Electronic Supplementary Information

One-step hydrothermal synthesis of monolayer MoS_2 quantum dots for highly efficient electrocatalytic hydrogen evolution

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Experimental Section

Reagents and materials

Sodium molybdate, dibenzyl disulfide and bulk MoS_2 powders were purchased from Aladdin Industrial Inc. H_2SO_4 was purchased from Tianjin Fuyu Chemical Reagent Co. Ltd., China. Pt and glassy carbon electrodes were purchased from Tianjin Aidahengsheng Technology. Co. Ltd., China. All chemicals were used as received without special purification. The water used throughout all experiments was deionized (DI) water purified through a Millipore system.

Preparation of MoS_2 QDs

In brief, 0.4 g of $Na_2MoO_4 \cdot 2H_2O$ was dissolved in 30 mL of water with ultrasonication for 20 min. Then, 0.38 g of dibenzyl disulfide and 30 mL of ethanol were added to the solution followed by ultrasonication for 30 min. The mixture was then transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 220 °C for 18 h. Upon cooling naturally to room temperature, drain the mother liquor and add new DI water into the autoclave. The resulting suspension was then centrifuged for 60 min at 12 000 rpm to separate the supernatant and centrifugate. The light brown supernatant (Fig. 1a) was MoS_2 QDs and the centrifugate (Fig. 1b) was the composite of MoS_2 QDs and micro-sized particles.

Characterization

The Transmission electron microscopy (TEM) images were taken with a JEM-2100. Field emission scanning electron microscope (FESEM) were performed on SU8020. Atomic force microscopy (AFM) images were obtained by using a Bruker

Multimode 8 in the tapping mode after the samples were deposited on a freshly cleaved mica surface by drop-casting method. X-ray photoelectron spectroscopy (XPS) experiments were conducted using an AXISULTRA X-ray photoelectron spectrometer using Al Kα as the exciting X-ray source. X-ray diffraction (XRD) was acquired by a SmartLab X-ray diffraction system. Photoluminescence (PL) spectra were carried out with a Hitachi F-7000 spectrophotometer. Ultraviolet-visible (UV–vis) spectroscopy was recorded on a Hitachi U-3900 spectrophotometer. Raman spectra were measured using a Renishawin Via micro-Raman spectrometer with the excitation laser line at 532 nm.

Electrochemical characterization

Electrochemical measurements were carried out with a computer-controlled IM6ex (Zahner, Germany) in a standard three-electrode cell using Ag/AgCl (in 3.5 M KCl solution) electrode as the reference electrode, a platinum foil as the counter electrode and a glassy carbon (GC) electrode modified by MoS_2 as the working electrode. The MoS_2 QD electrode was prepared as follows: (1) 80 μL Nafion solution (5 wt%) was dispersed in 1 mL MoS_2 QDs solution by sonicating for 10 min to form a homogeneous solution; (2) 5 μL portion of the resulting solution was drop cast onto a GC electrode with 3 mm diameter by a microliter syringe and dried at room temperature. The bulk MoS_2 electrode was prepared as follows: (1) 4 mg of sample and 80 μL Nafion solution (5 wt%) were dispersed in 1 mL water using sonication for 1 h to form a homogeneous ink; (2) This step is same as the preparation of MoS_2 QD electrode. The electrochemical impedance spectroscopy (EIS) was carried out in the

same configuration at η=0.3 V from 10^{-2} to 10^{6} Hz with an AC voltage amplitude of 5 mV.

