



## Short communication

# Graphene film-confined molybdenum sulfide nanoparticles: Facile one-step electrodeposition preparation and application as a highly active hydrogen evolution reaction electrocatalyst



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## H I G H L I G H T S

- We demonstrate the first one-step fabrication of graphene film-confined MoS<sub>x</sub> nanoparticles.
- Such hybrid film is used as a novel HER electrocatalyst in acidic solution.
- Such hybrid film shows high HER activity and good stability.

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## A B S T R A C T

MoS<sub>x</sub> nanoparticles–graphene hybrid film was deposited onto a glassy carbon electrode by a facile one-step electrodeposition approach using MoS<sub>4</sub><sup>2−</sup> and graphene oxide as precursors. As a novel hydrogen evolution reaction (HER) electrocatalyst, this hybrid film exhibits highly catalytic activity and good stability.

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## 1. Introduction

Hydrogen is an ideal candidate for the replacement of fossil fuels in the future [1]. Electrolysis of water, currently the simplest way to produce hydrogen of high purity at the most economical price, has attracted considerable attention [2,3]. The noble metals, such as platinum, have large cathodic current densities at low overpotentials in the hydrogen evolution reaction (HER) [4–6]. However, they suffer from high cost and resource scarcity, hindering their large-scale applications. Thus, replacement of Pt with earth-abundant metals is highly desirable.

Over the past few years, MoS<sub>2</sub> has been identified as promising alternatives for noble metals due to its earth abundance composition and excellent HER activity [7]. Both experimental and theoretical results suggest that the HER activity originates from the sulfur edges of MoS<sub>2</sub> layers, while the basal surfaces are catalytically inert [8–11]. Bulk MoS<sub>2</sub> shows poor HER activity [12], but such issue can be solved by designing MoS<sub>2</sub> nanostructures with more edge sites. The poor electrical conductivity issue of MoS<sub>2</sub> can be fixed by using conductive carbon as a support. Indeed, Dai and co-workers have developed reduced graphene oxide (GO) supported MoS<sub>2</sub> nanoparticles as highly efficient HER electrocatalysts [13]. For electrocatalytic application, the direct fabrication of catalyst film onto electrode surfaces has an obvious advantage of eliminating the immobilization step; however, the development of catalyst film based on MoS<sub>2</sub> for HER is scarcely reported. Until recently have Chang et al. deposited hydrothermally MoS<sub>x</sub> onto graphene-protected three-dimensional Ni foams for highly efficient

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hydrogen production [14]; however, it suffers from the involvement of dangerous gases ( $H_2$ ), high temperatures and a complicated procedure for catalyst film preparation.

In this communication, for the first time, we demonstrate the facile deposition of  $MoS_x$  nanoparticles–graphene ( $MoS_x$ –G) hybrid film onto a glassy carbon electrode (GCE) by a one-step electrodeposition approach with the use of  $MoS_4^{2-}$  and graphene oxide as precursors. We further show the utilization of such hybrid film as a highly active HER electrocatalyst with an overpotential of 200 mV at a cathodic current density of  $17 \text{ mA cm}^{-2}$ . A small Tafel slope of  $43 \text{ mV dec}^{-1}$  is observed, suggesting that the surface chemistry mechanism is responsible for HER. Such catalyst exhibits a good stability.

## 2. Experimental

### 2.1. Reagents and materials

$H_2SO_4$  was purchased from Tianjin Fuyu Chemical Reagent Co. Ltd., China.  $(NH_4)_2MoS_4$  was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) was purchased from Sigma–Aldrich. All chemicals were used as received without further purification. The water used throughout all experiments was deionized water purified through a Millipore system.

### 2.2. Preparation of $MoS_x$ –G hybrid film

The cyclic voltammograms (CVs) were performed for the electrochemical deposition of  $MoS_x$ –G hybrid film with the potential range from  $-1.2 \text{ V}$  to  $0.5 \text{ V}$  with a scan rate of  $30 \text{ mV s}^{-1}$  for different scan cycles [15]. The deposition bath used for the electrodeposition was simply composed of  $(NH_4)_2MoS_4$  (5 mM) and GO ( $1 \text{ mg mL}^{-1}$ ). GCE was used as working electrode for electrodeposition. A graphite electrode and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. For comparison, pure  $MoS_x$  was electrodeposited on GCE by the same route without adding GO into the deposition solution. The loading of  $MoS_x$ –G was about  $0.1 \text{ mg cm}^{-2}$ .

### 2.3. Structural characterizations

Scanning electron microscopy (SEM) images were taken on an XL30 ESEM. X-ray photoelectron spectroscopy (XPS) experiments were made on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

### 2.4. Electrochemical characterization

Electrochemical measurements are performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). The electrochemical properties of the prepared electrocatalysts were studied in a standard three-electrode system. The  $MoS_x$ –G or  $MoS_x$  modified GCE was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and graphite as the counter electrode. Electrical impedance spectroscopy (EIS) was recorded under the following conditions: AC voltage amplitude 5 mV, frequency ranges  $10^5$ –1 Hz.

