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ABSTRACT

In this study, we report an oxygen-doped MoS₂ quantum dot (O-MoS₂ QD) hybrid electrocatalyst for the hydrogen evolution reaction (HER). The O-MoS₂ QDs were prepared with a one-pot microwave method by hydrazine-mediated oxygen-doping. The synthetic method is straightforward, time-saving, and can be applied in large scale preparation. Ultra-small O-MoS₂ QDs with the average size of 5.83 nm and 1–4 layers can be uniformly distributed on the surface of reduced graphene oxide (RGO). Benefited from the unique structure and the doping effect of oxygen in the MoS₂ QDs and the great number of active sites, the O-MoS₂ QD hybrid displayed outstanding electrocatalytic performance toward HER. A low overpotential of 76 mV at 10 mA/cm² and a Tafel slope of 58 mV/dec were obtained in an acidic solution toward HER. Additionally, the resultant O-MoS₂ QD hybrid also exhibited excellent stability and durability toward HER, displaying negligible current density loss after 1000 cycles of cyclic voltammetry. The design and synthesis of the electrocatalyst in this work open up a prospective route to prepare active and stable electrocatalysts toward substituting precious metals for hydrogen generation.

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I. INTRODUCTION

Hydrogen possesses the highest energy density than any other fuel on Earth.^{1,2} Hydrogen produced from water by the electrocatalytic hydrogen evolution reaction (HER) is one of the promising technologies to develop a green energy economy.³ However, the electrocatalytic HER needs to overcome the high overpotential of the reaction. At present, platinum-based precious metal catalysts are the optimal catalysts toward HER, but their high-cost and limited abundance restrict their large-scale application. Hence, the exploration of low-cost and non-precious metal catalysts with excellent performance has attracted much attention.⁴

Over the past few decades, molybdenum disulfide (MoS₂) as a layered semiconductor has been extensively studied due to its unique S-Mo-S sandwich structure.^{5,6} Two-dimensional MoS₂ possesses reasonable electrocatalytic activity toward HER,⁷ which is mainly attributed to the fact that the layered crystal structure of MoS₂

allows effective electron transfer along its basal planes and interface adsorption.⁸ In addition, the edge position of MoS₂ is the thermodynamic active site for electrochemical hydrogen evolution. Inspired by previous works,^{9–12} downsizing MoS₂ can effectively improve its HER activity by creating more edge sites. In addition, the introduction of heteroatoms to MoS₂ can alter the electronic structure and thus improve HER activity.^{13–15} Along those lines, we rationally designed oxygen-doped MoS₂ quantum dots (QDs) where some sulfur atoms in MoS₂ QDs were displaced with oxygen to regulate the electronic structure and create a greater number of active sites simultaneously, which is likely to translate into the greater activity of HER.

Herein, oxygen-doped MoS₂ QDs were prepared with a rapid microwave method within 5 min. The oxygen dopant amount can be conveniently tuned by hydrazine. The synthetic strategy overcomes the shortcomings of a long reaction time and high reaction temperature encountered in hydrothermal or solvothermal

reactions and can be applied in large scale synthesis. Furthermore, the ultra-small O-MoS₂ QDs with a laminar size of 5.83 nm and 1–4 layers were evenly distributed on the surface of reduced graphene oxide (RGO). Such a homogeneous distribution makes the catalyst expose more active sites and high conductivity. Oxygen doping can regulate the electronic structure and further improve the intrinsic electrocatalytic activity. Hence, the O-MoS₂ QD hybrid electrocatalyst exhibits outstanding catalytic performance and durability toward HER under acidic condition.

II. EXPERIMENTAL SECTION

A. Chemicals and materials

Ammonium tetrathiomolybdate [(NH₄)₂MoS₄] was bought from Sigma-Aldrich (USA). Graphene oxide (GO) powder was purchased from Turing Evolution Technology Co. Ltd. (Shenzhen, China). Hydrazine was commercial from Shanghai Chemical Reagent Co. Ltd. Pt/C (20%) was obtained from McLean Chemical Reagent Co. Ltd. Deionized water was used throughout the whole experiment. All reagents were of analytical grade and were applied without further purification.

