Facile preparation of 3D MoS$_2$/MoSe$_2$ nanosheet–graphene networks as efficient electrocatalysts for the hydrogen evolution reaction†

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In this paper, 3D porous MoS$_2$/MoSe$_2$ nanosheet–graphene networks were successfully prepared by a simple mixing solvothermal treatment. The resulting products possessed highly conductive graphene networks on which highly exfoliated MoS$_2$/MoSe$_2$ nanosheets were decorated. This hybrid 3D architecture facilitated loading of 2D nanosheets (including some 0D quantum dots), exposure of active sites, and improvement of electron transfer between the electrode and the catalysts. The highly exfoliated and defect-rich structure of MoS$_2$/MoSe$_2$ nanosheets endowed these composites with plentiful active sites for the electrocatalysis of the hydrogen evolution reaction (HER). The MoSe$_2$ sample exhibited remarkable activity for the HER with a very small overpotential of approximately 70 mV and a low Tafel slope of 61 mV per dec, as well as excellent long-term durability. Moreover, due to the facile and relatively low-cost preparation method, our work might develop promising candidates for Pt-free HER catalysts for future commercial applications and provide an alternative facile approach to fabricate other layered materials confined in graphene hybrid 3D networks on a large scale.

Introduction

The world’s huge consumption of fossil fuels has resulted in serious energy crisis and environmental pollution. One potential way to solve these problems is to develop various types of sustainable energy conversion and storage systems. In particular, hydrogen production from electrochemical water splitting has attracted growing attention as a promising substitute for fossil fuels in the future. However, until now, the large-scale industrial application of hydrogen production has been impeded by the high cost of Pt-based catalysts and low efficiency of non-metallic materials. Therefore, the development of high-performance and cost-effective electrocatalysts for the hydrogen evolution reaction (HER) remains a major challenge.

Recently, it has been demonstrated that transition metal dichalcogenides (TMDs), such as molybdenum sulfide (MoS$_2$), tungsten disulfide (WS$_2$), molybdenum selenide (MoSe$_2$), etc., can be suitable electrocatalysts for the HER, since their hydrogen binding energy is close to that of Pt-group metals as well as their low cost and high electrochemical stability in acids. Unfortunately, the HER activity of such TMD composites is limited by intrinsic low electrical conductivity and rare active edges as well as relatively small special surface area.

In order to further improve the electrocatalytic activity, many strategies have been proposed. One approach is fabrication of layered transition metal dichalcogenide (LTMD) nanosheets to enhance the active edges and special surface area. The chemical vapor deposition (CVD) method enables us to efficiently synthesize monolayer TMDs on conductive supports and control the morphology of hybrids with impressive HER performance; however, the expensive equipment, complex procedure, and severe synthesis conditions hinder their widespread commercial applications. Although lithium intercalation is the most widely used method for the large-scale preparation of few-layer TMDs to date, in which the TMDs are exfoliated via lithium intercalation followed by a reaction with excess water resulting in force separation of the nanosheets, the drawbacks of this method is obvious. In the case of MoS$_2$ and WS$_2$, electron transfer from Li during intercalation leads to a metastable phase. Besides, the complex preparing process, their sensitivity to ambient conditions and the residual ionic species influencing their dispersibility in solution limit their large-scale use. Noticeably, a direct liquid exfoliation technique is proposed to synthesize few-layer TMD nanosheets by ultrasound sonication in solvents; compared with other methods, it is versatile, facile, green and low cost. Furthermore, the resulting dispersion can be directly deposited onto a glassy carbon electrode (GCE) substrate for the catalysis of the HER.
The second method to improve the electrocatalytic activity of TMDs is hybridization of TMDs with graphene, CNTs or metal nanoparticles to improve the electrical conductivity. Since Dai et al. first reported a MoS2/RGO (reduced graphene oxide) hybrid catalyst in 2011, it has sparked intensive research with various methods to synthesize TMDs coupled with graphene sheets. However, the most common method is solvothermally growing TMD nanoparticles on graphene usually accompanied by low HER activity, due to the difficulties in controlling the morphology of nanoparticles during the solvothermal process, that is, TMDs tend to randomly aggregate into irregular particles, which unfortunately conceal the active sites and restrain their catalytic activity for the HER. Hence, it is urgent and of considerable interest to synthesize TMD composites with controllable structure and more active sites which enables us to improve the catalytic activity.

Although plenty of studies have successfully fabricated TMD nanoparticle–graphene composites, as far as we know, reports on preparation of controllable 3D TMD nanosheet–graphene aerogels are relatively few. Chen et al. have attempted to fabricate a 3D MoS2–graphene hybrid nanostructure through hydrothermal treatment in isopropyl alcohol (IPA)/water. However, as a result of mismatched surface energies of TMDs and IPA/water, it failed to exfoliate nanosheets with a uniform few-layer height. More importantly, during the subsequent solvothermal process, IPA tends to evaporate due to its low boiling point, and thus it is incapable of further cutting the nanosheets into a defect-rich structure to provide more active sites for the HER. Consequently, the resulting 3D architecture is mainly endowed with high reversible capacity instead of effective HER activity. In contrast, according to our previous investigation, some high boiling point solvents, like N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), show strong exfoliation ability toward TMDs. Moreover, the solvothermal effect of these high boiling point solvents can not only keep the few-layer structure of TMDs but also cut these nanosheets into quantum dots to form a defect-rich structure which is beneficial to catalytic activity. Hence, if these nanosheets can be hybridized with highly conductive supports, the catalytic activity of these composites for the HER should be very remarkable.

