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Publication Date

2017-09-01

DOI

10.1016/j.apmt.2017.04.007

Peer reviewed

Contents lists available at ScienceDirect

Applied Materials Today

journal homepage: www.elsevier.com/locate/apmt

Hydrogen evolution activity of individual mono-, bi-, and few-layer MoS₂ towards photocatalysis

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ARTICLE INFO

Article history:

Received 20 January 2017

Received in revised form 5 April 2017

Accepted 16 April 2017

Keywords:

Transition metal dichalcogenide

MoS₂

HER

Photocatalysis

Electrochemical micro-cell

ABSTRACT

We investigate the hydrogen evolution activity in the dark and under illumination above the band gap of individual mono-, bi- and few-layer (bulk) MoS₂ flakes. We demonstrate that the electrocatalytic activity of 2H-MoS₂ immersed in 1 M H₂SO₄ increases with decreasing number of layers. For monolayers, we observe the highest exchange current density, which is one magnitude larger than in the bulk case. The onset potential scales with the number of layers, which is consistent with a previous report, suggesting that hopping transport across inter-layer barriers within the MoS₂ flakes is responsible for this scaling. A specially designed micro-sized catalytic cell enables us to investigate individual MoS₂ flakes with well-known geometry and edge-to-surface ratio. Taking these geometric parameters into account, we tentatively attribute the catalytic activity mainly to sulfur vacancies in the basal planes acting as active sites. The associated turn over frequencies (TOF) for mono- and bi-layer MoS₂ yield values higher than 10³ s⁻¹ at an overpotential of -0.2 V vs. RHE. In view of light driven hydrogen evolution as a means of solar energy conversion, we investigate the photocatalytic activity of few-layer MoS₂ under white light illumination.

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1. Introduction

There is an increasing need for alternatives to fossil fuels and for the generation of the so-called green energy [1,2]. One route to fulfill these challenges is the combination of an efficient solar energy conversion and the storage in chemical energy e.g. in hydrogen gas produced by the catalytic splitting of water [3,4]. The most efficient catalysts for the electrochemical hydrogen evolution reaction (HER) are rare and expensive noble metals such as Pt, with the electricity optionally delivered from solar cells [5]. In contrast, atomically thin, two-dimensional semiconducting transition metal dichalcogenides (TMDs), such as MoS₂, offer the unique combination of a band gap in the visible range of about 1.9 eV for monolayers

[6–8], high sunlight absorption of up to 15% [9–11], catalytically active sites for HER [4,12–16] or CO₂-reduction [17] and photocatalytic stability under harsh reaction conditions [18]. Moreover, semiconducting TMDs are earth abundant, inexpensive, and sustainable (photo-)catalysts which can be combined in lateral or vertical heterostructures [19–22]. All of such structures can be further integrated in hybrid devices based on carbon, gallium-nitride or silicon platforms. For instance, MoS₂ has been incorporated into a silicon tandem photo-electrochemical (PEC) water-splitting device acting simultaneously as a catalytically active material and as a corrosion protection layer for the silicon solar cell [2,23]. As far as their crystal structure is concerned, semiconducting TMDs are layered materials consisting of a triple layer in the smallest unit with a transition metal surrounded by two chalcogen atoms with strong covalent in-plane bonds [8,24]. The individual layers are weakly coupled by van der Waals interaction. Depending on the coordination of the atoms, TMDs exist in different polymorphs with different physical properties. For instance, the polymorph 2H-MoS₂ is a semiconductor with a band gap in the visible range holding outstanding optical, optoelectronic [24–29], and electronic properties

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[10,30,31] with a transition from an indirect to a direct band gap semiconductor in the monolayer limit [6,7] and with the already mentioned high sunlight absorbance [9–11].

The key parameters for PEC devices are a high sunlight-absorption (1), an efficient separation of e-h pairs e.g. across heterojunctions (2), the transport of charge carriers to active sites (3) and the catalytic activity (4). Parameters (1–3) are reasonably well fulfilled in TMDs and their heterostructures. Moreover, it was demonstrated that 2H-MoS₂ features catalytic active edge sites for HER along the (10–10)-direction [32], while the (11–20)-direction undergoes an anodic corrosion limiting the functionalization as a photo-anode for the oxygen evolution reaction (OER) [32]. The two-dimensional character of TMDs further offers opportunities for structural and defect engineering to locally increase the catalytic activity and to create anchoring sites for co-catalysis. It equally qualifies TMDs for a specific chemical treatment, e.g. to substantially increase the photoluminescence efficiency of certain sections to near unity quantum-yield [33,34]. The arrangement in vertical or lateral heterostructures allows for an efficient charge separation across the heterojunctions. So far, considerable efforts have been made to investigate the catalytic activity of various MoS₂ nanostructures, including nanoparticles [35–37], mesopores [38], nanowires [39], amorphous morphologies [40–42], thin films [43,32], MoS₂/graphene heterostructures [44], chemically exfoliated MoS₂ layers [45–47], metal nanoparticle-decorated MoS₂ [48], MoS₂ grown by chemical vapor deposition [49], or fabricated by mechanical exfoliation [50]. While there are already a considerable number of studies addressing the overall electrochemical properties of these nanostructures, there are only rare reports on the specific photo-electrochemical properties of MoS₂ with respect to the hydrogen evolution reaction (HER). For HER, both the intrinsic and extrinsic catalytic properties of MoS₂ are of interest. Material-related details are important, such as doping level, defects, strain, and polymorphic details. In addition, the pH-value and composition of the electrolyte, as well as the applied potential and the complementary illumination parameters including light intensity and photon energy are relevant [13].

