Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Communication

On the Upconversion Fluorescence in Carbon Nanodots and Graphene Quantum Dots

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Upconversion fluorescence has been frequently cited as an important feature in carbon nanodots (CNDs) and graphene quantum dots (GQDs); and some mechanisms and potential applications have been proposed. Contrary to such a general
10 **belief, we demonstrate in this report no observable upconversion fluorescence based on five different synthesized CNDs and GQDs. We confirm the so-called upconversion fluorescence actually originates from the normal fluorescence excited by the leaking component from the second diffraction**
15 **in the monochromator of the fluorescent spectrophotometer. Upconversion fluorescence can be identified by measuring the excitation intensity dependence of the fluorescence.**

Carbon nanodots (CNDs) and graphene quantum dots (GQDs) have emerged as promising carbon based nanomaterials due to
20 their unique features,[1-3] such as high quantum yields (QY, ~80%),[4] low cost and environmentally friendly,[5] nonblinking,[6] low photobleaching and high photostability, as well as large two-photon cross section.[7] Upconversion fluorescence has been observed and was frequently cited as an important feature in
25 CNDs and GQDs;[8-15] Some mechanisms and potential applications were proposed based on observed upconversion fluorescence, such as third generation photovoltaics.

Using the reported experimental conditions, we can observe so-called upconversion fluorescence in our five different synthesized
30 CNDs and GQDs in a commercial fluorescent spectrophotometer. However, we confirm the upconversion fluorescence actually originates from the normal fluorescence excited by the leaking component from the second diffraction in the monochromator of the fluorescent spectrophotometer. The leaking component and
35 thus upconversion fluorescence can be eliminated by adding a suitable long-pass filter in the excitation pathway of a fluorescent spectrophotometer. Intensity dependent experiment clearly confirms the so-called upconversion fluorescence is normal fluorescence with linear response, rather than multiple phonon
40 process. Our experiments suggest most of the CNDs and GQDs actually do not have detectable upconversion fluorescence. It is very necessary to eliminate the normal fluorescence when observing upconversion fluorescence.

The experimental samples used in this study include five different
45 synthesized CNDs and GQDs; the detailed synthesis and characterizations have been reported previously. (1) CND1: a green emitted CNDs synthesized by bottom-up approach developed by Fang;[16-18] (2) CND2: a blue emitted CNDs synthesized by similar bottom-up approach;[3, 16] (3) CND3:
50 synthesized by P_2O_5-based room temperature dehydration of acetic acid from banana.[16, 18, 19] (4) CND4: similar procedures to

CND3 from sweet potato;[20] (5) blue emitted GQDs synthesized by hydrothermal method using reoxidized graphene oxide.[21] Fluorescence spectra were recorded using a JASCO fluorescent
55 (FP-6300) spectrophotometer. Other excitation sources include femtosecond pulses from Ti:Sapphire oscillator (Tsunami, 100 fs, 78 MHz, 800 mW, wavelength tunable 700-900 nm), and a regenerative amplifier pumped optical parametric amplifier (100 fs, 1 KHz repetition rate and wavelength tunable from UV to
60 Near infrared).

Figure 1a shows the absorption and fluorescence (inset, excited at 400 nm) spectra of five samples. Similar to the previous studies in CNDs and GQDs, the absorption peaks in shorter wavelength can be ascribed to π-π* transition of aromatic C=C bonds; and the
65 shoulders at longer wavelength are attributed to n-π* transition of C=O bonds.[3, 16, 18] The fluorescence spectra basically are broad in the blue and green. It has been demonstrated that the broad fluorescence is ascribed to the extrinsic broadening of the functional groups and intrinsic broadening of strong electron-
70 electron scattering.[3] It should be noted that each CND or GQD exhibits wavelength dependent fluorescence more or less, that is, with increasing excitation wavelength the fluorescence peak red-shifts. Moreover, XPS measurement confirms that the functional groups of C-OH, C=O and COOH exist in each sample at
75 different extent. The lifetime was measured using the time correlated single photon counting technique, as shown in Figure 1b for CND1 and GQDs at 500 and 600 nm excited at 405 nm. The fluorescence evolution can be fitted by dual-exponential function and the average lifetime is determined by
80 $\tau_{av} = (A_1 \cdot \tau_1 + A_2 \cdot \tau_2)/(A_1 + A_2)$. Each sample has average lifetime between 1.5 and 4 ns at 500 nm; and slightly shorter at 600 nm. These results confirm that the used CNDs and GQDs have the similar features to the reported CNDs and GQDs.[14, 22]

