Molybdenum sulphides — efficient and viable materials for electro — and photoelectrocatalytic hydrogen evolution

Anders B. Laursen* Søren Kegnæs[†] Søren Dahl *
Ib Chorkendorff *

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1 Supplementary information

2 Experimental:

2.1 Equipment:

2.1.1 SEM-EDS

SEM-EDS analysis was done on a FE-SEM (FEI Quanta 200 F SEM) operated at 30 kV, using an Oxford Instruments X-max (51xmx0005) EDS running the INCA Suite v 4.15 software. Spectra were fitted using program standards and converted to atomic ratios. For all samples the ratio of Mo to S were close to the stoichiometric, the ratio of Mo to C was used to calculate the mass loading of MoS_2 on the MWCNT. The value is averaged over six measurements of different area of the pristine, annealed 2 h and annealed 8 h sample. The averaged loading is 46 wt%.

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*Center for Individual Nanoparticle Functionality, CINF, Department of Physics, Technical University of Denmark, DTU, Kgs. Lyngby. E-mail: `ibchork@fysik.dtu.dk`

[†] Centre for Catalysis and Sustainable Chemistry, CSC, Department of Chemistry, Technical University of Denmark, DTU, Kgs. Lyngby

2.1.2 TEM

The images were obtained by means of a JEOL 3000F microscope operated at an accelerating voltage of 300 kV. For sample preparation, ground powders were dispersed in ethanol and deposited on a 300 mesh copper grid coated with a holey carbon film.

2.2 Synthesis of MWMoS$_2$@MWCNT:

For the synthesis of the multi-walled MoS$_2$ on multi-walled carbon nanotubes (MW-CNT), MW-CNTS from Hyperion Catalysis International, Graphite FIBRIL type CC, consisting of > 90% MWCNT material according to low magnification TEM, were used. All other reagents were of reagent grade and used without further purifications: Thioacetamide, $Na_2MoO_4 \cdot 2\,H_2O$, water, 1M HCl(aq), and ethanol.

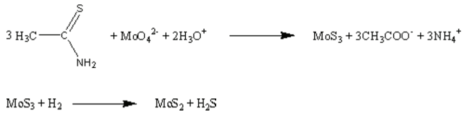

Figure 1: Reaction scheme for the acid catalysed MoS$_2$ deposition.

In the present work, multi-walled molybdenum(IV) sulfide (MoS$_2$) nanotubes coated on multi-walled carbon nanotubes (MW-CNT) were synthesized by precipitation of MoS$_3$ using thioacetamide in the present of carbon nanotubes using aqueous precursor solutions of sodium molybdate. Followed by high temperature reduction in a flow of hydrogen (see reaction in figure 1). In a typical synthesis of a precursor solution was prepared in a 50 ml Schlenk test tube by dissolving $Na_2MoO_4 \cdot 2\,H_2O$ (1 mmol, 0.2419 g) in distilled H$_2$O (10 ml) under stirring. To the solution MW-CNT (4 mmol of carbon, 0.048 g) was added and the mixture was sonicated at room temperature for 1 h. Thioacetamide (10 mmol, 0.75 g) together with a solution of HCl (10 ml, 1 M) was added to the suspension. The test tube was sealed and the suspension was sonicated for an additional 2 h. After this time, the mixture was left to stand over-night. The produced MoS$_3$ on MW-CNT was separated from the solution by filtration and washed with H$_2$O and ethanol. After drying, the MoS$_3$ was reduced to MoS$_2$. This was done by passing a gentle flow of AGA (90/10) Forming Gas (90% N$_2$, 10% H$_2$) over the sample at 450°C for 1 h using a heating ramp of 7°C /min. To make the coating layers of MoS_2 on the MW-CNT more homogeneous, the reduced samples were annealed by heating with 5°C /min to 800°C in a flow of argon for 2 h or 8 h.

2.3 Electrode preparation

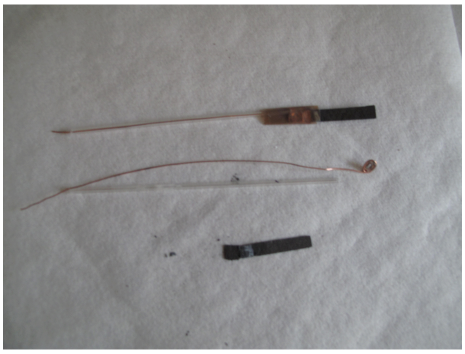

Figure 2: From the top down: A finished electrode, a separate glass tube, a separate copper wire with the end formed into a coil, a carbon paper electrode before mounting the connection.

The electrodes are made by depositing a catalyst ink onto a carbon paper (ETEK) electrode. Prior to deposition the carbon paper where impregnated with a ca. 0.5 cm brim of dispersed Teflon. A 10 by 3 cm piece of carbon paper was cut and heated to 90°C on a hotplate. Then drops of Teflon dispersion (Dyneon TF5032R PTFE) was put onto the carbon paper approximately 1 cm from the end that will become the circuit contact point; making an unbroken line parallel to the wide side of the carbon paper. The drops was allowed to dry in between addition and the drops was added until an unbroken white line of Teflon was visible. The purpose of this is to ensure that electrolyte that was sucked into the electrode do not reach the copper contact point allowing for copper corrosion to be a parasitic reaction. The strip of Toray paper was then cut into individual electrodes of 0.5 cm width and 3 cm length (see figure 2).

