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Photocatalytic Stability of Single- and Few-Layer MoS₂

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ABSTRACT

MoS₂ crystals exhibit excellent catalytic properties and great potential for photo-catalytic production of solar fuel such as hydrogen gas. In this regard, the photocatalytic stability of exfoliated single- and few-layer MoS₂ immersed in water is investigated by μ -Raman spectroscopy. We find that while the basal plane of MoS₂ can be treated as stable under

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3 photocatalytic conditions, the edge sites and presumably also defect sites are highly affected by a
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5 photo-induced corrosion process. The edge sites of MoS₂ monolayers are significantly more
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7 resistant to photocatalytic degradation compared to MoS₂ multi-layer edge sites. The photo-
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9 stability of MoS₂ edge sites depends on the photon energy with respect to the band gap in MoS₂
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11 and also on the presence of oxygen in the electrolyte. These findings are in agreement with an
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13 interpretation as oxidation process converting MoS₂ into MoO_x in the presence of oxygen and
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15 photo-induced charge carriers. The high stability of the MoS₂ basal plane under photocatalytic
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17 treatment with visible light irradiation of extreme light intensities in the order of $P \approx 10\text{mW}/\mu\text{m}^2$
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19 substantiates MoS₂'s potential as photocatalyst for solar hydrogen production.
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26 MoS₂ is a semiconducting two-dimensional 'van der Waals' material with outstanding
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28 electronic,^{1,2} optical³⁻⁵ and catalytic⁶⁻⁸ properties. MoS₂ undergoes a transition from an indirect
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30 to a direct band gap semiconductor in the single layer limit³ with a band gap of $E_{\text{gap}} = 1.9\text{ eV}$.⁴
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32 The high sunlight absorption of up to 10% for atomistic thin layers⁹ makes MoS₂ single- but also
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34 few-layers a promising material for optoelectronic applications and solar energy harvesting. For
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36 pH values between 0 and 7, a single layer of MoS₂ exhibits a suitable band edge alignment with
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38 respect to the redox potentials of the hydrogen evolution (H^+/H_2) (HER) and oxygen evolution
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40 ($\text{O}_2/\text{H}_2\text{O}$) (OER) reaction,^{10,11} which is an unambiguous requirement of a photo-catalyst for solar
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42 driven water splitting with an earth abundant electrolyte such as river or sea water. The
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44 peculiarity of MoS₂ is that it holds all requirements for a monolithic device for solar water
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46 splitting, because MoS₂ based materials offer not only catalytic activity,⁶⁻⁸ but also high
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48 absorption efficiency in the visible range.⁹ The basal planes feature the functionalization as photo
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50 absorber, built-in electric fields induced *e.g.* by lateral pn-junctions separate the e-h pairs¹² and
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52 the Mo edge along (10 $\bar{1}$ 0) direction is catalytically active.¹³ If a photon is absorbed by an
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interband absorption process, the incoming photon promotes an electron from the valence band to the conduction band leaving a hole in the valence band. Such photoexcited electrons can be directly transferred from the conduction band to the energetically preferred potential of the proton reduction. The transferred electron drives the hydrogen evolution reaction. The same applies for the photoexcited holes and the oxygen evolution reaction. Thus, single-layer MoS₂ serves as an ideal candidate for an efficient photocatalyst powering the sunlight-driven photocatalytic water splitting reaction.

