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Comment on "Strongly luminescent monolayered MoS2 prepared by effective ultrasound exfoliation" by V. Štengl and J. Henych, Nanoscale, 2013, 5, 3387

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Comment

Comment on “Strongly luminescent monolayered MoS2 prepared by effective ultrasound exfoliation” [Nanoscale 2013, 5, 3387]

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In a recent paper,[1] Štengl and Henych reported the fabrication of monolayered MoS_2 dots by refluxing MoS_2 nanosheets in ethylene glycol (EG) and the observation of excitation-dependent blue photoluminescence (PL), which was attributed to the formed MoS_2 dots. We repeated the same procedures with and without MoS_2, and found that refluxing MoS_2 in EG will form MoS_2 and carbon dots, and that refluxing pure EG will also effectively produce carbon dots. Both products show similar blue PL to the reported in reference 1. So, we suggest that carbon dots will be unavoidably formed when using the method in reference 1 and should be with responsibility for the observed blue PL.

Experiments

In Štengl and Henych’s work, the final MoS_2 dots were prepared through refluxing MoS_2 nanosheets in ethylene glycol (EG) at atmospheric pressure for 24 hours. In this method, three key points are refluxing, MoS_2 and EG. In order to check the real composition of the products fabricated by the method used in reference 1, two sets of preparation experiments were designed as sample A and sample B.

The first one applied the completely same procedures and same starting materials (MoS_2 + EG) as reference 1, denoted as sample A. The second applied the same procedures, but only EG but without MoS_2 was used in the starting materials, resulting in sample B. The formed samples were characterized by X-ray diffraction (XRD, Bruker), Raman spectra (JY HR800, 514 nm laser), UV-Vis absorption spectra (Shimadzu 2660), PL spectra (Varian Cary Eclipse), TEM (FEI Tecnai F30S-TWIN).

