

## Electronic Supplementary Information

# Synthesized Ultrathin MoS<sub>2</sub> Nanosheets Perpendicular to Graphene for Catalysis of Hydrogen Evolution Reaction

Z. H. Deng, L. Li, W. Ding, K. Xiong and Z. D. Wei\*

The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044; China

## Experimental section

**Preparation of the MoS<sub>2</sub>⊥RGO catalyst:** All agents were of analytical grade. All aqueous solutions were freshly prepared with distilled water (18 MΩ ·cm resistance). GO was obtained by refluxing a mixture of natural graphite powder, KMnO<sub>4</sub> and a 9:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> according to Marcano *et al* report.<sup>1</sup> GO with two different oxidation degrees were prepared by adjusting amount of KMnO<sub>4</sub> (1 or 3 g) for 0.5 g of graphite, which correspond to mildly and highly oxidized graphene, respectively. The MoS<sub>2</sub>⊥RGO catalyst was synthesized by a hydrothermal process. 30 mg oxidized graphene was dispersed in 40ml of DI water to obtain a yellow-brown aqueous suspension solution with the aid of ultrasonication for 1h, then 1/7 mmol of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and 8 mmol of H<sub>2</sub>NCSNH<sub>2</sub> (molar ratio Mo:S=1:8) were added into the solution, the mixture solution was strongly stirred for 30 min, then 40 μl N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was added with stirring. The homogeneous solution was transferred into a 100 mL Teflon-lined autoclave and heated in an oven at 180°C for 30 h. After that, the black precipitate was collected by centrifugation, washed several times with DI water and ethanol, and dried in an oven at 50°C for 12 h.

**Characterization of the MoS<sub>2</sub>⊥RGO catalyst:** Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were conducted on a Zeiss LIBRA 200 FETEM instrument using at 120 kV accelerating voltage. Field emission scanning electron microscope (FESEM) analysis was performed at an accelerating voltage of 5kV using a JSM-7800F scanning electron microscope instrument. X-ray diffraction (XRD) patterns were obtained on a XRD-6000 with Cu Kα radiation at a step rate of 1°·s<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM800 spectrometer equipped with a monochromatic Al X-ray source. Fourier transform infrared spectroscopy (FTIR) spectra were measured through a Nicolet iN10 spectrometer using the standard KBr pellet method. The Brunauer-Emmett-Teller (BET) surface areas measured by nitrogen adsorption-desorption at 77 K using an ASAP 2020M specific surface area and pore analyzer instrument.

**Electrochemical measurements:** All electrochemical experiments were performed in a standard three-electrode cell at room temperature. The cell consisted of a standard rotating disc electrode (RDE, 5 mm in diameter, PINE: AFEST050GC), an Ag/AgCl (saturated KCl) reference electrode, and a Pt wire counter electrode. All the potentials reported in this works were given relative to a reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst ink onto RDE. In brief, 2 mg of catalyst and 20 μl of 5wt% Nafion solution were dispersed in 400 μl of 3:1 V/V ethanol/water with at least 30 min sonication to form a homogeneous ink. Then 10 μl of the catalyst ink (containing 40 μg of catalyst) was pipetted onto a prepolished RDE. This is equivalent to MoS<sub>2</sub> loading of 0.204 mg·cm<sup>-2</sup>. After drying at room temperature, a drop of 0.5wt% Nafion solution was pipetted onto the surface of the catalyst layer to form a thin protective film. Linear sweep voltammetry (using the Versa STAT3-4000/V3) was conducted in N<sub>2</sub>-saturated 0.5M H<sub>2</sub>SO<sub>4</sub> solution from 0.30 to -0.50 V vs. RHE with a scan rate of 5 mV·s<sup>-1</sup> and rotation of 1600 rpm.

The electrical resistances of the MoS<sub>2</sub>⊥RGO(x) were determined by operating a homemade button cell (Fig. S11). The sample was inserted between two smooth polished steel discs. A Solartron SI 1287 electrochemical interface equipped with a Solartron SI 1260 impedance/gain-phase analyzer coupling system was used. The operating frequency range was between 10<sup>-1</sup> Hz and 10<sup>4</sup> Hz, the AC amplitude was 10 mV, and the DC potential was 0 V compared to an open circuit.

