

Supporting Information for the following paper:

MoS₂-graphene-CuNi₂S₄ Nanocomposite an Efficient Electrocatalyst for the Hydrogen Evolution Reaction

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Screen-Printed Electrode fabrication process

The fabrication of SPEs involves: first a carbon–graphite ink formulation product code: C2000802P2; Gwent Electronic Materials Ltd., U.K.) was screen-printed onto a polyester (Autostat, 250 mm thickness) flexible film. This layer was then cured in a fan oven at 60 °C for 30 minutes. Finally, a dielectric paste (product code: D2070423D5; Gwent Electronic Materials Ltd., U.K.) was then printed onto the polyester substrate to cover the connections. After a final curing at 60 °C for 30 minutes the SPEs are ready to be used and were connected *via* an edge connector to ensure a secure electrical connection.

Turn over frequency calculation (ToF)

The improved HER performance of the CuNi₂S₄, g-CuNi₂S₄, MoS₂-CuNi₂S₄ and MoS₂-g-CuNi₂S₄ composites may be explained by the calculation of hydrogen turnover frequency (ToF) per active basis. The ToF calculation was carried out using methodology reported by *Benson et al.*[1].

First, the electrochemically active surface area of the electrode (ESCA) was estimated from the ratio of the measured double layer capacitance with respect to the specific capacitance, utilizing the following equation:[1]

$$ESCA = \frac{C_{dl}(mFcm^{-2})}{C_{dl}(\mu Fcm^{-2})}$$

To evaluate the double-layer capacitance (C_{dl}) cyclic voltammograms (shown in ESI Figure S4.) were acquired in a non-faradaic region between 0.05 V to 0.30 V at various scan rates (5 to 100 mVs⁻¹). The difference in anodic and cathodic current density at a potential of +0.175 is shown in ESI Figure S5. where the C_{dl} was calculated from the slope of the straight line (i_c = vC_{dl}), when the charge current density (J (mA cm⁻²)) is plotted against scan rate. Using this relation, C_{dl} values were found to be 1.19 cm², 8.40 cm², 14.45 cm² and 23.08 cm² for CuNi₂S₄, g-CuNi₂S₄, MoS₂- CuNi₂S₄ and MoS₂-g-CuNi₂S₄, respectively.

Once the ESCA for each composite material was calculated, the following equation was used to calculate ToF per active site basis (H₂ s⁻¹):

