Super-aligned films of sub-1 nm Bi₂O₃-polyoxometalate nanowires as interlayers in lithium-sulfur batteries

Simin Zhang^{1†}, Haodong Shi^{2,3,4†}, Junwang Tang⁵, Wenxiong Shi^{6*}, Zhong-Shuai Wu^{2,3,4*} and Xun Wang^{1*}

ABSTRACT Sub-1 nm nanowires (SNWs) can not only be processed like polymers due to their polymer-analogue properties but also show multifunctions owing to their well-manipulated compositions and structures. Rationally designed and engineered multicomponent heterostructure SNWs can further enhance their multifunction performance while it is very challenging to achieve such SNWs at sub-nanoscale. Herein, we synthesized Bi₂O₃-polyoxometalate heterostructure SNWs (PMB SNWs), and fabricated super-aligned PMB SNWs films (S-PMB SNWs films), which can serve as interlayers to efficiently suppress lithium polysulfide (LPS) shuttling, intrinsically promote the redox kinetics of the LPS conversion and substantially protect the Li anode. The lithium-sulfur (Li-S) battery with the S-PMB SNWs film as the interlayer showcases an ultralow capacity decay rate with 0.013% per cycle over 850 cycles. This study demonstrates the potential of heterostructure SNWs to improve the performance of Li-S batteries.

Keywords: sub-1 nm nanowires, polymer-resembling films, lithium-ion batteries, interlayer

INTRODUCTION

Recently, lithium-sulfur (Li-S) batteries have gained much attention because they stand as the most attractive power supply devices owing to the ultrahigh theoretical capacity (1672 mA h g⁻¹) and energy density (2600 W h kg⁻¹), far more than that of lithium-ion bat-

teries (normally <400 W h kg⁻¹), but the shuttling effect of lithium polysulfides (LPSs), sluggish kinetics of LPS conversion and formation of Li dendrite lead to the poor stability, hindering their applications [1–4]. Although polymer films are being widely used as cell components at present, such as the Celgard separator in lithium-ion batteries, proton exchange membrane in proton exchange membrane fuel cells [5], the weak interactions between polymers and LPSs and poor electrocatalysis performance of polymers cannot meet the needs of Li-S batteries.

It is found that sub-1 nm nanowires (SNWs) not only show polymer- or biomolecule-analogue properties, but also show great potential in catalysis, photothermal conversion, and optics with well-manipulated compositions and structures [6–10]. Moreover, because the SNWs show polymer-analogue properties, they can be easily processed through some processing methods of polymers, such as electrospinning and wet-spinning [9,11]. Further incorporating multiple effective components to fabricate heterostructure SNWs is a potential way to improve the performance of SNWs and the basis for functional SNWs devices. However, until now, most of the synthesized SNWs were one-component because it is still a great challenge to achieve multicomponent SNWs at sub-nanoscale. Recently, it is founded that the polyoxometalate (POM) nanoclusters can interact with nuclei and pre-assemble into building units at the nucleation stage and further assemble into sub-1 nm architectures [12]. In

¹ Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China

² State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

³ Dalian National Laboratory for Clean Energy (DNL), Chinese Academy of Sciences (CAS), Dalian 116023, China

⁴ University of Chinese Academy of Sciences, Beijing 100049, China

⁵ Department of Chemical Engineering, University College London (UCL), WC1E 7JE London, United Kingdom

⁶ Institute for New Energy Materials and Low Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300387, China

[†] These authors contributed equally to this work.

* Corresponding authors (emails: wxshi2018@hotmail.com (Shi W); wuzs@dicp.ac.cn (Wu ZS); wangxun@mail.tsinghua.edu.cn (Wang X))

light of this, incorporating multiple effective components in SNWs mediated by POM to synergize immobilization and electrocatalysis of LPSs synchronously may greatly improve the performance of Li-S batteries.

