

## Electronic Supplementary Information (ESI)

### Graphene Oxide as a Highly Selective Substrate to Synthesize Layered MoS<sub>2</sub>/Graphene Hybrid Electrocatalyst\*\*

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#### Experimental Procedure

**Materials.** MoCl<sub>5</sub> (>95%) and butyl mercaptan – C<sub>4</sub>H<sub>10</sub>S (>98%) were purchased from Aldrich Chemical Co. The DMF and ethanol were purchased from Tedia Company, Inc. The GO was processed by a modified Hummers method <sup>1</sup>.

**Synthesis of MoS<sub>2</sub>/RGO hybrid.** The chemical compounds before the MW solvothermal treatment were manipulated inside a glove box under a controlled atmosphere. In a typical synthesis, 69 mg of MoCl<sub>5</sub> and 55 µL of butyl mercaptan were added to a Teflon tube with a colloidal dispersion of GO in DMF (200 mg of GO in 30 ml of DMF). After complete dissolution of the reagents, the sealed tube was removed from the glove box and heated in a MW reactor (Synthos 3000, Anton Paar) at 800 W during 60 min. After the reaction the product was collected by centrifugation (10000 rpm for 10 min.) and washed with ethanol. This procedure was repeated five times. Then the material was dried in vacuum for several hours. The synthesized material has a nominal [MoS<sub>2</sub>]/[RGO] ratio of 0.202. A similar procedure was repeated to process MoS<sub>2</sub>/RGO material with different [MoS<sub>2</sub>]/[RGO] ratios (hybrid materials with [MoS<sub>2</sub>]/[RGO] = 0.0202 and [MoS<sub>2</sub>]/[RGO] = 2.40). For the MoS<sub>2</sub>

synthesis without the GO addition, the same procedure was employed using 30 ml of DMF as the solvent.

**Characterization.** For the HRTEM /EDX analysis, a TECNAI F20 FEI microscope was used which was operated at 200 kV. The hybrid composite was dispersed in ethanol and dripped onto a hollow carbon coated copper grid. HRTEM multislice image simulations were generated using JEMS software, which were compared to experimental data. The hexagonal 2H MoS<sub>2</sub> structure was used as the basis for theoretical models.

After a drying step, the resulting powder was characterized by XRD using CuK $\alpha$  radiation (Rigaku D/MAX 2500 PC with a rotary anode operating at 150 kV and 40 mA). The dry powder was also subjected to Raman spectroscopy analysis.

For the AFM characterization, the ethanol dispersion of the MoS<sub>2</sub>/RGO and RGO were dripped onto a flash cleaved mica substrate. The measurement was performed using Nanosuff Easyscan2 equipment.

**Electrochemistry.** The electrochemical measurements were carried out in a standard three-electrode cell (working electrode, platinum as a counter electrode and a standard hydrogen electrode as a reference) in N<sub>2</sub> purged 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and a scan rate of 1 mV/s. For the preparation of the working electrode, the MoS<sub>2</sub>/RGO material (8 mg) and 160  $\mu$ L of 5%wt Nafion solution were dispersed in 800  $\mu$ L of water and 200  $\mu$ L of ethanol to form a viscous ink; 5  $\mu$ L of this ink was loaded onto a glassy carbon electrode (6 mm diameter). As reference point, high purity Pt disc was measured in the same experimental set-up. The current was normalized by the geometric area of the electrodes.

