


SCIENTIFIC REPORTS



OPEN

Control of Radiative Exciton Recombination by Charge Transfer Induced Surface Dipoles in MoS₂ and WS₂ Monolayers

Received: 15 November 2015

Accepted: 21 March 2016

Published: 07 April 2016

Peng Hu¹, Jun Ye², Xuexia He¹, Kezhao Du¹, Keke K. Zhang¹, Xingzhi Wang³, Qihua Xiong³, Zheng Liu¹, Hui Jiang¹ & Christian Kloc¹

Due to the two dimensional confinement of electrons in a monolayer of 2D materials, the properties of monolayer can be controlled by electrical field formed on the monolayer surface. F₄TCNQ was evaporated on MoS₂ and WS₂ monolayer forming dipoles between strong acceptor, F₄TCNQ, and monolayers of MoS₂ or WS₂. The strong acceptor attracts electrons (charge transfer) and decreases the number of the ionized excitons. Free excitons undergo radiative recombination in both MoS₂ and WS₂. Moreover, the photoluminescence enhancement is stronger in WS₂ where the exciton-phonon coupling is weaker. The theoretical model indicates that the surface dipole controls the radiative exciton recombination and enhances photoluminescence radiation. Deposition of F₄TCNQ on the 2D monolayers enables a convenient control of the radiative exciton recombination and leads to the applications of these materials in lasers or LEDs.

When an exciton, a quasiparticle consisting of an electron and a hole bound together by simple Coulomb interaction, recombines, i) photoluminescence occurs in the case of weak exciton-phonon coupling or ii) exciton recombines radiation-less increasing the phonon energy if this coupling is strong. In a monolayer of transition metal dichalcogenides (TMD), or a two dimensional electron gas, excitons can interact with free electrons forming charged excitons also known as trions, quasiparticles composed of two electrons and a hole¹. Due to the presence of these tightly bound negative trions, the number of non-bounded excitons available for radiative recombination is limited and the photoluminescence is suppressed. In other words, the non-bounded excitons cannot radiative recombine producing photon (light) because they are bonded with free electrons forming trions²⁻⁶. Therefore, to increase the photoluminescence, the concentration of trions needs to be reduced. A strong electrical field formed by gate electrode on the two-dimensional (2D) layer of TMD or dipoles on the surface of TMD monolayer can reduce the trion concentration¹.

In previous studies, a chemical doping method was used to enhance the photoluminescence by interaction of TMD monolayer with acceptor in solvent^{2,5}. Furthermore, some reports studied PL and optical properties controlled by the charge transfer between MoS₂ and metal nanoparticle⁷ or graphene quantum dots⁸. It was shown that not only the PL intensity has been changed, but also the phase transition in MoS₂ monolayer is caused by charge transfer⁹. In this work, we evaporate 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) on TMD monolayer forming dipoles between strong acceptor, F₄TCNQ and monolayers of MoS₂ or WS₂. The strong acceptor attracts electrons (charge transfer) and decreases the number of the ionized excitons. Free excitons undergo radiative recombination in both MoS₂ and WS₂. Moreover, the photoluminescence enhancement is stronger in WS₂ where the exciton-phonon coupling is weaker. No solvent was used, which provide a clean system to compare to theoretical calculations. The theoretical model indicates that the surface dipole is controlling the radiative exciton recombination, which further increases the photoluminescence.

¹School of Materials Science and Engineering, Nanyang Technological University, 639798 Singapore. ²Institute of High Performance Computing, Agency for Science, Technology and Research, 138632 Singapore. ³School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore. Correspondence and requests for materials should be addressed to Z.L. (email: z.liu@ntu.edu.sg) or H.J. (email: jianghui@ntu.edu.sg) or C.K. (email: ckloc@ntu.edu.sg)

