Solvatochromic Effect on the Photoluminescence of MoS_2 Monolayers

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Two-dimensional (2D) materials have attracted intense interest because of their unique structure[1] and physical properties.[2] Much work has been done on 2D transition-metal dichalcogenide monolayers because of their direct bandgaps,[1b,3] and potential nanoelectronic and optoelectronic applications.[1a,2f,4] For example, MoS_2 and WS_2 monolayers have intense and valley-selective photoluminescence (PL),[2f,4] which has potential applications in valleytronics. Transistors fabricated from MoS_2 monolayers showed high performance (>10^8 on/off ratio and moderate carrier mobility up to 200 $cm^2 Vs^{-1}$)[2d] and have been integrated into circuits.[2a,b] The optical and electrical properties of 2D semiconductors should change with the surrounding environment because of their atomically thin nature. This could be used in bandgap engineering, carrier mobility engineering,[2d,5] and sensing.[6] The carrier mobility of MoS_2 monolayers can be enhanced by about 100 times with high-κ dielectric gating[2d] or polymer electrolyte gating.[5]

Transition-energy shifts in different surrounding environments, traditionally called solvatochromism, have been widely investigated for fluorophores,[7] quantum dots,[8] and carbon nanotubes.[9] Depending on the molecule/nanomaterial and the surrounding solvent, solvatochromism (usually measured by absorption or fluorescence) can be positive (redshift) or

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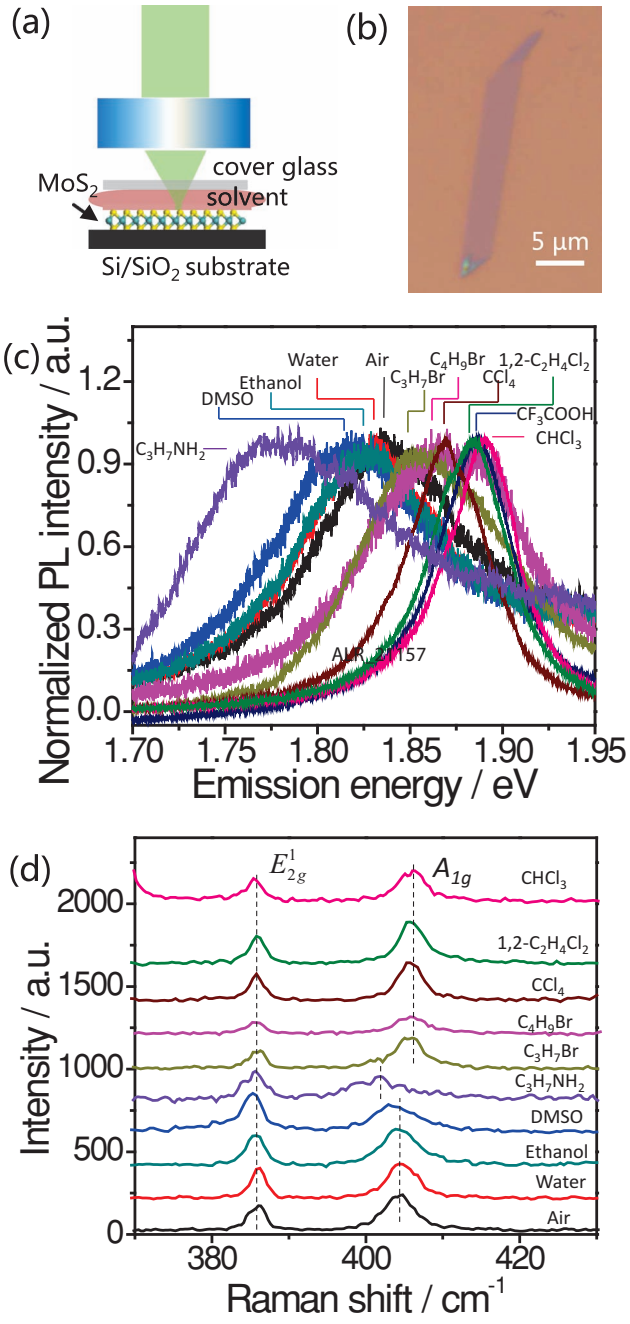

Figure 1. a) Illustration of the experimental configuration. b) Typical optical image of a MoS_2 monolayer. c) PL and d) Raman spectra of MoS_2 monolayers with different solvent surroundings.

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negative (blueshift) with maximum shifts up to hundreds of meV.[7b] Many applications have been explored based on solvatochromism, such as probing local polarity in micelles[10] and cells.[11] Since 2D monolayer semiconductors have a large exciton binding energy,[12] the excitonic transition energy should have a large solvatochromic shift. However, solvatochromism of 2D materials has not been reported yet. Herein, we investigate the effect of surrounding solvents on the PL of MoS_2 monolayers. It is revealed that, compared with PL in air, the PL from the MoS_2 monolayer shows redshifts (up to –60 meV) with nonhalogenated solvent surroundings, but blueshifts (up to 60 meV) and a large intensity increase (up to 50 times) with halogenated solvent surroundings.

