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## Editorial

## Application of metal sulfides in energy conversion and storage



Sulfides refer to a category of compounds formed by strong electro-positivity metal or non-metal combine with sulfur. Owing to its tunable stoichiometric composition, unique crystal structure, abundant redox centers, the synergy between transition metal ions, and strong corrosion resistance in alkaline environments [1–4], metal sulfides receive increasing attention in different fields such as batteries, capacitors, adsorption, catalysis/photocatalysis, electrochemistry and medicine. Compared with conventional materials, metal sulfides are a class of nanomaterials with high specific capacity. Various metal sulfides and their nanoscale composites exhibit significant enhancements in electrical conductivity, surface morphology, long-term durability and often metallic luster, and metal sulfides also exhibit unique physical and chemical sensitivity properties that can be effectively used in applications of energy storage and conversion applications [2,5–7].

Metal sulfides are widely utilized as battery electrode and capacitor materials. The reasons are: (i) Compared with metal oxides, metal sulfides have unique chemical and physical properties (e.g., mechanical and thermal stability), and they have an abundance of redox chemistry that contributes to higher specific capacity/capacitance. (ii) Many metal sulfides exhibit higher electron conductivity than their oxide counterparts. Because the electronegativity of sulfur is lower than that of oxygen, which prevents interlayer elongation leading to structural disintegration and allows for easy electron transport in the electrode [7]. (iii) Nanostructured metal sulfides with high surface area can provide abundant accessible reaction sites for charge storage, facilitate electron/ion transport, enhance electrolyte diffusion, and can mitigate the effects of structural deformation on embedding/de-embedding [2].

When metal sulfides are applied in battery materials, they are commonly loaded on a certain structure (such as nitrogen-doped porous carbon, carbon nanotubes/spheres, graphene), which is conducive to improving the electrochemical performance of the metal sulfide. Yang *et al.* used nitrogen-doped porous carbon as the substrate to load  $\text{Ni}_3\text{S}_2$  nanocrystals ( $\text{Ni}_3\text{S}_2@\text{NPC}$ ).  $\text{Ni}_3\text{S}_2$  nanocrystals can shorten the migration of  $\text{Na}^+$  and increase the electrochemical reaction kinetics. N-doped atoms can boost the conductivity of the carbon layer, providing defect vacancies for the transport and storage of  $\text{Na}^+$ , thereby improving the electrochemical performance [8]. Yang *et al.* designed a yolk-shell Ni-Fe sulfide@carbon as an anode for  $\text{K}^+/\text{Na}^+$  batteries by two steps (the infiltration method and sulfidation process). NFS@C yolk shell nanospheres as anode materials for KIBs and SIBs exhibit high reversible capacity, stable cycle life and excellent rate performance [9]. Wang *et al.* referred to a unique chain mail  $\text{Sb}_2\text{S}_3@\text{MoS}_2$  heterostructure as the

anode material of SIBs presenting excellent electrochemical performance. The sulfation step can enhance the mechanical strength of the electrode to adapt to the volume expansion of the battery, thus improving its stability [10]. Zhang *et al.* demonstrated that CoS embedded in carbon nanofibers were successfully prepared by an electrospinning technique combined with a solvothermal method, which can promote electron transfer and improve mechanical stability in batteries. In particular, the embedding of sulfide improves the electrical conductivity of the composite and reduces the volume expansion caused by charging and discharging [11]. Wan *et al.* reported a binary metal sulfide  $\text{CoS}@\text{SnS}$  heterostructure confined in carbon microspheres ( $(\text{CoSn})\text{S}/\text{C}$ ) for sodium ion battery anode materials.  $(\text{CoSn})\text{S}/\text{C}$  with micro/nanostructure can shorten the ion diffusion length, improve the mechanical strength of the electrode and can increase the intrinsic conductivity, which facilitates the rapid transfer of  $\text{Na}^+$  [12]. There are other structures that can also be used as carriers for metal sulfides.

When capacitor material is selected, metal sulfide materials have attracted significant attention due to their excellent electrical conductivity and superior electrochemical activity. Yu *et al.* prepared flower-like  $\text{Cu}_5\text{Sn}_2\text{S}_7/\text{ZnS}$  with excellent electrochemical properties by hydrothermal method, which provides a simple method for the preparation of capacitor materials. The substrate material can improve the conductivity of the electrode, and its three-dimensional structure can further expand the specific surface area of the electrode material and shorten the transmission distance of electrolyte ions [13]. Wang *et al.* designed P-doped CoS with S-defect two-dimensional nanosheets, which exhibits high energy density and excellent bending performance, providing new ideas for the design of the next generation of capacitors [14]. Therefore, the substrate loaded metal sulfide is often selected as the capacitor material. There are normally two types of substrate materials, one is the powder substrate, and the other is the film-structured substrate. Han *et al.* synthesized the vertically crosslinking  $\text{MoS}_2$ /three-dimensional graphene by hydrothermal method. Metal sulfides have the higher specific capacity and ionic conductivity than oxides, and the vertical  $\text{MoS}_2$  nanosheets increase the contact area with the electrolyte and the number of unsaturated bonds which improve the electron and ion transmission efficiency thus has excellent chemical properties [15]. Wu *et al.* prepared Ni-Co sulfide hollow nanoboxes for capacitor electrode, which has ultra-high specific capacity, superlative capacitance retention rate and cycle stability [16]. Metal sulfides are ordinarily grown on the film structure by hydrothermal or deposition methods. Liang *et al.* grew needle-like  $\text{NiCo}_2\text{S}_4$  nanowire on the surface of carbon cloth

by a simple two-step hydrothermal method. NiCo<sub>2</sub>S<sub>4</sub> nanowire provide fast ion/electron diffusion paths, abundant active sites and can increase the contact area, which improve the reversible capacitance and excellent electrochemical performance of the capacitor [17].