Herein, we directly integrate 2D graphene with LTMDs (MoS2 and MoSe2) into a 3D hybrid architecture by a mixed solvothermal treatment with NMP/water, in which the MoS2 and MoSe2 nanosheets of different lateral sizes assemble into a unique stack structure (i.e., some quantum dots interspersed in the nanosheets) and decorate on the highly conductive graphene network. The smaller size of MoS2 and MoSe2 nanosheets (including quantum dots) makes these catalysts possess a defect-rich structure which is beneficial to catalytic activity toward the HER. And with the electrical coupling effect on the highly conductive graphene substrates, it facilitates the electrical contact with the active sites. Moreover, the 3D porous interconnected network with high specific area, which provides an ideal matrix to load MoS2 and MoSe2 nanosheets and enhances the exposure of the active sites of MoS2 and MoSe2, also plays a crucial role in electrocatalytic activity with low overpotential and long-term durability toward the HER. The overpotential of MoSe2 hybrid aerogels is 70 mV which is very close to that of the commercial Pt-based catalysts to date. In addition, since the preparation method is versatile, facile and cost-effective, this work might provide a high-performance HER candidate and indicates a significant prospect for its further commercial applications.

Experimental section

Materials

MoS2 and MoSe2 were purchased from Alfa Aesar Corporation. Expandable graphite powders and potassium permanganate were purchased from Aladdin Industrial Corporation. NMP, H3PO4 (85 wt%), H2O2 (30 wt%), HCl (36 wt%) and H2SO4 (98 wt%) were supplied from Sinopharm Chemical Reagent Co. Ltd. Nafion solution (5 wt%) was purchased from Sigma-Aldrich. All reagents were of analytical grade and used without further purification. N2 with a purity of 99.9% was purchased from Shanghai Jifu Gas Co. Ltd.

Preparation of GO

GO was prepared by a slight modification method reported by Marcano et al. Briefly, 5 g of expandable graphite powder was dispersed in a mixture of 200 mL of H2SO4 and 40 mL of H3PO4 with magnetic stirring at a temperature below 10 °C for 30 min, followed by the slow addition of potassium permanganate (25 g). Then the temperature was increased to 40 °C and maintained for 4–5 h with vigorous stirring. After oxidation, the dark brown mixture was allowed to reach room temperature and then poured slowly in 600 mL of cold water followed by 40 mL of 30 wt% H2O2. The resulting suspension was filtered, washed with 5 wt% HCl, and dialyzed for a week to remove the remaining metal species. The GO aqueous dispersion was diluted to 8 mg mL−1 aqueous solution before being used.

Preparation of MoS2/MoSe2 nanosheets

Bulk MoS2/MoSe2 powder was directly exfoliated to nanosheets by a solvent exfoliation method. Typically, 1 g of MoS2/MoSe2 powder and 100 mL of NMP were added into a 150 mL serum bottle and kept under sonication for 8 h by using a sonicator (KQ5200DB) with an output power of 250 W to exfoliate the bulk MoS2/MoSe2 powder. Then the dispersion was kept undisturbed overnight and the few-layer MoS2/MoSe2 nanosheet suspension was collected. The concentration of MoS2 and MoSe2 nanosheet suspension is 0.5 g L−1 and 1.2 g L−1, respectively.

Preparation of MoS2/MoSe2–graphene hybrid aerogels

MoS2/MoSe2–graphene hybrid aerogels were synthesized by a facile solvothermal process followed by freeze-drying. Typically, 10 mL of GO aqueous solution (8 mg mL−1) was mixed with different amounts of NMP suspension of MoS2/MoSe2 nanosheets and then sealed in Teflon autoclaves at 180 °C for 24 h to obtain hybrid gels. After cooling to room temperature, the gels were immersed in de-ionized water for 5 days to remove the remaining NMP. The obtained hydrogels were quenched...
in liquid nitrogen and then freeze dried for 48 h to obtain the hybrid aerogels. The amounts of MoS$_2$ nanosheet suspension were 1 mL, 3 mL, 6 mL, 10 mL, 15 mL and 20 mL, while the amounts of MoSe$_2$ nanosheet suspension were 1 mL, 3 mL, 6 mL, 10 mL, 15 mL, 20 mL, 25 mL, 30 mL and 40 mL, and the as-prepared samples were marked as MoS$_2$-1, MoS$_2$-3, MoS$_2$-6, MoS$_2$-10, MoS$_2$-15, MoS$_2$-20, MoSe$_2$-1, MoSe$_2$-3, MoSe$_2$-6, MoSe$_2$-10, MoSe$_2$-15, MoSe$_2$-20, MoSe$_2$-25, MoSe$_2$-30 and MoSe$_2$-40, respectively.

