Supporting Information

A Polymer-Brush Templated Three-Dimensional Molybdenum Sulfide Catalyst for Hydrogen Evolution

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Experimental

Materials

Unless stated otherwise, commercially available materials were used as received. 4-Nitroaniline ($\text{C}_6\text{H}_6\text{N}_2\text{O}_2$, $\geq 99\%$, Aldrich), aniline ($\text{C}_6\text{H}_7\text{N}$, purum, $\geq 99.0\%$ (GC), Fluka), tetrafluoroboric acid solution (HBF_4 , 48 wt.% in water, Aldrich), sodium nitrite (NaNO_2 , RegaentPlus[®], $\geq 99.0\%$, Aldrich), tetrabutylammonium tetrafluoroborate (NBu_4BF_4 , 99%, Aldrich), acetonitrile (ACN, HPLC grade, Fischer), potassium chloride (KCl, puriss. p.a., $\geq 99.5\%$ (AT), Aldrich), hydrochloric acid (HCl, fuming 37% for analysis, VWR), iodomethane (methyl iodide, MeI, 99%, stabilized, Acros), 2,6-dimethylpyridine (2,6-lutidine, $\text{C}_7\text{H}_9\text{N}$, 99+%, Aldrich), 2-bromo-2-methylpropionyl bromide (BiBB, 98%, Aldrich), N,N-dimethylaminoethyl methacrylate (DMAEMA, 98%, Aldrich), 2,2'-bipyridine (bipyr, $\geq 99\%$, Aldrich), copper (I) bromide (CuBr , 99.999%, Aldrich), ethylenediaminetetraacetic acid (EDTA, $\geq 99\%$, Fluka), ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, 99.97% trace metals basis, Aldrich), platinum (II) chloride (PtCl_2 , 98%, Aldrich), ethylene glycol (EG, 99+%, extra pure, Acros), sodium perchlorate monohydrate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$, puriss, p.a., ACS reagent, $\geq 98\%$ (T), Aldrich), sulfuric acid (H_2SO_4 , volumetric, 1 M H_2SO_4 (2 N), Fluka). Triethylamine (Et_3N , $\geq 98\%$, Fluka) was distilled over KOH. Both toluene and DMF were purified and dried using a solvent-purification system (PureSolv). Organic solvents such acetone, dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), and diethyl ether (Et_2O) used for washing were of technical grade. The water used was first purified using Millipore Milli-Q[®] Integral water purification system (18.2 $\text{M}\Omega \cdot \text{cm}$ resistivity). DMAEMA was passed through basic alumina column to remove inhibitor just before a polymerization. 6-(chlorodimethylsilyl)hexyl 2-bromo-2-methylpropanoate was prepared according to previous literature report.¹ HOPG was used as substrate for the polymer brushes.

The HOPG ZYA plates were purchased from Optigraph. HOPG support was cleaved prior to use.

Synthesis of Benzenediazonium Tetrafluoroborate (BDT)

The synthesis of BDT followed the same procedure than that of 4-NDT synthesis. The difference consisted in using aniline (2.3 g) as starting material. Color changes were also affected by the change of starting material. The reagent concentrations were unchanged compared to the 4-NDT synthesis. Upon dissolution of the aniline, the solution turned white. The resulting product corresponds to a white paste (2.79 g). The reaction was quantitative.

^1H NMR (D_2O , 400 MHz): δ (ppm) 8.69-8.56 (m, 2H), 8.24-8.19 (m, 1H), 8.00-7.95 (m, 2H).

Physical Characterization

High resolution scanning electron microscopy images were taken on a ZEISS MERLIN. The treated HOPG plates were directly used for imaging. HRTEM images were taken on a FEI Tecnai Osiris equipped with an 11 megapixel Gatan Orius CCD camera. TEM images were taken on a Philips FEI CM12 with a LaB_6 source operated at 120 kV accelerating voltage. The samples were prepared by scrapping off HOPG plates using a scalpel. The extracted samples were then dispersed in ethanol and sonicated. The slurries were mixed with a micropipette by several suction-release cycles to ensure representative and reproducible TEM samples. A few drops of the mixed suspensions were deposited onto the carbon-coated grids.

To image the cross-section of HOPG ZYA samples, preparation of the sample through Focused ion beam was necessary. A TEM lamella was prepared by focused ion beam (FIB) milling using a Zeiss NVision40, applying ion beam voltages of 30 kV down to 5 kV for final thinning. During milling, the sample surface was protected by a layer of amorphous carbon made first by electron beam induced deposition and then by ion beam induced deposition.

Transmission electron microscopy (TEM) and scanning TEM (STEM) analyses of HOPG ZYA samples' cross sections were performed using an FEI Talos F200S, operated at 80 kV high tension in order to reduce the possibility of electron beam induced damage during imaging. Energy dispersive X-ray spectroscopy (EDXS) hyperspectral mapping was performed in STEM mode using a ~ 0.75 nA electron beam, with data recorded using Bruker Esprit software.

