



## Original Research Paper

# Hydrothermal synthesis of selenium-doped graphene-like molybdenum disulfide/graphene hybrid as an efficient electrocatalyst for hydrogen evolution



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## ABSTRACT

Se-doped graphene-like MoS<sub>2</sub>/graphene hybrid (Se-GL-MoS<sub>2</sub>/G) has been synthesized by an ionic liquid-assisted hydrothermal method and is also evaluated as an electrochemical catalyst for hydrogen evolution reaction (HER). The results indicate that Se-doped MoS<sub>2</sub> nanosheets are characteristic of monolayers with rich exposed active edges and are well dispersed in the highly conductive graphene networks. Consequently, the desirable microstructures endow the Se-GL-MoS<sub>2</sub>/G hybrid with significantly enhanced catalytic activity for HER compared with the bare MoS<sub>2</sub>.

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## 1. Introduction

To date, the energy issue is the most important topic and an excessive reliance on the combustion of nonrenewable fossil fuels brings not only ecological problems but also harsh ongoing impacts on the global economy and society [1]. There is a pressing requirement for cost-effective, efficient, and environmentally benign energy that can power energy demanding areas. As one kind of green energy, hydrogen has been vigorously pursued as a promising alternative fuel for traditional fossil fuels [2]. Electrocatalytic hydrogen evolution reaction (HER) is considered to be one of the most important pathways for hydrogen production without dependence on consumable resources [3]. Thereinto, electrocatalyst always plays an indispensable role in reducing the overpotential of electrodes, consequently promoting the reaction yield [4–6]. Currently, the most effective HER electrocatalysts are the Pt-group noble metals, which are known to catalyze HER at a significant rate with almost no overpotential [7]. However, the high costs and scarcity of Pt severely limit its widespread applications in HER and it still remains a great challenge to develop highly active and abundant HER catalysts.

Recent studies have shown that nanosized MoS<sub>2</sub> are impressive catalysts for HER [8]. Theoretical calculations and experiments has turned out that the catalytic activity arises from active sites located along the edges of MoS<sub>2</sub> layers and the edges of MoS<sub>2</sub>, particularly the terminated sulfur edges, are considered as active sites in catalysis for H<sub>2</sub> evolution, while the basal surfaces are catalytically inert [9]. Therefore, increasing the number of active sites of the catalyst is certainly an efficient pathway to enhance the HER activity. To date, a variety of strategies have been employed to fabricate MoS<sub>2</sub> nanostructures with preferentially exposed edges such as doublegyroid MoS<sub>2</sub> [10], vertically aligned MoS<sub>2</sub> layer films [11–14], porous MoS<sub>2</sub> films [15–18], ultrathin MoS<sub>2</sub> nanoplates [19–22], highly distorted or divided MoS<sub>2</sub> [23–25], amorphous MoS<sub>x</sub> [26–30], and MoS<sub>2</sub> nanoflowers [31–34]. Nevertheless, edges are usually the rare surface sites of layered materials due to their inherently high surface energy, which becomes a thermodynamic driving force impeding the formation of highly energetic and atomically undercoordinated edge sites at the surface relative to non-active basal sites [35]. Therefore, synthesis of nanosized MoS<sub>2</sub> with largely exposed edges is still confronted with a big challenge.

Besides engineering active edges, the HER activity of MoS<sub>2</sub> can also be tuned through tailoring its chemical composition. For instance, transition metal cationic doping including cobalt or nickel has been proved to promote the electrocatalytic performance of MoS<sub>2</sub> [36]. Additionally, sulfur in MoS<sub>2</sub> can be partially substituted with other chalcogens such as selenium. It has been

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suggested from theoretical calculations that hydrogen adsorption is slightly too weak on sulfided Mo edges but slightly too strong on selenided Mo edges [37,38]. The introduction of the polyelectronic Se atom can modulate the *d*-band electronic structure of molybdenum, probably leading to tuned hydrogen adsorption free energy and consequently electrocatalytic activity [39].

On the other hand, the inherent poor conductivity of MoS<sub>2</sub> is another pivotal issue that needs to be solved. Specially, the extremely low conductivity between two adjacent van der Waals bonded S-Mo-S layers would greatly compromise the catalytic performance [40,41]. In this aspect, effectively decreasing layer numbers is believed to be favorable to reducing the interlayered resistance and thus improving the hopping efficiency of electrons between MoS<sub>2</sub> layers [42]. Additionally, incorporation of highly conductive carbon-based materials such as graphite and its allotrope such as carbon nanotubes and graphene has also been confirmed to effectively promote electron transport from the active sites to the electrodes and accelerate the kinetics of electrode reaction [43–47,19]. Among, graphene has attracted considerable interest for its superior electrical conductivity, large surface area and excellent flexibility [48]. Moreover, graphene can act as an ideal platform to facilitate selective growth of MoS<sub>2</sub> and stabilize the high dispersion of MoS<sub>2</sub> [49].