Electrochemical measurements

Electrochemical measurements were carried out with a standard three-electrode cell using Ag/AgCl (in 3 M KCl solution) as a reference electrode and a platinum wire as a counter electrode. 1 mg of sample was first ultrasonically dispersed in 300 µL of Nafion solution (5 wt%), then the suspension (~10 µL) was attached onto a glassy carbon (GC) electrode with 3 mm diameter as a working electrode. For comparison, pure MoS$_2$/MoSe$_2$ nanosheets and commercial Pt (20 wt% Pt/C) catalysts were also measured as reported in our previous work. Typically, 5 µL of MoS$_2$/MoSe$_2$ nanosheet suspension or the commercial Pt catalyst was also dropped onto the glassy carbon electrode, and 5 µL of Nafion solution (5 wt%) was coated. After the suspension was dried, linear sweep voltamperometry (LSV) was performed in 0.5 M H$_2$SO$_4$ solution de-aerated with N$_2$ with a scan rate of 50 mV s$^{-1}$. The polarization curves and the Tafel slopes are not iR corrected. Electrochemical impedance spectroscopy (EIS) measurements were performed as reported before, from $10^6$ to 0.1 Hz at $\eta = 0.53$ V with an alternating current voltage of 10 mV. Cyclic Voltammetry (CV) measurements were performed in a potential range of 0.15–0.25 V vs. RHE according to a previous report.

Characterization

The transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were taken with a JEOL JEM2011 at 200 kV equipped with selected area electron diffraction (SAED). Field emission scanning electron microscope (FESEM) observations were performed on a Zeiss Ultra 55 with an energy dispersive X-ray spectroscopy (EDX). Atomic force microscopy (AFM) images were obtained by using a Multimode V8 in the tapping mode after the samples were deposited on a freshly cleaved mica surface by spin coating. X-ray photoelectron spectroscopy (XPS) spectra were acquired by using a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K$\alpha$ radiation ($hv = 1253.6$ eV). X-ray powder diffraction (XRD) data were acquired by using a D8 ADVANCE and DAVINCI.DESIGN (Bruker) X'pert diffractometer with Cu K$\alpha$ radiation. Raman spectra were recorded on an Xplora Laser Raman spectrometer equipped with a 638 nm helium/neon laser and a CCD detector. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer. Thermogravimetric analysis (TGA) was carried out at a heating rate of 20 K min$^{-1}$ on a Perkin-Elmer Pyris-I TGA in nitrogen at a flow rate of 40 cm$^3$ min$^{-1}$. The electrical conductivity of the aerogels was determined via a four-probe method on ST2263 double electrical logging digital Four-Point Probes (Suzhou Jingege electron Company, China).

Results and discussion

Preparation and characterization of MoS$_2$/MoSe$_2$-graphene hybrid aerogels

MoS$_2$/MoSe$_2$-graphene hybrid aerogels were fabricated via a mixed solvothermal method. During this process, graphene oxide (GO) sheets were reduced by the synergistic reduction effect of supercritical H$_2$O and NMP and assembled 3D porous architectures. Meanwhile, MoS$_2$/MoSe$_2$ nanosheets were able to uniformly decorate on graphene sheets due to the intersolvability of H$_2$O and NMP, as illustrated in Scheme 1. More details of the synthesis procedure can be found in the Experimental section. Transmission electron microscopy (TEM) images confirm that MoS$_2$/MoSe$_2$ nanosheets uniformly and tightly decorate on graphene sheets, and thus the 3D MoS$_2$/MoSe$_2$-graphene hybrid nanostructure was successfully prepared, as shown in Fig. 1 and 2. Apparently, abundant as-prepared MoS$_2$/MoSe$_2$ nanosheets have a thin and layered structure, indicating MoS$_2$ and MoSe$_2$ were efficiently exfoliated by sonication in NMP. The atomic force microscopy (AFM) images show that the height of MoS$_2$/MoSe$_2$ nanosheets is 1–4 nm after exfoliation, confirming that the layers of MoS$_2$/MoSe$_2$ nanosheets are less than 6 layers (Fig. S1†). The lateral sizes of these nanosheets are in a wide distribution, ranging from 15 to 200 nm for MoS$_2$ and from 5 nm to 150 nm for MoSe$_2$ (Fig. 1a and 2a). Moreover, for the larger nanosheets, the highly paralleled and ordered lattice fringe indicates that the larger MoS$_2$/MoSe$_2$ nanosheets are well crystallized (Fig. 1b, c, 2b and c). The sharp, single-crystalline selected area electron diffraction (SAED) patterns also demonstrate that the larger MoS$_2$/MoSe$_2$ nanosheets are well crystallized. The interlayer distance of MoS$_2$ nanosheets is 0.27 nm, corresponding to the (100) reflection index of MoS$_2$ crystals, as well as the interlayer distance of MoSe$_2$ nanosheets is around 0.285 nm, which also matches well with the (100) lattice spacing of 2H–MoSe$_2$.

