

Electronic Supporting Information

Floating Conductive Catalytic Nano-rafts at Soft Interfaces for Hydrogen Evolution

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Experimental

Chemicals. All chemicals were used as received with the exception of decamethylferrocene (DMFC, 99%, Alfa Aesar) which was purified by vacuum sublimation at 140 °C before use.¹ All aqueous solutions were prepared with ultrapure water (Millipore Milli-Q, specific resistivity 18.2 MΩ·cm). Ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, ≥99%), aniline (≥99%), and molybdenum carbide (Mo₂C, ~325 mesh, 99.5%), were purchased from Sigma-Aldrich. Multiwalled carbon nanotubes (MWNT, ≥97%) were provided by Shenzhen Nanotech Port Co. Ltd., China. No pre-treatment of the MWNTs prior to use was performed. Tetraethylammonium chloride (TEACl, >98.0%), lithium chloride (≥99%) and 1,2-dichloroethane (1,2-DCE, >99.8%) were ordered from Fluka. Hydrochloric acid (HCl, 37%) was bought from Merck. Lithium tetrakis(pentafluorophenyl)borate diethyl etherate (LiTB-DEE, Boulder Scientific) and bis(triphenylphosphoranylidene) ammonium chloride (BACl, 97%, Aldrich) were used to prepare bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate (BATB) by metathesis of equimolar solutions of BACl with LiTB-DEE in a methanol-water (2:1 v/v) mixture. The resulting precipitates were filtered, washed and recrystallised from acetone.²

Synthesis of nanoporous Mo₂C nanowires. Mo₂C nanowires consisting of an aggregation of individual Mo₂C nanocrystals were prepared *via* facile pyrolysis of a pre-prepared precursor, organic-inorganic Mo₃O₁₀(C₆H₈N)₂·2H₂O hybrid nanowires, according to the novel procedure developed by Tang and co-workers³ with some modifications. The intercalating amine molecules have a dual synthetic role acting as both the reducing agent and the source of carbon.³

Briefly, 2.48 g of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in 40 mL of ultrapure water. 3.20 g of aniline was subsequently added to this solution followed by the drop-wise addition of a 1 M HCl aqueous solution, with magnetic stirring at room temperature, until a white precipitate was obtained at pH 4~5. The reaction was allowed to proceed with stirring at 50 °C for 2~8 hours after which the product was filtered, washed with ethanol and dried at 50 °C for a further 10 hours. Air was expelled by argon at room temperature for 4 hours and the organic-inorganic Mo₃O₁₀(C₆H₈N)₂·2H₂O hybrid nanowires were obtained. These precursor

nanowires were heated to 725 °C for 5 hours in an argon flow yielding nanoporous Mo₂C nanowires and, finally, stored in a vacuum desiccator until use.

Synthesis of carbon nanotube supported Mo₂C nanoparticles (CNT/Mo₂C). The synthetic strategy developed to create nanoporous Mo₂C nanowires was extended in a follow-up paper by Tang and co-workers⁴ to efficiently load highly dispersed Mo₂C nanoparticles on a conductive CNT support. The precursor organic-inorganic Mo₃O₁₀(C₆H₈N)₂·2H₂O hybrid nanowires were once more prepared, as described above, and subsequently loaded on the CNT support (MWNT, ≥97%, BET surface area of 160 – 200 m² g⁻¹ and length 10- 50 μm) *via* an impregnation process in a water-ethanol solution.⁴ As for nanoporous Mo₂C nanowires, the amine in the hybrid acts as both a reducing agent and the source of carbon for the carbide.⁴

Briefly, 0.266 g of the Mo₃O₁₀(C₆H₈N)₂·2H₂O precursor was dispersed and dissolved in 80 mL of a water-ethanol (1:1 v/v) mixture to which 1.9 g of CNT were added. After stirring for 10 hours at room temperature, this mixture was dried at 50 °C. Finally, heating the obtained dry product to 725 °C for 5 hours in an argon flow yielded the CNT/Mo₂C catalysts which were then stored in a vacuum desiccator until used. CNT/Mo₂C has a theoretical stoichiometric total catalyst loading of 6.0 wt. %.

Particle characterization. The morphologies and sizes of the particles investigated were characterized by scanning electron microscopy (SEM) images recorded by a JEOL 6400 microscope operated at beam voltages of 10 keV. Transmission electron microscopy (TEM) studies were carried out using a JEOL JEM-2011 electron microscope at an acceleration voltage of 200 keV. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 advanced X-ray diffractometer using Ni-filtered Cu K α radiation (λ = 1.54056 Å, 40 mV working voltage and 40 mA working current).

Shake flask experiments. All shake flask experiments, whether characterized by gas chromatography or UV/vis spectroscopy, were prepared using aqueous and organic solutions thoroughly de-gassed with nitrogen, under anaerobic conditions in a glove box purged with nitrogen, in the dark and at an ambient temperature of 23 ± 2 °C.

