

SUPPORTING INFORMATION

The Synergistic Effect of Metallic Molybdenum Dioxide Nanoparticles Decorated Graphene as Active Electrocatalyst for Enhanced Hydrogen Evolution Reaction

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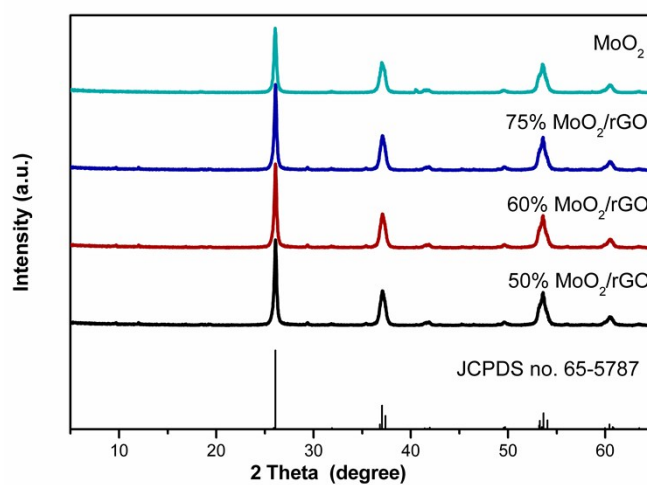


Fig. S1 XRD patterns of MoO₂ and MoO₂/rGO composites prepared with different contents of rGO under same conditions. The increase of rGO from 0 wt% to 50 wt% hardly influenced the crystal structure of MoO₂. All samples were crystallized into monoclinic phase by the hydrothermal treatment. Standard PDF card of the MoO₂ was given as reference.

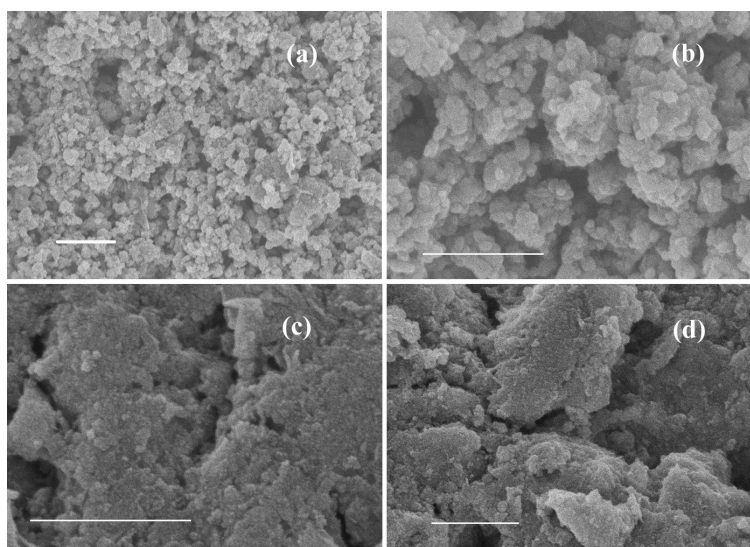


Fig. S2 SEM images of obtained MoO₂ and MoO₂/rGO composites with different contents: (a) MoO₂, (b) 75 wt% MoO₂/rGO, (c) 60 wt% MoO₂/rGO and (d) 50 wt% MoO₂/rGO. The scale bars are 500 nm.

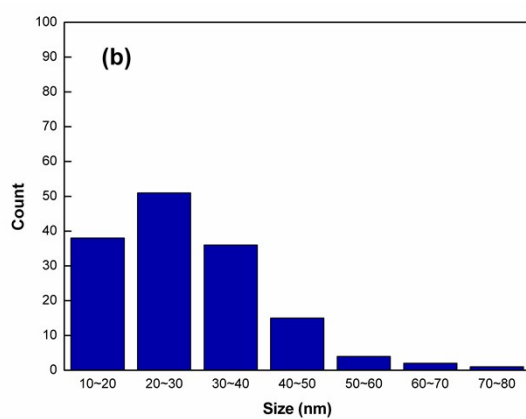
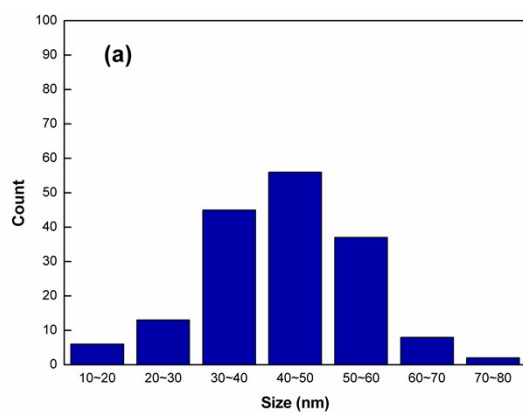


Fig. S3 Relevant size distribution of (a) MoO₂ and (b) 60 wt% MoO₂/rGO composite.