B. Preparation of O-MoS₂ QD hybrid electrocatalyst

The O-MoS₂ QDs were prepared by a microwave synthesis method. 50 mg of GO powder was scattered in 50 ml ethylene glycol and ultrasonicated for 10 min. Then, 0.42 mmol of (NH₄)₂MoS₄ was added into the above solution and stirred continuously until a homogeneous brown solution was formed. Subsequently, 1.0% (volume ratio) hydrazine was added to the above solution and stirred for 10 min. The mixture was transferred into a 100 ml flask and heated in the microwave oven at 140 °C for 5 min. After cooling down to ambient temperature naturally, the product was obtained by filtration and washed with acetone, ethanol, and deionized water three times, respectively. The resulting sample was freeze-dried for 12 h. For comparison, the MoS₂ nanoparticles (MoS₂ NPs) and RGO were also prepared in the same synthetic procedure without GO and (NH₄)₂MoS₄ in the process, respectively.

C. Characterizations

The morphology of the O-MoS₂ QD sample was characterized by field-emission scanning electron microscopy (SEM; Germany Zeiss Ultra 55, 5 kV) and transmission electron microscopy (TEM, FEI Tecnai G2F20). X-ray powder diffraction (XRD) was performed on an intelligent rotating target x-ray diffractometer (Smart Lab). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ESCAL ab220i-XL electron spectrometer. The Raman spectrum of power catalysts was collected using a DXR Raman microscope under the laser excitation wavelength of 532 nm.

D. Electrochemical measurements

All electrochemical data were obtained from an electrochemical workstation (CHI 760E, Shanghai, Chenhua) using a standard three-electrode system. The Ag/AgCl electrode (with saturated KCl), graphite rod, and catalyst loaded glassy carbon electrode (GCE) were used as the reference, auxiliary, and working electrode in this

three-electrode system, respectively. The working electrode was prepared as follows: 4 mg sample was dispersed in the mixture solution that contained 800 μ l deionized water and 200 μ l ethanol and subsequently sonicated to form a uniform ink. Then, 5 μ l catalyst ink (loading about 0.28 mg/cm²) was dropped onto the surface of the GCE with a diameter of 3 mm. After that, 3 μ l of 0.5% (volume ratio) Nafion solution was dropped onto the surface of the GCE. In addition, 20% Pt/C was used as a benchmark for the HER by depositing the corresponding dispersion onto GC substrates. The active material mass loading of the electrodes was 0.28 mg/cm² for Pt/C. Subsequently, linear sweep voltammetry (LSV) curves were acquired at a scan rate of 5 mV/s. iR drop compensation (100% compensation) was made by considering *i* as the measured working electrode current and *R* as the series resistance generated by the working electrode substrate and electrolyte resistances. Electrochemical impedance spectroscopy (EIS) was conducted in an N₂-saturated 0.5M H₂SO₄ solution from 0.01 Hz to 10⁵ Hz with a modulation amplitude of 5 mV at the potential of 76 mV [vs reversible hydrogen electrode (RHE)]. All the potential values in our manuscript were corrected based on the equation of hydrogen electrode potentials: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 + 0.059 \text{ pH}$ (measured pH = 0.3).

III. RESULTS AND DISCUSSION

A. Preparation and characterization of O-MoS₂ QD hybrid electrocatalyst

The O-MoS₂ QD hybrid was prepared by a one-pot microwave process with hydrazine tuning the oxygen doping and RGO as dispersing and stabilizing agents, as illustrated in Scheme 1. Here, hydrazine acts as the anchoring point and controls the nucleation of O-MoS₂ QDs. To better explain the essential role of hydrazine, we synthesized the MoS₂ hybrid without the addition of hydrazine in the synthesis process under the same condition. The SEM image (see Fig. S1a of the [supplementary material](#)) showed that MoS₂ sheets with large sizes were formed. On the contrary, O-MoS₂ QDs with ultra-small sizes can be successfully grown on the RGO surface after the addition of hydrazine in the preparation process [Fig. 1(a)]. Such a hybrid makes the electrocatalyst with a high electrical conductivity because of the close connection between the O-MoS₂ QDs and the RGO nanosheet. The ultra-small O-MoS₂ QDs [as seen in Figs. 1(a) and 1(b)] anchored on RGO could offer a great number of active sites for the HER and effectively prevent unwanted agglomeration.¹⁶ This is due to the fact that GO sheets provide a platform for nucleation and subsequent growth of O-MoS₂ QDs.¹⁷ A control experiment was performed under identical synthesis conditions to produce MoS₂ NPs without GO nanosheets. The result showed that MoS₂ NPs with bigger sizes were formed (see Scheme 1 and Fig. S1b of the [supplementary material](#)), evidencing the important role of GO as a dispersing agent for mediating the growth of O-MoS₂ QDs.¹⁸