In this manuscript, we describe the HER of individual mono-, bi- and few-layered MoS₂ flakes. In particular, we introduce a catalytic μ -cell suitable to characterize TMD-based micro- and nanostructures as well as related heterostructures on the basis of single flakes. The μ -cell features an optical access for a site-specific analysis of the photo-catalytic activity and for an in-situ characterization of the flakes. Via μ -Raman and photoluminescence measurements, structural changes such as phase transitions or degradation of the investigated flakes can be characterized with a lateral resolution as small as 1 μ m. The μ -cell features a carbon-based, catalytically inactive working electrode with several tens of microns in diameter. On top, the TMD flakes are implemented e.g. via mechanical exfoliation. Fig. 1 (a) sketches the μ -cell with all circuitries, and Fig. 1 (b) depicts a microscope image of the cell's working electrode with an implemented MoS₂ flake exhibiting mono-, bi-, tri- and few-layers (1L, 2L, 3L, and bulk). Generally, the investigated flakes are characterized by atomic force microscopy (AFM) a priori, and then, by the help of the μ -cell, via μ -Raman and photoluminescence spectroscopy with and without the aqueous electrolyte (1 M H₂SO₄). We find that the photoluminescence and Raman spectra of the flakes are different for both environments. The spectra suggest the interpretation that the intrinsic charge carrier density of the MoS₂ flakes is reduced in the presence of the electrolyte most presumably due to a charge transfer from the 2D material to the electrolyte [11,51]. Then, the catalytic activity for HER is investigated by linear sweep voltammetry (LSV) measurements with and without illumination. We find that the catalytic activity increases by decreasing the number of layers, and it is maximum for monolayer MoS₂ in agreement with reports in literature [49]. The μ -cell approach

Fig. 1. Device scheme. (a) General structure of the photo-electrochemical (PEC) μ -cell consisting of a substrate, a conducting back electrode, an isolation layer and the electrolyte. A circular window in the isolation layer enables the contact of the electrolyte and the back electrode, and it defines the working electrode of all electrochemical measurements. Single MoS₂ flakes with desired shape and structure are placed into the window on top of the conducting substrate. Additional platinum counter and silver/silver chloride reference electrodes are placed into the electrolyte to complete the electrochemical cell. The μ -cell is covered with a thin glass plate and installed in an optical microscope to enable optical and electrochemical measurements at the same time. (b) Optical microscope image of a circular working electrode with single- (1L), bi- (2L), tri- (3L) and few-layer (bulk) MoS₂ on glassy carbon and the surrounding isolation layer (SU-8). Inset shows the flake on PDMS prior to transfer for better distinction of layer numbers.

further allows us to access the geometry and edge-to-surface ratio of the investigated MoS₂ flakes. In turn, we can attribute the catalytic activity mainly to sulfur vacancies in the basal plane acting as active sites. We further demonstrate that the catalytic activity is increased when the flakes are illuminated using a white-light source. The activity monotonously increases with the light intensity, and we do not find evidence for structural changes of the MoS₂ catalyst up to high illumination intensities of 5×10^7 kW/m² staying at the cathodic current of the cyclic voltammetry. The developed method provides access to the intrinsic as well as extrinsic photocatalytic properties of two-dimensional photo-catalysts, such as MoS₂, and it is suitable to uncover structural changes reported post LSV measurements as e.g. oxidation of MoS₂ samples in air after LSV measurements when anodic potentials are applied [49].

2. Materials and experimental methods

2.1. Preparation of the PEC μ -cell

The PEC μ -cell comprises a carbon-based, conducting, and catalytically inactive substrate to host 2D photo-catalysts, such as TMDs. The supporting substrate also serves as the working electrode for the linear sweep voltammetry (LSV) measurements. To achieve a high enough sensitivity for individual TMDs flakes or other μ -sized catalytic materials, the active site of the working electrode is partially covered by a lithographically defined window of a catalytically inactive, electrically insulating layer made from SU-8 photoresist (MICROCHEM SU-8 2000.5). This photoresist has a thickness of about 700 nm, and it covers the residual, inactive part of the working electrode. In our studies, the shape of the active window is circular with a diameter ranging between 20 μ m and 100 μ m. TMDs flakes are mechanically transferred into the active window of the working electrode by viscoelastic stamping method as described in Section 2.2. The substrate hosting the (photo-) catalysts is then mounted in a standard chip-carrier, and the working electrode is connected to electronic contacts with silver paint. The overall framework is made from inert polytetrafluorethylene (PTF) glued with a silicon paint (Scrintec) on top of the protection layer such that all conducting parts except of the active window of the working electrode are isolated from the electrolyte (1 M H₂SO₄). The frame has a twofold functionality. On the one hand, it holds

the aqueous electrolyte and hosts the ring-shaped Pt counter electrode as well as a Ag/AgCl reference electrode to provide stable conditions for the LSV measurements. On the other hand, the frame has a flat surface serving as the mount for a thin glass cover sealing the PEC cell to protect the small amount of electrolyte against contamination. The volume of such a μ -cell holds approximately 200 μ l electrolyte. The glass cover also enables the optical access from the top. In particular, the electrochemical μ -cell can be placed below an optical microscope and it can be connected to illumination sources as well as to a spectrometer to analyze the outgoing light. The distance between the surface of the glass cover and the (photo-) catalysts is approximately 4 mm. The resulting spot size of a focused light spot in the visible range using a long-distance objective is as small as 1 μ m. Another advantage of the design of our PEC μ -cell is a very short distance between the electrodes, particularly between the reference electrode (RE) and the working electrode (WE).

We present results for two different material combinations as carbon working electrodes and substrates. The substrate is either a 3 mm thick glassy carbon (Hochtemperatur Werkstoffe GmbH SIGRADUR® G) or a 220 nm thick graphenic carbon layer directly grown by chemical vapor deposition (CVD) on a Si substrate [52]. Both working electrodes are characterized by atomic force microscopy, μ -Raman spectroscopy and cyclic voltammetry with 1 M H₂SO₄ as electrolyte to exclude parasitic effects to our measurements on the MoS₂ flakes. The LSV measurements verify that the catalytic activity of both carbon-based working electrodes is negligible compared to the MoS₂ flakes. Throughout the manuscript, the utilized working electrode material is mentioned in the figure captions for each measurement shown.

