This version of the article has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's AM terms of use (https://www.springernature.com/gp/open-research/policies/accepted-manuscript-terms), but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: https://doi.org/10.1007/s40843-019-1232-2

Lanthanide Near-infrared Emission and Energy Transfer in Layered WS_2/MoS_2 Heterostructure

Gongxun Bai^{1,2}, Yongxin Lyu¹, Zehan Wu¹, Shiqing Xu^{2*}, Jianhua Hao^{1*}

¹ Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, P. R. China

² Institute of Optoelectronic Materials and Devices, China Jiliang University, Hangzhou 310018, People's Republic of China

E-mail: jh.hao@polyu.edu.hk, shiqingxu@cjlu.edu.cn

Abstract

Lanthanide ions have drawn considerable attention due to their distinct photonic properties. The optoelectronic properties and device performance are greatly affected by the interfacial coupling between the layered van der Waals heterostructure, fabricated with two or more transition metal dichalcogenide (TMD) layers. In this work, lanthanide ions doped WS₂/MoS₂ layered heterostructures have been constructed through two synthesis steps. The prepared doped thin films were highly textured nanosheets on wafers. Importantly, the prepared stacked heterostructure is able to produce efficient near-infrared emission in the range of the telecommunication window, owing to energy transfer between lanthanide ions in the two TMD layers. The use of the layered heterostructure allows the decrease of deleterious cross-relaxation due to homogeneous doping or concentration quenching. The energy transfer process is studied in this work. The results suggest that lanthanide ions can effectively extend the emission band of TMD thin films and their heterostructures. The developed doped TMDs heterostructure is favourable for atomically thin near-infrared photonic devices.

Keywords: lanthanide ions, near-infrared luminescence, energy transfer, 2D transition metal dichalcogenide, heterostructure

Introduction

Recently, a large group of two-dimensional (2D) layered materials, classically well-known as the transition metal dichalcongenides (TMDs), such as WS₂, and MoS₂, have been intensified for electronic and optoelectronic applications at 2D limits due to their attractive physical and chemical properties.¹⁻³ Similar to graphene, layered TMD materials possess excellent physcial properties, for instance, high electrical conductivity, good thermal stability, flexibility, and outstanding mechanical strength.⁴ In particular, TMD materials show large exciton binding energies owing to their wide bandgap.⁵ Hence, TMD materials have presented considerably potential for next-generation optoelectronic devices and application, including optical sensors, information transmission, solar cells, photodetectors, light emitting diodes, and displays.^{6,7} Moreover, atomically thin optoelectronic devices can be created by stacking the layers of diverse 2D materials into van der Waals (vdW) heterostructures.⁸⁻ ¹⁰ However, the emisison of 2D TMD materials and devices are mostly confined in the spectral coverage from red to the near-infrared (NIR) edges. Tuning of the luminescence is mainly influenced by the excitons, layer number, and bandgaps. It should be considerably striking for both basic study and application of 2D materials and devices if their emission band can be extended to the wide-ranging NIR spectra, such as telecommunication window. As conventional techniques, doping methods can theoretically adjust the intrinsic properties of TMDs through tuning the band structure, magnetism, chemical sensitivty, semiconductor n- or p- type, etc. Some doping approaches have been used to modulate the photoluminscence and electroluminescence in 2D TMD materials and devices.¹¹ While doping transition metal ions can simply and slightly adjust the emitting wavelength in the reported doped TMDs.^{12,13} Thus, it is necessary to find a way to effectivcely extend the emission band of 2D TMD and their vdW heterostructures.¹⁻³

