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Surface Plasmon of Carbon Nanodots

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Luminescent ZnO quantum dots (QDs) have been prepared, and the fluorescence intensity of the QDs can be increased greatly with the introduction of carbon nanodots, meanwhile the fluorescence lifetime of the QDs decreases significantly. The fluorescence enhancement and lifetime decrement can be attributed to the surface plasmon effect of the carbon nanodots, and the calculated surface plasmon resonance frequency of the nanodots matches well with the fluorescence spectrum of the ZnO QDs.

Introduction

Surface plasmon has attracted much attention in recent years for its versatile potential applications in many interesting fields including but not limited to improving the resolution of microscopes,[1-5] enhancing the sensitivity of chemical and biological sensors,[6-11] increasing the quantum efficiency of light-emitting devices,[12-14] and killing cancerous tissues.[15-17] Classically, metal nanoparticles are utilized as the arena for surface plasmonic resonance,[18-22] but metal nanoparticles based surface plasmon usually has relatively large optical loss, which impairs the applications of such kind of surface plasmon greatly.[19,23,24] It has been reported that highly doped semiconductors can also serve as the arena for surface plasmon, but such surface plasmons can usually only cover the infrared region.[25-28] Nowadays, graphene has been demonstrated the ability to provide surface plasmons in various spectrum regions ranging from ultraviolet to infrared,[29-31] and the resonance peaks can be tuned by doping or regulating the sizes of graphene nanostructures.[32-35] As an emerging carbon based nanostructures, carbon nanodots have been a research focus in recent years for their high luminescent efficiency, tunable emission, and good bio-compatibility, etc.[36-39] Because of the above characters, carbon nanodots have great potential applications in light-emitting devices, bio-imaging and labeling, etc.[39-43] As carbon nanodots are complex carbon nanomaterial with a mix of amorphous carbon and graphite carbon,[44,45] the graphite part is supposed to support carbon nanodots working for surface plasmonic resonance. However, none such report can be found up to date.

In this work, we found that the fluorescence of ZnO quantum dots (QDs) solution can be enhanced greatly by introducing carbon nanodots, meanwhile the lifetime of the fluorescence is decreased significantly, and the above phenomenon can be attributed to the surface plasmon effect of the nanodots. Considering that none report on carbon nanodot surface plasmon can be found before, the results reported in this paper may open another potential application area for carbon nanodots.

Experimental

Materials and synthesis

The ZnO QDs in this study were synthesized via a sol-gel method.[46] Firstly, an Erlenmeyer flask loaded 0.3 g lithium hydroxide monohydrate and 40 ml ethyl alcohol was set in ultrasonic treatment for 15 minutes. Then a three-neck flask loaded 1.1 g zinc acetate dihydrate and a magnet rotor was installed with oil-bath and condenser pipe of which the straight part connecting with flask was sealed with nitrogen and the recycle part connecting with conduit was filled with water flow. After that the solution obtained in the first step was added into the three-neck flask and then the oil temperature was kept at 35°C and the magnet rotor was kept rotary. The zinc acetate dihydrate was totally dissolved for around 20 minutes. At last, the transparent and colourless solution was put into an Erlenmeyer flask and ultrasonic treated in ice water for half an hour. In this way, ZnO QDs in ethanol solution has been prepared. The carbon nanodots were synthesized by octadecylene, 1-hexadecylamine and anhydrous citric acid in a heating flask under argon flow. Jelly-like carbon nanodots were obtained after purified 5 times with acetone, and finally dissolved into toluene.[36,47]

Characterization and measurements

The morphology of the ZnO QDs was characterized using a Philips TF-F20 transmission electron microscope (TEM) operating at 200 kV and a Di3100 atomic force microscope (AFM). The Raman spectrum of the carbon nanodots were characterized in a JY630 micro-Raman spectrometer. The fluorescence spectra of the carbon nanodots and ZnO QDs were measured in a Shimadzu F4500 spectrometer with a Xe lamp as the excitation source. The transient spectrum of the ZnO QDs and carbon nanodots were measured in an Edinburgh

Instruments LTDZ FL920 time-corrected single photon counting system.

Results and discussion

The morphology and fluorescent characteristics of the ZnO QDs are displayed in Fig. 1. It can be seen that spherical shaped QDs have been obtained, and the size of the QDs is around 5 nm, as indicated in Fig. 1(a). The high-resolution TEM image of the ZnO QDs shown in Fig. 1(b) reveals clear lattice fringes, and the selected area electron diffraction pattern displayed in Fig. 1(c) indicates the high crystalline quality of the QDs. Fig. 1(d) exhibits the fluorescence spectrum of the ZnO QDs solution excited by a Xeon lamp. One can see two emission bands at around 370 nm and 530 nm, and the former can be attributed to the near band-edge emission of ZnO, while the latter from the deep-level related emissions of ZnO.[48]
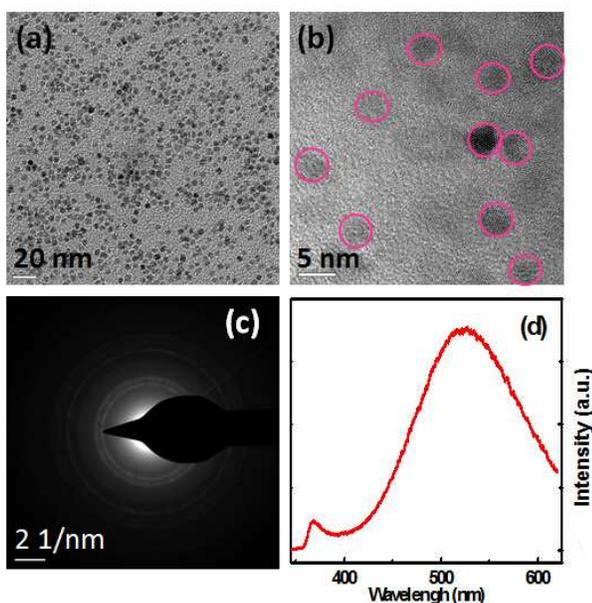
Figure 1. (a) Low-magnification TEM image and High resolution TEM image (b) of the ZnO QDs; (c) Selected area electron diffraction pattern of the ZnO QDs; (d) Fluorescence spectrum of the ZnO QDs.

