Molybdenum Sulfide Nanosheet-Based Hollow Porous Flat Boxes and Nanotubes for Efficient Electrochemical Hydrogen Evolution

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Introduction

As a potential substitute for Pt, nonprecious molybdenum disulfide (MoS$_2$) materials have been developed to catalyze the hydrogen evolution reaction (HER). In addition to MoS$_2$ materials, amorphous/quasiamorphous molybdenum sulfide (MoS$_x$) materials have been reported recently to be promising because of the exposed active sites from the intrinsically inert basal plane and the unique disulfide (S$_2^{2-}$) units. Although MoS$_x$ materials have been the focus of plenty of investigations, the endeavors to endow them with regular morphologies and hierarchical structures are inadequate. Thanks to their limited anisotropy and good deformability, MoS$_x$ materials have been deposited into 3D substrates/templates, the structures of which can be replicated and retained by the as-prepared MoS$_x$ materials. However, to date, almost no MoS$_x$ materials with a self-supported regular morphology composed of hierarchical structures such as nanosheet-based hollow porous flat boxes and nanotubes have been reported. As the structure of a material is very important for its catalytic performance, it is of great significance and necessity to explore and exploit regular morphologies and hierarchical structures of MoS$_x$ materials to extend their advantages.

Because MoS$_x$ is similar to MoS$_2$ and may be considered as a precursor of MoS$_2$, research on MoS$_x$ materials with regular hierarchical structures can shed light on the preparation of MoS$_2$ materials with unprecedented morphologies and structures. Initially, Feldman et al. confirmed the synthesis of MoS$_2$ fullerenes and nanotubes by a gas-phase reaction by virtue of the intermediate amorphous molybdenum trisulfide (MoS$_3$) phase obtained at elevated temperatures according to the ternary phase diagram of Mo–O–S.[9] After that, the merit of the intermediate amorphous MoS$_3$ phase was further proved and utilized by Nath et al. to develop a relatively simple thermal decomposition method of MoS$_3$ or MoS$_3$ precursors to prepare MoS$_2$ nanotubes.[10] Although these methods could be used to synthesize MoS$_2$ nanotubes and fullerenes, their applicability is restricted by the high reaction temperatures required and the nonhierarchical structures of the as-prepared MoS$_2$ fullerenes and nanotubes. Subsequently, liquid-phase methods have been developed to prepare nanosheet-based hierarchically structured MoS$_2$ nanotubes and nanocages with various templates under relatively mild conditions. Thanks to the hierarchical structures, nanosheet-based porous MoS$_2$ nanotubes and nanocages exhibited outstanding performances for hydrogen generation and lithium-ion battery anodes. Furthermore, porous MoS$_2$ nanotubes were also prepared without a template by the spontaneous self-assembly of MoS$_2$ nanosheets during growth in an ethanol-based mixed solvent under heating.[10] From previous studies on the preparation of MoS$_2$ materials with regular morphologies and hierarchical structures, it seemed that the amorphous MoS$_3$ precursor and the solvent component in the liquid-phase method were important factors to achieve regular hierarchical structures, although the mechanisms that influence this were not clear.

Inspired by the methods developed to prepare MoS$_2$ with regular morphologies and hierarchical structures, herein, for the first time, we have developed a facile template-free solvothermal method to synthesize MoS$_2$ nanosheet-based hollow porous flat boxes and nanotubes by adjusting the ethanol content in the reaction solvent. In the process, MoS$_2$ materials of low crystallinity and with characteristic S$_2^{2-}$ units are akin to the intermediate amorphous MoS$_3$ during the preparation of...
MoS$_2$ nanotubes. At the same time, the presence of ethanol may help to facilitate and stabilize the assembly of MoS$_2$ nanosheets at specific stages as reported previously$^{[9,10]}$. After reaction, the as-synthesized MoS$_2$ nanosheet-based hollow porous flat boxes are of 1–3 μm in length/width and 200–450 nm in thickness, and the nanotubes are several or more micrometers long with diameters of approximately 200–500 nm. For electrocatalytic hydrogen evolution, the MoS$_2$ nanosheet-based hollow porous flat boxes and nanotubes both demonstrate outstanding performances, and the overpotentials to achieve 10 mA cm$^{-2}$ current are approximately 206 and 210 mV, respectively.