Considerable efforts have been made to investigate the catalytic activity of various MoS₂ nanostructures such as nanoparticles,^{6,14,15} mesopores,¹⁶ nanowires,¹⁷ amorphous MoS₂,^{18–20} thin films²¹ and their nanostructure,¹³ MoS₂/graphene heterostructures,²² chemically exfoliated MoS₂ layers,^{7,23,24} metal nanoparticle-decorated MoS₂²⁵ and MoS₂ grown by chemical vapor deposition.⁸ Nonetheless, the long term photo-catalytical stability, and not only catalytical stability, is a crucial but often ignored requirement for photo-absorber and catalytic materials in water splitting devices.²⁶ For electro-catalysts, potential cycling with different scan rates and potential ranges in the dark are the most common methods to address the catalytic stability.^{21,22,27} For photocatalytically active materials, however, the catalytic stability in the presence of light irradiation is essential since catalytically stable materials are not per se stable under light irradiation. MoS₂ has been integrated in a silicon tandem photo-electrochemical water splitting device acting as electro-catalyst and simultaneously as corrosion protection for the Si photo-absorber.^{28,29} Stability in HER conditions measured by cyclic voltammetry under 1 sun red irradiation ($E_L < 1.95$ eV) has been demonstrated.²⁸ Bulk and nanostructured MoS₂ materials are efficient and stable photo-cathodes showing sun-light driven HER in a monolithic metal-free

architecture, however progressive photocorrosion under OER conditions limits its functionalization as photoanode because of anodic photo-corrosion along the $\langle 11\bar{2}0 \rangle$ direction.¹³

In this letter, we introduce μ -Raman spectroscopy in aqueous environment to microscopically investigate the stability of well-defined high-quality single- and few-layer MoS₂ crystals under photocatalytic conditions. Of particular interest is the role of the number of layers and hence the impact of the nature of the band gap as well as the role of exciton effects on the stability of the basal plane and edge sites in an earth abundant electrolyte - fresh water. The measurement scheme applies a monochromatic irradiation with high light intensities of $P \approx 10 \text{ mW}/\mu\text{m}^2$ what would be equivalent to 10^7 suns. Photostability under such challenging conditions certifies a material as durable and can be treated as long-term stable. Long-term stability of MoS₂ in aqueous solutions and in high humidity is not only important for solar-driven water splitting, but also for sensing applications, for functional corrosion protection layer and in general for electronic applications.

Thus, the photo-degradation of MoS₂ flakes immersed in water is *in situ* monitored with a high lateral resolution of about 300 nm and a time resolution of a few seconds. The photo-stability and the evolution of photo-degradation of MoS₂ in presence of water as electrolyte is studied in dependence of crystallographic site, number of layers, energy and intensity of the exposing light as well as the presence of oxygen gas in the electrolyte. We find that the more catalytically active edge sites^{30–33} show a much higher photo-degradation compared to the basal plane (a.k.a. terrace sites). We further observe that edge sites of MoS₂ monolayers exhibit a much lower degradation rate compared to edge sites of few-layers with corresponding decay rates of $\tau = 45 \text{ min}$ and $\tau = 1 \text{ min}$ for mono- and bilayer, respectively. Photo-degradation for flakes immersed in water takes place only under irradiation with energy larger than the band-gap of MoS₂. In addition, in our

experiments the presence of oxygen in the electrolyte is required to observe a considerable photo-degradation of the flakes edge sites. Overall, MoS₂ basal planes exhibit superior photo-stability in aqueous environment under extreme irradiation intensities and even the catalytically active edge sites are rather stable in the absence of O₂ in the electrolyte.

RESULTS AND DISCUSSION

The investigated MoS₂ flakes are micromechanically exfoliated from bulk crystals and transferred to Si/SiO₂ substrates by a dry stamping technique.³⁴ The SiO₂ thickness of 275 nm provides an excellent visibility contrast^{35,36} so that even single layers of MoS₂ are clearly distinguishable from bi-, tri- and few-layer regions by optical microscopy as well as by monochromatic reflectivity measurements. The samples are characterized prior and after the photocatalytic degradation studies by a set of microscopy and spectroscopy tools under ambient conditions. Size and changes in geometry are investigated by contrast images from optical microscopy, and monochromatic reflectivity measurements by scanning a laser with low power and high sampling rate over the sample and recording the reflected light with a photo-diode. The morphology is investigated by atomic force microscopy. From spatially resolved Raman spectroscopy, we gain access to various parameters such as the number of layers,³⁷ doping level³⁸ and even the presence of adsorbates.³⁹ Furthermore, the degradation process is monitored *in situ* by real-time Raman spectroscopy utilizing the irradiation laser of the photo-degradation studies for the Raman measurements. The most important figure of merit in the presented experiments is the time evolution of the phonon-mode energies as fingerprint for the number of layers and the change in the integrated intensity of the individual modes as sensor for the amount of unaffected and not photo-degraded crystalline volume. A high spatial resolution for all optical measurements in liquid is realized through a laser spot size of about 300 nm given by a water-