In this study, highly uniform Bi_2O_3 -POM heterostructure SNWs (PMB SNWs) were synthesized, which were composed of Bi_2O_3 and POM nanoclusters. The PMB SNWs showed strong absorbance and catalysis for LPSs in experiments. Then we fabricated polymer-resembling films with super-aligned PMB SNWs (S-PMB SNWs) through the wet-spinning method. The S-PMB SNWs films were highly flexible, which were subsequently used in Li-S batteries as interlayers, greatly improving the performance. The Li-S batteries with the S-PMB SNWs film as an interlayer delivered an initial specific capacity of 877 mA h g^{-1} and reserved 782 mA h g^{-1} after 850 cycles at 2 C, with only 0.013% capacity fading per cycle. Even at 5 C, the Li-S batteries with the separator of S-PMB SNWs film could cycle for 1000 times and decay at a low rate of 0.045% per cycle. It is demonstrated the S-PMB SNWs film can suppress LPS shuttling, promote the kinetics of the LPS conversion and protect the Li anode effectively, benefiting from its typical structures and combination of effective compositions. Taking advantage of the composition controllability and similarity to the polymers, this kind of heterostructure SNWs have broad application prospects.

RESULTS AND DISCUSSION

The morphologies of the PMB SNWs films were investigated through transmission electron microscopy (TEM) and atomic-resolution aberration-corrected TEM (AC TEM). As shown in Fig. 1a, the synthesized PMB SNWs were highly pure and several micrometers in length. And the PMB SNWs shown in Fig. S1 were highly winding, suggesting they were flexible. As shown in the inset of Fig. 1a, the PMB SNWs in a bundle were nearly parallel to each other. AC high-angle annular-dark field scanning TEM (AC HAADF STEM) image (Fig. 1b) revealed that a single SNW was comprised of some aligned clusters with hardly any lattice fringe. Moreover, energy dispersive X-ray spectroscopy (EDS) elemental mapping demonstrated that Bi, Mo and P were well dispersed in the PMB SNWs (Fig. 1c). The accurate proportions of Bi, Mo and P were determined by the elemental analysis (Table S1). As demonstrated by the atomic force microscopy (AFM) test (Fig. 1d, e), the diameter of the PMB SNWs was $\sim 1 \text{ nm}$, so they displayed an aspect ratio of several thousands. The structure was further investigated through the X-ray diffraction (XRD) pattern, solid-state

nuclear magnetic resonance (SSNMR), Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). As shown in Fig. S2a, the peaks in the XRD pattern were wide and could be roughly matched with the standard PDF card of Bi_2O_3 (card No. 27-0052), demonstrating there was Bi_2O_3 in the PMB SNWs. As shown in the FTIR spectrum of POM (Fig. S2b), the peak at 1064 and 964 cm^{-1} belonged to $\nu(\text{P}=\text{O})$ and $\nu(\text{Mo}=\text{O})$ respectively, and the peaks at 870 and 750 cm^{-1} belonged to $\nu(\text{Mo}-\text{O}-\text{Mo})$ [13]. These characteristic peaks also appeared in the FTIR spectrum of the PMB SNWs, indicating that POM existed in the PMB SNWs. By comparing ^{31}P SSNMR spectra of the PMB SNWs and POM (Fig. S2c), we found that there were two peaks and both had shifts compared with the ^{31}P peak in POM, suggesting there was local environment change of the P atom. As shown in Fig. S2d, the Mo 3d peaks in the spectrum of the PMB SNWs shifted to lower binding energies compared with POM, indicating the coexistence of Mo^{5+} and Mo^{6+} and demonstrating that some Mo^{6+} in POM were reduced in the reaction. And thus, we could know that the change of ^{31}P peak resulted from the existence of Mo^{5+} and Mo^{6+} and the influence of oleyamine and Bi_2O_3 in PMB SNWs. From the above, the PMB SNW could be clearly defined as a heterostructure comprised of modified POM nanoclusters and Bi_2O_3 . The formation mechanism of PMB SNWs was also investigated, and is shown in Figs S3 and S4. Molecular dynamics (MD) simulations were carried out to investigate the interactions between POM nanoclusters and Bi_2O_3 monomers and the structure stability of the PMB SNWs. As displayed in Fig. 1f, Bi_2O_3 was put around POM, and after the simulation was run, the Bi_2O_3 stayed in the vicinity of POM due to the van der Waals forces and Coulombic forces [12,14]. Subsequently, six of the PMB nanoclusters obtained previously pre-assembled into simply linear aggregates and 18 protonated oleyamine were added to keep the system electroneutral (Fig. 1g). After running MD, the density distribution of the PMB SNWs along the Z-axis illustrated the stable formation of $\sim 1 \text{ nm}$ diameter moiety (Fig. 1h). The density distribution of POM, Bi_2O_3 , and oleyamine along the X-axis illustrated that Bi_2O_3 arranged around POM and oleyamine attached to the SNWs uniformly (Fig. 1i). The main interactions between Bi_2O_3 and POM are van der Waals interactions and Coulombic interactions. The current synthesis strategy was also available for some other SNWs, such as Fe_3O_4 -POM and Y_2O_3 -POM SNWs.