Figure 1a shows the micro-Raman–PL experimental configuration, in which the top side of the MoS_2 monolayer was covered by different solvents during experiments. A typical optical image of the MoS_2 monolayer is shown in Figure 1b. MoS_2 monolayers showed a red contrast of about 10%, the $E_{2g}{}^1$ Raman mode at 386 cm^{-1}, and the A_{1g} Raman mode at 404 cm^{-1}.[13] With air surroundings, the MoS_2 monolayer showed a strong emission peak at ≈1.84 eV, corresponding to a direct excitonic transition at the K point.[1b,3] PL spectra of MoS_2 monolayers with different solvent surroundings are shown in Figure 1c, with an emission peak in the range of 1.78 to 1.90 eV. PL emission from the MoS_2 monolayer was redshifted when the surroundings changed from air to nonhalogenated solvents (water, ethanol, dimethyl sulfoxide (DMSO), propylamine), but blueshifted when the surroundings changed from air to halogenated solvents (trifluoroacetic acid, methylene chloride, chloroform, carbon tetrachloride, butyl bromide, propyl bromide). Raman characterization

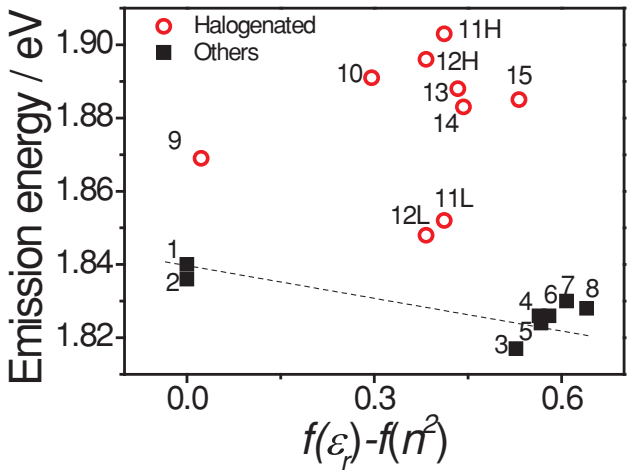

Figure 2. Plot of emission energy of the MoS_2 monolayer against $f(\varepsilon_r)$–$f(n^2)$ of surrounding solvents. The black dashed line is to guide the eye. The numbers near data points are the corresponding solvent numbers assigned in Table 1. The 11H/L and 12H/L represent two emission peaks for solvents 11 and 12, respectively.

showed that the A_{1g} mode of the MoS_2 monolayer upshifted by ≈1.5 cm^{-1} in halogenated solvents and downshifted by ≈4 cm^{-1} in propylamine, thus indicating significant p-doping and n-doping of the MoS_2 monolayer,[14] respectively. For other solvent surroundings, no obvious Raman shift was observed (Figure 1d and **Table 1**), which suggests no doping or straining of the MoS_2 monolayer.

Generally, the emission energy shift ΔE in solvatochromism is related to the dielectric constant ε_r and

Table 1. Refractive index, dielectric constant, and $f(\varepsilon_r)$–$f(n^2)$ of solvents used in the experiments, and MoS_2 monolayer emission energy, emission intensity, and A_{1g} frequency in different solvent surroundings. Only selected Raman and PL spectra for different solvent surroundings are shown in Figure 1c and d. The maximum emission intensity of MoS_2 monolayers in different solvents was calibrated by the Si 520 cm^{-1} Raman intensity.

Entry	Solvent	n[a)]	ε_r[a)]	$f(\varepsilon_r)$–$f(n^2)$	Emission energy [eV]	Emission intensity [a.u.]	A_{1g} frequency [cm^{-1}]
1	air	1.000	1	0.000	1.840	2.4×10^2	404.3
2	hexane	1.375	1.89	0.000	1.836	2.9×10^2	404.6
3	dimethyl sulfoxide	1.478	47.2	0.527	1.817	2.1×10^2	404.0
4	formamide	1.448	111	0.564	1.826	2.2×10^2	404.7
5	acetone	1.362	21.0	0.567	1.824	2.1×10^2	404.3
6	ethanol	1.361	25.3	0.580	1.826	2.4×10^2	404.3
7	acetonitrile	1.346	36.6	0.608	1.830	2.1×10^2	404.5
8	water	1.333	80.1	0.640	1.828	2.7×10^2	404.4
9	carbon tetrachloride	1.460	2.24	0.023	1.869	1.1×10^4	405.4
10	chloroform	1.446	4.81	0.296	1.891	1.0×10^4	405.9
11	propyl bromide	1.434	8.09	0.412	1.903/1.852[b)]	3.9×10^2	405.6
12	butyl bromide	1.440	7.01	0.383	1.896/1.848[b)]	4.1×10^2	405.9
13	methylene chloride	1.424	8.93	0.434	1.888	1.1×10^3	405.5
14	1,2-dichloroethane	1.444	10.4	0.443	1.883	1.0×10^4	405.7
15	trifluoroacetic acid	1.285	8.55	0.532	1.885	4.1×10^4	–[c)]
16	propylamine	1.388	5.31	0.349	1.774	82	400.8

