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Phase engineering of two-dimensional MoS_2 nanosheets

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Phase engineering has been emerging as an effective strategy to tune the properties of two-dimensional transition-metal dichalcogenides (TMDs) for a variety of applications including electronics, catalysis, energy storage and membrane separation [1]. Taking one of the most widely studied TMDs MoS_2 as an example, hexagonal 2H phase is the most stable structure of bulk MoS_2. MoS_2 also exists in many metastable phases including 1T, 1T′ and 1T″, distinguished by the formation of different superstructures [2]. Among these structural phases, 1T′ is the energetically preferred metastable phase in which Mo atoms are clustered into zigzag chains [2]. Chemical exfoliation of bulk 2H MoS_2 into single-layer nanosheets by Li intercalation leads to massive electron injection into MoS_2, inducing a phase transition from 2H to 1T′ [3]. The Li intercalation method can only produce a mixture of 1T′ and 2H phases with the 1T′ phase less than 80%, severely limiting their applications [3]. The raw materials used for intercalation and the intercalation method are two important factors that influence on the phase purity of MoS_2 nanosheets. In 2018, Zhang and coworkers [4] reported a facile annealing method to prepare 1T′ phase MoS_2 crystals in high purity. The intrinsic electrocatalytic activity of 1T′ phase MoS_2 was measured, revealing the high HER activity on the basal plane. By replacing small Li^+ ions with large quaternary ammonium ions to reduce the electron injection during intercalation, Duan and coworkers [5] prepared phase-pure 2H MoS_2 nanosheets for high-performance thin-film transistors. Therefore, phase engineering plays an important role in precise synthesis of MoS_2 nanosheets with different properties. Herein, we highlight recent progress in the fields of electrocatalysis (Fig. 1a–c) [6], smart membranes (Fig. 1d–f) [7] and Li-S batteries (Fig. 1g–i) [8] using MoS_2 nanosheets as building blocks and demonstrate how the properties of MoS_2 are influenced by their structural phases.

Single or few layer MoS_2 nanosheets have been widely used as supports of metal catalysts due to their ultrahigh surface area. It has been reported that many transition metal precursors can be reduced by 1T′ phase MoS_2 under mild conditions due to the presence of excess negative charges on their surface [9]. The redox reaction between metal precursors and 1T′ phase MoS_2 usually results in the formation of 2H phase MoS_2 supported metal nanoparticles [10]. Recently, by employing pure 1T′ phase K_xMoS_2 crystals as raw materials and a mild electrochemical intercalation method, Zhang and coworkers prepared 1T′ phase MoS_2 nanosheets with high purity. They found that the highly pure 1T′ phase MoS_2 templates (Fig. 1a) facilitate the grows of single-atomically dispersed Pt (s-Pt) atoms with Pt loading up to 10 wt% (s-Pt/1T′-MoS_2), whereas the 2H phase MoS_2 facilitate the epitaxial growth of ultrasmall Pt nanoparticles [6]. HAADF-STEM image in Fig. 1b revealed that s-Pt occupy three different locations: Pt substituting the Mo site (Pt_{sub}), Pt adsorbed on the top site of S ($Pt_{ads\text{-}S}$) and Pt adsorbed on the top site of Mo ($Pt_{ads\text{-}Mo}$). The as-developed mild photoreduction method ensures no phase transition of 1T′ MoS_2 after depositing Pt as confirmed by XPS and Raman. s-Pt/1T′-MoS_2 requires overpotential of (−19 ± 5) mV to reach geometric current density of 10 mA cm^{-2}. The mass activity of s-Pt/1T′-MoS_2 reaches (85 ± 23) A mg_{Pt}^{-1} at the overpotential of −50 mV and a mass-normalized exchange current density of 127 A mg_{Pt}^{-1} (Fig. 1c). The HER performance of s-Pt/1T′-MoS_2 is much higher than the commercial HiSPEC 9100 Pt/C and other previously reported Pt-based electrocatalysts. Moreover, the HER polarization curve exhibits no obvious degradation after 10,000 cyclic voltammetry cycles. Pt in s-Pt/1T′-MoS_2 remains single-atomically dispersed after the durability test as confirmed by various characterizations. Density functional theory (DFT) calculations indicate that $Pt_{ads\text{-}Mo}$ have a hydrogen adsorption free energy of close to zero, probably contributing to the superior hydrogen evolution reaction (HER) activity. This work demonstrates how the crystal phase of MoS_2 affects the growth of secondary material on its surface. The strong interactions between negatively charged 1T′ phase MoS_2 and Pt precursors prevent the direct reduction of Pt precursors into nanoparticles. The use of highly pure 1T′ phase MoS_2 and mild photoreduction method are crucial to prepare s-Pt/1T′-MoS_2 with high Pt loading.