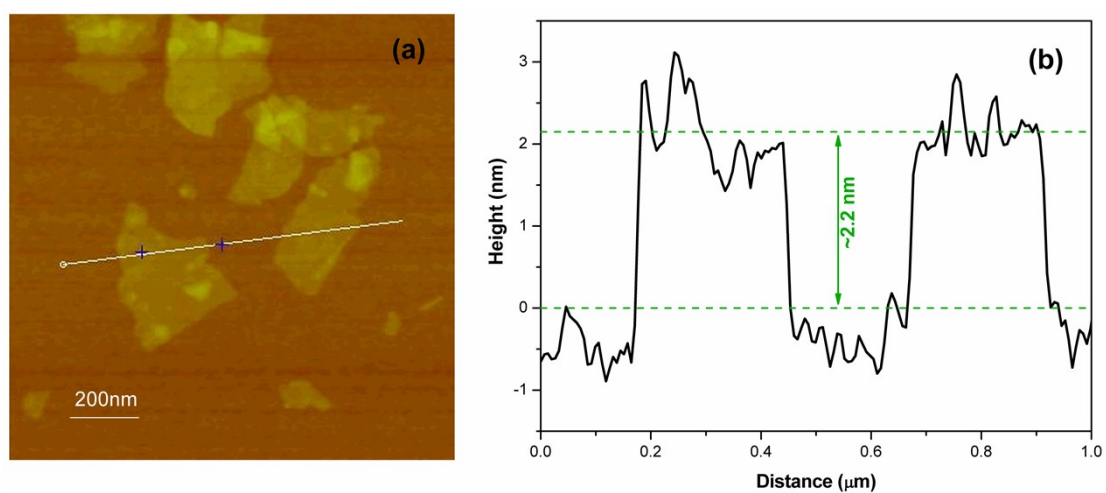


Fig. S4 (a) AFM image of the rGO nanosheets. (b) The corresponding height image of two random rGO nanosheets.

Table S1 Ratios of Mo atoms with different valence states in obtained MoO₂ NPs and 60 wt% MoO₂/rGO composite.

Percentage of Mo Atoms with Different Valence States in Samples	Mo IV	Mo V	Mo VI
MoO ₂	26.8%	30.2%	43.0%
MoO ₂ /rGO	45.3%	18.1%	36.6%

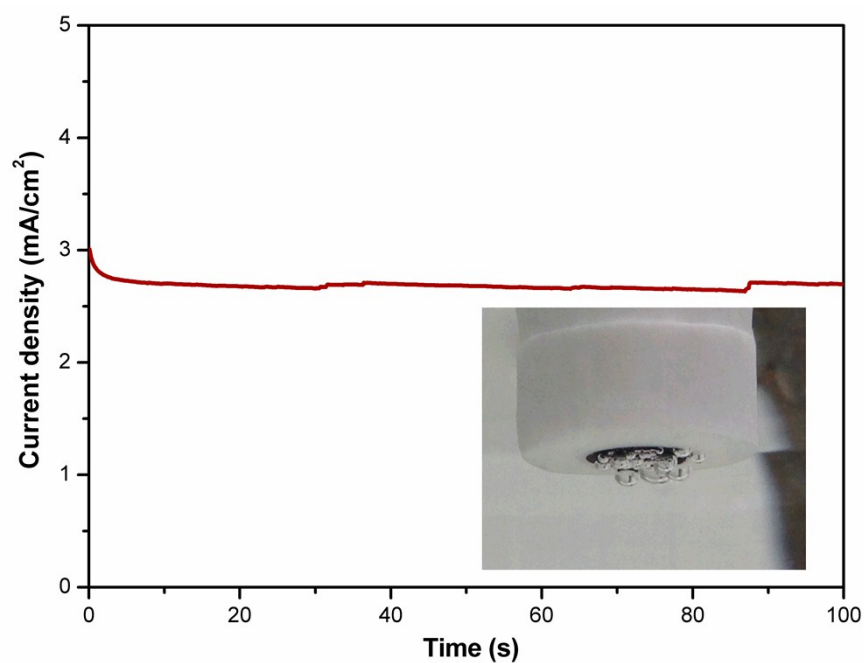


Fig. S5 Chronoamperometric responses recorded on 60 wt% MoO₂/rGO composite at a constant applied potential of -200 mV vs RHE. Inset digital photos show the H₂ bubbles formed on 60 wt% MoO₂/rGO composite modified GCE at the time point of 100 s. The measurements were performed in 0.5 M H₂SO₄ solution.

