Catalytic Behavior of Molybdenum Sulfide for the Hydrogen Evolution Reaction as a Function of Crystallinity and Particle Size Using Carbon Multiwall Nanotubes as Substrates

Abstract: Molybdenum sulfide is of interest as a noble metal-free catalyst for the hydrogen evolution reaction (HER). In crystallized form, it shows a typical stacking of planar S–Mo–S layers whereas the catalytically active centers are situated on the edges of these entities characterized by non-saturated bonds of the molybdenum atoms. In this study, 2H-MoS\textsubscript{2} is investigated as HER catalyst as a function of particle size using powder electrodes of different grain sizes and morphology. HER was also determined as a function of growth defects (bending of layers) and as a function of active sites employing MoS\textsubscript{2} nanoparticles (NP). To study the influence of the substrate on the perfection of the transition metal disulfide, MoS\textsubscript{2} nanosheets were deposited on multi-walled carbon nanotubes (MWCNTs) of different diameters. Highest activity was found for MoS\textsubscript{2} nanosheets deposited on MWCNTs with a diameter smaller than 8 nm. At diameters larger than 10 nm, a wrapping of the nanotubes by partially bended stacks of S–Mo–S layers occurs, while at diameters smaller than 10 nm, individual MoS\textsubscript{2} nanosheets of 3–5 S–Mo–S stacks of 3–4 nm in height and 10–20 nm in lateral extension surround the carbon nanotubes in form of hexagonal cylinders. The ratio of catalytically active non-van-der-Waals and hexagonal basal planes was determined electrochemically by electro-oxidation and correlated with HER activity.

Keywords: electro-oxidation; hydrogen evolution catalyst; molybdenum sulfide; multi wall carbon nanotubes; Raman spectra; reactive center.

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1 Introduction

Molybdenum disulfide can be used for different applications because of its highly anisotropic layer structure. It is used as a catalyst for the hydrodesulfurization process of crude oil [1], as transistor material using its semiconducting phase [2], but also as a solid lubricant [3]. It occurs in three different layer-type crystal structures, namely 2H-MoS$_2$, 3R-MoS$_2$ and 1T-MoS$_2$. Among them, 2H and 3R are the two main phases whereas the 2H phase is the dominant and most stable phase in nature. As shown in Figure 1, 2H-MoS$_2$ contains two S–Mo–S layer sequences per unit cell with a trigonal prismatic coordination of the molybdenum atoms by sulfur, while the unit cell of 3R-MoS$_2$ comprises three layer sequences [4]. The 1T-MoS$_2$ phase is characterized by an octahedral coordination of molybdenum by sulfur leading to a metallic property [5, 6]. Bulk 2H-MoS$_2$ is a compound semiconductor having an indirect band gap of 1.29 eV and a direct one of 1.8 eV, which is depending on the number of van der Waals layers in MoS$_2$ [7].

Among the non-precious metal catalysts that have been studied, molybdenum disulfide has stood out for its high catalytic activity of the HER and its high stability, especially under acidic conditions. Interestingly in former studies, MoS$_2$ was thought to only have low catalytic ability for HER [8]. However, according to theoretical calculations, the material should be relatively active for HER since it exhibits modest binding energies with atomic hydrogen and relatively high exchange current density as shown by Jaramillo et al. [9]. In the same paper, the authors describe that the exchange current density of the material is proportional to the edge length of a MoS$_2$ electrode. Therefore, the catalytically active sites of MoS$_2$ are found to be located on the edge site of the hexagonal layers.

![Fig. 1: Crystal structure of hexagonal MoS$_2$ crystallizing in the space group P6$_3$/mmc.](image)
Since then, researchers have put a lot of effort to increase the catalytic ability of MoS$_2$ for HER. One strategy to increase the catalytic activity is simply generating more active sites at the catalyst surface. To achieve this goal, Kibsgaard et al. [10] in 2012 engineered the surface structure of mesoporous MoS$_2$ thin films with a high degree of surface curvature to preferentially expose more edge sites than basal planes, leading to improved catalytic properties. Using high temperature hydrogen annealing, Kiriya et al. [11] discovered that the catalytic ability of different molybdenum sulfides, for instance, bulk, powder and nanoflakes of MoS$_2$, can be increased because of a higher surface area and more active sites due to thermal texturization. In 2016, Li et al. [12] increased the active site number by introducing and strain ing sulfur vacancies to activate the basal plane of MoS$_2$. DFT calculations suggested higher hydrogen adsorption and optimal Gibbs free energy of hydrogen adsorption ($\Delta G_{H^*}$) in the strained, S-vacancy activated MoS$_2$ catalyst, leading to a lower overpotential (170 mV at 10 mA/cm$^2$).

