Supplementary Materials

In situ study of graphene oxide quantum dot-MoS_x nanohybrids as hydrogen evolution catalysts

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Synthesis of graphene oxide quantum dots (GOQDs)

Graphene oxide quantum dots (GOQDs) were electrochemically synthesized from a graphene oxide (GO) foil. The synthesis was carried out in a standard three-electrode electrochemical cell, using a Pt gauze and an $Ag/AgCl/Cl^-_{(sat)}$ as counter and reference electrodes, respectively. A 0.1 M phosphate buffer solution (40 mL of NaH_2PO_4, PBS) with a pH of 6.86, adjusted by adding a 10 M NaOH solution, was used as electrolyte. 150 μL of a dispersion of GO in water (15 mg GO mL^{-1}) were drop casted on to a glassy carbon substrate and annealed in a tubular furnace at 150 °C for 30 min in N_2 atmosphere. Then, the GO film was cycled between -3.0 V and +3.0 V vs $Ag/AgCl/Cl^-_{(sat)}$ for 8 h at a scan rate of 0.5 V s^{-1}. Subsequently, the yellow solution was twice filtered, using cellulose acetate membranes (VWR) with 400 and 200 nm pore size, and dialyzed for five days (in DI water) with osmotic membranes (Spectra/Por, Molecular Weight Cut-Off (MWCO) of 1kD) to remove the electrolyte salt. Finally, the GOQDs solution was freeze-dried under low vacuum conditions and re-dispersed in Milli-Q water to obtain a 1 mg mL^{-1} solution.

In situ electrochemical cells

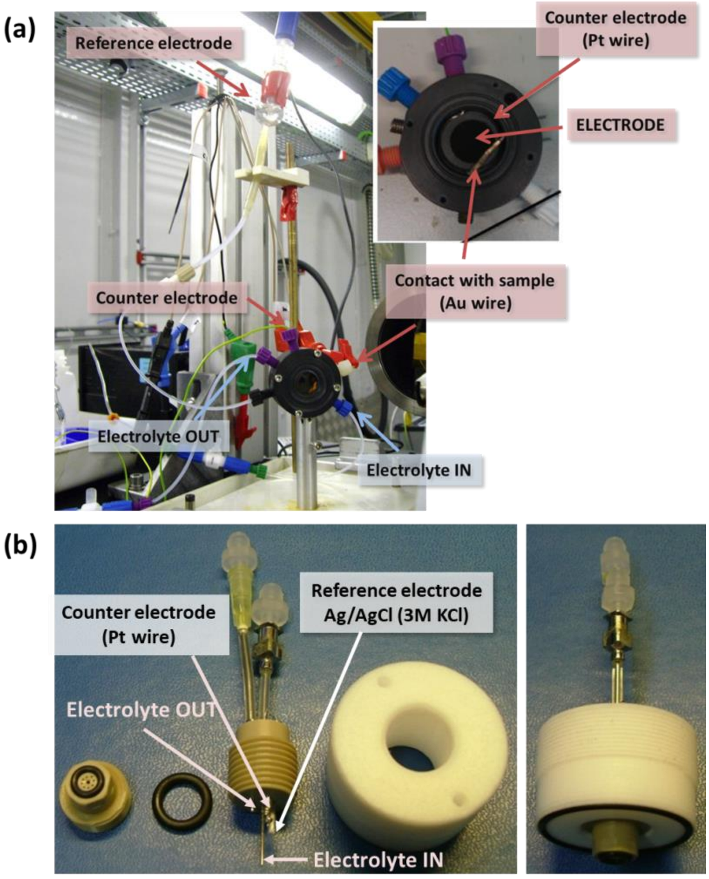

Figure S1. (a) *In situ* electrochemical cell used for the XAS measurements; and (b) *in situ* electrochemical cell used for the combined XPS/EC measurements.