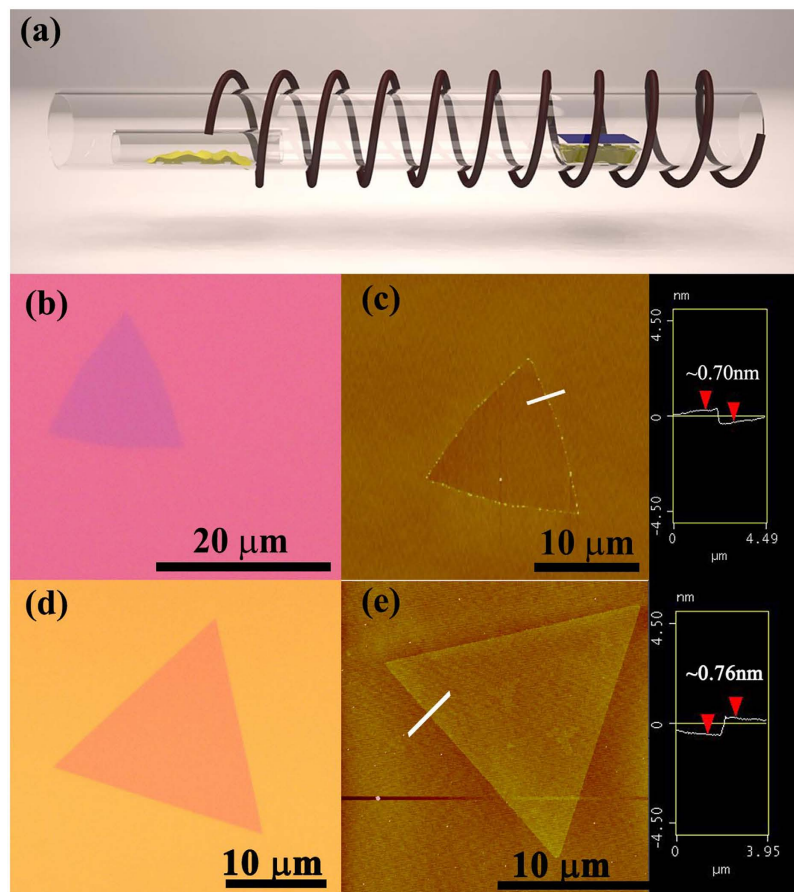


Figure 1. (a) Monolayer WS₂ and MoS₂ growth apparatus. (b) Optical image of triangle monolayer WS₂. (c) AFM image of a monolayer WS₂ on a SiO₂/Si substrate and the corresponding section analysis. (d) Optical image of triangle monolayer MoS₂. (e) AFM image of a monolayer MoS₂ on a SiO₂/Si substrate and the corresponding section analysis.

Results

MoS₂ and WS₂ monolayer growth and characterization. A triangle monolayer of WS₂ and MoS₂ was grown with the chemical vapor deposition (CVD) method onto a SiO₂/Si wafer. The monolayer growth apparatus is shown in Fig. 1(a). Triangular WS₂ and MoS₂ were grown at random locations on the substrate. Figure 1(b,d) show the optical images of the WS₂ and MoS₂, respectively. The thickness of the WS₂ and MoS₂ was determined by atomic force microscopy (AFM), as shown in Fig. 1(c,e). The AFM images indicate that both the WS₂ and MoS₂ have a smooth surface. The cross section height of the WS₂ and MoS₂ is approximately 0.70 nm and 0.76 nm, respectively, which corresponds to the monolayers of WS₂^{5,10} and MoS₂^{11–14}.

The monolayer structure of WS₂ and MoS₂ is further confirmed by the Raman spectrum shown in Fig. 2. The E_{2g}¹ and A_{1g} modes of monolayer WS₂ are located at approximately 355 and 417 cm⁻¹, respectively^{15–18}. With the number of layers increased, the in-plane vibrational E_{2g}¹ is slightly red-shifted, and the out-of-plane A_{1g} mode is blue-shifted. The energy difference between the Raman E_{2g}¹ and A_{1g} modes increased with the layer number. Thus, the energy difference can be used to identify the number of layers of WS₂. The energy difference shown in Fig. 2(a) is 62.5 cm⁻¹, which coincides with previous reports for monolayer WS₂^{15,19}. The same phenomenon is also observed in monolayer MoS₂. The in-plane vibrational E_{2g}¹ phonon mode is ~385 cm⁻¹, and the out-of-plane A_{1g} mode is ~404 cm⁻¹. The energy difference between the two modes is also dependent on the number of layers of MoS₂. The energy difference between the two modes is 18.2 cm⁻¹, as shown in Fig. 2(b), indicating that the MoS₂ is a monolayer^{2,14,17,20,21}.

Photoluminescence intensity after F₄TCNQ was deposited onto monolayer MoS₂/WS₂.

Figure 3(a) shows that the PL intensity before and after F₄TCNQ was deposited onto monolayer WS₂. The PL intensity is approximately fifty times higher after the F₄TCNQ deposition. The position of the PL peak of monolayer WS₂ is slightly blue-shifted, while the peak shape did not change, as shown in Fig. 3(b). The PL intensity is also increased by approximately ten times after the F₄TCNQ is deposited on MoS₂ monolayer. The position of the peak is also slightly blue-shifted, but the shape is not changed, as is shown in Fig. 3(c,d).

