

# Pt-MoS<sub>x</sub>/Graphene Nanocomposite for the Hydrogen Evolution Reaction

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**Abstract.** In this study, a catalyst was fabricated based on Pt nanoparticles on MoS<sub>2</sub>/graphene (MoS<sub>2</sub>/GN). The Pt-MoS<sub>2</sub>/GN was formed from graphite by modified Hummers and Offeman's method, hydrothermal method and polyol synthesis method. The graphene oxide (GO) sheets were synthesized by modified Hummers and Offeman's method. The graphene is to obtain by reduction of GO films by sodium tetrahydridoborate. Then, the graphene deposited with Pt particles were put in ethylene glycol for a reflux at 150 °C for 6 hours. Obtained Pt-MoS<sub>2</sub>/graphene catalysts were characterized by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Cyclic voltammetry (CV) was utilized to estimate the electrochemical performance of the Pt-MoS<sub>2</sub>/GN nanocomposites. The results show that the Pt-MoS<sub>2</sub>/GN nanocomposites modified glass carbon electrode (GCE) shows a high sensitivity and low detection limit for hydrogen peroxide and glucose detection. The activity of Pt-MoS<sub>2</sub>/GN nanocomposites can be enhanced after adding the 30 wt% MoS<sub>2</sub>. The Pt-MoS<sub>2</sub>/GN shows the highest current value reached -25 mA at -0.2V, which is higher than that of pure Pt/GN. The Pt-MoS<sub>2</sub>/GN nanocomposites also exhibit superior electrochemically active surface area (ECSA). The work may provide more insight into synthesizing hybrid photocatalytic materials with high activities for applications in solar energy conversion and utilization.

## Introduction

Hydrogen is an ideal clean and renewable energy carrier to replace fossil fuels in the future. Splitting water offers one simple way to produce hydrogen. However, efficient hydrogen generation requires advanced electrocatalysts [1,2]. The best hydrogen evolution reaction (HER) catalysts consist of Pt or Pt-based materials with negligible overpotentials [2]. But they are too expensive to be widely used. Replacement of Pt with earth-abundant elements would be desirable to facilitate the global scalability of such potential clean-energy technologies.

Recently nanometer-scale molybdenum disulfide (MoS<sub>2</sub>) with exposed edges has been identified as a promising electrocatalyst for the HER due to its low cost, high chemical stability and excellent electrocatalytic properties [3]. Molybdenum disulfide, a two-dimensional transition metal disulfide (TMD) has a layered structure comprising S-Mo-S layers plus the weak Van de Waal force interactions, nanoparticles/flake edge area of a large number of catalytic and there is a high active sites more suitable semiconductor material. Of about 1.2 eV when molybdenum disulfide structure form below to block material indirect bandgap, but a single form of molybdenum disulfide is a direct band gap of about 1.8 eV (similar to 2D graphene structure). (2-D) graphene has emerged as high potential material and increasingly attracted attention owing to its specific properties, including excellent electron mobility, large specific surface area, flexible structure, high transparency and stability at room temperature [4-7]. The integration of graphene, MoS<sub>2</sub> and nanoparticles (NPs) has been actively explored for applications in many areas. Loading of nanoparticles on highly conductive graphene nanosheets gives rise to hybrid nanocomposites. The hybrid nanomaterials could provide larger electrochemically active surface areas for the adsorption of biomolecules and effectively accelerate the electron transfer between electrode, making the hybrid nanocomposites ideal materials for high-performance electrocatalyst for the hydrogen evolution reaction. In this work, the Pt-MoS<sub>2</sub>/GN was formed from graphite by modified Hummers and Offeman's method, hydrothermal synthesis, and polyol synthesis method. The results show that

Pt-MoS<sub>2</sub>/GNnanocomposite exhibits an extremely high electrochemically active surface area (ECSA) value (350 m<sup>2</sup>g<sup>-1</sup>). The Pt-MoS<sub>2</sub>/GN shows the highest current value reached -25 mA at -0.2V, which is higher than that of pure Pt/GN.