2.2. Preparation of the (photo-)catalyst

MoS₂ flakes are micromechanically exfoliated from bulk crystals (SPI Supplies) using adhesive tape. Then, they are transferred with μ m precision onto the carbon-based working electrode. The typical dimensions of the flakes are several ten micrometers, typically 20 μ m to 100 μ m (compare Fig. 1). The transfer is accomplished by an all-dry viscoelastic stamping technique adapted from Ref. [53] using a polydimethylsiloxane (PDMS) thin film. During the transfer, the substrate is heated to approximately 100 °C to increase the transfer probability and to reduce parasitic PDMS residues on the 2D crystal surfaces that would alter the catalytic properties of the MoS₂ basal plane and edge sites. To ensure that the MoS₂ crystal is not covered by PDMS residues or other dirt, the samples are carefully cleaned immediately after the transfer process using acetone, isopropanol and dry nitrogen gas. The success of the sample preparation and cleaning process is inspected by optical microscopy as well as atomic force microscopy. The number of layers is determined from the optical contrast in optical microscopy (as in Fig. 1(b) and [54,55]). The determination of the number of layers is further verified by μ -Raman [6] and photoluminescence spectroscopy [7]. As a reference sample, a 20 nm thin Pt film on top of the carbon based working electrode is prepared by standard e-beam evaporation.

2.3. Characterization measurements

The morphology and surface roughness of the working electrodes as well as the transferred MoS₂ crystals are investigated by atomic force microscopy (AFM) under ambient conditions at room temperature. To this end, an AFM (Asylum MFP-3D) is operated in intermittent contact mode.

All optical measurements, including the μ -Raman, photoluminescence as well as cyclic voltammetry measurements with illumination, are performed with a homemade microscope set-up

using a 100x objective (Zeiss LD EC Epiplan-Neofluar 100x/0,75 DIC M27). For light in the visible range, the focused light spot is approximately 1 μ m in diameter on top of the MoS₂ flakes. The samples are either placed in a small home-built vacuum cell with a base pressure of $\sim 1 \times 10^{-3}$ mbar or in the PEC μ -cell. The μ -cells are mounted on an x-y-z piezo stack with a closed loop resolution of about 1 nm (Physik Instrumente P-611.3 NanoCube XYZ System). The position of the sample can be precisely controlled for all measurements. For the μ -Raman and photoluminescence measurements, the $\lambda = 488$ nm laser line of a Kr/Ar-ion gas laser is used. The scattered and emitted light is focused onto the entrance slit of a 500 mm spectrometer (Princeton Instruments), and it is dispersed by 1800 grooves/mm or 300 grooves/mm gratings for μ -Raman and photoluminescence measurements, respectively. The signal is then collected by a CCD camera (Princeton Instruments). The combined spectral resolution for μ -Raman measurements is 1 cm^{-1} . For the Raman measurements, a suitable ultra-sharp edge filter is used in front of the spectrometer to suppress the laser light. The laser power for the Raman and photoluminescence measurements is $P = 0.5$ mW.

For the LSV measurements under illumination, a supercontinuum fiber based laser source is used (NKT photonics SuperK EXTREME EXU-6). For the broadband white-light illumination, the infrared (IR) part of the spectrum is blocked, and a spectral band from $\lambda = 400$ nm to 653 nm is focused onto the sample. Use of this spectral range ensures optical excitation of monolayer MoS₂ above the direct band gap. The power of the exciting light is adjusted using neutral density filters.

2.4. Catalytic activity

The catalytic activity of MoS₂ with varying layer numbers is characterized by linear sweep voltammetry (LSV). The exchange current density of individual MoS₂ flakes is normalized to their surface area and background corrected by the small current of the carbon based working electrode. The exchange current density j and the required overpotential η to reach a current density of $j = 10 \text{ mA cm}^{-2}$ is used as a figure of merit for the overall catalytic performance. We note that all potentials applied versus the reversible hydrogen electrode (RHE) correspond directly to the overpotential to drive the HER. Thus, all applied potentials are called overpotential in the following. Moreover, an iR-correction is neglected in the discussions, because the electrolyte 1 M H₂SO₄ exhibits a high proton conductivity [56].

The electrode activity or the intrinsic activity of each active site is expressed by the turn over frequency (TOF). The latter provides the information about the processes taking place at every active site. However, it is challenging to determine this value for TMDs because of the small size of the flakes. In literature, most measurements describe the catalytic activity of the whole electrode surface containing a large amount of different TMD flakes that are averaged. The small active area is an advantage of the presented μ -cell approach. Therefore, we are able to give a good estimate of the catalytically active area for just single MoS₂ flakes. Moreover, we can calculate the average turn over frequency by assuming a constant density of active sites SA^{-1} :

$$\text{TOF}(\eta) = \frac{j(\eta)}{2e} \cdot \frac{A}{S}, \quad (1)$$

with the term $2 \cdot e$ accounting for the two elementary charges e necessary for the HER, A the active area of catalyst and S the number of active sites.

3. Results

3.1. Photoluminescence and Raman measurements with and without electrolyte

Fig. 2(a) shows photoluminescence spectra of a monolayer MoS₂ under vacuum conditions (black) and when the monolayer is immersed in 1 M H₂SO₄ (red). The photoluminescence energy is consistent with optical recombination processes at the K and K' points at the boundary of the first Brillouin zone in reciprocal space. We observe that the photoluminescence of the MoS₂ flakes is significantly altered in the electrolytes and that the alteration is most pronounced for the monolayers. The observed photoluminescence variation with and without electrolyte is in agreement to a molecular gating e.g. by H₂O molecules that effectively remove electrons from the MoS₂ [51]. In particular, in vacuum, the photoluminescence exhibits a rather broad asymmetric emission peak (Fig. 2(a)), which can be explained by a significant contribution from trion states to the overall emission. This finding points towards a high intrinsic charge carrier density of the MoS₂ flakes [57]. Accordingly, the emission energy appears to be red-shifted which can be explained by a doping induced band gap renormalization and a reduction of the exciton binding energy [58–60]. In comparison, in the electrolyte, the emission peak is blue-shifted and the FWHM of the photoluminescence intensity is reduced. This is consistent with the interpretation that the spectral weight of the trion is small compared to the neutral exciton. Fig. 2(b) shows the PL intensity map for the MoS₂ flake in vacuum. As can be seen, the flake exhibits mono-, bi-, and trilayer sections. The photoluminescence intensity is maximum for the monolayer section, which is typically referred

