



## Research paper

## Thermally reduced graphite oxide and molybdenum disulfide composite for enhanced hydrogen evolution reaction

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## ABSTRACT

We report an efficient molybdenum disulfide (MoS<sub>2</sub>) supported by thermally reduced graphite oxide (TRGO) for hydrogen evolution reaction (HER). The TRGO-MoS<sub>2</sub> composite exhibits excellent catalytic activity with a low overpotential of  $-0.23$  V, which is almost three and seven times lower than those of precursor MoS<sub>2</sub> and GO-MoS<sub>2</sub>. The high performance of HER attributes to TRGO, providing a conducting network for fast electron transport from MoS<sub>2</sub> to electrodes. The composite also shows high stability in which the overpotential remains constant after 1000 cycles and strong durability after 48 h, demonstrating a synergistic effect of MoS<sub>2</sub> and TRGO for efficient HER.

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## 1. Introduction

Nowadays, continuous and widespread use of fossil fuels has led to increased pollution and ecological problems. In this regard, substantial research efforts have been directed to the development of efficient and eco-friendly technologies for the production of energy conversion and storage devices as a solution to these problems [1–3]. Out of others, the energy from H<sub>2</sub> has been pursued as a clean and alternative source of fossil fuel. The hydrogen generated from water is the most important way which stands as a potential alternative to our energy demands. Different ways such as photochemical, photoelectrochemical and electrochemical have been broadly used for splitting of water [2,4,5]. But among them, the hydrogen produced by electrochemical method is widely adopted due to its higher efficiency, cost effectiveness, and easy instrumental setups [6,7]. However, the efficient conversion of H<sub>2</sub>O to H<sub>2</sub> strongly depends on the activity of the electrode materials [8]. The most common known as electrocatalysts for the hydrogen evolution reaction (HER) in acidic media are Pt group metals, which exhibit high catalytic reaction rates and lower overpotential nearly to zero [9,10]. However, its high price and extreme scarcity have posed tremendous limitations to widespread application. Therefore, to find alternative catalysts which are earth-abundant, as well as highly efficient is a crucial step towards a sustainable hydrogen production [11–13]. Studies on Transition metal chalcogenides

such as molybdenum and tungsten sulfide confirmed their potential to replace the expensive platinum as catalysts for hydrogen evolution reaction [14]. Currently, Molybdenum disulfide (MoS<sub>2</sub>) has attracted extensive attention as an effective hydrogen evolution reaction catalyst due to its excellent electrocatalytic properties [15,16]. Computational and experimental studies have confirmed that the hydrogen evolution reaction activity of MoS<sub>2</sub> comes from its sulfur edges, resulting of the electroactivity of MoS<sub>2</sub> to be directly proportional to number of exposed edges [16,17]. Although increasing the number of active edge sites can improve the electrochemical performance of MoS<sub>2</sub>, the intrinsic poor conductivity of MoS<sub>2</sub> greatly diminishes its electroactivity by limiting the electron-transfer efficiency [18]. Moreover, the strong van der Waals interactions among lamellar MoS<sub>2</sub> particles can result in their aggregation, decreasing the number of the exposed edges active sites as well as the electroactivity [19]. Therefore, the key challenge to apply MoS<sub>2</sub> in the hydrogen evolution reaction lies in the compensation for the conductivity while maintaining its nanosize.

In this regard, forming highly conducting MoS<sub>2</sub> is an ideal protocol to improve its catalytic activity for the hydrogen evolution reaction. As a result, various conductive materials, such as chemically reduced graphene oxide, carbon nanotubes (CNTs), and 3D graphene foam are chosen to support MoS<sub>2</sub>, to improve not only its conductivity but also efficiently prevents the aggregation of MoS<sub>2</sub> [11,20–23]. In our previous report, we have demonstrated that graphite oxide (GO) reduced through chemical and hydrothermal processes could support MoS<sub>2</sub> by increasing its conductivity, resulting in good performance of

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hydrogen evolution reaction due to synergistic effect of GO and MoS<sub>2</sub> [24].

Herein, the thermally reduced graphite oxide (TRGO) and MoS<sub>2</sub> composite was successfully synthesized with a good homogenous dispersion. The composite showed improvement of the electrocatalytic activity for hydrogen evolution reaction compared to precursor GO-MoS<sub>2</sub> or MoS<sub>2</sub> itself, demonstrating a synergistic effect of thermally reduced graphite oxide and MoS<sub>2</sub> on hydrogen evolution reaction.

## 2. Experimental

GO was synthesized from natural graphite (99.999% purity, –200 mesh, Alfar Aesar) by the modified Brodie's method as described elsewhere [25]. Briefly, 1 g of graphite, 30 ml of fuming nitric acid, and 6.5 g of sodium chloride oxide were mixed at room temperature and the mixture was stirred for 24 h to have more oxidation reaction. Thereafter, oxidized solution was washed many times by deionized (DI) water to remove the residue until pH is neutral and dried at 50 °C for 48 h to get GO powder after vacuum filtration. The GO powder was then heated at 900 °C with a heating rate of 15 °C min<sup>-1</sup> for 1 h in argon atmosphere to obtain thermally reduced graphite oxide. Then, 15 mg of thermally reduced graphite oxide was mixed with 15 mg of molybdenum disulfide from Sigma Aldrich and dispersed in 30 ml of DI water and ethanol and the dispersed solution was sonicated for 30 min at room temperature. The precursors of GO (Fig. 1a), TRGO (Fig. 1b) and MoS<sub>2</sub> (Fig. 1c) were also made for comparison with the obtained composite, named as TRGO-MoS<sub>2</sub> (Fig. 1d). Fig. 1 shows digital photos with schematic illustration of the samples.