Results and Discussion

If water is used as the solvent for the reaction of sodium molybdate dihydrate and thiourea in a sealed autoclave at 200 °C for 18 h, no observable solid substance is produced. However, if absolute ethanol is used instead of water, the outcome is completely different. A large amount of black product with excellent dispersity both in water and ethanol is obtained. As demonstrated by using SEM, the product is mainly hollow porous flat boxes with 2D nanosheets as building blocks (Figure 1a and b). As the synthesis is template free, the hollow porous flat boxes result from the self-assembly of nanosheets. The composition is measured by using energy-dispersive X-ray spectroscopy (EDS), and the results show that Mo and S atoms are distributed uniformly in the hollow porous flat boxes (Figure 1c–e). In Raman spectra, normally, the minor peak at $\tilde{v} = 404$ cm$^{-1}$ is an A$_{1g}$ model Raman shift of semiconductor-phase MoS$_2$ (Figure 1f). However, the missing MoS$_2$ E'$_{2g}$ model peak and the emerging peak at $\tilde{v} = 146$ cm$^{-1}$ (Mo–Mo stretching vibration of metallic phase MoS$_2$) imply that the flat boxes have Raman features similar to that of metallic-phase MoS$_2$ to some degree.$^{[11]}$ The peak at $\tilde{v} = 315$ cm$^{-1}$ is assigned to the $\nu$(Mo–S) vibration that corresponds to the existence of bridging S$_2^{2-}$ units.$^{[14]}$ As the Raman spectra do not show clear peaks in the region of $\tilde{v} = 520–550$ cm$^{-1}$ in which the $\nu$(S–S) vibrations generally lie, we suppose that the S$_2^{2-}$ units may not be dominant in the sample.$^{[15]}$ The composition and chemical states of the product are further confirmed by using X-ray photoelectron spectroscopy (XPS), and the result gives a Mo/S ratio of 1:2.72. By deconvolution, the characteristic high-resolution scan in the S 2p region can be fitted into two doublets (Figure 1g). One of the two doublets at a lower binding energy can be attributed to basal plane and apical S$^{2-}$, and the other doublet is caused by the existence of bridging and terminal S$^{2-}$ as reported previously.$^{[14]}$ Therefore, highly dispersed MoS$_2$ nanosheet-based hollow porous flat boxes have been synthesized by a template-free solvothermal method.

The crystallinity of the nanosheet-based hollow porous MoS$_2$ flat boxes is obtained by using selected-area electron diffraction (SAED) in high-resolution transmission electron microscopy (HRTEM) and XRD. The nanosheets that compose the hollow porous flat boxes are observed clearly by using HRTEM (Figure 2a–d). The layer distance is 1.02 nm, which is larger than the classical MoS$_2$ layer distance (0.62–0.65 nm). Therefore we conclude that the atomic layers in the nanosheets of flat boxes are packed loosely.$^{[15]}$ Although the fringes of the nanosheets show some kind of layer order, the SAED pattern of the flat box is broadened and blurry, which implies the imperfect order of the layers in the nanosheets and random arrangement of atoms in the layers as demonstrated by using HRTEM (Figure 2e). In addition, the powder XRD pattern of the product is quite similar to the patterns of amorphous/quasiamorphous MoS$_2$ materials$^{[16]}$ (Figure 2e). The peak at $2\theta = 8.7^\circ$ originates from loosely packed layers in the nanosheets, and the calculated layer distance is 1.02 nm, which is consistent with the value obtained by using TEM. Accordingly, the as-prepared nanosheet-based hollow porous boxes are MoS$_2$ with a low crystallinity and characteristic S$^{2-}$ units.

As ethanol can help to produce the nanosheet-based hollow porous MoS$_2$ flat boxes and ethanol is believed to have some impact on the self-assembly of nanosheets to form hierarchical MoS$_2$ structures,$^{[9,10]}$ the ethanol/water ratio in the solvent for the reaction is adjusted to check the influence of the ethanol.