Fig. 2. Optical in-situ characterization. (a) Normalized photoluminescence spectra of a monolayer MoS₂ measured in vacuum (black) and immersed in 1 M H₂SO₄ (red). (b) Photoluminescence intensity map of an exfoliated MoS₂ flake under vacuum conditions. (c) Normalized Raman spectra of the monolayer section in (b) for vacuum conditions (black) and immersed in 1 M H₂SO₄ (red). Experimental parameters are for vacuum (electrolyte) condition: 0.5 mW laser power, 1 × 120 s (1 × 300 s) integration time, and $p \sim 10^{-3}$ mbar. (d) Raman map of the same flake shown in (b) under vacuum conditions. The energy difference $\Delta E = |E(A_{1g}) - E(E'_{2g})|$ between the A_{1g} and E'_{2g} phonon modes in units of wavenumbers (cm^{-1}) is color-coded. All spectra are recorded using a laser with a wavelength of 488 nm. Supporting substrate: polished glassy carbon.

to as a transition from an indirect to a direct band gap from multi- to monolayers (e.g. [7]).

Fig. 2(c) displays typical μ -Raman spectra of MoS₂ with E' and A'_1 modes measured under vacuum condition (black spheres) and in the electrolyte (red spheres). The two Raman modes represent active zone center phonons characteristic for MoS₂. Whereas the in-plane LO phonon mode with E'_{2g} (E') symmetry for few-layer (monolayer) stiffens with decreasing number of layers, the homopolar out-of plane mode with A_{1g} (A'_1) symmetry for few-layer (monolayer) softens with decreasing number of layers [61]. Therefore, the frequency difference serves as a sensitive measure for the number of layer. This can be seen in Fig. 2(d), which depicts a Raman map of the same MoS₂ flake as in Fig. 2(b). The energy difference between the A_{1g} (A'_1) and the E'_{2g} (E')-modes is minimal for the monolayer section. In Fig. 2(c), individual Raman spectra for a monolayer section of the MoS₂ flake in vacuum (black spheres) and immersed in 1 M H₂SO₄ (red spheres) are plotted. The solid lines are fits to the spectra using two Lorentzians, respectively. The fit parameters are summarized in Table 1. The energy of the E' mode is identical for both vacuum and electrolyte environments, whereas the A'_1 mode is blue-shifted by more than 2 cm^{-1} within the electrolyte. Simultaneously, the FWHM is reduced. Both findings support the interpretation that the electron density of the MoS₂ flake is strongly reduced when the flake is immersed in the electrolyte. The extracted blue-shift of the A'_1 mode points towards a reduction of the charge density by around two orders of magnitude [62,63]. We explain this reduction by a charge transfer towards the electrolyte due to polar molecules such as H₂O [51,63]. An interesting related aspect is the impact of this reduction onto the catalytic activity due to an overall reduced electron mobility and hence reduced charge transfer rate at the catalytically active sites.

We further note that the phonon modes are not only a measure for the number of layers. The modes are also sensitive to structural changes, defects, strain, temperature as well as the mentioned doping level of the investigated MoS₂ flakes [19]. Therefore, an in-situ μ -Raman measurement as in Fig. 2(c) is a very sensitive and powerful method to investigate the intactness of the investigated MoS₂ flakes. In particular, we observe no structural changes, degradation or corrosion from the photoluminescence and Raman measurements in the aqueous electrolyte (1 M H₂SO₄). For monolayers, we do not observe evidence for degradation after more than 100 cycles taking roughly 1 hr. Bulk flakes are found to be stable for several hours, and even after drying them and immersing them again in the electrolyte we do not observe signatures for degradation. Monolayers, however, degrade after electrochemical measurements by drying and storing them in ambient conditions in agreement with the reports by Yu et al. [49].

3.2. Electrochemical characterization without illumination

Fig. 3(a) presents linear sweep voltammetry (LSV) measurements for MoS₂ of different layer thicknesses ranging from 1L, 2L and bulk as well as for a graphenic carbon electrode without any further catalyst on top and with a 20 nm thick layer of Pt as references. The polarization curves show the forward scan for an established equilibrium after 100 cycles. We find that the current densities of the investigated MoS₂ flakes are significantly higher compared to the carbon substrates. For Fig. 3(a), the measured current densities of the utilized graphenic carbon are close to zero in the investigated range of applied potentials (black line). In the shown representation, the polarization curves of the MoS₂ flakes are normalized to the surface area of the individual MoS₂ flakes and background corrected. The latter means that the small current value of the carbon electrode is subtracted for each voltage.

We observe the largest current densities for monolayer MoS₂, followed by bilayer and bulk flakes. At zero overpotential ($\eta = 0 \text{ V}$),

Table 1
Fitting parameters for Raman spectra in Fig. 2(c).

	E' mode		A ₁ ' mode		$\Delta\nu(A_1'-E')$ (cm ⁻¹)
	ν (cm ⁻¹)	FWHM (cm ⁻¹)	ν (cm ⁻¹)	FWHM (cm ⁻¹)	
vacuum	385.6	2.1	403.1	4.8	17.5
1 M H ₂ SO ₄	385.7	2.0	405.5	3.4	19.8

all current densities are close to zero. With an increasing overpotential, the current densities for all MoS₂ flakes increase. At an overpotential of $\eta = -0.3$ V, the current densities reach values of $j_{\text{bulk}} = -17 \text{ mA cm}^{-2}$, $j_{2\text{L}} = -32 \text{ mA cm}^{-2}$ and $j_{1\text{L}} = -65 \text{ mA cm}^{-2}$ for the bulk, bilayer and monolayer flakes, respectively. Higher overpotentials cause a larger energy shift between the band edges of the catalyst and the redox potential. The electron transfer across the electrode-electrolyte interface is facilitated, and the current density increases. We find, that the onset potential is shifted to lower overpotentials for reduced number of MoS₂-layers. The onset decreases from -0.12 V for the bulk material to approximately -0.03 V for the monolayer. The values are deduced by fitting the data to a bi-exponential Butler-Volmer model, considering anodic and cathodic currents.