However, metal sulfides still have shortcomings as battery and capacitor materials. During application, metal sulfides usually suffer from high irreversible capacity during charge/discharge cycles (low coulombic efficiency), poor multiplicative capability, low round-trip energy efficiency, and severe capacity decay during cycling (caused by sulfide expansion) [5,7].

Up to now, metal sulfides have high active in catalytic reactions due to their high valence, suitable electronic band gap, exposed active sites, synergistic interactions between metal ions and special electronic properties [18,19]. In addition, metal sulfide materials have a range of potential new properties because of their various shapes, sizes, crystalline forms, chemical compositions and excellent photonic response [20]. Catalysts usually include electrocatalysts, photocatalysts and advanced oxidation technology catalysts, *etc.* He *et al.* investigated that the Co<sub>1-x</sub>S@C materials synthesized with ZIF-67 as a template have low overpotential, small Tafel slope and can be used as efficient OER electrocatalyst materials [21]. Photocatalysts are commonly utilized to catalyze the decomposition of water to produce hydrogen or to degrade organic pollutants. Pan *et al.* synthesized a Ga-doped La<sub>5</sub>Ti<sub>2</sub>Cu<sub>0.9</sub>Ag<sub>0.1</sub>O<sub>7</sub>S<sub>5</sub> catalyst *via* reverse homogeneous precipitation and thermal sulfidation methods that can efficiently catalyze water decomposition to produce hydrogen [22]. Constructing heterojunction is an attractive way to improve separation efficiency and degrade organic pollutants. For example, CFs/TiO<sub>2</sub>/CdS heterojunctions also constructed for photocatalytic various pollutants from wastewater degradation [23]. In advanced oxidation, metal sulfides are utilized as Fenton-like and persulfate catalysts attributed to their excellent physicochemical properties. Persulfate includes peroxymonosulfate (PMS) and peroxydisulfate (PDS). Wang *et al.* prepared NiCo<sub>2</sub>S<sub>4</sub>/CS membrane as the precursor to active PDS for the removal of nimesulide in the wastewater. This is a promising catalyst because the sulfidation enhances the electron transfer between cobalt and nickel and improves the performance of the catalyst and prolongs the service life of the catalyst [24]. In addition, Yao *et al.* successfully synthesized CoS/CoS<sub>2</sub>/rGO as a low cost and high-performance fuel cell catalyst by one-pot hydrothermal method [25]. Liu *et al.* constructed a catalyst with Au/Ni<sub>3</sub>S<sub>2</sub>/NF nanosheet arrays, which exhibited excellent bifunctional activity and stability for HER and OER [26]. However, the quality and efficiency of laboratory metal sulfide production is not sufficient for commercial application of the system [20].

In addition to the applications mentioned above, metal sulfides are also used in adsorbents, photothermal agents, optical elements, microwave absorption, autotrophic denitrification and reductive dehalogenation. For example, MoS<sub>2</sub> nanosheets in polystyrene cation exchanger by hydrothermal method for adsorption and removal of lead ions. Hou *et al.* successfully prepared CoS nanospheres loaded with tumor therapeutic drugs by base-triggered polymerization, electrostatic interactions and Michael addition reactions. The results revealed a powerful chemotherapy-enhancing effect under near-infrared (NIR) light irradiation on the tumor surface without significant systemic toxicity [27]. MnS<sub>2</sub> has

a wide band gap, making it a short wavelength optoelectronic device. Meanwhile metal sulfides can also be used as light emitting diodes (LED) due to their high photosensitivity. Metal sulfides (such as MoS<sub>2</sub>, ZnS and Co<sub>x</sub>S<sub>1-x</sub>) have attracted great attention in microwave absorption materials attribute to their moderate dielectric constant, thin matching thickness, high dielectric loss and good chemical stability. Iron sulfide autotrophic denitrification (ISAD) can be used for nitrate pollution control and sustainable wastewater treatment. Iron sulfide also has a strong reduction capacity for dechlorination from chlorinated hydrocarbons present in soil and water.

Metal sulfides exhibit promising application prospects in environmental applications. Nevertheless, metal sulfide materials that can substantially improve electrochemical performance still require further exploration. In the future, metal sulfide catalysts with high catalytic activity should be considered, and the activity of metal sulfide electrocatalysts and photocatalysts can be improved by catalytic modification with single atoms to achieve excellent activity, charge capture, surface reaction, and surface reaction properties. Single atom can be loaded on the monolayer of metal sulfides as well as on the internal or external regions of metal sulfide nanoboxes, hollow shells and nanospheres. Scaling up production will further develop the industrial applications of metal sulfides as catalysts. In order to realize the future prospect of wide industrial applications, a simple, reliable, cheap, and less wasteful synthetic method is needed to realize large-scale production of metal sulfides. In addition, a trend toward the use of earth-abundant and non-toxic raw materials and green manufacturing processes must be established to ensure the continued development of energy storage and conversion without compromising cost effectiveness and environmental concerns. This editorial provides peers with new progress in the application of metal sulfides in the environment, and we hope it can bring some enlightenment to our world readers.

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