Physicochemical characterization

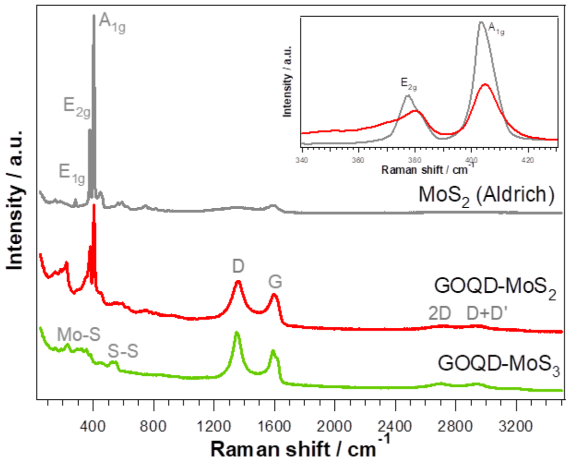

Figure S2. Raman spectra for the GOQD-MoS_x (x = 2, 3) nanohybrids and the commercial MoS_2 (Aldrich).

Operando X-ray absorption spectroscopy (XAS) measurements

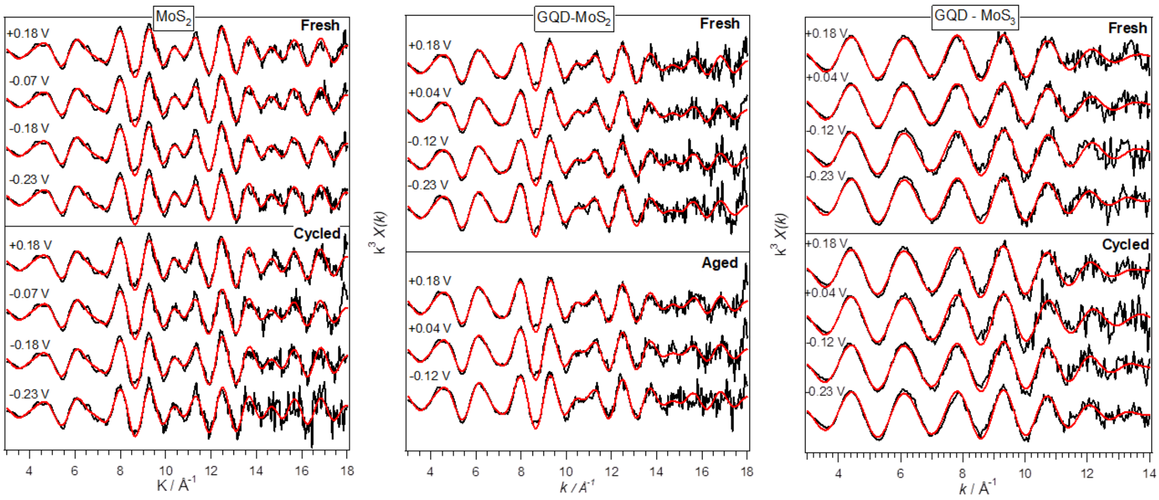

Figure S3. k^3 weighted experimental data (black) and fit (red) at Mo K edge for the fresh and aged MoS_2 (Aldrich) (a,d), GOQD-MoS_2 (b,e) and GOQD-MoS_3 (c,f) nanohybrids recorded at different applied potentials.

Table S1. Structural parameters obtained for the commercial MoS_2 (Aldrich) catalyst from fitting the Mo K edge EXAFS data acquired under potential control in 0.5 M H_2SO_4.