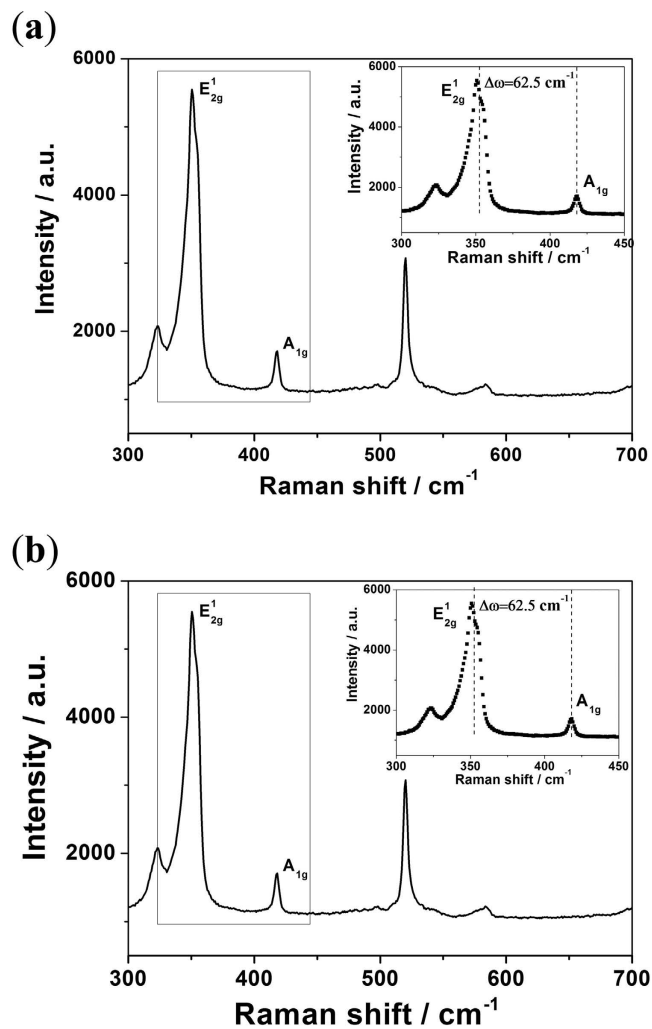


Figure 2. Raman spectra of a CVD-grown WS₂ monolayer (a) and MoS₂ monolayer (b). The inset shows the energy difference between the Raman E_{2g}¹ and A_{1g} modes.

Discussion

To understand the charge transfer from MoS₂/WS₂ to F₄TCNQ, we performed density functional (DFT) calculations²² on the model systems shown in Fig. 4. In both the F₄TCNQ-doped MoS₂ and WS₂ cases, electron density depletion (as indicated by the white isosurfaces) were found in the interface regions where the nitrogen atoms in the F₄TCNQ molecules are closest to the surface sulfur atoms in MoS₂ and WS₂, as shown in Fig. 4(a,c), respectively. The electron density depletion in the MoS₂ layer is slightly greater than that in the WS₂ layer according to the electron density difference plots. An electron density increase (red isosurfaces) is observed on the F₄TCNQ molecules in both cases, as shown in Fig. 4(a,c). Charge transfer occurs around the interface regions in both cases. The energy level of F₄TCNQ and MoS₂/WS₂ are shown in Supporting Information - Figure S1. In addition, the barycenters of the holes (white isosurfaces) shown in Fig. 4(b,d) clearly suggest that the holes are close to the MoS₂ and WS₂ surfaces, indicating the charge transfer from MoS₂ or WS₂ to F₄TCNQ. The charge transfer distance (D_{CT}) between MoS₂ and F₄TCNQ (calculated $D_{CT} = 1.299 \text{ \AA}$) is shorter than that between WS₂ and F₄TCNQ (calculated $D_{CT} = 1.391 \text{ \AA}$). However the charge transfer direction, indicated by arrows on the Fig. 4(b,d) is determined by the orientation of F₄TCNQ molecule relative to the surface of the TMD monolayer.

According to our discussion in introduction, the charge transfer between MoS₂ or WS₂ monolayer and acceptor, F₄TCNQ forms dipole layers at interface and reduces the ratio of charged exciton to neutral excitons. Therefore, the photoluminescence (PL) of both materials was enhanced due to the charge transfer.

The experimental results for PL enhancement for both MoS₂ and WS₂ are similar to the earlier reported photoluminescence of MoS₂ and WS₂ doped with F₄TCNQ from solution^{2,5}. In previous studies^{2,5}, mechanical exfoliated MoS₂ and WS₂ were used. Mechanical exfoliation is the easiest and the fastest method to obtain monolayers of MoS₂ and WS₂. However, only a small portion of MoS₂ and WS₂ crystals are exfoliate to monolayers, leaving a majority of samples as thicker flakes. In this study, we used the chemical vapor deposition to obtain large-area, high-quality monolayers of MoS₂ and WS₂. Therefore, after the F₄TCNQ deposition, our photoluminescence intensity of WS₂ and MoS₂ is approximately fifty times and ten times higher, respectively. Compared to