Generally, capacitive currents may constitute a significant fraction of the total current in the onset region [4]. Therefore, we use the values of overpotential which is needed to achieve a current density of 10 mA cm^{-2} [41,64] as figure of merit. Fig. 3(b) compares the corresponding values of the figure of merit for the investigated materials. To start with, the value for the graphenic carbon electrode is around -0.87 V exceeding the values found for the other materials. This approves the low catalytic activity of the substrate and hence, its low influence on the HER of the investigated MoS₂ flakes. For exfoliated bulk MoS₂, we find a value of -0.27 V. By decreasing the number of layers, the figure of merit of the investigated MoS₂ flakes decreases to -0.19 V (-0.17 V) for bilayer (monolayer). Only nanoparticles of MoS₂ tend to have similar low overpotentials at 10 mA cm^{-2} (-0.15 V). For comparison, the reference sample with Pt achieves values of -0.1 V, which is consistent with literature values [4,44,65].

The extracted values for the Tafel slopes shown in inset of Fig. 3(b) are 114 mV/dec, 210 mV/dec and 149 mV/dec for bulk, bi- and monolayer MoS₂, respectively. The rather high values for the Tafel slopes indicate the presence of the Volmer step describing the hydrogen adsorption to the catalyst as the rate limiting process. This is expected for high contact resistances between the MoS₂

catalyst and the working electrode causing an absence of electrons on the active sites [65]. The even higher Tafel slope for the bilayer flake might be explained by an even larger contact resistance. We would like to mention that the MoS₂ flakes are linked to the graphenic carbon substrate by van der Waals interactions, and consequently roughness of the substrate or residues, e.g. PDMS from the transfer process, are likely sources to alter the characteristic of the electric contact.

In a next step, we deduce the turn over frequency (TOF) of the MoS₂ flakes introduced above. We note that both the edge sites of MoS₂ and the sulfur vacancies at the inert basal plane play an important role for the HER [66]. We assume a constant density of sulfur vacancies of $SA^{-1} = (1.0 \pm 0.5) \cdot 10^{13} \text{ cm}^{-2}$ for our exfoliated MoS₂ flakes [67]. The number of edge sites can be estimated using a lattice constant of 0.32 nm [24] and a typical edge length in the order of $100 \mu\text{m}$. Consequently, the number of sulfur edge sites is approximately 2 orders of magnitude smaller than the number of sulfur vacancies in the basal plane. In turn, we use only the latter for the TOF calculations. Moreover, we assume that the whole measured Faradaic current contributes to the HER. All other potential reactions are neglected. For instance, we expect no diffusion limitations, because the protons have a high concentration in the utilized electrolyte. With these assumptions, we are able to deduce an overpotential dependence of the TOF for bulk-, 2L and 1L- MoS₂ flakes (Fig. 4). All TOFs are calculated and averaged using the polarization curves shown in Fig. 3(a). The TOF at 0 V reaches values of 0.5 s^{-1} for the bulk up to 1.1 s^{-1} for the bilayer. The values are in good agreement with reported ones obtained for thin layers of MoS₂ [68]. For an increasing overpotential, the TOFs of all samples increase (Fig. 4). At 0.3 V, the TOFs reach approximately $4 \cdot 10^3 \text{ s}^{-1}$, $1 \cdot 10^4 \text{ s}^{-1}$, and $2 \cdot 10^4 \text{ s}^{-1}$ for bulk, 2L and 1L MoS₂-flakes, respectively. These values are in excellent agreement with the reported values for monolayer MoS₂ by Voiry et al. [65], but rather high compared to other reports in literature with deduced TOFs of about $10\text{--}100 \text{ s}^{-1}$ [4,69].

Each of the micromechanically exfoliated MoS₂ crystals is unique as size as well as shape differ from sample to sample. Furthermore, the optoelectronic and catalytic properties depend not only on extrinsic parameters such as environment, doping or (electric) coupling to the supporting substrate but also on intrinsic properties such as quality of the bulk crystal used for exfoliation

Fig. 3. Layer dependent electrochemical characterization without illumination. (a) Polarization curves of bare graphenic carbon (GrC), bulk-, 2L- and 1L-MoS₂ flakes recorded on graphenic carbon in 1 M H₂SO₄. The curve for Pt is added as a reference value to assess the performance of the MoS₂. In all cases, the scan rate is 20 mVs^{-1} . For the MoS₂ flakes (Pt), the diameter of the active window made from glassy carbon is $100 \mu\text{m}$ ($30 \mu\text{m}$). For Pt, the whole area of the active window is covered with 20 nm of the metal, ensuring that no substrate is in contact with the electrolyte. (b) Extracted overpotentials required to reach a current density of 10 mA cm^{-2} for 1L-, 2L-, and bulk MoS₂ flakes, for Pt and for glassy carbon. The inset shows the corresponding Tafel slopes: GrC 273 mV/dec, bulk 114 mV/dec, 2L 210 mV/dec and 1L 149 mV/dec.

Fig. 4. Layer dependent TOF. Evolution of the turnover frequency with the applied overpotential of bulk-, 2L- and 1L-MoS₂ in blue, green and red, respectively. The TOFs were calculated from the polarization curves shown in Fig. 3 assuming a constant density of sulfur vacancies in the basal plane. A detailed description can be found in the following text.