Sample	Potential vs RHE	Shell	N	R /Å	σ^2 x 10^4 /Å^2	ΔE_0 /eV	R_f
Ex situ	---	Mo-S	5.80 ± 0.21	2.411 ± 0.003	27 ± 3	2.9 ±0.5	0.006
		Mo-Mo	5.66 ± 0.44	3.172 ± 0.003	33 ± 3		
Fresh	+0.18 V	Mo-S	5.34 ± 0.20	2.407 ± 0.003	27 ± 3	2.6 ±0.6	0.006
		Mo-Mo	5.14 ± 0.43	3.171 ± 0.003	34 ± 4		
	-0.07 V	Mo-S	5.35 ± 0.19	2.409 ± 0.003	27 ± 3	2.8 ± 0.5	0.004
		Mo-Mo	5.10 ± 0.41	3.172 ± 0.002	33 ± 3		
	-0.18 V	Mo-S	5.30 ± 0.19	2.409 ± 0.003	26 ± 3	2.8 ± 0.4	0.004
		Mo-Mo	5.21 ± 0.39	3.172 ± 0.002	34 ± 3		
	-0.23 V	Mo-S	5.38 ± 0.20	2.410 ± 0.004	27 ± 3	3.5 ± 0.5	0.005
		Mo-Mo	5.23 ± 0.41	3.172 ± 0.004	33 ± 3		
Cycled	+0.18 V	Mo-S	5.42 ± 0.21	2.411 ± 0.003	26 ± 3	3.3 ± 0.5	0.006
		Mo-Mo	5.00 ± 0.42	3.172 ± 0.003	31 ± 3		
	-0.07 V	Mo-S	5.53 ± 0.20	2.411 ± 0.003	27 ± 3	3.6 ± 0.5	0.003
		Mo-Mo	5.49 ± 0.44	3.173 ± 0.003	38 ± 4		
	-0.18 V	Mo-S	5.32 ± 0.22	2.409 ± 0.003	23 ± 3	3.3 ± 0.5	0.008
		Mo-Mo	5.45 ± 0.51	3.171 ± 0.003	36 ± 4		
	-0.23 V	Mo-S	5.50 ± 0.29	2.406 ± 0.004	28 ± 5	2.8 ± 0.7	0.013
		Mo-Mo	5.18 ± 0.59	3.169 ± 0.005	33 ± 5		

Table S2. Structural parameters obtained for the GOQD-MoS_2 catalyst from fitting the Mo K edge EXAFS data acquired under potential control in 0.5 M H_2SO_4.

Sample	Potential vs RHE	Shell	N	R /Å	σ^2 x 10^4 / Å^2	ΔE_0 /eV	R_f
Ex situ	---	Mo-S	4.15 ± 0.23	2.412± 0.005	31±5 36±9	3.6± 0.6	0.008
		Mo-Mo	2.53 ± 0.52	3.171± 0.006			
Fresh	+0.18 V	Mo-S	4.34 ± 0.21	2.411± 0.004	29±4	2.4± 0.6	0.004
		Mo-Mo	2.71 ± 0.48	3.168± 0.005	36±8		
	+0.04 V	Mo-S	4.40 ± 0.22	2.412± 0.004	32 ± 5	3.1± 0.6	0.005
		Mo-Mo	2.89 ± 0.52	3.172± 0.005	40±9		
	-0.12 V	Mo-S	4.43 ± 0.23	2.411± 0.004	32 ± 5	2.9± 0.6	0.005
		Mo-Mo	2.73 ± 0.51	3.171± 0.005	39± 9		
	-0.23 V	Mo-S	5.03 ± 0.24	2.411± 0.004	32± 5	2.5± 0.6	0.005
		Mo-Mo	3.39 ± 0.61	3.171± 0.005	45±9		
Cycled	+0.18 V	Mo-S	5.12 ± 0.26	2.411± 0.004	34± 5	2.8± 0.6	0.006
		Mo-Mo	3.19 ± 0.59	3.167± 0.005	41±9		
	+0.04 V	Mo-S	5.00 ± 0.29	2.411± 0.005	32± 6	2.6± 0.7	0.005
		Mo-Mo	3.38 ± 0.75	3.169± 0.006	45± 12		
	-0.12 V	Mo-S	5.12 ± 0.26	2.413± 0.004	32± 5	3.3± 0.6	0.003
		Mo-Mo	3.44 ± 0.67	3.172± 0.005	40±10		

Note: Due to the bubbles formed under the HER conditions that caused jumps in the spectrum for the cycled sample, it was not possible to fit the spectrum obtained at -0.23 V.