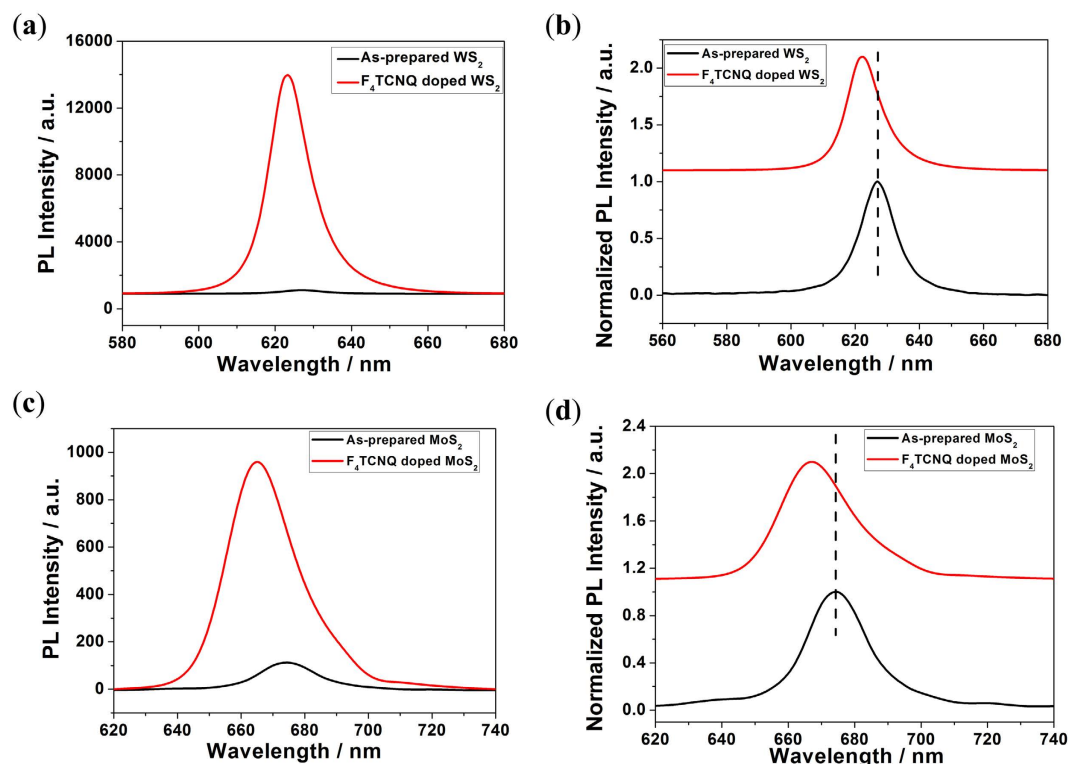


Figure 3. PL spectra of monolayer WS₂ (a) and monolayer MoS₂ (c) before and after F₄TCNQ doping. PL peak shift of monolayer WS₂ (b) and monolayer MoS₂ (d) before and after F₄TCNQ doping.

the solution-based chemical doping on MoS₂ monolayer², the PL increases approximately three times. During the vacuum deposition of F₄TCNQ on MoS₂ monolayer, there is no solvent contamination and interaction between MoS₂ and F₄TCNQ and therefore the PL increases stronger.

The optical properties of MoS₂ and WS₂, especially the photoluminescence, are affected by the number of layers^{6,23}. Few-layered MoS₂ and WS₂ have an indirect band gap and show low photoluminescence, while monolayers of MoS₂ and WS₂ have a direct bandgap and strong photoluminescence^{23,24}. To understand the effects of charge transfer, the photoluminescence peaks, which are due to the direct band gap transition, have been analyzed by fitting them with photoluminescence from trions and photoluminescence from neutral excitons represented by two Lorentzian functions, as shown in Fig. 5. For the all cases studied, the photoluminescence signal can be decomposed as A and B peaks, but the intensity of the B peak is negligible. The A peak can be further decomposed to trion (X⁻) and exciton (X) components. Peak positions from the fitting can be found in Table 1. The exciton binding energy of MoS₂ and WS₂ (1.85 eV and 1.985 eV) was determined in our work. The trion spectral weight I_{X^-}/I_{total} was also calculated and listed in Table 1.

For both WS₂ and MoS₂, the trion spectral weight I_{X^-}/I_{total} decreases after charge transfer, as shown in Table 1. This indicates that the charge transfer significantly decreases the concentration of trions by transferring electrons from the trions into acceptors, thereby enhancing the photoluminescence.

Upon the deposition of F₄TCNQ on the monolayers, the charge transfer reaches a maximum because the trion spectral weight reaches the saturation region at approximately 0.2. We observe that the peaks for the corresponding X⁻ and X of PL are sharper for WS₂ than for MoS₂. The wider peak width is associated with a stronger coupling strength or a larger Huang-Rhys factor *S* for a typical semiconductor^{25,26}, so that we may ascribe the narrower PL peaks for WS₂ samples compared to MoS₂ as indicative of slightly weaker exciton-phonon coupling²⁷. After charge transfer to the F₄TCNQ molecules, the peak width change is almost the same. The weaker exciton-phonon scattering of WS₂ results in narrower PL peaks with a larger amplitude.

The DFT calculated electron transferred from MoS₂ and WS₂ to F₄TCNQ was 0.271 and 0.237, respectively. These data are in good agreement with the trion spectral weight data (Table 1). Larger amount of charge transferred causes more trions to be dissociated to excitons, thereby leading to a lower trion spectral weight. The surface dipole is formed due to the charge transferred from MoS₂/WS₂ to F₄TCNQ. The amount of transferred charge can control the intensity and position of PL. The adding electrons to or withdrawing electrons from the 2D monolayer decreases⁷⁻⁹ or increases (this work) the intensity of PL.

It is worth to notice that a dipoles formed by charge transfer to acceptor deposited directly on 2D semiconductor is comparable to dipoles formed by Helmholtz double layer in an electrolyte double layer transistor (EDLT), where gate is a reference electrode in an ionic organic liquid. In an EDLT, the number of induced charges in the transistor channel is in the range of 10¹⁴ 1/cm². It is almost one order of magnitude larger than the charge induced by the layer of dipoles in our experiment, but two orders of magnitude larger than the charge induced

