Enhanced electrocatalytic activity for hydrogen evolution reaction from self-assembled monodispersed molybdenum sulfide nanoparticles on an Au electrode†

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Ultrasmall molybdenum sulfide nanoparticles with diameters of 1.47 ± 0.16 nm were fabricated from bulk MoS2 by a combination of ultrasonication and centrifugation. The nanoparticles were then assembled on an Au surface to form a film with high electrocatalytic activity for hydrogen evolution reaction (HER). A Tafel slope of 69 mV per decade was measured for this film and the onset potential was estimated to be −0.09 V. The small loading (1.03 μg cm−2) and the high current density (0.92 mA cm−2 at η = 0.15 V) demonstrated extremely high catalytic efficiency. X-ray photoelectron spectroscopic results revealed that the assembled nanoparticle film was sulfur enriched with abundant S edges and a structural rearrangement of the S rich particles might occur during the self-assembly process, resulting in significantly enhanced electrocatalytic activity for HER. Electrochemical impedance measurements suggested that the assembling process optimized the conductivity of the nanoparticle film, which contributed to the enhanced HER catalytic activity. Our research has provided a new way to synthesize active molybdenum sulfide nanoparticles for HER and a new approach to achieve enrichment of S edges on molybdenum sulfide, which might have potential use not only for electrocatalytic HER, but also for photoelectrocatalytic HER and plasmon-enhanced water splitting.

1 Introduction

The rapid depletion of fossil fuels and growing environmental concerns have created an enormous worldwide demand for alternative clean energy technologies. Compared with traditional fossil fuels, hydrogen is considered as an ideal energy carrier since it is clean and renewable. The most promising way to create hydrogen is through the splitting of water by either light or electricity. However, catalysts are necessary to achieve a highly efficient hydrogen production due to the existence of a large overpotential for hydrogen evolution reaction (HER). Pt-group metals are the most efficient catalysts for HER, but they are rare and expensive. In order to maintain the development of hydrogen energy, it is of great importance to find cheap catalysts with high HER activity. Molybdenum disulfide (MoS2), a low cost and easily obtained material with good catalytic property for HER, has attracted great attention. MoS2 is well known as a solid lubricant and also as a good catalyst for hydrodesulfurization reaction. Recent studies have shown that its sulfur edge is quite active for HER. As a result, much effort has been focused on trying to acquire MoS2 or MoS, nanomaterials with a plethora of sulfur edges. Here, we demonstrate a novel approach for synthesizing monodispersed molybdenum sulfide nanoparticles with ultrasmall diameters and a new strategy for achieving enrichment of active S edges on molybdenum sulfides by exploiting the covalent bonding of the nanocatalysts with the underlying gold electrode. The work is beneficial not only for the design of highly efficient molybdenum sulfide based HER catalysts but also for the synthesis of new catalysts for photoelectrocatalytic HER and plasmon-enhanced water splitting.

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by using graphene or carbon nanotubes as carriers.\textsuperscript{6,15,19} Besides, Fe, Co, and Ni doping was also used to improve the inherent activity of MoS\textsubscript{2} or MoS\textsubscript{3}.\textsuperscript{16,20} Previously, active MoS\textsubscript{2} was mainly synthesized by either chemical vapour deposition or incipient wetness impregnation.\textsuperscript{5} Even though it has been reported that bulk MoS\textsubscript{2} could be broken into nanoparticles\textsuperscript{21} and exfoliated to single layers by simple ultrasonication,\textsuperscript{22} no research has been conducted on the investigation of their catalytic properties towards HER. In this work, we report a strategy for preparing ultrasmall molybdenum sulfide nanoparticles with a narrow size distribution from bulk MoS\textsubscript{2} commercial powder by just applying ultrasonication and centrifugation. Then, in order to elucidate the importance of immediate coupling with the underneath electrode, we assembled them on an Au surface and obtained a high electroactive film with an onset potential as positive as $-0.09$ V for HER.