In addition to the larger nanosheets, there are plenty of smaller nanosheets or quantum dots adsorbed on graphene sheets; their size is smaller than 20 nm (Fig. 1d and 2d). Besides, some of the smaller nanosheets (including quantum dots) are also interspersed in the larger nanosheets. In our previous work, we have demonstrated that the solvothermal treatment can incise MoS$_2$ nanosheets into quantum dots. Therefore, these smaller nanosheets (quantum dots) probably resulted from the solvothermal effect. The HRTEM images also show that these smaller nanosheets (quantum dots) are crystallized with a clear and highly paralleled lattice fringe. Their interlayer distances are 0.27 and 0.285 nm, respectively, corresponding to the (100) reflection index of MoS$_2$ crystals.
successful preparation of MoS₂ or MoSe₂–graphene hybrid aerogels (Fig. 1d, 2d and e).

According to the TEM images, it is observed that the morphology and nanostructure of MoS₂ and MoSe₂–graphene hybrid aerogels are almost the same; however, one distinct difference between the samples should be noted: the lateral size of smaller MoSe₂ nanosheets (5 nm) is even much smaller than that of MoS₂ nanosheets (15 nm), as well as the amount of smaller MoSe₂ nanosheets is much more than that of smaller MoS₂ nanosheets. In some regions of the MoSe₂-20 sample, only smaller nanosheets or quantum dots can be observed on graphene sheets. As shown in Fig. S2† their size is less than 10 nm with a clear lattice fringe, the interlayer distance is 0.285 nm which is well consistent with larger MoSe₂ nanosheets. As discussed below, smaller nanosheets (or quantum dots) with more defect edges probably result in more active sites and enhanced catalytic activity for the HER.

The nanostructures of the MoS₂/MoSe₂–graphene hybrid aerogels were further characterized by field emission scanning electron microscopy (FESEM). According to Fig. 3, the structures of MoS₂–graphene aerogels (MoS₂-20) with interconnected pores ranging from several nanometers to several micrometers are similar to MoSe₂–graphene aerogels (MoSe₂-20). The specific surface area of MoS₂-20 and MoSe₂-20 is 180 and 260 m² g⁻¹ (Brunauer-Emmett-Teller (BET) method), which is higher than the pure graphene aerogel (GA) prepared under the same condition (Fig. S3†). The enhancement of specific surface area probably resulted from the hybridization of MoS₂/MoSe₂ nanosheets in graphene aerogels. The wrinkled paper-like graphene sheets construct a 3D architecture, which provides multiple effective electron transfer paths among 2D sheets and reduces transport limitation of the electrolyte at the cathode.38,39,46 Besides, the enlarged SEM images show that the MoS₂/MoSe₂ nanosheets are homogeneously and densely confined in these frameworks, no apparent aggregates can be observed. This unique 3D functional architecture not only promotes the exposure of the active edge sites of MoS₂/MoSe₂ nanosheets, but also

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**Fig. 1** TEM images of MoS₂–graphene hybrid aerogel (MoS₂-20). (a) is the panoramic TEM image; (b) is the TEM image of larger MoS₂ nanosheets; (c) is the HRTEM image of (b); (d) is the TEM image of smaller MoS₂ nanosheets; (e and f) are the HRTEM images of (d). The inset of (c) and (e) is the corresponding SAED pattern.
improves the electrical contact with these active edge sites, thereby greatly enhancing the electrocatalytic activity.

Based on the energy dispersive X-ray spectroscopy (EDX) measurements, the Mo, S/Se and C elements are clearly evidenced in the 3D hybrid aerogels (Fig. S4 and S5†). The elemental mapping images show that MoS₂/MoSe₂ nanosheets are uniformly distributed on graphene aerogels, which is well identified with the results of the FESEM image. Noticeably, the N elements are also observed in EDX patterns, it should be attributed to the doping of N on graphene during the solvothermal treatment in NMP and residue of NMP after dialysis. The contents of MoS₂ and MoSe₂ nanosheets are also calculated, the loading contents of MoS₂ and MoSe₂ nanosheets are 36.41 wt% (Mo and S total element contents) and 16.58 wt% (Mo and Se total element contents), relatively, which indicate the successful hybridization of these 2D nanosheets and the graphene aerogel. The lower content of MoSe₂ nanosheets on the graphene aerogel probably results from the weaker binding ability of dispersed MoSe₂ nanosheets.