## Experimental

In this work, the graphene oxide (GO) sheets were synthesized by modified Hummers and Offeman's method. Through this process, the natural graphite powder was exfoliated by strong oxidizing agent (KMnO<sub>4</sub>+ H<sub>2</sub>O<sub>2</sub>). The graphene is to obtain by reduction of GO films by sodium tetrahydridoborate. MoS<sub>2</sub>/GNnanocomposites were prepared hydrothermal method. 20mg of graphene oxide, various amounts (5-30mg) of sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub> 2H<sub>2</sub>O), various amounts (10-60 mg)thiosulfate acetamideand 60 mL of distilled water were added into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was sealed, maintained at 200 °C for 24 h and cooled to room temperature naturally. The product was filtered off, washed with distilled water and ethanol several times, and dried in a vacuum at 50 °C for 24 hours.The Pt-MoS<sub>2</sub>/GN was manufactured as follows: MoS<sub>2</sub>/GN (50 mg) was dispersed in 100 mL of ethylene glycol by ultrasonic treatment 30 min. Then 100 mg of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O were added to 100 mL of the as-obtained MoS<sub>2</sub>/GNs dispersion with magnetic stirring for 30 min. And the pH value of this mixture was adjusted to 3 using HCl. Finally the solution reflux at 150°C for 3 hours. After rinsing and filtrating, the Pt-MoS<sub>2</sub>/GN was dried at 70 °C for 12 hours.

The Pt-MoS<sub>2</sub>/GN was characterized by X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Powder X-ray diffraction (XRD) analyzes was performed on a Bruker D8 Advance diffractometer with Cu K<sub>α</sub> radiation. A scanning transmission electron microscope (SEM, JEOL JSM-6510LV) were used for the observation of microstructure of the Pt-MoS<sub>2</sub>/GN nanocomposites. Cyclic voltammetry (CV) was utilized to estimate the electrochemical performance of the Pt-MoS<sub>2</sub>/GN nanocomposites. The cyclic voltammetric (CV) was performed at a standard three-electrode electrochemical cell with Jiehan (make in Taiwan) electrochemical working station. CV measurements were performed in 0.1M Phosphate buffered solutions (PBS) (pH 7.0) solutions with a scan rate of 20 mV/s. PBS were prepared using 0.1 M Na<sub>2</sub>HPO<sub>4</sub> and 0.1M KH<sub>2</sub>PO<sub>4</sub>.Pt-MoS<sub>2</sub>/GN electrode was made by affixing the membrane to a glassy carbon electrode (3 mm in diameter, GCE) and used as the working electrode. A saturated calomel electrode (SCE, Hg/Hg<sub>2</sub>Cl<sub>2</sub> (sat.KCl)) was used as the reference and a platinum plate was used as the counter electrode. Prior to modification, GCE was polished with 1.0 μm, 0.3 μm and 0.05 μm alumina powders in sequence, rinsed thoroughly with DI water between each polishing step, sonicated in ethanol and DI water for 10 min respectively. Pt-MoS<sub>2</sub>/GN was dispersed in DI water with ultrasonication to achieve a 0.5mg/mL concentration. Then 5 μL of the above solution was carefully pipetted onto the GC electrode surface. The coatings were dried at room temperature for 1 h.

## Results and discussion

Fig. 1 (a)-(d) shows the XRD pattern of the graphite oxide (GO), graphene, MoS<sub>2</sub>/GN, and Pt-MoS<sub>2</sub>/GN nanocomposites, respectively. As observed in Figure 2(a), the characteristic peak of GO (002) is located at a 2θ angle of 11.3°, and the spacing between layers is 0.83 nm. Figure 2(b) presents the XRD spectrum of graphene, which was reduced from GO by sodium borohydride (NaBH<sub>4</sub>). Due to the relatively small number of graphite layers in the graphene film, the diffraction intensity of the graphene film is broaden, the diffraction peak of graphene at 26.5°. Fig.2 (c) shows the XRD patterns of MoS<sub>2</sub>/graphene. The diffraction peak angles are 13.5 °, 33 °, 39 °, 48.5 °, 58.7 °, 59.1 ° and 70.9 °, which correspond to 2H- molybdenum disulfide(002), (100), (103), (006), (105), (110), and (201), respectively. The XRD pattern of Pt-MoS<sub>2</sub>/GN sample shows diffraction peaks at 39.75°, 46.23°, and 67.45° which are in good agreement with the (1 1 1), (2 0 0), and (2 2 0) crystal planes of platinum with face-centered-cubic (fcc) phase (JCPDS 65-28680). This implies the successful synthesis ofPt-MoS<sub>2</sub>/GN nanocomposites.