Conversely, lanthanide ions normally doped into semiconductor or transparent insulator substrates as active centers to emit photons covering the ultraviolet (UV), visible, NIR, and mid-infrared (MIR) region.^{14,15} As lanthanide ions have abundant excited and emission energy states. The emission properties of lanthanide ions possess the benefits of high quantum yield, high optical stability, narrow bandwidth, and long lifetime.^{16,17} At present, lanthanide ions doped optical materials have been broadly applied in

many optoelectronic and photonic technology, including solid state lighting, and telecommunication, and biomedicine.^{18,19} For instance, Er³⁺ doped fiber amplifiers have been practicely used in optical fiber communication. Yb³⁺-Er³⁺, Yb³⁺-Tm³⁺ doped nanoparticlers with upconversion emisison have been applied in biological imaging and therapy.^{20,21} Presently, there are a few results about lanthanide ions doped 2D TMDs through chemical vapor deposition and hydrothermal synthesis.²² Specifically, Er³⁺ doped MoS₂ and Yb³⁺/Er³⁺ codoped WSe₂ with NIR emission have been prepared by CVD²³ and plused laser deposition²⁴ in our group. Kaczmarek et al. have developed Eu³⁺ doped MoS₂ 2D nanosheets for temperature sensing.²⁵ Hence, it has been confrimed that the doping of lanthanide ions can extend the instrinsic narrow band luminescence of 2D TMD materials. However, the doping concetration is usually limited in single compound of 2D materials. And the emission performancs often suffer from the deleterious cross relaxation when the lanthanide ions are doped in a homogeneous way.¹⁴ As a research trend, various heterostructures consisted of different 2D compounds are more helpful for constructing atomically thin optoelectronic devices. It is expected that lanthanide ions separately doped in the different layers could show more intriguing characterties, as the luminescent core-shell structure extensively studied in erailier reports.

In this work, Er^{3+} doped WS₂ and lanthanide ions doped TMDs vdW heterostructures have been fabricated for NIR emission and devices. As Er^{3+} ions can generate NIR emission around 1540 nm for telecommunication. Yb³⁺ ions have great absorption cross-section at 980 nm, which could be used as sensitizers. The crystal structure, chemical compostion, and optical properties have been studied with a serial of techniques. In particular, the energy transfer mechnism between the two TMD vdW heterostructure layers has been studied.

Experimental Section

The lanthanide doped TMD layered samples were fabricated by magnetron sputtering and chemical vapor deposition (CVD). First, the seed layers lanthanide Er doped W were deposited on SiO₂/Si substrates (SiO₂ 285 nm thickness) by sputtering the metal targets Er and W with different power. The thickness was controlled by the deposition time, nominal thickness of 0.5, 1, 1.5, 2.5 and 5 nm. Then Er doped layered WS₂ nanosheets were prepared by CVD. The layered thin films were synthesised in a horizontal tube furnace. The base pressure of the furnace was pumped down to 50 mTorr, after flush with Ar gas. Then the growth pressure was kept at 300 mTorr with a 50 sccm Ar flow. The growth temperature of the samples was aroused 750 °C for 20 min. During the reaction, the temperature of the upstream sulfur precusor was held around 200-350 °C. To fabricate the lanthanide doped layered leterostructure WS₂/MoS₂, the seed Yb doped Mo layer with 2.5 nm and Er doped W layer with 2.5 nm were first depostied. Then the lanthanide doped layered leterostructure was obtained after CVD.

The lanthanide doped thin films/heterostructures were recorded by a Raman microscopic Horiba Jobin Yvon HR800 system, under 488 nm illuination. The crystal structure was measured by a Rigaku SmartLab X-ray diffractometer. The XPS measurements were performed with an SKL-12 multitechnique system. The morphology and chemical compositions were studied by a scanning transmission electron microscope (STEM, JEOL ARM200F) equipped with an energy dispersive X-ray (EDX) spectrometer. The TEM sample was prepared by etching off the silica layer with NaOH and transferring the doped thin films on C/Cu TEM grids. The NIR emission spectra were recorded by a spectrophotometer (Edinburgh FLSP920) armed with a 980 nm laser diode.

Results and discussions



Figure 1. (a) The XRD result of the fabricated WS_2 :Er thin film. The XPS spectra of the (b) W 4f, (c) s 2p, and (d) Er 4d core levels.