To further investigate the morphology of MoS₂/MoSe₂ nanosheets interspersed in the aerogels, the as-prepared aerogels (MoS₂-20 and MoSe₂-20) were ultrasonically dispersed in de-ionized water and spin-coated on a freshly cleaved mica surface for AFM measurements (Fig. 4a and d). It also reveals that the 3D porous architecture of hybrid aerogels is constructed by graphene sheets and MoS₂/MoSe₂ nanosheets, which matches well with the high contrast images obtained by scanning transmission electron microscopy (STEM, Fig. 4c and f). Moreover, in AFM images, we can find there are smaller MoS₂/MoSe₂ nanosheets (including quantum dots) decorated on larger MoS₂/MoSe₂ nanosheets, which is well consistent with the TEM results. This structure is able to enlarge the exposed surface area and enhance the active site density, which is beneficial to the overall catalytic activity for the HER. The height of MoS₂/MoSe₂ nanosheets on the aerogel is about 3–5 nm, which is consistent with that of the as-prepared pure MoS₂/MoSe₂ nanosheets, indicating that MoS₂/MoSe₂ nanosheets would not randomly aggregate during the solvothermal process (Fig. 4b and e) and thus it avoids to conceal active sites. Therefore, these layered structures of MoS₂/MoSe₂–graphene
hybrid aerogels are different from MoS2/MoSe2 nanoparticles grown on graphene via bottom-up methods.\textsuperscript{20,37,48} X-ray photoelectron spectroscopy (XPS) measurements were also carried out to analyze the chemical composition of the hybrid aerogels and the chemical state of MoS2/MoSe2. In the spectra of MoS2-20 and MoSe2-20, distinct C 1s, N 1s, O 1s, Mo 3d and S 2p (Se 3d) peaks appear at 285.3, 400.7, 532.0, 229.3 and 162.2 (54.5) eV, respectively (Fig. S6a and b). The results of the high resolution C 1s spectra show the good reduction of GO after solvothermal treatment, which is also confirmed by Fourier transform infrared spectroscopy (FTIR) spectra (Fig. 5a, b and S7).\textsuperscript{49} Moreover, thermogravimetric analysis (TGA) results in Fig. S8 show that mass-loss peaks of graphene oxide located at 200–300 °C are suppressed with the addition of the MoS2 (MoSe2)/NMP suspension, that is, the amount of oxygen-functional groups in GO are decreased with the incorporation of NMP. This is probably due to the fact that the oxygen-scavenging property of NMP enables the further reduction of GO and thus renders hybrid aerogels highly conductive.\textsuperscript{49} which is also confirmed by electrochemical impedance spectroscopy (EIS) and electrical conductivity measurements as discussed below. According to the EDX results, there is a trace amount of nitrogen doped in the hybrid aerogels probably due to the incorporation of NMP in the mixing solvothermal procedure (Fig. S4 and S5). This result is confirmed by XPS, the high resolution N 1s reveals that some of the N in the composites is converted to pyridinic-like N, which demonstrates the doping of N in graphene sheets during the reduction process (Fig. S6e and f).\textsuperscript{49} It is worthwhile to notice that NMP acts as two significant roles in the mixing solvothermal process: (1) it facilitates to reduce GO due to its oxygen-scavenging property and dope N in graphene sheets, which results in a highly conductive network and improvement of electron transfer between the catalytic sites and the electrode;\textsuperscript{49} (2) as a result of its high boiling point (203 °C), the solvothermal effect of NMP is in favor of not only cutting the as-prepared nanosheets into smaller sizes (quantum dots) with increasing number of active sites but also resulting in a unique stack structure with high active site density.\textsuperscript{49}

As for the chemical state of MoS2/MoSe2 nanosheets in the hybrid aerogels, a small peak located at 235.9 eV is ascribed to partially-oxidative Mo edges (Mo(IV)) during the MoS2 exfoliation and mixing solvothermal process, which suggests a defect-rich structure of the nanosheets (Fig. 5c).\textsuperscript{37} The obvious and sharp peaks at 229.3 and 232.6 eV are assigned to Mo\textsuperscript{4+} 3d\textsubscript{5/2} and Mo\textsuperscript{4+} 3d\textsubscript{3/2} of MoS2 nanosheets, respectively, demonstrating that most of the MoS2 are undamaged. And a peak at 226.6 eV is ascribed to S 2s, while the S 2p peak is split into well-defined 2p\textsubscript{3/2} and 2p\textsubscript{1/2} peaks at 162.2 and 163.4 eV in the high-resolution spectrum of S (Fig. 5e).\textsuperscript{37} In the MoSe2-20 sample (Fig. 5d and f), a similar chemical state of Mo is observed. The peaks at 229.0 (Mo\textsuperscript{4+} 3d\textsubscript{5/2}) and 232.2 eV (Mo\textsuperscript{4+} 3d\textsubscript{3/2}) confirm that the molybdenum is basically in its Mo(IV) state, and a small peak of Mo\textsuperscript{6+} (235.4 eV) is also originated from the slight oxidation of Mo edges. And the peaks at 54.5 and 55.3 eV in the high-resolution spectrum of Se are attributed to Se 3d\textsubscript{5/2} and Se 3d\textsubscript{3/2}, respectively. Both results show that the MoS2 and MoSe2 nanosheets on the graphene aerogel are 2H phase crystals.\textsuperscript{37}

**Fig. 4** AFM (a and d) and STEM (c and f) images of MoS2-20 (top row) and MoSe2-20 (bottom row). (b) and (e) are the height of MoS2 and MoSe2 nanosheets in (a) and (d).

