Ultra-thin and porous MoSe$_2$ nanosheets: facile preparation and enhanced electrocatalytic activity towards the hydrogen evolution reaction†

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In this study, ultra-thin and porous molybdenum selenide (MoSe$_2$) nanosheets were prepared through a modified liquid exfoliation method as efficient electrocatalysts for the hydrogen evolution reaction (HER). This novel structure enables the exposure of more catalytically active sites and moreover maintains effective electron transport, resulting in a small peak potential of $\sim 75$ mV as well as long-term durability. In addition, due to the facile and economical preparation method as well as its eco-friendly synthetic conditions, this study provides a high-performance HER catalyst with promising commercial application prospects.

Hydrogen has attracted increasing research interests due to its great potential in sustainable energy harvesting and conversion field, and the fact that hydrogen energy conversion technologies are mainly limited by the development of highly active, acid-stable and inexpensive catalysts.$^1$ Recently, two-dimensional (2D) transition metal dichalcogenides (TMDs) have attracted more attention due to their potential electrocatalytic activity towards the hydrogen evolution reaction (HER).$^2$–$^6$ In general, it is predicted by theory that ultra-thin TMD nanostructures are favored for increasing surface areas with more exposed planes, and the edges of TMD nanosheets have higher activity towards the HER.$^7$ Therefore, if TMDs based catalysts are to realize their potential, there are two intractable problems that demand some ingenious solutions, i.e., achieving a facile method to obtain ultra-thin nanosheets and optimizing their nanostructures with high active site density.

Conventionally, 2D nanosheets are prepared by either top-down micromechanical cleavage$^8$ or bottom-up chemical-vapor deposition.$^9$–$^{10}$ These methods enable the production of single- or few-layer nanosheets, but they are unsuitable in practical applications on a large scale, which usually needs large quantities of materials in a processable form.$^{11}$ Although the massive preparation of TMDs nanosheets can be achieved via the Li-intercalation$^{12}$ and liquid exfoliation$^{13,14}$ methods, these strategies also suffer from drawbacks, where it is especially difficult to further tailor the morphology of TMDs. The Li-intercalation strategy needs extensive cleaning to get rid of impurities$^{15,16}$ and always sacrifices the pristine semiconducting properties of TMDs bulk crystals due to the structural destruction during Li intercalation.$^{16}$–$^{18}$ As for the traditional liquid-phase exfoliation technique, it is in favor of the scalable production of TMDs nanosheets and liquid-suspended nanosheets can be directly processed into films. However, unfortunately in this scalable process, the sonic energy and the interactions between the TMDs and the solvents are usually insufficient to thoroughly exfoliate the crystals,$^{13}$ and it is accompanied with the disadvantage of low exfoliation efficiency, i.e., long sonication time and thick nanosheets that are about several dozen nanometers. Overall, the liquid-phase exfoliation technique is the most appropriate method, but it is urgent to improve the efficiency of the exfoliation procedure and further tailor TMDs structures.

As for optimizing the HER catalytic activities of TMDs, there have been intensive efforts devoted to synthesizing TMDs nanostructures with a high density of active edge sites such as vertically aligned layers to expose the active edges of the TMDs,$^{19}$ controllable disorder ultrathin molybdenum sulfide (MoS$_x$) nanosheets with oxygen incorporation,$^{20}$ macroporous molybdenum selenide (MoSe$_x$) films$^{21}$ and unique stack structure of MoS$_x$ nanosheets.$^7$ All the abovementioned strategies suggest increasing active sites play a crucial role in higher HER activity, thus this inspires us to postulate that ultra-thin and porous TMDs nanosheets with abundant active edge sites might be a very promising candidate for highly active HER catalysts, which can replace traditional Pt noble metal catalysts.

Herein, to realize the facile preparation of superior HER electrocatalysts with an optimized nanostructure, a modified...
liquid exfoliation method is proposed, that is, an appropriate oxidant such as H$_2$O$_2$ is utilized to assist the exfoliation of bulk TMDs nanosheets. When H$_2$O$_2$ is employed during the exfoliation of bulk MoSe$_2$ flakes, even in the low-boiling-point solvent isopropyl alcohol (IPA), interestingly, the bulk MoSe$_2$ flakes are easily incised and exfoliated into a desirable ultra-thin and porous structure, which is probably ascribed to the oxidation and etching effect of H$_2$O$_2$. These ultra-thin and porous MoSe$_2$ nanosheets possess a high edge/basal ratio and exhibit excellent HER activity with a low overpotential of about 75 mV and long-term durability, which render them highly competitive with commercial Pt-based catalysts.