Fig. 5. Surface area and circumference dependent current densities. Polarization curves of single layer MoS₂ immersed in 1 M H₂SO₄. In all cases, the scan rate is 20 mVs⁻¹. (a) Background corrected current densities normalized to the surface area of the MoS₂ flakes. Pt and GIC are included for better comparison. (b) Background corrected current densities normalized to the circumference of the flakes.

but also on defects – predominantly sulfur vacancies – or strain induced by the manual handling during exfoliation with adhesive tape and transfer by viscoelastic stamping. For this reason, several MoS₂ samples with various shapes and sizes have been prepared and investigated as described above. LSV traces taken in the dark are plotted in Fig. 5 for several MoS₂ monolayers placed on glassy carbon (GIC). The LSV characteristics for Pt and the GIC substrate are included for better comparison. To corroborate our assumption that the catalytically active sulfur vacancies dominate the activity over the active edge site, we normalize the current densities to the sample area as well as to the length of their circumference. The results are composed in Fig. 5(a) and (b), respectively. While the polarization curves nicely collapse for normalization to the flake area, there is no correlation by normalization to the circumference. This comparison confirms our assumption that the HER activity is dominated by the number of catalytic active defect sites in the basal plane and not by the active edges. To further analyze the characteristics of the different samples, the key parameters from the electrochemical characterization are summarized for 7 MoS₂ monolayer devices in Table 2. For sample 0 (data shown in Figs. 3 and 4) graphenic carbon (GrC) is used as substrate and for the other samples (B–G) glassy carbon (GIC). Size, shape and also the ratio between area and length of the edge differ over a wide range. These investigations further substantiate the claim that the sulfur vacancies at the basal plane dominate the catalytic activity. We identify, however, also some differences between the samples. Besides sample C and G with glassy carbon as substrate, the extracted current densities at an overpotential of $\eta = -0.3$ V are in good agreement and constitute between 55 and 65 mA cm⁻² for all samples independent from the used carbon substrate. The difference for sample C and G is assumed to be caused by a reduced HER activity due to less active sites, e.g. less sulfur vacancies in the basal plane. This might also be the reason for the rather large flake sizes since less defected basal planes of bulk crystals are expected to be mechanically more stable under micromechanical exfoliation. We would like to mention that

we do not see differences in the Raman spectra between the different samples indicating that the interdefect distance in all samples is larger than approx. 5 nm [70].

The comparison of the samples indicates a correlation between Tafel slopes, required overpotentials $\eta(10)$ to get a current density of $j = 10$ mA cm⁻² and the WE or the quality of the electric contact to the substrate. The MoS₂ flakes and the carbon substrate are assembled by van der Waals interactions. For this reason, not only the electrical properties but also the surface roughness of the substrate are expected to be important for the performance of the electric contact that impacts Tafel slope and $\eta(10)$. For samples B, D, E and F, $\eta(10)$ constitutes between -0.09 V and -0.15 V and for sample 0, $\eta(10)$ is significantly lower with a value of -0.03 V. For samples C and G, $\eta(10)$ is much higher with values of -0.29 V and -0.25 V, respectively. The Tafel slopes for sample 0, C and G are approx. 150 mV/dec, whereas for samples A, D, E and F more than 170 mV/dec. The lower Tafel slopes together with the higher overpotentials $\eta(10)$ to get a current density of $j = 10$ mA cm⁻² can be attributed to a higher contact resistance between MoS₂ and the glassy carbon either by less contacted area due to the roughness of the GIC surface or by residues between the two materials as described above.

3.3. Laser power dependent photo-electrochemical activity of MoS₂

In the following, the catalytic properties of bulk (few-layered) MoS₂ under illumination are discussed. The illumination is realized using a broadband white-light supercontinuum laser source with a spot diameter less than 1 μ m. The laser is focused either on the basal plane (1) or the edge (2) of the sample as indicated by circles in the image of the flake in Fig. 6(f). The catalytic properties of MoS₂ are investigated via cyclic voltammetry. In Fig. 6(a)–(d), the illumination intensity is increased from $2 \cdot 10^6$ W cm⁻² to $5 \cdot 10^6$ W cm⁻² that corresponds to power densities of $2 \cdot 10^7$ kW m⁻² to $5 \cdot 10^7$ kW m⁻². We would like to mention that this power density is beyond realistic application, but is still suitable for fundamental studies and to explore the potential of MoS₂ for photocatalysis devices. All polarization curves presented show the forward scan for an established equilibrium. During such a scan, the illumination is periodically switched on and off (black top insets in Fig. 6(a)–(d)). We clearly see an increase of the currents when the laser is switched on (red) compared to the case when it is switched off (blue). The currents are absolute values, neither background corrected nor normalized by surface area. For zero overpotential $\eta = 0$ V, all currents are close to zero. For high overpotentials, the currents increase and reach a maximum value of approximately -3 nA at $\eta = -0.4$ V. For all data, the polarization curves without illumination are almost identical. This demonstrates a good reproducibility of the experimental methodology. In principle, the LSV curves under illumination have the same

Table 2

Key parameters extracted from electrochemical characterization in the dark for several 1L MoS₂ flakes with different aspect ratios placed on graphenic carbon (GrC) or glassy carbon (GIC), respectively. The current densities j at an overpotential of $\eta = -0.3$ V are given for a normalization of the measured current to either the area or the length of the circumference of a flake. Sample C and G are rather large monolayer flakes and the outstanding low current densities points towards a reduced number of catalytically active sites on the basal plane. Overall, we find a much better correlation between the samples for normalization to the areas compared to normalization to the perimeter. The deviations in the potential to achieve a current density of $j = 10$ mA cm⁻² coincides with the variations in the Tafel slopes and are assumed to be correlated with the quality of the electric contact to the working electrode that is assumed to be better for lower Tafel slope values.

sample	area/circumference [μ m ²]/[μ m]	$-j(-0.3 \text{ V})$ [mA cm ⁻²]/[nA μ m ⁻¹]	$\eta(10 \text{ mA cm}^{-2})$ [V]	Tafel slope [mV/dec]
0 (GrC)	108/70	65/0.1	-0.03	149
B (GIC)	149/88	55/0.9	-0.09	221
D (GIC)	30/32	55/0.5	-0.14	178
E (GIC)	94/89	65/0.7	-0.12	171
F (GIC)	574/196	60/1.7	-0.15	171
C (GIC)	236/111	15/0.2	-0.29	146
G (GIC)	1668/387	24/0.96	-0.25	141