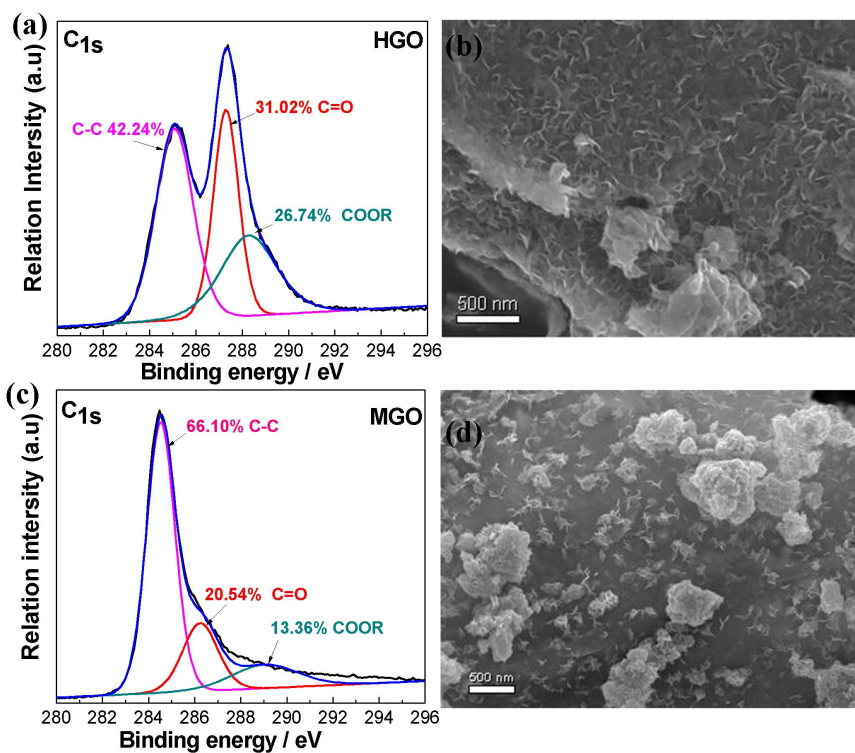
Double layer capacitance of the MoS<sub>2</sub> ⊥ RGO(x) was measured by cyclic voltammetry experiments in the potential range of 0.1 to 0.2 V vs. RHE in 0.5M H<sub>2</sub>SO<sub>4</sub> with varying scan rates from 20 to 140 mV·s<sup>-1</sup> (20, 40, 60, 80, 100, 120 and 140 mV·s<sup>-1</sup>). The C<sub>dl</sub> can be calculated from the scan rate dependence of charging current density at E=0.15 V vs. RHE, where the slope of the Δ*J* vs. scan rate curve is 2C<sub>dl</sub>.<sup>2</sup> The stability of the MoS<sub>2</sub> ⊥ RGO catalyst was checked by 3000 continuous cycles at 100 mV·s<sup>-1</sup> from -0.4 to 0.6 V in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at room temperature.