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component on the formation of regular morphologies and hierarchical structures. Different from the situation if 100% ethanol is used, the product is mainly nanosheet-based hollow porous nanotubes intermingled with some nanosheets clusters if 80 vol% ethanol and 20 vol% water are used as the solvent for the reaction. The nanosheet-based hollow porous nanotubes have outside diameters of 200–500 nm and thicknesses of 50–70 nm as revealed by using SEM (Figure 3 a and b) and TEM (Figure 3 c and d). Again, as with the above flat boxes, the Mo and S atoms are distributed uniformly in the hollow porous nanotubes (Figure 3 e–g). The XPS spectrum is used to calculate the Mo/S ratio, and the result is 1:2.54. In addition, the high-resolution scan in the S 2p region is fitted into two doublets, and the doublet at higher binding energy is attributed to the characteristic bridging and terminal $\text{S}_2\text{O}_2^-$ as for the above deconvolution of the S 2p spectrum of hollow porous flat boxes (Figure S1 a). The XRD pattern indicates that the sample is poorly crystalline (Figure S1 b). Therefore, MoS$_x$ nanosheet-based hollow porous nanotubes are synthesized by adjusting the ethanol concentration in the reaction solvent conveniently.

If the nanosheet-based hollow porous flat box has structure regularity in two dimensions, then the nanosheet-based hollow porous nanotube has structure regularity only in one dimension. So, possibly, the regularity of the hierarchical structure of the product may have a positive correlation with the ethanol concentration in the reaction solvent. If the ethanol content is reduced to 60 vol%, the still highly dispersed product only consists of nanosheets and the randomly packed nanosheet structure actually has no structure regularity (Figure 4 a and b). However, if the ethanol content is further reduced to 40 or 20 vol%, the products will become nondispersive and precipitate quickly and the apparent output decreases sharply (Figures S2 and S3). No solid product is harvested with pure water (0% ethanol) as the solvent for the reaction. The qualities and properties of the products prepared from low-ethanol-content solvents change dramatically and become clearly different from the highly dispersed products synthesized with high-ethanol-content solvents (Figures S3 and S4).

Consequently, with 60 vol% ethanol in the reaction solvent, only MoS$_x$ nanosheets are produced, and the nanosheets assemble randomly (Figure 4 c). If the ethanol content increases to approximately 80 vol%, the formed MoS$_x$ nanosheets can assemble gradually into 1 D regular hollow porous nanotubes of various aspect ratios. If the ethanol concentration is increased all the way to 100%, the assembly of the MoS$_x$ nanosheets will demonstrate more regularity and produce two-dimensionally regular hollow porous flat boxes with different aspect ratios.

Figure 2. Crystallinity and assembly of as-prepared MoS$_x$ nanosheet-based hollow porous flat boxes: a,b) TEM images of the nanosheet-based hollow porous flat boxes, the inset broadened and blurry SAED pattern in image a shows that the flat boxes have a low crystallinity; c,d) HRTEM images of the disordered atoms and loosely packed nanosheet layers in the hollow porous flat boxes; e) XRD pattern of the hollow porous flat boxes that indicates the loosely packed layers and poor crystallinity.

Figure 3. Morphology and composition of MoS$_x$ nanosheet-based hollow porous nanotubes: a,b) SEM and c,d) TEM images of as-prepared MoS$_x$ nanosheet-based hollow porous nanotubes; e–g) EDS results reveal the uniform distribution of Mo and S atoms in the hollow porous MoS$_x$ nanotubes.
Although the ethanol content in the solvent can indeed influence the assembly of the nanosheets to form regular morphologies and hierarchical structures, the amorphous/quasisubmorphous status of the intermediate phase or final product may also be an influential factor. Previously, amorphous MoS$_3$ has been an important intermediate phase in the formation of MoS$_2$ fullerene and nanotube structures. Here, the highly dispersed nanosheets and nanosheet-based hollow porous nanotubes and flat boxes are in a quasiamorphous status between amorphous MoS$_3$ and crystalline MoS$_2$. Hence, MoS$_x$ has the ability to assemble and transform into regular and hierarchical structures. As the higher concentration of S$_2^{2-}$ ensures the closer relationship of MoS$_x$ with MoS$_3$, MoS$_x$ materials with more S$_2^{2-}$ may form fascinating structures. From the fitting of the high-resolution spectra in the S 2p region, the concentrations of S$_2^{2-}$ of the three kinds of highly dispersed MoS$_x$ materials are calculated (Table 1). As expected, the MoS$_x$ nanosheet-based hollow porous flat boxes (100 vol% ethanol) have the highest S$_2^{2-}$ concentration followed by the hollow porous nanotubes (80 vol% ethanol) and the randomly packed nanosheets (60 vol% ethanol) has the lowest S$_2^{2-}$ concentration. For the particles prepared with a low ethanol concentration in the mixed solvent for the reaction, the XPS spectrum in the S 2p region will become totally different, and no S$_2^{2-}$ units could be quantified from the high-resolution scan (Figure S4b). We suppose that a specific concentration of ethanol in the reaction solvent can stabilize the MoS$_x$ at a certain amount of S$_2^{2-}$ units and meanwhile, the growing nanosheets would assemble under the influence of the existing ethanol (Figure 4c). The more ethanol in the solvent for the reaction, the larger the amount of S$_2^{2-}$ will be in the product and the more regular the hierarchical structure formed by the further assembly of the nanosheets. Other organic solvents for binary and ternary mixed solvents are under investigation to unravel the mechanisms of the influence of organic solvents on the S$_2^{2-}$ amount and the assembly of nanosheets, and we believe the realization of a controllable amount of S$_2^{2-}$ units and regular hierarchical structures may help us to prepare excellent MoS$_x$ catalysts.