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Results and discussion

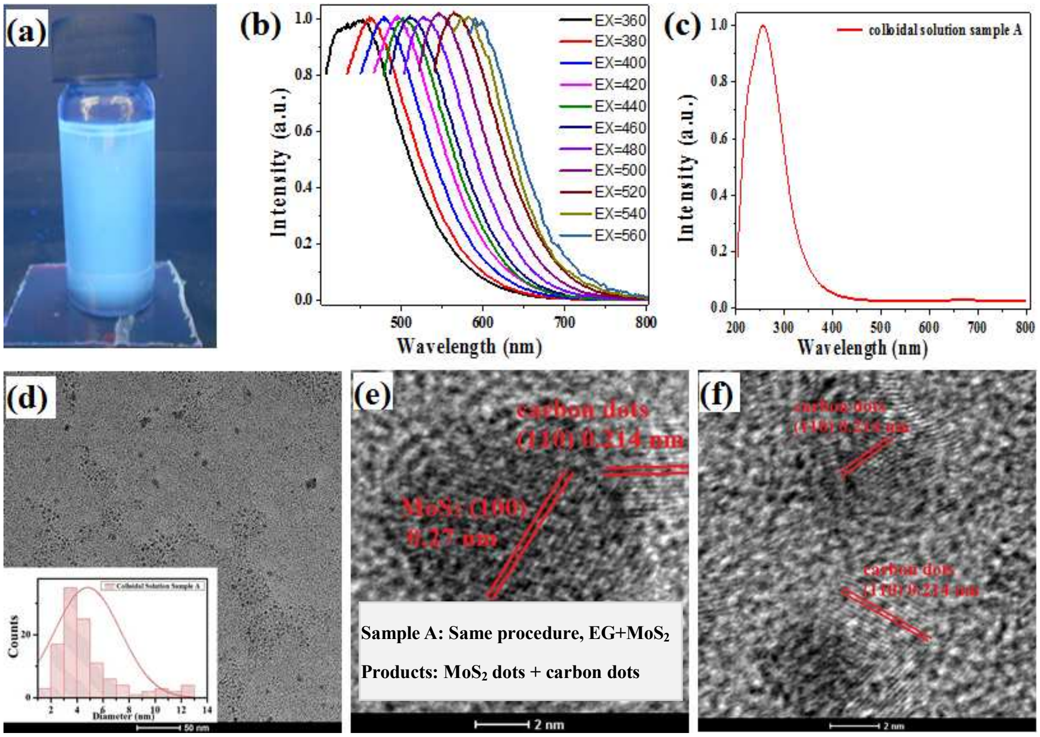

Figure 1. Characterizations of sample A, prepared by the same procedures and starting materials. The observed fluorescence photograph (a) under UV lamp, PL spectra (b) under different excition, UV absorption (c) and TEM image (d) all are very similar to the reported results in reference 1. But HRTEM images (e and f) show both MoS_2 and carbon dots in comparable yields. These results primally demonstrate that the MoS_2 dots have been contaminated by carbon dots and that the blue PL could come from MoS_2 or carbon dots.

The structure and optical properties of sample A were characterized as shown in Figure 1. The fluorescence photograph in Figure 1a shows that there is blue luminescence from this sample under UV excitation, which is further confirmed by PL measurement as shown in Figure 1b. Both the luminescence and absorption (Figure 1c) properties are the same as reported in reference 1. Combining with the very similar TEM image in Figure 1d and AFM image in Figure S1, these prove that we have successfully reproduced their experiment and products.

However, HRTEM images in Figure 1e and 1f clearly show both MoS_2 and carbon dots, and their numbers are comparable in HRTEM view range. These results primally

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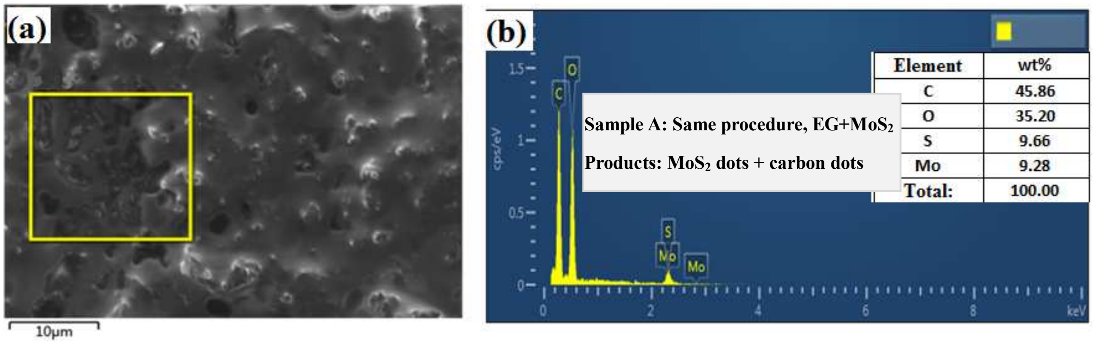
demonstrate that the MoS_2 dots produced by the method used in reference 1 have been contaminated by carbon dots and that the blue PL could come from MoS_2 or carbon dots. A typical crystalline M_OS_2 dots with hexagonal lattice structure is shown in Figure 1e, exhibiting clear (100) inter-planar distance of 0.27 nm.[3] Figure 1f presents two well crystallined carbon dots with hexagonal graphite structure evidenced by (001) inter-planar distance of 0.21 nm.[4] Considering the error of HRTEM observation from orientation of crystals and local view range, other tools with more sensitive and larger measuring-range were used, including EDS spectrum and Raman scattering spectrum.

The SEM image and corresponding EDS spectrum of sample A are shown in Figure 2. Very obviously, elements of C, O, S, and Mo have been detected. What should be noticed is that the ratio of carbon is highest, about 45.86% in weight, which is about 5 times of Mo. Considering the difference in molecular weight of them, the mole ratio of carbon to Mo is about 40:1. Although some detected carbon could be contributed to the environment or substrate, the results still obviously show that both MoS_2 and carbon products were formed, especially when considering the very high ratio of carbon to Mo. The detecting area of SEM-EDS is much larger than HRTEM. So, this result gives strong evidence that the product formed according to reference 1 is the mixture of MoS_2 and carbon, probably mainly carbon dots, and hence the blue PL could come from carbon dots.