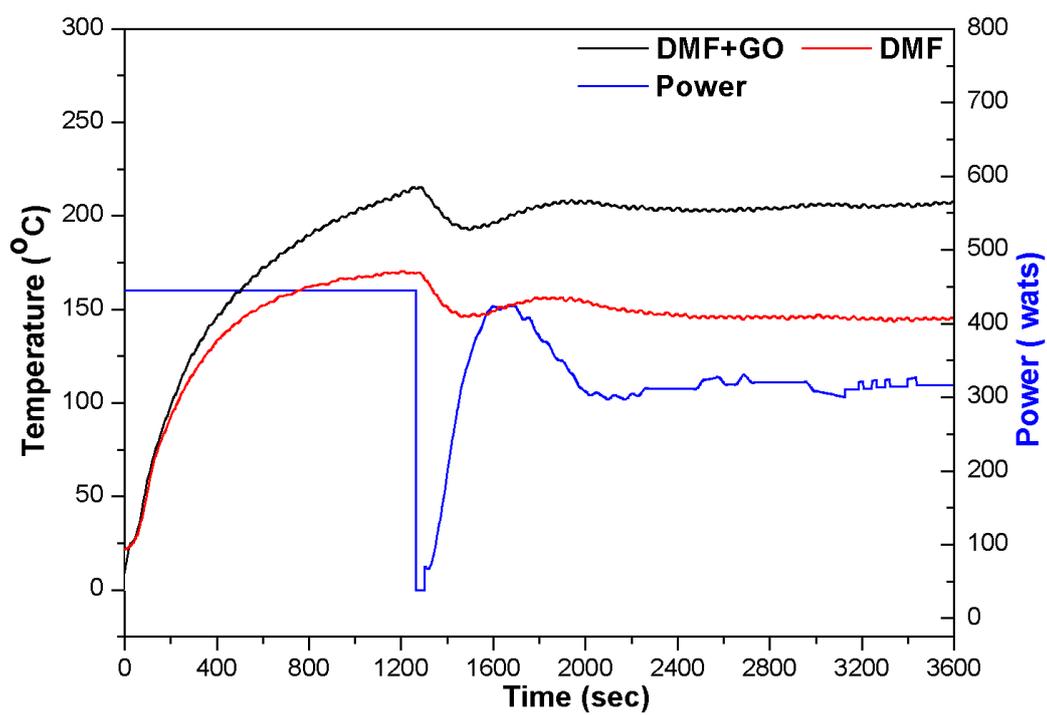


Figure S1 – Temperature and power profiles showing the high heating obtained by the addition of graphene oxide into the system.