dipping objective and mounting the sample on x - y - z piezo scanner. If not stated otherwise, deionized (DI) water is used as electrolyte.

Figure 1 demonstrates the photo-stability of a mono-/trilayer flake under irradiation with a focused laser with energy $E_{laser} = 2.54$ eV. This energy is larger than the band-gap of MoS₂ ($E_{gap} = 1.9$ eV). The region of interest (ROI) is marked on the optical microscopy image in Figure 1(a). The laser is scanned across a field consisting of monolayer (1L) and trilayer (3L) parts along the path shown on the reflectivity image in Figure 1(b) (on the right). The laser with a power of $P_{laser} = 1$ mW is kept at each spot for 20 s, and the step size during the scanning process is 250 nm. The sample is completely immersed in DI water during the whole scan. Figure 1(b) shows the reflectivity image taken prior (left side) and after exposure to laser light (right side). The right side discloses that the whole scanned 3L region is thinned down, whereas part of the 1L region seems to be unaffected. Other parts of the monolayer region are missing. In a next step, Raman measurements in ambient conditions are recorded on several positions on the MoS₂ flake [Figure 1(c)]: untreated 3L region (◆), thinned 3L region (▲), affected 1L (●) and untreated 1L region (■). The two characteristic zone-center phonons of MoS₂ are observable in the spectra. The E_{2g}^1 mode is an in-plane mode, with the atoms oscillating parallel to the basal plane and the A_{1g} mode is an out-of-plane oscillation with the sulfur atoms oscillating in opposite direction as sketched in Figure 2. The Raman measurements confirm the observation already seen from the reflectivity measurements. The Raman spectrum within the thinned area (▲) matches that of a monolayer, except a slight shift of the A_{1g} mode towards higher wavenumbers. This upshift in energy of ~ 0.3 cm⁻¹ can be explained by a decreased charge carrier density, consistent with an increased number of adsorbed molecules on defect sites.^{39–41} The reminiscent weak Raman intensities at the degraded monolayer region (●) is either attributed to a diluted amount of residual MoS₂

nanoflakes or to the fact that the spatial resolution of the water dipping objective is decreased by the measurements without liquid. The Raman spectra further demonstrate that the non-exposed 3L (◆) and 1L areas (■) are unaffected and consequently stable in water without illumination.

To study the photo-corrosion process in more detail, we repeatedly record Raman spectra on a different sample with bi-layer MoS₂ edges as well as basal planes. Again, the excitation energy is chosen to be above the band gap ($E_{laser} = 2.54$ eV). The measurements are carried out for various light intensities on various spots containing edge or terrace sites exemplarily demonstrated on the flake shown in Figure 2(a). The temporal evolution of energy as well as intensity of the two relevant phonon modes A_{1g} and E¹_{2g}, whose oscillation schemes are sketched in Figure 2(b), enable us to *in situ* monitor the photo-induced degradation process with a high spatial resolution by Raman scattering. Figures 2(c) and (d) depict the temporal evolution of the integrated intensities of the phonon modes recorded on the edge sites marked in Figure 2(a) for different light intensities. For clarity and better comparability, the peaks are normalized to their initial intensity. The related Raman spectra are plotted in Figure 2(e) for $t = 0$ sec (◆) and in Figure 2(f) after $t \approx 1$ min (○). At the beginning of the measurement ($t = 0$ sec) marked by (◆) in Figures 2(c,d), the energies of the relevant phonon modes are unambiguously corresponding to those of bi-layer MoS₂ [Figure 2(e)]. After approximately 1 minute, marked by (○) in panels (c,d), the signal of both Raman modes drop to about 50% of the initial intensities. Simultaneously, the E¹_{2g} Raman mode is blue-shifted and the A_{1g} Raman mode is redshifted. This change in the photon energies definitely marks the transition from a MoS₂ bi-layer to a MoS₂ monolayer³⁷ after ~1 min of light exposure [Figure 2(f)]. The photo-induced transition from bi- to monolayer MoS₂ is in line with the fact that the recorded Raman signals of both phonon modes disclose two distinct degradation rates. These rates exhibit an exponential decay rate of $\tau \approx 1$ min and $\tau \approx 45$ min,