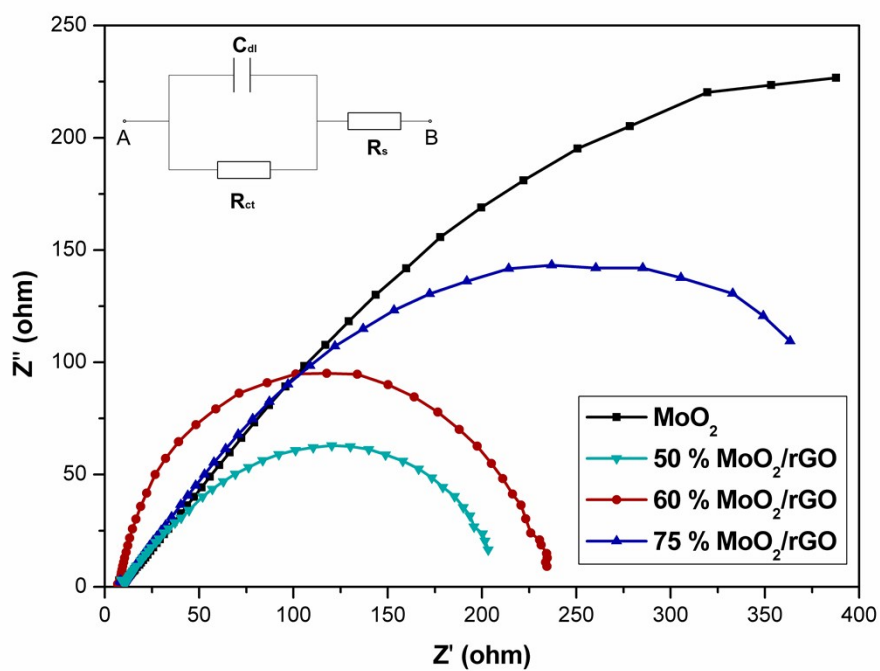


Fig. S6 Electrochemical impedance spectroscopy of MoO₂/rGO composites and MoO₂ at 250 mV vs. RHE. It can be seen when combined with rGO, the resistance of the sample decreased from 812 ohm (pure MoO₂) to 205 ohm (50 wt% MoO₂/rGO).

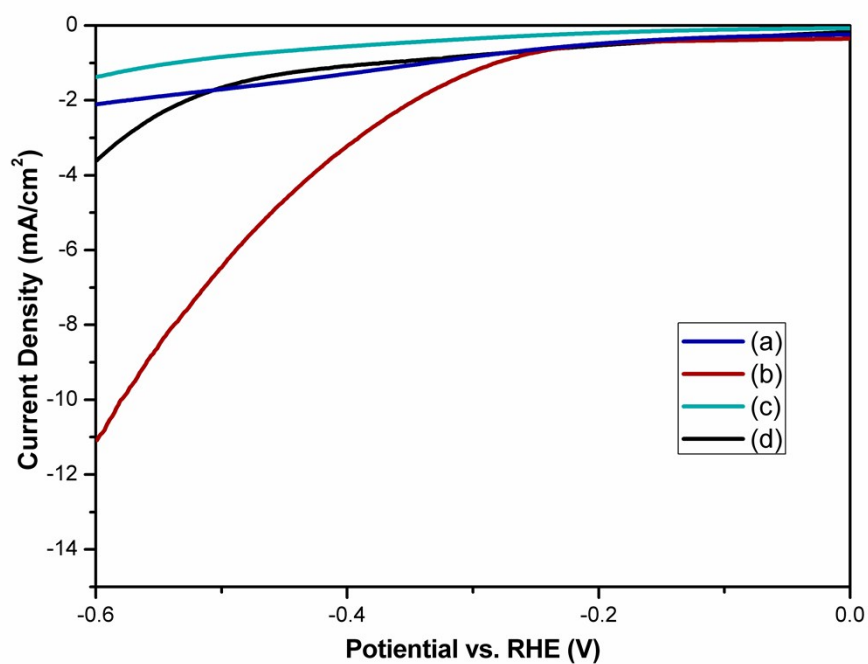


Fig. S7 Polarization curves of (a) 60 wt% MoO₂/rGO composite without calcination (b) 20 wt% MoO₂/rGO composite (c) MoO₃ NPs and (d) MoO₃/rGO composite. It is obvious that MoO₂/rGO composite have poor activity without calcination. MoO₃ NPs and MoO₃/rGO composite have low activity in HER.