Sample A: Same procedure, EG+MoS_2

Products: MoS_2 dots + carbon dots

Element	wt%
C	45.86
O	35.20
S	9.66
Mo	9.28
Total:	100.00

Figure 2. Composition checking of sample A. (a) SEM image and (b) corresponding EDS spectra of filtered and dried sample on a Si substrate. Although some detected carbon could come from the environment, the results still show that both MoS_2 and carbon products were formed, especially when considering the very high ratio of carbon to Mo.

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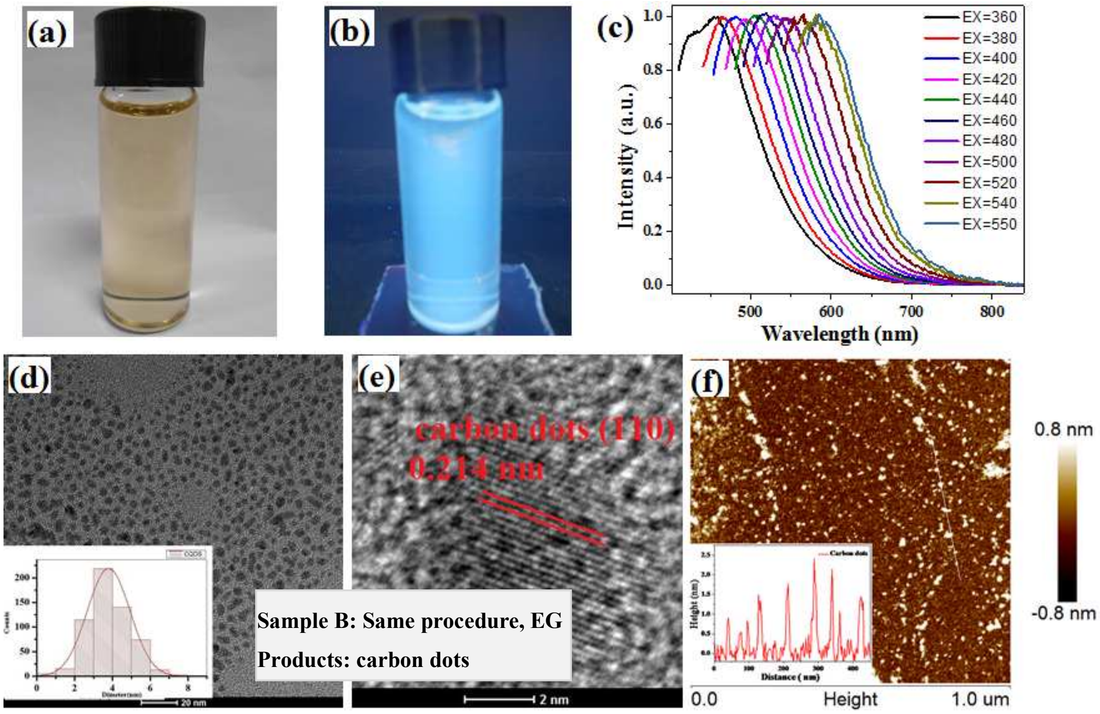

Figure 3. **Characterizations of sample B, prepared by the same procedure but only with EG.** The observed fluorescence photograph (a and b) under UV lamp, PL spectra (c) under different excition, TEM image (d) and AFM image (f) all are very similar to the reported results in reference 1. HRTEM images (e) show that all of the dot-like products are carbon dots with graphite structure, no any MoS_2 dots can be found. This is very resonable because only EG is applied as carbon source without any MoS_2. These results give convincing proof that carbon dots will be ineluctabilly and effectively produced during the refluxing of EG as used in reference 1 and that the observed blue PL should be attributed to these carbon dots.

To avoid the misgiving that the observed carbon could come from the post-treatment or from the prepration of SEM and TEM samples, no MoS_2 and only EG was used for the same fluxing procedure as reported in reference 1, resulting in sample B. The characterization of sample B is shown in Figure 3. Figure 3a, 3b, and 3c reveal that the product has similar blue and excitation-dependent luminescence to the reported results in reference 1. Furthermore, the TEM image in Figure 3d and AFM image in Figure 3f exhibit smimilar dot-like products. However, HRTEM image (e) shows that all of the dot-like products are actually carbon dots with clear graphite structure, no any MoS_2 dots can be found. This is very resonable because only EG is applied as carbon source without any MoS_2 in the starting material. These give convincing proof that carbon dots will be

