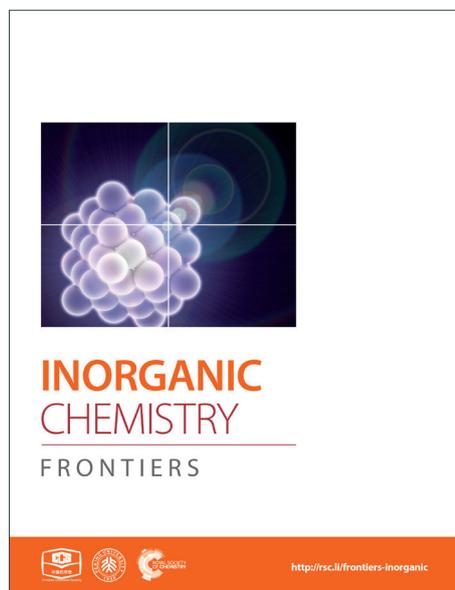
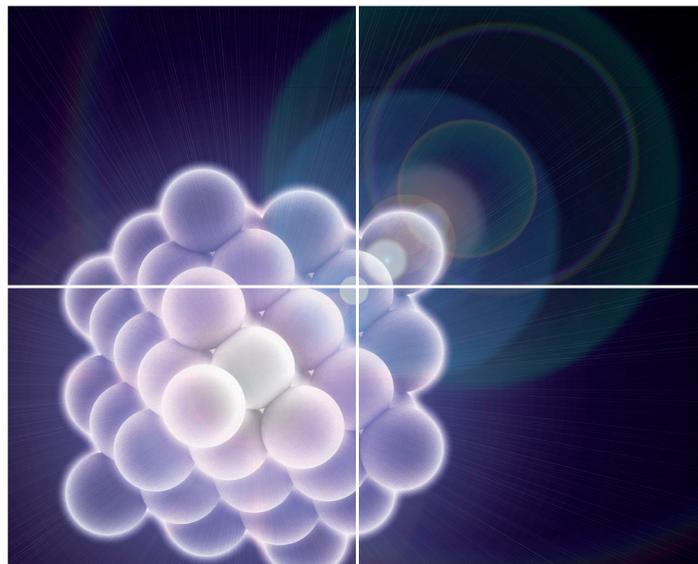


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## COMMUNICATION

## Nanosheet-Assembled MoSe<sub>2</sub> and S-doped MoSe<sub>2-x</sub> Nanostructures for Superior Lithium Storage Properties and Hydrogen Evolution Reactions

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The development of layered molybdenum chalcogenides with largely exposed active sites is receiving intense interest because of their potential applications in energy storage and catalysis. Here, we report a strategy for the synthesis of hierarchical MoSe<sub>2</sub> and S-doped MoSe<sub>2-x</sub> nanostructures resulting from the assembly of nanosheets. The incorporation of S exposes a large quantity of the active edge sites as well as abundant unsaturated sites. For example, the hierarchical S-doped MoSe<sub>2-x</sub> nanotubes show a high reversible capacity and excellent cycling performance as an anode material for lithium-ion batteries (LIB). In addition, the synthesized S-doped MoSe<sub>2-x</sub> nanosheets exhibit excellent catalytic activity and superior stability for the hydrogen evolution reaction (HER) in acidic medium. The excellent performance of S-doped MoSe<sub>2-x</sub> nanosheets has been attributed to the synergetic effect of the high density of active sites as well as the enhanced conductivity.

### Introduction

Layer-structured transition-metal dichalcogenides (TMDs), such as MoSe<sub>2</sub> and MoS<sub>2</sub>, have drawn great attention because of their interesting physical and chemical properties and wide potential applications in energy storage,<sup>1</sup> electronics,<sup>2</sup> optoelectronics,<sup>3</sup> and catalysis.<sup>4</sup> Particularly, two-dimensional (2D) and monolayered TMDs with exposed edges were demonstrated to be very promising electrocatalysts for the HER in recent years.<sup>5</sup> However, these nanosheets tend to restack seriously, which compromises their performance in many practical applications.<sup>6</sup> It has been suggested that self-assembly is considered to be one of the most efficient methods to maintain the advantages of the individual nanosheets.<sup>7</sup> As a consequence, assembling these 2D nanosheet building blocks into three-dimensional (3D) hierarchical architectures to maximize the number of edge sites and large specific surface area still remains a significant challenge.

MoSe<sub>2</sub>, as a typical layered TMDs semiconducting material, consists of Se-Mo-Se sandwich layers by weak van der Waals interactions.<sup>8</sup> Both computational and experimental results showed that catalytic active sites stem from the exposed planes on the edges rather than on the basal surfaces of nanosheets.<sup>9</sup> Besides, a high electrical conductivity of catalysts leads to faster reaction kinetic and electrocatalytic activity.<sup>10</sup> Recently, intense efforts have been devoted to increasing the density of the active sites and electrical conductivity.<sup>11</sup> Yan reported a

highly active ultrathin S-doped MoSe<sub>2</sub> nanosheets for efficient electrochemical hydrogen evolution.<sup>12</sup> Cui and coworkers synthesized vertically aligned MoSe<sub>2</sub> nanofilms on carbon fiber paper to maximally expose the active edges on the paper surface. HER activity of MoSe<sub>2</sub> has been further improved by Ni doping.<sup>13</sup> Li prepared ultrathin MoS<sub>2(1-x)</sub>Se<sub>2x</sub> alloy nanoflakes and found that alloy nanostructures showed more active HER performance than either pure MoS<sub>2</sub> or MoSe<sub>2</sub>.<sup>14</sup> These results suggest that anion-doping/substitution can be used as an effective strategy to promote the catalyst performance and to improve the electrical conductivity.