The optical and electric properties of the thin films are strongly depended by the chemical composition and crystal structure. Hence, it is important to check the doped TMDs phase. First, XRD was taken to study the crystallographic phase of the prepared samples. From the XRD pattern in Figure 1a, all peaks match very well with the standard database (JCPDS card No. 08-0237), which can be assigned to the hexagonal crystal WS₂. The existence of any other impurities such as Er_2S_3 can be ruled out. The reflection of only intense (00*l*) peaks suggests a highly textured WS₂ thin films prepared on a SiO₂/Si substrate with favoured alignment of c-axis. Usually, the texture development permits sputtering and CVD grown TMDs mostly perserving the excellent physical properties. Figure 1b, c and d show the binding energy profiles for W 4f, S 2p, and Er 4d in the fabricated samples, respectively. The distinct peaks placed around 32.38 and 34.55 eV can be assigned to the binding states of W 4f_{7/2} and W4f_{5/2} with spin-orbit split separation of 2.17 eV (Figure 1b). Similarly, two peaks belonging to the binding states of S $2p_{3/2}$ and S $2p_{1/2}$ are observed at 161.47 and 162.67 eV with peak sparation of 1.2 eV (Figure 1c). Moreover, the binding energy peaks at 185.9 and 173.1 eV can be assinged to the Er 4d core level (Figure 1d). The results match well with the previous reports about the WS₂ nanosheets. The XRD and XPS results indicate that the Er doped WS₂ crystal materials have been prepared.



Figure 2. (a) High-resolution TEM picture of the prepared WS_2 :Er thin film. (b) CS-STEM picture of the fabricated WS_2 :Er thin film. (c) The EDS spectrum of the fabricated WS_2 :Er thin film. (d) The HAADF intensity spectrum of the selected line.

Because the WS_2 :Er thin film is the actively luminescent layer, and the MoS_2 :Yb is the sensitivity layer. The microstructure of lanthanide ions doped MoS_2 thin films have been studied in previous reports. Hence, the WS_2 :Er thin films have been focused on research. The microstructure and doping profile of the prepared thin films have been recorded by TEM. Figure 2a shows the high-resolution TEM image of the fabricated WS_2 :Er nanosheet. The hexagonal arrangement of the fringes suggests that the WS_2 :Er layers are horizontally oriented. The inset electron diffraction pattern shows the

polycrystalline structure. Figure 2b presents the spherical aberration corrected STEM (CS-STEM) image of the WS₂:Er samples. The location of W and Er within the WS₂ lattice can be clearly observed by the high angle annular dark field (HAADF) mode. The EDS in Figure 2c shows the signals of W, S and Er, which confirms Er atoms doped in the WS₂ lattice. The Cu signal is originated from the TEM Cu grid. The transmitted electron intensity in Figure 2d is generated from the vertical direction of corresponding white line in Figure 2b. Due to the different atomic number, the Er atoms show higher compared to W atoms. The intensity spectrum indicates that Er atom can enter the site of W atoms. The EDS element mapping pictures are presented in Figure 3a-d. The distributions of W, S and Er elements are mainly co-localized for the WS₂:Er nanosheets, indicating that the lanthanide Er can be homogeneously doped within the fabricated WS₂ thin films.



Figure 3. EDS analysis mapping pictures of W, S, and Er in the fabricated WS₂:Er thin film.



Figure 4. (a) The Raman spectra of the fabricated undoped and doped WS_2 thin films. (b) The Raman spectra of the fabricated WS_2 :Er, MoS_2 :Yb, and TMD heterostructure thin films.

