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Tuning the optical emission of MoS$_2$ nanosheets using proximal photoswitchable azobenzene molecules

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We report photoluminescence measurements performed on monolayer- and two-layer-MoS$_2$ placed on two types of mixed self-assembled monolayers (mSAMs) of photoswitchable azobenzene molecules. The two mSAMs differ via the electronegative character of the azobenzene derivatives. Thin layers of a transition metal dichalcogenide—MoS$_2$—were mechanically exfoliated on mSAM to allow for direct interaction between the molecules and the MoS$_2$ layers. When the MoS$_2$ nanosheet is in contact with the electropositive azobenzene molecules in trans configuration, an emission side band at lower energies and at low excitation powers suggest n-type doping. The photoisomerization of the molecules from trans to cis configuration lowers the doping, quenching the side band and enhancing the overall PL efficiency by a factor of $\sim$3. Opposite results were observed with the chlorinated, more electronegative molecules, exhibiting a reversed trend in the PL efficiency between trans and cis, but with an overall larger intensity. The type of doping induced by the two types of mSAMs was determined by Kelvin probe force microscopy technique.

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Monolayer (1L)-MoS$_2$ is a two-dimensional (2D) material that has attracted considerable attention due to its semiconducting properties including band gap modulation, competitive mobility, and large field effect on/off ratios exceeding $10^5$. These properties make MoS$_2$ a promising material for developing the next generation of few atom-thin logic devices, photodetectors, and light emitting diodes.

When scaling down the number of atomic layers to one monolayer of MoS$_2$, a transition from indirect to direct energy gap occurs, enhancing the efficiency of the photoluminescence (PL) emission at visible wavelengths. Furthermore, due to the strong Coulomb interaction between the electron and hole pair, a stable PL can be measured at room temperature. Several approaches have been proposed to tune the optical properties of MoS$_2$. Recently, it has been predicted that straining MoS$_2$ modifies the size of the bandgap and the carrier effective masses. Alternatively, the PL intensity can be tuned via electrical gating. Knowing that the uncontrolled and undesired point defects are formed in the MoS$_2$ monolayer, we understand that in order to improve the quantum yield of this material, these point defects need to be neutralized. This was already demonstrated by Mouri et al., while measuring the PL intensity of 1L-MoS$_2$, which was drastically enhanced (reduced) when p(n)-type dopants cover its surface. The ability to modulate optical properties by means of external stimuli is highly sought for the design of displays and smart metamaterials. In this regard, optical tuning of devices represents a technological goal that can be achieved using photochromic compounds providing a straightforward way to realize photoswitchable devices. For instance, chemisorbed, highly ordered azobenzene self-assembled monolayers (SAMs) are widely known to photoisomerize between trans and cis conformations.

Among various tunable properties of SAMs, which serve as the basis for sensors, memory devices, and organic thin-film transistors, the quantum efficiency of a semiconductor in intimate contact can also be tuned. Therefore, heterostructures made by sandwiching SAMs between a metallic film and a monolayer of a 2D crystal are expected not only to tune the electronic properties of the 2D materials, as demonstrated previously by Margapoti et al., but also to optically modulate their spectroscopic properties. Therefore, keeping in mind that the optoelectronic properties of MoS$_2$ are influenced by substrate, it is expected that the use of photochromic molecules as electron donors/acceotors should result in the photo-tuning and -switching of the MoS$_2$ optical properties. In this work, we report photoswitchable optical properties of 1L- and two-layer (2L)-MoS$_2$ and the tunability of the MoS$_2$ optical properties by means of a proximal mixed self-assembled monolayers (mSAMs) of photochromic azobenzene molecules. We demonstrate that the proximal SAM facilitates optically gateable doping of the MoS$_2$ monolayer and gives rise to PL enhancement for p-type doping or quenching for n-type doping.