Beside using as electrocatalysts, MoS_2 nanosheets have attracted great attention as building blocks to prepare laminar membranes for water purification and gas separation [11,12]. Furthermore, MoS_2 is a strong candidate for making intelligent membranes because it can be controllably switched between several structural phases depending on external conditions. Recently, Nair and coworkers [7] reported the memory effects and stimuli-regulated transport of molecules through an intelligent 1T′ phase MoS_2 membrane in response to external pH (Fig. 1d). Water and ion permeation through 1T′ MoS_2 membranes follows a pH-dependent hysteresis with a permeation rate that switches by a few

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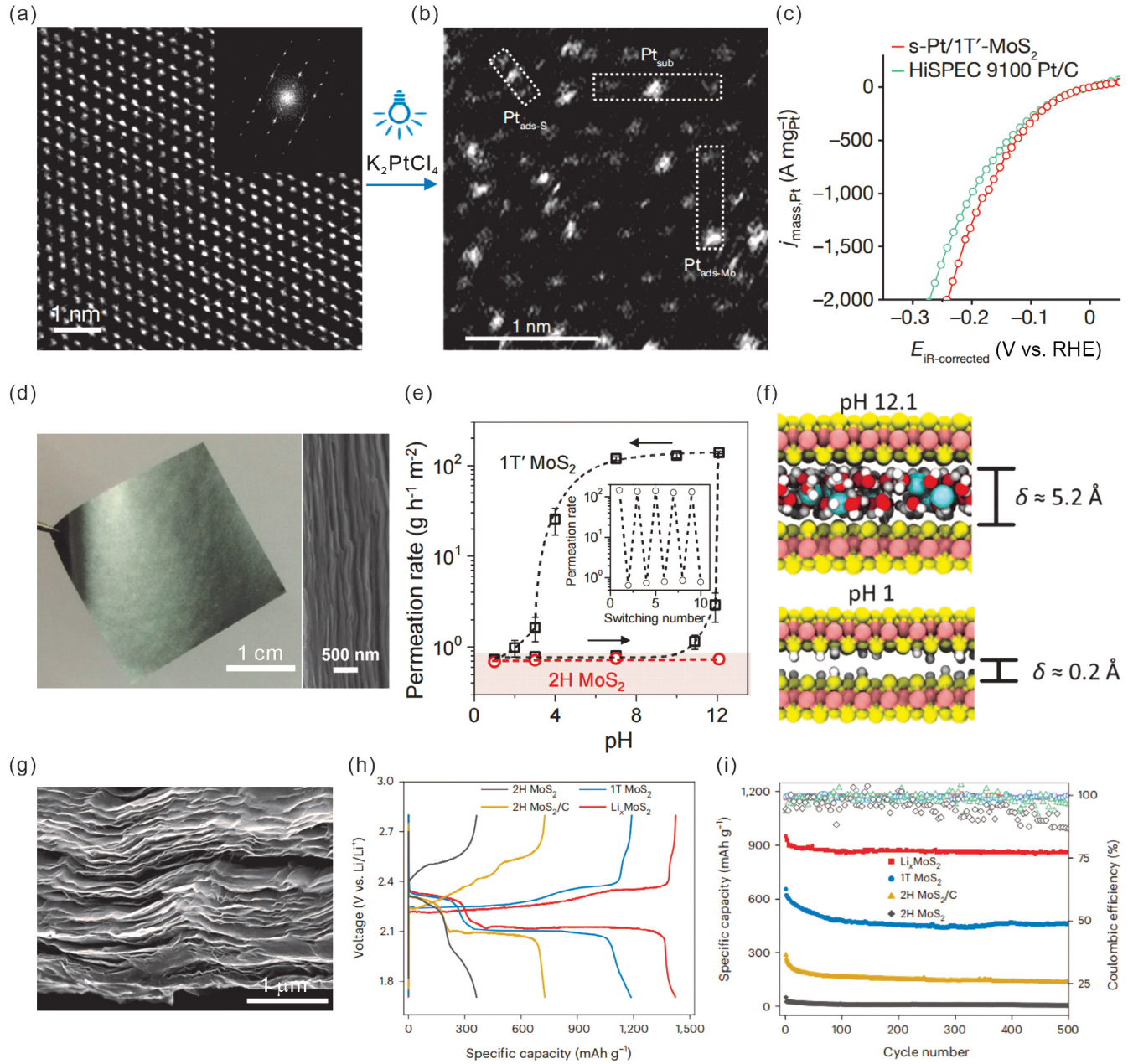