We herein report a facile bottom-up solution method to synthesize hierarchical MoSe<sub>2</sub> and S-doped MoSe<sub>2-x</sub> nanostructures resulting from the assembly of nanosheets. An interesting structural evolution from nanocaterpillars to nanosheets was observed by S-doping. The incorporation of S not only leads to a large quantity of exposed active sites, but also generates abundant unsaturated sites. Owing to the unique tubular structure with mesoporous, the obtained S-doped MoSe<sub>2-x</sub> nanotubes showed a highly reversible capacity and excellent cycling performance as an anode material for LIB. What is more, the resulting S-doped MoSe<sub>2-x</sub> nanosheets possess enhanced HER catalysis with low onset overpotential of ~95 mV and Tafel slope of 68 mV/decade, compared with MoSe<sub>2</sub> nanocaterpillars and S-doped MoSe<sub>2-x</sub> nanotubes. The enhanced catalytic activity of S-doped MoSe<sub>2-x</sub> nanosheets has

been attributed to the synergetic effect of the high density of active sites as well as the enhanced electrical conductivity.

## Experimental section

**Chemicals:** All chemicals were purchased from Sinopharm Chemical Reagent Beijing Company and were used as received without further purification. Deionized water was used throughout the experiment.

**Preparation of MoSe<sub>2</sub> nanocaterpillars:** In the synthesis of hierarchical MoSe<sub>2</sub> nanostructure, Selenium powder and ammonium molybdate are used as Se and Mo sources, respectively. A mixture of Se power (0.76 mmol) and ammonium molybdate [(NH)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] (0.05 mmol) were added in 15 mL of octylamine and 12 mL of oleyl alcohol in an 40 mL Teflon-lined autoclave under intense stirring. The sealed vessel was placed in an oven and heated at 200 °C for 12h. After cooling, the black product was washed with alcohol several times and finally dried at 60 °C by vacuum drying.

**Preparation of S-doped MoSe<sub>2-x</sub> nanosheets:** In a typical synthesis, a mixture of S power (0.32 mmol), Se power (0.76 mmol) and ammonium molybdate [(NH)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] (0.064 mmol) were added in 15 mL of octylamine and 12 mL of oleyl ethanol while other conditions are kept constant. The sealed vessel was placed in an oven and heated at 200 °C for 12h. After cooling, the black product was washed and finally dried at 60 °C by vacuum drying.

**Preparation of S-doped MoSe<sub>2-x</sub> nanotubes:** In a typical synthesis, a mixture of S power (1.08 mmol), Se power (1.27 mmol) and ammonium molybdate [(NH)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] (0.075 mmol) were added in 15 mL of octylamine and 12 mL of ethanol in an 40 mL Teflon-lined autoclave under intense stirring. The sealed vessel was placed in an oven and heated at 200 °C for 12h. After cooling, the black product was washed and finally dried at 60 °C by vacuum drying. For reparation of MoS<sub>2</sub>, MoS<sub>2</sub> were synthesized through the same process as that of S-doped MoSe<sub>2-x</sub> nanotubes except without adding Se power. All nanosheet-assembled samples were transferred to a quartz glass tube. The tube was then placed in a heating furnace and purged with Ar. The sample was calcined at 500 °C for 2 h, with a heating rate of 3 °C min<sup>-1</sup>.

## Characterization:

X-ray diffraction (XRD) characterization was carried on a Rigaku D/max-2400 X-ray diffractometer using CuK radiation ( $\lambda = 1.5418 \text{ \AA}$ ) ranging from 10° to 80° at 40 kV voltage and a 40 mA current. The morphologies and structures of the samples were determined by a HITACHI H-7700 TEM with an accelerating voltage of 100 kV, and a FEI Tecnai G2 F20 S-Twin high-resolution (HR) TEM equipped with energy dispersive spectrometer (EDS) analyses at 200 KV. The scanning electron microscope (SEM) was performed on a LEO 1530. Nitrogen adsorption/desorption measurements were conducted on a Quadasorb SI-MP instrument. X-ray photoelectron spectroscopy (XPS) experiments were conducted on scanning X-ray microprobe (Quantera SXM, ULVAC-PHI, INC) operated at 250 kV, 55 eV with monochromated Al K $\alpha$  radiation.

**Lithium ion battery measurements:** The working electrodes were prepared by mixing the samples, conductive carbon black (Super-P), and poly(vinylidene fluoride) (PVDF) at a weight ratio of 75:15:10 and pasted on pure copper foil. The slurry was

uniformly pasted onto Cu foil with a blade. The electrodes were dried at 120 °C in a vacuum oven for 12 h to remove the solvent before pressing. Cell assembly was carried out in an Ar-filled glove box with moisture and oxygen concentrations below 1.0 ppm, using lithium metal as the counter electrode. The electrolyte is 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate and diethyl carbonate (1:1 by weight). The cycling and rate performances were recorded on a LAND celltest 2001A system with a voltage of 0.01-3 V vs. Li<sup>+</sup>/Li.