The enhancement for p-type doping can be explained as the suppression of extra negative charges from negative triions, enhancing the PL recombination of the neutral exciton. In contrast, the n-type doping increases the injection of additional electrons, resulting in a decreasing of the neutral
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exciton peak. This can be understood considering a three level model. The trion ($I_t^{(-)}$) to neutral ($I_n$) PL-intensity-ratio can be written as $I_t^{(-)}/I_n = \gamma_t \Gamma_t / \gamma_n \Gamma_n$, where $\gamma_{n(\kappa)}$ is the neutral exciton (trion) radiative decay rate, $\Gamma_n$ is the trion decay rate, and $\Gamma_t$ is the trion formation decay.\cite{12} Therefore, increasing the trion intensity $I_t^{(-)}$ increases the population of the intermediate trion level through $\gamma_t$ with the consequent lowering of the radiative exciton decay rate $\gamma_n$. Moreover, we report on the tunability and reversibility of this effect simply by switching the azobenzene molecules from trans to cis, which can shift the Fermi level of the system.

We describe the PL effect and Kelvin probe force microscopy (KPFM) on a 1L-MoS$_2$ and multilayers when directly exfoliated on mSAM. A solid-state laser diode (532 nm) was used for the PL measurements focused to $\sim 0.8 \mu m^2$ using a Mitutoyo Apo Plan SL objective (NA = 0.55). The maximum excitation power used was maintained below 1190 W/mm$^2$ to avoid damaging the MoS$_2$ flake and mSAM. The PL signal was detected using a liquid-nitrogen-cooled CCD camera via a 0.55 m monochromator. The sample was cooled to $\sim 10$ K using a cold finger cryostat. The KPFM characterization were performed using an Asylum Research scanning probe microscope employing a Pt-Ir coated Si cantilever with a spring constant of $\sim 2$ N/m. The KPFM measurements were conducted in a non-contact mode, and the tip was scanned above the sample at a height of 10 nm with a drive frequency of 67 kHz and AC voltage amplitude of 3 V.

The mixed SAMs (mSAM) consist of the well-known\cite{22,25} photoisomerizable azobenzene derivative (E)-6-(4-(phenyl diazenyl)phenoxy)hexane-1-thiol (HS-C$_6$AZO) mixed with spacer-molecules, 2-(2-mercapto)-1-hexanol, in the ratio 1:1, such as to prevent aggregation of the photomediated molecular conformational switching.\cite{25}Spacer molecules and HS-C$_6$AZO were purchased from Sigma-Aldrich and Prochimia Surfaces Sp., respectively. The HS-C$_6$AZO is considered to be electropositive whereas the use of (E)-6-(4-(4-chlorophenyl)diazenyl)phenoxy)hexane-1-thiol (HS-C$_6$AZO-Cl) also mixed with the -(2-mercapto)-1-hexanol in the ratio 1:1 should lead to an electronegative behaviour. The HS-C$_6$AZO-Cl was synthesized as reported in literature.\cite{26,27} The mSAM in this case is defined as mSAM-Cl.

MoS$_2$ flakes (left most panels in Fig. 1(b)) were mechanically exfoliated from bulk crystals onto the functionalised Au-quartz substrate. A scheme of the configuration is shown in Fig. 1(a). Photoisomerization experiments were performed by irradiating the sample with 366 nm UV-laser for 60 min inducing conformational isomerization from trans to cis. The switching back of the azobenzene molecules from cis to trans was reached irradiating the sample with a 475 nm laser for 60 min. Typical integrated PL map intensity modulation between trans and cis of 2L-MoS$_2$-mSAM is shown in Fig. 1(b). Here, the weak PL intensity (second left image) for the HS-C$_6$AZO in trans can be optically tuned by irradiating the sample with the UV-light. The consecutive panels were recorded at different illumination times up to 60 min, after which the PL map intensity is now much brighter and the azobenzene molecules should be completely switched in cis.

The switching back of the molecules to trans is shown in the last panel. The integrated PL spectra for the exposure time, t = 0, before UV-light exposure (red spectrum), after 60 min of UV-light exposure (blue spectrum), and after 60 min of exposure with 475 nm laser (orange spectrum) are shown in Fig. 1(c).