Fig. 1. (Color online) Phase engineering of two-dimensional MoS_2 for various applications. (a) HAADF-STEM image of a typical 1T′-MoS_2 (inset: the corresponding fast Fourier transform pattern). (b) Atomic-resolution HAADF-STEM image of s-Pt/1T′-MoS_2 showing the isolated Pt atomically dispersed on 1T′-MoS_2. (c) HER polarization curves for s-Pt/1T′-MoS_2 and HiSPEC 9100 Pt/C showing the mass-normalized current densities. (d) Photograph of a 2-μm-thick freestanding 1T′ MoS_2 membrane with the corresponding SEM cross-sectional image showing the closely packed lamellar structure. (e) Water vapor permeation rate of 2H and 1T′ MoS_2 membranes as a function of pH treatment. Inset: reversible change in water permeation by alternating acid (0.1 mol L^{-1} HCl) and base (0.1 mol L^{-1} LiOH) treatment. (f) Schematic showing available free space (δ) in base and acid treated MoS_2 membranes. Yellow, sulfur; pink, molybdenum; teal, lithium; red, oxygen; white, hydrogen. (g) A cross-sectional SEM image of the Li_xMoS_2 film. (h) Galvanostatic charge–discharge curves at a current density of 0.1 C and (i) cycling stability at a current density of 1 C of different MoS_2-based cathodes in Li-S coin cells. (a)–(c) reproduced from Ref. [6], (d)–(f) reproduced from Ref. [7], (g)–(i) reproduced from Ref. [8] with permission from Nature Publishing Group, Copyright © 2023.

orders of magnitude (Fig. 1e). In comparison, the 2H MoS_2 membranes remained impermeable throughout this pH range (Fig. 1e). No degradation of membrane performance was observed after ten alternating pH changes, confirming the reversible and robust of 1T′ MoS_2 membranes (inset of Fig. 1e). X-ray diffraction (XRD) results revealed that 1T′ phase MoS_2 membranes have an interlayer spacing of 11.4 Å (available free space δ 5.2 Å). By contrast, 2H phase and acid treated 1T′ phase MoS_2 membranes have an interlayer spacing of 6.4 Å (available free space δ 0.2 Å) (Fig. 1f). Systematic studies revealed that the concentration of Li^+ in 1T′ phase MoS_2 membranes followed an identical trend with water permeation rate as a function of pH. The water permeation rate sharply decreased when Li/Mo ratio was lower than 0.1. Molecular dynamics simulations revealed the spontaneous swelling of MoS_2 bilayers in the presence of Li ions within the channels due to osmotic pressure-driven intercalation of water. In comparison, water molecules did not enter the channels in the absence of Li ions (2H and acid-treated MoS_2). The as-developed intelligent MoS_2 membranes show potential applications in autonomous wound infection monitoring and pH-dependent nanofiltration. A 1T′ MoS_2 membrane with pH-responsive permeation properties was used to build a pH sensor for wound monitoring. No permeation was observed for simulated wound exudate with pH $\leq$ 5 (healing wound). The membrane became permeable when the