2 Results and discussion

2.1 Synthesis and characterization of monodispersed molybdenum sulfide nanoparticles

Monodispersed molybdenum sulfide nanoparticles were synthesized by a combination of ultrasonication, which aimed at exfoliating the bulk MoS\textsubscript{2}, and gradient centrifugation, which aimed at separating the mixture. A systemic work has been reported on the exfoliation of bulk layered materials into two-dimensional nanosheets by long time sonication.\textsuperscript{22} However, in addition to nanosheets, nanoparticles could also be obtained through this method. In our work, bulk MoS\textsubscript{2} powder was mixed with N,N-dimethylformamide (DMF) and long-time ultrasonication was performed to obtain a black suspension. Then the suspension was centrifuged at 6000 $r$ min$^{-1}$ for 30 min to remove the relatively large particles. After that the supernatant was centrifuged at 12 000 $r$ min$^{-1}$ for 30 min, the precipitation was collected and redispersed into DMF to form a transparent homogeneous light yellow solution. The concentration of this nanoparticle solution was estimated to be 10 $\mu$g mL$^{-1}$. The Tyndall effect, demonstrated clearly in Fig. 1, indicated the existence of very small particles in the solution. In addition, the UV-vis absorption spectrum showed several peaks at 298 nm, 388 nm, 450 nm, 613 nm, and 667 nm separately (Fig. 1), which matched well with the characteristic absorption bands of molybdenum sulfide nanoparticles in the solution.\textsuperscript{23,24}

The transmission electron microscopy (TEM) was used to characterize the size and structure of these nanoparticles. The result (Fig. 2a) showed that the sizes of these particles were nearly the same with diameters of $1.47 \pm 0.16$ nm (Fig. 2b). The lattices of the nanoparticles could hardly be observed, which implied that their structures were not so uniform even though their sizes were similar. The selected area electron diffraction result of the sample also suggested that the structure of these nanoparticles was amorphous as no typical diffraction pattern could be observed (Fig. S1, ESI$^\dagger$).

2.2 Construction of assembled molybdenum sulfide nanoparticle films and their electrocatalytic investigation for HER

Since these monodispersed particles are so small and amorphous in the solution, it could be easily conjectured that they have more sulfur edges than molybdenum sulfide prepared by other techniques.\textsuperscript{5,6,19} On the other hand, the HER activity had

![Image](image_url)
been correlated with the number of edge sites on the molybdenum sulfide catalysts\textsuperscript{12–14} and Au[111] was suggested to be a good carrier for molybdenum disulfide to exhibit its catalytic property for HER.\textsuperscript{6} The electrocatalytic activities of these molybdenum sulfide nanoparticles for HER were investigated by assembling them onto an Au surface. A well cleaned Au electrode was incubated in the monodispersed molybdenum sulfide nanoparticle solution overnight, followed by washing with DMF and acetone respectively. Then its catalytic performance was measured in 0.5 M H\textsubscript{2}SO\textsubscript{4} with a three-electrode system. The catalytic property of the electrode for HER was enhanced significantly by the self-assembly of these nanoparticles onto the surface of the Au electrode (Fig. 3). A bare Au electrode showed an onset potential of about −0.2 V. However, after molybdenum sulfide nanoparticles were self-assembled onto the surface of the Au electrode, obvious hydrogen evolution current could be observed at −0.09 V. This is one of the most positive onset potentials for electrocatalytic HER among the reported molybdenum sulfide based materials.\textsuperscript{5,6} A traditional drop-casting method was also used to study the catalytic activity of the molybdenum sulfide nanoparticles on the Au surface. 3 μL of molybdenum sulfide nanoparticle solution was dropped onto a bare Au electrode and dried at room temperature (22 ± 2 °C) to form a drop-cast film. In high contrast, the activity of this film for HER was not as high as the assembled one. Its onset potential was about −0.15 V, which was similar to the MoS\textsubscript{2} nanoplatelets grown on Au[111].\textsuperscript{13} Furthermore, the current density of the drop-cast film was smaller than that of the assembled one.