**Table S1.** A Summary of Various MoS<sub>2</sub> HER Catalysts

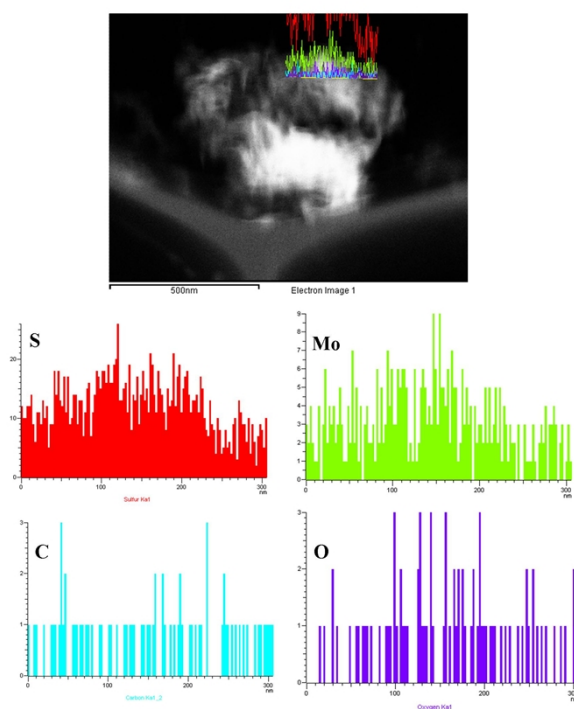
| Samples/morphology  | $\eta_{10}/\text{mv}$ | Tafel slope/ $\text{mv}\cdot\text{dec}^{-1}$ | Loading/ $\mu\text{g}\cdot\text{cm}^{-2}$ |
|---|-----------------------|--|---|
| 1T-MoS <sub>2</sub> <sup>11</sup>                         | 187                   | 43   | -   |
| Amorphous MoS <sub>2</sub> <sup>5</sup>                   | 198-204               | 53-65  | -   |
| MoS <sub>2</sub> ultrathin nanoplates <sup>9</sup>        | ~175                  | 53   | 136                                       |
| MoS <sub>2</sub> PTFs <sup>8</sup>                        | 180-225               | 1-44   | -   |
| MoO <sub>3</sub> /MoS <sub>2</sub> nanowires <sup>3</sup> | 250                   | 50-60  | -   |
| MoS <sub>2</sub> /WC/RGO <sup>7</sup>                     | 200                   | 41   | 104                                       |
| MoS <sub>2</sub> /RGO nanoplates <sup>14</sup>            | 155                   | 41   | 285                                       |
| MoS <sub>2</sub> /RGO nanosheets <sup>6</sup>             | ~180                  | 41   | 200                                       |
| MoS <sub>2</sub> $\perp$ RGO(in this work)                | 172                   | 43   | 204                                       |

**Table S2.** The double layer capacitance and the relative active edge sites of MoS<sub>2</sub> $\perp$ RGO (x)

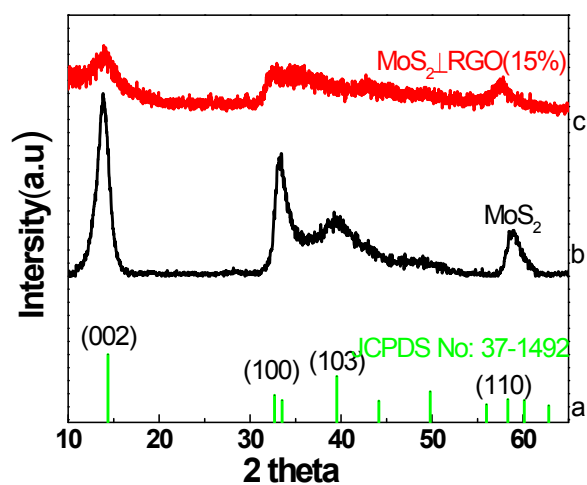
| Samples                            | C <sub>dl</sub> ( $\mu\text{F}/\text{cm}^2$ ) | Relative active edge site |
|------------------------------------|---|---------------------------|
| MoS <sub>2</sub>                   | 446   | 1.0                       |
| MoS <sub>2</sub> $\perp$ RGO (10%) | 3465  | 7.8                       |
| MoS <sub>2</sub> $\perp$ RGO (20%) | 4907  | 11.0                      |
| MoS <sub>2</sub> $\perp$ RGO (15%) | 6045  | 13.6                      |



