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Published in:
A C S Applied Materials and Interfaces

Link to article, DOI:
[10.1021/acsami.8b09797](https://doi.org/10.1021/acsami.8b09797)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Ly, T. H., Deng, Q., Doan, M. H., Li, L.-J., & Zhao, J. (2018). Facile Doping in Two-Dimensional Transition Metal Dichalcogenides by UV Light. *A C S Applied Materials and Interfaces*, 10(35), 29893-29901. <https://doi.org/10.1021/acsami.8b09797>

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Facile Doping in Two-Dimensional Transition Metal Dichalcogenides by UV Light

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KEYWORDS

two dimensional, transition metal dichalcogenides, doping, atomic defects, atomic force microscopy, transmission electron microscopy

ABSTRACT

Two-dimensional (2D) materials have been emerging as potential candidates for the next generation materials in various technology fields. The performance of the devices based on these 2D materials depends on their intrinsic band structures as well as the extrinsic (doping) effects such as surrounding chemicals and environmental oxygen/moisture, which strongly determines their Fermi energy level. Herein, we report the UV treatments on the 2D transition metal dichalcogenides (TMdCs), to controllably dope the samples without damaging the crystal structures or quenching the luminescence properties. More surprisingly, both n type and p type doping can be achieved depending on the initial status of the sample and the UV treatment conditions. The doping mechanisms were elaborated on the atomic scale with transmission electron microscopy and ab-initio calculations. The facile doping by UV light has potential to be integrated with photolithography processes, aiming for the large scale integrated device/circuits design and fabrications.

INTRODUCTION

Two-dimensional (2D)-layered materials have attracted great attentions for their extraordinary properties, e.g. the electron confinement without interlayer interaction, high mechanical flexibility as well as optical transparency.¹ Particularly, graphene has zero bandgap which made difficulties for the applications in industry.² On the contrary, 2D transition metal dichalcogenides (TMdCs), with direct gaps from 1.0 to 2.5 eV,¹ are more suitable for various electronic or optoelectronic applications. Doping is a common process for tailoring the properties of semiconductors. So far a few doping methods for the 2D-TMdCs have been reported, e.g. heat treatment approaches such as chemical vapor deposition (CVD) were enabled for stoichiometric control³ or Nb doping in MoS₂,⁴ while wet chemistry methods could be applied for atomic doping in TMdCs as well.⁵ However, most of existed doping methods involve either thermal or chemical processes, which are difficult to control or integrated with other processes during large scale fabrications. Some other doping methods, such as plasma treatment approaches⁶⁻⁸ were proposed for the carrier control in MoS₂ monolayers as well, and they have indeed paved the way for the 2D TMDs towards scalable industrial fabrications.

On the other hand, currently the detailed structures of defects⁹⁻¹⁶ and oxygen passivation effects on the defects^{17,18} in 2D TMdCs remain under hot debate. Several previous works¹⁹⁻²³ have shown that the enhancement of photoluminescence (PL) intensity achieved by thermal annealing or weak plasma irradiation is closely related to strong oxygen bonding at the defect sites of 1L-MoS₂^{19,22,23} and the quenching of PL intensity by strong plasma irradiation is associated with the lattice distortion or creation of MoO₃ defects.¹⁹⁻²¹ The gradual oxidation of TMdCs are prevalent for these atomic-thick layer when exposed to air, even under ambient conditions.²⁴⁻²⁷ The environmental effects play key roles on the optical and electronic properties of monolayer TMdCs. Therefore, it is imperative to have a systematic study with careful engineering on all control parameters and rationalize the influences on associated structural/property changes, further, for understanding the underlying mechanisms of oxidation.

Distinct to the previous approaches, in this work we apply a facile and industrial friendly method to dope the 2D-TMdCs in both types (n/p). During the initial stage of UV light exposure with humidity, which has been used to oxidize and observe the grain boundaries of graphene²⁷ and TMdCs,²⁸ the monolayer TMdCs were successfully doped and modified without compromising the structures. According to the summary in Supporting Table S1, the initial stage can last few min, depending on the specific conditions. By careful characterizations with the PL spectroscopy, Raman spectroscopy, XPS, TEM/STEM, density functional theory (DFT) simulation and C-AFM, it is clearly revealed that under a controlled UV irradiation dose and humid level, the chemical doping process can adjust the carriers in bands of 2D-TMdCs, without lattice periodicity/band structure perturbation or sample damage.

