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Monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots on monolayered MoS₂ flakes with enhanced photoluminescence

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The precise control of the morphology and crystal shape of MoS₂ nanostructures is of particular importance for their application in nanoelectronic and optoelectronic devices. Here, we describe a single step route for the synthesis of monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots on monolayered MoS₂ flakes using a chemical vapor deposition method. First-principles calculations demonstrated that the bandgap of the pyramid-like MoS₂ nanodot is a direct bandgap. Enhanced local photoluminescence emission was observed in the pyramid-like MoS₂ nanodot, in comparison with monolayered MoS₂ flakes. The findings presented here provide new opportunities to tailor the physical properties of MoS₂ *via* morphology-controlled synthesis.

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Introduction

Monolayered molybdenum disulfide (MoS₂), composed of three layers of atoms where Mo atoms are sandwiched between two layers of S atoms, has attracted much attention from researchers because of its direct bandgap electronic structure and unique excitonic properties.^{1,2} In particular, MoS₂ in its monolayer form has broad applications in photonic devices,^{3,4} including light-emitting devices,⁵ photodetectors,⁶ solar cells,⁷ and so forth. The performances of these devices are determined by the physical properties of MoS₂ layered materials, which are, fundamentally, determined by the material characteristics, such as morphology and quality. So, it is essential to synthesize high quality MoS₂ films with the desired morphology and physical properties.⁸ In general, the fabrication methods for monolayered MoS₂ flakes from bulk MoS₂ include mechanical exfoliation,⁹ intercalation assisted exfoliation,^{10,11} liquid exfoliation,¹² physical vapor deposition,¹³ hydrothermal synthesis,¹⁴ and thermolysis of the single precursor containing Mo and S.¹⁵ Using these synthetic methods,

relatively large-sized monolayered MoS₂ with a lateral dimension size up to submicron has been reported.

To develop high performance MoS₂-based photonic devices, the tunability of the optical properties of the material is important, such as photoluminescence (PL) emission. Currently, the PL emission of MoS₂ can be tuned in several ways, such as chemical doping,¹⁶ electrical doping,¹⁷ changing the temperature,¹⁸ strain engineering,¹⁹ alloying,²⁰ modification of interlayer coupling,²¹ and so forth. It has also been demonstrated that the interplay between photogenerated carriers, excitons, and the surface acoustic wave (SAW) induced electro-acoustic field leads to strong dependence of the PL intensity on the SAW amplitude and excitation intensity.²² However, another important approach to tune the optical properties is to utilize the quantum confinement effect, which can be achieved, for instance *via* reducing the material size from bulk to large area monolayer to nanodots.²³ However, most of the recent attention has been focused on the fabrication, property and application studies of MoS₂ flakes with the relevant exploration of MoS₂ nanodots being ignored, which present new physical properties and important device applications.

In this paper, we have demonstrated the growth of monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots on monolayered MoS₂ flakes using a chemical vapor deposition (CVD) method. First-principles calculations demonstrated that the bandgap of the pyramid-like MoS₂ nanodot is a direct bandgap. Because of the significant enhancement of the PL efficiency caused by the monolayers of pyramid-like MoS₂ nanodots, strong PL enhancement was observed from this unique morphology of MoS₂ nanostructures. The findings

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presented here bring new opportunities to engineer the properties of MoS₂ *via* morphology-controlled synthesis.

Experimental

Pyramid-like MoS₂ nanodots on monolayered MoS₂ flakes were fabricated *via* a one-step approach with the CVD method. A two temperature zone tube furnace was used to provide accurate temperature control of the solid MoO₃ and sulfur (S), respectively. An alumina boat with S powders (99.9% purity) was placed upstream in the low-temperature zone. Another alumina boat containing MoO₃ (99.9% purity) was placed downstream in the high-temperature zone. A piece of Si wafer with a 300 nm SiO₂ layer substrate was placed face down to the MoO₃ powder. The distance between these two alumina boats is 14 cm. The temperature of S and the substrate was increased concurrently to 200 °C and 750 °C under an Ar flow, respectively. The sample was synthesized by evaporating S and MoO₃ powders simultaneously with a stoichiometric Mo to S ratio of 4 : 1 at an Ar flow rate of 30 sccm. After 3 minutes, the furnace was cooled down naturally to room temperature. The morphology of the MoS₂ nanostructures was examined by using Park system atomic force microscopy (AFM). The crystal structure and quality of MoS₂ nanostructures were examined by using a Rigaku X-ray diffractometer (XRD) with Cu K α radiation. Raman spectra were recorded by using a Horiba Jobin Yvon Raman microscopic system. The solid-state excitation laser has a wavelength of 532 nm, and the laser spot size was 1 μ m in diameter and a 100 \times objective was used to focus the laser beam. The PL measurements were also performed with the same laser by using the PL mode of the Raman microscopic system.

