Revealing the Heterogeneity of Large-Area MoS\textsubscript{2} Layers in the Electrocatalytic Hydrogen Evolution Reaction

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The electrocatalytic activity concerning the hydrogen evolution reaction (HER) of micrometer-sized MoS\textsubscript{2} layers transferred on a glassy carbon surface was evaluated by scanning electrochemical cell microscopy (SECCM) in a high-throughput approach. Multiple areas on single or multiple MoS\textsubscript{2} layers were assessed using a hopping mode nanocapillary positioning with a hopping distance of 500 nm and a nanopipette size of around 55 nm. The locally recorded linear sweep voltammograms revealed a high lateral heterogeneity over the MoS\textsubscript{2} sheet regarding their HER activity, with currents between $-40$ and $-60$ pA recorded at $-0.89$ V vs. reversible hydrogen electrode over about 4400 different measured areas on the MoS\textsubscript{2} sheet. Stacked MoS\textsubscript{2} layers did not show different electrocatalytic activity than the single MoS\textsubscript{2} sheet, suggesting that the interlayer resistance influences the electrocatalytic activity less than the resistances induced by possible polymer residues or water layers formed between the transferred MoS\textsubscript{2} sheet and the glassy carbon electrode.

Introduction

Two dimensional (2D) materials emerged in the last decades due to their unique properties, which open the way to new applications. Among those, transition metal dichalcogenides (TMDs) were extensively studied for electrochemical applications, where they were used as electrocatalyst materials or to fabricate electrodes for different analyte detection.\cite{3–7} Inspired by nature, where hydrogenase enzymes contain Mo, Fe and Ni, nanosized MoS\textsubscript{2} was predicted by theory to be an efficient hydrogen evolution reaction (HER) electrocatalyst almost 20 years ago.\cite{8–10} Since then, many studies have confirmed the potential of MoS\textsubscript{2} as a highly active HER electrocatalyst.\cite{11,12}

Single MoS\textsubscript{2} layers show unique properties. They can be synthesised either in a bottom-up, e.g., chemical vapour deposition (CVD)\cite{13–15} or top-down, e.g., exfoliation, approach.\cite{16,17} While the latter generally offers high-quality 2D materials, it fails to produce large-scale single layers independently of the substrate and hence lacks scalability.\cite{18} Often, the transfer of MoS\textsubscript{2} layers on different supports is required, and recent studies indicate that this may also influence the properties of the MoS\textsubscript{2}.\cite{19} Apart from the influence of the substrate itself, it was recently shown that intercalated water layers between the MoS\textsubscript{2} layers and the substrate substantially alter the MoS\textsubscript{2} electronic properties.\cite{20,21}

MoS\textsubscript{2} is seen as an abundant and lower-cost alternative for Pt as HER electrocatalyst.\cite{22} Improving the electrocatalytic activity of MoS\textsubscript{2} was attempted by different methods, such as doping with other elements,\cite{23–25} by introducing defects,\cite{26} or by applying strain.\cite{27} Multiple studies\cite{28–30} investigated the electrocatalytic activity of MoS\textsubscript{2} obtained via different synthesis routes at the macro- and nanoscale, leading to a debate about the location of active sites on MoS\textsubscript{2}.\cite{31} While classical measurements performed at the macroscale can confirm an overall change in the electrocatalytic activity, they do not provide information about the active areas on the catalyst layer.

Scanning electrochemical cell microscopy (SECCM) demonstrated its power over the last decade in evaluating electrocatalyst materials at the nanoscale.\cite{32,33} In SECCM, a nanopipette filled with electrolyte is approached to the surface to be investigated. Upon contact, the hanging nano-droplet forms an electrochemical cell that allows the exclusive electrochemical evaluation of the wetted area. By automatically retracting and repositioning the nanopipette at different electrode areas, a high-throughput evaluation of the sample surface is achieved in a relatively short time.\cite{34} The technique is ideal for studying the lateral heterogeneity at the micro- and nanoscale and was used to evaluate electron-transfer rates or electrocatalytic activity of a broad range of materials such as Pt,\cite{35} carbon nanotubes,\cite{36} graphene,\cite{37–40} MoS\textsubscript{2},\cite{21,32,33} pentlandite crystals,\cite{41} Co(OH)\textsubscript{2} crystals,\cite{42} high-entropy alloys,\cite{43} etc.