In specific, our PL and Raman spectroscopy measurements unveiled the different carrier and lattice vibration behaviors according to the UV irradiation time, humidity level. The PL intensity of exfoliated monolayer (1L) MoS₂ gradually increased with significant blue shift of A exciton peak, distinct to the PL quenching with red shift of A exciton peak observed in CVD grown 1L MoS₂, indicating different doping effects in these two kinds of samples. Meanwhile, a significant peak shift of the E_{2g}¹ and A_{1g} modes in the Raman spectra for all samples has been observed. The origin of the different doping effects which can be attributed to different defective structures after treatment was unraveled by the high resolution TEM/STEM imaging. Finally, the increased electrical current level on the CVD grown MoS₂ samples in the conducting atomic force

microscopy (C-AFM) results also confirmed the doping. Our work manifests the capability of controlled UV light treatment for tuning the electrical and optical properties of the 2D TMdCs. This process has great advantage over other doping methods and potential for industry use, in particular for the compatibility with current lithography techniques.

RESULTS AND DISCUSSIONS

The fabrication, preparation and characterization specifications of the 2D TMdCs can be referred to the METHODS. As the first example, the 1L MoS₂ flakes were exfoliated on 300nm SiO₂/Si substrate using Scotch-tape method (pristine samples in Supporting information Figure S1) and applied treatment with UV irradiation at humidity level of 60-65% (Figure 1a-h). Several bright spots/holes were observed in Figure 1a in the monolayer portion, whereas the thicker portion does not have any noticeable effect. The thickness of monolayer was ~ 0.8 nm verified by AFM (Figure 1b,e). The roughness in monolayer part was less than 0.2 nm. The bright spots in Figure 1a were correlated with the dark spots in Figure 1b, showing the formation of nanoholes after UV irradiation under 60% humidity. The edge height increased to 4 nm, indicating the highly active edges were preferably oxidized as in our previous reports.²⁸ The formation of holes and edge oxidation are related to the initial oxidation and etching of 1L MoS₂ under UV treatment. It should be noted that except for several discrete spots, the samples under UV exposure for 6 min and 60% humidity kept globally uniform and exhibited well-preserved uniformity (Figure 1e) as well as crystallinity in 1L MoS₂, double-confirmed by our TEM characterizations shown later.

In contrast, increasing of 5% humidity gave different results. For 65% humidity and 6 min UV exposure samples, there were continuous bright lines and bright spots appeared in the AFM images (Figure 1d,f). Even in the >1L portions there were some changes in morphology. Line patterns emerged with height ~ 0.8 nm and width ~ 50 nm, roughness was also increased to ~3 nm (Figure 1f), which probably comes from the functionalization groups after oxidation of MoS₂¹⁹⁻²². Meanwhile, stress corrosion cracking (SCC)²⁹ was also initiated, with cracking depth 0.8 nm (1L thickness) and width ~ 50 nm.

To investigate the physical properties after UV treatment, we performed spectroscopic analysis by Raman and photoluminescence (PL) on the initially oxidized samples. Figure 1g,h exhibit the results on the 6 min UV and 60% humidity treatment samples. Firstly, the two

characteristic peaks from Raman spectra for original monolayer MoS₂ at 384.2 cm⁻¹, assigned to E_{2g}¹ mode, and 401.5 cm⁻¹, assigned to A_{1g} mode, were observed.⁸ After UV oxidation for 6 min, the E_{2g}¹ peak was slightly shifted to 383.6 cm⁻¹ and A_{1g} peak was shifted to 402.5 cm⁻¹. In the PL results, The A exciton peak (excited by a 532 nm laser) of 1L MoS₂ near 1.82 eV was blue-shifted with enhanced peak intensity. Accordingly, the intensity of the B exciton peak near 805 nm was significantly reduced without appreciable peak shifting. These results are all in consistent with the p type doping effects^{5,30} for the 2D MoS₂. Based on the Raman peak shift we obtained, the actual free electron density reduction (p doping) was estimated to be 2×10¹² cm⁻².³⁰ The increased total PL intensity is well contrasted to the behavior after other thermal and plasma treatments,³¹ whereas the PL intensity is normally reduced significantly.