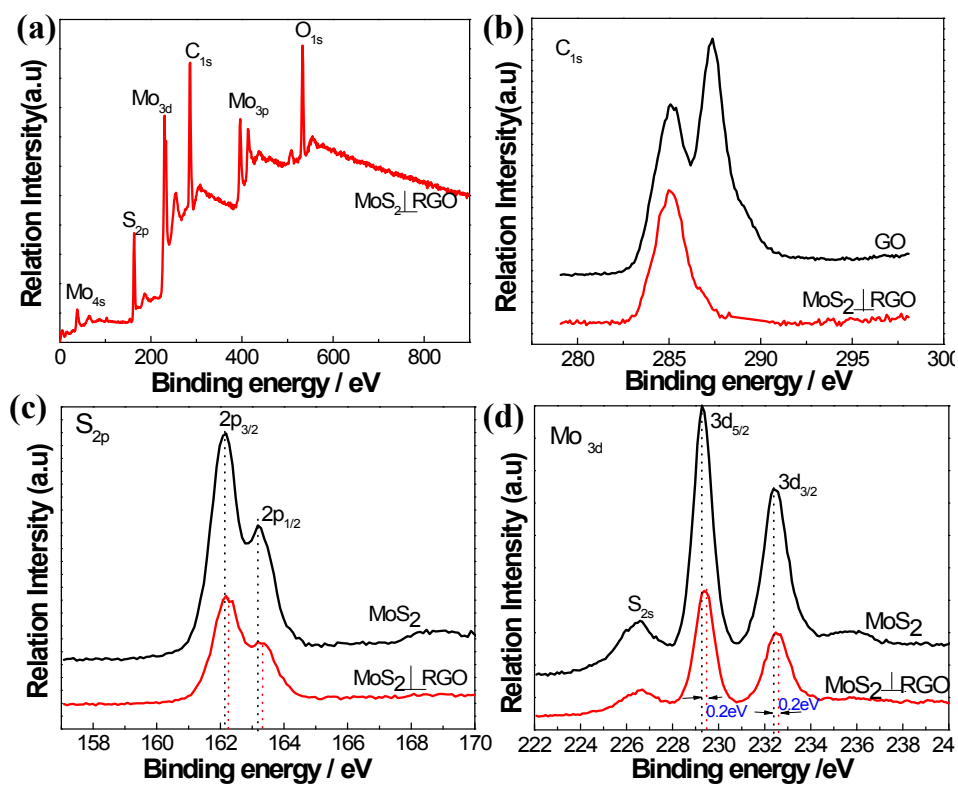
**Fig.S1** XPS images and FESEM images of as-synthesized MoS<sub>2</sub> sample using the highly oxidized graphene and the mildly oxidized graphene



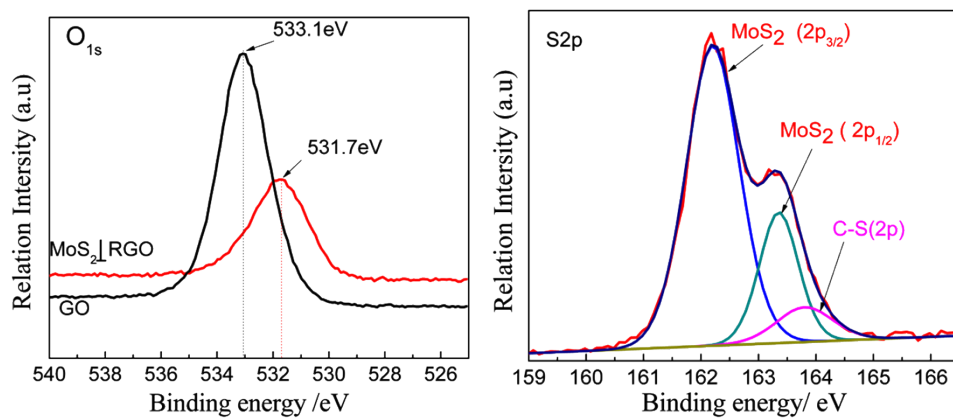
**Fig.S2** A typical electron energy loss spectrum (EELS) taken from the MoS<sub>2</sub> region indicates an elemental ratio of Mo: S close to 1:2.31