$$ToF = \frac{JN_A}{2FnESCA}$$

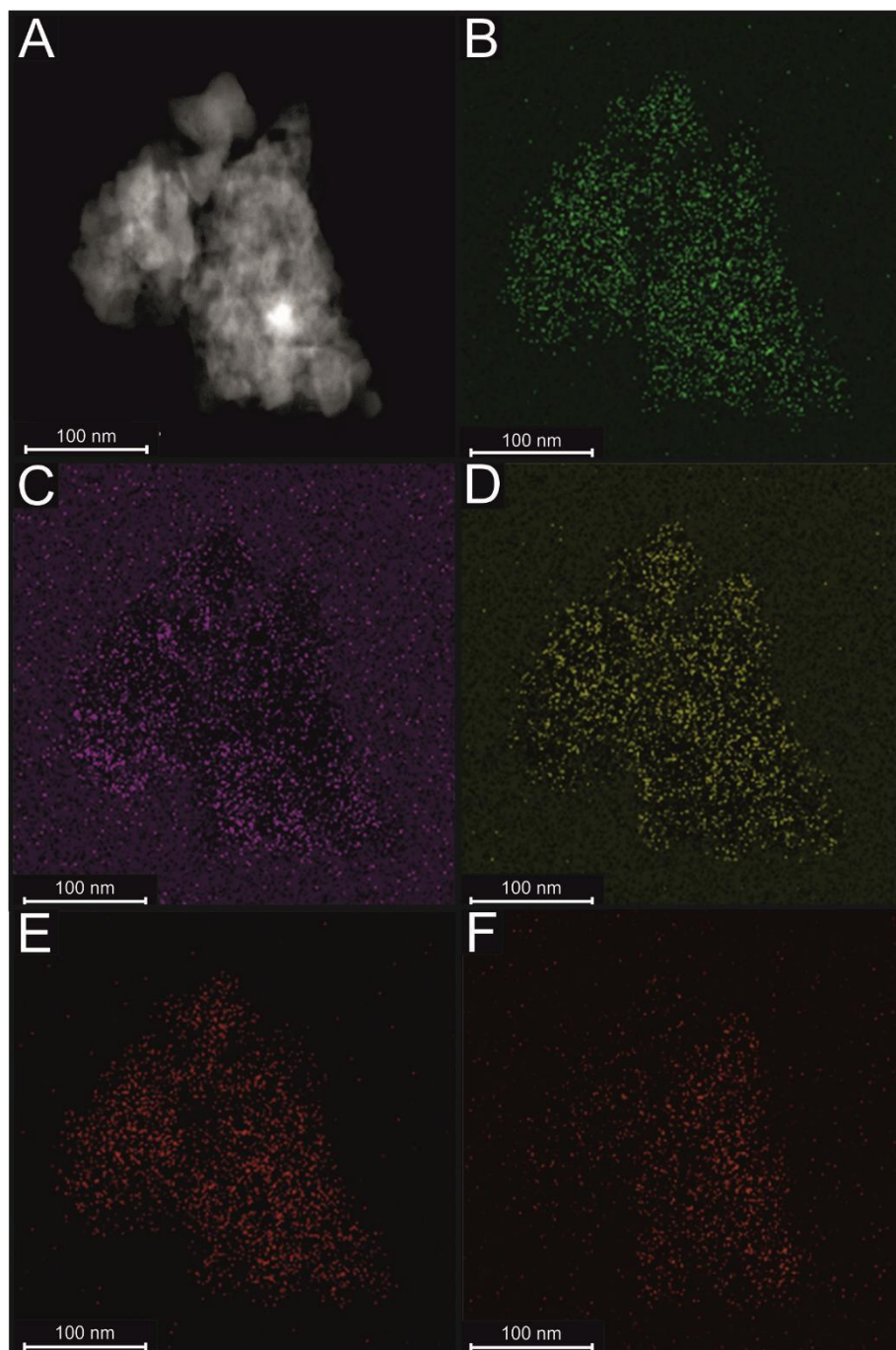
where J is the current density, “2” represents the stoichiometric number of electrons consumed in the electrode HER reaction, ESCA is the electrochemically active surface area of the electrode (cm²), F is the Faraday constant (F= 96485 C mol⁻¹), N_A is Avogadro’s number (N_A=6.022 × 10²³ H₂ molecules mol⁻¹) and n is the number of active sites (n= 1.28 × 10¹⁴ cm⁻²) in a flat 1 cm² surface sample. Using this relation, ToF values of 0.083, 0.19, 0.53, and 0.73 H₂ s⁻¹ were calculated for the CuNi₂S₄, g-CuNi₂S₄, MoS₂- CuNi₂S₄ and MoS₂-g-CuNi₂S₄ electrodes, respectively.

ESI Table 1. Elemental composition of the MoS₂-g-CuNi₂S₄ at five separate sites specified in Figure 2 deduced using EDX analysis.