The Tafel plot of the assembled nanoparticle film fits well with the Tafel equation when the overpotential was between 0.09 V and 0.19 V. The Tafel slope was calculated to be 69 mV per decade and the exchange current density was 9.3 × 10\textsuperscript{−6} A cm\textsuperscript{−2} (Fig. 4). The experimental results displayed a quite large exchange current density and a relatively small Tafel slope at such low overpotential compared with those reported in the literature.\textsuperscript{6,16,17} The large exchange current density illustrated that the electron transfer rate of the assembled film was very fast, which should be responsible for the high activity of this film.

The stability of the self-assembled film was also tested. We applied cyclic potential scan from −0.3 V to +0.7 V at a scan rate of 100 mV s\textsuperscript{−1}.\textsuperscript{19} Only a slight activity loss was observed after 1000 cycles, which implied that the durability of the assembled film was very good (Fig. 5).

Since it seemed that the assembly process onto the Au surface played an important role in fabricating highly active molybdenum sulfide films, the relationship between the assembling time and the HER activity of the assembled film was carefully investigated. Fig. 6 shows the polarization curves of assembled molybdenum sulfide nanoparticle films with different assembling times. It was found that the film incubated overnight showed the best performance. Both too short and too long incubation times would result in a decrease in HER activity of the film. A possible explanation for this behaviour was that one hour was too short to form the self-assembled film, whereas prolonged incubation for two days resulted in the agglomeration of the particles. The agglomerated nanoparticle film might be similar to the film prepared by drop-casting and showed inferior catalytic property. In fact, the Tafel slopes of the
two-day-assembled film and the drop-cast film on Au were similar (Fig. S2 and S3, ESIF). Their slopes were both about 100 mV per decade, which proved that their hydrogen evolution mechanism might be similar. Their slopes were larger than the slope of the assembled film under the optimized conditions (69 mV per decade), which is most likely associated with a larger internal resistance of the films on the electrode.\(^6\)

2.3 Surface analysis of the assembled molybdenum sulfide nanoparticle films

The morphologies of the assembled films were further surveyed by atomic force microscopic (AFM) characterization (the morphology of the drop-cast film was too rough to be characterized by AFM). Fig. 7a shows the morphology of the molybdenum sulfide nanoparticle films assembled for 1 h. We could see that the distribution of the nanoparticles was rarefactive. Two kinds of structures could be observed: tiny dots with the diameters of several nanometers and larger spots with the diameters of tens of nanometers. The heights of the tiny dots were below 2 nm and the heights of the larger spots were measured to be in the range of 2 to 5 nm (Fig. 7d). The size and height of these tiny dots matched well with the TEM image in Fig. 2a. We could also observe that most of the large spots consist of groups of tiny dots, which indicate that agglomeration of small nanoparticles accompanied the assembly process. This explains the origin of a large amount of large spots in Fig. 7b and c. After an overnight assembly, the distribution of the nanoparticles was much denser and the proportion of the larger spots increased (Fig. 7b). The heights of those tiny dots were still below 2 nm, but the average height of the nanoparticles increased due to the agglomeration of these particles (Fig. 7e). After incubating for two days, tiny dots disappeared from the AFM image (Fig. 7c). Only molybdenum sulfide particle clusters with the diameters of tens of nanometers could be observed. In addition, the height of this assembled film also increased compared with molybdenum sulfide assembled overnight. These observations illustrated that the assembled molybdenum sulfide nanoparticle film was not a uniform monolayer, which was different from the assembled Mo\(_{3}\)S\(_4\) monolayer as reported previously.\(^5\) A possible explanation for the structure of the film was that the solution of the monodispersed molybdenum sulfide nanoparticles was not as stable as that of Mo\(_{3}\)S\(_4\). They would aggregate during the long-time self-assembly process, both in the solution and on the Au surface. The over aggregation of the molybdenum sulfide nanoparticles might increase the resistance of the assembled film and reduce the amount of the active S edges, thus leading to an inferior HER activity of the film. On the other hand, a very short assembly time would result in a sparse nanoparticle distribution and hence too few active sites with unfavourable effects on the HER activity film.