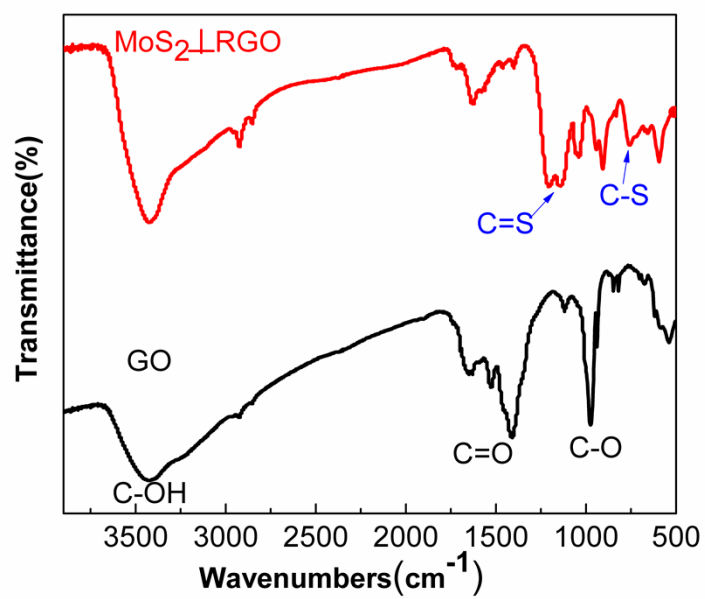
**Fig.S3** XRD patterns of the standard crystallographic spectrum of 2H-MoS<sub>2</sub> (JCPDS No: 37-1492) (a), the support-free MoS<sub>2</sub> (b) and MoS<sub>2</sub>/RGO (c).



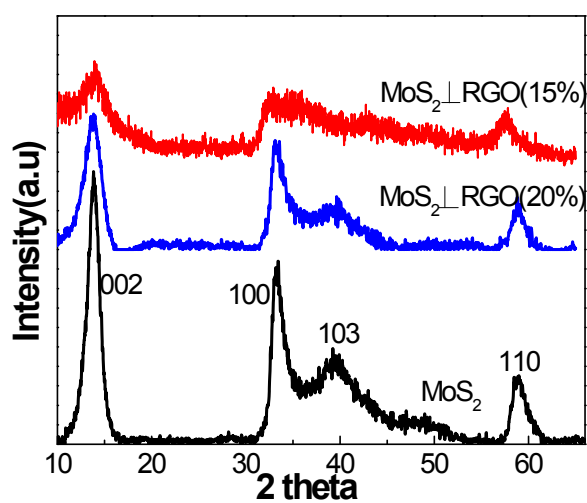
**Fig.S4** XPS spectra of survey (a), C<sub>1s</sub> (b), S<sub>2p</sub> (c) and Mo<sub>3d</sub> (d) on the MoS<sub>2</sub>/RGO catalyst.



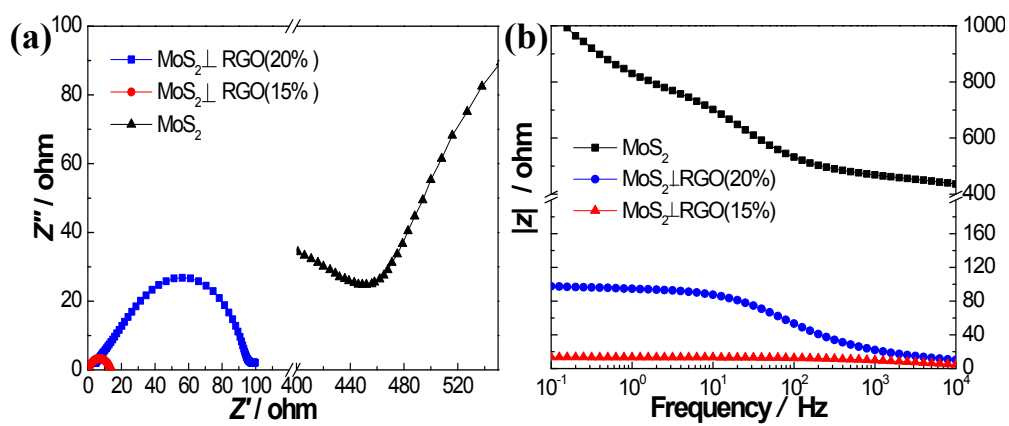
**Fig.S5** The high resolution XPS of O1s and S2p on the MoS<sub>2</sub>/LRGO catalyst.