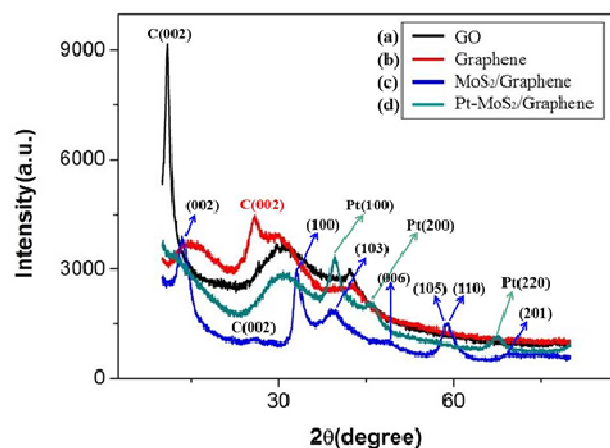


Fig. 1 XRD pattern of the graphite oxide (GO), graphene, MoS<sub>2</sub>/GN, and Pt-MoS<sub>2</sub>/GN nanocomposites, respectively.

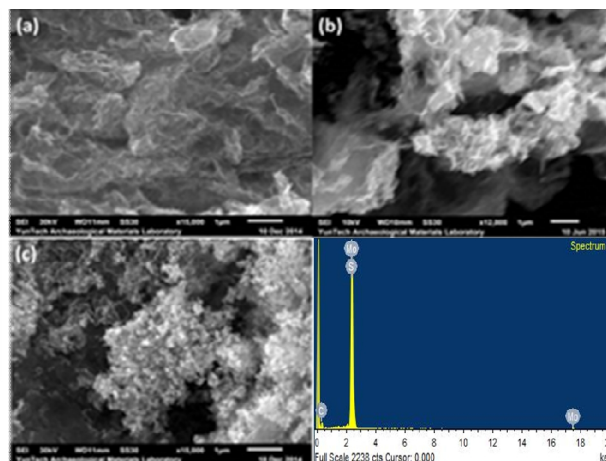


Fig. 2 (a) and (b) SEM images of MoS<sub>2</sub>/GN, (c) SEM images of Pt-MoS<sub>2</sub>/GN, (d) EDS of MoS<sub>2</sub>/GN.

Fig. 2 (a) and (b) shows the SEM image of the obtained MoS<sub>2</sub>/GN. It clearly illustrates MoS<sub>2</sub> is supported on the GN surface. Figure 2 (c) shows the SEM image of Pt-MoS<sub>2</sub>/GN nanocomposites. It can be found that the platinum nanoparticles well dispersive on MoS<sub>2</sub>/GN. EDS was used to determine the composition of the layered MoS<sub>2</sub>/GN nanocomposite. The results showed that the samples contain C, Mo (62.1), and S (31.35). The calculated atomic ratio of S to Mo element was about 2, approaching the theoretical value of MoS<sub>2</sub>. These values indicate that the products are stoichiometric MoS<sub>2</sub>.