The spectra show a clear enhancement of the intensity of the PL intensity by a factor of three times, switching the HS-C$_6$AZO from trans to cis, and results show that the process is reversible. It is worth to mention that during the recording time of the spectra (30 s), the 532 nm wavelength of the excitation laser is not provoking any conformational changes of the photochromic molecules.

Notably, similar experiments were conducted on 1L-MoS$_2$-mSAM and 1L-MoS$_2$-mSAM-Cl. Fig. 2(a) shows the normalised integrated PL spectra when the HS-C$_6$AZO are in trans for excitation powers $P_0 = 1.23$ W/mm$^2$, $P_1 = 6.13$ W/mm$^2$, $P_2 = 47.7$ W/mm$^2$, $P_3 = 45$ W/mm$^2$, and $P_4 = 1060$ W/mm$^2$. At lowest excitation power ($P_0$), the recorded PL (red spectrum) is asymmetric, showing a main neutral excitonic peak ($X_0$) at $\sim 1.943$ eV as well as a broad side-band (D), on the lower energy side. At higher excitation powers, the intensity of the $X_0$ peak increases linearly, while the D peak slowly saturates. At the excitation power $P_2$, the spectrum starts to decrease, while the PL red shifts and the...
FWHM becomes broader. Similarly, in cis (Fig. 2(b)) the PL spectrum (∼1.894 eV; P0) is red shifted with the excitation power and the FWHM increases. However, the D-peak is now completely suppressed. Both measurements, performed in trans and in cis, show a clear red-shift of the spectra as the laser power is enhanced and also the FWHM increases. The size of the red-shift differs between the trans and the cis configuration, being ΔE1T = 80 meV in trans and ΔE1C = 40 meV in cis.

We now consider the results obtained using mSAM-Cl (Figs. 2(c)–2(d)). Here, the PL spectral recorded either in trans or in cis shows no D-peak and the PL intensity shows opposite behaviour compared to the sample with the mSAM discussed above. At low excitation powers, the PL spectra are symmetric at ∼1.92 eV in trans (Fig. 2(c)) and asymmetric in cis with a maximum at ∼1.945 eV and a feature on the higher energy side of the PL spectrum at ∼1.98 eV (Fig. 2(d)). By increasing the excitation power, the PL spectra get broader and red-shift by about ΔE2T = 24 meV in trans and of ΔE2C = 40 meV in cis. Notice that the red-shift upon increasing the excitation power is higher in cis than in trans for the sample MoS2-mSAM-Cl, in contrast to MoS2-mSAM, where the observed red-shift in trans is almost twice as that for cis.

The unexpected red-shift of the PL spectra depend on excitation power, observed for both the two types of samples (1L-MoS2-mSAM and 1L-MoS2-mSAM-Cl), cannot be attributed to molecular switching induced by the laser, because there is a reversible PL behaviour anytime we increase and reduce the laser power. Therefore, we exclude any correlation with the molecules. Furthermore, the switching of the molecules from trans to cis shows a clear PL intensity enhancement as reported in the respective integrated PL intensity maps in the inset of Figs. 2(a) and 2(b).

Another possible reason of the red-shift and broadening of the spectra upon increasing the excitation power can be attributed to heating. In order to find the cause of this effect, we need to compare these results with reference samples. Indeed, changing the substrate, using SiO2 instead of quartz, the increase of the excitation power up to P4 = 1060 W/mm² does not lead to red-shift as neither to broadening or quenching of the PL emission. The main difference in using the two substrates, SiO2 or quartz, lies on the formation of Au grains with size of 30 ± 10 nm in diameter and 4 ± 1 nm in height, obtained evaporating Au on the quartz substrate.28 Therefore, we attribute this universal red-shift and the PL intensity decrease upon increasing the excitation power to excitation of localized surface plasmons at grain boundaries. The enhancement or the quenching of the PL emission of the active material can be dictated by the distance between the active material and the metal grains,13,29 which is usually optimal at 10 nm for PL enhancement.13,30,31 On the other hand, an additional recognized plasmonic effect is the PL red-shift when the emitter and the metal grains are too close (below 10 nm), which can be explained as a dipole-dipole interaction between the emitter and the metal grain.31,32