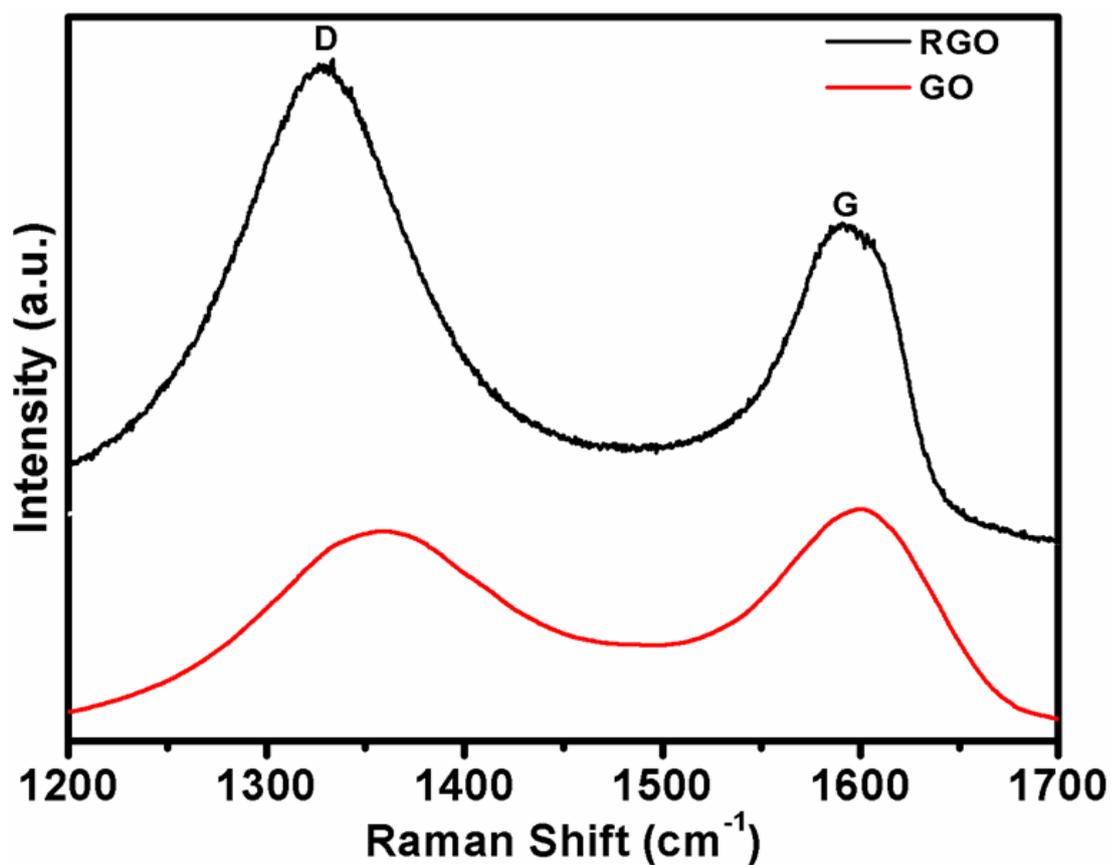


Figure S2 – Raman spectroscopy analysis of the GO before and after the MW treatment. The Raman spectrum presents two characteristic bands at approximately 1595 cm<sup>-1</sup> (G band) and 1350 cm<sup>-1</sup> (D band). The higher relative intensity of the D band compared to the G band can be observed in all hybrid material after the MW synthesis <sup>2</sup>. This observation confirms the mild reduction of GO during the reaction time in the microwave.