As investigated before, the PMB SNWs were similar to polymer chains in dimension and they would intertwine

Figure 1 Characterization of the PMB SNWs. (a) A TEM image of the PMB SNWs at a low magnification. The inset shows a TEM image at a high magnification. (b) AC HAADF-STEM image of a PMB SNW. (c) HAADF-STEM image and the corresponding EDS elemental mapping images of the PMB SNWs. (d) Typical AFM topographic image of an isolated PMB SNW on a freshly cleaved highly oriented pyrolytic graphite substrate. Inset: line profile along the dashed line. (e) 3D AFM image of the corresponding PMB SNW. The MD simulation of the formation of (f) PMB nanoclusters and (g) PMB SNWs with oleyamine. The density distributions of POM clusters, Bi_2O_3 and oleyamine in a PMB SNW (h) along the Z-axis and (i) X-axis. The blue model represents the POM; the red-green model represents the Bi_2O_3 molecule; the blue chain model represents the oleyamine molecule.

with each other in the dispersion. As shown in Fig. S5, the dispersion of PMB SNWs could transform to a gel after standing for a while, and the flowing dispersion of PMB SNWs became viscous and could be drawn into silk by a glass bar. Fig. 2a and Supplementary Movie 1 show the fabrication process of the PMB SNWs film. Successive PMB SNWs films could be obtained by injecting the PMB SNWs dispersion (30 wt% dispersed in octane) into a

mixed solution of absolute ethanol and octane (1:1, v/v). The mechanical property of the PMB SNWs film is shown in Fig. S6. The structure of the PMB SNWs film was further examined through the scanning electron microscopy (SEM), showing a thickness of $\sim 100 \mu\text{m}$ (Fig. S7), and the PMB SNWs were oriented axially in the film. We also tried to control the thickness of membranes through regulating the viscosity and flow velocity, and the results

Figure 2 The free-standing PMB SNWs film. (a) The fabrication process of PMB SNWs films. The PMB SNWs film could be loaded on glass, twisted on a glass rod and folded into different shapes. The SAXS 2D patterns of the (b) S-PMB SNWs film and (c) D-PMB SNWs film. The insets of (b, c) are photos of the S-PMB SNWs film and D-PMB SNWs film, respectively.