respectively. Therefore, the initial fast decay rate can be interpreted as the stability of the bi-layer edge site, whereas the much slower decay rate is the stability of the monolayer. For comparison, Figure 2(g) depicts the temporal evolution of the normalized integrated intensity of the silicon TO-phonon mode. The intensity of the Si-phonon mode increases by a similar amount as the intensity of the two MoS₂-phonon modes decreases approaching the intensity value of the Si-mode on the pristine substrate. This opposite trend of the intensities of Si and MoS₂ phonon modes, respectively, corroborates the above given interpretation that the drop in intensity of the Raman modes of the photo-excited MoS₂ is because of photo-degradation of the material and that it is not caused by spurious effects like the loss of laser focus. The overall exponential decay is power independent between 0.5 mW and 1.5 mW [Figures 2(c) and (d)]. This is interpreted such that the corrosion process is already saturated with a laser power of 0.5 mW. The photo-degradation is most likely limited by a rather slow oxidation rate linked to the density of mobile holes η_{th} in MoS₂, but not directly linked to the absolute density of photo-excited charge carriers η and the oxidation rate is presumably also affected by the diffusion of reactive species present in the electrolyte. The rate is expected to be slower than the turn over frequency (TOF) for the HER reported to be $\text{TOF} = 0.02 \text{ s}^{-1}$ per MoS₂ edge site.³⁰ The density of photo-induced e-h pairs constitutes approximately $\eta > 10^{11} \text{ cm}^{-2}$ for a spot diameter of $\sim 300 \text{ nm}$, laser wavelength of 488 nm , an absorption efficiency of $\sim 10\%$ and an e-h recombination slower than 1 ps .⁴² The number of freely mobile holes η_{th} is expected to be larger for the bilayer because of the combined effect of a reduced exciton binding energy from 0.64 eV ⁴³ for the monolayer to less than 0.21 eV (number for MoSe₂, similar value expected for MoS₂)⁴⁴ for bilayers and by an increased lifetime of the holes as expected for an indirect bandgap semiconductors.

We now reveal the role of number of layers as well as the difference between edge and terrace sites for the photo-corrosion process. We illuminate several MoS₂ samples consisting of mono- and few-layer regions with three different geometries: either scanning the laser across a field on the sample in a specific pattern as shown *e.g.* in Figure 1, illuminating a spot either on the samples' edge or basal plane (see Figure 2) or scanning the laser along a line from the substrate onto the flake across steps from mono- to multilayer region or *vice versa* and back from the flake to the substrate as demonstrated on the MoS₂ flake in Figure 3.

Figure 3 depicts an optical micrograph and an atomic force microscopy (AFM) image with corresponding height profile before and after a laser line scan from the substrate across a trilayer to a protruding monolayer area. The transition from substrate over the edge of the trilayer region is marked as (1), the transition from trilayer to the protruding monolayer with (2) and over the monolayer edge site to the substrate with (3). The laser scan is performed with the sample immersed in DI water, a laser excitation energy of 2.54 eV (488 nm), a step size of 100 nm and a dose of 200 μ W x 120 s at each spot. The removal of the trilayer part starting at the edge site (1) is clearly visible, while the single layer seems almost unaffected as evident in the AFM height profiles perpendicular to the line of the laser scan. The monolayer seems to be undamaged at transition (2) from tri- to monolayer without hitting a monolayer edge and is visibly only affected at the step (3) from the monolayer region to the substrate. This linescan shows that the edge sites are degraded after illumination in water, whereas the basal plane remains visibly unaffected in agreement with the previous reported findings.