In a typical fluorescent spectrophotometer, the excitation light is
85 obtained by utilizing a grating monochromator in which the continuous spectrum from a xenon lamp passes through a diffraction grating and the grating splits the light in different directions. Namely only a single wavelength light can pass through the slit as a monochromatic excitation source. When light
90 is incident on the grating at an angle of θ_i (assuming a plane wave), the diffracted light will exhibit the maxima at angles θ_m given by $\theta_m = \arcsin(m\lambda/d - \sin\theta_i)$, where λ is the wavelength of the light and d is grating spacing; and integer m=0, ±1, ±2.. etc. is order of the diffraction maxima. The zero order, $m = 0$,
95 corresponds to specular reflection for a reflection grating or direct

transmission for a transmission grating. The non-zero integer m represents the others of diffraction maxima on both sides of the zero order beam. The first order maximum is generally chosen as excitation beam because of the largest intensity. It should be
5 emphasized the second order maximum of the light with half wavelength of the designated excitation wavelength can also pass though the slit simultaneously, in such a configuration. This component generally has much lower intensity than that of the first order maximum. For example, when choosing 800 nm as
10 excitation, a weaker 400 nm beam can also pass through the slit simultaneously. It should be noted that the detection sensitivity of a state of the art fluorescent spectrophotometer is very high so that it is easy to detect any weak fluorescence component if the background is clear. Therefore, the fluorescence detected for
15 excitation of 800 nm actually is the sum excited by both 800 and 400 nm, if without a filter.

Shown in Figure 2 is the fluorescence spectrum of CNDs (CND1) excited at 400 nm. A similar spectrum but at lower intensity can be obtained with 800 nm excitation without a filter in the
20 excitation pathway of the fluorescent spectrophotometer. The fluorescence disappears when a long pass filter was inserted in the excitation pathway. This clarifies that the observed fluorescence actually originates from the second order output of 400 nm. Each other sample also exhibits the same phenomenon.

25 Upconversion fluorescence is defined as the emission photon energies are higher than those of the excitation, i.e., an emission photon at shorter wavelength than the excitation wavelength is generated by absorbing two or more photons. A typical example is absorbing multiple infrared photons and emitting one visible
30 photon. In principle, three mechanisms can result in upconversion fluorescence, energy transfer upconversion, excited-state absorption and photon avalanche.[23, 24] Upconversion fluorescence is basically a multiple photon process but should be distinguishes from two-photon absorption and second harmonic generation.[23, 24]
35 It is generally very difficult to observe upconversion fluorescence in a commercial fluorescent spectrophotometer because the excitation resource is an incoherent and low intensity xenon lamp and thus the efficiency of upconversion is extremely low. By using a long pass filter, we confirm there is no observable
40 upconversion fluorescence for each CNDs and GQDs used in this study. Figure 3 shows (a) a bright fluorescence in solution of CNDs excited by 400 nm laser with power of 5 mW. The CNDs and GQDs have high fluorescence quantum yield, usually more than 20%. When changing the excitation laser to 800 nm with 20
45 times higher power, 100 mW, obviously there is no observable upconversion fluorescence, Figure 3b.

Phosphorescence with tens to hundreds of millisecond lifetime has been observed in each our CNDs and GQDs sample, similar to the previous reports.[25, 26] Therefore, cascade excitation induced
50 fluorescence is possible mechanism in which the triplet state acts as an intermediate state. However, there is no obvious fluorescence observed with excitation of 800 nm ultrashort pulses, both at 1 KHz and 80 MHz. This confirms the efficiency of this mechanism is also very low.