Results and discussion

Fig. 1(a) shows the optical microscopy image of MoS₂ flakes synthesized on the SiO₂/Si substrate with a pure Ar carrier gas flow rate of 30 sccm. The brighter-contrast flakes on the surface indicate the MoS₂ flakes, and the surrounding regions correspond to the SiO₂/Si substrate. A high density of flakes with a fairly uniform lateral size is formed over the surface of the substrate. Most importantly, it can be found that there is a shining spot on every MoS₂ flake and the thicknesses of these spots decrease from centers to edges. In order to further confirm the morphology and thickness of these MoS₂ flakes, AFM was used to examine the MoS₂ flakes. Fig. 1(b) illustrates the AFM image of a representative MoS₂ flake. The smooth surface morphology of the MoS₂ flake can be observed clearly, suggesting that the one layered structure of MoS₂ is formed. The MoS₂ flake has a dodecagonal shape, which corresponds to the Mo-rich conditions.²⁴ This is consistent with our synthesis conditions that the Mo : S ratio is much larger than 1 : 2. More interestingly, there is a MoS₂ nanodot decorated at the centre of the MoS₂ flake. The nanodot overall looks like pyra-

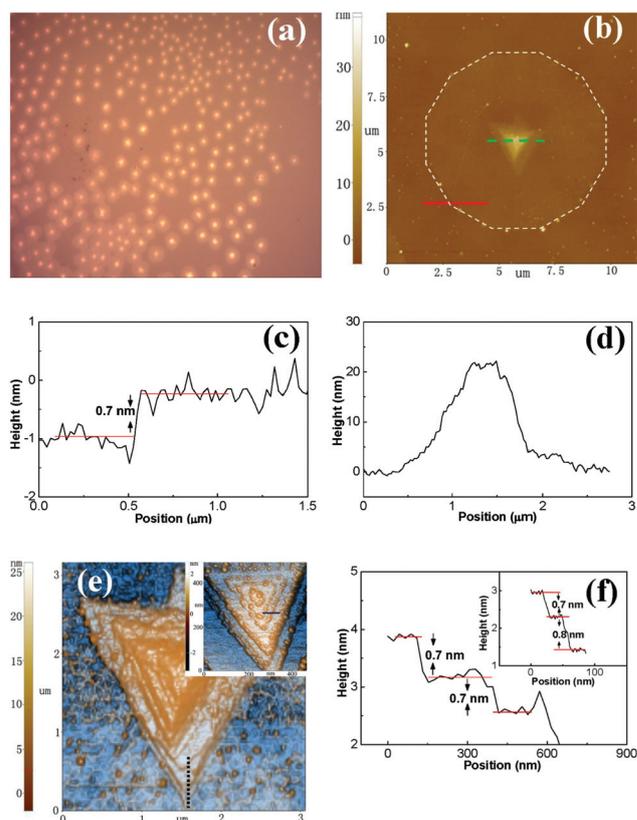


Fig. 1 (a) Optical microscopy image of MoS₂ flakes deposited on the SiO₂/Si substrate; (b) a typical AFM image of the MoS₂ flake; (c) height profile of the MoS₂ flake; (d) height profile of a pyramid-like MoS₂ nanodot; (e) side view of the high resolution AFM image of a pyramid-like MoS₂ nanodot; the top view of the high resolution AFM image of a pyramid-like MoS₂ nanodot in the top right corner; (f) step height profile of the corresponding region of the side viewed MoS₂ nanodot; step height profile of the corresponding region of the top viewed MoS₂ nanodot in the top right corner.