Other than modifying the structure of MoS$_2$ itself, molybdenum sulfides with different structures were also studied. For example, cluster-type molybdenum sulfides with a large number of edge atoms per unit area are expected to be a hydrogen evolution catalyst (HEC) of high performance. The incomplete cubane-typed [Mo$_3$S$_4$]$_2^{-}$ cluster was used as HEC in 2008 by Jaramillo et al. The [Mo$_3$S$_4$]$_2^{-}$ cluster obtained a similar overpotential compared with MoS$_2$ NPs of about 300 mV at $-10$ mA/cm$^2$ [13]. Then in 2014, the thiomolybdate cluster [Mo$_3$S$_{13}$]$_2^{-}$ was described as an efficient HER catalyst with a high number of sulfur atoms located at the edges of the cluster units exhibiting an overpotential of 180 mV at $-10$ mA/cm$^2$ and high stability (10–20 mV increase of overpotential at 10 mA/cm$^2$ after 1000 cycles of cyclic voltammetry in the potential range from 0.2 to $-0.3$ V with a 100 mV/s scan rate) [14].

Besides, amorphous MoS$_x$ was also discovered for its excellent catalytic activity. The amorphous MoS$_x$ has a different structure other than layer structured MoS$_2$ which gave the material an unique catalytic behavior. Amorphous MoS$_x$ can be synthesized through electrodeposition [15], wet chemical reaction [16], and sulfurization without thermal treatment [17, 18]. The origin of the high catalytic performance of amorphous MoS$_x$ was not clear for a long time. The high surface area [19] and the existence of bridging and terminal [S$_2$]$^{2-}$ were thought to be possible reasons [16]. In 2016, Yeo et al. [20] found that the composition of S species in amorphous MoS$_x$ was changed during HER. In the meantime, Artero et al. [21] observed loss of terminal [S$_2$]$^{2-}$ during HER condition, also suggesting that MoS$_x$ went through structural changes in HER catalysis process. In the previous study of our group [22], the structural transformation of amorphous MoS$_x$ from a [Mo$_3$S$_{13}$]$_2^{-}$ cluster-like material to a MoS$_{2-x}$ layer-type material was identified.
There are still other methods to improve the catalytic ability of molybdenum sulfide. Literatures have already shown that doping MoS$_x$ with elements such as Co, Fe and Ni could improve its catalytic ability [19]. Besides, by electrochemical exfoliation, the thermodynamically favored 2H-MoS$_2$ can be partially transformed to a 1T polymorph which has more metallic character and more competitive HER activity [23]. However, even though much progress has been achieved during the past, the catalytic performance of MoS$_2$ as HER catalyst, in both activity and stability, is still much inferior to that of platinum and the catalytic mechanism of MoS$_2$ is partially not yet understood. For this reason, efforts still need to be made for further improvement of its catalytic ability and a detailed understanding of its catalytic mechanism.

In this paper, we compare MoS$_2$ powders of different grain size with MoS$_2$ nanosheets deposited on multi-walled carbon nanotubes (MWCNTs). Owing to two oxidation peaks found in cyclic voltammetry (CV) measurements electro-oxidizing MoS$_2$, the area of catalytically active edges of the hexagonal material in contact with the electrolyte can be determined and compared with the areas of the chemically inert basal planes. Using the surfactant Tween 80, which reacts with unsaturated metal ions located at the layer edges and therefore blocks the active centers, the first oxidation peak has been assigned to the oxidation of the catalytic centers. Thus, the ratio of edge to basal planes in MoS$_2$ can be determined by electrochemical CV measurements.

2 Experimental

2.1 MoS$_2$ electrodes preparation

2.1.1 MoS$_2$ preparation

MoS$_2$ single crystals, used as a reference material in this work, were grown by chemical vapor transport using MoO$_3$ and IBr as transporting agents. In a first step, MoS$_2$ (2 g) and MoO$_3$ powder (25 mg) were placed at the closed end of a 190 mm long and closed quartz glass tube of 20 mm diameter. Afterwards, the ampoule was evacuated and prior to sealing IBr (365 mg) was sublimed at the cooled end of the ampoule. The tube was placed into a two zone furnace. In a temperature gradient $\Delta T = 1173 - 1123$ K endothermal transport was observed from hot to cold. After 200 h, crystals up to 5–10 mm edge length were grown in the growth chamber of the ampoule. Crystals investigated in this paper as hydrogen evolving catalysts showed typical growth spirals on the basal planes which have step sizes of several hundred nanometers.
MoS$_2$ powder (# DS-315) was prepared by a precipitation reaction dissolving sodium molybdate and thioacetamide in an acid solution: a 10 mM thioacetamid solution dissolved in 1 M HCl was added to an aqueous 1 mM Na$_2$MoO$_4$ · 2H$_2$O solution. Afterwards, the mixture was stirred for 12 h and finally the molybdenum sulfide particles were filtered using a PTFE filter. The obtained product was heated in forming gas (10% H$_2$ in N$_2$) at 450 °C for 1 h before the product was heated at 800 °C for 2 h under argon gas. The powder sample (# SF) was synthesized from the elements at 500 °C in an evacuated and sealed quartz glass ampoule for 50 h by weighing-in molybdenum and sulfur in the mass ratio of 1:2. The samples Sigma Aldrich I & II (shortly SA I & II), Molykote µ-size, and Molykote z-size were purchased from Sigma Aldrich and Dow Chemicals, respectively. The preparation method of these powders is unknown and not specified by the manufacturer. Molykote powders are produced by the manufacturer as lubricants for metals. According to the data sheet, the particle size of the Molykote µ-size preparation is 0.65–0.75 µm and that of the Molykote z-powder 3–4 µm. According to the supplier the particle size was determined using the Fischer method. The preparation of the samples SA I & II is also unknown and also the method by which the particle size was determined is not described. Looking at SEM images, a high size distribution of the hexagonal platelets can be seen for all commercial samples. The particles appear to be mechanically fractured and show numerous crystallite fragments (see Figure 2). Sample DS-315 has a particle size of <200 nm, the particles of the powder #SF have a particle size ranging from 50 to 1000 nm.