**Fig. 5** XPS spectra of MoS2-20 (left column) and MoSe2-20 (right column). (a) and (b) are the high resolution C 1s XPS spectra; (c) and (d) are the high resolution Mo 3d XPS spectra; (e) is the high resolution S 2p XPS spectra; (f) is the high resolution Se 3d XPS spectra.
nаносheets loaded on graphene aerogels (Fig. S9 and S10†). From the SAED patterns, when the dosage of MoS2/MoSe2 is only a little, the aureole is very dim. With the increase of MoS2/MoSe2, the aureole becomes bright and clear and plenty of independent facula appear. The FESEM images also show that the content of MoS2/MoSe2 nanosheets loaded on graphene aerogels increases with the enhancement of initial dosage of the MoS2/MoSe2 suspension and the nanosheets are still segregated and uniformly distributed on graphene when the dosage of MoS2/MoSe2 is very high (Fig. S11 and S12†).

The crystal structures of MoS2/MoSe2 nanosheets in these as-prepared hybrid aerogels were systematically investigated by X-ray diffraction (XRD) patterns (Fig. 6a and b) and Raman spectra (Fig. 6c and d). After solvothermal treatment, the diffraction peak of GO at 2θ = 11.5° disappears, instead, a broad peak at 2θ of ~24° present in all of the samples corresponds to the stacking-related C{002} diffraction peaks of graphite, indicating an amorphous structure and the good exfoliation and reduction of GO sheets (Fig. S13a†).† In Fig. 6a, a very strong diffraction peak at 2θ = 14.4° and two lower peaks at 2θ = 39.6° and 2θ = 49.8° are assigned to (002), (103), and (105) reflection indices of 2H–MoS2, respectively (JCPDF 37-1492).† Importantly, all of the peaks are broadened compared with raw MoS2, indicating that most structures of MoS2 in the composites are nanosheets, which is well consistent with the previous results of TEM and AFM images (Fig. 1–3). The XRD patterns of MoSe2–graphene aerogels are very similar to those of MoS2–graphene aerogels. Three main peaks at 13.7, 37.8, and 47.5° are assigned to (002), (103) and (105) reflection indices of hexagonal 2H–MoSe2 (JCPDF 77-1715) [Fig. 6b].† And these peaks are also broadened compared with raw MoSe2. Interestingly, the intensity of diffraction peaks is significantly enhanced with the increase of MoS2/MoSe2, indicating that much more MoS2/MoSe2 is hybridized in graphene aerogels.

Raman analysis is regarded as a universal and facile measurement to characterize the layered materials. As we know, for graphitic derivatives, the D band is assigned to the disordered carbon, defects and edges, while the G band is attributed to the ordered sp²-bonded carbon (Brillouin zone center E²g mode). According to the Raman spectra, the G band of GO at 1588 cm⁻¹ shifts to 1591 cm⁻¹ as well as the intensity ratio of D/G (I_D/I_G) increases from 1.01 to 1.15, suggesting the decrease of sp² domains during the reduction of GO in the solvothermal process (Fig. S13b†).† The Raman spectrum of MoS2 powder is well known with two main modes, the out-of-plane A1g and the in-plane E1g vibrational modes, located at ~408 and ~383 cm⁻¹, respectively. In this work, the A1g and E1g peak of MoS2–graphene hybrid aerogels shift to 405 and 381 cm⁻¹ (Fig. 6c). Previous work has demonstrated that the A1g peak of MoS2 would redshift with the decrease of layers. Therefore, the A1g peak at 405 cm⁻¹ indicates the bi-layer or tri-layer structure of these MoS2 nanosheets. As for the MoSe2 samples, the Raman modes A1g of MoSe2 are identified at 238.5 cm⁻¹, also showing a redshift compared with bulk MoSe2 materials, it suggests that 2H–MoSe2 nanosheets are decorated in the hybrid aerogels (Fig. 6d). While the absence of the in-plane (E1g) mode is probably due to a high intensity ratio between the A1g and E1g modes, also indicating a fewer-layer structure and relatively weak layer–layer interactions in the MoSe2 samples. Noticeably, the intensity of diffraction peaks of MoS2/MoSe2 is also significantly enhanced with the increase of MoS2/MoSe2 dosage, which is identified with XRD.