In line with our AFM morphology results, the increased PL intensity after UV exposure confirmed that the crystal structure of 2D MoS₂ has not been degraded, otherwise the prevalent dangling bonds will serve as non-recombination centers and reduce the PL intensity. A exciton peak is combined with the negative trion peak (~1.84 eV) and exciton peak (~1.88 eV).⁵ Compared to the as-exfoliated MoS₂ samples, the blue shift of A exciton peak and peak intensity enhancement at around 1.88 eV after UV oxidation can be attributed to the transition of negative trion recombination to direct exciton recombination,⁴ in congruent with the decrease of free electrons due to p type doping. The 65 % humidity and 6 min UV treated samples (Figure 1d,f) have much lower PL intensity than the 60 % humidity and 6 min UV treated samples (Supporting Figure S1), exhibiting they have been severely oxidized and damaged.

The mechanical exfoliated samples usually contain less atomic defects compared to the CVD grown samples, especially the atomic vacancies in 2D TMdCs.¹⁴ As the second example, CVD-grown monolayer MoS₂ on sapphire³² was tested without transferring substrates to reduce unexpected artifacts caused by the transfer process. The high quality pristine samples before UV exposure were shown in Supporting Figure S2. While after UV irradiation under 65% humid level for 6 min, Figure 2a showed the topographic AFM image demonstrating the uniformity of the triangle shape 1L MoS₂ (thickness ~ 0.8 nm, roughness ~ 0.1 nm). Only several brighter lines caused by the SCC cracks due to initial oxidation and large strain mismatch between the flake and sapphire substrate^{29,33}. It is also reasonable that the CVD grown samples were cracked under a lower humidity level than mechanical exfoliated samples with same exposure time, because the

CVD samples intrinsically possess more atomic defects or vacancies than the mechanical exfoliated samples.

To further understand the oxidation effects, we prepared samples with different UV exposure times, while the humidity level maintained at 65% and 60%. The series of AFM results for 65% humidity were presented in Supporting Figure S3, and the height profiles confirmed the uniform morphologies except some cracks or oxidized edges/boundaries starting to emerge at 4 min while larger particles were seen after 6 min. The series of Raman and PL spectra for 65% humidity was shown in Figure 2b-e, and the respective Raman and PL (mapping) data were presented in Supporting Figure S4-S7. It can be seen that the Raman intensity kept spatially uniform in the initial stage but the total intensity was increased after UV irradiation until 4 min and then start to rapidly decrease from 6 min (Figure 2d). The enhanced Raman intensity could be ascribed to plasmonic effects from the oxidation process.⁴ Figure 2f showed the peak position evolution of E_{2g}^1 and A_{1g} . Both E_{2g}^1 and A_{1g} peaks were shifted to lower wavenumber with the increasing UV exposure time (0-4 min), and then shift back higher wavenumber for longer exposure time (> 4 min). The initial and subsequent shifting of E_{2g}^1 peak can be well explained by the strain effects³⁴⁻³⁶ in response to the UV irradiation. With more atomic defects/vacancies created, the tensile stress across the sample was increased, thereby the sample started to have SCC cracks and the tensile stress was eventually released. On the other hand, the A_{1g} peak position is more closely related to the doping concentrations.³⁰ The corresponding PL spectra also presented the crossover of n/p doping by A exciton peaks at around 2~3 min UV exposure (Supporting Figure S4b). The crossover is earlier than the A_{1g} peak in Raman spectra (crossover at 4 min), which is probably due to the effect of in-plane strain mixed with doping in the PL results, say, the tensile strains cause similar effect as p doping for PL. The above results indicate in the initial stage of UV treatment, n type doping tends to occur first in the CVD grown samples followed by p type doping, in contrast to the direct p type doping by UV in the mechanical exfoliated samples.