Atomic force microscopy was performed in tapping mode on a Veeco Multimode Nanoscope IIIa SPM controller (Digital Instruments, Santa Barbara, CA) using NSC14/no Al MikroMasch (Tallinn, Estonia) cantilevers. Micropatterned initiator-coated substrates were prepared using a protocol previously reported in the literature.² The prepared patterns on HOPG were used to determine the height profile of polymer-coated HOPG.

Reduction of the Nitro Functional Groups to Amino Moieties

Electrochemical reduction was performed in an electrolyte composed of 1 M HCl and 1 M KCl. A 2 L stock solution of the electrolyte was prepared prior to reduction. The HOPG plates, bearing nitro groups after electrografting, were immersed in the electrolyte and were employed as working electrodes. Three consecutive cyclic voltammetry scans were performed to ensure large conversion of the nitro groups. The starting and ending potential of the cyclic scan was of 0.8 V *vs.* RHE, the vertex potential was of -0.4 V *vs.* RHE. The scan rate applied was of 20 mV s⁻¹. After reduction, the HOPG sample was carefully washed with water and dried with nitrogen gas. The counter and reference electrode were both washed with water, acetone and dried under nitrogen between each reduction. The electrolyte was renewed between each HOPG samples' reduction.

Fabrication of a Monolayer of Trimethylammonium onto HOPG

For comparison purposes with the polymer composites on HOPG ZYH electrodes, monolayer of trimethylammonium were fabricated on HOPG electrodes; which were previously modified with 4-NDT followed by reduction. The electrode tips were immersed into a 2 mL solution of DMF including 50 μ L of methyl iodide (114 mg, 0.8 mmol) and 5 μ L of 2,6-lutidine (4.6 mg, 0.04 mmol) for 16 h at room temperature. Thereafter, the electrodes were washed with deionized water and dried under compressed air.

Attachment of the ATRP Initiator on HOPG Plates

The prepared HOPG plates were then placed within a PEEK holder into a glass reactor. Once the reactor was sealed, it was evacuated and backfilled with nitrogen 3 times. Dry toluene (20 mL) was added to the reactor. Freshly distilled trimethylamine (0.4 mL) was then added and the mixture is well stirred. The system was then cooled down to 0 °C in ice bath. Afterwards, BiBB, the ATRP initiator, is added dropwise (0.4 mL) to the solution. The reaction was kept at 0 °C for 1 h, then the ice bath was removed and the reaction is kept at room temperature for 16 hours. The HOPG plates were then washed extensively with toluene, dichloromethane for 5 minutes and dried with nitrogen.

Attachment of the ATRP Initiator on Si Substrates

Silicon wafers (0.8x1.0 cm) were sonicated 5 minutes in acetone, 5 minutes in ethanol and 5 minutes in distilled water. The wafers were dried using compressed air flow. The substrates were then exposed to microwave-induced oxygen plasma (200 W, Diner electronic GmbH, Germany) for 15 minutes. The wafers were then immersed for 16 h at room temperature under inert atmosphere in a 2 mM solution of 6-(chlorodimethylsilyl)hexyl 2-bromo-2-methylpropanoate

in dry toluene. The prepared wafers were rinsed with dichloromethane and methanol, and dried under nitrogen flow.

Insulation of HOPG ZYA Plates Prior to Anion Exchange

The HOPG ZYA samples were insulated so that only one face of the HOPG was exposed to the electrolyte (cf. Fig. S7). To ensure conductivity of the isolated material, Ag paste was used to attach a Cu wire at the back of the HOPG support. Once connected, the assembly was isolated so that the HOPG face opposite to the silver paste is exposed. After insulation, the surface area exposed to the electrolyte was determined by means of optical photography (prior to HER). The pixel area of the exposed surface was then determined. By comparison with a sample, whose pixel and geometric area is known, the exact geometric area of the sample was calculated. In addition, the edge sites of HOPG were isolated from deposition of molybdenum sulphide.

Oxidation to Obtain the MoS₃ Precatalyst

MoS₄-incorporated polymers underwent electrochemical oxidation to form the MoS₃ precatalyst prior to the HER. The electrolyte solution contained 0.1 M of NaClO₄. The potentiostatic oxidation was performed at a potential of 0.3 V *vs.* RHE for several minutes. In all cases, the oxidation was complete before 10 minutes of reaction. The oxidation was stopped when the current change between two consecutive minutes was in the order sub-micro-ampere. The oxidized samples were washed with water and dried under nitrogen. Both the counter and reference electrodes were washed with water and acetone and dried using nitrogen gas. In regard of the small amount of currents generated during oxidation, the electrolyte solution was not renewed between each sample.