Electrocatalytic properties of MoS2/MoSe2–graphene hybrid aerogels

As a typical application, MoS2/MoSe2–graphene hybrid aerogels were explored as electrocatalysts for the HER. The HER activity of these materials was measured using the standard three electrode electrochemical configuration in the N2 saturated 0.5 M H2SO4 electrolyte with a scan rate of 50 mV s⁻¹. For comparison, pure MoS2/MoSe2 nanosheets and commercial Pt (20 wt% Pt/C) catalysts were also included. As seen in the polarization curves (Fig. 7a), the pure graphene aerogel exhibits almost no HER activity. However, for the hybrid aerogels, when only 1 mL of MoS2 nanosheet suspension is added, the onset potential of hybrid aerogels shifts to ~350 mV which is close to that of pure MoS2 nanosheets (Fig. S14†). With the increase of MoS2 nanosheets, the onset potential of hybrid aerogels shifts to a much lower value. Especially, upon the addition of 10 mL of MoS2 NMP suspension, the overpotential value is close to ~130 mV which is comparable to or even smaller than that of the many monolayer or few-layer MoS2 nanosheets. Thus it demonstrates that MoS2 nanosheets are the core catalyst with abundant active edges for the HER while graphene sheets provide a conductive substrate for them. With the further addition of MoS2, although the current density is improved, the onset potential only slightly shifts, i.e., the onset potential shifts from ~130 mV for MoS2-10 to ~115 mV for MoS2-20. Undoubtedly, it suggests that the aerogel has already carried an adequate load of MoS2 nanosheets when the MoS2 NMP suspension is approaching 10 mL.

Compared with MoS2–graphene hybrid aerogels, MoSe2–graphene hybrid aerogels manifest a similar tendency toward the HER and seem to share the same catalysis mechanism (Fig. 7b). MoSe2–graphene samples have even higher HER activity than MoS2–graphene samples. It might be due to the smaller band gap in MoSe2 accompanied by the inherent superior catalytic activity of MoSe2 nanosheets and smaller sizes (more quantum dots) affording more active edge sites as observed in Fig. 1 and 2. When only 1 mL of MoSe2 nanosheet suspension is hybridized in the graphene aerogel, the onset potential exhibits a sharp positive shift to ~120 mV which is close to the MoS2-10 sample and much more positive than the MoS2-1 sample and pure MoSe2 nanosheets (~220 mV). With the increase of MoSe2 nanosheets on the graphene aerogel, the onset potential further shifts to ~70 mV, which is comparable to or even better than many MoSe2 composites.

The impressive catalytic activity of hybrid aerogels is probably attributed to the synergistic effect of three factors. As seen in the TEM and AFM images (Fig. 1, 2, 4a and d), the adequate addition of MoS2/MoSe2 nanosheets is in favor of increasing the number of active sites of the catalysts. And it is worthwhile to notice that some smaller MoS2/MoSe2 nanosheets (including
some quantum dots) stack on larger nanosheets during the solvothermal procedure, which results in an unique stack structure with higher edge/basal ratios (i.e., more edge sites in a specific size of the basal plane), and hence improves the density of active sites for the HER. Moreover, the electrical coupling between the underlying graphene sheets and the active sites also play a crucial role in improving the integral catalytic activity. Especially with the incorporation of NMP suspension, it facilitates to form highly conductive networks and thus reduces electronic transfer limitations, as discussed in TGA, EDX and XPS results and further confirmed in EIS and electrical conductivity results (Fig. S15† and S16†). Nyquist plots reveal an obvious decrease in charge-transfer resistance ($R_{ct}$) for the hybrid aerogel with the incorporation of NMP (i.e., the $R_{ct}$ of MoS$_2$-20 is 17 $\Omega$ and the $R_{ct}$ of MoSe$_2$-40 is 14 $\Omega$) compared to the graphene aerogel (25 $\Omega$) (Fig. S15†), which is in line with the electrical conductivity results (Fig. S16†). Moreover, the electrochemical active surface area is also obviously enhanced with the increase of MoS$_2$/MoSe$_2$ NMP suspension (Fig. S17, Tables S1 and S2†). These results demonstrate that the synergistic reduction effect of NMP indeed enables effective electrical integration and improves the charge transfer efficiency. Besides the intrinsic activity of MoS$_2$/MoSe$_2$ nanosheets, the 3D interconnected porous aerogel network is also a probable reason for the high activity of the HER, in which it efficiently enlarges the exposed surface area of active sites.

As an intrinsic property of the electrocatalyst materials, the Tafel slope, which is associated with the rate-limiting step of the HER, has also been driven from Tafel plots where their linear portions are fit well with the Tafel equation ($\eta = b \log j + a$, where $j$ is the current density and $b$ is the Tafel slope). As shown in Fig. 7c, the Tafel slope of commercial Pt (20 wt% Pt/C) is $\sim 33$ mV per dec, which is close to previous work. For the Tafel plots in the MoS$_2$-1 sample, the Tafel slope is 159 mV per dec which is even worse than pure MoS$_2$ nanosheets, since the amount of MoS$_2$ nanosheets is only a little and the catalytic activity is affected by the graphene aerogel. This result is well consistent with the polarization curves. When the dosage of MoS$_2$ nanosheets is increased to 20 mL, as we have mentioned before, the aerogel has already carried an adequate load of MoS$_2$ nanosheets and the Tafel slope shifts to 71 mV per dec which is comparable to other MoS$_2$ catalysts.\footnote{18,51}