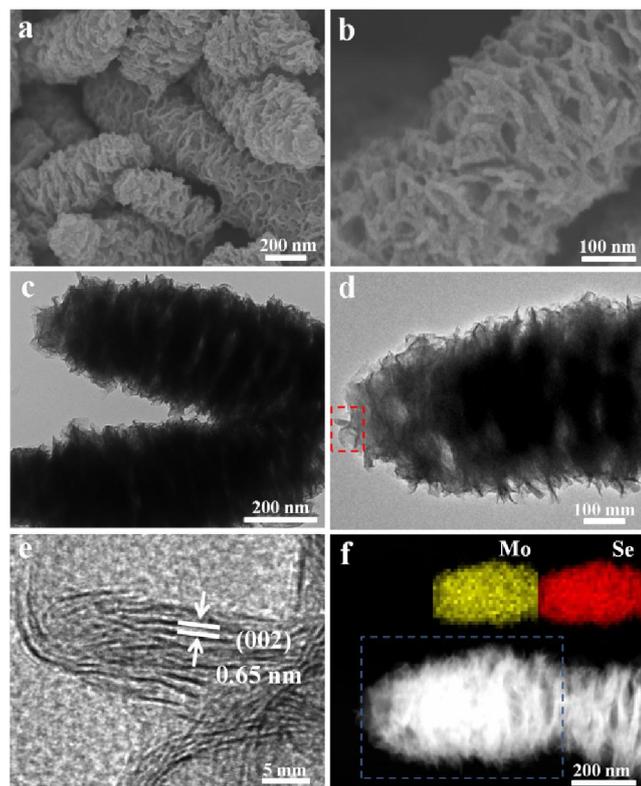
**Electrochemical Measurements:** The electrochemical measurements were conducted using an electrochemical workstation (CHI660E) in a typical three-electrode setup with an electrolyte solution of 0.5 M H<sub>2</sub>SO<sub>4</sub>, Pt plates as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Typically, 5 mg of catalyst and 50  $\mu$ L of Nafion solution (5 wt%) were dispersed in 1 mL water-ethanol solution (1:3) by sonicating for 1 h to form a homogeneous ink. Then 10  $\mu$ L of the catalyst ink was loaded onto a glassy carbon electrode of 5 mm in diameter (loading  $\sim 0.25 \text{ mg/cm}^2$ ). Linear sweep voltammetry (LS) was conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> with a scan rate of 5 mV s<sup>-1</sup>. Prior to measurement, a resistance test was made and the iR compensation was applied by using the CHI software. Electrochemical impedance spectroscopy (EIS) measurements were also carried out in the frequency range of 100 kHz–0.1 Hz using a Princeton PARSTAT P4000 of AMETEK Co. Ltd. electrochemistry workstation. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). RHE calibration was performed experimentally according to reported method. In 0.5M H<sub>2</sub>SO<sub>4</sub>, E(RHE)=E(SCE)+0.281V.

## Results and discussion

In the synthesis of hierarchical MoSe<sub>2</sub> nanostructure, selenium powder and ammonium molybdate are used as Se and Mo resources, respectively. The morphology of the sample is initially characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) at different magnifications. It is obvious to see that the products exhibit worm-like shape with a diameter of about 300 nm and a length of several micrometers (Fig. 1a-b and Fig. S1). As can be clearly seen from Fig. 1c, the obtained sample is composed of numerous curled MoSe<sub>2</sub> layers. Fig. 1e shows the typical high-resolution TEM (HRTEM) image taken from the selected area marked in Fig. 1d. The obvious lamellar structures with an interlayer spacing of 0.65 nm are observed, indicating the nature of layer structure. The HRTEM image in Fig. S2 shows that the interplanar distance between lattice fringes is 0.28 nm, which is consistent with the (100) planes of the hexagonal MoSe<sub>2</sub> phase. In addition, the selected area electron diffraction (SAED) pattern with concentric diffraction rings represents the polycrystalline structure of the sample (inset in Fig. S2). The high-angle annular dark-field scanning TEM (HAADF-STEM) and the corresponding energy-dispersive X-ray (EDX) mapping (Fig. 1f and Fig. S3) show the uniform distribution of molybdenum and selenium throughout the whole structure.

X-ray diffraction (XRD) was carried out to identify the crystallographic structure, as shown in Fig. S3. Compared with the standard values, all of the broad diffraction peaks indicate the nanoscale structure and the peaks are shifted to the left side. The obvious (002) diffraction can be attributed to the well-stacked nanosheets. The X-ray photoelectron spectroscopy (XPS) was used to further investigate the chemical states of Mo and Se in the products (Fig. S4). The peaks at 228.7 eV and

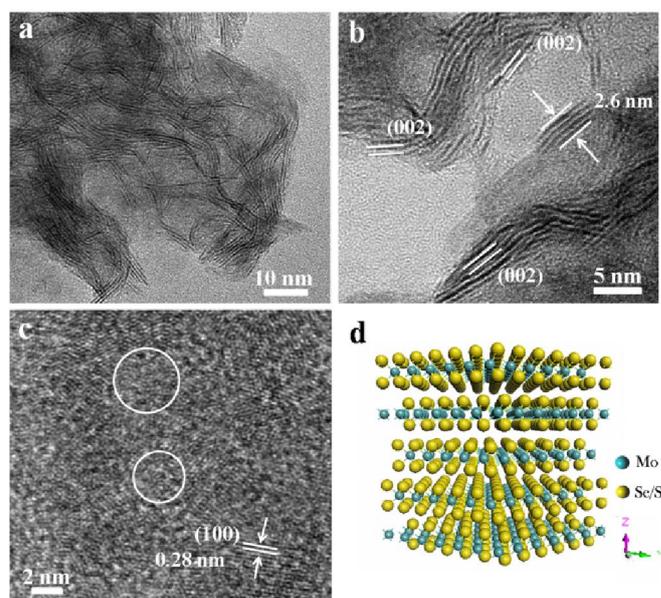
231.9 eV results from the Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub>, respectively. Whereas the peak at 55.1 eV represent the binding energies of Se 3d. The Mo 3d and Se 3d spectra indicate that the valence states of elements Mo and Se are +4 and -2,<sup>15</sup> respectively. In order to further improve the structure, the Raman spectrum was carried out, as shown in Fig. S5. The characteristic A<sub>1g</sub> and E<sub>12g</sub> Raman modes located at 236 cm<sup>-1</sup> and 280 cm<sup>-1</sup> represent the out-of-plane mode and in-plane mode of MoSe<sub>2</sub>, which confirmed the composition of the products as MoSe<sub>2</sub>.<sup>5c</sup> The corresponding Ion coupled plasma atomic emission spectrometry (ICP-AES) also shows that the atomic ratio of Mo : Se is about 1 : 2.1. These results demonstrate that nanosheet-assembled MoSe<sub>2</sub> nanostructures has been successfully prepared through this facile solvothermal method.