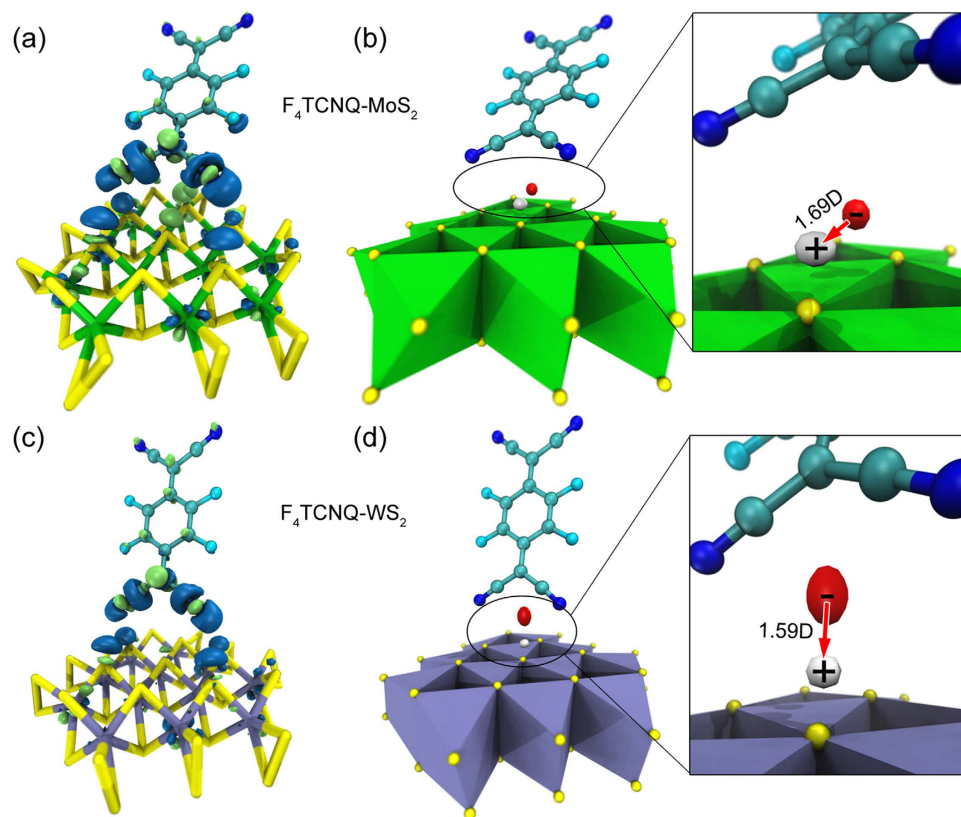


Figure 4. (a) Electron density differences (with \pm isovalues of 0.005 a.u.) and (b) barycenters (with \pm isovalues of 0.0001 a.u.) of an F_4TCNQ -doped MoS_2 cluster model. Electron density differences (with \pm isovalues of 0.005 a.u.) and barycenters (with \pm isovalues of 0.0001 a.u.) for F_4TCNQ -doped WS_2 cluster model are given in (c,d), respectively. Green and blue isosurfaces indicate positive and negative values in electron density differences, while red and white isosurfaces indicate plus (electron density increase) and minus (electron density depletion) values of barycenters in (b,d). The dipole moment variation before and after charge transfer are also displayed in the enlarged view of (c,d), with \pm sign indicating virtual charge of the barycenters due to electron density depletion/increase.

in MoS_2 transistor with 280 nm SiO_2 and gate voltage of $-70 V^1$. Such high concentration of charge induced in a monolayer of TMD semiconductors should lead to correlated effects like ferromagnetism or to superconductivity in EDLT MoS_2 system²⁸. Additionally acceptor layer deposited on the surface on 2D semiconductors can be considered as a stable gate that doesn't required additional connector for gate voltage.

Conclusion

In summary, triangle monolayer WS_2 and MoS_2 were grown using the chemical vapor deposition (CVD) method. The formation of the monolayers was confirmed by both AFM and Raman spectra. The PL increased after a thin layer of F_4TCNQ was deposited on the surface of the WS_2 and MoS_2 monolayers. The ratio of charged excitons, trions, to neutral excitons decreases due to the charge transfer from monolayer WS_2 and MoS_2 to strong acceptor, F_4TCNQ . The weaker exciton-phonon interaction of WS_2 results in narrower PL peaks with larger amplitudes than in MoS_2 where this interaction is strong. Acceptors or donators deposited on the surface of MoS_2 or WS_2 and also on other 2D monolayers provides an effective mechanism for controlling the electron distribution in such heterojunctions. In this way, it is a convenient method of tuning the optoelectronic properties of 2D materials and leads to the application of these materials in lasers or LEDs.

Methods

Chemicals and materials. WO_3 (>99.5%), MoO_3 (>99.5%) and sulfur (>99.95%) powders were purchased from Sigma-Aldrich and used without any purification. F_4TCNQ (>99.5%) was purchased from Jilin OLED Materials Tech. Co. Ltd. and purified at 220 °C via physical vapor transport (PVT).