Electrochemical impedance measurement was used to characterize the conductivity of the produced films on Au. Fig. 8 shows the electrochemical impedance spectra of the drop-cast and assembled molybdenum sulfide films on Au electrodes together with that of the bare Au electrode. The equivalent circuit is shown in Fig. S4.\(^\dagger\) We could see that the charge transfer resistance of the electrode increased greatly (from 10 \(\Omega\) to about 1000 \(\Omega\)) after the drop-casting of the molybdenum sulfide nanoparticle solution onto the Au electrode. However, the charge transfer resistance of the assembled film was much smaller. The film assembled for 1 h showed a charge transfer resistance of only about 40 \(\Omega\). After an overnight assembly, the charge transfer resistance increased to 80–100 \(\Omega\), whereas upon further assembly for two days, it reached 300–400 \(\Omega\), which was still smaller than that of the drop-cast film even though its loading was larger. These results suggest that the conductivity of the assembled films is much higher than that of the drop-cast film, which indicates a much faster electron transfer process during electrochemical reaction. Thus we presume that the formation of the self-assembled film on Au resulted in the integration of the nanoparticles with the electrode, which might increase the electrical conductivity of the assembled film on Au and improve its activity. Besides, the larger film resistance of the drop-cast film and the two day assembled film could also explain their larger Tafel slopes compared with that of the film assembled overnight.

A quartz crystal microbalance (QCM) was used to measure the loading of the assembly process. After incubating for 1 h, the loading of the nanoparticles was about 0.14 \(\mu\)g cm\(^{-2}\). The loading was increased to 1.03 \(\mu\)g cm\(^{-2}\) after an overnight incubation. After a two day assembly, the loading reached 1.85 \(\mu\)g cm\(^{-2}\). The loading of the drop-cast film was about 1 \(\mu\)g cm\(^{-2}\), which is similar to that of the film assembled overnight. But its HER activity was inferior. The current density of the film assembled overnight at \(\eta = 0.15\) V was 0.92 mA cm\(^{-2}\), which was larger than most of those molybdenum sulfide based HER catalysts,\(^6\) but still smaller than those of the MoS\(_2\)-graphene oxide hybrid (9 mA cm\(^{-2}\))\(^9\) and the Fe–MoS\(_2\) film (1.55 mA cm\(^{-2}\)).\(^10\) However, it is important to emphasize that the loadings of the nanoparticles decreased by two orders of magnitude compared with that of the MoS\(_2\)-graphene oxide hybrid.
and reduced by one order of magnitude compared with that of the Fe–MoS₃ film, which attested that its efficiency was extremely high.