Figures 1(a) and 1(b) present TEM images of the O-MoS₂ QD hybrid at different magnifications. The laminar structured MoS₂ dots anchored on the surface of the crumpled RGO [Fig. 1(a)]. The O-MoS₂ QDs (red circles) with an average laminar size of 5.83 nm were evenly distributed on the surface of RGO [as displayed in Fig. 1(b) and inset]. From the HRTEM images of the

SCHEME 1. Schematic illustration of the process of O-MoS₂ QD hybrid electrocatalyst.

O-MoS₂ QD hybrid, MoS₂ QDs with 1–4 layers and an inter-layer spacing of 0.63 nm were grown intimately on the RGO sheets [Fig. 1(c)]. Figure 1(d) indicates the hexagonal atomic lattices in the MoS₂ basal planes and a large number of open edges of the quantum dot. The element mapping analysis of the O-MoS₂ QD hybrid further confirmed C, O, Mo, and S as the primary elemental components.

XRD was carried out to explore the structural information. In Fig. 2(a), the (002) peak of GO at 11.0° was not detected in the RGO and O-MoS₂ QD hybrid. Such an observation indicated that GO was efficiently reduced in the microwave synthesis. Moreover, the XRD patterns of the O-MoS₂ QD hybrid displayed four peaks at 9°, 24.3°, 32.9°, and 57.5°, which can be ascribed to the doping of oxygen atoms, (002) of RGO, and (100) and (110) planes of the 2H MoS₂, respectively. Moreover, the absence of the typical (002) peak of MoS₂ located at 14.0° (XRD of MoS₂ NPs shown in Fig. S2 of the supplementary material) indicated that the O-MoS₂ QDs had been successfully prepared.¹⁹ Furthermore, these weak and broad peaks of the O-MoS₂ QD hybrid suggested its low crystallinity. With the addition of hydrazine, a new and broad peak emerged at 9.0° in the low-angle region [brown line in Fig. 2(b)]. However, the peak diminished when the content of hydrazine exceeded 1.0% (volume ratio). This verified the critical role played by hydrazine in the formation of the oxygen-doped structure. The amounts of hydrazine make a difference in the final catalyst of the oxygen content (see Table S1 of the supplementary material). When the hydrazine amount

(volume ratio) is 1.0%, the doping content of the oxygen atom reached the highest, and at the same time, the O-MoS₂ QDs have been successfully prepared by applying the atomic ratio of S:Mo closest to 2:1 in the XPS measurement. Meanwhile, through EDS characterization, it was found that the atom ratio of C and O in RGO had no obvious change in the absence and presence of hydrazine in the reduction process at 140 °C (see Figs. S5a and S5b of the supplementary material). Further LSV measurement indicated that little activity of RGO was observed in the absence and presence of hydrazine (see Fig. S6a of the supplementary material). These results suggested that the addition of hydrazine plays a critical role in oxygen doping in MoS₂, not for the regulation oxygen content in RGO.

Raman spectroscopy was performed, as shown in Fig. 2(c). The D and G bands at 1345 cm⁻¹ and 1586 cm⁻¹ can be observed in the O-MoS₂ QD hybrid, RGO, and GO. The reduction of GO resulted in the enhancement of D bands in the O-MoS₂ QD hybrid and RGO.²⁰ The characteristic peaks of the O-MoS₂ QDs within the range of 250–500 cm⁻¹ were observed in the Raman spectra of the O-MoS₂ QD hybrid. The peaks were located at about 380 cm⁻¹ and 404 cm⁻¹, which can be attributed to the vibrational modes of in-plane E_{2g} and out-of-plane A_{1g} in the MoS₂ structure, respectively,^{16,21} while the peaks at 282 cm⁻¹ and 338 cm⁻¹ can be identified as the vibrational modes of B_{2g} and B_{1g} for Mo–O bonds,²² thus proving that the oxygen atom has been incorporated in the lattice of MoS₂ QDs [Fig. 2(d)]. The difference of peak frequencies between