Preparation of MoS_2 and WS_2 monolayers. For both the triangular shaped MoS_2 and WS_2 monolayers, we used the same method of chemical vapor deposition (CVD). The growth process for the two materials is almost the same, with the only difference being the precursor. Commercially available SiO_2/Si substrates were used in this study. All the substrates were successively cleaned with acetone, methanol, H_2O_2/H_2SO_4 (1 volume/4 volume) and distilled water in an ultrasonic bath for 5 min and then dried in ambient N_2 . First, fine WO_3 or MoO_3 powder was spread on the bottom of the crucible. One piece of SiO_2/Si substrate (1 × 1 cm) was

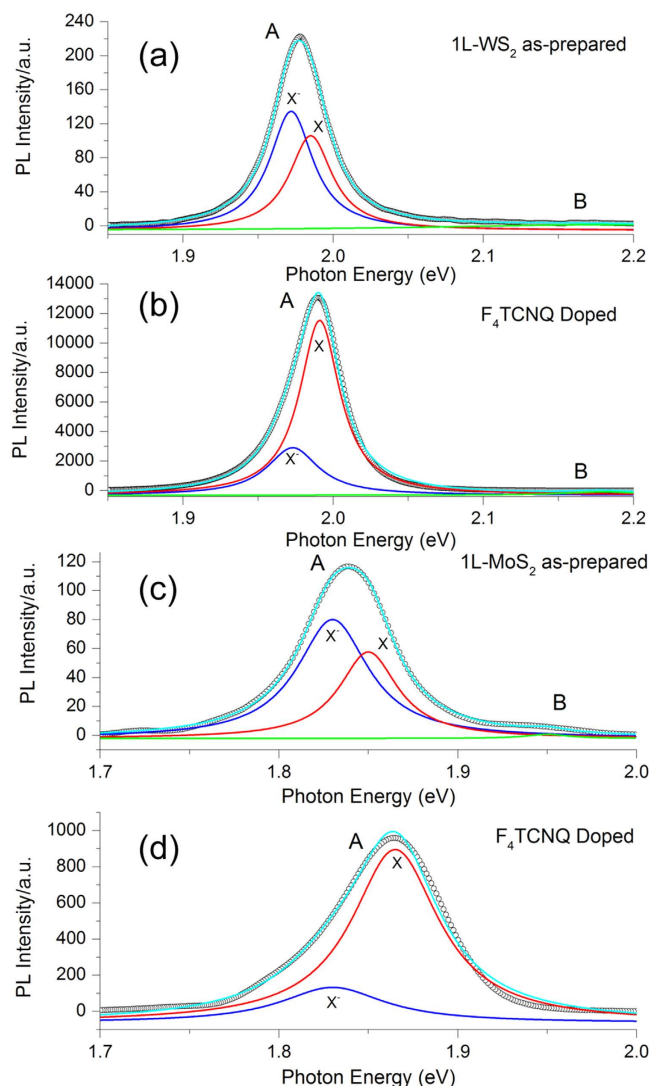


Figure 5. Fitted PL spectra of monolayer WS₂ (a) before and (b) after F₄TCNQ doping. Fitted PL spectra of monolayer MoS₂ (c) before and after F₄TCNQ doping (d). Lorentzian functions were used to fit the A and B peaks, with A peaks assumed to be composed of trions (X⁻) and excitons (X).

Sample	Peak name	Peak Position (eV)	FWHM(meV)	I_{X^-}/I_{total}
1 L WS ₂ as-prepared	X ⁻ trion	1.972 (1.96)	35	0.63
	X exciton	1.985	35	
F ₄ TCNQ doped 1 L WS ₂	X ⁻ trion	1.973 (1.98)	42	0.25
	X exciton	1.991 (2.02)	33	
1 L MoS ₂ as-prepared	X ⁻ trion	1.83 (1.84)	48	0.70
	X exciton	1.85 (1.88)	40	
F ₄ TCNQ doped 1 L MoS ₂	X ⁻ trion	1.83 (1.84)	70	0.20
	X exciton	1.865 (1.88)	60	

Table 1. Peak position and width for Lorentzian functions used to fit PL peak A in Fig. 5. (The values in brackets for peak positions were previously reported^{2,5}).

placed face-down on the crucible, and the crucible was put in the center of the growth furnace. Another small crucible with approximately 50 mg sulfur powder was put in another part of the furnace near the gas input side at a temperature of 200 °C. The furnace was heated to 750 °C at 25 °C/min and then maintained at that temperature for 20 min before naturally being cooled down to room temperature. Argon gas was provided during the whole growth process at 60 sccm.

Preparation of F₄TCNQ layers on WS₂ and MoS₂ monolayers. 2-nm F₄TCNQ was deposited on the WS₂ and MoS₂ monolayers by the evaporation of F₄TCNQ in a Tectra mini-coater (Germany) with a deposition rate of 0.1 angstrom per second.

Characterization. Photoluminescence was measured at the same area before and after F₄TCNQ deposition. Both the laser beams (solid-state laser, 473 nm and Nd:YAG solid-state laser, 532 nm) were collimated and focused through a $\times 100$ objective onto the sample surface. All the spectra were collected using a confocal triple-grating spectrometer (Horiba-JY T64000). Raman spectra were recorded using a Renishaw Raman microscope configured with a charge-coupled device array detector with the excitation laser line of 532 nm. Atomic force microscopy was performed on a Digital Instruments 3100.