Evaluation of the HER Activity of the MoS_x-Polymer Brush Composite

The prepared samples were subjected to electrolysis in 1 M H₂SO₄. 10 consecutive LSV scans were performed using a potential window of 0.1 V to -0.4 V *vs.* RHE. These measurements prior to the catalytic activity recordings were performed without iR drop correction. The preliminary scans ensured the effective transformation of the MoS₃ pre-catalyst to the catalytic active species, *i.e.*, MoS_x.³ The 11th LSV was thus used to evaluate the catalytic performance of the MoS_x-polymer brush composite for HER. The potential window of this LSV scan was similar, that is the potential ranged from 0.1 V to -0.4 V *vs.* RHE. However, in this instance, the iR drop was corrected using the current interrupt method. After electrolysis, the samples were washed with water, dried with nitrogen gas and stored under inert atmosphere. The auxiliary and reference electrodes were both rinsed with water and acetone and dried using nitrogen in between each sample measurement. The electrolyte was renewed for each sample.

Evaluation of the TOF of the MoS_x-Polymer Composite and References

This Work

Based on the following electrochemical oxidation reaction (corresponding to the step 7 in Fig. 1),³

it was possible to determine the electrochemical active loading of catalyst using the following relation

$$\text{Loading } [\mu\text{g cm}^{-2}] = \frac{Q [\text{C}] \times 10^6 [\mu\text{g/g}] \times 192 [\text{g/mol}_{\text{MoS}_3}]}{2 [\text{mol}_{\text{e}^-}/\text{mol}_{\text{MoS}_3}] \times 96485 [\text{C/mol}_{\text{e}^-}] \times A [\text{cm}^2]} \quad (\text{Eq. S2})$$

By assuming that all catalyst molecules included in the loading act as active sites for HER, the TOF was determined by:

$$TOF [H_2 s^{-1}] = \frac{j \left[\frac{mA}{cm^2} \right] \times 10^{-3} \left[\frac{A}{mA} \right] \times \frac{1}{96485} \left[\frac{mol_{e^-}}{A \cdot s} \right] \times \frac{1}{2} \left[\frac{mol_{H_2}}{mol_{e^-}} \right] \times 6.022 \times 10^{23} \left[\frac{molecules H_2}{mol_{H_2}} \right]}{cat. loading \left[\frac{g_{cat.}}{cm^2} \right] \times M_{cat.}^{-1} \left[\frac{mol_{cat.}}{g_{cat.}} \right] \times 6.022 \times 10^{23} \left[\frac{molecules cat.}{mol_{cat.}} \right]} \quad (Eq. S3)$$

Upon simplification we obtain:

$$TOF [H_2 s^{-1}] = \frac{3.12 \times 10^{15} \times j}{\# active sites/cm^2} \quad (Eq. S4)$$

A samples' batch consisted of 3 to 4 samples with identical preparation conditions (identical polymerization time and grafting density). The TOFs for the samples in a batch were calculated individually. TOFs described in the main-text and shown in Fig. 8 correspond to the average of the TOFs obtained for the samples from the same batch. The standard deviation was determined and is depicted as error-bar in the corresponding figure.

TOF of electrodeposited MoS_{2+x} ³

It was based on the given catalytic loading ($15 \mu g cm^{-2}$) and the calculated current density at 200 and 250 mV of overpotential. The latter current density was determined using the Tafel slope, and exchange current density given in the report. Once the values were obtained, the relation Eq. S4 was applied.

TOF of $[Mo_3S_{13}]^{2-}$ clusters⁴

The TOF values at both overpotential are given within the maintext. Detailed calculations of the TOF are given in the corresponding literature and are similar to the method employed for this work.

*TOF of CS-MoO₃/MoS₂*⁵

Determined on the basis of the reported value of active site $7.4 \cdot 10^{16}$ MoS₂/cm² and of the current densities at 200 and 250 mV overpotential. Using these parameters, Eq. S4 was applied.

*TOF of MoS₂ RGO*⁶

Based on the reported loading ($285 \mu\text{g cm}^{-2}$), the active site value was calculated using the molecular mass of MoS₂. The current density at 200 mV and 250 mV of overpotential were calculated using an extrapolation of the catalytic activity reported. Using these parameters, Eq. S4 was applied.

*TOF of DG MoS₂*⁷

Based on the reported loading ($60 \mu\text{g cm}^{-2}$), the active site value was calculated using the molecular mass of MoS₂. The current density at 200 mV overpotential is given in the corresponding report. The current density at 250 mV was calculated using an extrapolation of the catalytic activity reported. Using these parameters, Eq. S4 was applied.

*TOF of MoS_x-polypyrrole composite*⁸

It was based on the reported value of active site ($5 \cdot 10^{-8}$ molMoS₂/cm²) and on the current densities at 200 and 250 mV overpotential. Using these parameters, Eq. S4 was applied.