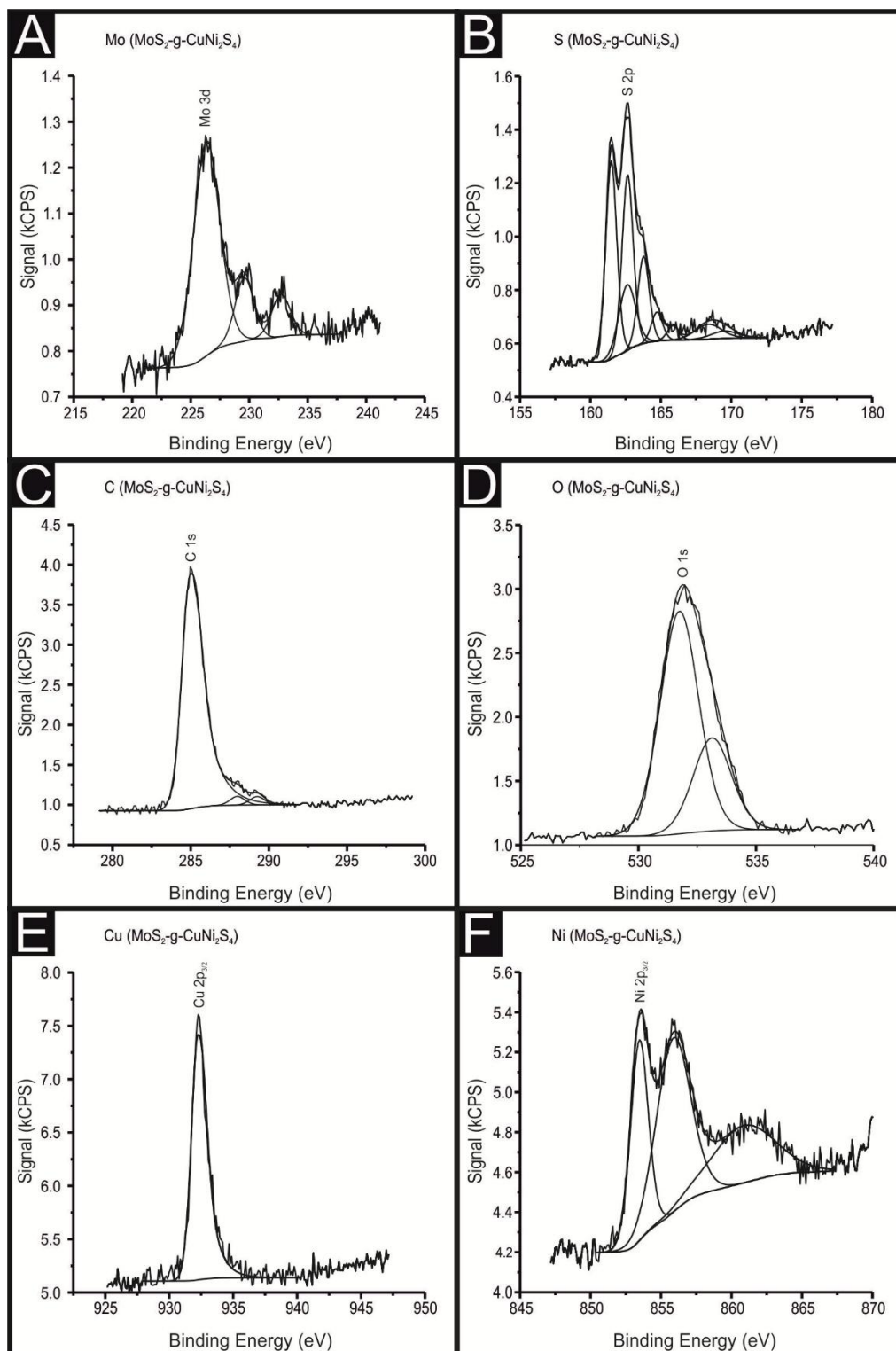
Spectrum Site	C	O	Si	S	Ni	Cu*	Mo
Spectrum 1	86.22	1.48	0.55	1.53	0.71	9.48	0.03
Spectrum 2	61.9	1.39	0.21	14.67	1.36	18.94	1.53
Spectrum 3	85.7	1.26	0.43	4.7	3.5	4.06	0.35
Spectrum 4	77.68	1.24	0.25	7.27	6.8	6.31	0.44
Spectrum 5	64.85	1.28	0.28	11.73	0.64	19.87	1.35

Key: *; the high presence of elemental Cu can be prescribed to the supporting Cu grid used within the TEM analysis

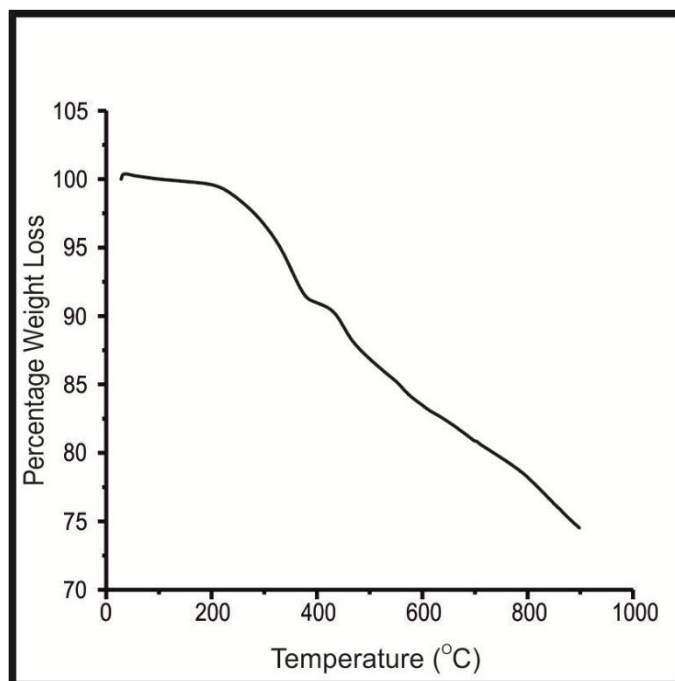
ESI Figure S1. SEM of the MoS₂-g-CuNi₂S₄ nanocomposite (A) with EDAX analysis highlighting the Sulfur (B, green), Copper (C, purple), Nickel (D, yellow), molybdenum (E, red) and Oxygen (F, brown) coverage, respectively.