Density functional theory calculations. The geometry of the F₄TCNQ on the surface of the MoS₂/WS₂ was optimized using the DMol³^{29,30} with the dispersion-corrected (OBS) PW91 (GGA) functional at the level of the DNP basis set. The geometry of the models is regarded as converged when the total energy difference is less than 1×10^{-5} Ha, the total force difference is less than 4×10^{-3} Ha/Å, and the maximum displacement of atoms is less than 5×10^{-3} Å during the optimization. The optimized geometries of the models were subsequently fed into the ORCA 3.0.3 package³¹ to perform single-point energy calculations (with SCF convergence criteria set as 1×10^{-6} Ha) at the level of B3LYP/6-31G(d,p) (with Mo and W atoms treated using SDD effective core potentials³²). To facilitate the charge transfer analysis, the MultiWFN 3.3.7 package³³ was used to calculate the charge transfer based on electron density difference.

References

- Mak, K. F. *et al.* Tightly bound trions in monolayer MoS₂. *Nat. Mater.* **12**, 207–211 (2013).
- Mouri, S., Miyauchi, Y. & Matsuda, K. Tunable Photoluminescence of Monolayer MoS₂ via Chemical Doping. *Nano Lett.* **13**, 5944–5948 (2013).
- Newaz, A. K. M. *et al.* Electrical control of optical properties of monolayer MoS₂. *Solid State Commun.* **155**, 49–52 (2013).
- Tongay, S. *et al.* Broad-Range Modulation of Light Emission in Two-Dimensional Semiconductors by Molecular Physisorption Gating. *Nano Lett.* **13**, 2831–2836 (2013).
- Peimyoo, N. *et al.* Chemically Driven Tunable Light Emission of Charged and Neutral Excitons in Monolayer WS₂. *ACS Nano* **8**, 11320–11329 (2014).
- Dhall, R. *et al.* Direct Bandgap Transition in Many-Layer MoS₂ by Plasma-Induced Layer Decoupling. *Adv. Mater.* **27**, 1573–1578 (2015).
- Li, Z. *et al.* Active Light Control of the MoS₂ Monolayer Exciton Binding Energy. *ACS Nano* **9**, 10158–10164 (2015).
- Li, Z. *et al.* Graphene Quantum Dots Doping of MoS₂ Monolayers. *Adv. Mater.* **27**, 5235–5240 (2015).
- Kang, Y. *et al.* Plasmonic Hot Electron Induced Structural Phase Transition in a MoS₂ Monolayer. *Adv. Mater.* **26**, 6467–6471 (2014).
- Peimyoo, N. *et al.* Nonblinking, Intense Two-Dimensional Light Emitter: Monolayer WS₂ Triangles. *ACS Nano* **7**, 10985–10994 (2013).
- Salehzadeh, O., Tran, N. H., Liu, X., Shih, I. & Mi, Z. Exciton Kinetics, Quantum Efficiency, and Efficiency Droop of Monolayer MoS₂ Light-Emitting Devices. *Nano Lett.* **14**, 4125–4130 (2014).
- Lee, Y.-H. *et al.* Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Adv. Mater.* **24**, 2320–2325 (2012).
- Zhan, Y., Liu, Z., Najmaei, S., Ajayan, P. M. & Lou, J. Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate. *Small* **8**, 966–971 (2012).
- Najmaei, S. *et al.* Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat. Mater.* **12**, 754–759 (2013).
- Zhang, Y. *et al.* Controlled Growth of High-Quality Monolayer WS₂ Layers on Sapphire and Imaging Its Grain Boundary. *ACS Nano* **7**, 8963–8971 (2013).
- Berkdemir, A. *et al.* Identification of individual and few layers of WS₂ using Raman Spectroscopy. *Sci. Rep.* **3**, 1755 (2013).
- Huo, N. *et al.* Interlayer coupling and optoelectronic properties of ultrathin two-dimensional heterostructures based on graphene, MoS₂ and WS₂. *J. Mater. Chem. C* **3**, 5467–5473 (2015).
- Wang, X. H. *et al.* Photoluminescence and Raman mapping characterization of WS₂ monolayers prepared using top-down and bottom-up methods. *J. Mater. Chem. C* **3**, 2589–2592 (2015).
- Gutiérrez, H. R. *et al.* Extraordinary Room-Temperature Photoluminescence in Triangular WS₂ Monolayers. *Nano Lett.* **13**, 3447–3454 (2013).
- Zhang, W. *et al.* High-Gain Phototransistors Based on a CVD MoS₂ Monolayer. *Adv. Mater.* **25**, 3456–3461 (2013).
- Nan, H. *et al.* Strong Photoluminescence Enhancement of MoS₂ through Defect Engineering and Oxygen Bonding. *ACS Nano* **8**, 5738–5745 (2014).
- Le Bahers, T., Adamo, C. & Ciofini, I. A Qualitative Index of Spatial Extent in Charge-Transfer Excitations. *J. Chem. Theory Comput.* **7**, 2498–2506 (2011).
- Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
- Splendiani, A. *et al.* Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **10**, 1271–1275 (2010).
- Chakraborty, B. *et al.* Symmetry-dependent phonon renormalization in monolayer MoS₂ transistor. *Phys. Rev. B* **85**, 161403 (2012).
- Ye, J., Zhao, Y., Ng, N. & Cao, J. Width of Phonon Sidebands in the Brownian Oscillator Model. *J. Phys. Chem. B* **113**, 5897–5904 (2009).
- Ho, C. H., Wu, C. S., Huang, Y. S., Liao, P. C. & Tiong, K. K. Temperature dependence of energies and broadening parameters of the band-edge excitons of Mo_{1-x}W_xS₂ single crystals. *J. Phys. Condens. Matter* **10**, 9317–9328 (1998).
- Ye, J. T. *et al.* Superconducting Dome in a Gate-Tuned Band Insulator. *Science* **338**, 1193–1196 (2012).
- Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.* **92**, 508–517 (1990).
- Delley, B. From molecules to solids with the DMol³ approach. *J. Chem. Phys.* **113**, 7756–7764 (2000).
- Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 73–78 (2012).
- Andrae, D., Häußermann, U., Dolg, M., Stoll, H. & Preuß, H. Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theoret. Chim. Acta* **77**, 123–141 (1990).
- Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580–592 (2012).