mids. Each basal plane has a triangular shape and shrinks gradually to the summit point. Fig. 1(c) shows the cross-sectional step height profile of the MoS₂ flake along the red line indicated in Fig. 1(b). From the height profile, it can be found that the MoS₂ flake has a thickness of about 0.7 nm, which is consistent with the previous report¹¹ for a monolayered MoS₂ grown on the SiO₂/Si substrate. Fig. 1(d) shows the cross-sectional height profile of the pyramid-like MoS₂ nanodots decorated at the centre of the MoS₂ flake along the green dashed line indicated in Fig. 1(b). From the height profile, it can be found that the pyramid-like MoS₂ nanodot has a height of about 20 nm and a lateral size of about 1.5 μ m. Fig. 1(e) shows the side view of the high resolution AFM image of a MoS₂ nanodot decorated at the centre of the MoS₂ flake. The insert is the top view of the high resolution AFM image of the pyramid-like MoS₂ nanodot. Obviously, pyramid-like features can be clearly observed as shown in the AFM images, and each basal plane has a triangular shape. The triangles stack up layer by layer and shrink gradually to the center

summit point. During the growth process of MoS₂ nanodots, the upper layers are formed later and have a shorter time to grow. Thus, the lateral layer size decreases with the height, and monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots form. Fig. 1(f) shows the step height profile of the corresponding region of the side viewed MoS₂ nanodot marked by the black dotted line displayed in Fig. 1(e). The insert is the step height profile of the corresponding region of the top viewed MoS₂ nanodot marked by the blue line displayed in the inset of Fig. 1(e). The height profile shows an obvious step height of about 0.7–0.8 nm, which matches the thickness of the MoS₂ monolayer. Therefore, it can be confirmed that the pyramid-like MoS₂ nanodot is stacked with monolayer-by-monolayer MoS₂.

In order to clarify the crystal structure and quality of the pyramid-like MoS₂ nanodot decorated MoS₂ flakes, XRD measurements were performed. Fig. 2(a) shows the XRD pattern of the MoS₂ nanostructures. All the diffraction peaks in the pattern can be indexed as hexagonal-phase MoS₂ with the space group *P63/mmc* (JCPDS no. 77-1716). No diffraction peaks from impurities are observed in the XRD pattern. From Fig. 2(a), the dominant peak reflecting the (002) plane was observed. This reflects the nature of the MoS₂ nanostructures which consist of MoS₂ layers with mostly (002) planes. Meanwhile, the very sharp peaks with high intensity and the strong (002) peak in the pattern of MoS₂ nanostructures also indicate good crystallization and a well-stacked layered structure. This result is in good agreement with the AFM observation that the nanostructured MoS₂ composed of monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots on the monolayered MoS₂. Moreover, the XRD pattern is matched against a simulated XRD pattern generated by using Java Electron Microscopy Simulation (JEMS) software.²⁵ As shown in Fig. 2(b), the lattice constants of MoS₂ calculated from this XRD pattern are $a = b = 3.16 \text{ \AA}$ and $c = 12.35 \text{ \AA}$. The former is very close to the standard value of MoS₂ ($a = 3.16 \text{ \AA}$), but the latter shows an obvious increase in comparison with that of MoS₂ ($c = 12.29 \text{ \AA}$). The results indicate that the distance between neighboring MoS₂ layers increases but their in-plane structure is preserved.

The pyramid-like MoS₂ nanodot decorated MoS₂ flakes are further examined by Raman spectroscopy measurements. The solid-state excitation laser has a wavelength of 532 nm and the

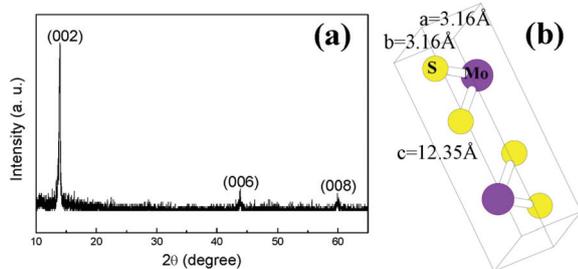


Fig. 2 (a) XRD pattern of MoS₂ flakes decorated with pyramid-like MoS₂ nanodots; (b) schematic image of MoS₂ unit cells.