are shown in Fig. S8. In addition, we also fabricated the PMB SNWs film through the evaporation method, which was relatively disordered rather than super-aligned (Fig. S9). The structure of the PMB SNWs films was further investigated by synchrotron radiation small-angle X-ray scattering (SAXS). As shown in Fig. 2b, c, the SAXS two-dimensional (2D) pattern of the PMB SNWs film prepared through wet-spinning was obviously anisotropic, demonstrating its super-aligned structure, while the SAXS 2D pattern of the PMB SNWs film prepared through evaporation was isotropic, indicative of no preferred orientation of SNWs. It is worth noting that the S-PMB SNWs film was highly flexible. As shown in Fig. 2a, the films could be folded in half, wrapped on the glass rod and folded into different shapes without any crack. All of these demonstrated the excellent flexibility of the S-PMB SNWs film, which might be attributed to the high aspect ratio and ultrathin diameter of the PMB SNWs essentially. The free-standing and flexible features of the S-PMB SNWs films would be significant in practical applications.

Subsequently, the synchronous immobilization and electrocatalysis of LPSs by the S-PMB SNWs films were investigated. The adsorption of LPS species was the precondition for the redox conversion on the S-PMB SNWs film. As shown in Fig. 3a, after adsorbing LPSs, the ratio of Mo^{5+} in PMB SNWs increased. The POM could be seen as Lewis acid and can accept electrons from Lewis base. And LPSs can be seen as Lewis bases. After LPSs were adsorbed on the PMB SNWs film, electrons transferred from LPSs to Mo^{6+} in the POM, so the ratio of Mo^{5+} increased, demonstrating the interactions between

Mo and LPSs. As shown in Fig. 3b, Bi existed in the PMB SNWs with a valence of +3, and the peak shifted to lower binding energy after adsorbing LPSs, suggesting the interactions between Bi and LPSs. The adsorption of the LPSs on PMB SNWs was intuitively observed by adding some PMB SNWs into Li_2S_4 /tetraglyme solution (Fig. 3c). And the absorption peak of Li_2S_4 in ultraviolet-visible (UV-vis) spectra disappeared, demonstrating there were rich anchoring sites of LPS species on PMB SNWs. The results of Li_2S_4 permeation experiments could also demonstrate that LPSs were adsorbed by the PMB SNWs film effectively (Fig. S10). The “sulfiphilicity” of the PMB SNWs was the important first step for electrocatalysis of LPSs’ redox conversion. The electrocatalytic performance of the S-PMB SNWs film was evaluated through cyclic voltammetry (CV) profiles of the Li-S batteries, CV profiles obtained at a scan rate of 100 mV s^{-1} of symmetric batteries and the potentiostatic discharge/charge curves of Li_2S_8 /tetraglyme solution measured at 2.05 V with an S-PMB SNWs film or a polypropylene (PP) film. As shown in Fig. 3d, the cathodic peaks at 2.29–2.51 and 1.71–2.01 V were attributed to the reduction of S_8 to Li_2S_x ($4 \leq x \leq 8$) and further reduction to Li_2S_2 and Li_2S while the anodic peak at 2.39–2.80 V was attributed to the oxidation of Li_2S_x to S_8 [4]. Compared with the Li-S battery with only a PP film, the cathodic and anodic peaks of the Li-S battery with the S-PMB SNWs film shifted to higher and lower potential respectively, suggesting enhanced kinetics of LPS conversion [15]. As shown in Fig. 3e, the symmetric battery with the S-PMB SNWs film exhibited higher polarization current than the battery with only a PP film, suggesting enhanced interfacial ki-

Figure 3 The S-PMB SNWs films for LPS adsorption and conversion. (a) Mo 3d spectrum and (b) Bi 4f spectrum of the PMB SNWs before and after charge-discharge. (c) The UV-vis spectra of Li₂S₄/tetraglyme solution before and after addition of PMB SNWs. The inset is the photograph of Li₂S₄/tetraglyme solutions before and after addition of PMB SNWs. (d) CV profiles of Li-S batteries with an S-PMB SNWs film or PP film. (e) CV profiles obtained at a scan rate of 100 mV s⁻¹ of symmetric batteries with an S-PMB SNWs film or PP film. (f) The potentiostatic discharge curves of Li₂S₈/tetraglyme solution measured at 2.05 V with an S-PMB SNWs film or a PP film. (g) DFT-based geometry and binding energy optimization of the PMB SNWs with LPS species. (h) Fraction of contribution from each component of the PMB SNWs to the binding energy with LPS species.