**Fig. 1** (a-b) SEM images of as-prepared MoSe<sub>2</sub> nanocaterpillars. (c-d) TEM and HRTEM images of MoSe<sub>2</sub> nanocaterpillars. (e) HRTEM analysis taken from the selected area marked by rectangle in (d). (f) HAADF-STEM image of MoSe<sub>2</sub> nanostructure. The insets are the corresponding EDS mapping images, which show that molybdenum and selenium are homogeneously distributed throughout the whole nanostructure.

Sulfur powder was directly added into this amine-oleyl ethanol solution, the S-doped MoSe<sub>2-x</sub> nanosheets can be obtained. Fig. S6a show the XRD pattern of S-doped MoSe<sub>2-x</sub> nanosheets. Compared with the MoSe<sub>2</sub>, it is interesting to note that the (002) peak of S-doped MoSe<sub>2-x</sub> nanosheets is diminished. In addition, the diffraction peaks at  $2\theta = 56.6^\circ$  is shifted to higher angles compared to that of pure MoSe<sub>2</sub> (Fig. S6b). Such a right shift of peaks can be ascribed to a smaller ionic radius of S.<sup>10</sup> As shown in Fig. 2a, the morphology of sample changes into a three dimensional network stemming from the disorderly assembly of nanosheets. HRTEM observation clearly reveals the formation of nanosheets with ripple structures and large quantity of exposed edge sites of the (002) plane. The thicknesses of the nanosheets are measured to be in the range of 0.65-2.6 nm with a

thickness of 2-5 atomic layers (Fig. 2b, 2d). What is more, the spacings between adjacent (002) planes were measured ranging from 6.5 Å to 7.5 Å (Fig. S7). The curvature of the edge of (002) plane is attributed to the introduction of S, which tends to expose more basal planes as terminating surface. STEM-EDX mapping image (Fig. S7c) indicates the incorporation of S in nanosheets and the uniform distribution of Mo and Se. The ICP-AES analysis also indicate that the atomic ratio of Mo : Se is 1 : 1.55, suggesting Mo-rich with a lot of Se vacancy. It is believed that this unsaturated structure results in the formation of more active edge sites. In addition, the HRTEM image in Fig. 2c shows the existence of nanodomains with polycrystalline structure in the basal plane. The nanodomains will provide additional structural defects in their basal planes because of the addition of S. Therefore, this defect-rich S-doped MoSe<sub>2-x</sub> nanosheets possess many active unsaturated Se atoms and active sites along the basal edges, which is advantageous for electrocatalytic applications.

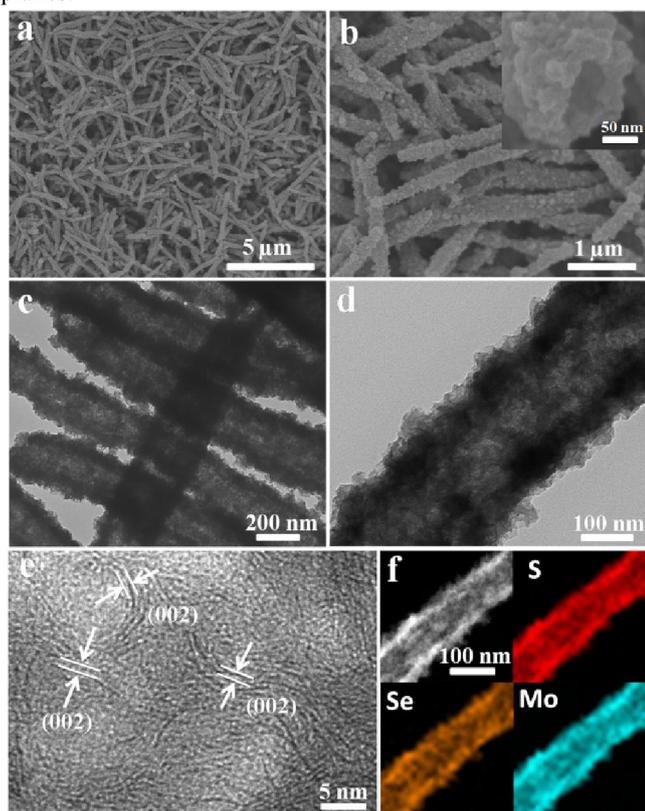


**Fig. 2** (a) TEM image of as-prepared S-doped MoSe<sub>2-x</sub> nanosheets. (b) HRTEM image of the folded edge of the stacking nanosheets with different atomic layers. (c) HRTEM image of the basal plane of the nanosheet, indicating the existence of nanodomains with random atomic arrangements. (d) The corresponding atomic stacking models in (b). Thicknesses of the curled edges are measured to be 2.6 nm.