FIG. 1. [(a) and (b)] TEM images with different magnifications of the O-MoS₂ QD hybrid. Inset of (b): particle size distribution of O-MoS₂ QDs. [(c) and (d)] HRTEM images of the O-MoS₂ QD hybrid with different magnifications. Scale bars are 5 nm and 2 nm, respectively. [(e)–(h)] Element mapping of C, Mo, O, and S in the O-MoS₂ QD hybrid.

E_{12g}^{1} and A_{1g} in the O-MoS₂ QD hybrid is 24 cm^{-1} , which indicated a limited number of layers in MoS₂, and this result is consistent with the HRTEM observation [Fig. 1(c)].²³ Moreover, to compare with MoS₂ sheets, the shrinkage in the frequency of E_{12g}^{1} and A_{1g} of the O-MoS₂ QD hybrid indicated that the interaction between the Mo precursor and the RGO could effectively refrain MoS₂ from aggregation.²⁴ The results are consistent with the SEM and TEM observations.

The bonding state and surface chemical properties of the O-MoS₂ QD hybrid were examined by XPS. The elements Mo, C, S, and O were distinctly shown in the XPS survey (see Fig. S3 of the [supplementary material](#)). The peaks of Mo3d and S2p in MoS₂ also appeared in the survey spectra, which confirmed the successful integration of the O-MoS₂ QDs with the RGO sheets. In Fig. 3(a), there are four characteristic peaks located at 235.9 eV, 232.4 eV, 228.5 eV, and 226.5 eV in the Mo3d region, which correspond to Mo⁵⁺3d, Mo⁴⁺d3/2, Mo⁴⁺d5/2, and S2s, respectively, according to the literature.²⁴ Figure 3(b) depicts the appearance of the S 2p spectrum, which can be deconvoluted into four peaks of S 2p1/2, S 2p3/2, S₂²⁻, or S²⁻ ligands and the S⁴⁺ of sulfate groups located at 163.3 eV, 162.0 eV, 164.6 eV, and 168.9 eV, respectively.^{20,25} The existence of S₂²⁻ or S²⁻ may be due to the incorporation of oxygen into MoS₂. As seen from Fig. 3(c), the peak of O 1s located at 531.0 eV can be attributed to the binding energy of the Mo–O bond, suggesting the existence of MoO₂,

thus proving the presence of chemical bonding rather than the surface oxidation. The peak at 532.1 eV can be ascribed to the adsorbed water molecules. In Fig. 3(d), the fine XPS spectrum of C 1s could be deconvoluted into four main peaks at 284.5 eV, 286.0 eV, 287.9 eV, and 290.0 eV, corresponding to C=C/C–C, C–O, C=O, and –COO–, respectively, which is consistent with the literature.²⁶ The difference in binding energy between C=C/C–C (284.5 eV) in the O-MoS₂ QD hybrid and the graphitized carbon peak of pristine GO (284.9 eV) was 0.4 eV²⁷ (XPS spectrum of C 1s for GO shown in Fig. S4 of the [supplementary material](#)). This result indicated a tremendous amount of charge transfer from RGO to O-MoS₂ QDs, which can enhance both the current density and catalytic activity of the composite. The binding energy of –COO– is extremely weak, which indicated that GO was successfully reduced to RGO during the reaction, agreeing well with the result of the XRD and Raman analysis. The existence of the C–O/C=O bond proved that a small portion of oxygen atoms existed in the RGO surface.