MoS$_2$ grown on MWCNTs was prepared using the same method as described for the preparation of DS-315 powder. In an aqueous 1 mM Na$_2$MoO$_4$ · 2H$_2$O solution 48 mg of MWCNTs were dispersed and ultrasonically homogenized at RT. After 1 h treatment, a 10 mM thioacetamid solution dissolved in 1 M HCl was added and homogenized for 2 h in an ultrasonic bath. Afterwards, the mixture was stirred for 12 h and finally MWCNT supported molybdenum sulfide was filtered using a PTFE filter. The obtained product was in a first step heated in forming gas (10% H$_2$ in N$_2$) at 450 °C for 1 h and then at 800 °C for 2 h under argon gas (Ar).

### 2.1.2 Electrode preparation

Ten milligrams MoS$_2$ powder catalyst or MoS$_2$ catalyst deposited on MWCNT were mixed with 1 mL poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS), which was diluted before in water in a ratio 0.3:7. After homogenizing the dispersion in an ultrasonic bath, 10 µL of the mixture was drop-casted on a FTO substrate of 10 × 20 cm$^2$ in size. The samples were first dried in air at RT
Fig. 2: SEM images of different MoS\textsubscript{2} powders: (a) DS-315 (<200 nm particle size), (b) SF (50 nm–1000 nm), (c) Molykote μ-size (0.65–0.75 μm), (d) Sigma Aldrich I, (e) Molykote z-powder (mean particle size 3–4 μm), and (f) Sigma Aldrich II (<8 μm).

and afterwards at 125 °C. To perform XRD measurements, the MoS\textsubscript{2} powders and MoS\textsubscript{2} deposited on MWCNTs particles were deposited on 111-oriented Si wafers.

2.2 Structural and morphological characterization

The morphology of the films was measured by field emission scanning electron microscopy (FESEM) using a LEO GEMINI 1530 instrument from ZEISS, operated with an acceleration voltage of 5 kV. For transmission electron microscopy (TEM) analysis, MoS\textsubscript{2} catalyst deposited on top of MWCNTs were prepared ultramicrotomically. In the first step, the MoS\textsubscript{2} coated nanotubes were embedded in an acryl
resin (LR-White). Prior to cutting the small polymer blocks by ultramicrotomy (ULTRACUT E from Reichert & Jung), it was trimmed and acuminated. Ultrathin slices (40–60 nm thick) were cut from the resin tip and were floated on a water surface from where they were subsequently fixed on carbon film covered grids. Alternatively, small slices (0.5 mm thick) were cut from the tiny resin block and glued face to face. Afterwards these samples were sanded and polished perpendicular to the glued interface down to a thickness of 4–6 μm before they were fixed to a molybdenum ring. At the end the samples were ion-milled (5 kV, 2 mA) using Ar ions under an incidence angle of 6° until parts of the sample became transparent for the electron beam. Finally, the so prepared samples were investigated by a transmission electron microscope (Cm 12 from Philips, equipped with a LaB₆ cathode) and electron micrographs were taken at an acceleration voltage of 120 kV. A Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) was used to obtain glancing incidence X-ray diffractiongrams (GIXRD). The angle of incidence was 0.5° and the measured detection angle (2θ) was varied from 10° to 60°. Raman spectroscopy was performed using a LabRam spectrometer from Horiba Jobin Yvon under excitation conditions using a He/Ne laser with λ = 632.82 nm, which was focused via a microscope (Olympus BX 40) on the surface of the samples. A CCD camera detected the Raman peaks.

2.3 Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed using a VersaSTAT3 potentiostat in a three-electrode configuration. MoS₂ electrodes deposited on FTO were used as working electrodes (WE) while an Ag/AgCl electrode in saturated KCl solution (−0.197 V vs. reversible hydrogen electrode (RHE)) served as reference electrode (RE), and a platinum wire as counter electrode (CE). The electrolyte used was a 0.5 M H₂SO₄ aqueous solution (pH 0.3). The contacting area of the sample with the electrolyte was fixed using an O-ring of 0.63 cm diameter which is equivalent to an electrode area of 0.3117 cm². The iR drop of the sample in the electrolyte was calculated by measuring the resistance of the sample in the electrolyte at 100 kHz using electrochemical impedance spectroscopy (EIS). The current density was evaluated from cyclic voltammetry (CV) measurements. The CV measurements were performed within the potential range from 0.6 V to −0.4 V vs. RHE with a scan rate of 10 mV/s. The double layer capacitance (Cdl) of the CV curves shown in Figure 4 and Figure 8 were extracted calculating Δj = ja – jc (ja and jc represent anodic and cathodic current densities) at a potential U = 0 V using the equation jₐ – jₖ = Cdl dU/dt. The obtained value was added to the jₖ-V curves. The corrected curves are shown in the Figures S2 and S3 of the Supplementary information. The edge sites of the MoS₂ nanoparticles were catalytically
passivated by immersing the electrodes in 5 m% Tween80 solution for 2 days under continuous stirring.