The intriguing MoS$_x$ nanosheet-based hollow porous flat boxes and nanotubes are applied to catalyze the hydrogen evolution reaction with a classical three-electrode setup in 0.5 M H$_2$SO$_4$ solution. Unsurprisingly, the nanosheet-based hollow porous MoS$_x$ flat boxes and nanotubes demonstrate excellent performances, and the required overpotentials to reach 10 mA cm$^{-2}$ current are only approximately 206 and 210 mV, respectively, as indicated by the polarization curves (Figure 5a). For comparison, highly dispersed randomly packed nanosheets are also tested, and the performance is approximately 215 mV overpotential.
to achieve $10 \text{ mA cm}^{-2}$ current) is slightly worse than that of the two hollow porous samples. This may be because of the increasing number of $S_{2}^{2-}$ units and the increasing stability of nanosheets arrangements to expose sufficient active sites in the hollow porous samples with regular morphologies and hierarchical structures (Table 1 and Figures 1 a and b, 3 a and b, and 4 a and b). In addition, the performances of the three highly dispersed nanosheets and nanosheet-based samples are significantly superior to that of the undispersed particles, which do not have the characteristic high-resolution $2p$ spectrum that contains $S_{2}^{2-}$ units (Figure S4b). The results indicate that a good amount of $S_{2}^{2-}$ units, good material dispersity, and regular hierarchical structure stability are probably important factors to achieve excellent HER catalytic performances. Furthermore, Tafel slopes of the samples are obtained by the linear fitting of the polarization curves, and the Tafel slopes are quite similar and lie in the region of 58–65 mV/decade for the highly dispersed nanosheets and nanosheet-based samples. As for cycling stability, it seems that the two nanosheet-based hollow porous samples may be slightly more stable than the nanosheets sample (Figure S6). Accordingly, the MoS$_{x}$ nanosheet-based hollow porous flat boxes and nanotubes have competitive catalytic performances (206–210 mV) and their performances are among the best (200–230 mV) of amorphous/quasiamorphous MoS$_{2}$ materials prepared in the liquid phase under relatively convenient conditions.$^{[14a,14b,17]}$ Moreover, the nanosheet-based hollow porous MoS$_{2}$ flat boxes and nanotubes may act as exceedingly effective supporters/templates to prepare other multifunctional catalysts.

**Conclusion**

We have synthesized MoS$_{2}$ nanosheet-based hollow porous flat boxes and nanotubes by a facile template-free water/ethanol thermal method. With 60 vol.% ethanol in the mixed solvent for the reaction, the highly dispersed black product consists of randomly packed nanosheets. As the ethanol concentration increases further, the components of the consistently highly dispersed products change from nanosheets to nanosheet-based hollow porous nanotubes and ultimately to nanosheet-based hollow porous flat boxes with increasing structural hierarchy/regularity. The presence of certain concentrations of ethanol may freeze the MoS$_{2}$ in a quasiamorphous status with specific amounts of $S_{2}^{2-}$ units and then the MoS$_{2}$ nanosheets would grow and assemble into regular hollow porous nanotubes and flat boxes. The catalytic performances of MoS$_{2}$ nanosheet-based hollow porous flat boxes and nanotubes in the hydrogen evolution reaction are outstanding, and the overpotentials to achieve $10 \text{ mA cm}^{-2}$ current are approximately 206 and 210 mV, respectively. Therefore, nanosheet-based hollow porous MoS$_{2}$ flat boxes and nanotubes are synthesized by a versatile water/ethanol thermal method, and the nanosheet-based hollow porous flat boxes and nanotubes can be used as synergistic supports/templates to prepare catalysts with heterostructures.