Focusing the laser on a single spot on the basal plane of a trilayer yields no corrosion of the flake on a similar timescale and irradiation dose. Such a difference in the photo-degradation between edge and basal plane has been observed for all investigated flakes. The terrace site can

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3 be treated as stable under the assumption that the photo-corrosion observed *e.g.* in Figure 1 on
4 the 1L part starts on defect sites. Like edge sites, defect sites imply dangling bonds that are
5 expected to be responsible for the enlarged catalytic activity compared to the basal plane. The
6 absence of dangling bonds at the basal planes is characteristic for van-der Waals layered
7 materials such as MoS₂.
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16 We find that the photo-excitation of electron-hole pairs is essential for the photo-degradation
17 process. The MoS₂ edge sites only degrade under light exposure with energies larger than the
18 band gap. Figure 4 contrasts two optical images of the same flake after laser scans conducted
19 with an energy of $E_{laser} = 1.59$ eV and $E_{laser} = 2.54$ eV, corresponding to illumination with energy
20 smaller and larger than the direct band gap of MoS₂, respectively. For the lower irradiation
21 energy, no corrosion shows up neither on the MoS₂ edge nor on the illuminated basal planes
22 (laser power $P_{laser} = 1.5$ W). The complementary scan with light energy of 2.54 eV ($P_{laser} = 0.5$
23 W), however, clearly displays a decomposition of the flake over a large area. From the scan
24 direction of the laser, marked by the arrows in Figure 4, we again see that the photo-degradation
25 predominantly starts at the step-edges of the individual planes.
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41 Let us now turn to the role of reactive species in the electrolyte. The power-independence of
42 the photo-degradation rate [Figure 2(e) and (f)] points already towards the importance of reactive
43 species and their amount on the interface between MoS₂ and electrolyte. Their role is
44 investigated on example of oxygen as reactive species by changing the amount of dissolved
45 oxygen in the DI water. To this end, the photo-stability of edge sites of a bi-layer flake immersed
46 in degased DI water is studied with parameters similar to those shown in Figure 2. The DI water
47 is degased with inert nitrogen gas in order to reduce the amount of naturally dissolved oxygen.
48 The photo-degradation rates of MoS₂ bilayers immersed in water with and without oxygen are
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3 compared in Figure 5. The drop in the MoS₂ Raman intensities monitoring the degradation is
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5 indeed significantly reduced, when the sample is immersed in water with a strongly reduced
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7 oxygen concentration. The remaining degradation rate might be influenced by the steadily
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9 increasing oxygen content in the DI water over time. During the measurements, the surface of
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11 the water basin is in contact to ambient air and consequently it is expected that the nitrogen gas
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13 dissolved in the electrolyte is again replaced by oxygen gas.
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18 Overall, all our observations are in agreement with the interpretation that MoS₂ terrace sites
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20 immersed in water as electrolyte can be treated as stable under photocatalytic conditions even
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22 under extreme irradiation intensity of 10 mW/μm². Edges and presumably also defects sites,
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24 however, exhibit a significant, photo-generated charge carrier driven catalytic degradation in the
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26 presence of reactive species such as oxygen. Opposite to reported laser thinning, where thermal
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28 ablation caused by laser heating is used to thin MoS₂ to monolayers,⁴⁵ the process reported here
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30 is of significant different origin. Thermal ablation causes are unlikely to produce the observed
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32 photodegradation because of the low laser power, absence of a power dependence, the distinct
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34 difference between edge sites and basal plane and also the absence of degradation for light
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36 energy below the band gap. We propose a charge carrier driven photo-catalytic oxidation process
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38 converting MoS₂ into MoO₃ or more general into MoO_x as the underlying process for the photo-
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40 degradation. The MoO_x then dissolves in the electrolyte⁸ in agreement with the absence of any
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42 MoO_x signatures in a suitable energy range in Raman spectroscopy. This photo-corrosion
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44 process is believed to be responsible for the photo-degradation of MoS₂ at area-scans, line-scans
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46 as well as spot-like exposure of edge sites with light above the band-gap. The amount of
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48 dissolved MoO_x in the electrolyte from a 1 μm x 1 μm oxidized area of a flake would result in
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50 approximately 10⁻¹⁴ g of MoO_x in more than 1 ml water in a petri dish that is not sealed against
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the environment. For this reason it is not possible in this study to further investigate the MoO_x compound *e.g.* by inductively coupled plasma mass spectrometry.