Evaluation of the mass activity (j_m) and specific activity (j_s)

Mass activities were obtained by a simple operation. The current density was divided by the catalytic loading.

Specific activities were determined by normalizing the current generated with the electrochemical surface area (ESCA). The ESCA was determined by the ratio of the double layer

capacitance with the specific capacity. A general specific capacity value of 0.035 mF cm^{-2} was used for acidic electrolyte.⁹

If not reported, the double layer capacitance was determined with the charge passed during oxidation of the molybdenum sulfide species. Given the charge and the oxidation potential, the capacitance was determined as the ratio of the coulombic charge over the oxidation potential.

Discussion of XPS signals

Fig. S7 shows the XPS spectra of the composites at different stages of fabrication. Survey spectra suggest successful preparation of the MoS_x -polymer composite (Fig. S7a, d, g, k, o and r). Silicon signals were due to frequently reported XPS chamber contamination. The N 1s high resolution XPS spectra (Fig. S7b, e, h and l) of the samples revealed the NO_2 signal (406 eV) at several stages of the sample preparation.^{10,11} The signal at 400 eV after the electrografting might be attributed to azo groups formed during electrografting. Alternatively partial reduction of nitro groups to amines by the X-ray in XPS measurements might give rise to this signal.¹¹

The presence of the nitro group after electrochemical reduction underlines that the conversion was not complete. Interestingly, signals corresponding to partial reduction of the nitro group into azo (399.9 eV), hydroxylamine (401.8 eV, Fig. S7b, e, h magenta curve) and nitroso (402.4 eV, Fig. S7b, e, h cyan curve) moieties were observed.¹¹⁻¹³ Small features at 403.8 eV and 405.1 eV (Fig. S7b, e, h green and dark green curve) were attributed to the diazonium moiety.^{14,15} The feature at 407 eV has been previously observed but the origin of this signal is yet unexplained.^{11,13} After polymerization, traces signals from the previous reaction steps were not observed. The sharp feature at 399 eV (Fig. S7l, blue curve “D”) is attributed to the amine moiety.¹⁶ The 401 eV was attributed to the amine group under hydrogen binding environment (Fig. S7l, turquoise curve).¹⁷ Adventitious traces of water after polymerization growth might

explain this observation. The signal at 402 eV has been previously observed and corresponds to the partial protonation of the PDMAEMA amine (Fig. S7l, light cyan curve).^{16,17} Due to significant overlap between the Mo 3p and N 1s signals, deconvolution of the N 1s features after catalyst incorporation was not possible.

High resolution C 1s XPS spectra are shown in Fig. S7c, f, i, m, p and s. Prior to polymerization, five main features can be considered. At 284.6 eV the signal corresponding to the HOPG substrate was observed (Fig. S7c, f, i, dark grey “0” curve).¹⁸⁻²⁰ The most important signal, 284.9 eV, corresponded to the C=C bond (Fig. S7c, f, i, orange “1” curve).²¹ The feature at *ca.* 286 eV was attributed to C-N species (Fig. S7c, f grey “2” curve).^{21,22} Upon initiator attachment a signal feature at 286 eV increased and was attributed to the C-Br bond.²³ The trace feature at about 289 eV was correlated with carbonate moieties and might arise from air oxidation of the samples.²² After polymerization, several features corresponding to carbon in PDMAEMA, PMETAI were observed (Fig. S7m, p and s). C sp³ signal was observed at 284.8 eV (Fig. S7m, p and s, blue “7” curve).^{16,24,25} The characteristic C-O-C=O, C-O-C=O and C-C=O signals of PDMAEMA were observed at 289.3 eV, 286.9 eV and 285.3 eV, respectively (Fig. S7m, p and s, pink, curve “8”, “9” and “10”, respectively).^{16,24} The tertiary amine and its quaternized counterpart were observed at a binding energy of 285.9 eV and 286.3 eV, respectively.^{16,24}

The broad feature at 533 eV on Fig. S7j explains the significant O 1s peaks in the XPS survey spectra of the composite at precedent fabrication's steps; the observed signal corresponds to the binding energy of oxygen in nitro groups.²⁶ This indicates that residual electrografted nitrophenyl groups remain on the surface prior to polymerization. A broad feature above at 534 eV was attributed to the C=O bond after initiator attachment (Fig. S7j, blue “a” curve).¹⁶ After

polymerization three signals corresponding to the oxygen of the PDMAEMA polymer were observed Fig. S7n, q and t, curve “b”, “c” and “d”). The O-C=O and O-C signals were found at 533.5 eV and 531 eV, respectively.²⁷ The C=O binding energy is of 532.5 eV.¹⁶ Water traces are the cause of the small feature at high binding energy on Fig. S7n and q.²⁸

Table S1. Summary of catalytic activity measured on different MoS_x-polymer composites films grafted from HOPG ZYH electrodes highlighting the irreproducibility of data due to the use of HOPG ZYH electrodes; the catalytic activity was measured in 1 M sulfuric acid.