**Experimental Section**

**Synthesis of MoS$_{2}$ materials**

For the synthesis of MoS$_{2}$ nanosheet-based hollow porous flat boxes, sodium molybdate (20 mg; Sigma ≥99.5%) and thiourea (15 mg; Sigma ≥99.0%) were dispersed in ethanol (10 mL) by stirring for 1 h. The uniform suspension was transferred into a 25 mL PTFE-lined steel autoclave reactor, and the reactor was put into a 200 °C oven for 18 h. After reaction, the autoclave reactor was taken out to cool down naturally. The black dispersed MoS$_{2}$ nanosheet-based hollow porous flat boxes product was obtained and washed with deionized water and ethanol each for at least three times.

For the synthesis of MoS$_{2}$ nanosheet-based hollow porous nanotubes, sodium molybdate (20 mg) and thiourea (15 mg) were dissolved in a mixed solvent of ethanol (8 mL) and deionized water (2 mL). The transparent liquid was poured into a 25 mL PTFE-lined steel autoclave reactor. After heating at 200 °C for 18 h, the highly dispersed black product consisted of MoS$_{2}$ nanosheet-based hollow porous nanotubes was produced. The product was washed with deionized water and ethanol each for at least three times.

With the same amount of reactants, if ethanol (6 mL) and deionized water (4 mL) was used as the solvent for the reaction in the autoclave reactor under 200 °C for 18 h, a highly dispersed black product of randomly packed nanosheets was harvested. If even less ethanol was applied in the mixed solvent for the reaction under the same conditions, only a small amount of undispersed product of particles was obtained. All the products were washed with deionized water and ethanol at least three times each.

**Characterization**

The morphologies and structures of the materials were imaged by using SEM (Hitachi SL4800) at 3 kV and by using HRTEM (JEOL 2010F). The atomic distribution was revealed by using EDS with a CuK$_{α}$ X-ray source (λ = 1.4866 keV, line width ≈0.3 eV). To fit the high-resolution XPS curves in the Mo 3d and S 2p regions, a doublet between S 2p$_{3/2}$ and S 2p$_{1/2}$ was (1.2 eV). Raman spectroscopy was performed by using a LabRam HR8000 with a scan rate of $1 \text{ m}^{-1}$. XPS spectra were measured by using a Thermo Scientific K-Alpha XPS system equipped with a monochromatic soft A1K, X-ray source ($hν$ = 1.4866 keV, line width ≈0.3 eV). For the high-resolution XPS curves in the Mo 3d and S 2p regions, the peak area ratio of each doublet was determined according to the degeneracy of the spin state. The binding energy separation of the doublet between S 2p$_{3/2}$ and S 2p$_{1/2}$ was (1.2 ± 0.1) eV. For the electrochemical measurements, a classical three-electrode setup with a working electrode (glassy carbon), a counter electrode (Pt plate), and a reference electrode (saturated calomel electrode; SCE) was used for the electrochemical measurements of the HER. The SCE reference electrode was calibrated by using a reversible hydrogen electrode (RHE). The calibration was conducted in 0.5 M H$_{2}$SO$_{4}$, $E$(RHE) = $E$(SCE) + 0.31 V, and all the potentials in this work were referenced to the RHE. All the samples were dispersed in a mixture of solvents (80 vol.% deion-
ized water and 20 vol% ethanol) to prepare solutions of 1.32 mg mL$^{-1}$ catalyst. Then, 20 µl of each suspension was dropped onto the 5 mm diameter glassy carbon electrode and dried under ambient conditions. Linear sweep voltammetry was performed at a scan rate of 3 mVs$^{-1}$ in an electrolyte of 0.5 m sulfuric acid solution by using a Biologic potentiostat.

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**Conflict of interest**

The authors declare no conflict of interest.

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Out of the box: We diversify MoS$_x$ morphologies and structures by a facile template-free solvothermal method to prepare fascinating MoS$_x$ nanosheet-based hollow porous flat boxes and nanotubes. Catalytic measurements demonstrate that the hollow porous MoS$_x$ flat boxes and nanotubes have similar outstanding performances for the hydrogen evolution reaction and can reach 10 mA cm$^{-2}$ current at overpotentials of approximately 206 and 210 mV, respectively.