Fig. 6. Laser power dependent photo-activity. Illumination intensity dependent polarization curves of bulk MoS₂ on unpolished glassy carbon in 1 M H₂SO₄. (a)–(d) Illumination intensity dependent currents as measured (without background correction and normalization). The scan rate is 5 mVs⁻¹. The illumination intensity is increased from $2 \cdot 10^6 \text{ W cm}^{-2}$ to $5 \cdot 10^6 \text{ W cm}^{-2}$. Dark current and current under illumination are shown in blue and red, respectively. The black lines on top represent the periodic switching of the laser. Illumination and dark periods are indicated by higher and lower values, respectively. (e) Illumination intensity dependent current gain. The difference signals from (a)–(d) are normalized to the size of the laser spot (diameter around 1 μm). The striped areas between upper and lower bounds on the difference current represent the rather high uncertainties. (f) Optical microscope image of the investigated flake. The inset shows the investigated part of the flake and the white circles indicate the position of the laser spots.

shape as the dark currents within the apparent noise. Moreover, with increasing illumination intensity, the difference between the dark and illuminated curves rises. Fig. 6(e) depicts the illumination intensity dependent current density gain for illumination at the basal plane (spot 1) of the bulk sample pictured in Fig. 6(f). In order to determine the current densities, the difference signals from (a)–(d) are normalized to the laser spot size of about 1 μm . The laser intensities of $2 \cdot 10^6 \text{ W cm}^{-2}$, $3 \cdot 10^6 \text{ W cm}^{-2}$, $4 \cdot 10^6 \text{ W cm}^{-2}$ and $5 \cdot 10^6 \text{ W cm}^{-2}$ are shown in black, blue, green, red, respectively. Due to the rather high uncertainties, the calculated errors are included as striped areas. For an overpotential of $\eta = -0.4 \text{ V}$, the current density gains are approximately 11 mA cm⁻², 20 mA cm⁻², 27 mA cm⁻² and 42 mA cm⁻² for the above given illumination intensities. Within the range of investigated intensities, the current density increases approximately linear with intensity. In other words, the difference between the blue, green and red curves stays constant within Fig. 6(e). For all illumination intensities, an onset of a saturation is observed around -0.3 V . Diffusion limitations can

be neglected, again due to the high concentration of protons in the electrolyte [71]. The maximum current density can be increased with increasing light intensity. This suggests that all available charge carriers at the active sites react for high overpotentials, and that the slow catalytic processes (μs – ms) start to limit the overall dynamics. In addition, the maximum current density can be further increased by illumination of the edge of the bulk sample consisting of steps with small terraces from bulk to only a very few layers as shown in Fig. 6(f) (spot 2). Under highest illumination intensity and at an overpotential of $\eta = -0.4 \text{ V}$, a current density gain of 70 mA cm^{-2} is observed that is almost doubled compared to the bulk value of 42 mA cm^{-2} . The increased photo-activity is assumed to be due to an effective separation of the photo-generated electron hole pairs by internal electric fields across the individual steps [72]. Due to the thickness-dependent band structure of MoS₂ these steps effectively function as multiple lateral heterojunctions [72] reducing the loss of the photo-generated charge carriers by radiative recombination. Hence, more electrons reach the catalytically active sites and contribute to the HER. Within the experimental error, we identify an increase of the current densities under illumination in LSV measurements for a MoS₂ monolayer, too. The illumination dependent increase in the current densities for the highest illumination intensity is found to be approximately 6 times higher for the monolayer compared to the bulk. Overall, the uncertainties in the photocurrent amplitude are significantly larger for the monolayer flake since the flake size is much smaller compared to the bulk flake. Hence, the illumination dependent increase in the currents is close to the noise level of the experimental setting. Reasons for the enlarged photocurrent for the monolayer compared to the bulk might be caused by a higher absorbance for monolayers [11,19]. Overall, the increase in current density is rather low compared to the high illumination intensities. Due to the combined effect of exciton binding energy, exciton localization and short lifetime in the order of picoseconds and the slow catalytic processes in the order of μs to ms , the majority of photo-generated charge carriers are lost by radiative or non-radiative relaxation processes [31]. These loss channels are expected to be significantly reduced for lateral or vertical van der Waals heterostructures with a type-II band alignment such as WS₂/MoS₂ [73]. The in-plane electric field across the heterojunction will effectively separate the photo-generated charge carriers causing an accumulation of electrons in one layer and of holes in the other layer.

4. Discussion

Generally, our observations on the catalytic properties of MoS₂ are in good agreement with literature values. Most publications show a reduced current density for an increasing number of layers and an elevated onset potential [4,35], which can be explained by a reduced electron transfer to the active sites on the surface of the catalyst [49,54]. The vertical interlayer potential barrier in the bi- and few-layers hinders the electron transfer between two consequent layers. With increasing number of layers the overall transition probability decreases drastically. In this picture, the limited electron density at the active sites limits the current density. The obtained current densities for the single layer flakes are in good accordance with other more complex MoS₂ structures (70 – 80 mA cm^{-2}) [65,68]. These structures exhibit low numbers of MoS₂-layers and a large amount of edge- and defect-sites, which seem to be highly catalytically active.

The extracted TOF, the number of produced molecules per active site per second, yield values higher than 10^3 s^{-1} at an overpotential of -0.2 V vs. RHE for mono- and bi-layer MoS₂. These numbers are in good agreement with reported values for 1L MoS₂ by Voiry et al. [65], but high compared to other reports in literature with

TOFs of about $10\text{--}100\text{ s}^{-1}$ [4,69]. Overall, the TOF increases for more negative overpotentials as expected, and the determined TOF at 0 V is in the range of about 1 s^{-1} , again in good agreement with literature values for thin MoS_2 layers [68]. Furthermore, with decreasing number of layers, the TOFs increase in agreement with the trend of the observed onset potential and the defined figure of merit, the overpotential η required to reach a current density of $j = 10\text{ mA cm}^{-2}$. Given the investigation of single flakes with well-known geometry and edge to surface ratio, we attribute the catalytic activity mainly to sulfur vacancies in the basal plane acting as active sites. We would like to mention that for the evaluation of the TOF, the whole measured Faradaic current is assumed to contribute to the HER. Another uncertainty in the evaluation of TOF is the estimation of the density of catalytically active sites. We assume a constant density of sulfur vacancies for exfoliated MoS_2 of $\text{SA}^{-1} = (1.0 \pm 0.5) 10^{13}\text{ cm}^{-2}$ [67] that is estimated to be 2 orders of magnitude larger than the number of edge sites for the investigated MoS_2 flakes deduced from the determined circumference of the MoS_2 flakes. However, even within the large uncertainties in the estimation of catalytically active sites at the basal plane, it is obvious that the dominant contribution to the HER is from the MoS_2 basal plain and not from the edge sites. The latter would result in unphysical large numbers for the TOF, therefore the estimated numbers of catalytically active sulphuric vacancies is used to calculate the TOF.