3 Results and discussion

3.1 MoS$_2$ powder electrodes

Six kinds of MoS$_2$ powders were compared with each other with respect to their HER activity. The morphology of the electrodes prepared from different MoS$_2$ powders is shown in the SEM images of Figure 2. According to the morphology, sample DS-315 has the smallest and most isotropic particle sizes ranging from 100 to 200 nm (Figure 2a). The typical platelet-like hexagonal growth features of 2H-MoS$_2$ occur in the powder sample #SF (Figure 2b). The other four commercial samples (Figure 2c–e) have a totally different morphology. Their shapes point at fractured hexagonal platelets with 1–10 µm extension of the (001) facets. Therefore, it is difficult to predict which of these samples has the highest fraction of small MoS$_2$ fragments.

According to the XRD patterns in Figure 3a, all six powders show the typical diffraction pattern of 2H-MoS$_2$. However, sample DS-315 also shows peaks of MoO$_2$ which could be from the residual reactant sodium molybdate (Na$_2$MoO$_4$). The increasing intensity of the 00.2 diffraction peak at 14.4 °C in the XRD patterns represents an increasing crystallinity. Sample DS-315 has the lowest peak intensity and highest full width half maximum (FWHM), which means that the sample

![Fig. 3: (a) XRD patterns of MoS$_2$ powders with standard 2H-MoS$_2$ pattern (red) and MoO$_2$ pattern (green) displayed at the bottom of the figure; (b) Raman spectra of different MoS$_2$ powders including commercial products (Sigma Aldrich I (SA I), Sigma Aldrich II (SA II), Molykote z-size, Molykote µ-size), MoS$_2$ prepared by precipitation (DS-315), and chemical synthesis under vacuum (SF), in relation to a MoS$_2$ single crystal. In addition, schemes for the vibrational modes (E$_{2g}^1$ and A$_{1g}$) of hexagonal MoS$_2$ are shown.](image-url)
has lower crystallinity and smaller particle sizes as compared to the other five samples.

In addition, the 00.2 peak is slightly shifted to a smaller 2θ-value of about 0.35° indicating an increased distance between the S–Mo–S layers unities due to a disturbed stacking of the S–Mo–S slabs. The 10.1 peak appears to be shifted to a higher 2θ-value pointing at a smaller a₀ lattice constant possibly caused by sulfur point defects. Using Scherrer’s equation, coherently scattering crystallites of about 7 nm in height were determined from the broadening of the 00.2 peak which relates to about twelve S–Mo–S stacks.

Figure 3b shows the Raman spectra of the MoS₂ powders. In this figure, a MoS₂ single crystal was used as reference material. Its Raman spectrum shows strong characteristic peaks at 382 cm⁻¹ due to in-plane vibration of Mo–S bonding in the layer structure of 2H-MoS₂, namely E₂g¹ mode and at 407 cm⁻¹ owing to an out of plane vibration of the S–S bonding, which could be assigned as A₁g mode (see scheme in Figure 3b) [24–26]. All powder samples show a red shift of the E₂g¹ peak by 8 cm⁻¹ and of the A₁g mode by 7 cm⁻¹ and additional broadening of the peaks. In general, the peak shift and broadening of the Raman peaks could be affected by different factors, such as crystallite size [27], numbers of stacked S–Mo–S layer entities or extension of the van-der-Waals surface area [28], strain in the layers [29], changes in composition [30], and degree of oxidation [31].

CV measurements were used to investigate the electrochemical activity of the MoS₂ powders. Figure 4a shows the CV curves of the powder electrodes. The sample DS-315, which has the smallest particle size according to the morphology shown in Figure 2a, exhibited the highest current density (1 mA cm⁻² at a potential of −0.3 V vs. RHE) owing to small areas of the (00.1) basal planes but a large number of sulfur determined edges ((hk.0) facets). Interestingly, the catalytic

![Fig. 4:](image-url) (a) CV curves of the MoS₂ powder electrodes; measured in 0.5 M H₂SO₄ at a scan rate of 10 mV/s; the data were iR-corrected according to the procedure described in the experimental section; for Cdl corrected curves see Figure S2; (b) dependence of the current density at −0.3 V vs. RHE on particle size, the data were taken from Figure 4 (a).
activity of sample #SF is worse than that of the commercial powder SA II, indicating that the number of active sites in sample SA II is higher although its mean particle size is much larger. This effect could be explained by a high number of smaller fragments in this sample which is underestimated in the particle size determination from Figure 2f. Figure 4b shows the current density of different electrodes at the reversal point of the potential scan at $-0.3 \text{ V vs. RHE}$ as a function of particle size of the MoS$_2$ powder. At this highest applied potential the Faraday current has the largest contribution to the measured total current, so that it is the most suitable point for a comparison of the HER activity. It should be noted, however, that these data also include a certain amount of capacitive effects (see corrected curves in Figures S2 and S3). The current density of the electrode increases strongly as soon as the particle size becomes smaller than 1 $\mu$m. This result is in consistent with the fact that only the edge sites of MoS$_2$ layers are catalytically active.

