

Comment on “Upconversion and Downconversion Fluorescent Graphene Quantum Dots: Ultrasonic Preparation and Photocatalysis”

■ In a recent paper, Zhuo *et al.*¹ reported a facile method for preparation of graphene quantum dots (GQDs) with efficient “upconversion” and “downconversion” luminescence properties. They also demonstrated high photocatalytic performance of the complex of rutile (or anatase) TiO₂ and GQDs under visible light (>420 nm) irradiation and proposed that the enhancement of photocatalytic activity of the complex could be attributed to the upconversion luminescence behavior of the GQDs and the enhanced photoinduced electron and hole separation. However, their results and discussions are quite questionable.

In their experiments for measurement of upconversion luminescence, monochromatic light from a xenon lamp passing through gratings was used as an excitation source. It is a well-known fact that, for low intensity light excitations, the efficiency of upconversion luminescence caused by excited state absorption, energy transfer, *etc.* is very small. In particular, the probability of multiphoton excited luminescence is extremely low. Therefore, a high flux of excitation photons is typically required, and usually a laser with high light intensity is used as the excitation source.^{2–4} Multiphoton excited upconversion luminescence is rarely detected directly by the normal spectrofluorimeter using an incoherent monochromatic light from a xenon lamp as an excitation source. To the best of our knowledge, there have been very rare related reports besides the papers published by the authors' group up to now.

We consider that the upconversion luminescence reported in ref 1 may not be real upconversion luminescence but normal luminescence due to the excitation by second-order diffraction light of wavelength $\lambda/2$, which coexists in the selected light (first-order) of wavelength λ from the monochromators of the spectrofluorimeter.^{5,6} To confirm our speculation, we prepared carbon quantum dots by laser ablation in ethanol and observed strong visible luminescence excited at 400 nm from the monochromator of a Fluoromax-3 spectrofluorimeter. Similarly, we detected upconversion luminescence when we selected 800 nm monochromatic light from the monochromators as the excitation light. As shown in Figure 1, the upconversion luminescence intensity excited at 800 nm is about 1/100 of the normal luminescence intensity excited at 400 nm, which is very similar to the results reported in ref 1 for upconversion and downconversion luminescence. However, if we put a 420 nm cutoff filter in the excitation channel (between the excitation source and the sample in order to eliminate the light at 400 nm (800/2) from light source), no upconversion luminescence could be detected, as shown in Figure 1. Second-order diffraction light ($\lambda/2$) is always present in the selected excitation light (λ) due to limitation of diffraction gratings used in the monochromators

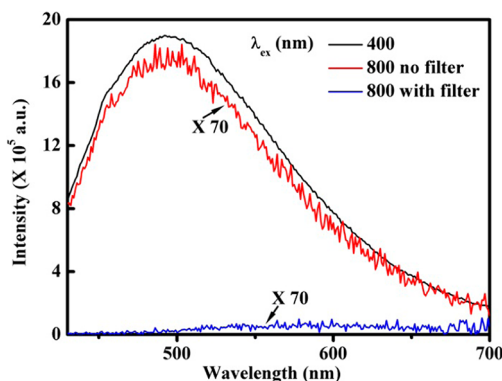


Figure 1. Emission spectra excited at 400 nm (black), 800 nm without (red) and with (blue) a 420 nm cutoff filter in the excitation channel.

of the spectrofluorimeter.^{5,6} Therefore, the so-called upconversion luminescence in ref 1 may not be real upconversion luminescence but normal luminescence excited by the second-order diffraction light of wavelength $\lambda/2$. In Figure 4 of ref 1, all of the detecting range in the emission spectra did not contain the half wavelength of the selected excitation light. Especially, the detecting range was changed to avoid detecting the half wavelength of the selected excitation light when excited at 660 and 700 nm, implying that there was second-order diffraction light of wavelength $\lambda/2$ in the selected excitation light, which is the real excitation light for the upconversion luminescence.

In fact, the discussions about the high photocatalytic performance of the rutile (or anatase) TiO₂/GQD complex under visible light irradiation are also questionable. When we carefully compare Figures 7 and 5S of ref 1, no apparent difference can be observed on the photocatalytic rate under the conditions with or without the 420 nm cutoff filter, especially for the rutile/TiO₂ complex. This result just indicates that light with wavelength longer than 420 nm plays an important role, but it does not mean that upconversion luminescence behavior is dominant for the high photocatalysis. There have been many reports on high photocatalysis of carbon-doped TiO₂ or TiO₂/graphene complex under visible light irradiation. The possible reasons for the enhanced photocatalytic performance of these complexes can be the red shift of the absorption edge, enhanced absorptivity in the visible range, *etc.*^{7–10}

In addition, downconversion usually means that one high-energy photon is “cut” to obtain two or more lower energy photons. Therefore, the downconversion luminescence reported in the ref 1 is only normal photoluminescence (one to one), not real downconversion luminescence. Though the preparation of rutile (or anatase) TiO₂ and GQD complex is interesting and normal photoluminescence is true, the upconversion photoluminescence may be an artificial technical error and the discussion about catalysis of the complex is not exact. Considering a lot of related literature about upconversion luminescence behavior of carbon and graphene quantum dots published recently in many prestigious journals by

the authors' group, we think it is necessary to recheck the luminescence properties of the related materials urgently.

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