In view of solar driven hydrogen evolution, we also report on the photocatalytic activity of few-layer MoS_2 under white light illumination, an important factor for future application in the field of solar energy conversion. By illumination above the band gap of MoS_2 , photogenerated electrons from the valence band are promoted to the conduction band and expected to diffuse to active sites. These charge dynamics should increase the catalytic activity. Indeed, we experimentally observe an increase of the catalytic HER activity under illumination. The clear and linear power dependence of this increase substantiates that photogenerated electrons transferred to the active site enhances the catalytic activity of MoS_2 . This observation corroborates the great potential of MoS_2 for direct sunlight driven production of hydrogen gas by water splitting.

The developed photo-electrochemical μ -cell enables not only the ultra-sensitive electrochemical measurement of individual MoS_2 flakes exhibiting low signal due to their small surface areas, but also for illumination of the catalyst during electrochemical investigations and in-situ Raman and photoluminescence measurements. From the complementary inspection of the samples by optical characterization measurements, we do not find evidence that the working samples are significantly degraded during the photo-electrochemical measurements. Furthermore, a comparison of Raman and photoluminescence measurements of the MoS_2 flakes in vacuum and immersed in the electrolyte indicate that the intrinsic electron density is reduced by at least two-orders of magnitude in the presence of the electrolyte most likely due to a molecular gating effect due to the dipolar moment of some molecules, e.g. H_2O [63]. An interesting related aspect is the impact of this reduction onto the catalytic activity due to an overall reduced sheet conductivity and hence reduced charge transfer rate at the catalytically active sites [65]. In addition, there are less intrinsic electrons available that can be promoted to the active sites. Substitutional doping of MoS_2 might be a possible route to increase the catalytic activity of MoS_2 . In this context, another source for improvement of the electrochemical performance can be the electronic coupling between carbon based working electrodes [65] to provide efficient electron transfer rate from the working electrode to the electrolyte. As already discussed as source for the reduced catalytic activity for MoS_2 few-layers compared to monolayers, also the electron transfer rate across the van der Waals gap between

working electrode and MoS_2 is expected to limit the overall device performance. The coupling between substrate and MoS_2 can be increased e.g. by careful cleaning process to avoid e.g. water, resist residues or other dirt at the interface and by moderate annealing steps.

An important step to enhance the photo-catalytic performance of a device is the successfully separation of photogenerated electron-hole pairs and their promotion to catalytic active sites as already indicated by the comparison of illumination dependent measurements of MoS_2 bulk and bulk terraces. A promising way is the preparation and implementation of vertical or lateral van der Waals (vdW) heterostructures [19,74,75] into the PEC μ -cell. At the interface between two different semiconducting TMDs a type-II band alignment results in a promotion across the heterojunction of electrons to one material and hole to the other one [19]. In such a way, photogenerated electron-hole pairs are efficiently separated across the heterojunction what is expected to result in an increased number of charge at the active sites and therefore, in an increased photo-catalytic activity of heterostructures compared to the two individual 2D flakes.

5. Conclusion

In summary, we studied the photo-electrochemical properties of individual micromechanically exfoliated MoS_2 mono-, bi- and few-layer flakes towards solar driven HER. A PEC μ -cell is developed to achieve the required sensitivity in electrochemical measurements of individual just a few tens of micrometer large MoS_2 flakes together with full optical access with $1\text{ }\mu\text{m}$ resolution. By placing the PEC under a microscope, not only electrochemical measurement under site selective illumination of edge or basal planes can be performed, but also in-situ μ -Raman and photoluminescence measurements. Therefore, the photo-physical system immersed in the electrolyte ($1\text{ M H}_2\text{SO}_4$) can be tested in real operating conditions. In agreement with recent reports in literature, we find that the catalytic activity for HER is increasing with decreasing number of layers. Particularly, the exchange current density is one order of magnitude larger for monolayer MoS_2 compared to bulk material. The onset potentials scale monotonously with the number of layers, too, and are largest for bulk material. The reduced activity can be assigned to a reduced electron transfer between the individual van der Waals coupled layers due to hopping transport. Estimating the TOF by taking into account the edge-to-surface ratio from the well-known geometries of the investigated flakes, the catalytic activity seems to be dominated by the catalytically active sulfur vacancies at the basal planes and not by the also active edge sites. At an overpotential of -0.2 V vs. RHE, the TOF for all investigated number of layers is larger than 10^3 s^{-1} . The catalytic activity measured by the cathodic current in cyclic voltammetry is increased for all applied overpotentials by white-light illumination with a nearly linear dependence from the light intensity. From complementary Raman and photoluminescence measurements, we do not see evidence for degradation processes for much more than 100 cycles and we learned that the electron density for MoS_2 flakes immersed in the aqueous electrolyte is reduced by at least two orders of magnitude. The reduced charge carrier density is discussed as well as the implementation of van der Waals heterostructure to spatially separate photo-generated electron hole pairs to increase the amount of electrons promoted to the active sites. Overall, our results demonstrate the great potential of MoS_2 and related van der Waals heterostructures for future application in solar energy conversion and storage with photo-catalytic devices made from rather cheap earth abundant and sustainable materials.

Acknowledgements

We acknowledge NKT photonics for support with the super continuum laser source for broadband white light illumination with high light intensity. We further acknowledge financial support by Deutsche Forschungsgemeinschaft (DFG) via excellence cluster 'Nanosystems Initiative Munich' (NIM), through the TUM International Graduate School of Science and Engineering (IGSSE) and DFG projects WU 637/4-1, HO3324/9-1 and BaCaTeC.

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