### 3.2 MoS$_2$ deposited on MWCNTs

In order to further increase the area of non-van-der-Waals planes where the catalytically active centers are located, MoS$_2$ nanosheets were grown by the precipitation reaction described above on MWCNT substrates of different diameters. Four different series of samples were produced varying the MWCNT diameter from $<8 \text{ nm}$ to $\geq 50 \text{ nm}$. The diameters of the MWCNTs used as substrates for MoS$_2$ nanosheets, namely ARKM00x, are shown in Table 1.

The MoS$_2$ samples deposited on MWCNTs were compared with the DS-315 powder sample prepared by the same protocol. According to the XRD patterns in Figure 5, they all show both the 00.2-reflection and the representative reflections of (hk.0) and (h0.1) lattice planes as well. The (hk.0) reflections referred to lattice planes parallel to the c-axis of related crystallites. In case of (h0.1) reflections, the planes intersect the a$_0$- as well as the c$_0$-axis. In addition to the characteristics of MoS$_2$, the XRD patterns also exhibit peaks belonging to MoO$_2$. The presence of this phase can be explained by residual reactant sodium molybdate (Na$_2$MoO$_4$) in the

**Tab. 1:** The diameters of MWCNTs used as carriers for MoS$_2$.

| MWCNT   | Diameter (nm) |
|---------|---------------|
| ARKM001 | $<8$          |
| ARKM002 | 10–20         |
| ARKM004 | 40–50         |
| ARKM005 | $>50$         |
Fig. 5: (a) XRD of MoS$_2$ layers on MWCNTs with various tube diameters: ARKM001 ø < 8 nm, ARKM002 ø 10–20 nm, ARKM005 ø > 50 nm. Standard patterns of 2H-MoS$_2$ (purple) and MoO$_2$ (green) are shown on the bottom of the graph; (b) Raman spectra of MoS$_2$ nanosheets deposited on MWCNTs, compared with MoS$_2$ single crystal.

batch or by a partial oxidation of the nanosheets in contact with air. Figure 5b displays the corresponding Raman spectra of MoS$_2$ deposited on different MWCNTs. All samples show the MoS$_2$ typical vibrational modes, which could be addressed as $E_{2g}^1$ and $A_{1g}$. Compared with the Raman spectrum of a MoS$_2$ single crystal they are red shifted and show a broadening of the peaks indicating structural defects, partial oxidation or deviations from stoichiometry as also discussed in Figure 3b [27, 29, 31–34]. In Figure S1 of the supporting information, the Raman spectra of the MWCNT supports are also shown. From the spectra it can be concluded that the most perfect nanotubes had a diameter $\leq$ 8 nm [35, 36]. As explained in the following, structural nanotube perfection presumably does indirectly influence the performance of the HER catalyst (see below).

Figure 6 shows four TEM images of MoS$_2$ deposited on MWCNTs (diameters ranging from 20 to 40 nm) in transverse and longitudinal cross sections. As shown, MoS$_2$ nanosheets surround MWCNTs whereas S–Mo–S layer units appear as stacks of distinctive bold black lines on the MWCNT substrates. The carbon layers beneath are represented as black lines of lower intensity and thickness. Besides, the line distances can also be used to distinguish MoS$_2$ from the carbon substrate. Graphite like MWCNT has a lattice distance of around 3.4 Å while 2H-MoS$_2$ is characterized by a S–Mo–S layer distance of around 6.4 Å [10]. The MoS$_2$ nanosheets partially adapt to the bending of the carbon nanotubes, but in most cases the MoS$_2$ nanosheets show no bending and appear as individual flat MoS$_2$ nanosheets showing small extension of the (00.1) planes compared to the nanosheet thickness. This observation is consistent with the model that the
Fig. 6: TEM images of transverse and longitudinal cross sections of MWCNTs surrounded by S–Mo–S layer stacks. (a) Unbent S–Mo–S stacks with gaps between the particles with an extension of 5–10 nm, (b) slightly bent S–Mo–S units with a length <30 nm which are oriented parallel to carbon fibers, (c) facetted growth of MoS$_2$ nanoparticles enveloping a multiwall carbon nanofiber, (d) partly bent MoS$_2$ particles enveloping a carbon fiber.

bending behavior of MoS$_2$ is limited as shown schematically in Figure 7. As a consequence, MoS$_2$ nanosheets are separated from each other by a small gap with decreasing MWCNT diameter (see Figure 6a). The surfaces of the S–Mo–S layers are 10 nm–20 nm broad and at least 50 nm long, the S–Mo–S stack number varies from 1 to 7 layer units. Encapsulation of MWCNTs by stacks of S–Mo–S layers can be understood as a hexagonal cylinder enclosing the individual carbon nanotubes under ideal conditions. Ideally, the gaps between the individual nanosheets are expected be large enough that protons in the electrolyte have access to the edges
Fig. 7: Scheme of MoS$_2$ nanosheets grown on MWCNT substrates with different diameters.

of the S–Mo–S units. Best catalytic material is expected to have a high stacking number of S–Mo–S entities which then offer a large number of reactive sites at the particle electrolyte.