In order to further elucidate the origin of the enhanced electrocatalytic activity for HER by self-assembling molybdenum sulfide nanoparticles onto an Au electrode, X-ray photoelectron spectroscopic (XPS) analysis of both the assembled nanoparticle film and the drop-cast film on the Au surface was conducted as well as those particles, and the results showed quite interesting findings. Bulk MoS₂ showed typical S and Mo peaks before sonication. It exhibited S 2p₃/2 binding energy at 162.2 eV (Fig. S5, ESI†) and Mo 3d₅/₂ binding energy at 229.4 eV (Fig. S6, ESI†). After sonication, the S and Mo binding energies of the obtained nanoparticles increased. It exhibited S 2p₃/2 binding energy at 162.7 eV (Fig. S7, ESI†) and Mo 3d₅/₂ binding energy at 229.7 eV, respectively (Fig. S8, ESI†). This increase might be due to the significant decrease of the particle size. However, when assembled onto the Au surface, an obvious change in the S spectrum could be observed (Fig. 9). Besides the S 2p₃/2 binding energy at around 162.7 eV (1 S), a new S 2p₃/2 peak at about 161.8 eV (II S) could be identified. The ratio of the peak at 161.8 eV to the peak at 162.7 eV decreased over the assembly time. For 1 h it was 2.8 : 1. After incubating overnight, the ratio reduced to 1.8 : 1. When the assembly time extended to two days, the ratio decreased to 1.3 : 1. There are two possible explanations for the existence of this new doublet and this tendency in the S spectrum. In one aspect, the generation of the assembled film meant that there should be an interaction between the nanoparticle and Au. It has been reported that a partial electron transfer from Au to S would lead to a decrease of the binding energy for S, attesting the presence of the S–Au interaction.
Taking into consideration this statement, since the binding energy of this new S 2p3/2 peak matched well with that of the S–Au bond, we speculated that the new peak should be attributed to the formation of the S–Au bond during assembling. Besides, the slightly higher 4f7/2 binding energy of the Au substrate at 84.4 eV after the self-assembly process compared with the Au element at 84.0 eV might also imply the existence of a partial electron transfer from Au to S and the formation of the S–Au bond (Fig. S9–S11, ESI†). At the beginning of the assembly process, most of the nanoparticles interacted directly with Au, which resulted in a high relative intensity of the S doublet at lower binding energy. But when the assembly time increased, the nanoparticles would not only interact with Au, but also with each other due to self-agglomeration, which led to a decrease of the relative intensity of the S doublet at 161.8 eV and a corresponding increase of the relative intensity of the typical molybdenum sulfide nanoparticle peak at 162.7 eV. From another point of view, Hu and his co-workers reported that terminal S2− and S2− of amorphous MoS2 showed a lower binding energy at 162.0 eV compared with that of bridging S2− and apical S2−, and those materials with S–S bonds are more active for HER than simple MoS2. So we could also attribute the new S doublet in the assembled film to the terminal S2−. Since these amorphous nanoparticles were so small, they should possess a large amount of surface defects and would not be very stable. Thus structural rearrangement of the particles might occur during the assembly process on Au, which might result in the formation of terminal S2−. During incubation, the proportion of terminal S2− decreased due to the agglomeration of the particles. This assumption also interpreted the high activity of the assembled film due to the generation of S–S bonds. The binding energies of S in the two suppositions were similar and hard to be distinguished. Maybe both of them contributed to the lower binding energy doublet in the S spectrum. The S spectrum of the drop-cast film on Au was also obtained (Fig. S12, ESI†). The S 2P3/2 peak at about 161.8 eV (II S) could be observed as well, but its relative intensity was much lower. The intensity ratio of the peak at 161.8 eV to the peak at 162.7 eV was 0.2 : 1. This was due to the obvious accumulation of the particles during the drying process. Besides, its Au binding energy was also slightly upshifted compared with that of element Au (Fig. S13†).