It is worth noting that ultralong nanotube can be obtained in large quantities by increasing the amount of sulfur in amine-ethanol system. The SEM images (Fig. 3a and Fig. S8) show that the obtained nanotubes are highly uniform with a diameter about 200-300 nm and a length of 4-5 μm. A representative SEM was shown in Fig. 3b. From this cross-sectional image, the samples possess a well-defined tubular void structure with a pore size of 50 nm. The hierarchical structure was further characterized by TEM (Fig. 3c-d), which shows that the obtained nanotubes are also constructed by flexible sheet-like subunits. The HRTEM images in Fig. 3e and Fig. S8 show that these visible curled edges assembled by disordered nanosheets are measured about 0.7 nm. The EDS elemental mapping shows that the elements S, Se and Mo are uniformly distributed throughout the whole nanotubes (Fig. 3f and Fig. S9) and the ratio of Se : S is about 1.1 : 1 (Table S1). XRD analysis (Fig. S6) shows that the crystal structure of S-doped MoSe<sub>2-x</sub> nanotubes. Noted that increasing the sulfur content results in a continuous right shift

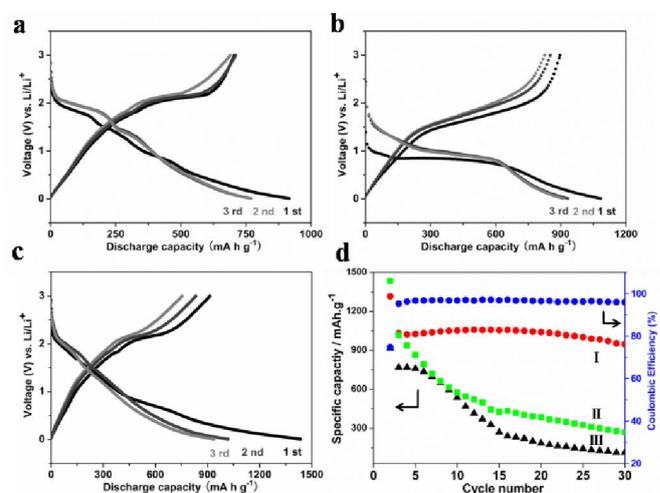
for the diffraction (110) peaks, indicating the scompaction of unit cells. Dotted lines in Fig. S6b are added to facilitate in tracking the shifting of (110) peak. This result is in agreement with the previous reports.<sup>14</sup> In order to better investigate the chemical states of S-doped MoSe<sub>2-x</sub> nanotubes, XPS analysis was carried out. As shown in Fig. S10, two characteristic peaks located at 229.1 eV and 232.4 eV can be assigned to Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub>, respectively.<sup>14, 15, 21a</sup> The binding energies of Se 3d<sub>5/2</sub> and Se 3d<sub>3/2</sub> are 54.6 eV and 55.2 eV. And the minor peak at 162.1 eV and 163.4 eV correspond to binding energies of S 2p<sub>3/2</sub> and 2p<sub>1/2</sub>, suggesting the presence of Mo-S bonding.<sup>12</sup>

It should be emphasized that alcohols are critical to form sheets-assembled architecture for amine-based synthetical system. It has been found experimentally that the assemblies depend on the dipole-dipole interactions for primary crystal nuclei, and as a result affect the interaction between nuclei and determine the initial assembly.<sup>16-17</sup> The function of various alcohols was investigated in details, For example, microspheres and irregular structure can be obtained using heptanol and ethanol while other conditions are kept constant (Fig. S11). In such synthesis systems, oleyl alcohol serves not only as the solvent, but also as a surfactant to limit the growth of the basal plane. Only a microsized structure was obtained without oleyl alcohol (Fig. S11a). With S-doping, the morphology of MoSe<sub>2</sub> changed from nanocaterpillars to nanosheets. In addition, the incorporation of S results in a large quantity of exposed active sites and generates abundant unsaturated sites in their basal planes.



**Fig. 3** (a-b) SEM images of as-prepared S-doped MoSe<sub>2-x</sub> nanotubes. The inset in b represents typical tubular structure. (c-e) TEM and HRTEM images of S-doped MoSe<sub>2-x</sub> nanotubes. (f) HAADF-STEM image and the corresponding EDS mapping images, indicating that sulphur, molybdenum and selenium are distributed throughout the whole nanostructure.