B. Electrocatalytic activity toward HER

The overpotential at 10 mA/cm² current density has been set as the standard requirement for the measurement to evaluate the HER performance of the catalyst as the value is related to solar fuel synthesis.²⁸ The HER performance of the as-prepared O-MoS₂QD

FIG. 2. (a) XRD patterns of GO, RGO, and O-MoS₂ QD hybrid. (b) XRD patterns of O-MoS₂ QD hybrid prepared with different amounts of hydrazine. (c) Raman spectra of GO, RGO, and O-MoS₂ QD hybrid. (d) Raman spectra of O-MoS₂ QD hybrid within the range of 250–500 cm⁻¹.

hybrid catalyst was investigated in a 0.5M N₂-saturated H₂SO₄ (pH = 0.3) electrolyte using a scan rate of 5 mV s⁻¹. Figure 4(a) described the linear sweep voltammetry (LSV) curve of the O-MoS₂ QD hybrid in the cathodic potential window of 0 to -0.45 V vs RHE. For a fair comparison, the HER catalytic activity of the MoS₂ NPs, RGO (prepared with the same process), and commercial 20% Pt/C was also investigated under the same conditions, as shown in Fig. 4(a). Evidently, besides the 20% Pt/C catalyst possessed the supreme HER performance, the O-MoS₂ QD hybrid showed excellent activity, showing an overpotential of 76 mV at 10 mA/cm² and an onset potential of 16 mV at 1.0 mA/cm². In contrast, RGO had almost no HER activity and MoS₂ NPs have a relatively poor activity toward HER (reached 167 mV at 10 mA/cm²). From Fig. 4(c), one could see that, compared with MoS₂ NPs, the overpotential required to drive an HER current density of 10 mV, 20 mV, and 50 mV/cm² with the O-MoS₂ QD hybrid was reduced to 76 mV, 100 mV, and 131 mV, respectively. The increment in the activity of the O-MoS₂ QD hybrid toward HER may be attributed to the following factors: First, the unique lamellar structure of the O-MoS₂ QD hybrid exposes more catalytic active sites, allows free diffusion

of the electrolyte, and results in shortened path lengths for electron transfer over the whole electrode. Second, ultra-small O-MoS₂ QDs are uniformly distributed in the highly conductive RGO carbon matrix, serving as active sites for the HER. It is known that proton discharge is the initial step in the acidic solution for the HER and H₃O⁺ can be easily adsorbed at Lewis base sites. Here, the O dopants, some sulfur atoms in the structure of MoS₂ QDs were replaced by oxygen atoms, form a Lewis base on adjacent molybdenum, and this is thought to accelerate the HER in these systems. In the meantime, oxygen doped in the structure of MoS₂ QDs can also effectively adjust the electronic structure of the electrocatalyst, thus enhancing the intrinsic activity.²⁹ Finally, the enhancement in the intrinsic activity of the O-MoS₂ QD hybrid could also be caused by the synergy between RGO and O-MoS₂ QDs with ultra-small sizes. Furthermore, the effect of the oxygen dopant amount in O-MoS₂ QDs on the HER activity was investigated, as shown in Fig. S6b (supplementary material). The O-MoS₂ QD hybrid with 22.73% (atom%) oxygen doping (corresponding the addition of 1.0% hydrazine) shows an optimized HER activity (see Table S1 of the supplementary material). Meanwhile, from the EDS of the optimal O-MoS₂

FIG. 3. (a) Mo 3d, (b) S 2p, (c) O 1s, and (d) C 1s high-resolution XPS spectra of the O-MoS₂ QD hybrid.

QD hybrid (see Table S3 of the [supplementary material](#)), we could see that the content of oxygen is 22.8% and the atomic ratio of S: Mo is 2.02:1. These results are consistent with the XPS and Raman results.

Moreover, the Tafel slope was calculated from the linear portion of the Tafel plots [Figs. 4(b) and 4(d)], which can help us to understand the specific reaction mechanism of HER. The Tafel slope can be acquired by the Tafel equation,³⁰

$$\eta = a + b \log j,$$

where a , b , and j correspond to the constant, the Tafel slope, and current density, respectively.

In the acidic environment, there are three main reaction steps involved in HER,^{31–33} as shown below:

- Volmer reaction: $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$, $b = 120$ mV/dec.
- Heyrovsky reaction: $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$, $b = 40$ mV/dec.
- Tafel reaction: $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$, $b = 30$ mV/dec.