**Fig.S6** FTIR spectra of the GO and MoS<sub>2</sub>/LRGO.

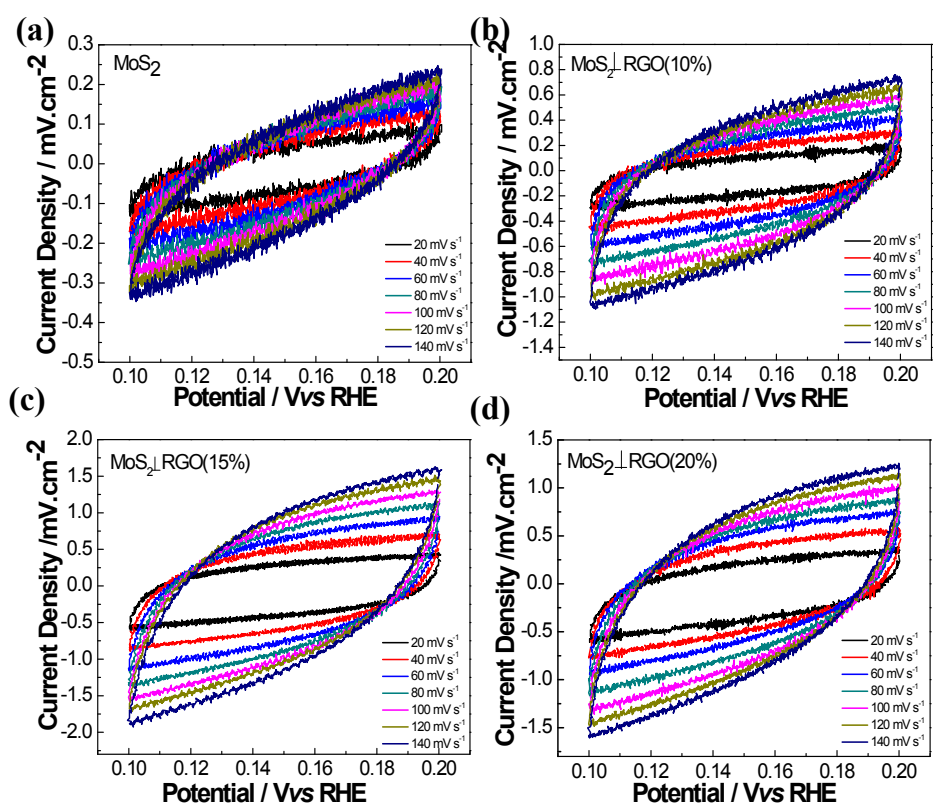


**Fig.S7** XRD patterns of  $\text{MoS}_2 \perp \text{RGO}$  (x)

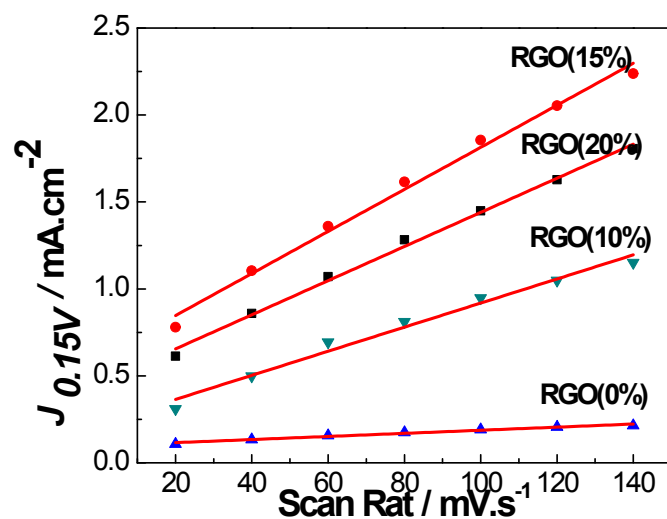


**Fig.S8** Nyquist (a) and Bode (b) plots obtained through the application of a sine wave with an amplitude of 100mv from 0.1 to 10kHz for  $\text{MoS}_2 \perp \text{RGO}$  (x).