Catalyst	Grafting density [%]	Polymer brush film thickness [nm]	Anion-exchange solvent	Oxidation time [hour]	Loading [$\mu\text{g cm}^{-2}$]	η_{10} ^a [mV]	Tafel slope [mV dec ⁻¹]	TOF ₂₀₀ ^b [s ⁻¹]
	100	44	DMF	1	0.23	N/A	179	0.18
		44			0.62	N/A	66	N/A
		44			2	497	51	0.02
		100			0.03	384	50	2.53
	10	25	DMF	3	0.06	N/A	92	0.85
		30			0.1	235	91	39.48
		34			0.79	327	66	0.19
PtCl ₂	10	34	DMF	1	N/A	35	24	N/A

^a η_{10} corresponds to the overpotential value obtained at a current density of 10 mA cm⁻². ^b TOF₂₀₀ corresponds to the turnover frequency at an overpotential value of 200 mV.

Table S2. Catalytic parameters of MoS_x/polymer composites on HOPG ZYA electrodes at 100% grafting density.

Sample	Polymerization time	Loading	$\eta_{0.5}$ ^a	Tafel slope	Exchange current density
	[min]	[$\mu\text{g cm}^{-2}$]	[mV]	[mV dec ⁻¹]	[A cm ⁻²]
1	1	0.78	321	132	$-1.4 \cdot 10^{-6}$
2		0.33	321	111	$-6.4 \cdot 10^{-7}$
3		0.10	N/A	137	$-6.5 \cdot 10^{-7}$
4	5	0.28	348	172	$-4.6 \cdot 10^{-6}$
5		0.18	351	136	$-1.3 \cdot 10^{-6}$
6		0.15	379	140	$-1.1 \cdot 10^{-6}$
7	20	0.38	296	141	$-3.6 \cdot 10^{-6}$
8		0.12	354	152	$-2.5 \cdot 10^{-6}$
9		0.17	344	148	$-2.0 \cdot 10^{-6}$

^a $\eta_{0.5}$ corresponds to the overpotential required to attain a current density of 0.5 mA cm⁻².

Table S3. Catalytic parameters of representative MoS_x/polymer composites on HOPG ZYA electrodes at different grafting densities.

Sample	Grafting density [%]	Polymerization time [min]	Loading [$\mu\text{g cm}^{-2}$]	$\eta_{0.5}$ ^a [mV]	Tafel slope [mV dec ⁻¹]	TOF @ $\eta = 200$ mV [s ⁻¹]	TOF @ $\eta = 250$ mV [s ⁻¹]	Exchange current density [A cm ⁻²]
1	100	1	0.10	N/A	137	N/A	0.50	$-6.5 \cdot 10^{-7}$
2		5	0.18	351	136	0.02	0.47	$-1.3 \cdot 10^{-6}$
3		20	0.17	344	148	0.06	0.53	$-2.0 \cdot 10^{-6}$
4	50	1	0.05	350	147	0.76	2.15	$-2.1 \cdot 10^{-6}$
5		5	0.15	251	114	0.69	3.21	$-2.8 \cdot 10^{-6}$
6		20	0.12	254	106	0.88	3.81	$-1.9 \cdot 10^{-6}$
7	10	1	0.04	345	145	0.97	3.46	$-2.1 \cdot 10^{-6}$
8		5	0.05	306	134	1.19	3.64	$-2.4 \cdot 10^{-6}$
9		20	0.35	211	104	0.98	4.77	$-5.4 \cdot 10^{-6}$

^a $\eta_{0.5}$ corresponds to the overpotential required to attain a current density of 0.5 mA cm^{-2} .

Table S4. Catalytic parameters of several molybdenum sulfide catalyst systems^a

Catalyst	Loading [$\mu\text{g cm}^{-2}$]	j_{200} [mA cm ⁻²]	j_{250} [mA cm ⁻²]	$j_{m\ 200}$ [mA μg^{-1}]	j_{m250} [mA μg^{-1}]	$j_{s\ 200}$ [mA cm ⁻²]	j_{s250} [mA cm ⁻²]	Ref.
MoS_x polymer composite	0.35	-0.34	-1.65	-0.97	-4.71	-0.01	-0.05	This work
Electrodeposited	15	-11.5	-196	-0.77	-13	N/A	N/A	3
MoS _{2+x} [Mo ₃ S ₁₃] ⁻² clusters	N/A	-0.03	-0.18	N/A	N/A	N/A	N/A	4
CS- MoO ₃ /MoS ₂	60	-1	-8.5	-0.02	-0.07	-0.22	-1.83	5
MoS ₂ RGO	280	-32.9	-100.9	-0.12	-0.36	N/A	N/A	6
DG MoS ₂	60	-4	-16.1	-0.07	-0.27	-0.03	-0.12	7
MoS _x polypyrrole composite	8	-0.1	-0.4	-0.01	-0.05	N/A	N/A	8

^a j , j_m , j_s correspond respectively to the current density, the mass activity and the specific activity. Current density is normalized over the geometric surface area while the specific activity is normalized over the ESCA. The subscripts related to these activities indicate the overpotential value at which the current is calculated. For the three variables, the overpotential evaluated are 200 and 250 mV of overpotential.