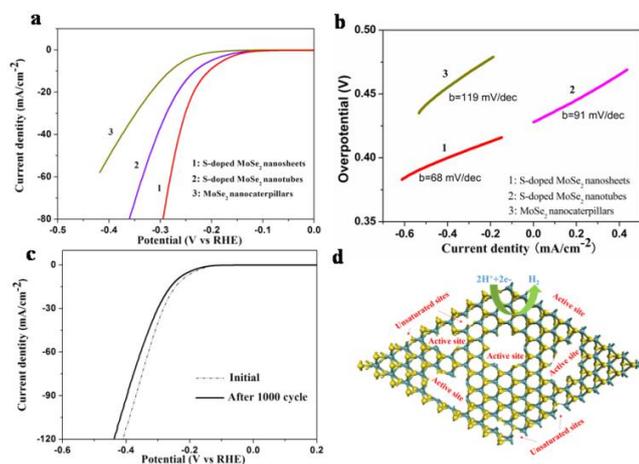
In view of the hollow structure and the ultrathin nanosheet-assembled feature, nitrogen adsorption-desorption isotherms and pore size distribution measurements were carried out to investigate the permanent porosity of the samples. Brunauer-Emmett-Teller (BET) surface area (Fig. S12) of S-doped MoSe<sub>2-x</sub> nanotubes is 49.8 m<sup>2</sup> g<sup>-1</sup> (Langmuir surface area, 72.4 m<sup>2</sup> g<sup>-1</sup>). The corresponding pore size distribution is about 30 nm and 4 nm. The later is likely associated with the channels resulting from the assembly of the nanosheets. In addition, BET specific surface area of MoSe<sub>2</sub> nanocaterpillars and S-doped MoSe<sub>2-x</sub> nanosheets are 13.3 m<sup>2</sup> g<sup>-1</sup> and 23.0 m<sup>2</sup> g<sup>-1</sup>, respectively (Fig. S12c-d). In order to get rid of the residual oleylamine and expose more active site of the samples, the as-synthesized samples were heated at 500 °C under Ar atmosphere. After annealing, the tubular morphology is still well retained (Fig. S13), indicating excellent structural stability. Given that these sheets-assembled structures have large quantities of exposed edge sites, the as-prepared samples could be useful in energy storage and electrocatalytic hydrogen evolution.



**Fig. 4** Discharge-charge curves of different samples for the 1st, 2nd, and 3rd cycles. (a) MoSe<sub>2</sub> nanocaterpillars; (b) S-doped MoSe<sub>2-x</sub> nanotubes. (c) S-doped MoSe<sub>2-x</sub> nanosheets. (d) Specific discharge capacity of S-doped MoSe<sub>2-x</sub> nanotubes (I), S-doped MoSe<sub>2-x</sub> nanosheets (II), MoSe<sub>2</sub> nanocaterpillars (III) and the coulombic efficiency of S-doped MoSe<sub>2</sub> nanotubes. The tests are conducted at a current density of 100 mA g<sup>-1</sup> between 0.01-3.0 V vs. Li/Li<sup>+</sup>.

To demonstrate the advantages of these sheets-assembled assemblies, we first evaluated their lithium storage properties as anode materials for LIBs. Fig. 4a-c show the first three discharge/charge profiles of the MoSe<sub>2</sub> nanocaterpillars, S-doped MoSe<sub>2-x</sub> nanotubes, and S-doped MoSe<sub>2-x</sub> nanosheets electrode at a current rate of 100 mA g<sup>-1</sup> between 0.01 and 3.00 V versus Li<sup>+</sup>/Li. These electrodes display similar electrochemical storage characteristics, which is very similar to those of metal dichalcogenides.<sup>18</sup> For S-doped MoSe<sub>2-x</sub> nanotubes, There are two notable voltage plateaus in the discharge-charge curves at around 0.9 V and 1.5 V, respectively, indicating the lithium insertion/de-insertion process. The corresponding CV curves of S-doped MoSe<sub>2-x</sub> nanotubes during the first three cycles are presented in Fig. S14a. The reduction peak at ~0.8 V during the first cycle may be attributed to the formation of LiMoS<sub>x</sub>Se<sub>2-x</sub>, and other peak at ~0.3 V corresponds to the conversion reaction process. These peaks disappear in the subsequent cycles with the appearance of new peaks at ~1.7 V, which is similar to the previous metal

dichalcogenides results.<sup>18</sup> The initial discharge capacity of the S-doped MoSe<sub>2-x</sub> nanotubes and S-doped MoSe<sub>2-x</sub> nanosheets electrode is 1316 and 1400 mA h g<sup>-1</sup>, which is superior to the theoretical capacity of MoSe<sub>2</sub>.<sup>18</sup> The high initial lithium discharge capacity might be attributed to the nanosheet-assembled nanoarchitecture with porous structure, which is a common phenomenon for the nanostructured anode material. A large electrode–electrolyte contact area and shortened solid-state diffusion paths for both electronic and ionic transfer allow the material to achieve a high lithium-ion intercalation capability. The obvious irreversible capacity for all samples in the initial cycle is ascribed to the formation of a solid electrolyte interface layer. As shown in Fig. 4d, the cycling performance of the above three samples electrode between 0.01 and 3.00 V were compared. Owing to the unique tubular structure, S-doped MoSe<sub>2</sub> nanotubes exhibited the highest reversible capacity of 947 mA h g<sup>-1</sup> in the 30th cycle and the correspondingly coulombic efficiency maintained about 95%. Noted that the capability of S-doped MoSe<sub>2-x</sub> nanotubes is superior to those metal dichalcogenides anodes results previously reported.<sup>19–20</sup> By contrast, the capacities of the MoSe<sub>2</sub> nanocaterpillars and S-doped MoSe<sub>2-x</sub> nanosheets decrease dramatically after 30 cycles. Moreover, S-doped MoSe<sub>2</sub> nanotubes also exhibit excellent rate capability at different current densities, as shown in Fig. S15. When the discharge/charge rate increases from 50 to 500 mA g<sup>-1</sup>, the capacity decreases from 1054 to 1020, 982, and 667 mA h g<sup>-1</sup>. Moreover, the capacity can restore about 1000 mA h g<sup>-1</sup> when the current changes into 100 mA g<sup>-1</sup>. The outstanding energy storage performance of the S-doped MoSe<sub>2-x</sub> nanotubes could be probably summarized from several aspects. Firstly, the hollow architecture not only can facilitate penetration of the electrolyte in the electrode, but also can buffer the stress caused by the volume excursions in charging and discharging reactions (Fig. S16). Furthermore, the S-doped MoSe<sub>2-x</sub> nanotubes with mesoporous may benefit the transport of Li<sup>+</sup> ions, resulting in the enhanced Li storage property.