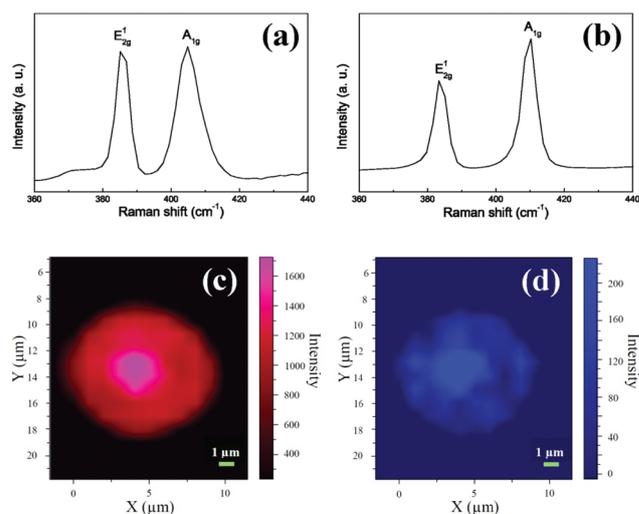


Fig. 3 (a) Raman spectra of the MoS₂ flake region; (b) Raman spectra of the pyramid-like MoS₂ nanodot region; Raman intensity mappings of (c) E_{2g} and (d) A_{1g} of the MoS₂ flakes decorated with pyramid-like MoS₂ nanodots.

laser spot size was 1 μm in diameter. The Raman spectra of the monolayered MoS₂ flake region and the pyramid-like MoS₂ nanodot region are shown in Fig. 3(a) and (b), respectively. It can be found that the two characteristic Raman vibration modes E_{2g} and A_{1g} can be observed in the spectra of the monolayered MoS₂ flake and the pyramid-like MoS₂ nanodot. The E_{2g} mode is associated with the in-plane vibrations, *i.e.*, two S atoms are displaced in one direction and the Mo atom is displaced in the opposite direction. The A_{1g} mode is related to the perpendicular vibrations, *i.e.*, two S atoms are displaced in the opposite directions while the Mo atom does not move. These two Raman modes, E_{2g} and A_{1g}, exhibit a sensitive layer thickness dependence,²⁶ which provides a convenient and reliable means for determining the layer thickness with atomic precision. Obviously, the frequency difference between the E_{2g} and A_{1g} Raman modes is 19 cm⁻¹ in Fig. 3(a) and 25 cm⁻¹ in Fig. 3(b), which confirm the MoS₂ flake is monolayer and the pyramid-like MoS₂ nanodot is multilayer. This is consistent with the AFM results that the MoS₂ flake is monolayered MoS₂ and the pyramid-like MoS₂ nanodot is stacked with monolayer-by-monolayer MoS₂. As shown in Fig. 1(d) and (f), the MoS₂ nanodots are composed of a few tens of monolayers and the interlayer distance is about 0.7 nm. The effective interlayer mechanical coupling is still relatively strong, which can modify the phonon vibrations in multilayered MoS₂ nanodots. Therefore, a frequency difference of 25 cm⁻¹ between the E_{2g} and A_{1g} Raman modes can be observed in the pyramid-like MoS₂ nanodot. Moreover, this frequency difference of the monolayered region suggests the good quality of the MoS₂ flake, and the frequency difference values of the pyramid-like MoS₂ nanodot indicate good preservation of the MoS₂ nanodot quality.²⁷ Raman mapping of the whole region further confirms the observation, as shown in Fig. 3(c) and (d). Mapping

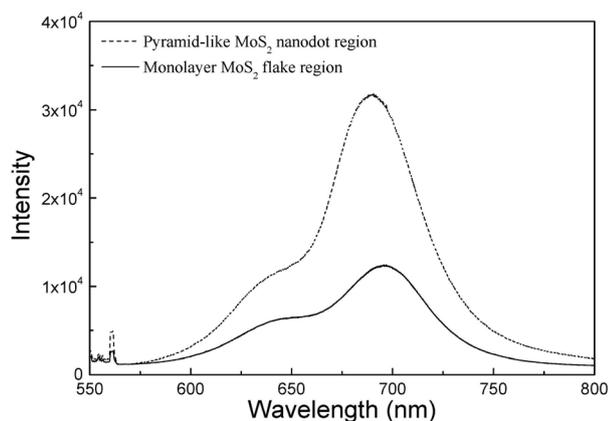


Fig. 4 PL spectra of a typical monolayered MoS₂ flake region and the pyramid-like MoS₂ nanodot region.

of the integrated intensity of the E_{2g} and A_{1g} peaks shows that the pyramid-like MoS₂ nanodot region is brighter than the monolayered MoS₂ flake region.