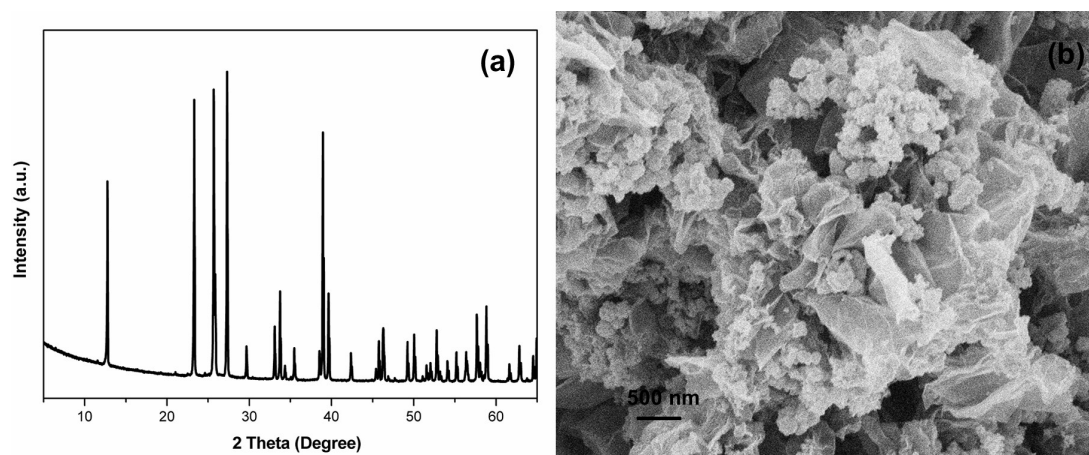


Fig. S8 (a) XRD pattern and (b) SEM image of as-prepared MoO₃/rGO composite.

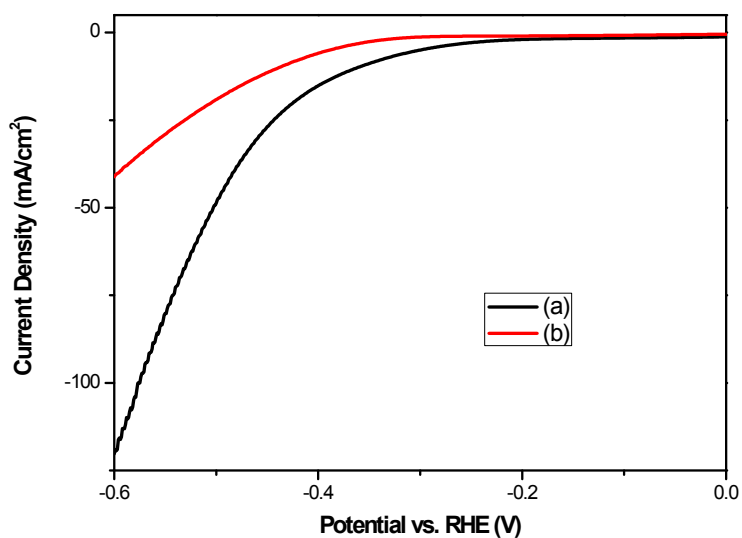
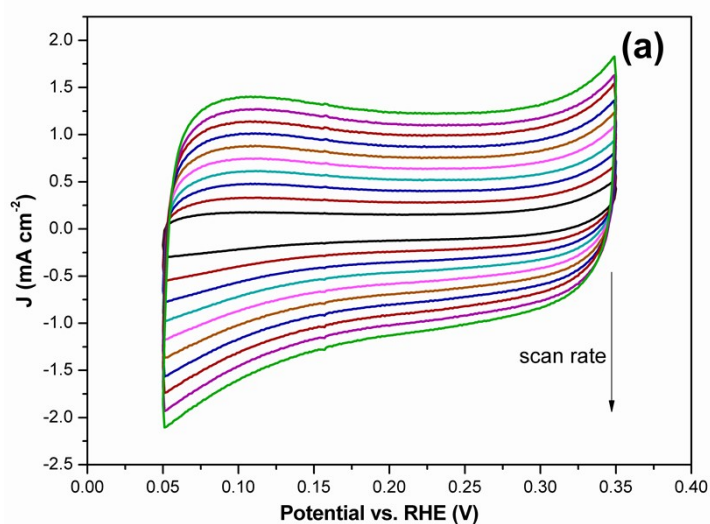