Anaerobic conditions were necessary to avoid competing side-reactions of DMFc with oxygen, such as H₂O₂ generation, as previously demonstrated.⁵

Two-phase reactions were performed in a septum sealed glass vial. 2 mL of an acidic aqueous phase containing LiTB-DEE, with or without a catalyst, was contacted with an equal volume of 1,2-DCE containing the lipophilic electron donor DMFc. Magnetic stirring (900 rpm) was used to emulsify the two phases for the duration of each experiment. The liquid-liquid interface was polarized chemically by distribution of a common ion (highly hydrophobic TB⁻, initially present in the aqueous phase) across the interface. The expected reaction products from the shake flasks, the precise compositions of which are outlined in Scheme 1, were H₂ and DMFc⁺, see eqn (1), main text. Post-shake flask reaction, 1 mL samples of the headspace gas were obtained using a lock-in syringe with a push-pull valve (SGE Analytical Sciences) in a glovebox and subsequently analysed by gas chromatography (GC) using a Perkin-Elmer GC (Clarus 400, equipped with 5 Å molecular sieves and an 80/100 mesh) with a thermal conductivity detector (TCD) and argon as a carrier gas.

Kinetics measurements. The composition of the shake flasks used for kinetic studies were identical to those analyzed by GC, see Scheme 1, main text. The kinetics of the biphasic HER were analysed by monitoring the variation of the intensity of the UV/vis absorbance peak of the reaction product DMFc⁺, and hence the *in situ* variation of [DMFc⁺], with time. The UV/vis spectra were measured in a glovebox on an Ocean Optics CHEM2000 spectrophotometer using a quartz cuvette with a path length of 1 cm, volume of 4 mL, and equipped with a Teflon cap to prevent evaporation of the organic phase during analysis (1 mL of each phase was added to the quartz cuvette). UV/vis scans were taken at regular intervals, typically every 30 seconds, for a period of time and during scan intervals the solution in the cuvette was constantly agitated using a magnetic stirrer (900 rpm). Quantitative determination of [DMFc⁺] in 1,2-DCE by UV/vis spectroscopy was possible as the molar extinction coefficient (ϵ) of DMFc⁺ in 1,2-DCE was determined previously as 0.632 mM⁻¹·cm⁻¹.⁶

Electrochemical measurements at the polarized liquid|liquid interface. Ion-transfer voltammetry experiments at the water-1,2-DCE interface were performed in a four-electrode configuration using a PGSTAT 30 potentiostat (Metrohm, CH). Two platinum counter electrodes were positioned in the aqueous and organic phases,

respectively, to supply the current flow. An external potential was applied by means of silver/silver chloride (Ag/AgCl) reference electrodes which were connected to the aqueous and organic phases, respectively, *via* a Luggin capillary as illustrated previously.⁶ The Galvani potential difference across the interface ($\Delta_o^w\phi$) was estimated by taking the formal ion transfer potential of tetraethylammonium cation (TEA^+) as 0.019 V.⁷ No *iR* compensation was applied to the cell. The area of the liquid-liquid interface was 1.53 cm². The generic composition of the four-electrode cells studied is given in Scheme 2, main text. All voltammetry experiments were completed using aqueous and organic phases thoroughly de-gassed with nitrogen, under anaerobic conditions in a glovebox filled with nitrogen, in the dark and at an ambient temperature of 23 ± 2 °C.

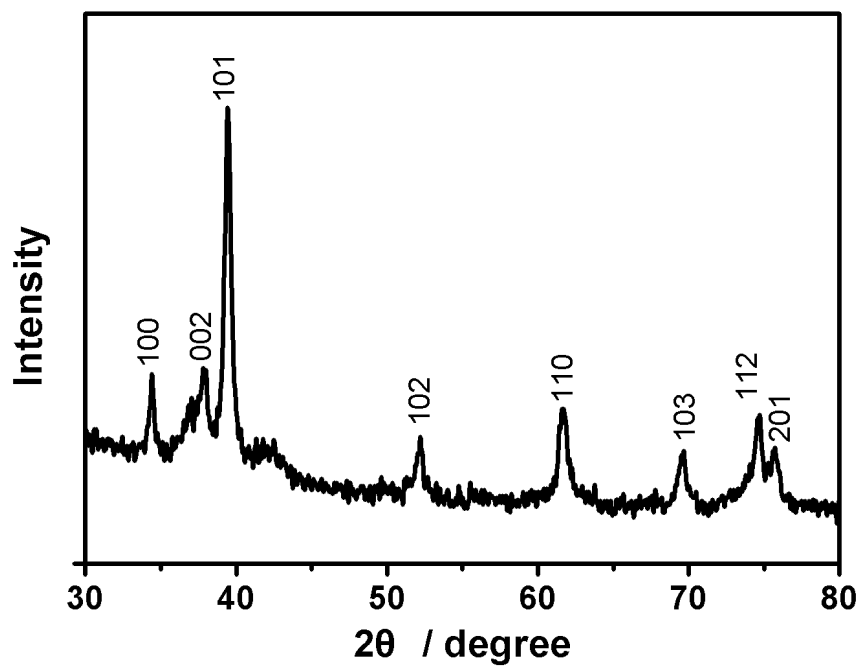


Fig. S1 X-ray diffraction (XRD) pattern of nanowire Mo_2C ; consistent with the presence of the pure hexagonal $\beta\text{-Mo}_2\text{C}$ phase (JCPDS: 35-0787).

Image of the 4-electrode electrochemical cell



Fig. S2 The 4-electrode cell used in this study. Note the positions of the aqueous and organic Pt counter electrodes to the left of centre and the aqueous and organic luggin capillaries to the right of centre. The design of this cell influences the movement of CNTs at the interface when an interfacial potential difference is applied, as shown in the movie in the supporting information and Fig. 8, main text.

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