Figure 8a shows the catalytic activity of the MoS$_2$ grown on MWCNTs. As already explained in Figure 4, again a splitting of the curves between the forward and reverse scan due to capacitive effects can be seen. The capacitance corrected curves are shown in Figure S3. The sample deposited on the smallest diameter MWCNTs (<8 nm) obtained a current density of 2 mA/cm$^2$ at the potential of $-0.3$ V vs. RHE, which is the highest activity. The current densities of the other samples at the same potential are ranging from 1.4 to 1.0 mA/cm$^2$. The light grey

Fig. 8: (a) CV-curves of MWCNT supported MoS$_2$ nanoparticles in comparison to DS-315 and a pure MoO$_2$ electrode; data were measured in 0.5 M H$_2$SO$_4$ with a scan rate of 10 mV/s; the data were iR-corrected according to the procedure described in the experimental section; for $C_{dl}$ corrected curves see Figure S3; (b) dependency of the current density at a voltage of $-0.3$ V vs. RHE as a function of the diameter of MWCNTs; data were taken from Figure 8 (a).
curve shows the CV curve of MoO$_2$ which proves that this phase has only a moderate catalytic activity. In neither the MoS$_2$ powders nor the MoS$_2$ layer sequences grown on the carbon MWCNTs, hydrogen sulfide evolution ($H_2S$) as a corrosion product has been detected investigating the released gases by a mass spectrometer coupled to our electrochemical cell. Figure 8b shows the current density as a function of the average diameter of MWCNTs at a potential of $-0.3$ V vs. RHE. As explained above (see Figure 4) at this highest applied potential the Faraday current has the highest contribution to the overall current density. The result is comparable to the dependence of the current density of MoS$_2$ powders on the particle size (see Figure 4b). In the case of MoS$_2$ deposited on MWCNTs of 8 nm diameter, the improved catalytic performance can be explained by a higher number of catalytic sites at the edges of S–Mo–S units owing to a higher number of stacks which are accessible by the electrolyte. To prove this assumption, clarification of the catalytic centers in different MoS$_2$ electrodes were investigated by electro-oxidation.

Since MoS$_2$ is highly anisotropic the question arises how far the electrical conductivity influences the catalytic behavior considering changes of the particle dimension and the orientation of the nanosheets with respect to the carbon nanotubes. It is known that bulk 2H-MoS$_2$ is a compound semiconductor with an indirect band gap of $E_g = 1.4$ eV followed by a direct one at $E_g = 1.9$ eV. In 1983, Thakurta and Dutta studied the specific conductance of highly doped natural crystals perpendicular ($s_\perp$) and parallel ($s_\parallel$) to the hexagonal c-axis [37]. They found a specific conductance for $s_\perp$ ranging from 0.078–1.09 $W^{-1}cm^{-1}$ while $s_\parallel$ was four orders of magnitude smaller ranging from $3.0–4.6 \times 10^{-4}$ $W^{-1}cm^{-1}$. This means that the conductivity parallel to the hexagonal surface is high compared to the conductivity perpendicular to the hexagonal c-axis. Since the number of S–Mo–S is typically four to seven in our case (see Figure 6) electron transport from the carbon tubes via the stacked S–Mo–S layers to the catalytically active centers is small compared the conductivity in the S–Mo–S layers. This means that both particle dimension and number of stacks determine the transport velocity of electrons from the carbon nanotube via the MoS$_2$ nanosheets to the catalytically active centers. Since in our MWCNT supported MoS$_2$ catalyst nanoparticles the S–Mo–S stacking number did not change when lowering the particle extension of the 00.1 facets the number of edges is mainly determining the catalytic performance as will be discussed and demonstrated in the following chapter.

3.3 Clarification of the catalytic center by electro-oxidation

Bonde et al. [32] analyzed MoS$_2$ samples by a surface-sensitive method, X-ray photoelectron microscopy (XPS) before and after electro-oxidation. They could show
that the intensities of the Mo 3d and Mo 3p signals as well as the S 2s and S 2p decreased after the experiment. This can be explained by a number of reasons: a) MoS₂ could delaminate from the surface of the conductive support or b) MoS₂ is oxidized to MoO₃ (Mo³⁺) which could be soluble in the electrolyte. According to the work of n-type photoactive MoS₂ single crystals, sulfur compounds such as SO₄²⁻, S₂²⁻ and MoO₃ are formed after electrochemical measurements in potassium nitrate (KNO₃) [38].

The reaction equation of the oxidation at the edges can be expressed by the equation [32]:

\[
\text{MoS}_2 + 7\text{H}_2\text{O} \rightarrow \text{MoO}_3 + \text{SO}_4^{2-} + \frac{1}{2} \text{S}_2^{2-} + 14 \text{H}^+ + 11 \text{e}^{-} \tag{1}
\]

According to the literature [9], the catalytically active centers of molybdenum disulfide are located at Mo atoms piercing out of hk.0 and h0.1 surfaces of the crystalline material. Since the edge Mo atoms with dangling bonds and Mo atoms of complete coordination of sulfur sandwiched between sulfur layers (basal planes) have different electrochemical properties, the electro-oxidation of these two kinds of atoms should appear as two separate peaks in CV curves under anodic conditions. Therefore by electro-oxidation, the edges should be distinguishable from basal planes. This process could be verified by passivating the edges with a nonionic surfactant, e.g. Tween 80 as demonstrated in the following discussion.

