–sulfur battery, it is shown that 2D arrays of several nitrides can achieve a high initial capacity of >1000 mAh g\(^{-1}\) at 0.2 C and only about 13% degradation over 1000 cycles at 1 C under a high areal sulfur loading (>5 mg cm\(^{-2}\)).

Abstract: Polymer electrolytes have attracted great interest for next-generation lithium (Li)-based batteries in terms of high energy density and safety. In this review, we summarize the ion-transport mechanisms, fundamental properties, and preparation techniques of various classes of polymer electrolytes, such as solvent-free polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and composite polymer electrolytes (CPEs). We also introduce the recent advances of non-aqueous Li-based battery systems, in which their performances can be intrinsically enhanced by polymer electrolytes. Those include high-voltage Li-ion batteries, flexible Li-ion batteries, Li-metal batteries, lithium-sulfur (Li-S) batteries, lithium-oxygen (Li-O$_2$) batteries, and smart Li-ion batteries. Especially, the advantages of polymer electrolytes beyond safety improvement are highlighted. Finally, the remaining challenges and future perspectives are outlined to provide strategies to develop novel polymer electrolytes for high-performance Li-based batteries.

Abstract: It is essential to develop a facile and effective method to enhance the electrochemical performance of lithium metal anodes for building high-energy-density Li-metal based batteries. Herein, we explored the temperature-dependent Li nucleation and growth behaviour and constructed a dendrite-free Li metal anode by elevating temperature from room temperature (20 °C) to 60 °C. A series of ex situ and in situ microscopy investigations demonstrate that increasing Li deposition temperature results in large nuclei size, low nucleation density, and compact growth of Li metal. We reveal that the enhanced lithiophilicity and the increased Li-ion diffusion coefficient in aprotic electrolytes at high temperature are essential factors contributing to the dendrite-free Li growth behaviour. As anodes in both half cells and full cells, the compact deposited Li with minimized specific surface area delivered high Coulombic efficiencies and long cycling stability at 60 °C.


Abstract: The low Coulombic efficiency and serious safety issues resulting from uncontrollable dendrite growth have severely impeded the practical applications of lithium (Li) metal anodes. Herein we report a stable quasi-solid-state Li metal battery by employing a hierarchical multifunctional polymer electrolyte (HMPE). This hybrid electrolyte was fabricated via in situ copolymerizing lithium 1-[3-(methacryloyloxy)propylsulfonyle]-1-(trifluoromethanesulfonylimide (LiMTFSI) and pentaerythritol tetraacrylate (PETEA) monomers in traditional liquid electrolyte, which is absorbed in a poly(3,3-dimethylacrylic acid lithium) (PDAALi)-coated glass fiber membrane. The well-designed HMPE simultaneously exhibits high ionic conductivity ($2.24 \times 10^{-3}$ S cm$^{-1}$ at 25°C), near-single ion conducting behavior (Li ion transference number of 0.75), good mechanical strength and remarkable suppression for Li dendrite growth. More intriguingly, the cation permselective HMPE efficiently prevents the migration of negatively charged iodine (I) species, which provides the as-developed Li-I batteries with high capacity and long cycling stability.


**Abstract:** Molecular-scale modulation of interfaces between different unilamellar nanosheets in superlattices is promising for efficient catalytic activities. Here, three kinds of superlattices from alternate restacking of any two of the three unilamellar nanosheets of MoS$_2$, NiFe-layered double hydroxide (NiFe-LDH), and graphene are systematically investigated for electrocatalytic water splitting. The MoS$_2$/NiFe-LDH superlattice exhibits a low overpotential of 210 and 110 mV at 10 mA cm$^{-2}$ for oxygen evolution reaction (OER) and alkaline hydrogen evolution reaction (HER), respectively, superior than MoS$_2$/graphene and NiFe-LDH/graphene superlattices. High activity and stability toward the overall water splitting are also demonstrated on the MoS$_2$/NiFe-LDH superlattice bifunctional electrocatalyst, outperforming the commercial Pt/C-RuO$_2$ couple. This outstanding performance can be attributed to optimal adsorption energies of both HER and OER intermediates on the MoS$_2$/NiFe-LDH superlattice, which originates from a strong electronic coupling effect at the heterointerfaces. These results herald the interface modulation of superlattices providing a promising approach for designing advanced electrocatalysts.