The Mo binding energies of the assembled films and the drop-cast film were similar to those of the as-prepared nanoparticles (Fig. 10 and S14, ESI†). They all showed a doublet with Mo 3d5/2 at 229.8 ± 0.1 eV. But there was a noticeable difference in the Mo to S ratios. Bulk MoS2 showed a Mo to S ratio of 1 : 2.0, which matched well with its structure. After sonication, the obtained nanoparticles exhibited a Mo to S ratio of about 1 : 2.1, which increased slightly compared with that of the bulk materials. The Mo to S ratio of the drop-cast film on Au was 1 : 2.3, this deviation might be attributed to the innegligible noise of the XPS signal for the drop-cast film since the signal was too weak. However, the assembly process produced molybdenum sulfide films with much larger S proportion. For the 1 h assembled film, the relative intensity of the Mo doublet was so weak that it was a little hard to distinguish it from the background noise (Fig. 10a). Thus it was not reasonable to calculate the Mo to S ratio of this film. However, we could observe that the relative intensity of S in this film was much higher than the film assembled overnight (Fig. 10b). The overnight assembled film demonstrated a Mo to S ratio of 1 : 5.0, while the Mo to S ratio of the film incubated for two days was 1 : 3.4. All of these values are smaller than the statistical average of the as-prepared nanoparticles. So compared with the name “assembled molybdenum disulfide film”, maybe it is more suitable to name our film as “assembled molybdenum sulfide film” despite the fact that these nanoparticles were synthesized from MoS2. Besides, we could also find that the XPS signals of S and Mo for the film assembled for two days were not as strong as those for the film assembled overnight even though the loading of the two-day assembled film was larger. A possible explanation was that the film assembled for two days would exhibit a larger effective surface area, thus would be more easily polluted by the environment. The inevitable pollution on the surface of the film would reduce the absolute intensities of S and Mo signals significantly as their signals were so weak. The survey spectrum of the film assembled for two days showed relatively stronger C and O signals compared with the film assembled for a shorter time (Fig. S17–S19, ESI†), which might prove that the two-day assembled film was more seriously polluted with an increase of the assembly time. The C and O contaminations would probably have influence on the HER activity of the assembled film since they might block the HER active sites of the assembled molybdenum sulfide film and reduce its conductivity. This might be another reason for the inferior HER activity of the two-day assembled film.
Since the TEM image showed that the nanoparticles were amorphous, we speculated that the structures of these particles were quite different even though their size was nearly the same. Some of the nanoparticles might have a higher amount of S on the surface than the average, thus might show a better catalytic property for HER. During self-assembling, the nanoparticles with more S surface sites would more easily interact with the Au surface to form the S–Au bond, thus forming a film with a higher S proportion than average. The assembled films showed a tendency of decline in the S proportion with increase of the assembly time, which proves our supposition. When Au was immersed into the solution of molybdenum sulfide nanoparticles, the particles with the highest number of surface S sites might adsorb on Au in 1 h, which leads to the formation of a nanoparticle film with a very high ratio of S and nearly no Mo. With the increase of the assembly time, particles with less surface S would slowly adsorb and agglomerate onto the Au surface, which results in a decrease in the S ratio. Besides, the assembled films also showed a possibility of structural rearrangement to form terminal $S_2^{2-}$ since their formulae were more close to MoS$_3$. This agreed well with the second hypothesis explaining the S spectrum. Therefore we believe that the assembly process on the Au surface played a key role in fabricating molybdenum sulfide films with high activity for HER. The Au selectively adsorbed those ultrasmall molybdenum sulfide nanoparticles with more S edges and formed a film with more active sites for HER compared with other molybdenum sulfide based catalysts.\cite{6,5,15} Under optimized conditions it could show ultra high activity. The possible rearrangement of the particles during assembling might form a more active S–S structure, which would also contribute to the improvement of HER activity of the assembled film. Besides, the formation of the S–Au bond during incubation could result in the integration of the nanoparticles with the electrode, which resulted in an increased conductivity of the assembled film on Au and improvement of its activity.

### 2.4 The origin of the enhanced HER activity of the assembled film

The experimental results presented in this work suggest that the excellent catalytic property of the assembled molybdenum sulfide nanoparticle film is derived from four aspects. Firstly, the synthesized ultrasmall molybdenum sulfide nanoparticles are amorphous with diameters of less than 2 nm, possessing a higher proportion of surface S active sites than their larger particles. Secondly, the high S to Mo ratio of the assembled film and the decrease of S to Mo ratio during the assembly process prove that Au selectively adsorbs those nanoparticles with the highest number of surface S sites during the assembling process and formed a film with highly rich S edges, which may increase the activity of the film significantly. Thirdly, XPS characterization shows the existence of the lower binding energy peaks in S spectra,\cite{15} indicating that structural rearrangement of the S rich nanoparticles may occur when it interacts with Au during the assembling process, which would lead to the formation of the terminal S–S bond and increase the activity of this material. Fourthly, the formation of the S–Au bond ensures the integration of the assembled film with Au and improves the conductivity of the system. As shown in Fig. 8, the charge transfer resistance of the assembled film is much smaller than the simply drop-cast film even when the loading of the assembled film was larger. These factors coordinated with each other have led to the great enhancement for the HER catalytic activity of the assembled molybdenum sulfide film on Au. The electrode constructed in this experiment is somewhat similar to one of the idealised MoS$_2$ photocathode designs that were proposed by Chorkendorff and his co-workers despite the fact that the Au electrode was used instead of semiconductor pillars.\cite{6} It may have potential applications in not only electrocatalytic HER, but also photocatalytic HER and plasmon-enhanced water splitting.