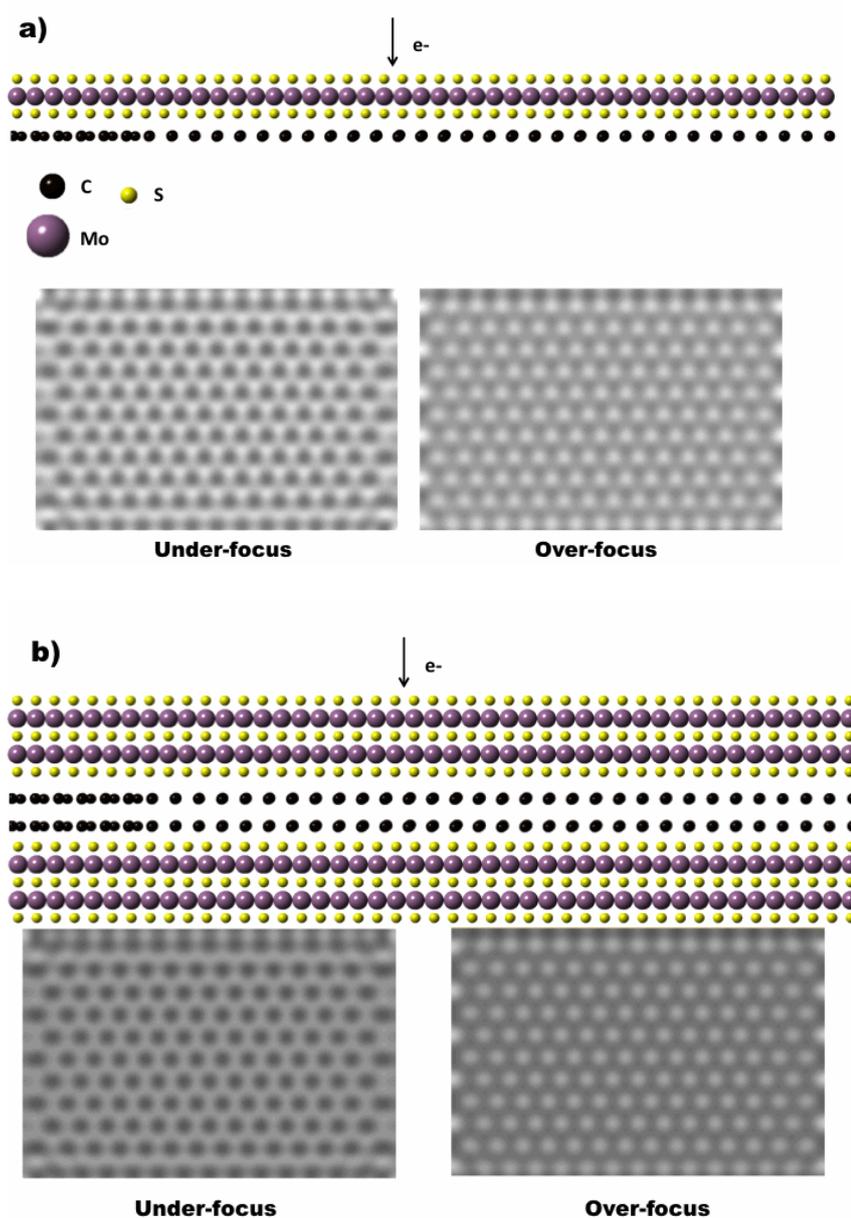


Figure S5 - HRTEM multislice image simulations<sup>3</sup>: a) Considering one single layer of MoS<sub>2</sub>/graphene; b) considering four layers of MoS<sub>2</sub> and two layers of graphene. Under-focus and over-focus conditions are reported for both images. Several others MoS<sub>2</sub>/graphene layers were simulated. However no significant contrast variation is observed. Even one single layer of MoS<sub>2</sub> shows good contrast at 200kV; a single layer of graphene showed no contrast at 200kV.