The Tafel slope of the O-MoS₂ QD hybrid catalyst is 58 mV/dec, suggesting that the electrochemical process is carried out

according to the Volmer–Heyrovsky reaction. The lower Tafel slope showed that the HER follows the Volmer–Heyrovsky mechanism and the desorption of hydrogen was the rate-limiting step in our case.³⁴ Besides, even compared with other MoS₂ QDs based materials as well as other transition metal dichalcogenide QDs reported in the literature, the electrocatalytic activity of the O-MoS₂ QD hybrid for the HER is still outstanding (see Table S2 of the [supplementary material](#)).

C. Electrocatalytic mechanism

To illustrate the mechanism of the O-MoS₂ QD hybrid toward HER, as shown in Fig. 5, RGO and O-MoS₂ QDs that act as a conductive carrier and active substance can provide electrons and active sites, respectively. The H_3O^+ will be adsorbed to the surface of the active substance of the O-MoS₂ QDs when it contacted with the catalyst fully. The intermediate adsorbed hydrogen atom will be produced under the action of electric current and it will combine with the proton in the electrolyte and release electrons from O-MoS₂ QDs, thus producing hydrogen gas. During the hydrogen evolution reaction, the chemical interaction between

FIG. 4. (a) LSV curves of MoS₂ NPs, O-MoS₂ QD hybrid, RGO, and 20% Pt/C. (b) The corresponding Tafel plots of MoS₂ NPs, O-MoS₂ QD hybrid, RGO, and 20% Pt/C. (c) Overpotential against the current density of 10 mA, 20 mA, and 50 mA/cm² for 20% Pt/C, O-MoS₂ QD hybrid, and MoS₂ NPs, respectively. (d) The Tafel slope histogram of 20% Pt/C, O-MoS₂ QD hybrid, MoS₂ NPs, and RGO.

RGO and O-MoS₂ QDs played an important role for the HER. The main reasons are as follows: (1) RGO with high specific surface areas is an ideal scaffold candidate.³⁵ (2) Moreover, the design of the RGO-based hybrid could enhance the HER activity of the O-MoS₂ QDs by reducing their ΔG^0_{H} .³⁶ (3) The presence of RGO

FIG. 5. The diagram of the HER mechanism of the O-MoS₂ QD hybrid.

to O-MoS₂ QDs inhibits the agglomeration and restacking effects, leading to a uniform distribution of O-MoS₂ QDs on the 2D platform.^{37,38}

In order to further research the prominent electrochemical activity mechanism of the O-MoS₂ QD hybrid toward HER, we analyzed the electrochemical active surface area (ECSA) and electrochemical impedance spectra (EIS) of the O-MoS₂ QD hybrid, MoS₂ NPs, and RGO. The ECSA of the electrocatalyst was estimated using the double-layer capacitance (C_{dl}) parameter.³⁹ Meanwhile, the cyclic voltammetry was used to calculate the C_{dl} , as displayed in Fig. S6 of the [supplementary material](#). The C_{dl} was obtained using the function of capacitive current (the difference of positive and negative current densities at an intermediate value of the potential window) against different scan rates (10–90 mV/s), as shown in Fig. 6(a). The half of the slopes in Fig. 6(a) corresponds to the value of C_{dl} in which we could estimate the double-layer capacitance to be 11.80 mF/cm² for the O-MoS₂ QD hybrid electrocatalyst, which is larger than that of MoS₂ NPs (3.50 mF/cm²) and RGO (0.45 mF/cm²). This result indicated that large ECSA (295 cm²) of the O-MoS₂ QD hybrid catalyst might improve hydrogen evolution activity. The EIS

FIG. 6. (a) Current density against scan rate plots of MoS₂ NPs, O-MoS₂ QD hybrid, and RGO. (b) EIS spectra of MoS₂ NPs, O-MoS₂ QD hybrid, and RGO in an N₂-saturated 0.5M H₂SO₄ electrolyte.

measurement was conducted to study the charge transfer resistance (R_{ct}) of HER. Obviously, RGO and MoS₂ NPs presented much larger R_{ct} because of the absence of the active site toward HER or intrinsic semiconductor properties, respectively. Compared with MoS₂ NPs

and RGO alone, the as-prepared O-MoS₂ QD hybrid composite displayed a lower R_{ct} , and the corresponding impedance equivalent circuit diagram was shown in Fig. S7 (supplementary material). More charges transferred from the active surface to the conductive carrier