The initial n type doping effect for CVD samples was confirmed by the PL measurements. The A exciton peak was red-shifted (Figure 2c) for 5 min UV irradiated sample. This red-shift A exciton peak can be attributed to n type doping⁵ or tensile straining,³⁰ however the 5 min UV sample was already SCC cracked (Figure 2a), therefore most of the tensile stress is already released, precluding the tensile strain effect. Nevertheless, n type doping is supposed to dominate

the initial stage during the UV oxidation process in the CVD grown samples. The maximum electron density (n doping) estimated by Raman shift was increased by $6 \times 10^{12} \text{ cm}^{-2}$ after UV doping. Finally after around 6 min by the UV treatment, the 1L MoS₂ started to be damaged (Supporting Figure S8), which significantly reduced the Raman and PL intensities.

Hence we have demonstrated the morphology and optical responses of the monolayer MoS₂ samples, both mechanical exfoliated and CVD grown, can be controllably modified by the UV light and rich humid exposure. Conditions including the thickness of sample, particularly monolayer, as well as the exposure time and humidity level will result in distinct reaction rates. Importantly, during the initial stage (e.g. <6 min under 60% humidity or <4 min under 65% humidity, using current UV exposure intensity and dose, see *METHODS*) of treatment, doping effect on the monolayer MoS₂ were clearly observed while uniform morphologies can be preserved. As the monolayers intrinsically have higher chemical reactivity than thicker flakes due to fluctuations in morphology, higher surface ratios and higher defect concentrations, they suit such mild UV oxidative treatment for doping. Because 5 min UV exposure is under the threshold between the mild doping (initial stage) and the stronger oxidation/damage, in the following we mainly use the 5 min UV exposure sample to demonstrate the doping effect.

The MoS₂ layer was further studied by the X-ray photoelectron spectroscopy (XPS) for elemental analysis. Figure 3 showed the XPS spectra of the Mo-3d and S-2s of pristine and post UV treatment 1L MoS₂. After 5 min UV irradiation, the S-2s peak was suddenly reduced (Figure 3 upper panel), shown in Table 1, by around 50%. Note the sapphire substrates also contribute in the O signals. The oxygen content after 5 min UV treatment was significantly increased (Table 1). The accuracy of Mo/S ratio determined by XPS may be disturbed by X ray beam damage, however it clearly exhibited the trend of replacement of S by O during the UV treatment. In addition, the individual peak of Mo3d⁶⁺ which related to oxidation was significantly increased after UV, and the core level of S-2p and Mo-3d peaks was red shifted simultaneously by around 1.5 eV due to UV exposure and chemical doping (Figure 3).

By using high resolution TEM and STEM techniques, we have been able to observe the local atomic structures of the UV treated TMdCs (Figure 4a-f). The annular dark field (STEM-ADF) image (Figure 4a) showed the CVD grown 1L MoS₂ have perfect crystal lattice even after 5 min UV irradiation under 60% humidity, and the mechanical exfoliation samples have similar results.

Although there are some atomic vacancies in S sublattice (Figure 4d), the Mo sublattice is non-affected. The oxygen substitution into the S atomic positions cannot be clearly resolved by ADF because the O and S are both light elements and quite close in Z contrast, however the localized EELS spectrum over defective zones (Figure 4b,c) confirmed the trace of oxygen. While in pristine MoS₂ monolayer samples without UV treatment, it is hardly to find trace of oxygen in the EELS spectra for local areas (Supporting Figure S9). Therefore, the O substitution of S or O atom/OH functional group (caused by the photochemical dissociation of H₂O) attaching to S vacancies will deplete the original n type carriers (electrons) in conduction band caused by S vacancies, leading to significant p-doping effect, which is in consistent with the PL and Raman spectroscopy results (Figure 1).

In addition, in CVD grown samples, by using ADF imaging we frequently observed sulphur vacancies (Figure 4d) and additional Mo atoms replacing S atoms (Figure 4e,f), which can enhance n-type doping by excess electron (by additional Mo atoms) injection into the conduction band. As more atomic defects and S vacancies were found in as-prepared CVD grown samples, the creation of extra sulphur vacancies can be easier than less defective exfoliated MoS₂, because the S₂ vacancies in MoS₂ are energy favorable.¹⁶ On another hand, the Mo atoms in the original lattice are more active upon oxidation conditions. Additional Mo atoms may also come from the MoO_x sources used for CVD process. The n-doping effect can be saturated due to exhaustion of S vacancies or Mo sources, which is followed by p doping effect similar to the mechanical exfoliated samples. Elongated UV exposure time (>8 min) or levitated humidity level on the samples will quickly damage or even destroy the samples.