Table S5. TOF of several molybdenum sulfide systems at 200 and 250 mV of overpotential

Catalyst	TOF @ $\eta = 200$ mV [s ⁻¹]	TOF @ $\eta = 250$ mV [s ⁻¹]	Ref.
MoS_x polymer composite	1.31	4.92	This work
Electrodeposited MoS _{2+x}	0.76	13	3
[Mo ₃ S ₁₃] ⁻² clusters	0.67	7.91	4
CS-MoO ₃ /MoS ₂	0.04	0.36	5
MoS ₂ RGO	0.10	0.30	6
DG MoS ₂	0.06	0.22	7
MoS _x polypyrrole composite	0.05	0.08	8
MoS _x /N-doped CNT forest	3.5	-	29
[Mo ₃ S ₁₃] ⁻² clusters	3.3 ^a	22 ^a	4
UHV MoS ₂	8 ^{a,b}	-	4

^a TOF determined by active sites count. ^b TOF at an overpotential of 150 mV.

Figure S1. (a) Optical photograph of low-grade HOPG ZYH plate (ca. 1x1x0.2 cm). (b - c) High resolution SEM (HRSEM) images of the HOPG plate. (b) Top-view. (c) Cross-section view.

Figure S2. (a - n) XPS spectra of the MoS_x-polymer brush composites on HOPG ZYH at different stages of the assembly fabrication on HOPG. Each row of spectra corresponds to the composite at a different step of the process shown in Fig. 1. The corresponding chemical structure of the assembly is shown for reference. The numbers and letters displayed on the structure refer to specific atoms on the corresponding chemical structure. (a, d, g, k) XPS survey spectra at different stages of the assembly preparation. (b, e, h, l) High resolution N 1s XPS spectra. (c, f, i, m) High-resolution C 1s XPS spectra. (j, n) High-resolution O 1s XPS spectra.

Figure S3. Water-contact angle measurements at different stages during the fabrication of the MoS_x composite films on HOPG ZYH (water droplets of 5 μ L). (a) Prior to and (b) after step 3. (c) Prior to and (d) after step 5. The step number refers to the steps indicated in Fig. 1 of the article.

Figure S4. AFM images of non-functionalized HOPG ZYH plates (a) before and (b) after mechanical polishing. (a) Average roughness (Ra) = 54.7 nm, roughness mean square (Rms) = 68.3 nm, (b) Ra = 30.4 nm, Rms = 41.3 nm. Mechanical polishing did not sufficiently improve topography of the surface.

Figure S5. (a) Optical photograph of the HOPG ZYA. Plate dimension: 10x10x0.5 mm. (b) AFM image of the HOPG ZYA. (c) Optical photograph depicting the simple scotch-tape technique to cleave and renew the HOPG ZYA surface.

Figure S6. (a) AFM image representative of bare HOPG ZYA surface after cleaving. The roughness of the material on the micron scale and the possible defects underline the difficulty of accurate AFM measurements on HOPG grown polymers. Average roughness = 5.4 nm, roughness mean square = 6.9 nm. (b) Evolution of polymer brush film thickness as a function of polymerization time on both Si wafers (black squares) and HOPG (red circles). The height profile was determined by AFM measurements. Around 20 minutes of polymerization, the polymer growth slows down on Si wafer.

Figure S7. (a - t) XPS spectra of MoS_x-polymer brush composite films on HOPG ZYA at different stages of fabrication. Each row of spectra corresponds to the sample at a different step of the process shown in Fig. 1. The corresponding chemical structure of the assembly is shown

for reference. The numbers and letters displayed on the spectra refer to specific atoms on the corresponding chemical structure. The deconvolution follows a simple color code: the experimental data correspond to the black dots, the fitting envelope is the red line. For the same element, each color represents a unique moiety. Peaks of similar colors indicate, thus, the same signal at different stages of the polymer fabrication. (a, d, g, k, o, r) XPS survey spectra at different stages of the assembly preparation. (b, e, h, l) High resolution N 1s XPS spectra. (c, f, i, m, p, s) High-resolution C 1s XPS spectra. (j, n, q, t) High-resolution O 1s XPS spectra.