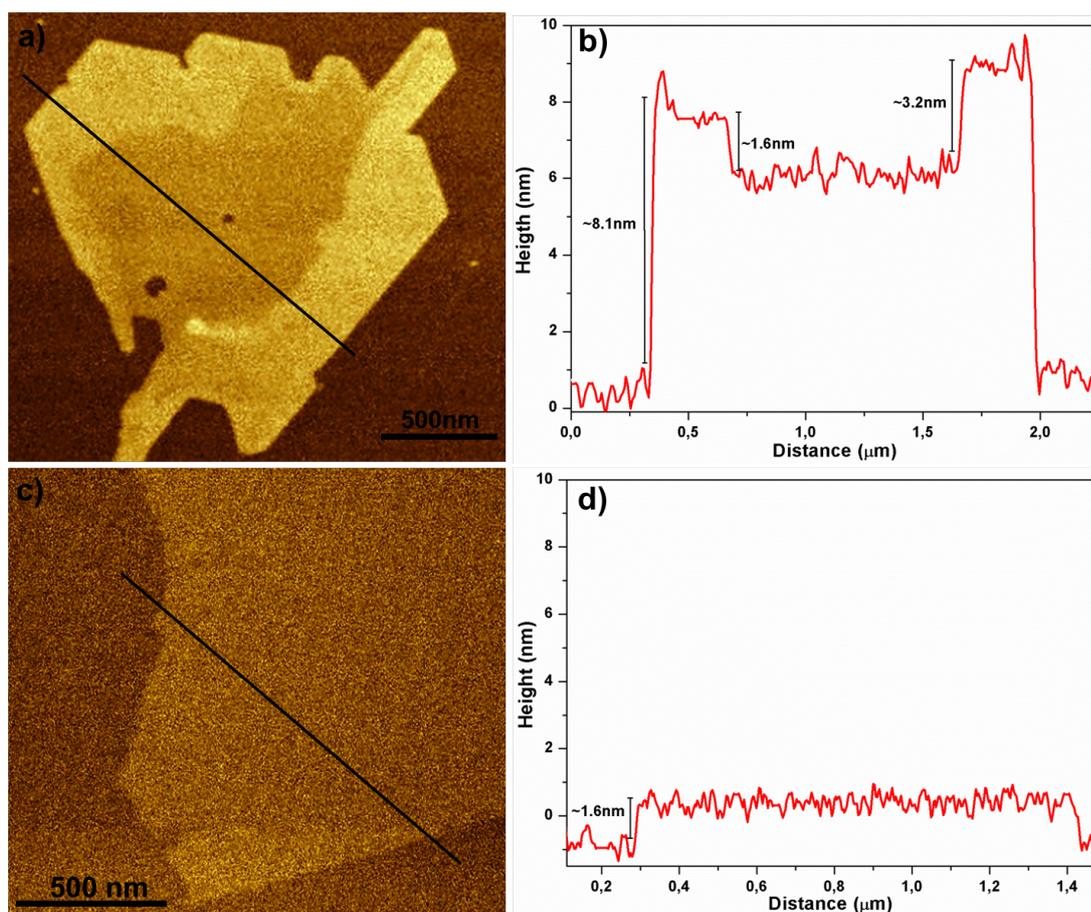


Figure S6 – a) AFM image of the MoS<sub>2</sub>/graphene composite with the graphene covered by layers of MoS<sub>2</sub>. The height profile analysis reveals steps of 1.6 and 3.2 nm (see Figure S6b). These steps were not observed in the GO sheets (see Figure S6c). Figure S6d shows the GO platelet with micrometer-sized homogeneity displayed over the entire lateral dimension.

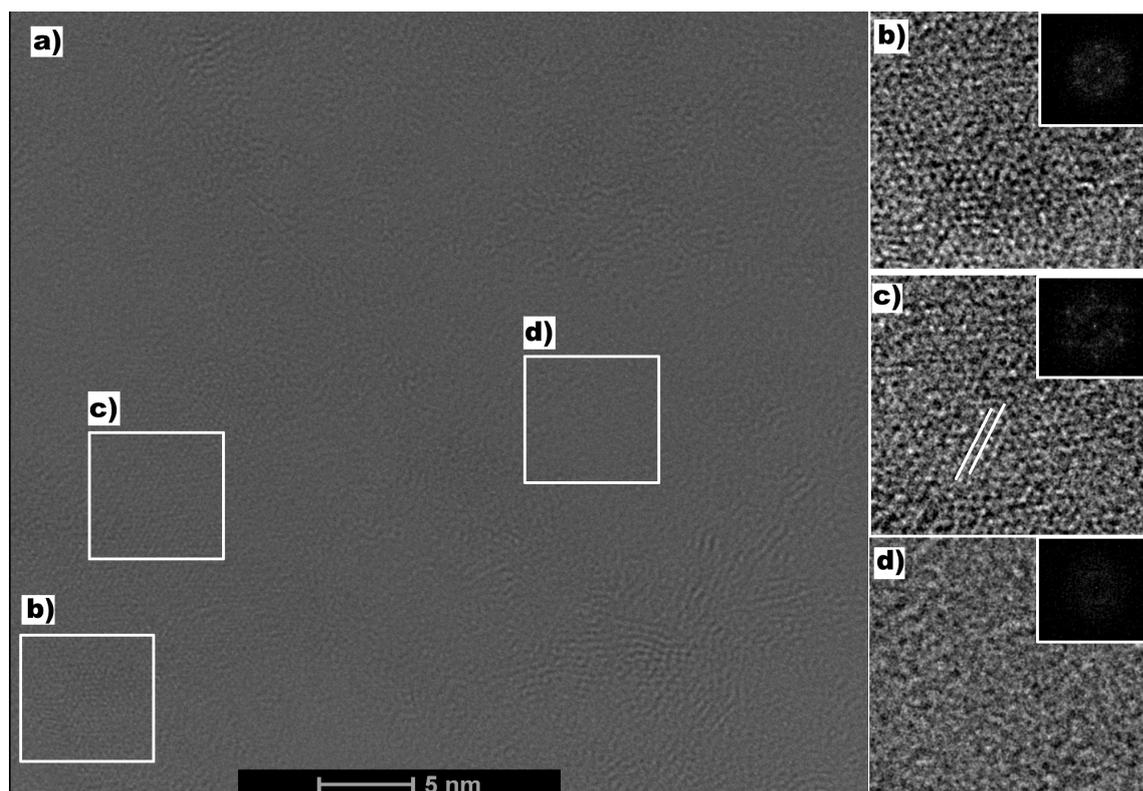


Figure S7 – HRTEM images of the MoS<sub>2</sub>/RGO hybrid material with a low [MoS<sub>2</sub>]/[RGO] ratio (0.0202) a) Representative HRTEM images; b) and c) details showing a single layer of MoS<sub>2</sub> over RGO; d) Area without MoS<sub>2</sub> layer (with graphene only).