## 3. Results and discussion

Fig. 1a shows the low-magnification scanning electron microscopy (SEM) image of the resulting hybrid film on GCE, indicating the film consists of a large amount of nanoparticles and graphene sheets. The high-magnification SEM image (Fig. 1b) further reveals

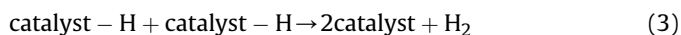
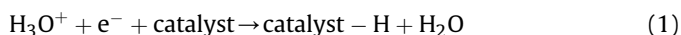
the formation of  $MoS_x$  nanoparticles–graphene hybrid film. The deposition of graphene film from GO suspension can be rationally explained as follows [16]: GO in direct contact with GCE accepts electrons and is electrochemically reduced into graphene during cathodic scan. Because of their poor solubility in water, these graphene sheets are directly attached to GCE surface to form film. It is of importance to mention that electrodeposition without the presence of GO only produces film of pure molybdenum sulfide nanoparticles (Fig. 1c). The high-magnification SEM image (Fig. 1d) shows that the nanoparticles are nanoparticle aggregates or cross-linked nanoparticles. These results suggest that graphene film can effectively prevent the aggregation of the nanoparticles thus generated.

The chemical states of Mo and S in the hybrid film were further investigated by X-ray photoelectron spectroscopy (XPS). Fig. 2 displays the detailed XPS scans for the Mo and S binding energies for these  $MoS_x$  catalysts. The binding energies of Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  are 228.9 eV and 232.1 eV, respectively, which can be assigned to  $Mo^{4+}$  [17–19]. The peaks, corresponding to the S  $2p_{1/2}$  and  $2p_{3/2}$  orbitals of divalent sulfide ions ( $S^{2-}$ ) are observed at 162.9 and 161.8 eV. The S: Mo stoichiometric ratio is 2.1, suggesting that the nanoparticle is close to  $MoS_2$ . In addition to the XPS peaks for  $MoS_2$  structure, other sets of peaks are also observed. The observation of Mo  $3d_{3/2}$  and Mo  $3d_{5/2}$  binding energies at 233.1 and 230 eV suggests the presence of  $Mo^{5+}$  ions. The peak at 235.6 eV is that for  $3d_{3/2}$  of  $Mo^{6+}$  [20]. The peak at 226.3 eV corresponds to the S 2s component [21]. Meanwhile, the S  $2p_{1/2}$  and S  $2p_{3/2}$  energies at 164.3 and 163.2 eV indicate the existence of bridging  $S_2^{2-}$  or apical  $S^{2-}$  [22,23]. The S 2p spectrum can be fit with two S 2p doublets, which is similar to those of amorphous  $MoS_3$ . These observations imply the coexistence of  $MoS_2$  and  $MoS_3$  [24].

The  $MoS_x$ –G hybrid film is prepared by CVs with the potential range from  $-1.2 \text{ V}$  to  $0.5 \text{ V}$  with a scan rate of  $30 \text{ mV s}^{-1}$  for 30 scan cycles, as shown in Fig. 3a. Electrochemical measurements of the hybrid film were conducted in a three-electrode cell. The linear scan voltammograms (LSVs) measurements were used to test HER properties of  $MoS_x$ –G hybrid film and  $MoS_x$  film with a scan rate of  $5 \text{ mV s}^{-1}$  in  $0.5 \text{ M H}_2SO_4$ . Meanwhile, the commercial Pt/C catalyst was also tested with the same measurements. Fig. 3b shows the polarization curves of  $MoS_x$ –G,  $MoS_x$  and Pt/C. The  $MoS_x$ –G shows a small onset overpotential ( $\eta$ ) of 130 mV for HER, which is smaller than that of  $MoS_x$  ( $\eta = 160 \text{ mV}$ ). And the Pt/C exhibits the best HER catalytic performance ( $\eta = 20 \text{ mV}$ ). Likewise, the highly catalytic activity is demonstrated by comparing the current density of  $MoS_x$ –G and  $MoS_x$ . For achieving a catalytic current density of  $10 \text{ mA cm}^{-2}$ , the overpotentials need to be 183 mV and 208 mV for  $MoS_x$ –G and  $MoS_x$ , respectively. Such performance of  $MoS_x$ –G is comparable to that of previous reports [7,9,24,25].

Tafel plots of these catalysts were recorded with the linear regions fitted into the Tafel equation ( $\eta = a + b \log j$ , where  $j$  is the current density and  $b$  is the Tafel slope) [26]. The Tafel slopes for Pt/C,  $MoS_x$ –G and  $MoS_x$  are  $\sim 30$ ,  $\sim 43$  and  $\sim 50 \text{ mV dec}^{-1}$ , respectively (Fig. 3c).

In acid solutions, three principal reactions are assumed to predominate when hydrogen is evolved on a metal catalyst, commonly named the Volmer [Equation (1)], Heyrovsky [Equation (2)], and Tafel reactions [Equation (3)] [27].



The Tafel slope is an inherent property of the catalyst. When the Volmer reaction is the rate-determining step of the HER, Tafel

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