As shown in Scheme 1, bulk MoSe$_2$ flakes are exfoliated and incised into ultra-thin and porous nanosheets with the assistance of H$_2$O$_2$. Atomic force microscopy (AFM) images show that the MoSe$_2$ nanosheets are almost single- or double-layer with the thickness of 1–1.5 nm, which indicates their highly exfoliated nature, and their average lateral size is several hundred nanometers (Fig. 1). However, the layer thickness of the MoSe$_2$ flakes exfoliated in IPA exceeds a few tens of nanometers, as shown in Fig. S1b (ESI†), which is probably due to the mismatched surface energies of IPA and TMDs.13 Even in the case of MoSe$_2$ nanosheets exfoliated in better solvents with strong exfoliating ability for TMDs such as N-methyl-2-pyrrolidone (NMP),13,22 it is also intractable to exfoliate the nanosheets into single- or double-layer and further tailor their morphologies (Fig. S1c, ESI†). Nevertheless, the height profile of the MoSe$_2$ nanosheets sharply decreases in the presence of H$_2$O$_2$, and more importantly the morphology of these ultra-thin MoSe$_2$ nanosheets is significantly different from those exfoliated from common solvents. As a consequence of the H$_2$O$_2$ etching effect, the nanosheets are tailored into an optimized structure for the HER, in which plenty of pores and irregular lateral edges significantly improve the edge/basal ratio of the nanosheets and thus enhance their active surface areas with a higher catalytic active site density. Transmission electron microscope (TEM) images also confirm the porous and defect-rich morphology, as shown in Fig. 1c. The lattice fringe is 0.285 nm in the high resolution TEM (HRTEM) images, which corresponds to the (100) face of the MoSe$_2$ crystal.23 In addition, field emission scanning electron microscope (FESEM) images and element mapping results further confirm the morphology and successful preparation of the ultra-thin and porous MoSe$_2$ nanosheets, as shown in Fig. S2 (ESI†), although the presence of oxygen element might suggest the slight oxidation of some Mo edges, and this will be further discussed in the XPS results. Moreover, we carefully measured the concentration of the ultra-thin and porous MoSe$_2$ nanosheets, which is about 0.7 mg mL$^{-1}$, and therefore the yield is 7% (the initial amount of MoSe$_2$/IPA was 10 mg mL$^{-1}$). The concentration and yield of the ultra-thin and porous MoSe$_2$ nanosheets are comparable to or even better than some previous reports on the liquid exfoliation of TMDs,22,24,25 thus indicating the high efficiency of this modified method.

The crystal structure of the ultra-thin and porous nanosheets was further systematically investigated via X-ray powder diffraction (XRD) measurements and Raman spectroscopy. According to Fig. 2a, several main peaks at 13.7°, 37.8°, 47.5°, 55.8° and 56.7° are assigned to the (002), (103), (105), (110) and (008) faces of hexagonal 2H-MoSe$_2$ (JCPDF (65-3481)). Compared with raw MoSe$_2$, the (002) peak is clearly broadened, which indicates the highly exfoliated nature of the MoSe$_2$ nanosheets. This is well consistent with the previous results of TEM and AFM, which also confirm the strong exfoliating ability of this mixing solvent system with H$_2$O$_2$ assistance. Moreover, the well-matched peaks suggest that the highly-exfoliated porous nanosheets still retain the pristine structure of 2H-MoSe$_2$. This is also confirmed in a typical UV-vis spectrum of the porous MoSe$_2$ nanosheets, as shown in Fig. S3 (ESI†). There are four characteristic absorption bands observed, which are in good agreement with previously reported studies, and these indicate no disturbance of the intrinsic MoSe$_2$ crystal structure.26,27 Raman analysis is also applied to identify such layered materials. The Raman mode A$_{1g}$ of bulk MoSe$_2$ is identified at 247.3 cm$^{-1}$, whereas the A$_{1g}$ mode of the ultra-thin and porous MoSe$_2$ nanosheets is identified...
peaks located at 228.9 (Mo 4+ 3d5/2) and 232 eV (Mo 4+ 3d3/2) confirm that molybdenum is basically in the Mo(IV) state, and the small and broad peak of Mo 6+ (235 eV) is probably ascribed respectively.30,31 These results further confirm that the as-prepared exfoliated features of the as-prepared MoSe2 nanosheets.

The chemical state of the porous nanosheets was further investigated via X-ray photoelectron spectroscopy (XPS). The peaks located at 228.9 (Mo4+ 3d5/2) and 232 eV (Mo4+ 3d3/2) confirm that molybdenum is basically in the Mo(IV) state, and the small and broad peak of Mo6+ (235 eV) is probably ascribed to the slight oxidation of some Mo edges, which should result from the oxidization of Mo(0) in the presence of H2O2. The peaks identified at 55.3 and 54.5 eV in the high-resolution spectrum of Se are generally attributed to Se 3d3/2 and Se 3d5/2, respectively.30,31 These results further confirm that the as-prepared porous nanosheets mainly are MoSe2.