In our study electro-oxidation is performed using MoS₂ nanosheets grown on MWCNTs. The edge-basal plane-ratio of the samples has been determined by electro-oxidation and the correlation between the current density and the edge-basal plane-ratio is discussed.

### 3.3.1 Passivation of the edges with Tween 80

By treating a HEC characterized by a layer structure with organic detergents, the CV characteristics can be influenced, since the detergents are specifically attaching to the reactive edges of the individual layer units. To investigate this behavior, organic detergents with ligands that act as electron donors and molecules with large functional groups, which affect and limit the reaction due to steric hindrance, are used. Chemical treatment of photocatalysts were first described by Parkinson et al. [39]. In their experiments, treatments with organic ligands such as 1,2-bis (diphenylphosphino) ethane (diphos), which is commonly used for rodium-catalyzed hydroformylation [40], showed a lower dark current and a higher open-circuit voltage. In the treatment of tungsten diselenide (WSe₂) single crystals, the phosphorous atom of the diphos reacts with tungsten atoms at
the edges or on steps of (00.l) facets of hexagonal crystals. Other ligands such as isocyanides, thiocarbamates [41], ethylenediamine tetraacetate (EDTA) [42], and 1,2-diaminobenzene (OPD) [43], also show a reduction of the dark current due to passivation of recombination centers on the (00.l) planes and crystal edges.

In this work, the nonionic surfactant Tween 80, which is used as an oil/water emulsifier [44], was chosen as passivation material. Tween 80 is an ethoxylated sorbitan fatty acid ester with the trade name Tween. The structure of Tween 80 is shown in Figure 9. The sorbitans differ in their fatty acid, the middle number of the polyoxyethylene units of the molecule, and the degree of esterification. In Tween 80, the number 8 stands for the oleic acid and number 0 stands for a monoester with 20 polyethylene units.

After the MoS$_2$ samples were impregnated with Tween 80, the influence of the surfactant on the catalytic activity has been investigated by electrochemical measurements. After treatment of MoS$_2$ with Tween 80, the surfactant covers the edges of the S–Mo–S slabs, which are considered as the reaction centers for the HER. This experiment can additionally clarify the meaning of the oxidation peaks in the CV curves shown below (Figure 11), which are attributed to an electro-oxidation of the catalyst.

Figure 10 shows the CV characteristic of a MoS$_2$ single crystal in the potential range from 0.6 V to $-0.4$ V vs. RHE with and without Tween 80. The initial cycle was measured up to a potential of 1.7 V vs. RHE to clean the surface. This effect is noticeable in Figure 10 by an increased current density in the following CV cycles as shown by the black arrow. The current density of the MoS$_2$ single crystal electrode after cleaning is about 0.5 mA/cm$^2$ at $-0.4$ V vs. RHE. After passivation of the active sites by Tween 80, the current density reduces to $-0.05$ mA/cm$^2$ at the same potential (orange curve in Figure 10). As the number of CV cycles increases, the current density in hydrogen evolution of the sample treated with Tween

![Fig. 9: Structure of the non-ionic surfactant Tween 80 (w + x + y + z = 20).](image-url)
80 increases as well. The surfactant is apparently reversibly coordinating the edges.

Figure 11a displays the CV curve of MoS$_2$ nanosheets grown on ARKM005 MWCNTs (diameter $>50$ nm) with and without Tween 80 taken in the positive potential range. The surfactant slightly also alters the second oxidation peak since the surfactant partially covers the (00.1) surfaces. However, the intensity of the first oxidation peak is significantly reduced after the treatment with Tween 80 and the peak position is shifted by about 50 mV (see Figure 11b). According to the CV of the electrode before and after the treatment with Tween 80 in Figure 11c, Tween 80 is obviously attached to the edge sites of S–Mo–S entities passivating the catalytically active centers because the current density at negative potential decreases dramatically, which was also found for the MoS$_2$ single crystal (see Figure 9). From the change of the two electro-oxidation peaks in Figure 11a, it can be concluded that the first electro-oxidation peak is connected with an oxidation of the edge sites while the second peak is correlated to the oxidation of the basal planes. Since the first peak is still visible after the treatment of Tween 80, only a part of the catalytically active centers was passivated by Tween 80. The reason could be that the surfactant has a large steric hindrance due to the presence of the polyoxoethylene group. Therefore, it is not able to coordinate to all metal atoms at the MoS$_2$ edges. This fact is also the reason why the evolution of hydrogen of the cathode does not completely disappear after Tween 80 treatment in Figure 11c.
3.3.2 Electro-oxidation of MoS$_2$ nanosheets grown on MWCNTs with different diameters

Since the edges and basal planes in MoS$_2$ can be identified and also quantified by electro-oxidation, the catalytic properties of MoS$_2$ nanosheets grown on MWCNTs of different diameter were studied by CV. In this study, the correlations between the current density and the edge-to-basal-plane-ratio for MoS$_2$ nanosheets deposited on MWCNTs were determined.