55 To judge if the observed fluorescence originates from upconversion, a conventional method is to measure the excitation intensity dependence of fluorescence. Basically, upconversion fluorescence originates from a multiple photon process and thus the intensity will exhibit an excitation intensity dependent
60 fluorescence $(I_{ex})^n$ for n photon dominant process. For a simple two-photon dominant fluorescence, the intensity can be described

as $I_{PL} \propto (I_{ex})^2$. Therefore, in double-logarithmic coordinate the slope should be close to 2. Instead, the slope should be approximately 1 for a normal fluorescence. We measured the
65 excitation intensity dependence of the fluorescence of CNDs (CND1), as shown in Figure 4 in a double-logarithmic scale. It is evident that the slope of the $\log(I_{PL}) - \log(I_{ex})$ curve is approximately 1 for both excitations of 400 and 800 nm; which clearly confirms the fluorescence at 800 nm excitation does not
70 originate from upconversion.

### Synthesis of CNDs from glacial acetic acid, ethylene glycol, banana and sweet potato

The acetic acid CNDs (CND1) were synthesized by P_2O_5-based room temperature dehydration of acetic acid.[18] Briefly speaking,
75 a mixture solution of 1 mL glacial acetic acid and 80 μL H_2O was quickly added to 2.5 g of P_2O_5 without additional heating. The carbon nanodots were collected by dispersing into 5 mL deionized water for further optical measurements.

The ethylene glycol CNDs (CND2) were prepared by a vigorous
80 stirring mixture of 5 mL of ethylene glycol with 7 mL of concentrated H_2SO_4 at 80 ℃.[20] A black solution was obtained after 3 mins. 15 mL of deionized water was quickly injected into the solution and kept stirring for another 30 mins. A dark CNDs solution was obtained by filtration.

85 The banana and sweet potato CNDs (CND3 and CND4) were synthesized from banana/sweet potato juice (ca. 80 g banana/sweet potato with 100 mL of water) by using a juice extractor.[20] Then 20 mL of the juice was taken with 20 mL of ethanol in a 60 mL glass bottle and heated at constant
90 temperature of 150 ℃ in an oven for 4 h. Dark brown products were obtained after cooling to room temperature. They were dissolved in 20 mL of water and the residues were separated by filtration.

Synthesis of GQDs

95 For synthesis of GQDs,[21] 5 mg graphene oxide was reoxidized in concentrated H_2SO_4 (30 mL) and HNO_3 (10 mL) for 5 h under ultrasonic conditions. The mixture was then diluted with deionized water (200 mL) and centrifuged (12,000 rpm for 10 min) 3 times to remove the acids. The reoxidized GO was
100 dissolved in deionized water (50 mL) and the pH was tuned to 12 with KOH. Then the suspension was transferred to a polytetrafluoroethylene Teflon-lined autoclave (100 mL) and heated at 180 ℃ for 10 h. When cooling to 25 ℃, the black suspension was filtered. The brown solution was further dialyzed
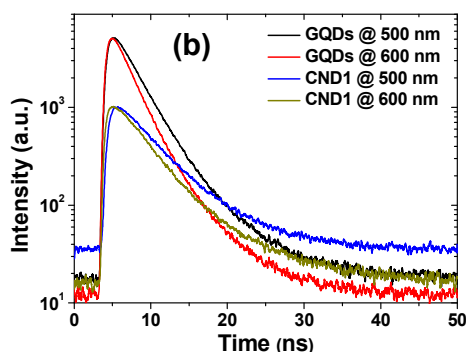105 (retained molecular weight: 8000–14,000 Da) overnight.
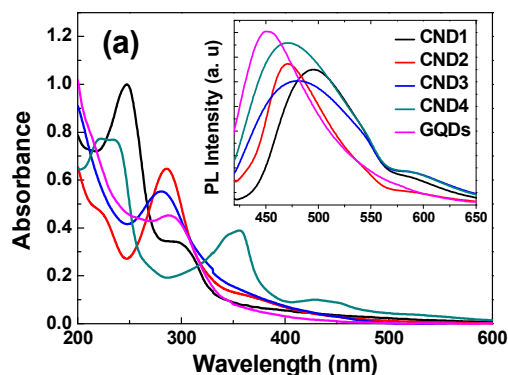
Figure 1. (a) Absorption and fluorescence (inset) spectra of CNDs and GQDs.(b) fluorescence decay curves of GQDs and CND1 at 500 and 600 nm measured by TCSPC, excited at 405nm.
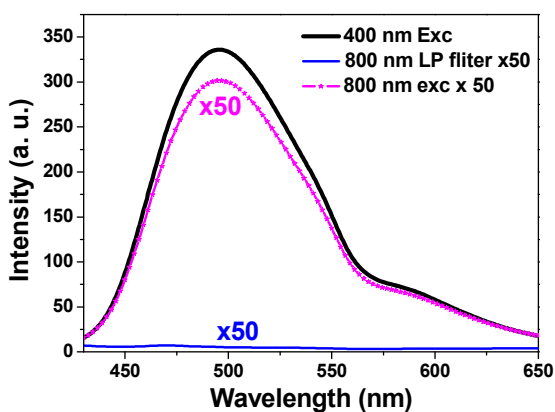