To further study the optical properties of the prepared lanthanide doped TMDs thin films, Raman and photoluminescence (PL) spectroscopy have been employed to analyse the films with various layers. The Raman spectra can be used to confirm the characteristic in-plane (E') and out of plane (A'₁) vibration modes of TMDs thin films.²⁷ Here, the resonance Raman spectra of undoped and doped lanthanide ions doped WS₂ thin films are recorded under 488 nm excitation. Figure 4a displays the Raman spectra of the fabricated WS₂:Er thin films with different nominal layers. All the samples present two distinct peaks, which can be attributed to E^{1}_{2g} and A_{1g} modes, respectively. For the monolayer WS₂ sample, the modes E_{2g}^{1} and A_{1g} are peaked at 352.1 and 417.3 cm⁻¹, respectively. After doping lanthanide ions, the resonate transitions of monolayer shows shift towards 417.4 cm⁻¹ (A_{1g} mode). With increasing the layer number up to 5, the Raman peak (E¹_{2g} mode) shifts to 352.3 cm⁻¹, and the Raman peak (A_{1g} mode) shifts to 420.1 cm⁻¹. The lanthanide ions doping seems to show small effect on the Raman signature. Figure 4b presents a comparison among the Raman spectra of single-kind WS2:Er, MoS2:Yb and their heterostructure. The Er doped WS₂ layers show Raman peaks at 356.1 and 421.3 cm⁻¹, originating from the E^{1}_{2g} and A_{1g} modes in WS₂ nanosheets, respectively. The Yb doped MoS₂ layers present Raman peaks at 384.2 and 408.8 cm⁻¹, generating by the E_{2g}^{1} and A_{1g} modes in MoS₂ nanosheets, respectively. This result suggests that we have obtained a WS₂:Er, MoS₂:Yb heterostructure rather than an alloyed W_xMo_{1-x}S₂ thin film, as there would be two main Raman peaks due to the E_{2g}^1 and A_{1g} modes in an alloyed W_xMo_1 .

 $_x$ S₂ thin film. The peak spacing between the E' and A'₁ modes recorded from the individual WS₂:Er and MoS₂:Yb thin films were 65.2 and 24.6 cm⁻¹, respectively, which match with the formation of ~5 layers in each TMD thin film.



Figure 5. (a) The photoluminescence spectra of undoped and doped WS_2 thin films under 488 nm excitation. (b) The photoluminescence spectra of the fabricated TMDs heterostructure thin films under 980 nm excitation.



Figure 6. (a) The prepared lanthanide ions doped TMDs heterostructure system. (b)The proposed energy transfer mechanism, CB is short for conduction band, VB is short for valence band.

Under 488 nm excitation, Figure 5a shows the PL spectra of the prepared WS₂:Er thin films with different nominal layers at room temperature. When increasing the layer number of the thin films, the peaks of emitting wavelength present progressively shift to lower energy from 620 to 710 nm. The monolayer undoped and doped lanthanide ions doped WS₂ thin film generate the most intensive emission because of the direct band gap. The undoped WS₂ thin film only shows red emission. In the WS₂:Er thin film and WS₂:Er/MoS₂:Yb heterostructure, both the samples show the down shifting emission around 1550 nm, under the excitation at 980 nm. The NIR emission