**Fig. 5** a) Polarization curves of MoSe<sub>2</sub> nanocaterpillars, S-doped MoSe<sub>2-x</sub> nanosheets and S-doped MoSe<sub>2-x</sub> nanotubes; and (b) the corresponding Tafel plots; (c) Durability test for the S-doped MoSe<sub>2-x</sub> nanosheets after 1000 CV cycles. (d) Schematic illustration of the unsaturated edges on the nanosheet (100) basal plane and edge-rich ultrathin nanosheets for HER

The HER catalytic activity of the samples were further evaluated in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution using a rotating disc electrode (RDE) in a typical three-electrode setup on a glassy carbon electrode. Fig. 5a shows the polarization curves of the samples measured with a scan rate of 2 mV/s. The polarization

curves of S-doped MoSe<sub>2-x</sub> nanosheets exhibit high activity with a small overpotential of ~95 mV. And the overpotential is as small as 235 mV vs. RHE at a HER current of 20 mA cm<sup>-2</sup>, while the S-doped MoSe<sub>2</sub> nanotubes and MoSe<sub>2</sub> nanocaterpillars exhibited comparatively poor HRE activity with 266 mV and 318 mV, respectively. Therefore, S-doped MoSe<sub>2</sub> nanosheets are much superior in catalytic activity to MoSe<sub>2</sub> nanocaterpillars and S-doped MoSe<sub>2</sub> nanotubes. It can be inferred that S-doped MoSe<sub>2</sub> nanosheets with large quantities of exposed edge sites lead to a higher current at low overpotential.

The Tafel slopes were further investigated the intrinsic activity of all samples. The linear portions of the Tafel plots (Fig. 5b) were fit to the Tafel equation ( $\eta = b \log j + a$ )<sup>21</sup> yielding Tafel slopes of 68, 91, 119 mV per decade for S-doped MoSe<sub>2-x</sub> nanosheets, S-doped MoSe<sub>2-x</sub> nanotubes and MoSe<sub>2</sub> nanocaterpillars, respectively. The small Tafel slope usually means that hydrogen generation rate increase faster with increasing overpotential. Such a small Tafel slope of 68 mV per decade means that the rate-limiting step of S-doped MoSe<sub>2-x</sub> nanosheets was the electrochemical desorption and the Volmer-Heyrovsky mechanism.<sup>22</sup> In addition, the electrical conductivity of samples can be increased by S-doping, which confirms by electrochemical impedance spectroscopy (EIS) analysis, as shown in Fig. S17. The semicircle indicates the charge transfer resistance ( $R_{ct}$ ) of H<sup>+</sup> reduction.<sup>23</sup> The S-doped MoSe<sub>2</sub> nanosheets exhibited much lower charge transfer impedance of 176  $\Omega$  than S-doped MoSe<sub>2-x</sub> nanotubes (234.2  $\Omega$ ) and MoSe<sub>2</sub> nanocaterpillars (800  $\Omega$ ), which is consistent with the polarization measurements. The reduced impedance will provide faster electron transfer and facilitate the kinetics of the HER. The stability of the S-doped MoSe<sub>2-x</sub> nanosheets was evaluated by cycling the electrode at a scan rate of 100 mV/s. As shown in Fig. 5c, the performance of the S-doped MoSe<sub>2</sub> nanosheets after 1000 cycles showed only slight degradation compared with the fresh electrode, indicating a good cycling performance. This loss may be attributed to the consumption of H<sup>+</sup> in the solution or remaining H<sub>2</sub> bubbles on the surface of the electrode that hinder the reaction.<sup>11a,24</sup> The existence of unsaturated Se atoms and edge-rich ultrathin nanosheets are active site for proton adsorption (Fig. 5d). Therefore, a high density of active sites and good electrical conductivity of S-doped MoSe<sub>2</sub> nanosheets are responsible for the high catalytic performance.

## Conclusions

In summary, we report a facile solvothermal method method to prepare hierarchical MoSe<sub>2</sub> nanocaterpillars and S-doped MoSe<sub>2-x</sub> nanostructures. An interesting structural evolution from nanocaterpillars to nanosheets was observed by S-doping. When evaluated as an anode material for LIB, the as-synthesized S-doped MoSe<sub>2-x</sub> nanotubes manifested a high specific capacity and good cycling performance because of unique tubular structure, which is much better than that of synthesized MoSe<sub>2</sub> nanocaterpillars and S-doped MoSe<sub>2-x</sub> nanosheets. Besides, the resulting S-doped MoSe<sub>2-x</sub> nanosheets are rich in both unsaturated Se atoms as well as active sites along the basal edges, which exhibits high HER catalytic activity and good stability. Such a high performance has been attributed to the synergetic effect of the high density of active sites as well as the enhanced conductivity. The present work suggests that the catalyst performance can be enhanced by anion doping. Significantly, this effective strategy might be extended to design other MoSe<sub>2</sub>-based materials for high-performance HER catalysis and other applications.