The fact that we observe photo-corrosion predominantly on edge sites can be explained by a more favored transfer of charge carriers to the electrolyte from edge and defect sites due to existent dangling bonds compared to the basal plane without dangling bonds. The found degradation on some individual spots on the basal plane suggest to start at lattice defects. Such individual defects of the crystal are beyond the resolution in our experiments and therefore we can only conjecture about the role of defect sites. The observed layer dependence is interpreted in terms of an increased density of freely mobile holes η_{fh} for MoS₂ bi- and multilayers compared to the monolayer because of a much larger exciton-binding energy for the monolayer resulting in a reduced e-h separation efficiency. The observed layer dependence might be further amplified by an increased life-time of photo-generated charge carriers due to the reduced recombination rate for the indirect band-gap of MoS₂ bi-, tri- and multilayers compared to the direct band gap in the monolayer limit. A role of the supporting substrate is unlikely since we assume a thin water layer between the MoS₂ flake and the hydrophilic SiO₂ substrates as the exfoliation process has not been done in inert atmosphere. This assumption is supported by atomic force microscopy height profile revealing a step height from substrate to MoS₂ monolayer of about 3 nm, whereas the step height from monolayer to bilayer constitutes 0.7 nm close to the theoretical value.

CONCLUSION

In summary, we find that the MoS₂ edge sites are subject to significant photo-corrosion under light exposure with a laser energy larger than the direct band gap, when immersed in an

electrolyte with dissolved oxygen. The photo-corrosion process is found to take place on edge and most likely also defect sites. The photo-degradation rate is much faster for bi- and multi-layer ($\tau_l \sim 1$ min) compared to monolayer ($\tau_2 \sim 45$ min) MoS₂ and is explained by the transition from an indirect to a direct semiconductor resulting in an decreased amount of freely mobile photogenerated holes η_{th} due to an increased exciton binding energy and reduced lifetime of the charge carriers. The degradation process is interpreted in terms of an oxidation process driven by the photo-generated charge carriers converting MoS₂ *e.g.* into MoO_x that is expected to be dissolved in the electrolyte. The role of photo-generated charge carriers as driving force can explain the layer-dependence as well as the superior catalytic degradation of the edges compared to basal planes.

The MoS₂ basal plane is found to exhibit a high level of photocatalytic stability even in the presence of reactive species such as oxygen in the electrolyte and under irradiation with visible light of intensities exceeding 10 mW/ μm^2 . The stability in photocatalytic conditions is an unambiguous requirement of a photo-absorber for photocatalytic splitting of water, but also for sensing applications, transparent corrosion protection layer with further functionality and general for optoelectronic device applications in aqueous or humid environment. The stability under challenging conditions together with high absorption in the visible range and the electro-catalytic activity strengthen MoS₂'s potential for sunlight driven overall hydrogen production by water splitting in a durable monolithic device without any metals utilizing the earth abundant electrolyte fresh water.

METHODS

MoS₂ flakes are prepared by standard micromechanical exfoliation from bulk crystal (SPI supplies) and then transferred to a p-type doped Si substrate with a 275 nm thick thermal oxide layer on top. The transfer is accomplished by an all-dry viscoelastic stamping technique³⁴ using a polydimethylsiloxane (PDMS) thin film. The flakes are investigated by optical contrast, scanning reflectivity measurements, atomic force microscopy as well as Raman spectroscopy.