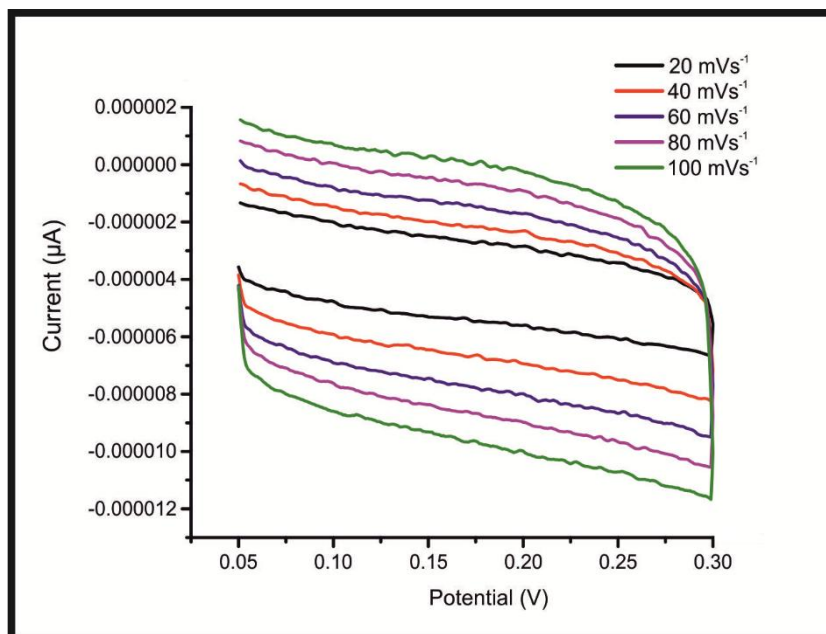
ESI Figure S2. High resolution XPS analysis of the (A) Mo, (B) S, (C) C, (D) O, (E) Cu and (F) Ni components of the $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$.



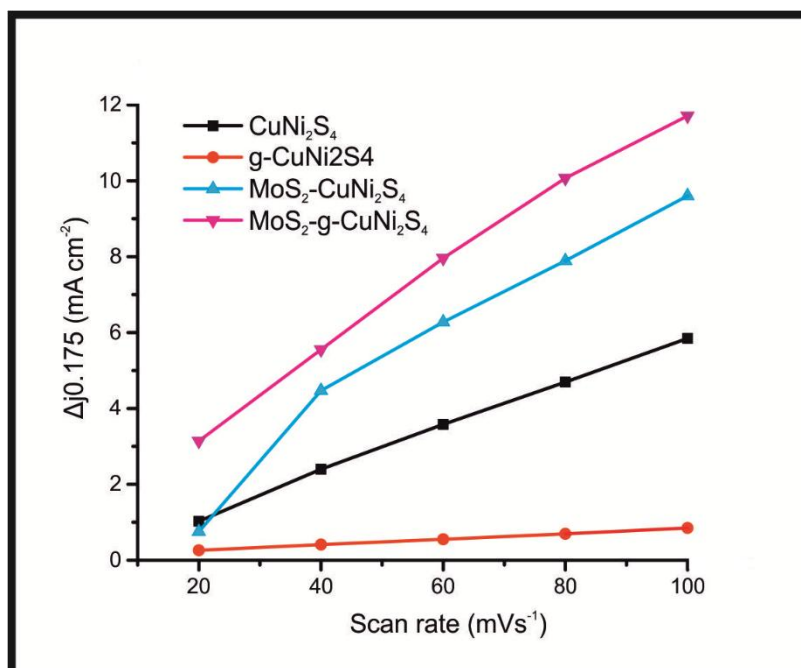
ESI Figure S3. TGA analysis of the MoS₂-g-CuNi₂S₄.