Figure 2. Fluorescence spectra of CNDs excitation at 400nm; and 800 nm with and without a long pass filter.
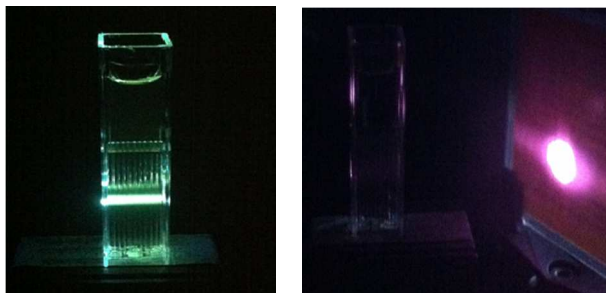

Figure 3. The photographs of the same CNDs solution excited with (a) 400 nm with 5 mW, (b) 800 nm with 100 mW (the bright spot on the left is laser on infrared detection paper).
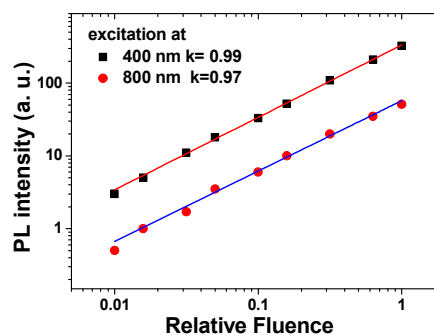

Figure 4. Excitation intensity dependence of fluorescence with excitation at 400 (black squares) and 800 nm (red circles) in a fluorescent spectrophotometer.

Conclusions

In summary, we demonstrate the five different synthesized CNDs and GQDs do not exhibit observable upconversion fluorescence. Due to the second order grating diffraction of a Xenon lamp at $\lambda/2$, a common problem is the normal fluorescence may be referred to as upconversion fluorescence. By simply insert a long pass filter in the excitation pathway the wrong excitation can be removed. Upconversion fluorescence should be identified by measuring the excitation intensity dependence of the fluorescence.