To study the electrocatalytic activity of the Pt-MoS<sub>2</sub>/GN, the Pt-MoS<sub>2</sub>/GN was deposited on glassy carbon electrode (GCE) and evaluated in 0.5 M H<sub>2</sub>SO<sub>4</sub> with a scan rate of 20 mV/s. The Pt/GN was also tested for comparison. Figure 3 shows the polarization curves of Pt-MoS<sub>2</sub>/GN with different amounts of MoS<sub>2</sub> and Pt/GN. The Pt-(30wt%)MoS<sub>2</sub>/GN electrodes produced current densities of -25 mA cm<sup>-2</sup> at overpotentials of -0.2 V. The electrocatalytic HER activity of the Pt-(30wt%)MoS<sub>2</sub>/GN electrodes also compares to other Pt-MoS<sub>2</sub>/GN with different amounts of MoS<sub>2</sub>, including Pt-(10 wt%)MoS<sub>2</sub>/GN (-4.2 mA/cm<sup>2</sup>), Pt-(50wt%)MoS<sub>2</sub>/GN (-13.8 mA/cm<sup>2</sup>), Pt-(90wt%)MoS<sub>2</sub>/GN (-8.2 mA/cm<sup>2</sup>), and Pt/GN (-18.9 mA/cm<sup>2</sup>). The cathodic current density reached 25 mA/cm<sup>2</sup> at 200 mV over Pt-(30wt%)MoS<sub>2</sub>/GN material, showing 6-fold, 2-fold and 4-fold enhancement with those of Pt-(X wt%)MoS<sub>2</sub>/GN material with 10wt% MoS<sub>2</sub>, 50wt% MoS<sub>2</sub>, and 90wt% MoS<sub>2</sub>, respectively. The HER activity of Pt-MoS<sub>2</sub>/GN increases first and reaches the maximum value when the MoS<sub>2</sub> content is 30 wt. %, then drops down afterward, which indicates that the synergistic effect is not obvious when the amount of MoS<sub>2</sub> is low or large. Fig. 4 shows the current density variation with voltage in CV test for Pt-(30wt%)MoS<sub>2</sub>/GN nanocomposites sample. The ECSAs for Pt-(30wt%)MoS<sub>2</sub>/GN electrode was estimated to be 350 m<sup>2</sup>g<sup>-1</sup>. The integrated area of the hydrogen absorption and desorption peaks for Pt-(30wt%)MoS<sub>2</sub>/GN is larger than those of Pt-(X wt%)MoS<sub>2</sub>/GN material with 10 wt% MoS<sub>2</sub>, 50 wt% MoS<sub>2</sub>, and 90 wt% MoS<sub>2</sub> electrode, respectively. The larger ECSAs indicate that Pt-(30wt%)MoS<sub>2</sub>/GN electrode has more active sites in the electrocatalytic process, suggesting that the Pt-MoS<sub>2</sub>/GN might have great potential in practical HER application.

## Summary

In this work the MoS<sub>2</sub>/GN nanocomposites were prepared by hydrothermal method. Then electrode catalyst Pt particles were reduced on their surface in ethylene glycol and application to hydrogen evolution reaction. The high electrochemical active surface area with 350 m<sup>2</sup>/g can be obtained in Pt-(30 wt%)MoS<sub>2</sub>/GN sample. The cathodic current density reached 25 mA/cm<sup>2</sup> at 200 mV over Pt-(30 wt%)MoS<sub>2</sub>/GN material, showing 6-fold, 2-fold and 4-fold enhancement with those of Pt-(X wt%)MoS<sub>2</sub>/GN material with 10 wt% MoS<sub>2</sub>, 50 wt% MoS<sub>2</sub>, and 90 wt% MoS<sub>2</sub>, respectively. The

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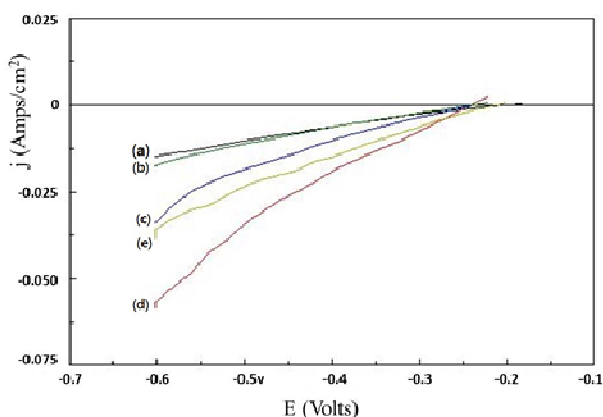


Fig. 3 the polarization curves of Pt-MoS<sub>2</sub>/GN with different amounts of MoS<sub>2</sub> and Pt/GN..

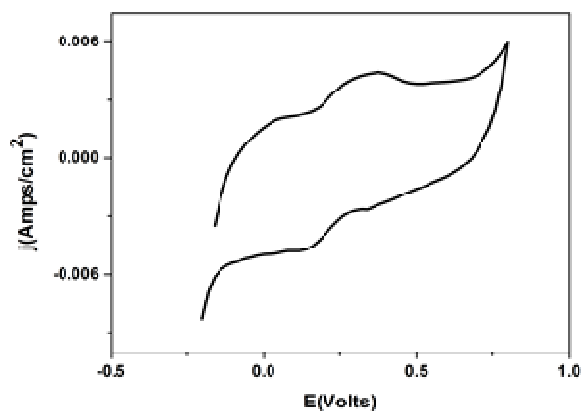


Fig. 4 the current density variation with voltage in CV test for Pt-(30 wt%)MoS<sub>2</sub>/GN nanocomposites sample.

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