netics of LPS liquid-liquid conversion on the S-PMB SNWs film. As shown in Fig. 3f, the discharge current peak of Li-S battery with the S-PMB SNWs film was much earlier and higher than the battery with only a PP film. Moreover, the capacity of Li₂S deposited on the S-PMB SNWs film (145 mA h g⁻¹) was higher than that of PP film (86 mA h g⁻¹), clearly suggesting enhanced nucleation and deposition of LPSs on the S-PMB SNWs film [15,16]. As seen in the SEM image (Fig. S11), Li₂S was deposited on the S-PMB SNWs film sufficiently and uniformly, demonstrating the excellent affinity between LPSs and the PMB SNWs. The anomalous 3D deposition

of Li₂S endowed the PMB SNWs with high utilization of LPSs, efficiently suppressing the diffusion of LPSs into electrolytes [17]. And the charge current peak of the battery with an S-PMB SNWs film appeared earlier and higher than the battery with a PP film (Fig. S12), validating the promoted Li₂S dissolution on the PMB SNWs film [18]. All of the above results proved the efficient adsorption of LPSs and acceleration of LPS conversion kinetics on the S-PMB SNWs film. Then, the separate Bi₂O₃ and POM were prepared (Fig. S4). The adsorption of LPSs and the kinetics of the LPS conversion on Bi₂O₃ and POM were investigated, respectively. They both

showed adsorption of LPSs, and POM showed stronger adsorption of LPSs than Bi_2O_3 (Fig. S13a). The Bi_2O_3 and POM were loaded on the carbon papers, and the symmetric battery with Bi_2O_3 or POM exhibited higher polarization current than the bare carbon paper. The battery with Bi_2O_3 exhibited higher polarization current than the battery with POM, suggesting higher interfacial kinetics of LPS liquid-liquid conversion on Bi_2O_3 . Incorporating Bi_2O_3 and POM in PMB SNWs could synergize the immobilization and electrocatalysis of polysulfides synchronously. In addition, Bi_2O_3 and POM were powders while PMB was SNWs. The structure of free-standing PMB SNWs films was more stable than some Bi_2O_3 and POM powders loaded on substrates. The intrinsic adsorption and conversion of LPSs on the S-PMB SNWs were further investigated through density functional theory (DFT) simulations. As shown in Fig. 3g, with the exception of S_8 conversion to Li_2S_8 , the subsequent conversions were all endothermic and the conversion from Li_2S_4 to Li_2S_2 was the rate-determining step during discharging [17,19]. It is demonstrated that all the components of the PMB NWs hindered the LPSs shuttling synergistically, and POM played a major role (Fig. 3h), consistent with the experimental results.

Considering that lithium dendrite was one of the trickiest problems obstructing the practical application of Li-S batteries, the ability of S-PMB SNWs film to stabilize Li metal in the Li/Li symmetric cell during its electroplating and stripping process was investigated. As shown in Fig. S14a, the overpotential of the Li/Li symmetric cell with an S-PMB SNWs film remained constant for 237 cycles. In contrast, the overpotential of the Li/Li symmetric cell with a PP film fluctuated during the first 32 cycles and suddenly jumped at the 33rd cycle. Compared with the cell with a PMB SNWs film, the Li foil in the cell with only a PP film was seriously fragmented (Fig. S14b–e) due to the formation of lithium dendrites and “dead lithium” during the cycling process. The S-PMB SNWs films could improve the distribution uniformity of lithium deposition, reduce the effective current density and reduce the side reaction between the lithium anode and electrolyte, so the stability of the Li foil is improved [20]. As shown in Fig. S14f, when the current density increased to 2, 3, 4, 5 and 7 mA cm^{-2} , the S-PMB SNWs film was also effective in stabilizing the Li electrode. The Li/Li symmetric cell with a bare PP film, however, showed drastically fluctuating overpotentials. Even at a high current density of 3 mA cm^{-2} , the symmetric cell with an S-PMB SNWs film also possessed excellent rate performance (Fig. S15). It is demonstrated that the S-PMB

SNWs film could protect the Li anode effectively during the plating/stripping process.