To confirm the electronic structures of the O/Mo doped 1L-MoS₂, we carried out DFT calculations (Figure 5). The single S_O defect and S_{Mo} doping defects which were observed by TEM experiments are mainly investigated. The structure and local density of states (LDOS) of monolayer MoS₂ shows a band gap of ca. 1.8 eV in Figure 5b, which are consistent with previous DFT calculations^{37,38}. The gap is mainly derived from 4d orbits of Mo atoms. The symmetry of LDOS is kept as shown as in Figure 5c by substituting one S atom with O. The 2p orbitals of O locate far from the Fermi level (<-2.4 eV) indicating slightly effect of the chemical properties by substitution S with O. Therefore, the O doping will deplete the n doping levels caused by original S vacancies. For Mo doping, the impurity states distributed around Fermi

level are mainly contributed from 4d orbits of Mo as dopants in Figure 5d, and the dopant Mo 4d defect orbits (in pink, Figure 5d) also locate at the conduction band edges, thereby enhancing n-doping. In brief, the TEM/STEM studies on the post UV samples and DFT calculations have explained the origin of the distinct n/p doping effects on the atomic scale.

The electrical properties of the 2D TMdCs after doping were studied by the conductive atomic force microscopy (C-AFM) measurements. The SiO₂ layer of 300 nm SiO₂/ Si substrate was etched away instantly in buffer etching oxide (BOE) solution before the CVD grown MoS₂ transferred on the new substrate. The idea here is to use the MoS₂ layer as the protection layer for the Si substrate from re-oxidation after etching away the surface oxide. Si was used as the counter electrode for the C-AFM measurements. The C-AFM can provide local I-V responses in correspondence to the topographic information obtained by AFM. The AFM topographic image of the 1L MoS₂ (thickness~0.8 nm) after UV treatment are shown in Figure 6a. Accordingly, Figure 6b showed the current mapping at a bias voltage of 1V and contact force of -1 nN. Note there is no much contrast in current level between MoS₂ and Si substrate. It can be seen that after UV irradiation for 5 min, brighter spots emerged in the topography image as well as the C-AFM images. The height profiles in Figure 6c,d clearly showed the morphology change of MoS₂ after UV irradiation. The peak marked by green arrow in Figure 6c highlighted points with high level of current/conductivity as in Figure 6d, indicating the synchronized increase of current (C-AFM) and height (AFM) in MoS₂ due to cracking and severe oxidation. Except for these, the red arrows in Figure 6d also highlighted the high current spots which locate in the uniform/flat areas (no corresponding peaks in height profile in Figure 6c). They can be attributed to the Mo substitution, leading to the enhanced n-doping and increased density of carriers (electrons). The measured current level at the brighter spots in Figure 6d increased approximately by one order of magnitude, from 0.08 A in pristine samples to 0.8 A in UV exposed samples, implying the carrier (electron) density increased by one order of magnitude in MoS₂. With the initial room temperature carrier (electron) density on order of 10^{12} cm^{-2} in CVD MoS₂ monolayers,^{39,40} the n doping concentration after UV exposure can reach around $1 \times 10^{13} \text{ cm}^{-2}$ based on our C-AFM results, which is comparable with the previous results (increase by $5 \times 10^{12} \text{ cm}^{-2}$) by optical measurements. The slight difference between them may come from the local characteristics of the C-AFM experiment and the averaging effect in optical measurements.