Initial studies at the nanoscale, reported by Bentley et al.,\cite{44} showed that the bulk MoS\textsubscript{2} basal plane possesses a high activity...
towards HER, which significantly increases over the edge plane. The study of Takahashi et al. confirmed the existence of active sites on the basal space of small triangular MoS₂ layers having ~130 nm in length. They showed that on freshly prepared MoS₂, an increased activity could be observed for edges compared with the basal plane, a difference no longer visible when MoS₂ was exposed to air for several months. Cabre et al. evaluated the electron transfer rate for TMDCs exfoliated from bulk crystals on Au substrates. Plechinger et al. showed that CVD-grown MoS₂ could have a similar quality as exfoliated MoS₂ while having the advantage of larger and coherent single layers. These large single layers enable low-resolution and non-localised measurement methods, such as X-ray photoelectron spectroscopy (XPS), and open the door for the investigation of various structural modification methods, e.g., ion- or electron irradiation and etching. In catalytic and electrochemical applications, large reproducible single layers with a high surface coverage are desirable to maximise the surface-to-volume ratio.

In the present work, we evaluated the surface of large areas of single-sheet MoS₂ grown by CVD, which were transferred on a glassy carbon (GC) electrode using the classical polymer-assisted method. By probing 4941 different spots over an area of 30 μm × 40 μm (~4400 on the MoS₂ sheet), a variation of electrocatalytic HER activities was observed, and possible reasons for the increased lateral heterogeneity are discussed.

**Results and Discussion**

The single-layer MoS₂ sheet grown on a SiO₂/Si substrate, as previously reported, was transferred onto a GC electrode to enable mapping of the electrochemical activity of MoS₂ by SECCM. The GC electrode was used to establish the electrical connection (in the so-called bottom-contacted mode) and was further used as a working electrode (WE) in SECCM experiments. The mode of contacting the MoS₂ layers was shown to impact the measured electrocatalytic activity of MoS₂ by SECCM, since different pathways for the electrons transport are established. In top contact, the lateral electron transport along the layer occurs, while in bottom contact, the electron transfer occurs from the substrate to the upper MoS₂ sheet, where the reaction takes place. For example, in the case of bulk MoS₂ measuring with a top contact proved to be beneficial as compared to measuring with a bottom contact, as it prevented the recording linear sweep voltammograms (LSVs) with artefacts. On the other hand, for single to few-layer MoS₂, the bottom contact was successfully used to perform SECCM. For the large single-sheet MoS₂ used in this study, the recorded LSVs during the SECCM measurement show no artefacts (Figure S1), indicating that electrical conductivity between the MoS₂ sheet and the GC current collector is not limited.

SECCM measurements were performed with a capillary size of 55 nm in a hopping mode with a hopping step of 500 nm (Figure 1).

Based on the recorded LSVs, current maps are derived by plotting the currents recorded at defined potentials. At lower overpotentials [−0.6 V vs. reversible hydrogen electrode (RHE)], Figure S2], slightly higher currents are recorded on the GC compared with the MoS₂ sheet. At overpotentials lower than −0.6 V vs. RHE, we see a sudden increase in the currents recorded on the MoS₂ sheet compared to the GC (Figure 2, S2). Overall, over the MoS₂ sheet, we see a high variation of currents at −0.89 V vs. RHE, ranging from −20 to −60 pA (Figure S1), corresponding to current densities ranging from −0.45 to −1.36 A/cm² (Figure S3), in agreement with the results of Bentley et al. Exemplary LSVs from different locations are illustrated in Figure 2c. We compared the currents recorded on the GC at the beginning of the scan with those at the end of the scan to confirm the technical robustness of our experiment (white and black areas marked in Figure 2b).