Since the S-PMB SNWs film could suppress the LPS shuttling, enhance the LPS conversion kinetics and protect the Li anode effectively, it was applied in the Li-S batteries as a functional interlayer (Fig. S16). The electrochemical tests of the Li-S batteries with the S-PMB SNWs films were performed. As shown in the electrochemical impedance spectra (EIS, Fig. 4a), the semicircle in high frequency was attributed to the capacitance and resistance of the solid electrolyte interface (SEI) layer of Li anode and S cathode. The second semicircle was attributed to the $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ insulating layer formed on the surface of Li anode [21]. The Li-S batteries with a PP film displayed two large semicircles, while the semicircles of the Li-S batteries with a PMB SNWs film were smaller, indicating that the problem of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ insulating layer and thick SEI were effectively alleviated by the S-PMB SNWs film. As shown in Fig. 4b and Fig. S17, the capacities of the Li-S battery with an S-PMB SNWs film at rates of 0.3, 0.5, 1, 2, 3 and 5 C were 1126, 1061, 973, 923, 897 and 851 mA h g^{-1} , respectively, much higher than that of PP film. After the current density was recovered to 0.5 C, the capacity of the Li-S battery with an S-PMB SNWs film recovered to 1042 mA h g^{-1} , demonstrating outstanding rate performance of the Li-S battery with an S-PMB SNWs film. High areal capacity and energy density are important for achieving practical applications of Li-S batteries and realizing high S loading is critical. As shown in Fig. 4c, the Li-S battery with an S-PMB SNWs film delivered a high areal capacity of 5.6 mA h cm^{-2} after cycling at 0.3 C for 100 cycles. The long-term cycling performance of the Li-S battery with an S-PMB SNWs film was tested at 0.5, 2 and 5 C (Fig. 4d, Figs S18 and S19). The Li-S battery with an S-PMB SNWs film showed an initial specific capacity of 877 mA h g^{-1} and retained 782 mAh g^{-1} after 850 cycles at 2 C, with only 0.013% capacity fading per cycle (Fig. 4d). However, when the disordered PMB SNWs film (D-PMB SNWs film) was fabricated through the traditional evaporation method, the performance was inferior. The capacity of the Li-S battery with such a PMB SNWs film decayed at a rate of 0.023% per cycle, which might be due to the structure difference. The S-PMB SNWs film was flat and compact while the D-PMB SNWs film was relatively loose and there were some small defects on it (Figs S7 and S9). But the Li-S battery with an S- or D-PMB SNWs film exhibited better performance than the Li-S battery with only a PP film. When cycling at 0.5 C, the Li-S battery with an S-PMB SNWs film decayed at a rate of 0.030% per cycle

Figure 4 The electrochemical performance of the Li-S batteries with the PMB SNWs films. (a) Nyquist plots and (b) rate performance of Li-S batteries with a PP film or S-PMB SNWs film. (c) Areal capacity of the Li-S battery with the S-PMB SNWs film obtained at 0.3 C with high S loading of 9.6 mg cm^{-2} . (d) Cyclic performance obtained at 2 C of Li-S battery with an S-PMB SNWs film, D-PMB SNWs film or a PP film. Comparison of performance of Li-S batteries with S-PMB SNWs films and other results reported before cycling at rates of (e) 2 C [15–17,21–25] and (f) 0.5 C [16,25–35]. The content in brackets means S loading (mg cm^{-2}), and cycle number.

and cycled for 500 times (Fig. S18). Even at 5 C, the Li-S battery with an S-PMB SNWs film could cycle for 1000 times and decay at a rate of 0.045% per cycle (Fig. S19). The above electrochemical tests proved the effectiveness of the S-PMB SNWs film as interlayer in Li-S batteries. The performance of Li-S batteries with S-PMB SNWs films far outperformed the performance of many Li-S batteries reported previously, as shown in Fig. 4e, f.