Fig. S9 Polarization curves of (a) 60 wt% MoO₂/rGO composite and (b) a mechanical mixed sample of 60 wt% MoO₂ and 40 wt% rGO. In sharp contrast, 60 wt% MoO₂/rGO composite exhibit an overpotential of only 190 mV, which is markedly better than the mechanical mixed sample under the same catalyst loading. The enhanced performance in HER indicates that a strong synergistic effect was appeared during the synthesis process.



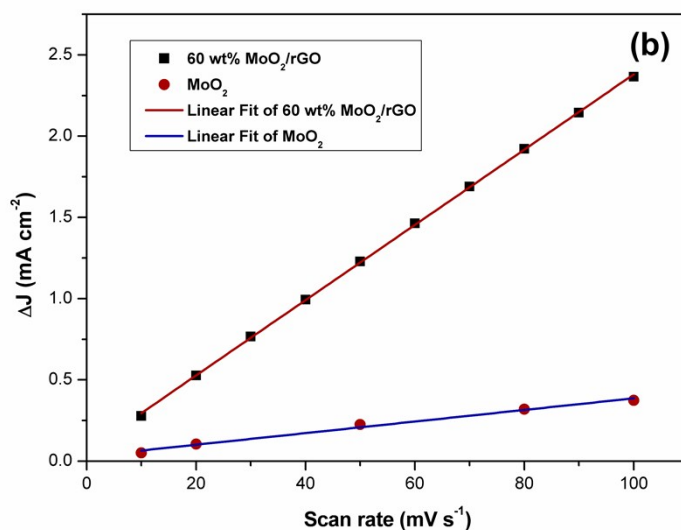


Fig. S10 (a) Cyclic voltammograms of 60 wt% MoO₂/rGO composite measured at different scanning rates (10-100 mV s⁻¹) in 0.5 M H₂SO₄ with the same loading. (b) Corresponding scanning rate dependence of the current density of 60 wt% MoO₂/rGO and MoO₂ at 0.2 V vs. RHE.

It is generally supposed that the amount of active sites in HER is directly proportional to electrochemically active surface area. The electrochemically active surface area was assessed by capacitance measurements as it is presumed to be linearly proportional to the double layer capacitance (C_{dl}).^{1, 2} Therefore, the relative value of electrochemically active surface area can be obtained by normalization of C_{dl} . It can be seen from Fig. S10b that the slope of 60 wt% MoO₂/rGO is almost 10 times bigger than that of MoO₂, clearly demonstrating that with the presence of rGO, the MoO₂/rGO composite has much larger amount of active sites in HER.

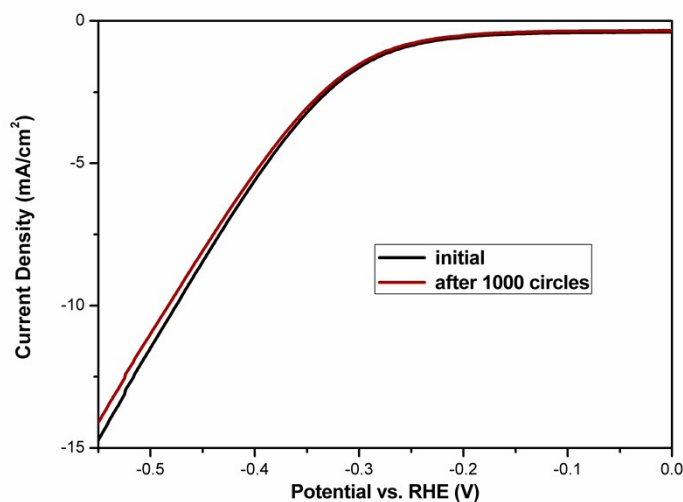


Fig. S11 Linear sweep voltammograms of 60 wt% MoO₂/rGO composite on the GC electrode

before and after 1000 cycles in alkaline condition (0.1 M KOH); at the scan rate of 5 mV s⁻¹.

References:

- (1) D. Merki, S. Fierro, H. Vrubel, and X. L. Hu, *Chem. Sci.* 2011, **2**, 1262-1267.
- (2) J. D. Benck, Z. B. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.* 2012, **2**, 1916-1923.