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## References

- X. Zhang, Y. Xie, *Chem. Soc. Rev.*, 2013, **42**, 8187-8199.
- L. Jia, X. Sun, Y. Jiang, S. Yu, C. Wang, *Adv. Funct. Mater.*, 2015, **25**, 1814-1820.
- L. Zhang, H. B. Wu, Y. Yan, X. Wang, X. W. Lou, *Energy Environ. Sci.*, 2014, **7**, 3302-3306; b) F. Zhou, S. Xin, H. W. Liang, L. T. Song, S. H. Yu, *Angew. Chem. Int. Ed.*, 2014, **53**, 11552-11556.
- S. Zhuo, Y. Xu, W. Zhao, J. Zhang, B. Zhang, *Angew. Chem. Int. Ed.*, 2013, **52**, 8602-8606.
- (a) H. Vrubel, D. Merki, X. Hu, *Energy Environ. Sci.*, 2012, **5**, 6136-6144; (b) H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* 2012, **335**, 698-702; (c) L. P. Jia, X. Sun, Y. M. Jiang, S. J. Yu, C. M. Wang, *Adv. Funct. Mater.*, 2015, **25**, 1814-1820.
- M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh and H. Zhang, *Nat. Chem.*, 2013, **5**, 263-275.
- M. Xu, T. Liang, M. Shi, H. Chen, *Chem. Rev.*, 2013, **113**, 3766-3798.
- (a) D. Sun, S. Feng, M. Terrones, R. E. Schaak, *Chem. Mat.*, 2015, **27**, 3167-3175; (b) Y. N. Ko, S. H. Choi, S. B. Park, Y. C. Kang, *Nanoscale*, 2014, **6**, 10511-10515.
- J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou, Y. Xie, *Adv. Mater.*, 2013, **25**, 5807-5813.
- H. Tang, K. Dou, C. Kaun, Q. Kuang, S. Yang, *J. Mater. Chem. A.*, 2014, **2**, 360-364.
- (a) X. Zhou, J. Jiang, T. Ding, J. Zhang, B. Pan, J. Zuo, Q. Yang, *Nanoscale*, 2014, **6**, 11046-11051; (b) Z. H. Deng, L. Li, W. Ding, K. Xiong, Z. D. Wei, *Chem. Commun.*, 2015, **51**, 1893-1896; (c) Y. Jiang, X. Li, S. Yu, L. Jia, X. Zhao, C. Wang, *Adv. Funct. Mater.*, 2015, **25**, 2693-2700; (d) D. Merki, H. Vrubel, L. Rovelli, S. Fierro, X. Hu, *Chem Sci.*, 2012, **3**, 2515-2525.
- C. Xu, S. J. Peng, C. L. Tan, H. X. Ang, H. T. Tan, H. Zhang, Q. Y. Yan, *J. Mater. Chem. A.*, 2014, **2**, 360-364.
- (a) H. Wang, D. Kong, P. Johanes, J. J. Cha, G. Zheng, K. Yan, N. Liu, Y. Cui, *Nano Lett.*, 2013, **13**, 3426-3433; (b) H. Wang, C. Tsai, D. Kong, K. Chan, F. Abild-Pedersen, J. K. Nørskov, Y. Cui, *Nano Res.*, 2015, **8**, 566-575; (c) D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, *Nano Lett.*, 2013, **13**, 1341-1347.
- Q. Gong, L. Cheng, C. Liu, M. Zhang, Q. Feng, H. Ye, M. Zeng, L. Xie, Z. Liu, Y. Li, *ACS Catal.*, 2015, **5**, 2213-2219.
- H. Tang, K. Dou, C. Kaun, Q. Kuang, S. Yang, *J. Mater. Chem. A.*, 2014, **2**, 360-364.
- P. Wang, Y. Yang, J. Zhuang, X. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 6834-6837.
- P. Wang, H. Sun, Y. Ji, W. Li, X. Wang, *Adv. Mater.*, 2014, **26**, 964-969.
- (a) Y. Shi, C. Hua, B. Li, X. Fang, C. Yao, Y. Zhang, Y. Hu, Z. Wang, L. Chen, D. Zhao, G. D. Stucky, *Adv. Funct. Mater.*, 2013, **23**, 1832-1838; (b) C. Zhu, X. Mu, P. A. van Aken, Y. Yu, J. Maier, *Angew. Chem. Int. Ed.*, 2014, **53**, 2152-2156; (c) X. H. Cao, Y. M. Shi, W. H. Shi, H. Rui, Q. Y. Yan, J. Kong, H. Zhang, *Small*, 2013, **47**, 3433-3438;
- (a) K. Chang, W. X. Chen, *Chem. Commun.*, 2011, **47**, 4252-4254; (b) S. K. Park, S. H. Yu, S. Woo, J. Ha, J. Shin, Y. E. Sung, Y. Piao, *CrystEngComm.*, 2012, **14**, 8323-8325; (c) S. J. Ding, D. Y. Zhang, J. S. Chen, X. W. Lou, *Nanoscale*, 2012, **4**, 95-98.
- (a) K. Chang and W. X. Chen, *ACS Nano.*, 2011, **5**, 4720-4728; (b) S. K. Park, S. H. Yu, S. Woo, B. Quan, D. C. Lee, M. K. Kim, Y. E. Sung and Y. Piao, *Dalton Trans.*, 2013, **42**, 2399-2405.
- (a) H. Vrubel, D. Merki, X. Hu, *Energy Environ. Sci.*, 2012, **5**, 6136-6144; (b) Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 7296-7299.
- Y. Yan, B. Xia, X. Ge, Z. Liu, J. Wang, X. Wang, *ACS Appl. Mater. Interface.*, 2013, **5**, 12794-12798.
- (a) B.E. Conway, B.V. Tilak, *Electrochim Acta.*, 2002, **47**, 3571-3594; (b) B. Qu, X. B. Yu, Y. J. Chen, C. L. Zhu, C. Y. Li, Z. X. Yin, X. T. Zhang, *ACS Appl. Mater. Inter.* 2015, **7**, 14170-14175.
- J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan, Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 17881-17888.

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