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Abstract: Lithium-sulfur (Li-S) batteries have been regarded as one of the most promising candidates for next-generation energy storage owing to their high energy density and low cost. However, the practical deployment of Li-S batteries has been largely impeded by the low conductivity of sulfur, the shuttle effect of polysulfides, and the low areal sulfur loading. Herein, we report the synthesis of uniform Co-Fe mixed metal phosphide (Co-Fe-P) nanocubes with highly interconnected-pore architecture to overcome the main bottlenecks of Li-S batteries. With the highly interconnected-pore architecture, inherently metallic conductivity, and polar characteristic, the Co-Fe-P nanocubes not only offer sufficient electrical contact to the insulating sulfur for high sulfur utilization and fast redox reaction kinetics but also provide abundant adsorption sites for trapping and catalyzing the conversion of lithium polysulfides to suppress the shuttle effect, which is verified by both the comprehensive experiments and density functional theory calculations. As a result, the sulfur-loaded Co-Fe-P (S@Co-Fe-P) nanocubes delivered a high discharge capacity of 1243 mAh g\(^{-1}\) at 0.1 C and excellent cycling stability for 500 cycles with an average capacity decay rate of only 0.043% per cycle at 1C. Furthermore, the S@Co-Fe-P electrode showed a high areal capacity of 4.6 mAh cm\(^{-2}\) with superior stability when the sulfur loading was increased to 5.5 mg cm\(^{-2}\). More impressively, the prototype soft-package Li-S batteries based on S@Co-Fe-P cathodes also exhibited superior cycling stability with great flexibility, demonstrating their great potential for practical applications.

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Abstract: Sodium–sulfur batteries using abundant elements offer an attractive alternative to currently used batteries, but they need better sulfur host materials to compete with lithium-ion batteries in capacity and cyclability. We report an in situ sulfur-doping strategy to functionalize MXene nanosheets by introducing heteroatomic sulfur into the MXene structure from the MAX phase precursor. By employing the vacuum freeze-drying method, a three-dimensional (3D) wrinkled MXene nanoarchitecture with the high specific surface area was prepared. The tailor-made wrinkled sulfur-doped MXene (S–Ti$_3$C$_2$Tx) nanosheets were applied as an electrode host material in room temperature sodium–sulfur batteries. The S–Ti$_3$C$_2$Tx matrix shows high polarity with sodium polysulfides, restricting the diffusion of sodium polysulfides. The MXene/sulfur electrode can achieve high areal sulfur loading up to 4.5 mg cm$^{-2}$ as well as good electrochemical performance (reversible capacity of 577 mAh g$^{-1}$ at 2 C after 500 cycles).

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Abstract: Potassium-ion batteries (KIBs) have attracted increasing attention for grid-scale energy storage due to the abundance of potassium resources, low cost, and competitive energy density. The key challenge for KIBs is to develop high-performance electrode materials. However, the exploration of high-capacity and ultrastable electrodes for KIBs remains challenging because of the sluggish diffusion kinetics of K⁺ ions during the charging/discharging processes. This study reports for the first time a facile ion-intercalation-mediated exfoliation method with Mg²⁺ cations and NO₃⁻ anions as ion assistants for the fabrication of expanded few-layered ternary Ta₂NiSe₅ (EF-TNS) flakes with interlayer spacing up to 1.1 nm and abundant Se sites (NiSe₄ tetrahedra/TaSe₆ octahedra clusters) for superior potassium-ion storage. The EF-TNS deliver a high capacity of 315 mAh g⁻¹, excellent rate capability (121 mAh g⁻¹ at a current density of 1000 mA g⁻¹), and ultrastable cycling performance (81.4% capacity retention after 1100 cycles). Detailed theoretical analysis via first-principles calculations and experimental results elucidate that K⁺ ions intercalate through the expanded interlayers effectively and prefer to transport along zigzag pathways in layered Ta₂NiSe₅. This work provides a new avenue for designing novel ternary intercalation/pseudocapacitance-type KIBs with high capacity, excellent rate capability, and superior long-term cycling performance.