is attributed to radiative transition of lanthanide Er^{3+} : ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$. Compared with the WS₂:Er thin film, the WS₂:Er/MoS₂:Yb heterostructure presents more intensive emission around 1550 nm. The emission can be improved by about twice. It is deduced that the enhanced NIR emission can be attributed to energy transfer and the improved absorption section at 980 nm owing to the introduction of MoS₂:Yb heterostructure. The mechanism of energy transfer will be discussed later in detail. It is well acknowledged that 1550 nm low loss window is extensively applied in NIR photonic and optical communication. The ultimate objective of fabricating atomically thin optoelectronic devices prompts the present intensive exploration on 2D TMD and their heterostructure. Thus, our results in Figure 5b suggest that the WS₂:Er thin film and WS₂:Er/MoS₂:Yb heterostructure not only importantly expanded emission of 2D TMDs to NIR range valuable to fundamental investigation but also offers a novel opportunity to the advance of atomically thin optoelectronic devices in NIR spectra. Figure 6 shows the schematic of the WS₂:Er/MoS₂:Yb heterostructure and its corresponding energy level scheme of a WS₂:Er, MoS₂:Yb heterostructure and energy transfer between the lanthanide ions doped heterostructure under 980 nm excitation. At first, the electrons of Er^{3+} ions at ${}^{4}I_{15/2}$ state are populated to the $Er^{3+}:{}^{4}I_{11/2}$ state via ground state absorption (GSA) in WS2:Er, under 980 nm excitation. Meanwhile, the electrons of Yb^{3+} ions at ${}^{2}F_{7/2}$ state are populated to the Yb³⁺:²F_{5/2} state via GSA in MoS₂:Yb under 980 nm photon pumping. As the absorption section of the Yb^{3+} : $^{2}F_{5/2}$ state is much larger than that of the Er^{3+} : ${}^{4}\mathrm{I}_{15/2}$ state. The energy transfer occurs from the populated Yb³⁺: ${}^{2}\mathrm{F}_{5/2}$ state to the Er^{3+} :⁴ $I_{11/2}$ state. And then the electrons at the Er^{3+} :⁴ $I_{11/2}$ state relax to the excited Er^{3+} : ${}^{4}\mathrm{I}_{13/2}$ state by radiative or non-radiative way. Finally, the electrons in the Er^{3+} : ${}^{4}I_{13/2}$ state radioactively relax to the ground state Er^{3+} : ${}^{4}I_{15/2}$ and NIR photon with wavelength ~1550 nm emission occurs. Hence, enhanced NIR emission is generated from the WS₂:Er, MoS₂:Yb heterostructure owing to the lanthanide doping and energy transfer.

In conclusion, we have designed and fabricated lanthanide doped TMDs thin film and stacked heterostructure through a combination of magnetron sputtering and CVD methods. Comprehensive structural and chemical characterizations suggested that the prepared lanthanide Er^{3+} doped WS₂ thin film was highly textured nanosheets, and lanthanide ions could be substitutionally introduced into the TMD lattice. Importantly, the emission of TMD materials under a 980 nm laser diode excitation can be extended to the telecommunication range. In particular, the lanthanide doped TMDs stacked heterostructure produces efficient NIR emission as a result of energy transfer between WS₂:Er and MoS₂:Yb layers. The developed lanthanide doped TMDs stacked heterostructure are promising for application in atomically thin NIR optoelectronic and photonic devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge grants from Chinese National Natural Science Foundation (No 61705214) and the Research Grants Council (RGC) of Hong Kong (RGC GRF No. PolyU 153281/16P).

References

- [1] Y. Liu, N. O. Weiss, X. Duan, H.-C. Cheng, Y. Huang, X. Duan, *Nat. Rev. Mater.* **2016**, *1*, 16042.
- [2] S. B. Desai, S. R. Madhvapathy, A. B. Sachid, J. P. Llinas, Q. Wang, G. H. Ahn, G. Pitner, M. J. Kim, J. Bokor, C. Hu, *Science* 2016, *354*, 99-102.
- [3] W. Xu, W. Liu, J. F. Schmidt, W. Zhao, X. Lu, T. Raab, C. Diederichs,
 W. Gao, D. V. Seletskiy, Q. Xiong, *Nature* 2017, 541, 62-67.
- [4] Z. Yang, J. Hao, J. Mater. Chem. C 2016, 4, 8859-8878.
- [5] C. Tan, X. Cao, X. J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G. H. Nam, M. Sindoro, H. Zhang, *Chem. Rev.* 2017, *117*, 6225-6331.
- [6] F. Withers, O. Del Pozo-Zamudio, A. Mishchenko, A. P. Rooney, A. Gholinia, K. Watanabe, T. Taniguchi, S. J. Haigh, A. K. Geim, A. I. Tartakovskii, K. S. Novoselov, *Nat. Mater.* 2015, 14, 301-306.
- [7] S. Wu, S. Buckley, J. R. Schaibley, L. Feng, J. Yan, D. G. Mandrus, F. Hatami, W. Yao, J. Vuckovic, A. Majumdar, X. Xu, *Nature* 2015, 520, 69-72.
- [8] W. Jie, Z. Yang, G. Bai, J. Hao, Adv. Opt. Mater. 2018, 6, 1701296.
- [9] M. Chhowalla, D. Jena, H. Zhang, Nat. Rev. Mater. 2016, 1, 16052.
- [10] Z. Li, J. Zheng, Y. Zhang, C. Zheng, W. Y. Woon, M. C. Chuang, H. C. Tsai, C. H. Chen, A. Davis, Z. Q. Xu, J. Lin, H. Zhang, Q. Bao, *ACS Appl. Mater. Inter.* 2017, *9*, 34204-34212.