PL spectra recorded from the sample MoS2-mSAM and MoS2-mSAM-Cl (red spectra) are presented in Figs. 3(a) and 3(b), showing clearly the impact that the two types of azobenzene molecules have on the 2D crystal. That is a symmetric PL spectrum and 8× more intensity for the case of HS-C6AZO-Cl with respect to the HS-C6AZO, when both types of molecules are in trans. Switching the molecules in cis (blue spectra) improves the PL signal only for the sample with HS-C6AZO of about 2.5× (Fig. 3(a)) and...
instead, lower the PL of the same amount for the sample with HS-C6Azo-Cl (Fig. 3(b)). Therefore, by carefully choosing the type of the molecules, one can tune the optical properties of the 2D crystals.

In order to understand the reason behind the switchable optical properties as well as the opposite behaviour of the two azobenzene molecules, we performed KPFM measurements for both the two samples MoS2–mSAM-Au and MoS2–mSAM-Cl-Au, in trans and in cis.

Figs. 4(a) and 4(b) show the KPFM measurements of the surface potential (SP) of MoS2–trans–mSAM-Cl and MoS2–trans–mSAM, respectively. The highest SP is found for MoS2–mSAM hybrids. In absolute terms, an increase of the SP is associated with a lower work function, thus increasing the n-doping character. Likewise, in relative terms, an increase of the SP from multilayer (>3L) MoS2–mSAM to the 1L-MoS2–mSAM (Fig. 4(a)) indicates that the Fermi level goes upward, thereby suggesting n-type of doping on the 1L-MoS2. For MoS2–mSAM-Cl, the absolute surface potential values are lower and the trend is reversed, indicating a lower doping or even p-doped (Fig. 4(b)). Figure 4(c) qualitatively illustrates these observations.

The observation of a higher n-type doping level for MoS2–trans–mSAM is in agreement with drastic quenching of the integrated PL intensity,12 as reported in Fig. 3(a) (red spectrum). Accordingly, the PL intensity is higher for trans–mSAM-Cl where a lower doping level in trans (red spectrum) is present. When the molecules switch in cis, the surface potential is strongly shifted to lower values by up to 300 mV.28

Thus, the Fermi energy for both cis forms of the molecules shifts the Fermi level towards lower energy, increasing the neutral exciton efficiency (blue spectrum in Fig. 3(a)). It is interesting to note that the sample MoS2–mSAM-Cl in trans has higher PL intensity than the molecules in cis. This can be understood as a lower p-doping level in MoS2–trans–mSAM-Cl as compared to the cis counterparts. The more asymmetric shape in cis compared to trans, showing a broadening at ~1.98 eV, can be attributed to an excess of positively charged density that in this case might create positive trions, thereby decreasing the overall PL intensity. Note that our observations extend and complement those by Mauri et al.12 While p-doping does increase the PL yield relative to n-doping, it decreases the PL yield relative to the undoped material.

In conclusion, we presented a study on the optical properties of the MoS2 mono- and multi-layers exfoliated on top of Au substrate functionalized with azobenzene molecules. An increase of PL emission between trans–mSAM and cis–mSAM was recorded using a photo-tunable n-type of doping, and opposite behaviour was recorded for the photoswitchable p-type of doping. This was possible using photoswitching azobenzene molecules proximal to MoS2 monolayer, which tune the Fermi level of the proximal material, tuning the doping between trans and cis. Through KPFM, we confirm the type of doping induced by the two mixed monolayers mSAM and mSAM-Cl, by looking at the surface potentials both in trans and in cis for the different layer thicknesses.

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