## Notes and references

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1.   M. Bernardi, J. Lohrman, P. V. Kumar, A. Kirkeminde, N. Ferralis, J. C. Grossman and S. Ren, *ACS nano*, 2012, **6**, 8896.
2.   M. P. Ramuz, M. Vosgueritchian, P. Wei, C. Wang, Y. Gao, Y. Wu, Y. Chen and Z. Bao, *ACS nano*, 2012, **6**, 10384.
3.   X. Wen, P. Yu, Y.-R. Toh, X. Hao and J. Tang, *Advanced Optical Materials*, 2013, **1**, 173.
4.   S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang and B. Yang, *Angewandte Chemie*, 2013, **125**, 4045.
5.   Q. Wang, X. Huang, Y. Long, X. Wang, H. Zhang, R. Zhu, L. Liang, P. Teng and H. Zheng, *Carbon*, 2013, **59**, 192.
6.   Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang and H. Wang, *Journal of the American Chemical Society*, 2006, **128**, 7756.
7.   L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca and D. Murray, *Journal of the American Chemical Society*, 2007, **129**, 11318.
8.   X. Jia, J. Li and E. Wang, *Nanoscale*, 2012, **4**, 5572.
9.   J. Shen, Y. Zhu, C. Chen, X. Yang and C. Li, *Chem. Commun.*, 2011, **47**, 2580.
10. S. Zhuo, M. Shao and S.-T. Lee, *ACS nano*, 2012, **6**, 1059.
11. M. Li, W. Wu, W. Ren, H.-M. Cheng, N. Tang, W. Zhong and Y. Du, *Appl. Phys. Lett.*, 2012, **101**, 103107.

12. C. Wang, X. Wu, X. Li, W. Wang, L. Wang, M. Gu and Q. Li, *J. Mater. Chem.*, 2012, **22**, 15522.

13. C. Zhu, J. Zhai and S. Dong, *Chem. Commun.*, 2012, **48**, 9367.

14. H. Li, Z. Kang, Y. Liu and S.-T. Lee, *J. Mater. Chem.*, 2012, **22**, 24230.

15. J. Jiang, Y. He, S. Li and H. Cui, *Chem. Commun.*, 2012, **48**, 9634.

16. Y. Fang, S. Guo, D. Li, C. Zhu, W. Ren, S. Dong and E. Wang, *Acs Nano*, 2012, **6**, 400.

17. X. M. Wen, P. Yu, Y. R. Toh, Y. C. Lee, A. C. Hsu and J. Tang, *Appl. Phys. Lett.*, 2012, **101**, 163107.

18. P. Yu, X. Wen, Y. R. Toh and J. Tang, *J. Phys. Chem. C*, 2012, **116**, 25552.

19. C. Liu, Y. Liu and Z.-y. Zhang, *J. Mater. Chem. C*, 2013, **1**, 4902.

20. B. De and N. Karak, *RSC Adv.*, 2013, **3**, 8286.

21. F. Wang, Z. Gu, W. Lei, W. Wang, X. Xia and Q. Hao, *Sensors and Actuators B: Chemical*, 2014, **190**, 516.

22. L. Li, G. Wu, G. Yang, J. Peng, J. Zhao and J.-J. Zhu, *Nanoscale*, 2013, **5**, 4015.

23. D. Matsuura, *Appl. Phys. Lett.*, 2002, **81**, 4526.

24. M. Pollnau, D. Gamelin, S. Lüthi, H. Güdel and M. Hehlen, *Phys. Rev. B*, 2000, **61**, 3337.

25. Y. Deng, D. Zhao, X. Chen, F. Wang, H. Song and D. Shen, *Chem. Commun.*, 2013, **49**, 5751.

26. H. Tetsuka, R. Asahi, A. Nagoya, K. Okamoto, I. Tajima, R. Ohta and A. Okamoto, *Adv. Mater.*, 2012, **24**, 5333.

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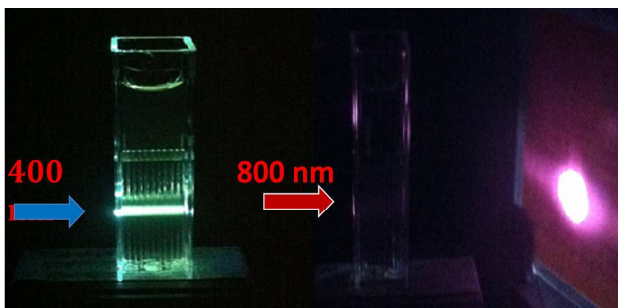
So-called upconversion fluorescence in CNDs and GQDs is confirmed originating from a measurement mistake; therefore cross-check is very necessary.