Figure S8. Insulated HOPG ZYA electrode. The exposed surface shown in (a) is in direct contact with the electrolyte. (b) Silver paste was used to connect a Cu wire to the back of the HOPG electrode. The connection was also insulated prior to treatment of the electrode. Insulation of the electrode is made after successful SI-ATRP (Fig. 1, step 5). The remaining steps in the catalytic process were done on isolated electrodes. The process ensures that only the exposed surface is affected by the subsequent chemical modifications operated on the electrode assembly. The exposed surface area was determined by means of optical photography and

subsequent image analysis. Any shape could be selected and the software provided a number of pixels of the selected area, which could be related to a real value in cm^2 .

Figure S9. Water-contact angle measurements at different stages of the composite fabrication on HOPG ZYA (water droplets of 5 μL). (a) After step 2. (b) Image after step 3. (c) After step 5 (d) After step 6. (e) After pre-catalyst formation (step 7). (f) After HER catalysis (step 8). The step number refers to the steps indicated in Fig. 1.

Figure S10. LSV scans of MoS_x-polymer brush assemblies, prepared using different polymerization times and different grafting densities, in 1 M H₂SO₄. (a) 100% Grafting density; (b) 50% Grafting density; (c) 10% Grafting density. The assemblies underwent 10 consecutive LSV scans from 0.1 V to -0.4 V vs. RHE in 1 M H₂SO₄ to convert the precatalyst MoS₃ to the catalytic active species MoS_x. The scans displayed correspond to the 11th LSV measurement performed on the assemblies. Conditions: scan rate 5 mV s⁻¹, IR drop corrected. The catalytic activities correspond to the samples described in Table S3.

Figure S11. Comparison of TOF between a representative MoS_x polymer composite at 10% grafting density and a bare substrate sample dipped in catalyst solution for 1 hour. Details of the TOF calculations are given in the supporting information (Eq. S4).

References

- (1) Schüwer, N.; Klok, H. A. A Potassium-Selective Quartz Crystal Microbalance Sensor Based on Crown-Ether Functionalized Polymer Brushes *Adv. Mater.*, **2010**, 22, 3251–3255.
- (2) Tugulu, S.; Harms, M.; Fricke, M.; Volkmer, D.; Klok, H.-A. Polymer Brushes as Ionotropic Matrices for the Directed Fabrication of Microstructured Calcite Thin Films *Angew. Chem. Int. Ed.*, **2006**, 45, 7458–7461.
- (3) Vrubel, H.; Hu, X. Growth and Activation of an Amorphous Molybdenum Sulfide Hydrogen Evolving Catalyst *ACS Catal.*, **2013**, 3, 2002–2011.
- (4) Kibsgaard, J.; Jaramillo, T. F.; Besenbacher, F.; Building an Appropriate Active-Site Motif into a Hydrogen-Evolution Catalyst with Zhiomolybdate $[\text{Mo}_3\text{S}_{13}]^{2-}$ Clusters *Nat. Chem.*, **2014**, 6, 248–253.
- (5) Chen, Z.; Cummins, D.; Reinecke, B. N.; Clark, E.; Sunkara, M. K.; Jaramillo, T. F. Core–Shell MoO_3 – MoS_2 Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials *Nano Lett.*, **2011**, 11, 4168–4175.
- (6) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong G.; Dai, H. MoS_2 Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction *J. Am. Chem. Soc.*, **2011**, 133, 7296–7299.
- (7) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. Engineering the surface structure of MoS_2 to preferentially expose active edge sites for electrocatalysis. *Nat. Mater.*, **2012**, 11, 963–969.
- (8) Lattach, Y.; Deronzier, A.; Moutet, J. C. Electrocatalytic Hydrogen Evolution from Molybdenum Sulfide-Polymer Composite Films on Carbon Electrode *ACS Appl. Mater. Interfaces*, **2015**, 7, 15866–15875.

- (9) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T.F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices *J. Am. Chem. Soc.*, **2015**, 137, 4347-4357.
- (10) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J. M. Covalent Modification of Carbon Surfaces by Aryl Radicals Generated from the Electrochemical Reduction of Diazonium Salts *J. Am. Chem. Soc.*, 1997, 119, 201–207.
- (11) Yu, S. S.; Tan, E. S.; Jane, R. T.; Downard, A. J. An Electrochemical and XPS Study of Reduction of Nitrophenyl Films Covalently Grafted to Planar Carbon Surfaces *Langmuir*, **2007**, 23, 11074–11082.
- (12) Gui, A. L.; Liu, G.; Chockalingam, M.; Le Saux, G.; Luais, E.; Harper, J. B.; Gooding, J. J. A Comparative Study of Electrochemical Reduction of 4-Nitrophenyl Covalently Grafted on Gold and Carbon *Electroanalysis*, **2010**, 22, 1824–1830.
- (13) Menanteau, T.; Levillain, E.; Downard, A. J.; Breton, T. Evidence of Monolayer Formation via Diazonium Grafting with a Radical Scavenger: Electrochemical, AFM and XPS Monitoring. *Phys. Chem. Chem. Phys.*, **2015**, 17, 13137–13142.
- (14) Finn, P.; Jolly, W. L. Nitrogen 1s Binding Energies of Some Azide, Dinitrogen, and Nitride Complexes of Transition Metals *Inorg. Chem.*, **1972**, 11, 1434–1435.
- (15) Ullien, D.; Thüne, P. C.; Jager, W. F.; Sudhölter, E. J.; de Smet, L. C. Controlled Amino-Functionalization by Electrochemical Reduction of Bromo and Nitro Azobenzene Layers Bound to Si(111) Surfaces *Phys. Chem. Chem. Phys.*, **2014**, 16, 19258–19265.
- (16) Zengin, A.; Karakose, G.; Caykara, T. Poly(2-(dimethylamino)ethyl methacrylate) Brushes Fabricated by Surface-Mediated RAFT Polymerization and Their Response to pH *Eur. Polym. J.*, **2013**, 49, 3350–3358.