The electrochemical measurements for hydrogen evolution reaction were carried out by a three-electrode cell system in aqueous electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>) by Potentiostat/ Galvanostat with impedance spectroscopy (Bio-Logic SAS, SP-150). The GO, TRGO, MoS<sub>2</sub> or TRGO-MoS<sub>2</sub> samples, were mixed with 20 μl of nafion solution and sonicated for 30 min to form homogeneous suspension in DI water and ethanol (1:1). Then, 10 μl of homogeneous dispersion was drop casted on a glassy carbon electrode (GCE, Biologic SAS, SP-150) to make a working electrode, and the three electrode system was consisted with Ag/AgCl and platinum foil as a reference and counter electrode, respectively. Linear sweep voltammetry (LSV) was conducted with scan rate of 10 mVs<sup>-1</sup>, and electrochemical impedance spectroscopy (EIS) was performed in the same configuration at the frequency range from 100 mHz to 100 kHz with the modulation amplitude of 5 mV.

Morphology of samples was investigated by using scanning electron microscopy (SEM, HITACHI, S-4300). X-ray energy dispersive spectroscopy (EDS, HITACHI, S-4300) and X-ray diffraction

(XRD, HITACHI, S-4300) were used to investigate elemental composition and crystallinity of samples, respectively. Raman spectrum of the samples was recorded on an In Via-Reflex Raman microscopy with a laser excitation wavelength of 532 nm to investigate vibrational modes of samples and the effect of TRGO on MoS<sub>2</sub> structure.

## 3. Results and discussion

Fig. 2 shows morphology of GO, TRGO, MoS<sub>2</sub>, GO-MoS<sub>2</sub> and TRGO-MoS<sub>2</sub>. GO (Fig. 2a) has flat, smooth, and two dimensional layers stacked together, and TRGO (Fig. 2b) presents defects or gap on its surface, resulting in high specific surface area by the larger interlayer distance and high conductivity [25]. However, the surface of MoS<sub>2</sub> (Fig. 2c) was rough like cumulus clouds. MoS<sub>2</sub> is likely to be agglomerated, and the agglomeration of it has been known to restrict the catalytic behavior [26]. GO-MoS<sub>2</sub> (Fig. 2d and e) show the flat GO layers and MoS<sub>2</sub> flakes on top and between the layers of GO. The final TRGO-MoS<sub>2</sub> composite (Fig. 2f) presented exfoliated thermally reduced graphite oxide with non-agglomerated MoS<sub>2</sub> of smaller size compared to that of GO-MoS<sub>2</sub>. The size of MoS<sub>2</sub> in TRGO-MoS<sub>2</sub> is smaller than that of MoS<sub>2</sub> itself, and it is distributed uniformly on the surface of thermally reduced graphite oxide layers, indicating that TRGO supporting MoS<sub>2</sub> without an agglomeration of MoS<sub>2</sub> will provide an electrical network for the electron transport during hydrogen evolution reaction process.

The elemental composition of samples obtained from EDS is shown in Table 1. The carbon and oxygen atomic percentages of GO and TRGO are 68, 32, 87, and 13 at%, respectively. GO-MoS<sub>2</sub> presented carbon, oxygen, molybdenum, and sulfur elements which were 68, 12, 7, and 13 at%, respectively. TRGO-MoS<sub>2</sub>, however, shows reduced oxygen amount from 32 at% to 7 at%, meaning that GO was successfully reduced, and the atomic ratio of Mo and S was 1–2. It is, therefore, expected that the TRGO-MoS<sub>2</sub> composite will provide better conductivity and positive performance of hydrogen evolution reaction.

Crystallinity of the samples was determined by using XRD measurement (Fig. 3a). The interlayer distance of GO was 6.00 ± 0.12 Å, corresponding to the (0 0 2) peak near 14.5 degree and the peak intensity was reduced and shifted to 17 degree after the thermal reduction. The main peak (0 0 2) of MoS<sub>2</sub> is also located at the same position of that of GO with additional small bumps at 33, 34, and 36 degree, corresponding to (1 0 0), (1 0 1) and (1 0 2), which are typical MoS<sub>2</sub> peaks [27]. The TRGO-MoS<sub>2</sub> composite shows the (0 0 2) peak with lower intensity compared to that of MoS<sub>2</sub> (Fig. 3b) and two peaks at 20 and 24 degree originated from TRGO with the small bumps originated from MoS<sub>2</sub>, proving that two

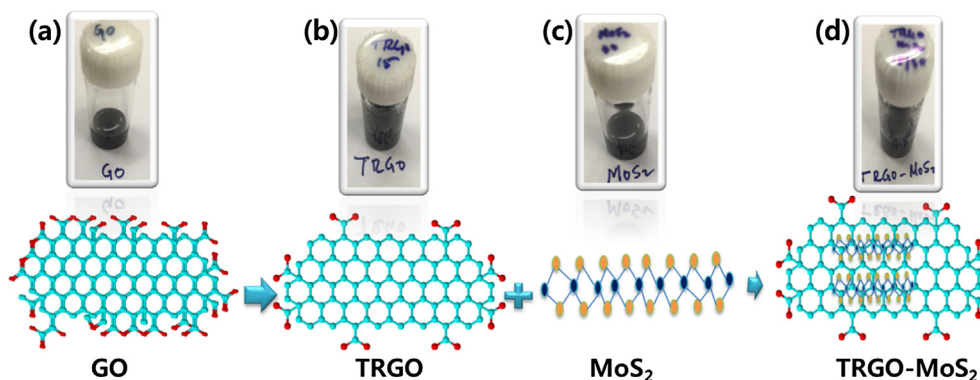


Fig. 1. Schematic illustration of the samples and their digital photos.

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