[a)]Data are from Lange's Handbook of Chemistry, 15th edition; [b)]Two emission components were observed and fitted; [c)]The A_{1g} mode was not observed due to high background.

refractive index n of the solvent, and further can be expressed by[7a,9a] $\Delta E \propto -(\alpha_e - \alpha_g)[f(\varepsilon_r) - f(n^2)]$ where α_e and α_g are the polarizabilities of the excited state and the ground state, respectively, and $f(x) = \frac{2(x-1)}{2x+1}$ is the Onsager polarity function; $f(\varepsilon_r)$–$f(n^2)$ is responsible for different interaction terms, such as dipole–dipole, dipole–induced dipole, and dispersion interactions.[7a] Table 1 shows the MoS_2 monolayer emission energy, emission intensity, and A_{1g} frequency, together with ε_r and n of the surrounding solvents.

Figure 2 plots the MoS_2 monolayer emission energy in dependence on $f(\varepsilon_r)$–$f(n^2)$. Since there is significant doping for halogenated solvents (entries 9–15 in Table 1) and propylamine (entry 16 in Table 1), we first looked into other solvents (entries 1–8 in Table 1). For solvents 1–8, the PL emission redshifts as $f(\varepsilon_r)$–$f(n^2)$ increases (black squares in Figure 2), which means more stabilization for the excited state in polar solvents. This is similar to the observed redshift of the transition energy for quantum dots[8] and carbon nanotubes[9] in polar solvents, mainly attributable to the larger dielectric screening in polar solvents.

In contrast to the redshift observed for nonhalogenated solvent surroundings, the PL from MoS_2 monolayers in halogenated solvent surroundings showed blueshifts. Specific bonding of halogen atoms to MoS_2 could affect the emission energy of the MoS_2 monolayer. Reference work has shown that chlorine and bromine can bind to the van der Waals gap between MoS_2[15] and WS_2[16] layers, respectively, which can give intense PL at low temperature. This is attributed to the bound excitons near neutral halogen atoms. However, bound excitons near halogen atoms should show a redshift,[15,16] and cannot explain the blueshift of PL from MoS_2 monolayers in halogenated solvent surroundings.

Several other studies also reported that bound excitons near impurities could introduce an emission peak at the lower-energy side.[17] But this is also not the case here because 1) the MoS_2 monolayer samples were cleaved from high-quality single crystals and should have a high quality; 2) emission from bound excitons near impurities can only be observed at low temperatures (T<175 K)[17b,c] and not at room temperature; and 3) emission from bound excitons near impurities is located at ≈1.80 eV, significantly lower than the observed emission peaks in this work (1.82–1.84 eV in solvents without doping effect and 1.85–1.90 eV for halogenated solvents).

One possibility for the abnormal blueshift observed for halogenated solvent surroundings could be p-doping-induced dissociation of charged excitons (i.e., trions) to neutral excitons. Electrical gating experiments have shown trion formation in MoS_2 and $MoSe_2$ monolayers.[18] Trion emission even dominates the PL spectrum of the as-prepared MoS_2 monolayer due to the intrinsic n-type nature of MoS_2 monolayers.[18a] The trion binding energy is ≈20–50 meV depending on the carrier concentration.[18] By applying a negative gate, electrons can be extracted from the MoS_2 monolayer and then negative trions dissociate to neutral excitons. In PL measurements, the low-energy trion emission disappeared and higher-energy exciton emission was observed.[18a] For MoS_2 monolayers in air, the electron density is ≈10^{13} cm^{-2},[2d,14,18a,19] whereas for MoS_2 monolayers with halogenated solvent surroundings, the carrier (electron) density decreased by ≈4 × 10^{12} cm^{-2} according to the A_{1g} upshift of ≈1.5 cm^{-1}.[14] Therefore halogenated solvents extracted electrons from MoS_2, and then played a similar role to negative electrical gating. As a result, a blueshift was observed for MoS_2 monolayers with halogenated solvent surroundings due to the spectrum weight shift from trion emission to exciton emission.