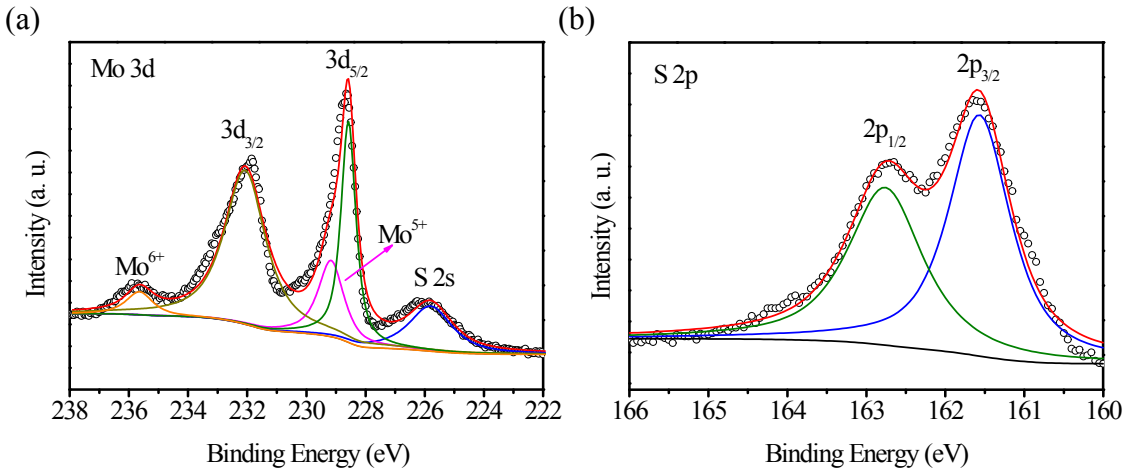

Fig. S1. High-resolution XPS of (a) Mo 3d and (b) S2p spectra of the MoS_2 QDs.

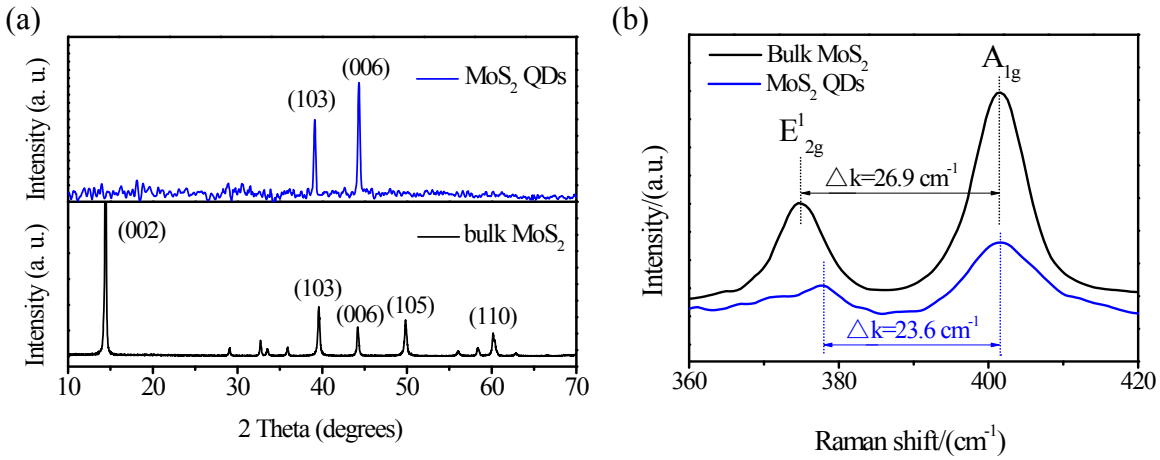

Fig. S2. (a) XRD patterns of MoS_2 QDs and bulk MoS_2. (b) Raman spectra recorded using a 532 nm laser for MoS_2 QDs and bulk MoS_2.

Table S1. Comparion of HER performance in acidic media for MoS_2 QDs with other MoS_2-based HER electrocatalysts.

Catalyst		Onset potential (mV)	Tafel slope (mV/dec)	References
Regular MoS_2	Defect-free MoS_2 Nanosheets	-180	87	[37]
	Nanosized bulk MoS_2	-0.280	82	[38]
	Pure MoS_2 nanoparticles	-0.160	77	[39]
Structural modified MoS_2	Defect-rich MoS_2 nanosheets	-120	50	[37]
	Disorder engineering in oxygen-incorporated MoS_2	-120	55	[40]
MoS_2/conductive substrates composites	MoS_2/Graphene/Ni-foam	-109	42.8	[41]
	MoS_2 /RGO	-100	41	[42]
	MoS_2/CNF mats	-120	45	[43]
	MoS_2 QDs	-160	58	This work

RGO: Reduction graphene oxide

CNF: Carbon fiber foam