Fig. 4 shows the PL spectra recorded on a monolayered MoS₂ flake region and a pyramid-like MoS₂ nanodot region with a 532 nm laser source at room temperature. PL measurements were performed with the same laser excitation source and conditions as that for Raman spectroscopy. Two peaks can be observed in the PL spectra, 690 nm and 645 nm, which can be attributed to the B₁ and A₁ excitons of MoS₂, respectively.⁹ Similar PL structures can be found for both the monolayered MoS₂ flake region and the pyramid-like MoS₂ nanodot region. Interestingly, in contrast to the silent PL emission of the bulk MoS₂, the PL emission of the pyramid-like MoS₂ nanodot is much stronger than that of the monolayered MoS₂ flake. It should be noted that the PL intensity of the MoS₂ nanodot is almost 3 times stronger than that of the monolayered MoS₂ flake.

To understand the PL of pyramid-like MoS₂ nanodots, we studied the electronic structural properties of MoS₂ with different phases using first-principles calculations based on density functional theory (DFT) and generalized gradient approximation (GGA). The projector augmented wave (PAW)

scheme as incorporated in the Vienna ab initio simulation package (VASP) is used in the study. In addition, the van der Waals interaction between two adjacent MoS₂ layers for bulk phases is also taken into account in our calculations. The calculated energy band structures of bulk 2H-MoS₂, MoS₂ monolayer and bulk 1H-MoS₂ are shown in Fig. 5. According to Fig. 5(a) and (b), the indirect bandgap and direct bandgap for bulk 2H-MoS₂ and MoS₂ monolayer respectively are in good agreement with previous reports.^{4,28} As we know, there is no PL for bulk 2H-MoS₂, which is directly related to its indirect bandgap. However, the direct bandgap results in the PL in the MoS₂ monolayer. Based on our experimental results, the pyramid-like MoS₂ nanodots have strong PL, which suggests that the pyramid-like MoS₂ nanodots should not have the stacking sequence ABAB...(2H phase) for MoS₂ monolayers. Therefore, we propose that the pyramid-like MoS₂ nanodots could possess the AAAA... stacking sequence (1H phase). In order to confirm this, we calculate the band structure (Fig. 5(c)) of bulk 1H-MoS₂ with the distance between two adjacent layers of 0.7 nm, which basically corresponds to the inter-layer distance in our samples. It is obviously found that the bandgap is direct. A direct bandgap means the easy appearance of PL. As a consequence, the strong PL of pyramid-like MoS₂ nanodots is closely related to the stacking sequence of MoS₂ monolayers. Furthermore, due to the greater number of monolayers of pyramid-like MoS₂ structures, the PL intensity of pyramid-like MoS₂ nanodots is significantly higher than that of the MoS₂ monolayer, as observed in Fig. 4.

Conclusion

In conclusion, we have demonstrated the growth of monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots on monolayered MoS₂ flakes using a CVD method. Strong local PL emission has been observed for the pyramid-like MoS₂ nanostructures. First-principles calculations demonstrated that the bandgap of monolayer-by-monolayer stacked pyramid-like MoS₂ nanodots is a direct bandgap. It leads to stronger PL emission of the pyramid-like MoS₂ nanodot in comparison with that of monolayered MoS₂ flakes. The findings presented here provide new opportunities to tailor the properties of MoS₂ via morphology-controlled synthesis.

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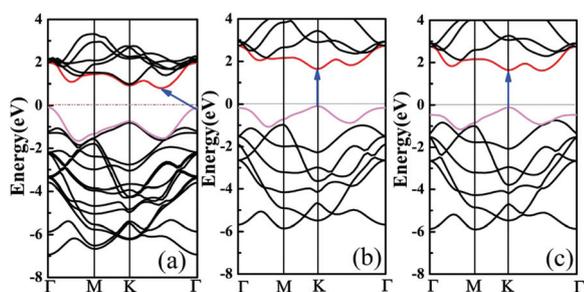


Fig. 5 Energy band structures of (a) bulk 2H-MoS₂; (b) MoS₂ monolayer; (c) bulk 1H-MoS₂.