- [11] J. Suh, T.-E. Park, D.-Y. Lin, D. Fu, J. Park, H. J. Jung, Y. Chen, C. Ko, C. Jang, Y. Sun, R. Sinclair, J. Chang, S. Tongay, J. Wu, *Nano Lett.* **2014**, *14*, 6976-6982.
- [12] Q.-C. Sun, L. Yadgarov, R. Rosentsveig, G. Seifert, R. Tenne, J. L. Musfeldt, Acs Nano 2013, 7, 3506-3511.
- [13] J. Gao, Y. D. Kim, L. Liang, J. C. Idrobo, P. Chow, J. Tan, B. Li, L. Li, B. G. Sumpter, T. M. Lu, V. Meunier, J. Hone, N. Koratkar, *Adv. Mater.* 2016, 28, 9735-9743.
- [14] B. Zhou, B. Shi, D. Jin, X. Liu, Nat Nanotechnol 2015, 10, 924-936.
- [15] Y. Zhang, J. Hao, J. Mater. Chem. C 2013, 1, 5607-5618.
- [16] S. Han, X. Qin, Z. An, Y. Zhu, L. Liang, Y. Han, W. Huang and X. Liu, *Nat. Commun.*, 2016, 7, 13059.
- [17] J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, Chem. Rev. 2015, 115, 395-465.
- [18] R. Deng, F. Qin, R. Chen, W. Huang, M. Hong, X. Liu, Nat. Nanotech. 2015, 10, 237-242.
- [19] G. Bai, M.-K. Tsang, J. Hao, Adv. Funct. Mater. 2016, 26, 6330-6350.
- [20] X. Wu, Y. Zhang, K. Takle, O. Bilsel, Z. Li, H. Lee, Z. Zhang, D. Li, W. Fan, C. Duan, E. M. Chan, C. Lois, Y. Xiang, G. Han, *ACS Nano* 2016, *10*, 1060-1066.
- [21] H. Dong, L. D. Sun and C. H. Yan, Chem. Soc. Rev., 2015, 44, 1608-1634.
- [22] C. Y. Liang Cheng, Sida Shen, Xuan Yi, Hua Gong, Kai Yang, and Zhuang Liu, *ACS Nano* 2015, *9*, 11090-11101.
- [23] G. Bai, S. Yuan, Y. Zhao, Z. Yang, S. Y. Choi, Y. Chai, S. F. Yu, S. P. Lau, J. Hao, *Adv. Mater.* 2016, *28*, 7472-7477.
- [24] G. Bai, Z. Yang, H. Lin, W. Jie, J. Hao, Nanoscale 2018, 10, 9261-9267.
- [25] J. Liu, R. Van Deun, A. M. Kaczmarek, J. Mater. Chem. C 2016, 4, 9937-9941.
- [26] D. Xu, W. Chen, M. Zeng, H. Xue, Y. Chen, X. Sang, Y. Xiao, T. Zhang, R. R. Unocic, K. Xiao, L. Fu, *Angew. Chem. Int. Ed.* 2018, 57, 755-759.
- [27] B. Liu, W. Zhao, Z. Ding, I. Verzhbitskiy, L. Li, J. Lu, J. Chen, G. Eda,
 K. P. Loh, *Adv. Mater.* 2016, 28, 6457-6464.