In general, the above doping approach by UV irradiation on 2D MoS₂ can be extended to other TMdC materials such as WSe₂ (Supporting Figure S10). The reaction kinetics directly depend on the humidity level and UV exposure time, and the photochemistry of the doping process can be understood as follows. The dissociation of H₂O molecules are at first triggered by the direct UV absorption. The wavelength of the UV light (185 nm) we applied has satisfied the energy requirement (<239 nm) of the H₂O molecule dissociations.⁴¹ The full photochemical reactions have been listed in *METHODS* section. The chalcogenide vacancies in the as prepared samples serve as the anchoring sites for the –O or –OH functional groups, which will induce p type doping. If oxidation processes involve more chalcogenide vacancies such as in CVD grown samples, the encapsulated transition metal atoms become more active and some dissociated metal atoms will act as the n-type dopants. Subsequently, the enhanced oxidization level will turn n-doping into p-doping by oxygen atom substitution similar to mechanical exfoliated samples, after certain amount of UV light and humidity exposure. Eventually, uncontrolled oxidation by UV will cause sample damage and severely deteriorate all the physical properties.

We have summarized the doping results depending on different MoS₂ samples, UV doses and humidity levels in supporting Table S1, as a guideline for the doping process and conditions. It is also noted the ideal humid level (process window) for doping in MoS₂ should be around 60%~65%. Lower or higher humidity will cause too slow or too fast doping reactions which become less controllable. The humidity level is critical to doping due to the introduction of OH* radicals, meanwhile the effect of O₃ on MoS₂ is mainly oxidation (with structure damage) rather than doping. Thus under lower humid condition the doping is slower, while more O₃ remained in the chamber which can cause faster oxidation (damage) in the sample. The exfoliated MoS₂ may have less possibility to react with O₃ because they have less defects, therefore the oxidation (damage) is slower. The competition between oxidation (by O₃) and doping (by OH*) exist in the UV process.

In conclusion, we have systematically studied the doping effect of UV irradiation on monolayer TMdCs under humid environment. Controlled n type or p type doping is feasible in the initial stage, which can be readily applied for electrical/optical device design and fabrications. By the characterizations using SEM, AFM, TEM, Raman and photoluminescence spectroscopy combined with DFT simulations, we directly compared CVD-grown MoS₂ to the mechanical

exfoliated MoS₂ after UV exposure. The PL and Raman spectrum enhancement as well as the electrical conductivity enhancement by C-AFM in the UV treated samples have been observed. This UV approach is facile and compatible with lithography techniques used for industry. It requests only conventional lithography UV dose and ambient humid condition, expected to be cost-effective. In fabrications, the exposure to humid may preclude some processes which require moisture isolation. Meanwhile, the stress in the sample needs to be controlled to prevent SCC cracking. However, this approach still has great potential for the scalable and flexible doping in 2D-TMDCs.

METHODS.

Sample Preparation.

Molybdenum dioxide growth on sapphire. The MoO₃ powder (0.3 g) was placed in a ceramic boat located in the heating zone center of the furnace. The S powders were placed in a separate ceramic boat at the upper stream side maintained at 150°C during the reaction. The sapphire substrate for growing MoS₂ was located at the downstream side, where the S and MoO₃ vapors were brought to the targeting sapphire substrate by an Ar carrier gas (70 sccm, chamber pressure = 40 Torr). The center heating zone was heated to 635 °C with a ramping rate 15 °C/min. After reaching 635 °C, the heating zone was kept for 30 minutes and the furnace was then naturally cooled down to room temperature.

Preparation of exfoliated 1L-MoS₂ on Si/SiO₂ substrate. MoS₂ flake was purchased from 2D-Materials Company, MoS₂ was prepared on 300 nm SiO₂/ Si substrate using conventional mechanical exfoliation methods using the semiconductor transfer tape (USI Blue Adhesive Plastic Film).

Ultraviolet Oxidization of MoS₂. MoS₂ was placed into a chamber equipped with a low-pressure Hg lamp (LH-arc, Lichtzen, with an output of 20 mW cm⁻²), with the majority of emitted light at a wavelength of 254 nm and approximately 10 % of emitted light at a wavelength of 185 nm. Humidity was introduced into chamber by connecting it to a humidifier. The humidity level in the chamber was monitored using a hydro-thermometer (accuracy of ±3 %), where the chamber

was continuously ventilated to maintain a constant pressure. After reaching the required humidity level, the humidifier was disconnected from the chamber. MoS₂ was then irradiated under UV light for different times (2, 4, 6, 8 and 10 min). Radicals are generated under UV and humidity conditions as follows:

Sample Characterization. Raman and PL spectroscopy (NT-MDT) was performed with an excitation energy of 2.33 eV (532 nm), AFM (SPA400, SEIKO), SEM (FESEM, JSM7000F, JEOL), and TEM (JEM ARM 200F, JEOL Ltd.) were used to characterize the sample. We describe the details of each characterization as below.