Contact to the carbon electrode was made by attaching the electrode contact point to a copper wire with one end formed into a coil (see figure 2); then the contact point and the coil are painted with Ag-paste (HighPurity Ag paint, SPI Supplies). It was allowed to dry and the remaining Cu tape was wrapped twice around the electrode and wire junction. A small glass tube was slid onto the copper wire and finally the whole connection area was wrapped in adhesive tefon tape to make a water-proof seal from the glass tube to the Teflon brim on the electrode (see figure 2).

The catalyst ink was made by mixing 1.5 mg catalyst in 0.4 ml isopropanol (Sigma-Aldrich, Laboratory reagent $\geq$ 99.5%), 0.6 ml milli-Q®water (18.2 MΩ· cm @ 25°C), and 0.004 ml 5 % w/w Perflourosulfonic acid (PTFE) copolymer (Alfa Aesar) solution. This suspension was sonicated for ca. 200 min in a Branson 8510 ultra-sonicator, immediately after 50 μL of this suspension was deposited on each electrode, then they were dried at 80°C on a hotplate. Electrodes for the oxidation-experiment was prepared by the same technique a above, only the suspension was 0.1 wt% in N,N-dimethylformamide (DMF, Merck) and 5 μL of this suspension was deposited on each electrode. The difference is due to the easier observation of the oxidation features at lower loadings of catalyst.

2.4 Electrochemical testing

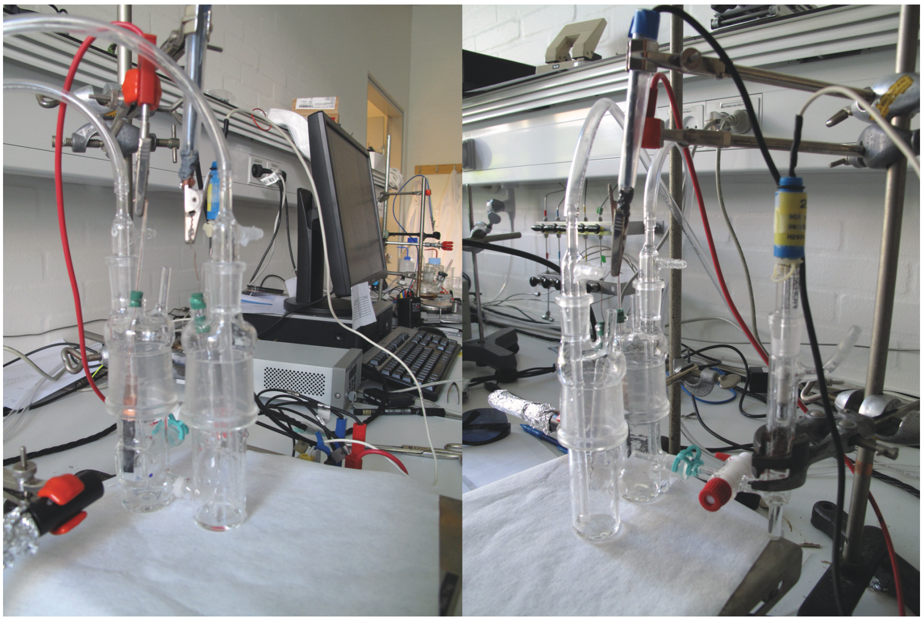

Figure 3: The 3-compartment cell setup.

Electrochemical tests was performed in a 2-compartment cell with a luggin capillary reference electrode compartment (see figure 3) using a BioLogic VSP potentiostat running EC-Lab v 10.2. All compartments are separated from each other by glass frits. Any Pt-ions coming from the Pt mesh counter electrode is kept from diffusion to the working electrode by the aforementioned frit. The luggin was filled with a saturated sodium chloride (Merck, analysis pure) solution as an ion-bridge. The reference electrode is a saturated calomel electrode (SCE) and all potential were recalculated to refer to the reversible hydrogen electrode (RHE). A 0.1 M $HClO_4$ (Merck, SupraPur®70%) in milli-Q®water solution was used as electrolyte, the pH was measured to be 1.24. Before catalytic testing the cell is purged with Ar for at least 30 min, then with H_2 for 5 min. During measurements a steady hydrogen flow was bubbled through both the working and counter electrode compartments.

The recorded potentials are re-calculated to refer to RHE by the following $E_{actual} = E_{measured} + E_{SCE} + 0.059V \cdot pH - R_{ohmic} \cdot I_{measured}$ so $E_{actual} = E_{measured} + 0.244V + 0.059V \cdot 1.24 - R_{ohmic} \cdot I_{measured}$. This also takes into account the ohmic resistance of the electrode (R_{ohmic}); this resistance is estimated from impedance spectroscopy measurements (at -0.6 V vs SCE (pH 1.24) 2 kHz to 5 Hz with a sinusoidal 10 mV amplitude). From this measurement the ohmic resistance was seen to be less than 11 Ω, which is low. However, the exact resistance could not be resolved. Hence, the resistance correction is omitted. To lessen the effect of the ohmic resistance on the Tafel slope, the slope is only evaluated at low currents (and thus low overpotentials) as the resistance is directly proportional to the current drawn. The error is estimated to be within 1 percent.