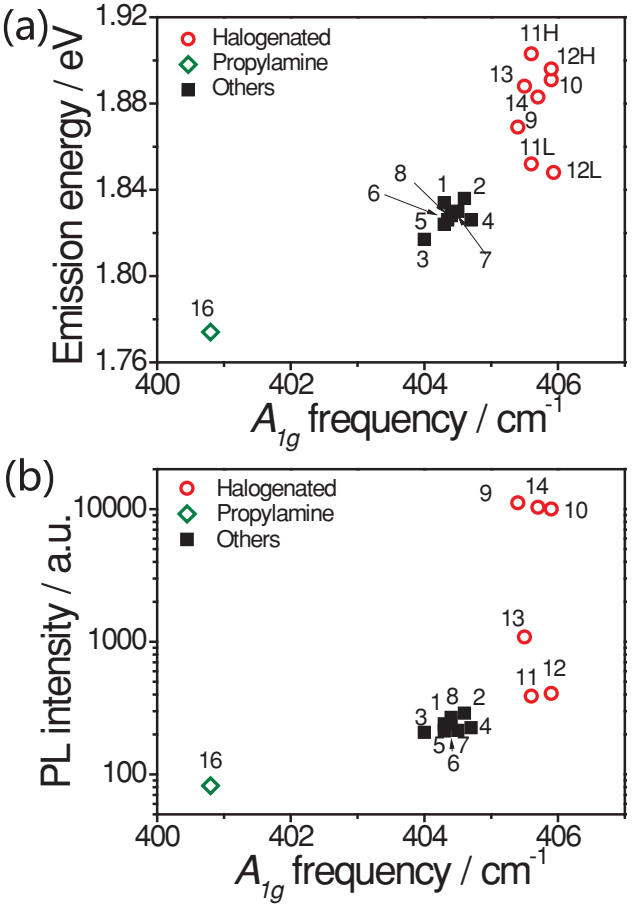

Figure 3. Plots of a) emission energy and b) emission intensity against A_{1g} frequency for MoS_2 monolayers in different solvent surroundings. The numbers near data points are the corresponding solvent numbers assigned in Table 1. The 11H/L and 12H/L represent two emission peaks for solvents 11 and 12, respectively.

Figure 3a and b show emission peak energy and emission intensity against A_{1g} frequency. The emission energy difference (10–60 meV) between MoS_2 monolayers in halogenated solvents and in air matches well with the trion and exciton energy difference (20–50 meV).[18a] Additionally, about 2–50 times stronger PL was observed in halogenated solvents than in air (Figure 3b). This emission intensity increase is consistent with higher PL emission for excitons than that for trions observed in electrical gating experiments.[18a] The low emission intensity for trions could be due to faster nonradiative decays.[20] Additionally, the emission spectra of MoS_2 monolayers in propyl bromide and butyl bromide show two emission components, which could be due to simultaneous trion and exciton emissions, but this needs further verification. Finally, for propylamine surroundings, the large redshift could be due to increased trion binding energy when the MoS_2 monolayer is more n-doped.[18a]

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In conclusion, the effect of solvent surroundings on 2D MoS_2 monolayer has been investigated, and shows emission energy tuned from 1.78 to 1.90 eV. The general solvatochromism mechanism still works for solvents without doping effect. For halogenated solvents showing a doping effect, an abnormal blueshift and large PL intensity increase were observed, which were attributed to dissociation of negative trions to neutral excitons. The environment-sensitive PL emission of MoS_2 monolayers could have potential applications in sensing and bioimaging.

Experimental Section

MoS_2 single crystals were purchased from SPI Supplies. MoS_2 monolayers were mechanically exfoliated on Si/SiO_2 substrates (oxide thickness of 300 nm). Optical images were taken on an Olympus BX51 microscope equipped with a 100× objective and DP71 camera. Micro-Raman–PL measurements were performed on a JY Horiba HR800 system. A long-working-distance 50× objective was used for laser focusing and signal collecting. An 1800 grooves mm^{-1} grating was used to disperse the Raman–PL signal, corresponding to a spectral resolution of ≈0.4 cm^{-1}. Optical contrast (red contrast of ≈10%) and Raman characterization ($E_{2g}{}^1$ at 404 cm^{-1} and A_{1g} at 386 cm^{-1}) were used to locate and identify monolayers.[13]

All solvents were of analytical purity and purchased from Beijing Tongguang Fine Chemical Company. In micro-Raman–PL measurements, the solvent layer was kept as thin as ≈100 μm to avoid focus distortion. All measurements were performed at room temperature. To avoid laser heating on MoS_2 monolayers in different surroundings, the laser power was kept at ≈0.7 mW, corresponding to a power density of ≈0.7 mW μm^{-2}. No Raman or PL shift was observed at or below this laser power.

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