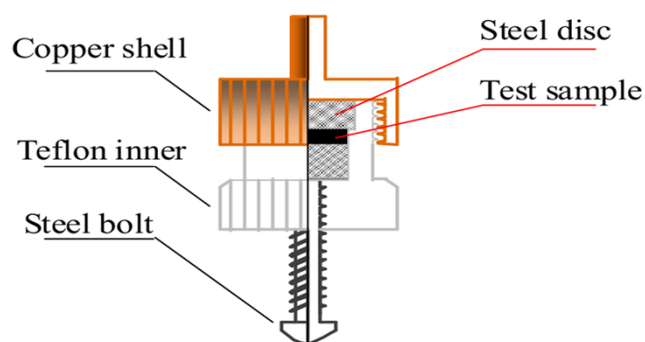




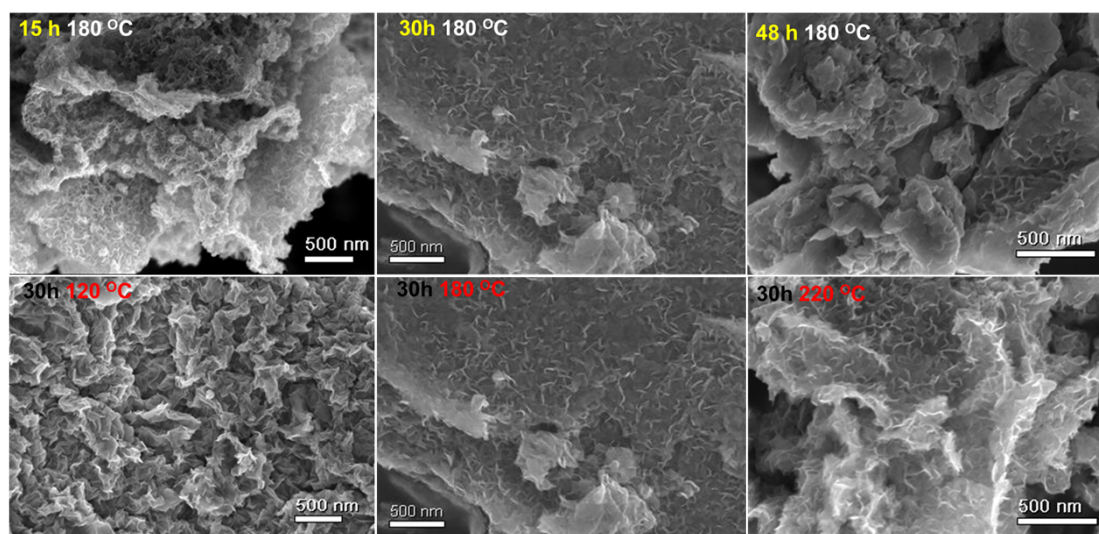
**Fig.S9** Cyclic voltammograms in the region of 0.1~0.2 V vs. RHE for the  $\text{MoS}_2/\text{RGO}(x)$ .



**Fig.S10** Scan rate dependence of the current density at  $E=0.15\text{V}$  vs. RHE for  $\text{MoS}_2/\text{RGO}(x)$ .



**Fig.S11** The simple illustration of a homemade button cell.



**Fig.S12** FESEM images of the as-synthesis MoS<sub>2</sub> under different reaction time and synthesis temperature.

The influence of different reaction time and synthesis temperatures for the MoS<sub>2</sub>⊥RGO catalysts has been provided as shown in Fig.S12. With the increase of the reaction time, it was found that the MoS<sub>2</sub> nanosheets became such larger that the nanosheets crimped and wrapped in the graphene substrate for 48 h. As the synthesis temperature changes, the MoS<sub>2</sub> nanosheets could not be formed on the RGO at 120 °C for 30h, except for bare stacking graphene. When the temperature increased to 180 °C, the vertical MoS<sub>2</sub> nanosheets were well grown on the RGO. For the MoS<sub>2</sub>⊥RGO catalyst synthesized over higher temperature, up to 220 °C, the MoS<sub>2</sub> nanosheets became further larger and the by-product hydrogen sulfide gas has been formed. Therefore, the optimal condition of the ultrathin MoS<sub>2</sub> nanosheets perpendicular to RGO is at 180 °C for 30h during the hydrothermal reactions.

## References

- 1 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano*. 2010. **4**. 4806.
- 2 E. Gileadi, *Physical Electrochemistry*, Wiley-VCH, Weinheim. 2011.