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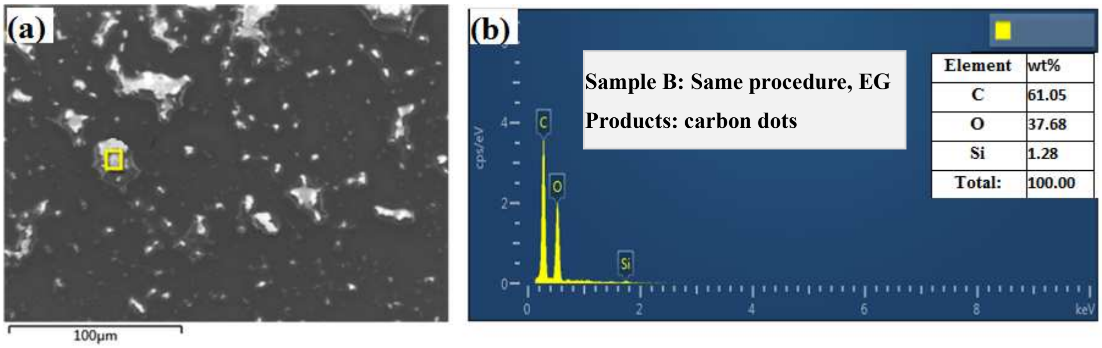
ineluctabilly and effectively produced during the refluxing of EG as used in reference 1 and that the observed blue PL should be attributed to these carbon dots. Actually, similar method has been widely used to fabricate blue-luminescent carbon dots, there are many related literatures. This result is strongly confirmed by EDS in a large measuring range, as shown in Figure 4, where only carbon is detected without any MoS_2.



Element	wt%
C	61.05
O	37.68
Si	1.28
Total:	100.00

Figure 4. Composition checking of sample B. When only EG source was used, sample B were formed by the same procedure as reported in ref. 1(a) SEM image and (b) EDS (SEM-EDS) spectrum of the resulted sample, showing only carbon dots, besides oxygen from surface groups and Si from substrate. This also proved carbon dots can be inescapability formed when applying the procedure and EG source as reported in ref.1.

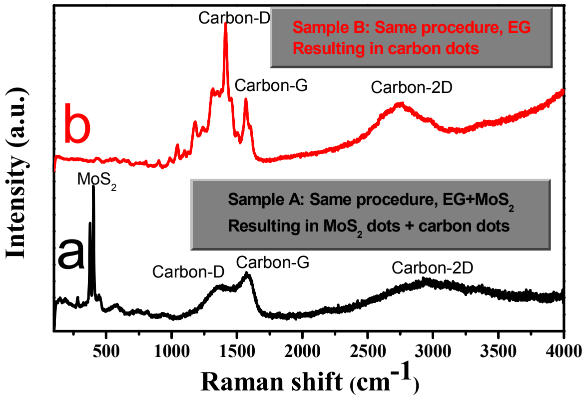


Figure 5. Raman checking of sample A and sample B. Sample A, using the same procedure and starting materials as reported in reference 1, exhibits characteristic peaks of both MoS_2 and carbon. However, sample B only shows contributions of carbon dots. This demonstrates that according to the procedure applied in reference 1, MoS_2 and EG will results in MoS_2 and carbon dots, only EG can also produce carbon dots. So, carbon dots cannot be avoided in reference 1.

In order to accurately identify the formed compound structure besides elements, above

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sample A and B were measured by Raman scattering spectrum as shown in Figure 5. The Raman spectrum of sample A shows scattering peaks from both MoS_2 and carbon, but sample B only exhibits carbon scattering peaks. Details of Raman peaks are listed as following: 377.4 and 401.6 cm^{-1} peaks are corresponding to E^1_{2g} and A_{1g} vibrational modes of MoS_2; 1590, 1320, and 2700 cm^{-1} peaks are typical G-band (sp^2), D-band (sp^3), and 2D-band (double resonance) of carbon. The Raman checking reveals that the carbon dots will be unavoidably formed by reference 1 method when EG was used, so the products should be mixture, but not MoS_2 dots as claimed in reference 1. This demonstrates that according to the procedure applied in reference 1, after fluxing, MoS_2 and EG will results in MoS_2 and carbon dots, only EG can also effectively produce carbon dots. So, carbon dots cannot be avoided in reference 1. Considering that bright blue luminescence can be observed in both cases, we suggest that such observed blue PL comes from carbon dots. Actually, blue luminescence and its excitation-dependence behaviors have been very frequently reported recently from carbon dots fabricated by similar process.