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Figure 2. (a) Scanning electron microscopy (SEM) image of the MoS$_2$ sheet transferred on the GC on which the SECCM scan, containing 61 x 81 measured points, was performed. The SECCM scan spreads over an area of 40 μm x 30 μm with a hopping distance of 500 nm and a nanopipette tip size of ~95 nm. (b) Corresponding currents maps of the area marked in (a) derived by plotting the currents extracted from the recorded LSVs as a function of the measured position at −0.89 V vs. RHE. (c) Exemplary LSVs from different regions of the scan (GC top: X = 19.5 μm, Y = 1 μm; GC bottom: X = 29.5 μm, Y = 24 μm; MoS$_2$ high activity: X = 34 μm, Y = 15.5 μm; MoS$_2$ lower activity: X = 9.5 μm, Y = 23.5 μm). (d) Histograms showing the number of measured points for which different currents are recorded at −0.89 V vs. RHE in the areas marked with pink and red. The currents marked with white and black bars are currents recorded on the GC electrode. (e) SEM images of the areas marked with pink in which the presence of multiple MoS$_2$ layers (highlighted in Figure 3a) can be observed and SEM image of the area marked with red where no multi-layer MoS$_2$ can be identified.
air, e.g., oxidation. After 30 min, the samples can be retrieved. To transfer the grown MoS$_2$ flakes onto the glassy carbon substrate, poly(methyl methacrylate) (PMMA) was spin-coated onto the samples. Then, the sample was placed into a 0.1 M KOH bath, slowly etching the SiO$_2$ and separating the PMMA/MoS$_2$ layer from the silicon piece. After that, the resulting layer of PMMA/MoS$_2$ was transferred into a water bath to clean it, and it could then be scooped off with the glassy carbon substrate. The glassy carbon was purchased (HTW Hochtemperatur-Werkstoffe GmbH) in a polished condition. The roughness of the glassy carbon surface was measured in an atomic force microscope (AFM) to 2.5 ± 0.5 nm. In the last step, acetone was applied to the PMMA/MoS$_2$ layer to dissolve the remaining PMMA.

Scanning Electrochemical Cell Microscopy

Single barrel pipettes with nanometer-sized tip openings were fabricated by laser pulling single barrel quartz glass capillaries using a CO$_2$-laser puller (P-2000; Sutter Instruments). A one-line program with the following pulling parameters was used: HEAT 790, FIL 4, VEL 40, DEL 130, PUL 110, generating a nanopipette with an opening diameter of approximately 55 nm (Figure S5). The obtained nanopipettes were filled with 0.1 M HClO$_4$ using a MicroFil syringe, and a Ag/AgCl wire was inserted and used as quasi reference counter electrode (QRCE) during the SECCM experiments. To fabricate the Ag/AgCl QRCE, a polished Ag wire (diameter: 0.125 mm, Goodfellow, 99.99 %) was immersed in a 3 M KCl $+ 0.1$ M HCl solution, and a potential of $+5$ V versus a Pt electrode was applied for 10 min. The QRCE open circuit potential was measured vs a Ag$|$AgCl$|3$ M KCl reference electrode before and after the SECCM measurement. The filled nanopipette and the Ag/AgCl/3 M KCl were immersed in a one-compartment cell filled with 0.1 M HClO$_4$ and the open circuit potential ($E_{OCP}$) was measured with a digital potentiometer. The conversion of the potentials applied during the SECCM measurements vs. the Ag/AgCl QRCE to the RHE scale was performed using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.210 + E_{\text{OCP}} + 0.059 \, \text{pH},$$

where $E_{\text{Ag/AgCl}}$ is the applied potential to the working electrode versus the QRCE, 0.210 V is the standard potential of the Ag$|$AgCl$|3$ M KCl reference electrode, and $E_{\text{OCP}}$ is the correction factor of the open circuit potential measured against the commercial reference electrode (31 mV). 0.059 is the result of $(RT)/nF$, with $R$ the universal gas constant, $T$ the temperature (25°C = 298 K), $F$ the Faraday constant and $n$ equals 1.
Electrochemical measurements were performed in a home-built SECCM workstation. A sample holder supporting the GC/MoS$_2$ sample is mounted on a 3-axis step motor microscrew system (Owis) and controlled by an L-Step PCIe controller card (Lang). This enables a coarse positioning and first approach of the pipette tip to approximately 50 μm above the surface.

The filled single barrel capillary with the QRCE is mounted at a 3-amplifier (E-664, Physik Instrumente) is used. For fine positioning of the pipette tip above the surface, an analog pipette (Owis) and controlled by an L-Step PCIe controller card (Lang). This setup is used.

Scanning Electron Microscopy
For the characterisation of the nanopipette tip (size measurement of the opening) and the analysis of the landing species during the SECCM scan, a Quanta 3D ESEM (FEI) microscope was used.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: chemical vapour deposition · hydrogen evolution reaction · molybdenum disulphide · scanning electrochemical cell microscopy · thin film materials

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