Table 2 shows the calculated area of the first ($A_1$) and the second ($A_2$) electro-oxidation peak, respectively, as well as the edge-to-basal-plane-ratio for different MWCNT/MoS$_2$ electrodes. According to Table 2, the four MWCNT/MoS$_2$ samples with different diameters have similar $A_2$ values, suggesting similar basal plane areas. However, the $A_1$ value of ARKM001/MoS$_2$ was significantly higher.
Tab. 2: Calculation of peak areas and edge-to-basal plane-ratios of MoS$_2$ deposited on MWCNTs.

| Sample                  | Peak area $A_1$ (Q, C/cm$^2$) | Peak area $A_2$ (Q, C/cm$^2$) | Edge-to-basal plane-ratio $A_1/A_2$ (%) |
|-------------------------|---------------------------------|---------------------------------|----------------------------------------|
| ARKM001/MoS$_2$ Ø < 8 nm| 0.040                           | 1.421                           | 2.8                                    |
| ARKM002/MoS$_2$ 10–20 nm| 0.013                           | 1.292                           | 1.0                                    |
| ARKM004/MoS$_2$ 40–50 nm| 0.014                           | 1.489                           | 0.9                                    |
| ARKM005/MoS$_2$ Ø > 50 nm| 0.012                           | 1.704                           | 0.7                                    |

than in the other three samples. Therefore, this sample also obtains the highest edge-to-basal-plane-ratio.

In the following, the current densities of the MWCNT/MoS$_2$ electrodes were compared with the edge-to-basal-plane-ratios to further study the impact of these ratios on the catalytic property of samples. Figure 12a compares the obtained geometric current density with the edge-to-basal-plane ratio as a function of MWCNT diameter.
diameter. The sample with the smallest diameter shows the largest current density and the largest edge-to-basal-plane ratio. The left y-axis in Figure 12b visualizes the current divided by the geometric area of the MWCNTs. As expected, the trend of this geometric current density is also consistent with the edge-to-basal-plane ratio. Figure 12c shows the comparison between the current density divided by the area of the second electro-oxidation peak and edge-to-basal-plane ratio correlating well with each other. In Figure 12d, the comparison of the current density divided by the Helmholtz double layer capacitance ($C_d$) and the edge-to-basal-plane ratio is shown. The capacitance $C_d$ is measured by CV in a potential region where no electrochemical reaction is occurring. In this region, the capacitive current is proportional to the scan rate ($df/dt$) according to Eq. 2. The unit of the capacitance is As/V or F (Farad) [45].

$$i_C = \frac{dQ}{dt} = \frac{\delta Q}{\delta \phi} \frac{d\phi}{dt} = C_d \frac{d\phi}{dt}$$

In this equation, $i_C$ stands for the capacitive current, $Q$ stands for the electric charge, $t$ is the time, and $f$ is the potential, $C_d$ stands for the Helmholtz double layer capacitance. As shown in Figure 12d, the edge-to-basal-plane-area ratio and the current densities as a function of capacitance do not correlate, the current divided by capacitance remains constant. The reason could be that MWCNTs have a large electrochemical capacitance which overlays the material-specific capacitance of the MoS$_2$.

From this comparison, one could speculate that the large edge-to-basal-plane ratio in sample ARKM001/MoS$_2$ is the main reason for its high current density, which leads to a higher number of active sites at the catalyst surface. In summary, HER active MoS$_2$ catalysts should have a high edge-area to van-der-Waals-plane ratio and at the same time a large FWHM in the $E_{2g}^1$ Raman peaks.

### 4 Conclusion

Electrodes made from powders and nanosheets of the molybdenum sulfide phase 2H-MoS$_2$ have been investigated as hydrogen evolution catalysts under acidic conditions. The catalytic center was identified at the edges of the hexagonal particles. Powders with a diameter >200 nm and carbon-supported MoS$_2$ nanosheets were fixed using PEDOT:PSS on conductive glass substrates (FTO). MoS$_2$ nanosheet deposited chemically on MWCNTs of different diameters had sizes in the range from 3 to 5 nm (particle height in 00.1 direction) and from 10 to 50 nm (extension of basal planes surrounding MWCNTs in transversal and longitudinal direction). The hydrogen evolution reaction was studied as a function of particle size
and especially as a function of the edge-to-basal-plane-area ratios of MoS$_2$. MWCNTs of different diameters were tested as support to study their influence on the growth and defects of MoS$_2$ particles. Among all samples, the MoS$_2$ grown on MWCNTs with smallest diameter (Ø < 8 nm) obtained the highest catalytic activity (2 mA/cm$^2$ at $-0.3$ V vs. RHE). By electro-oxidation, the catalytically active edge atoms could be distinguished from the inert atoms on the basal planes. This effect is confirmed by the passivation of edge sites using Tween 80 as surfactant, which mainly protects edge atoms from electro-oxidation. From these measurements, the edge-to-basal-plane ratios in different MoS$_2$ samples could be determined. During the comparison of different electrodes, the sample with highest catalytic activity was found to have the highest edge-to-basal plane-ratio, which means that the high catalytic activity of this sample is due to the high number of active edge atoms on the catalyst non-van-der-Waals surfaces.

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