In a liquid-phase approach toward synthesis of graphene and its composites, graphene oxide sheets (GO) are usually utilized as precursors owing to their abundance of oxygen-containing functional groups on the GO surface and edges, thereby leading to their better dispersion and accessibility [49]. However, the exfoliated GO are inclined to reaggregating or restacking due to their van der Waals forces. As a result, the advantages of the separated nanosheets disappear, leading to significantly different properties that are characteristic for isolated atomic layers [50]. Additionally, the oxygen-containing functional groups render the GO surface negatively charged, which would interfere the interaction between GO and negatively charged inorganic species such as MoS<sub>4</sub><sup>2-</sup>. Recently, ionic liquids (ILs) have been widely employed for synthesis of inorganic nanomaterials and electrochemical applications owing to their unique properties [51]. It was reported that ILs could not only untangle bundles of carbon nanotubes and exfoliate graphite into graphene, but also functionalize GO or graphene to improve their hydrophilic properties, dispersibility and processability [52]. Moreover, it has been demonstrated that ILs can stabilize highly energetic, thermodynamically unstable under-coordinated surfaces and increase exposed active edges of MoS<sub>2</sub> [53]. Furthermore, adsorption of ILs onto the basal planes of the MoS<sub>2</sub> layers has been shown to be energetically favorable, which is in favor of disruption of the van der Waals interactions holding the MoS<sub>2</sub> layers together to form de-layered structures [54].

Herein, we present a facile IL-assisted hydrothermal route to fabricate Se-doped graphene-like MoS<sub>2</sub>/graphene hybrid (Se-GL-MoS<sub>2</sub>/G), which highlights a scalable pathway to accomplish the task of exfoliating MoS<sub>2</sub> nanosheets into single-layered structures and simultaneously increasing exposed active edge sites and conductivity of the hybrids.

## 2. Experimental section

### 2.1. Hydrothermal synthesis of Se-GL-MoS<sub>2</sub>/G hybrid

Graphene oxide (GO) was prepared using the modified Hummer's method [52]. In a typical synthesis, 1.5 mL of IL (1-ethyl-3-methylimidazolium bisfluorosulfonylimide, EMIMFSI) was dropped into 30 mL aqueous dispersion of GO (3.0 mmol) under vigorous stirring to allow cation [EMIM]<sup>+</sup> well adsorbed on the GO surface. After that, 15 mL 100 mM of ammonium tetrathiomolybdate

(NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> solution and 15 mL hydrazine hydrate-Se solution (0.3 mmol of Se powder) were dropped into the above mixture slowly. Afterwards, the resultant mixture was transferred into the 100 mL Teflon-lined stainless steel autoclave, which was heated and maintained at 210 °C for 24 h. After cooling naturally, the product was collected by centrifugation and washed several times and dried in the vacuum oven at 60 °C for 12 h. For comparison, the bare MoS<sub>2</sub> and MoS<sub>2</sub>/G samples were also prepared by a similar method.

### 2.2. Characterizations

XRD patterns were recorded with a Thermo X'TRA X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm). The morphologies of the samples were observed by using a SIRION-100 field emission SEM. HRTEM was performed on a JEOL JFL-2010 TEM operating at 200 kV. X-ray photoelectron spectra (XPS) were processed on a Perkin-Elmer PHI5000c XPS, using C 1s (B. E. 284.6 eV) as a reference. Raman spectra were recorded with 514 nm Ar ion laser at 6 mW for 50 s employing a Jobin Yvon Lab-Ram HR spectrometer.

### 2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system at an electrochemical station (CHI660D). Typically, 4 mg of catalyst and 80  $\mu$ L Nafion solution (5 wt%) were dispersed in 1 mL water-ethanol solution with volume ratio of 4:1 by sonicating for 1 h to form a homogeneous ink. Then 6  $\mu$ L of the dispersion was loaded onto a glassy carbon electrode with 5 mm diameter to prepare working electrode. Linear sweep voltammetry with scan rate of 5 mV s<sup>-1</sup> was conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> using saturated calomel as the reference electrode, a Pt plate as the counter electrode. All the potentials were calibrated to a reversible hydrogen electrode (RHE).

## 3. Results and discussion

### 3.1. Microstructure and morphology of Se-GL-MoS<sub>2</sub>/G hybrid

The XRD patterns of the MoS<sub>2</sub>, MoS<sub>2</sub>/G and Se-GL-MoS<sub>2</sub>/G hybrid plotted in Fig. 1 are in good agreement with a hexagonal structure (JCPDS 37-1492). As for the bare MoS<sub>2</sub>, the appearance of the high and sharp (002) peak at  $2\theta = 14.0^\circ$  in Fig. 1a signifies a well stacked layered structure and the *d*-spacing is calculated about 0.63 nm. When graphene is introduced, it can be seen from

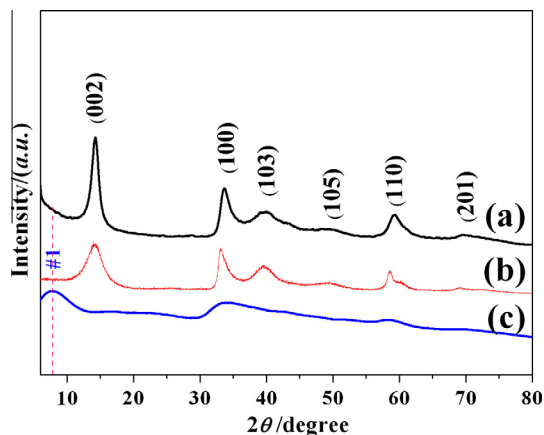


Fig. 1. XRD patterns of (a) bare MoS<sub>2</sub>; (b) MoS<sub>2</sub>/G and (c) Se-GL-MoS<sub>2</sub>/G hybrid.

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