### 3 Conclusions

In conclusion, we developed a very easy way to fabricate ultrasmall molybdenum sulfide nanoparticles with a narrow size distribution by just using ultrasonication and centrifugation steps. The self-assembled molybdenum sulfide nanoparticle film on the Au surface exhibited an outstanding HER electrocatalytic activity with an onset potential of $-0.09$ V and a Tafel slope of 69 mV per decade. This is the most positive onset potential with a relatively small Tafel slope that has been reported to date based on MoS$_2$ materials. The loading of the nanoparticles was as low as 1.03 $\mu$g cm$^{-2}$, which demonstrates that the catalytic efficiency of this assembled film is extremely high. The improved performance is due to the presence of
highly catalytic S edges as revealed by a low ratio of Mo to S and the possible rearrangement of the S rich nanoparticles on Au, as well as the excellent electrical coupling to the underlying Au electrode via the formation of the Au–S bond. Our research has offered a new way to synthesize monodispersed molybdenum sulfide nanoparticles and a new approach to achieve the enrichment of active S edges on molybdenum sulfides, which is highly beneficial for the design of highly efficient molybdenum sulfide based HER catalysts.

4 Experimental

4.1 Preparation of monodispersed MoS2 nanoparticles

DMF was selected as the exfoliation solvent for MoS2 since it was suggested to be efficient and was easily obtainable.21 MoS2 (99%, Aldrich) with an average diameter of several micrometers was mixed with DMF (99.9% Aldrich) at a concentration of 1 mg mL−1. This mixture was ultrasonicated by an SB-2200 sonifier (Shanghai Branson, China) at room temperature for 4 h to form a black suspension. After this process, the suspension was centrifuged at 6000 r min−1 for 30 min with a GS-15R centrifugation system (Beckman, America) to remove the particles with large size. Then the light yellow supernatant was collected and centrifuged at 12 000 r min−1 for 30 min and the precipitation was gathered. Ultrasmall monodispersed molybdenum sulfide nanoparticle solution was prepared by redispersing the precipitation into DMF with the same volume before centrifugation.

4.2 Fabrication of assembled and drop-cast molybdenum sulfide films onto Au surfaces

An Au electrode with a diameter of 2 mm was polished with 1.0 μm and 0.05 μm Al2O3 power respectively, followed by sonicating in deionised water for 3 min. Then the electrode was electrochemically cleaned by applying continuous potential cycles from 0 V to 1.6 V (vs. SCE) at a scan rate of 0.5 V s−1 in 0.5 M H2SO4 (typically 200 cycles were applied). After that the electrode was washed with deionised water and dried in a N2 atmosphere. The clean electrode was then immersed into the fresh molybdenum sulfide nanoparticle solution and incubated at room temperature overnight. Next the electrode was rinsed with DMF and acetone, respectively, and dried in a N2 atmosphere. The drop-cast film was fabricated by successive addition of 3 μL fresh molybdenum sulfide nanoparticle solution on a well cleaned Au electrode (2 mm in diameter). The electrode was dried in the air.

4.3 Characterization

Polarization curves were obtained by linear sweep voltammetry with a scan rate of 2 mV s−1 on a CHI 660D (Chenhua, China) at room temperature in a protective layer of N2 gas. An Au electrode was used as the counter electrode and an Au or modified Au electrode was used as the working electrode. A saturated calomel electrode was used as the reference electrode for all the electrochemical tests and the potential was calibrated to the standard hydrogen electrode (SHE) at the end (the potential of the saturated calomel electrode was 0.248 V vs. SHE at 20 °C). Electrochemical impedance spectra were recorded on an Autolab PGSTAT 302 (ECO Chemie, The Netherlands) in 0.1 M KCl–0.01 M phosphate buffer solution (pH = 7.4) containing 5 mM K3Fe(CN)6–K4Fe(CN)6 (1 : 1) at 0.21 V (vs. SCE). The frequency ranged from 100 000 Hz to 0.1 Hz and the applied voltage was 5 mV. The loading of the assembly process was evaluated by a quartz crystal microbalance (QCM) on a CHI 420B (Chenhua, China, see the ESI† for more detail). UV-vis absorption spectra were recorded on a U-4100 UV-vis-NIR spectrophotometer (Hitachi, Japan). Transmission electron microscopy (TEM) images were acquired on a Nanoscope III AFM (Veeco, America) and the samples were assembled onto Au pieces with ultrasmooth surface.

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References