As a typical application, the ultra-thin and porous MoSe2 nanosheets were explored as electrocatalysts for the HER. The HER activity was measured using the standard three electrode electrochemical configurations in N2 saturated 0.5 M H2SO4 electrolyte with a scan rate of 50 mV s−1.22,32 For comparison, few-layer MoSe2 nanosheets and commercial Pt (20 wt% Pt/C) catalysts were also included. As expected, the ultra-thin and porous MoSe2 nanosheets have better HER activity than the few-layer MoSe2 nanosheets (Fig. 3a). The onset potential manifests a significant positive shift to ~75 mV, which is much better than few-layer MoSe2 nanosheets. Moreover, the overpotential of the porous MoSe2 nanosheets required for clear hydrogen evolution (~10 mA cm−2) is ~150 mV, which is significantly lower than that of few-layer MoSe2 nanosheets (~300 mV). Moreover, we have summarized the HER performance of the TMDs nanosheet (film) catalysts in Fig. S4 and Tables S1–S4 (ESI†), wherein it is obvious that the ultra-thin and porous MoSe2 nanosheets possess impressive HER activity among the state-of-the-art TMDs nanosheet (film) catalysts.

As an intrinsic property of electrocatalyst materials, the Tafel slope (Fig. 3b), which is associated with the rate-limiting step of the HER, has also been derived from Tafel plots, wherein their linear portions fit well with the Tafel equation (η = b × log j + a), where j is the current density and b is the Tafel slope. As shown in Fig. 3b, the Tafel slope of commercial Pt (20 wt% Pt/C) is ~33 mV dec−1, which is close to that reported in previous studies; this suggests that the HER on a Pt surface proceeds through the Volmer–Tafel mechanism and the Tafel reaction is the rate-limiting step at low overpotentials.33,34 Although the reaction mechanism on MoSe2 remained inconclusive, the Tafel slope of the porous MoSe2 nanosheets is 80 mV dec−1, which is similar to the MoSe2 nanosheets (82 mV dec−1) and comparable to the previous reports.30 This suggests a relative fast enhancement of the HER rate with the increase of overpotential.35

In addition to the onset potential and Tafel slope, the stability of electrocatalysts, as a key factor of catalytic activity, was also evaluated, as shown in Fig. 3c. The polarization curves before and after 1000 cycles are almost identical, and especially the onset potential is almost unchanged, indicating the good stability of the catalysts in a long-term electrochemical process.

To throw some light on the impressive HER performance of these ultra-thin and porous MoSe2 nanosheets, we further calculated their electrochemical active surface areas and investigated the
electrochemical impedance spectra of the ultra-thin and porous MoSe₂ nanosheets and few-layer MoSe₂ nanosheets exfoliated in NMP. The estimation of the electrochemical active surface areas of the catalysts was conducted by measurement of the electrochemical double-layer capacitance in the potential region with no faradaic response using a simple cyclic voltammetry (CV) method.\(^\text{32-36,37}\) The CV results suggest that the electrochemical active surface area value for the ultra-thin and porous MoSe₂ nanosheets is enhanced more than five-fold compared with that for the few-layer MoSe₂ nanosheets, as shown in Fig. S5 and summarized in Table S5 (ESI\(^\dagger\)). Moreover, because the morphology characterization from the AFM and TEM images and structural analysis from the XRD and Raman results consistently confirm their highly exfoliated nature and porous defect-rich structure, this obvious increase in surface area is reasonable. Moreover, according to the EIS results in Fig. S6 (ESI\(^\dagger\)), the electrode kinetics of the ultra-thin porous MoSe₂ nanosheets is similar to that of few-layer MoSe₂ nanosheets, in which the charge transfer resistance (R\(_\text{ct}\)) of the porous MoSe₂ nanosheets is 25 Ω, which is slightly smaller than that of MoSe₂ nanosheets (30 Ω), thus suggesting an even smaller charge transfer resistance in the optimized porous structure. Therefore, the impressive HER performance of the porous MoSe₂ nanosheets is mainly attributed to two factors. On the one hand, it originates from the optimized structure of the ultra-thin and porous MoSe₂ nanosheets. The porous structure results in a higher electrochemical active surface area and thus leads to a higher ratio of active edges and basal planes with more active edge sites.\(^8\) Thereby, the exposed surface area of the active sites contributes to the higher HER activity. On the other hand, the remaining continuous flat nanosheets also provide effective electrical contact between the electrode and the active sites. As confirmed in EIS results (Fig. S6, ESI\(^\dagger\)), the electrode kinetics of the porous MoSe₂ nanosheets is slightly faster than that of the MoSe₂ nanosheets.

In summary, we have developed a modified liquid exfoliation method to prepare ultra-thin and porous MoSe₂ nanosheets. With the assistance of H\(_2\)O\(_2\), bulk MoSe₂ is easily exfoliated into an ultrathin and porous structure. This facilitates the exposure of the active sites of the nanosheets and moreover the lamellar structure maintains effective electron transfer between the electrode and the catalytic sites. The resulting products exhibit impressive HER catalytic activity with a small onset potential of \(~75\) mV, a Tafel slope of 80 mV dec\(^{-1}\), as well as long-term durability, which is even comparable to Pt-based HER catalysts. In addition, considering the facile and low-cost procedure, the ultra-thin and porous MoSe₂ nanosheets is proposed to be a promising candidate for commercial HER catalysts in the future.

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