Abstract: It is desirable to design nonprecious metal nanocatalysts with high stability and catalytic performance for fine chemicals production. Here, a method is reported for the preparation of cobalt metal and cobalt oxide cores confined within nanoporous nitrogen-doped hollow carbon capsules. Core–shell structured Zn/Co-ZIF@polymer materials are fabricated through a facile coating polymer strategy on the surface of zeolitic imidazolate frameworks (ZIF). A series of hollow carbon capsules with cobalt metal and cobalt oxide are derived from a facile confined pyrolysis of Zn/Co-ZIF@polymer. The hollow Co-CoO$_x$@N-C capsules can prevent sintering and agglomeration of the cobalt nanoparticles and the nanoporous shell allows for efficient mass transport. The specific surface area and Co particle size are optimized through finely tuning the original Zn content in ZIF particles, thus enhancing overall catalytic activity. The yolk–shell structured Zn$_4$Co$_1$O$_x$@carbon hollow capsules are shown to be a highly active and selective catalyst (selectivity $>$99%) for hydrogenation of nitrobenzene to aniline. Furthermore, Zn$_4$Co$_1$O$_x$@carbon hollow particles show superior catalytic stability, and no deactivation after 8 cycles of reaction. The hollow Co-CoO$_x$@N-C capsules may shed light on a green and sustainable catalytic process for fine chemicals production.


Abstract: The commercialization of high-energy-density and low-cost lithium-sulphur batteries has been severely impeded by capacity fading and electrochemical polarization. Here we report a strategy to entrap polysulphides and boost the cathodic redox kinetics by embedding the surface oxidized quantum-dot-size TiN (TiN-O) within the highly ordered mesoporous carbon matrix. While the carbon scaffold offers sufficient electrical contact to the insulate sulphur, benefiting the full usage of sulphur and physical confinement of polysulphides. The surface oxygen renders TiN-O with a stronger charge polarization effect for polysulphides via S-O-Ti bond as verified experimentally and theoretically. The suppressed shuttle effect and high lithium ion diffusion coefficient (7.9×10⁻⁸ cm² s⁻¹) lead to a high capacity of 1264 mA h g⁻¹ at 0.2 C with a negligible capacity fading rate of 0.06% per cycle. Remarkably, TiN-O based prototype soft-package cells also exhibit excellent cycling stability with great flexibility, demonstrating their potential for practical applications.

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Abstract: Benefiting from the natural abundance and low standard redox potential of potassium, potassium-ion batteries (PIBs) are regarded as one of the most promising alternatives to lithium-ion batteries for low-cost energy storage. However, most PIB electrode materials suffer from sluggish thermodynamic kinetics and dramatic volume expansion during K⁺ (de)intercalation. Herein, it is reported on carbon-coated K₂Ti₂O₅ microspheres (S-KTO@C) synthesized through a facile spray drying method. Taking advantage of both the porous microstructure and carbon coating, S-KTO@C shows excellent rate capability and cycling stability as an anode material for PIBs. Furthermore, the intimate integration of carbon coating through chemical vapor deposition technology significantly enhances the K⁺ intercalation pseudocapacitive behavior. As a proof of concept, a potassium-ion hybrid capacitor is constructed with the S-KTO@C (battery-type anode material) and the activated carbon (capacitor-type cathode material). The assembled device shows a high energy density, high power density, and excellent capacity retention. This work can pave the way for the development of high-performance potassium-based energy storage devices.
Abstract: Sodium-selenium (Na-Se) battery has been emerging as a new rechargeable energy storage system with high capacity, low cost and high rate capability. However, the shuttling of polyselenides from the cathode to the anode causes dramatic capacity decay, severely impeding their practical applications. Herein, we report a combinational strategy of nitrogen and sulphur dual-doped hierarchical porous carbon with interconnected conductive polyaniline (PANI) coating to incorporate Se as stable cathodes (i-PANI@NSHPC/Se) for Na-Se batteries. Ex situ characterizations and density functional theory (DFT) calculations demonstrate that the i-PANI@NSHPC/Se cathode can provide both physical diffusion barrier and strong chemical affinity for polyselenides. In addition, the interconnected conductive polyaniline network enhances the conductivity for electrons and ions. With this strategy, the i-PANI@NSHPC/Se cathode delivered a high reversible capacity of 617 mAh g⁻¹ after 200 cycles at 0.2 C with a low capacity decay rate of 0.013% per cycle and an excellent rate capability at 20 C. Importantly, stable cycling performances were achieved with high capacities at different Se areal mass loadings (1.2, 2.3, 3.5 mg cm⁻²). This work could provide an efficient approach for developing Na-Se batteries with high active material mass loading, high rate capacity and long cycle life.

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Preview

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