

Synergetic effect of CoNPs and graphene as cocatalysts for enhanced electrocatalytic hydrogen evolution activity of MoS₂

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Electronic supplementary information

S.1. Preparation of graphene oxide

Graphene oxide was prepared by a modified Hummers' method [1-3]. Typically, 50 ml of concentrated sulfuric acid (98%) was added to 0.375 g of graphite powder and 2.0 g of KMnO₄ in a beaker. The reaction was then heated to 50 °C and stirred for 24 h. The formed brownish slurry was then added slowly into 138 ml of cold DI water under stirring for 10 min. Afterwards, 420 ml of warm water (~45 °C) was added followed by a slow addition of 30 ml of H₂O₂ to get a yellow suspension. After that, the mixture was centrifuged (8000 rpm for 5 min) and washed repeatedly by a mixed aqueous solution of 6 wt% H₂SO₄ and 1 wt% H₂O₂, and then by DI water until the PH of the suspension closes to 7.0.

S-2. Calculation of active sites

Cyclic voltammetry measurements were carried out in 1.0 mol L⁻¹ phosphate buffer solution (PBS, pH = 7) only (blank measurements) with a scan rate of 20 mV·s⁻¹ (Figure S-3). Later, the absolute components of the voltammetric charges (cathodic and anodic)

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reported during one single blank measurement were added. Assuming a one electron redox process, this absolute charge was divided by two. The value was then divided by the Faraday constant to get the number of active sites of the film. Following this procedure, the number of active sites (in mol) was determined.

S-2. Turnover frequency (TOF) calculations

When the number of active sites is known, TOF can be calculated with the following equation:

$$TOF = \frac{I}{2Fn}$$

Where F is Faraday constant ($96485 \text{ C}\cdot\text{mol}^{-1}$), I is current (in A) during the linear sweep measurement and n is active sites number (in mol). The factor 1/2 in the equation represents that two electrons are required to form one hydrogen molecule from two protons.

For the Co-MoS₂/rGO, Q is $9.112 \times 10^{-2} \text{ C}$, $n \text{ (mol)} = 4.419 \times 10^{-2} / (2 \times 96485) \text{ mol} = 4.72 \times 10^{-7} \text{ mol}$. For the MoS₂/rGO, Q is $1.90 \times 10^{-2} \text{ C}$, $n \text{ (mol)} = 1.737 \times 10^{-2} / (2 \times 96485) \text{ mol} = 9.85 \times 10^{-8} \text{ mol}$. For the Co-MoS₂, Q is $1.79 \times 10^{-2} \text{ C}$, $n \text{ (mol)} = 1.565 \times 10^{-2} / (2 \times 96485) \text{ mol} = 9.28 \times 10^{-8} \text{ mol}$. For the MoS₂, Q is $1.027 \times 10^{-2} \text{ C}$, $n \text{ (mol)} = 1.027 \times 10^{-2} / (2 \times 96485) \text{ mol} = 5.32 \times 10^{-8} \text{ mol}$.

Table S-1. Calculation of the exchange current densities of the hybrid catalysts.

Sample	Log j (mA cm ⁻¹) at $\eta=0$	Exchange current density (mA cm ⁻¹)
Pt/C	-0.26	0.55
Co-MoS ₂ /rGO	-1.54	2.9×10^{-2}
MoS ₂ /rGO	-2.10	7.9×10^{-3}
Co-MoS ₂	-2.21	6.2×10^{-3}
MoS ₂	-2.28	5.2×10^{-3}

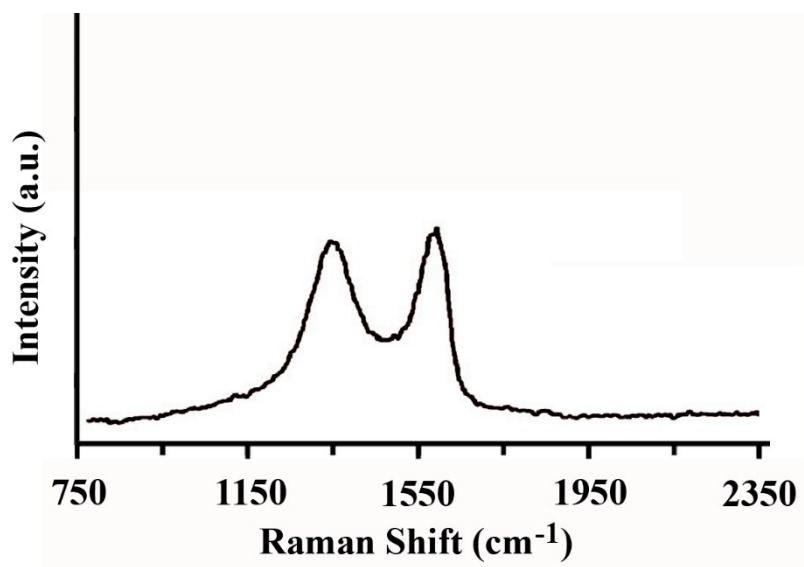


Figure S-1. Raman spectrum of the bare GO sheets.

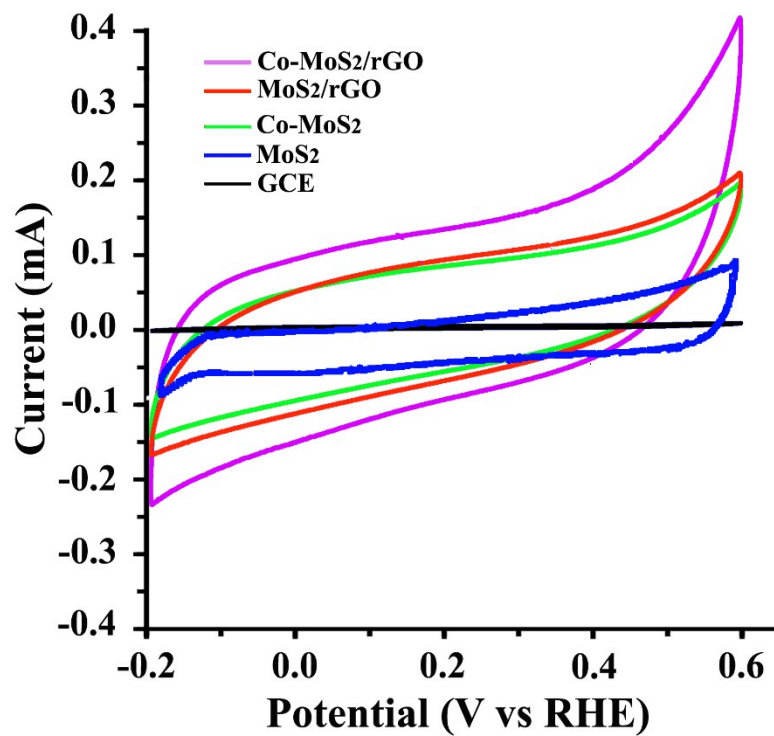


Figure S-2. CVs of the Co-MoS₂/rGO, MoS₂/rGO, Co-MoS₂, MoS₂, and bare GCE at a scan rate of 20 mV·s⁻¹ in 1.0 mol L⁻¹ PBS (pH=7).

1. W. S. Hummers, R. E. Offeman, *Journal of the American Chemical Society*, 1958, 80, 1339-1339.
2. P. Lian, X. Zhu, S. Liang, Z. Li, W. Yang and H. Wang, *Electrochim. Acta*, 2010, 55, 3909-3914.
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