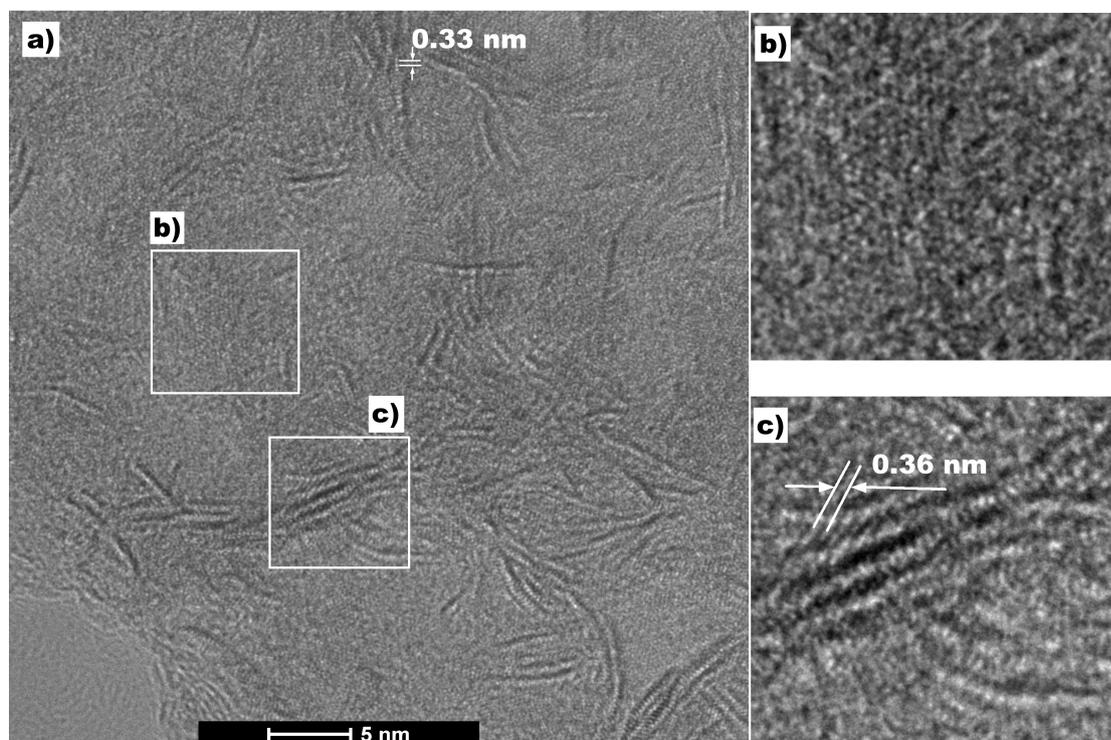


Figure S8 - HRTEM images of the MoS<sub>2</sub>/RGO hybrid material with a high [MoS<sub>2</sub>]/[RGO] ratio (2.40): a) Representative HRTEM images; b) and c) details

In a very low [MoS<sub>2</sub>]/[RGO] ratio, isolated island of MoS<sub>2</sub> oriented along the [001] direction and areas without the sulfide layer are visible (see Figure S7). Increasing the [MoS<sub>2</sub>]/[RGO] ratio produces a high concentration of dark fringes related to the folded edges of the MoS<sub>2</sub> layers (see Figure S8). The details in Figure S8b and Figure S8c show the folded edge of the MoS<sub>2</sub> layers and a MoS<sub>2</sub> layer over graphene, respectively.

#### References

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