Fig. 6 XRD patterns (top row) and Raman spectra (bottom row) of MoS$_2$–graphene hybrid aerogels (a and c) and MoSe$_2$–graphene hybrid aerogels (b and d) prepared with different dosages of MoS$_2$ and MoSe$_2$: (I) 1 mL; (II) 3 mL; (III) 6 mL; (IV) 10 mL; (V) 15 mL; (VI) 20 mL; (VII) 25 mL; (VIII) 30 mL; (IX) 40 mL. The parameters of crystal are referenced to JCPDF (37-1492) and (77-1715).
According to theoretical calculations, the Gibbs free energy for hydrogen adsorption onto MoSe₂ edges is lower than that of MoS₂ and thus results in higher coverage of hydrogen adsorption. Moreover, many studies have demonstrated that MoSe₂ has higher intrinsic electrical conductivity than MoS₂ since the more metallic nature of Se, the unsaturated Se-edges in MoSe₂ is more electrocatalytically active and beneficial for the HER. In our work, the Tafel slope of pure MoSe₂ nanosheets is about 88 mV per dec, which is much lower than pure MoS₂ nanosheets, indicating the more excellent catalytic activity of MoSe₂. For the MoSe₂-1 sample, although the onset potential has a positive shift, the Tafel slope is almost unchanged (91 mV per dec) or even worse than pure MoSe₂, which also resulted from the content of MoSe₂ nanosheets on graphene aerogel nanosheets that is very little. While the dosage of MoSe₂ nanosheets is enhanced to 40 mL, the Tafel slope shifts to 61 mV per dec. For practical applications, the small Tafel slope is advantageous, since it results in the faster enhancement of HER rate with the increase in overpotential. Compared with pure MoSe₂ nanosheets, the smaller Tafel slope of MoSe₂-40 also suggests that, in addition to the superior intrinsic property of MoSe₂, the abundant exposed edge sites on the 3D conductive substrates and the unique stack structure of MoSe₂ nanosheets (smaller nanosheets or quantum dots stack on the relatively larger nanosheets) are beneficial to improve the active site density, optimize the adsorption conditions of active sites and hence improve the HER efficiency.

In addition to the onset potential and Tafel slope, the lifetime or durability of electrocatalysts is also a key factor to evaluate the catalytic activity. Fig. 7d shows the polarization curves of MoS₂-20 and MoSe₂-40 samples before and after 1000 cycles. The almost identical curves indicate the good stability of these catalysts in a long-term electrochemical process. Hence these materials can be excellent catalytic catalysts for the HER.

Compared with the previous reports, the most significant difference of the present work is that we directly integrate 2D MoS₂/MoSe₂ nanosheets (including some 0D quantum dots) with graphene sheets into a 3D highly conductive architecture with abundant active sites, instead of a lamellar structure by depositing MoS₂/MoSe₂ nanosheets on conductive supports or growing MoS₂/MoSe₂ nanoparticles (with plenty of layers) on graphene. It endows these composite catalysts with three characteristics: (1) small-sized...
and few-layer MoS2/MoSe2 nanosheets (including quantum dots) which are homogeneously distributed throughout the frameworks affording abundant active sites, (2) the unique stack structure of various sizes of defect-rich MoS2/MoSe2 nanosheets (i.e., some quantum dots stack on the nanosheets) resulting in a high ratio of the active edge and basal plane and (3) a 3D porous structure with high surface area and high electrical conductivity providing multiple effective electron transfer paths and improving the electrical contact between the electrode and the active sites. Thus, the synergistic effect of graphene substrates and MoS2/MoSe2 nanosheets results in an excellent HER performance with a small overpotential and Tafel slope, suggesting that these materials can be an alternative substitute for commercial Pt as high-performance electrocatalysts toward the HER. Moreover, it also indicates that the combination of sonication and solvothermal treatment might be a facile and versatile method to prepare other TMD nanosheet–graphene 3D porous materials.

Conclusions

In summary, we developed a facile and versatile method to prepare high-performance HER catalysts integrating graphene sheets and MoS2/MoSe2 nanosheets (including quantum dots) into a unique 3D architecture by a simple mixing solvothermal process. During the mixing solvothermal process, highly conductive graphene 3D networks with large surface area were fabricated by the synergistic reduction effect of NMP and supercritical H2O, meanwhile the highly exfoliated MoS2/MoSe2 nanosheets with a defect-rich stack structure (i.e., some quantum dots intersperse in the nanosheets) were uniformly decorated on the porous network. This hybrid 3D architecture facilitated the exposure of active sites of nanosheets, enhancement of the active site density, and improvement of electron transfer between the electrode and the catalysts. Both MoS2–graphene and MoSe2–graphene hybrid aerogels present impressive HER catalytic activity with a small onset potential and long-term durability. The MoSe2–40 sample exhibits the most outstanding catalytic performance with a small onset potential of ~70 mV and a Tafel slope of 61 mV per dec, as well as the long-term durability, which is also very competitive compared with Pt-based HER catalysts. Moreover, considering the facile and relatively low-cost preparation method, this work develops promising candidates for Pt-free HER catalysts for future commercial applications.

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Notes and references