Table S3. Structural parameters obtained for the GOQD-MoS_3 catalyst from fitting the Mo K edge EXAFS data acquired under potential control in 0.5 M H_2SO_4.

Sample	Potential vs RHE	Shell	N	R /Å	σ^2 x 10^4 / Å^2	ΔE_0 /eV	R_f
Ex situ	---	Mo-S	4.10 ± 0.62	2.440± 0.013	58±21	1.9 ±1.5	0.017
		Mo-Mo	0.50 ± 0.45	2.790± 0.026	76±58		
Fresh	+0.18 V	Mo-S	3.84 ± 0.46	2.440± 0.010	57±16	1.8 ±1.1	0.016
		Mo-Mo	1.27 ± 0.98	2.790± 0.021	76±59		
	+0.04 V	Mo-S	3.96 ± 0.51	2.440± 0.011	61±18	1.9± 1.2	0.013
		Mo-Mo	1.11 ± 1.00	2.784± 0.023	69±67		
	-0.12 V	Mo-S	4.00 ± 0.30	2.444± 0.007	66± 10	2.6± 0.7	0.008
		Mo-Mo	0.83 ± 0.34	2.785± 0.010	37 ± 21		
	-0.23 V	Mo-S	4.21 ± 0.42	2.440± 0.009	66±13	1.9±1.0	0.022[a]
		Mo-Mo	0.90 ± 0.55	2.789± 0.016	46±33		
Cycled	+0.18 V	Mo-S	4.18 ± 0.56	2.441± 0.011	58± 18	1.6± 1.2	0.018
		Mo-Mo	1.27 ± 1.04	2.791± 0.021	64±59		
	+0.04 V	Mo-S	4.14 ± 0.63	2.435± 0.012	42± 12	1.1± 1.4	0.026
		Mo-Mo	1.63 ± 1.51	2.783± 0.026	87± 77		
	-0.12 V	Mo-S	4.28 ± 0.58	2.439± 0.019	61± 18	1.2± 1.2	0.019
		Mo-Mo	1.09 ± 0.95	2.783± 0.020	54±59		
	-0.23 V	Mo-S	4.45 ± 0.21	2.440± 0.012	67± 20	1.7± 1.3	0.019
		Mo-Mo	1.08 ± 0.99	2.788± 0.061	53±61		