Optical microscopy. Optical microscopy (100x magnification, Olympus, Japan, numerical aperture=0.9) was used to obtain images of the surface morphologies of samples.

Raman and PL spectroscopy. Confocal Raman, PL mapping (NT-MDT, 532 nm wavelength, NTEGRA Spectra PNL, x100 lens, 0.7 N.A.) was performed using a laser (532 nm) with ~ 30 μW power. The scanned image was obtained at 128 x 128 pixels with a grating of 600 g/mm to yield a spectral resolution of < 0.1 cm⁻¹ for confocal Raman mapping and with a grating of 1800 g/mm to yield a spatial resolution of 200 nm for confocal PL mapping. The accumulation time for each spectrum was one second for image scanning and 30 seconds for a single spectrum. An area filter was used to extract the Raman spectrum map with an integration of E_{2g}¹ peak (368 to 386 cm⁻¹), and PL intensity map (625 to 775 nm).

Atomic force microscopy (AFM). AFM images were obtained using a SPA400 system (SEIKO, Japan) in tapping mode. A NSC14-type silicon tip (MikroMasch, Estonia) with an approximately 10 nm tip radius was used. In general, the force constant and resonant frequencies of the tips were approximately 5 N/m and 160 kHz, respectively.

Conductive atomic force microscopy (C-AFM) measurements. A Au tip with an approximately 10 nm tip radius was used. The force constant and resonant frequencies of the tips were approximately 1.6N/m and 28 kHz, respectively C-AFM study was done monolayer MoS₂ transferred on pre-etched Si substrate. IV measurements from -1 V to 1 V were done with C-AFM.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Field-emission scanning electron microscopy (FESEM) (JSM7000F, Jeol, Japan) was used to examine the surface morphology of samples at different accelerating voltages to obtain a high level of contrast at different magnifications. An X-Max Silicon Drift Detector in a FESEM-JSM7600F system was used for EDS mapping for 10 min. An accelerating voltage of 3 keV was used to obtain sufficiently pronounced signals while retaining sensitivity to the sample surface.

X-ray photoelectron spectroscopy (XPS). XPS was performed using an Al K α X-ray source (XPS, ESCA2000, VG Microtech). Mo3d, S2s, O1s peak data were collected to analyze the extent of oxidation of monolayer MoS₂. X-ray photoelectron spectroscopy (XPS) (QUANTUM 2000, Physical electronics, USA) was performed using focused monochromatic Al K α radiation (1486.6 eV).

TEM and DF-TEM. TEM imaging was conducted using a JEM ARM 200F machine operated at 80 kV, which did not cause any apparent damage to the sample. Acquisition time for dark field (DF) images was one second using the smallest objective lens aperture. The HRTEM imaging acquisition time was 1 s.

ADF-STEM. Annular dark field (ADF)-STEM imaging was conducted using a probe aberration corrected JEM ARM200F, operated at 80 kV. High angle annular dark field (HAADF) images were acquired using a 20 mrad convergence angle. Because the low-voltage electron beam was below the damage threshold energy, the pristine MoS₂ lattice remains stable and defect-free with regular scans. Images presented in the main text were acquired with the medium-angle annular dark field detector with angle between 50 mrad to 180 mrad and acquisition times of 1 μ s per pixel.

EELS. EELS spectrometer (Enfinium, Gatan) working under 80 kV accelerating voltage was applied. The beam current during the experiments were ca. 120 pA. The spectrometer was 0.5 eV per channel dispersion with exposure time 0.1s per spectrum.