FIG. 7. (a) Current density against time curves (i - t curves) of the O-MoS₂ QD hybrid catalyst under the overpotential of 76 mV (vs RHE) for 20 h. Inset: LSV curves before and after 1000 cycles with a scan rate of 50 mV/s. (b) LSV curves of RGO and (c) LSV curves of MoS₂ NPs before and after 1000 cycles with a scan rate of 50 mV/s. (d) Current density against time curves (i - t curves) of the O-MoS₂ QD hybrid catalyst under the overpotential of 76 mV (vs RHE) for 20 h after six months. Inset of (d): LSV curves of the O-MoS₂ QD hybrid before and after six months with a scan rate of 5 mV/s.

for the O–MoS₂ QD hybrid, thus resulting in the catalytic efficiency, agreeing well with the above LSV analysis.

D. Stability of the electrocatalyst

Stability is a very significant indicator for the practical application of electrocatalysts. The time-dependent current density curve (*i*–*t* curve) of the O–MoS₂ QD hybrid was used to depict the stability of the catalyst under an overpotential of 76 mV (vs RHE). As shown in Fig. 7(a), the current densities of the O–MoS₂ QD hybrid catalyst remained stable even after continuous electrolysis for 20 h in the acidic solution, and only a slight decrease in the current density was observed, which may be due to the H₂ adsorption on the electrode surface and the depletion of H⁺ during the test process.⁴⁰ The inset of Fig. 7(a) shows that the LSV curves of the O–MoS₂ QD hybrid after 1000 cycles in 0.5M H₂SO₄ media almost overlapped with the initial curves at this current density. These facts suggested that the catalyst possesses relatively high stability toward HER. Furthermore, the O–MoS₂ QD hybrid and RGO both exhibited slight loss of the current density after 1000 cycles (the inset of Figs. 7(a) and 7(b)). Weak catalytic activity was observed in MoS₂ NPs after only 1000 CV cycles [Fig. 7(c)], implying the extremely poor stability of pure MoS₂ NPs. The increased stability of the O–MoS₂ QD hybrid for the HER is derived from the protection system built by the O–MoS₂ QDs anchored on the RGO nanosheet. To demonstrate the chemical stability of the catalyst, Fig. 7(d) and the inset of Fig. 7(d) present the stability of the O–MoS₂ QD hybrid after six months at room temperature. It was found that the current density of the O–MoS₂ QD hybrid after six months almost did not decline [inset Fig. 7(d)]. These facts suggested that the O–MoS₂ QD hybrid not only has stable electrochemical properties but also has outstanding chemical stability. Notably, XRD and Raman analysis revealed that no obvious structural changes were observed for the O–MoS₂ QD hybrid after *i*–*t* measurements in the acid electrolyte (see Fig. S9 of the supplementary material). These results further demonstrated the stability of the O–MoS₂ QD hybrid as well as MoS₂ based nanomaterials in previous studies.⁴¹ To sum up, all the above results indicated that the O–MoS₂ QD hybrid exhibited outstanding stability and durability toward HER in the acidic electrolyte.

IV. CONCLUSION

In summary, a simple microwave synthesis method for one-pot and direct synthesis of O–MoS₂ QDs anchored on RGO sheets was demonstrated. The unique structure and the doping of the oxygen atom not only expose abundant active sites but also efficiently regulate the electronic structure of MoS₂ QDs, which leads to the outstanding performance of O–MoS₂ QDs hybrid toward HER. The O–MoS₂ QD hybrid catalyst possessed excellent catalytic activity and durability for the hydrogen evolution reaction. What is more important is that the synthetic strategy is convenient, cost-effective, and time-saving, and the reaction conditions are relatively mild, which makes it very promising for large-scale applications.

SUPPLEMENTAL MATERIAL

See the supplementary material for additional details on the structure and morphology characterization of contrast catalysts,

oxygen doping content and its effect on hydrogen evolution activity, the comparison results of our electrocatalyst with other reported electrocatalysts, and structure characterization of the catalyst after electrochemical tests.

AUTHOR'S CONTRIBUTION

J.P. and X.Y. contributed equally to this work.

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There are no conflicts to declare.

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