pH of simulated wound exudate increased to 8 (infected wound). The pH-responsive MoS_2 membranes can be used not only for sensing but also for intelligent drug delivery in the future. The pressure filtration of salt solutions was performed through 1T′ MoS_2 membranes treated at different pH. The rejection of $K_3[Fe(CN)_6]$ can be regulated between 18% and 97% and follows a hysteresis with a reverse trend of water flux through the membrane. This work demonstrates the pH-dependent hysteresis in water permeation through 1T′ phase MoS_2 membranes. This phenomenon is unique to the 1T′ phase of MoS_2 due to the presence of surface charge and exchangeable ions on the surface.

Restacked 1T′ phase MoS_2 nanosheets have been considered as promising electrode materials for energy storage devices due to the high electrical conductivity and efficient intercalation of various ions [13,14]. Recently, Chhowalla and coworkers [8] reported the use of lithiated 1T′ phase MoS_2 (Li_xMoS_2) as a binder-free conducting cathodes (Fig. 1g) for high-performance Li–S batteries. Li_xMoS_2 cathodes show specific capacity of 1425 mAh g^{-1} at 0.1 C in coin cells, which is much higher than cathodes made from semiconducting 2H MoS_2, 2H MoS_2 mixed with conductive carbons and non-lithiated 1T′ MoS_2 (Fig. 1h). The improved immobilization of lithium polysulfides in compact electrodes enables capacity retention of 91% for the Li_xMoS_2 cathode after 500 cycles at 1 C (Fig. 1i). The improved battery performance can be largely attributed to the increased adsorption of lithium polysulfides, enhanced Li^+ transport, accelerated electrochemical reaction kinetics and superior electrocatalytic activity for polysulfide conversion. The high affinity of Li_xMoS_2 host for polysulfides can be ascribed to the polar nature of its metallic 1T′ phase and the additional binding sites introduced by lithiation. The Li^+ ion diffusion coefficient in Li_xMoS_2 cathodes was found to be ~ 70% higher than that in 1T′ MoS_2 cathodes due to intercalated lithium between 1T′ phase MoS_2 nanosheets facilitating Li^+ ion transport. Electrochemical impedance spectroscopy measurements revealed that Li_xMoS_2 cathode possess the lowest charge transfer resistance and activation energy among different cathodes. Li_xMoS_2 cathode also shows the highest electrocatalytic activity for Li_2S_4 reduction with an electron transfer number of 10.6, which is in good agreement with sulfur utilization rate of 85.1% obtained from coin cells. Pouch cell batteries fabricated with Li_xMoS_2 cathode and Li-metal anode show superior areal capacity, energy density and cycling stability compared with state-of-the-art Li-S and Li-ion batteries. This work demonstrates the design of practical Li-S cathode using both conductive and electrocatalytically active lithiated 1T′ phase MoS_2. The improved adsorption of polysulfides, enhanced Li^+ transport and accelerated electrochemical kinetics collectively mitigate the sluggish ionic transport and shuttling effects in practical Li-S batteries under lean electrolyte conditions, thus improve the energy density and cycling stability.

In conclusion, the rich chemistry of MoS_2 nanosheets offers many opportunities for both of fundamental studies and practical applications. The ability to tune the chemistry by phase engineering allows new properties to be realized with MoS_2. However, the phase stability of 1T′ MoS_2 is the key challenge for practical applications, especially under high-temperature or strong oxidizing conditions. Covalent surface functionalization will be a promising way to improve the phase stability as well as to introduce new properties [15].

Conflict of interest

The authors declare that they have no conflict of interest.

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