CONCLUSION

In summary, heterostructure PMB SNWs were synthesized and polymer-resembling films of S-PMB SNWs with excellent flexibility were fabricated. Due to the combination of effective components in PMB SNWs and typical structures of the S-PMB SNWs film, it showed

effective synchronous immobilization and electrocatalysis of LPSs and could protect the Li anode at the same time. Thus, the Li-S batteries with S-PMB SNWs films delivered exceptional performance, giving researchers new insights into improving the performance of Li-S batteries. More importantly, incorporating multiple effective compositions in SNWs through the method in this work and manipulating the structures SNWs assemblies can improve their performance and pave the way for their practical applications in different fields including optics, electronics, and energy.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Simin Zhang received her PhD degree in Prof. Xun Wang's group from Tsinghua University in 2020. Currently, she is a post-doctor researcher in Prof. Xun Wang's group at the Department of Chemistry, Tsinghua University. Her current research focuses on the synthesis and application of sub-1 nm nanowires/nanobelts.

Haodong Shi received his bachelor's degree in applied chemistry from Northeastern University in 2016. He is pursuing the PhD degree from Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS), under the supervision of Prof. Zhong-Shuai Wu. His research interests focus on graphene and 2D materials for high-energy batteries.

Wenxiong Shi received his PhD degree from the Institute of Chemistry, CAS. And he is a professor at Tianjin University of Technology. His research interest focuses on simulation of polyoxometalate clusters and metal-organic frameworks.

Zhong-Shuai Wu received his PhD degree from the Institute for Metal Research, CAS, in 2011 and worked as a postdoctoral fellow at the Max Planck Institute for Polymer Research in Mainz, Germany, from 2011 to 2015. He is a DICP chair professor now. His research interests include graphene and 2D materials, surface- and nanoelectrochemistry, microscale electrochemical energy storage devices, supercapacitors, batteries and catalysts.

Xun Wang received his PhD degree from the Department of Chemistry, Tsinghua University in 2004. He then joined the faculty of the Department of Chemistry, Tsinghua University in 2004, and was promoted to associate professor and full professor in 2005 and 2007, respectively. His current research interests include the synthetic methodology, formation mechanism, and properties of monodisperse nanocrystals.

超顺排的 Bi_2O_3 -多酸亚纳米线薄膜用于锂硫电池中间层

张思敏^{1†}, 石浩东^{2,3,4†}, 唐军旺⁵, 匙文雄^{6*}, 吴忠帅^{2,3,4*}, 王训^{1*}

摘要 亚纳米线(SNWs)具有类高分子的性质, 可以像高分子一样进行加工, 而且其组成和结构易于调控, 具有丰富的功能. 合理设计多组分异质结构SNWs可以进一步提高其功能性, 然而目前合成这种SNWs仍然面临着巨大的挑战. 本文合成了 Bi_2O_3 -多酸异质结构SNWs(PMB SNWs), 并制备了超顺排的PMB SNWs薄膜(S-PMB SNWs薄膜), 该薄膜可以作为中间层, 有效抑制多硫化锂(LPSs)的穿梭, 从本质上促进LPSs氧化还原转化动力学, 并对锂阳极起到保护作用. 以S-PMB SNWs膜作为中间层的锂硫(Li-S)电池在850次循环中表现出超低的容量衰减率, 每循环一圈只衰减0.013%. 本研究证明了这种异质结构的SNWs具有改善锂硫电池性能的潜力.