All optical measurements, reflectivity scans as well as μ -Raman spectroscopy and laser cutting with the sample immersed in the electrolyte are performed using a 63x water immersion objective (Carl Zeiss Objective W N-Achroplan 63x/0.9 M27) in combination with a piezo stack with a closed-loop resolution of 1 nm (Physik Instrumente P-611.3 NanoCube® XYZ-System). This combination allows us to reach a spatial resolution of roughly 300 nm in our measurements with the sample in the electrolyte. The position of the flake is monitored before and after each measurement in order to exclude any influence due to lateral drifts. Laser excitation energies below ($\lambda = 780$ nm) and above the direct band gap energy ($\lambda = 488$ nm) are accessed utilizing a Ti:Sapphire and Ar-ion gas laser, respectively, as excitation light source.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

HER, hydrogen evolution reaction; OER, oxygen evolution reaction; e-h, electron-hole; DI, deionized; atomic force microscopy (AFM);

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Figure 1. (a) Optical microscopy image (100x) of exfoliated single- (1L) and tri-layer (3L) MoS₂ on a Si/SiO₂ substrate. (b) Monochromatic reflectivity map of before (left) and after (right) a laser scan in the electrolyte of the ROI defined in (a). The arrows indicate scan direction. Step size 250 nm, dose 1 mW x 20 s at each spot. (c) Raman spectra of the spots marked in (b) of untreated, unaffected and photo-degraded regions.

Figure 2. (a) Monochromatic reflectivity map of a MoS₂ bilayer sample after extensive photo-degradation measurements immersed in water (circles mark the corroded spots used for time-resolved measurements. More spots on the flake have been investigated). (b) Scheme of the direction of movement of Mo and S atoms for the two Raman active phonon modes E_{2g}^1 and A_{1g} , respectively. (c) and (d) Normalized Raman peak area intensity of the E_{2g}^1 (c) and A_{1g} (d) mode

of the spectra shown in (e) and (f) as a function of laser illumination time for the MoS₂ flake immersed in DI water for various light intensities. The fits show two different decay rates for the bilayer and the remaining monolayer-flake. (e) and (f) Raman spectra showing the E_{2g}¹ and A_{1g} modes of an initial MoS₂ bilayer-flake (e) at the beginning of laser irradiation (◊) and (f) after degradation from bi- to a monolayer after 1 min (○). (g) Raman peak area intensity of the silicon TO-phonon mode that depicts the complementary increase of the Raman signal originating from the substrate.

Figure 3. (a, c) Optical microscopy (100x) and (b, d) AFM image of exfoliated single- and trilayer flake on a Si/SiO₂ substrate before (top) and after (bottom) laser linescan immersed in electrolyte. The dashed arrow indicates the scan direction. The steps from substrate to trilayer (1), from trilayer to monolayer (2) and from monolayer to substrate (3) are highlighted with labels. Photo-degradation takes predominantly place on edge sites. The corresponding AFM height-profiles at the trilayer regions are depicted on the right (red lines). Scale bars 5 μm.

Figure 4. Optical microscopy image of a multi-layer MoS₂ flake before (left) and after (right) area illumination scans with a laser energy below (1.59 eV) and above (2.54 eV) the direct band gap, respectively. The MoS₂ flake is unaffected for exposure to light with energy smaller than the band-gap (red marked area). In case of illumination with energy larger than the band gap, corrosion of the MoS₂ flake is clearly visible (black marked areas). Scan parameters: step size 250 nm, illumination at each spot: 21 s.

Figure 5. Normalized Raman peak area of the E_{2g}^1 and A_{1g} mode as a function of laser illumination time on the edge site of a bilayer-flake. The upper curve (blue) corresponds to a flake immersed in water with reduced oxygen concentration in the electrolyte, the lower curve (red) to water with a natural amount of dissolved oxygen.