In order to confirm that the solvent has no effect on the results and avoid cross-contamination during ultrasonic treatment, we tested the PL spectra of the solvent without any treatment and only refluxing for 24 h at the boiling point without ultrasonic treatment. There is no PL for the solvent and the Raman characteristic peaks vary from different excitation wavelength in the spectra (**Figure S3**). On the other hand, the PL results of the sample after the process of refluxing, which is the same as that of carbon dots. Moreover, the TEM image is the same as figure 3d, revealing the formation of carbon dots. This suggested that carbon dots were formed during the process of refluxing (**Figure S3**).

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Conclusions

Aiming to the produced MoS_2 dots by refluxing MoS_2 nanosheets in ethylene glycol (EG) and the corresponding blue PL, we repeated the same procedures with and without MoS_2. Our results demonstrated that fluxing MoS_2 in EG will form MoS_2 and carbon dots, and that fluxing pure EG will also and very effectively produce carbon dots. Both cases show similar blue PL to the reported in reference 1. So, we suggest that carbon dots will be unavoidably formed when using the method in reference 1 and should be with responsibility for the observed blue PL.

Acknowledgements

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References

[1] V. Štengl, and J. Henych, Strongly luminescent monolayered MoS_2 prepared by effective ultrasound exfoliation, *nanoscale*., 2013, **5**, 3387 – 3394.

[2] J. Shen, Y. Zhu, X. Yang, J. Zong, J. Zhang and C. Li, One-pot hydrothermal synthesis of graphene quantum dots surface-passivated by polyethylene glycol and their photoelectric conversion under near-infrared light, *New J. Chem.*, 2012, **36**, 97-101.

[3] Y. L. Liu, H. Y. Nan, X. Wu, W. Pan, W. H. Wang, J. Bai, W. W. Zhao, L. T. Sun, X. R. Wang, Z. H. Ni, Layer-by-Layer Thinning of MoS_2 by Plasma, *ACS Nano*., 2013, **7**, 4202-4209.

[4] L. B. Tang, R. B. Ji, X. K. Cao, J. Y. Lin, H. X. Jiang, X. M. Li, K. S. Teng, C. M. Luk, S. J. Zeng, J. H. Hao and S. P. Lau, Deep Ultraviolet Photoluminescence of Water-Soluble Self-Passivated Graphene Quantum Dots, *ACS Nano*., 2012, **6**, 5102-5110.

[5] F. Wang, S. P. Pang, L. Wang, Q. Li, M. Kreiter and C. Y. Liu, One-Step Synthesis of Highly Luminescent Carbon Dots in Noncoordinating Solvents, *Chem. Mater*., 2010, **22**, 4528-4530.

[6] H. T. Li, X. D. He, Z. H. Kang, H. Huang, Y. Liu, J. L. Liu, S. Y. Lian, C. H. Tsang, X. B. Yang, and S. T. Lee, Water-Soluble Fluorescent Carbon Quantum Dots and Photocatalyst Design, *Angew. Chem. Int. Ed*., 2010, **49**, 4430-4434.

Nanoscale

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Comment

[7] Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M.J. Meziani, B. A. Harruff, X. W, H. F. Wang, P. J. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca, and S. Y. Xie, Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence, *J. Am. Chem. Soc.*, 2006, **128**, 7756-7757

[8] Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. G. Hong, and H. J. Dai, MoS_2 Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction, *J. Am. Chem.Soc.*, 2011, **133**, 7296–7299

[9] Z. Y. Yin, H. Li, H. Li, L. Jiang, Y. M. Shi, Y. H. Sun, G. Lu, Q. Zhang, X. D. Chen, H. Zhang, Single-Layer MoS2 Phototransistors, *ACS Nano.*, 2012, **1**, 74–80.