DFT calculations. Spin-polarized density function theory (DFT) calculations are carried out using the Vienna *ab initio* simulation package (VASP) program package^{42,43} within the projector augmented wave (PAW) pseudo-potentials (PAW). The exchange-correlation functions are described with the generalized gradient approximation (GGA) in the form of the Perdew, Burke, and Ernzerhof (PBE) functional. The kinetic energy cutoff for the plane-wave basis set is chosen as 500 eV. The distance of vacuum layer is set to be more than 20 Å, which is sufficient large to avoid interlayer interactions. The electronic SCF tolerance is set to 10^{-5} eV. Fully relaxed geometries and lattice constant are obtained by optimizing all atomic positions until the Hellmann–Feynman forces are less than 0.02 eV/Å. The k-points samplings are $4\times 4\times 1$ in the Brillouin zone for structural optimizations, while $8\times 8\times 1$ are used for the local density of states (LDOS) calculations.

Figures and Figure Legends

Figure 1. Analysis of UV treatment effect on mechanical exfoliated MoS₂. a,c, SEM and b,d, AFM topographic images for the mechanical exfoliated 1L MoS₂ after 6 min UV treatment under 60% humidity and 65% humidity. The black arrows in a marked the nanoholes after UV exposure. Scale bars, a,b, 2 μ m, c,d, 1 μ m. e,f, Height profiles corresponding to dashed lines in b,d. g, Raman and h, PL spectra for the pristine and post-UV treatment samples.

Figure 2. Analysis of CVD grown 1L MoS₂ pre and post UV treatment. **a**, AFM topographic image for the 1L MoS₂ after 5 min UV treatment under 65% humidity. Scale bar, 4 μm. **b,c**, Raman and PL analysis of the pristine and 5 min UV treatment sample under 65% humidity. **d,e**, Raman and PL analysis of the series of 1L MoS₂ samples by different UV treatment times under 65% humidity. **f**, Time evolution of Raman peaks by UV treatment corresponding to **d**.

Figure 3. Chemical components of CVD-MoS₂ grown on sapphire before (lower panel) and after 5min UV treatment under 65% humidity (upper panel) by XPS.

Figure 4. The TEM characterizations of post UV exposure MoS₂ samples. False colors are applied for clarity. a, STEM-ADF image for the 5 min UV treatment under 60% humidity 1L MoS₂, scale bar 1 nm. b, STEM-ADF image for the 1L MoS₂ under same condition as a, scale bar 500 pm. c, EELS spectra acquired in the area highlighted in b. d, Filtered ADF image for S vacancy area in 1L MoS₂ after 5 min UV exposure. Scale bar, 500 pm. e, Magnified ADF image for the Mo doping area in 1L MoS₂ after 5 min UV exposure, scale bar, 300 pm. f, Intensity profiles of two dashed lines in e.

Figure 5. Optimized structure of MoS₂ with targeting doping site labelled in red. a, The atomic structures of single atomic doping by O or Mo substitution for S in MoS₂ (red dopant atom, O or Mo). Spin-polarized local density of states (LDOS) of **b**, pristine MoS₂, **c**, O doped MoS₂, **d**, Mo doped MoS₂ projected on 4d (pink lines) orbitals of Mo as well as *p* orbitals of S and O (green and blue lines), and the total DOS (TDOS) are black lines. The Fermi level is set to zero.

Figure 6. Morphology and conductivity mapping on UV-treated MoS₂ on SiO₂/Si substrate using C-AFM. **a**, Topography images of CVD grown MoS₂ after 5 min UV treatment, scale bar 4 μm. **b**, The C-AFM current mapping for the same position as in **a**. **c,d**, The line profiles correspond to the thin white lines in **a** and **b**, and the pristine samples.

Table 1. The detailed data extracted from deconvolution of Mo3d, S2p, and O1s peaks in XPS. Atomic weight calibrated to Mo%.

	Pristine	5 min UV
(Mo3d) Mo	1.00	1.00
(S2p) S	2.24	1.10
(O1s) O	12.80	14.06

ASSOCIATED CONTENT
Supporting Information.

Supporting information includes Figure S1 to S11 and Table S1. This material is available free of charge via the internet at <http://pubs.acs.org>.

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Note

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from City University of Hong Kong (Project No. 7200551, 9610387), the Hong Kong Polytechnic University Grant (No. 1-ZE8C), National Science Foundation of China (21703076), the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement no. 609405 (COFUNDPostdocDTU), Natural Science Foundation of Jiangsu Province of China (BK20170466).

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