- (17) Yang, Y.; Liu, L.; Zhang, J.; Li, C.; Zhao, H. PMMA Colloid Particles Stabilized by Layered Silicate with PMMA-b-PDMAEMA Block Copolymer Brushes. *Langmuir*, **2007**, 23, 2867–2873.
- (18) Fujimoto, A.; Yamada, Y.; Koinuma, M.; Sato, S. Origins of sp^3C peaks in C_{1s} X-ray Photoelectron Spectra of Carbon Materials *Anal. Chem.*, **2016**, 88, 6110–6114.
- (19) Yang, D.-Q.; Sacher, E. Carbon 1s X-ray Photoemission Line Shape Analysis of Highly Oriented Pyrolytic Graphite: The Influence of Structural Damage on Peak Asymmetry *Langmuir*, **2006**, 22, 860–862.
- (20) Schmieg, S. J.; Belton, D. N. Highly Oriented Pyrolytic Graphite by XPS *Surf. Sci. Spectra*, **1992**, 1, 333–336.
- (21) Chuang, C. H.; Ray, S. C.; Mazumder, D.; Sharma, S.; Ganguly, A.; Papakonstantinou, P.; Chiou, J.-W.; Tsai, H.-M.; Shiu, H.-W.; Chen, C.-H.; Lin, H.-J.; Guo, J.; Pong, W. F. Chemical Modification of Graphene Oxide by Nitrogenation: An X-ray Absorption and Emission Spectroscopy Study *Sci. Rep.*, **2017**, 7, 42235.
- (22) Moulder, J. F.; Stickle, W. F.; Sobol P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics, Inc., Minnesota, 1995.
- (23) Matrab, T.; Chancolon, J.; L’hermite, M. M.; Rouzaud, J. N.; Deniau, G.; Boudou, J. P.; Chehimi, M. M.; Delamar, M. Atom Transfer Radical Polymerization (ATRP) Initiated by Aryl Diazonium Salts: A New Route for Surface Modification of Multiwalled Carbon Nanotubes by Tethered Polymer Chains. *Colloids Surf. Physicochem. Eng. Asp.*, **2006**, 287, 217–221.
- (24) T. Bilgiç Tune, Polymer Brushes - Engineered Model Interfaces and Functional Surface Coatings for DNA Biosensing and Electrocatalysis, Ph. D. Thesis, EPFL, Lausanne, 2015.

- (25) Karamdoust, S.; Yu, B.; Bonduelle, C. V.; Liu, Y.; Davidson, G.; Stojcevic, G.; Yang, J.; Lau, W. M.; Gillies, E. R. Preparation of Antibacterial Surfaces by Hyperthermal Hydrogen Induced Cross-Linking of Polymer Thin Films *J. Mater. Chem.*, **2012**, 22, 4881–4889.
- (26) Folkesson, B.; Sundberg, P. A Reinvestigation of the Binding Energy Versus Atomic Charge Relation for Oxygen From X-Ray Photoelectron Spectroscopy *Spectrosc. Lett.*, **1987**, 20, 193–200.
- (27) Endo, K.; Maeda, S.; Aida, M. Simulation of C1s Spectra of C- and O-Containing Polymers in XPS by Ab Initio MO Calculations Using Model Oligomers *Polym. J.*, **1997**, 29, 171–181.
- (28) Schulze, P. D.; Shaffer, S. L.; Hance, R. L.; Utley, D. L. Adsorption of water on rhenium studied by XPS *J. Vac. Sci. Technol. Vac. Surf. Films*, **1983**, 1, 97–99.
- (29) Li, D. J.; Maiti, U. N.; Lim, J.; Choi, D. S.; Lee, W. J.; Oh, Y.; Lee, G. Y.; Kim, S. O. Molybdenum Sulfide/N-Doped CNT Forest Hybrid Catalysts for High-Performance Hydrogen Evolution Reaction *Nano Lett.*, **2014**, 14, 1228–1233.