Notes and references

- 1 Y. Zhang, T. T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen and F. Wang, *Nature*, 2009, **459**, 820.
- 2 W. Z. Wu, L. Wang, Y. L. Li, F. Zhang, L. Lin, S. M. Niu, D. Chenet, X. Zhang, Y. F. Hao, T. F. Heinz, J. Hone and Z. L. Wang, *Nature*, 2014, **514**, 470.
- 3 A. K. Geim and I. V. Grigorieva, *Nature*, 2013, **499**, 419.
- 4 Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman and M. S. Strano, *Nat. Nanotechnol.*, 2012, **7**, 699.
- 5 R. Sundaram, R. Engel, A. Lombardo, R. Krupke, A. Ferrari, P. Avouris and M. Steiner, *Nano Lett.*, 2013, **13**, 1416–1421.
- 6 O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic and A. Kis, *Nat. Nanotechnol.*, 2013, **8**, 497.
- 7 M. L. Tsai, S. H. Su, J. K. Chang, D. S. Tsai, C. H. Chen, C. I. Wu, L. J. Li, L. J. Chen and J. H. He, *ACS Nano*, 2014, **8**, 8317.
- 8 Y. J. Cao, X. F. Luo, S. M. Han, C. L. Yuan, Y. Yang, Q. L. Li, T. Yu and S. L. Ye, *Chem. Phys. Lett.*, 2015, **631–632**, 30.
- 9 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli and F. Wang, *Nano Lett.*, 2010, **10**, 1271.
- 10 H. S. S. R. Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2010, **49**, 4059.
- 11 Z. Y. Zeng, Z. Y. Yin, X. Huang, H. Li, Q. Y. He, G. Lu, F. Boey and H. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 11093.
- 12 K. G. Zhou, N. N. Mao, H. X. Wang, Y. Peng and H. L. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 10839.
- 13 J. V. Lauritsen, J. Kibsgaard, S. Helveg, H. Topsoe, B. S. Clausen, E. Lagsgaard and F. Besenbacher, *Nat. Nanotechnol.*, 2007, **2**, 53.
- 14 Y. Y. Peng, Z. Y. Meng, C. Zhong, J. Lu, W. C. Yu, Y. B. Jia and Y. T. Qian, *Chem. Lett.*, 2001, **8**, 772.
- 15 C. Altavilla, M. Sarno and P. Ciambelli, *Chem. Mater.*, 2011, **23**, 3879.
- 16 S. Mouri, Y. Miyauchi and K. Matsuda, *Nano Lett.*, 2013, **13**, 5944.
- 17 K. Eshun, H. D. Xiong, S. Yu and Q. L. Li, *Solid-State Electron.*, 2015, **106**, 44.
- 18 T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler and C. Schüller, *Appl. Phys. Lett.*, 2011, **99**, 102109.
- 19 A. Castellanos-Gomez, R. Roldán, E. Cappelluti, E. Buscema, F. Guinea, H. van der Zant and G. Steele, *Nano Lett.*, 2013, **13**, 5361.
- 20 Y. F. Chen, J. Y. Xi, D. O. Dumcenco, Z. Liu, K. Suenaga, D. Wang, Z. G. Shuai, Y. S. Huang and L. M. Xie, *ACS Nano*, 2013, **7**, 4610.
- 21 K. H. Liu, L. M. Zhang, T. Cao, C. H. Jin, D. N. Qiu, Q. Zhou, A. Zettl, P. D. Yang, S. G. Louie and F. Wang, *Nat. Commun.*, 2014, **5**, 4966.
- 22 A. R. Rezk, S. Walia, R. Ramanathan, H. Nili, J. Z. Ou, V. Bansal, J. R. Friend, M. Bhaskaran, L. Y. Yeo and S. Sriram, *Adv. Opt. Mater.*, 2015, **3**, 888.
- 23 B. L. Li, L. X. Chen, H. L. Zou, J. L. Lei, H. Q. Luo and N. B. Li, *Nanoscale*, 2014, **6**, 9831.
- 24 D. Cao, T. Shen, P. Liang, X. S. Chen and H. B. Shu, *J. Phys. Chem. C*, 2015, **119**, 4294.
- 25 P. A. Stadelmann, *Ultramicroscopy*, 1987, **21**, 131.
- 26 H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier and D. Baillargeat, *Adv. Funct. Mater.*, 2012, **22**, 1385.
- 27 L. Liang and V. Meunier, *Nanoscale*, 2014, **6**, 5394.
- 28 W. S. Yun, S. W. Han, S. C. Hong, I. G. Kim and J. D. Lee, *Phys. Rev. B: Condens. Matter*, 2012, **85**, 033305.