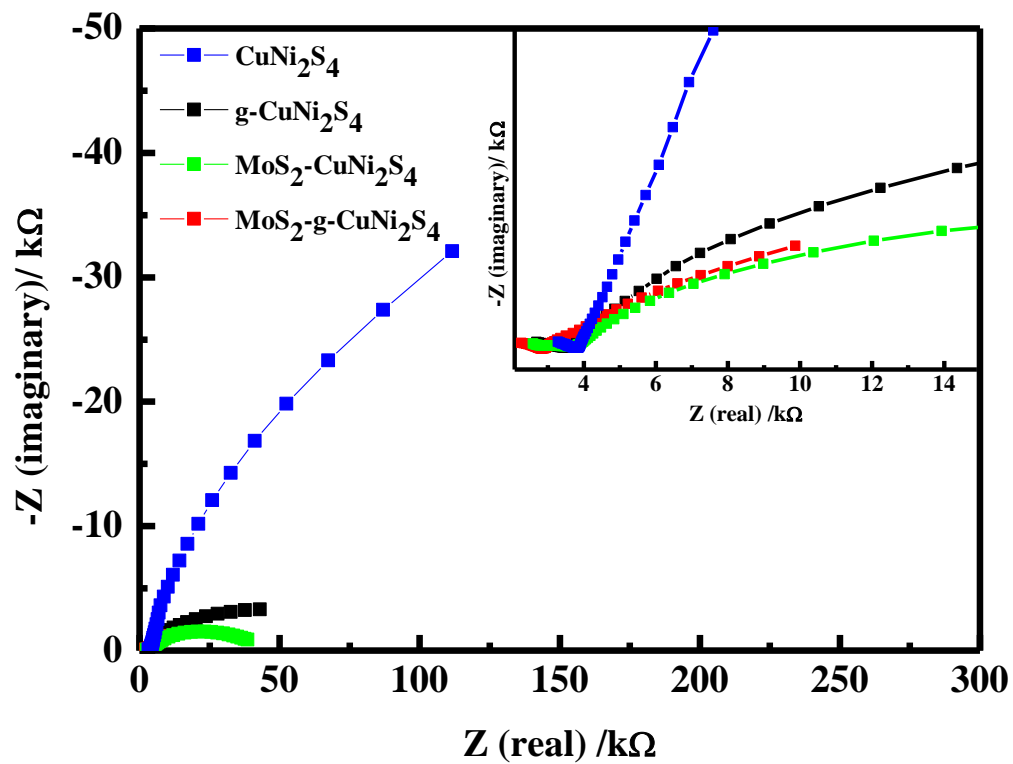
ESI Figure S4. Cyclic voltammograms recorded in a 0.5 M H₂SO₄ electrolyte using the MoS₂-g-CuNi₂S₄ electrode in the scan rate range: 20-100 mV s⁻¹.



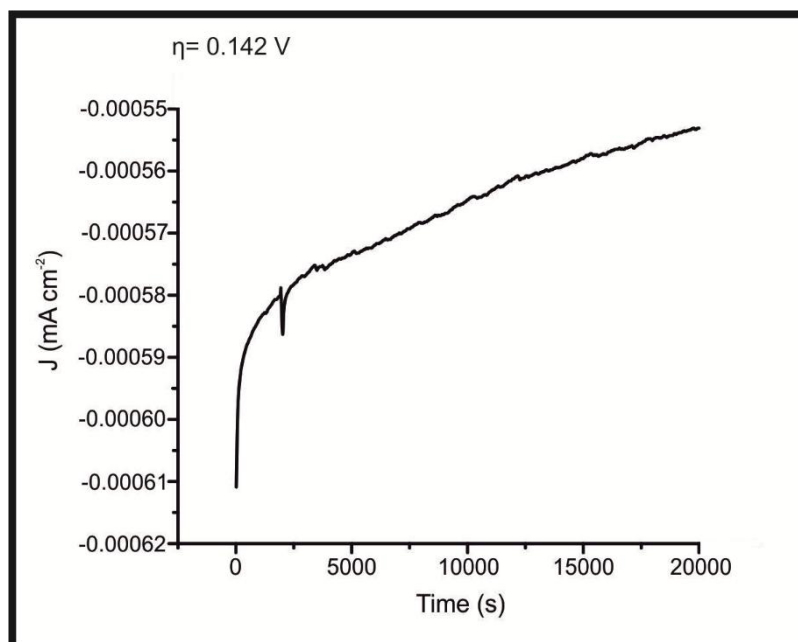
ESI Figure S5. The difference in anodic and cathodic current density at a potential of +0.175 V against scan rate (mVs^{-1}) (vs. RHE). The slope of each data set indicates the value of double layer capacitance (C_{dl} : mF cm^{-2}).



ESI Figure S6. Electrochemical impedance spectroscopy analysis of the synthesized CuNi_2S_4 , $\text{g-CuNi}_2\text{S}_4$, $\text{MoS}_2\text{-CuNi}_2\text{S}_4$ and $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$ nanocomposites.



ESI Figure S7. The current observed using chronoamperometry with the potential held at -0.142 V (vs. RHE) for 20,000 seconds using the $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$ electrode recorded in 0.5 M H_2SO_4 .



References:

1. Benson, J., et al., *Electrocatalytic Hydrogen Evolution Reaction on Edges of a Few Layer Molybdenum Disulfide Nanodots*. ACS Applied Materials & Interfaces, 2015. **7**(25): p. 14113-14122.