In situ photoemission and electrochemical measurements

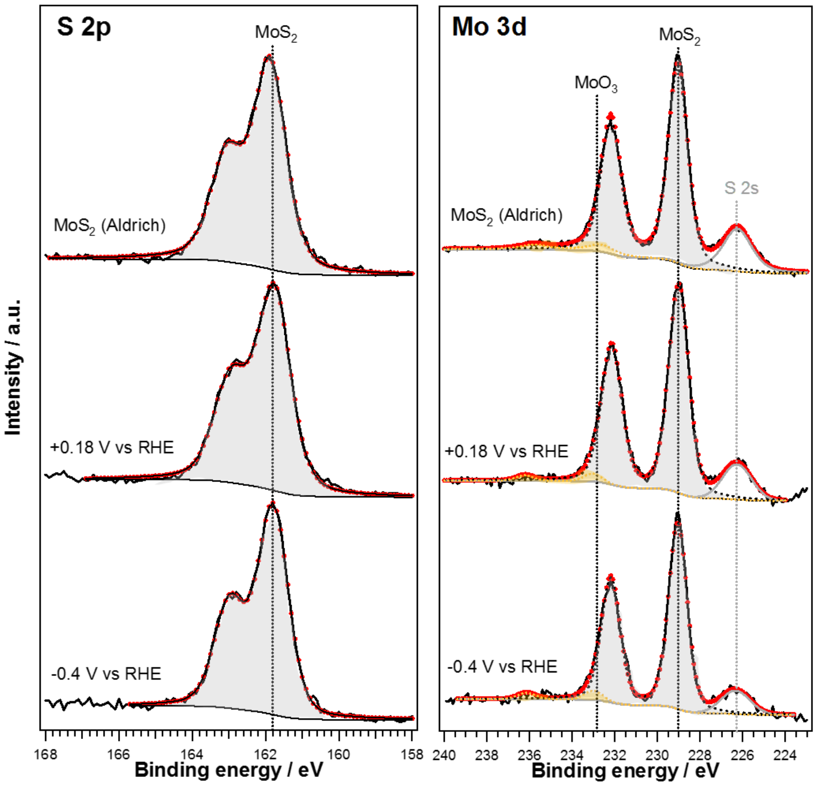

Figure S4. S 2*p* and Mo 3*d* photoemission lines and their deconvolution into chemical shifted components for the commercial MoS_2 (Aldrich) before and after the electrochemical measurements in 0.1 M $HClO_4$ at different potentials. The black and red curves represent the experimental data and the corresponding fit, respectively.

Table S4. Analysis of the single chemical components of the S 2p and Mo 3*d* regions, as well as the atomic Mo:S ratio calculated from the XPS data. For each single chemical component, the BE (eV) and amount (at. %) values are given.

		S 2*p*		**Mo 3*d***			**Atomic Mo:S ratio**
		MoS_2	**MoS_3**	**MoS_2**	**MoS_3**	**$MoO_2(OH)$**	
MoS_2 Aldrich	Pristine	161.9 eV 1.1 100 %	---	229.0 eV 1.11 93.9 %	---	---	1 : 2.0
	+0.18 V (pre HER)	161.8 eV 1.1 100 %	---	229.0 eV 1.13 89.7 %	---	231.4 eV 1.1 2.8 %	1 : 2.0
	-0.40 V (HER)	161.8 eV 1.0 100 %	---	229.0 eV 1.03 91.4 %	---	231.5 eV 1.0 4.8 %	1 : 2.0
GOQD-MoS_2	Pristine	161.7 eV 1.2 80.6 %	163.1 eV 1.5 19.4 %	228.8 eV 1.2 87.4 %	229.5 eV 1.2 12.6 %	---	1 : 2.1 (32:68)
	+0.18 V (pre HER)	161.6 eV 1.2 83.0 %	163.1 eV 1.2 17.0 %	228.7 eV 1.2 81.0 %	229.5 eV 1.2 15.6 %	231.5 eV 1.5 3.4 %	1 : 2.1 (32:68)
	-0.40 V (HER)	161.7 eV 1.2 82.1 %	163.1 eV 1.3 17.9 %	228.8 eV 1.2 73.3 %	229.5 eV 1.2 13.2 %	232.3 eV 1.4 13.5 %	1 : 2.0 (33:67)
GOQD-MoS_3	Pristine	161.6 eV 1.5 42.8 %	163.0 eV 1.5 57.2 %	228.7 eV 1.2 34.3 %	229.5 eV 1.3 65.7 %	---	1 : 2.7 (27:73)
	+0.18 V (pre HER)	161.6 eV 1.5 43.2 %	163.0 eV 1.5 56.8 %	228.7 eV 1.2 34.4 %	229.5 eV 1.2 50.9 %	231.2 eV 1.2 14.7 %	1 : 2.7 (27:73)
	-0.40 V (HER)	161.6 eV 1.5 56.4 %	163.0 eV 1.5 43.6 %	228.7 eV 1.5 48.0 %	229.5 eV 1.5 39.1 %	231.4 eV 1.5 12.9 %	1 : 2.2 (31:69)