Acknowledgements

This research was conducted by the NTU-HUJ-BGU Nanomaterials for Energy and Water Management Programme under the Campus for Research Excellence and Technological Enterprise (CREATE), which is supported by the National Research Foundation, Prime Minister's Office, Singapore. Z.L. thanks Singapore National Research Foundation for NRF RF Award No. NRF-RF2013-08 and the start-up funding from Nanyang Technological University (M4081137.070). Q.X. and C.K. gratefully thanks Singapore Ministry of Education for the strong support via an AcRF tier2 grant (MOE2012-T2-2-086) and AcRT RG125/4 grant. J.Y. would like to thank the support from the Institute of High Performance Computing, Agency for Science, Technology and Research, Singapore.

Author Contributions

P.H., X.H., H.J., Z.L. and C.K. conceived the experiments. P.H. and X.H. performed the experiments including monolayers growth, characterization and data analysis. K.D., K.K.Z., X.W. and Q.X. performed the PL measurement. J.Y. performed all theoretical calculations and wrote respective discussions. J.Y. also prepared Fig. 4 and assist fitting of Fig. 5 and preparation of Table 1. P.H., X.H., H.J. and C.K. co-wrote the manuscript. Z.L., H.J. and C.K. supervised the project. All of the authors reviewed the manuscript, discussed the data and gave profound suggestions.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Hu, P. *et al.* Control of Radiative Exciton Recombination by Charge Transfer Induced Surface Dipoles in MoS₂ and WS₂ Monolayers. *Sci. Rep.* **6**, 24105; doi: 10.1038/srep24105 (2016).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

SCIENTIFIC REPORTS

OPEN

Corrigendum: Control of Radiative Exciton Recombination by Charge Transfer Induced Surface Dipoles in MoS₂ and WS₂ Monolayers

Peng Hu, Jun Ye, Xuexia He, Kezhao Du, Keke K. Zhang, Xingzhi Wang, Qihua Xiong, Zheng Liu, Hui Jiang & Christian Kloc

Correction to: *Scientific Reports* <https://doi.org/10.1038/srep24105>; published online 07 April 2016; updated 05 April 2018

This article contains an error in Figure 2, where the same image was inadvertently shown in both panel (a) and (b). The correct Figure 2 appears below:

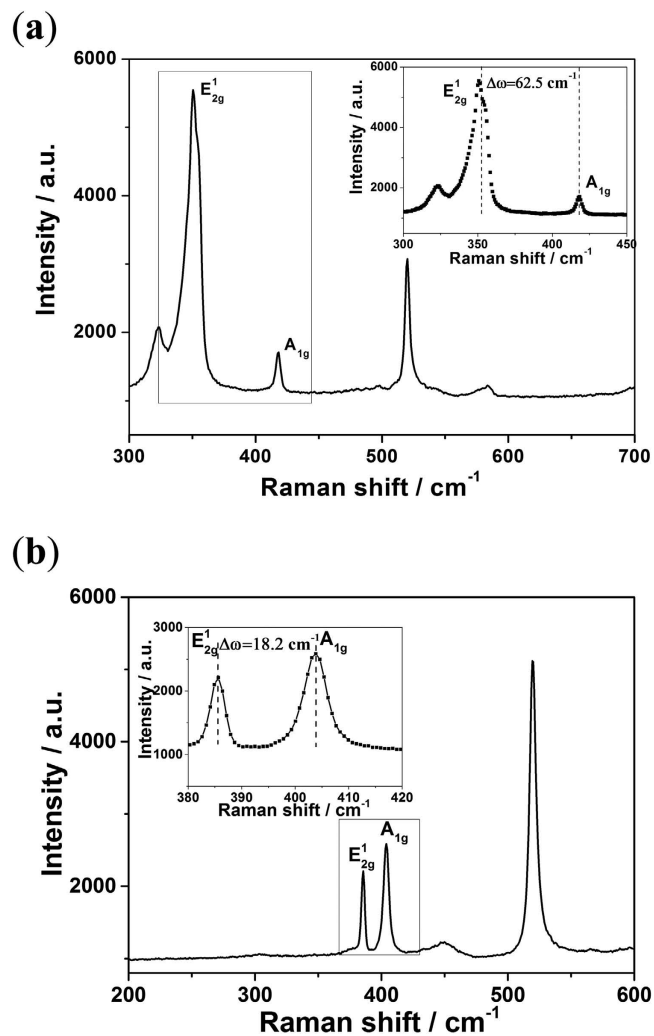


Figure 2.



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

© The Author(s) 2018