Interestingly, the introduction of carbon nanodots into the ZnO QDs solution increases the luminescence intensity of the QDs greatly, as shown in Fig. 2. One can see from the figure that under the excitation of 320 nm line of a Xeon lamp, when 1/5000 mole ratio of carbon nanodots were added into the ZnO QD solution, the emission of the QDs can be increased significantly while the emission shape remains. With further increase the mole ratio of the carbon nanodots, the emission of the ZnO QDs was increased further. The inset of Fig. 2 shows the dependence of the enhancement ratio on the ZnO/carbon ratio, it is evidenced that with the carbon mole ratio increases from 1/5000 to 1/250, the emission enhancement ratio of has been increased from 1.6 to 3.9. The above data reveals the

carbon can enhance the emission intensity of the ZnO QDs greatly. To explore the enhancement mechanism caused by the introduction of carbon nanodots, the properties of carbon nanodots were studied, as indicated below.
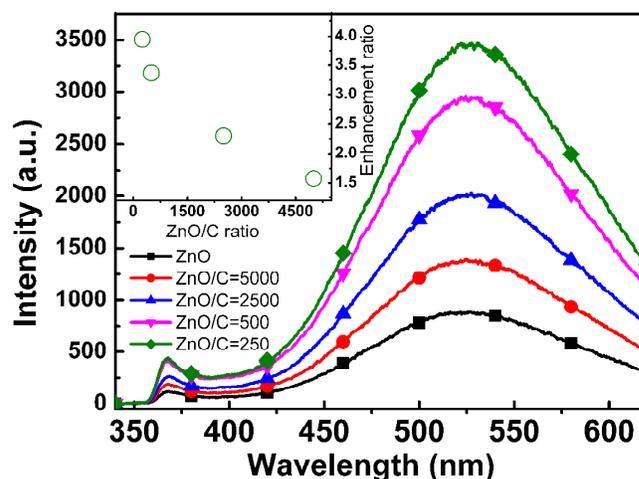
Figure 2. Fluorescence spectra of the mixed solutions of ZnO QDs and carbon nanodots with different mole ratios under the excitation of 320 nm line of a Xeon lamp, and the inset shows the dependence of the emission enhancement ratio on the ZnO/carbon ratio.

The morphology of the carbon nanodots are pictured in Fig. 3. As shown in Fig. 3(a), the size of the carbon nanodots are from 8 nm to 15 nm, and the high-resolution TEM image of the carbon nanodots indicated in Fig. 3(b) shows one typical nanodot, and round shaped nanodot with the diameter of around 8 nm can be seen in the figure. In order to exhibit the 3D morphology of the carbon nanodots, the AFM image of the nanodots are illustrated in Fig. 4. The diameter of the investigated carbon nanodots is in the order of ten of nanometres, which is consistent with the TEM image shown in
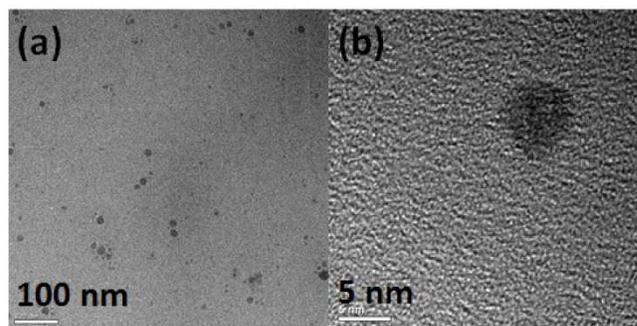
Figure 3. Low-magnification TEM image (a) and High resolution TEM images (b) of the carbon nanodots.

Fig. 3(a). It is noteworthy that the height of the nanodots is from 0.35 nm to 2 nm, which corresponds to several atomic layers, indicating that the carbon nanodots are shaped in round

disks with diameter of 8- 15 nm and height of several atomic layers. Actually, this kind of carbon atomic layers is graphite structure, which can be confirmed by Raman spectrum shown in Fig. 5, where D band at around 1360 cm^{-1} is an indication of amorphous carbon, while G band at around 1580 cm^{-1} is the indication of graphite structured carbon.[44,45]
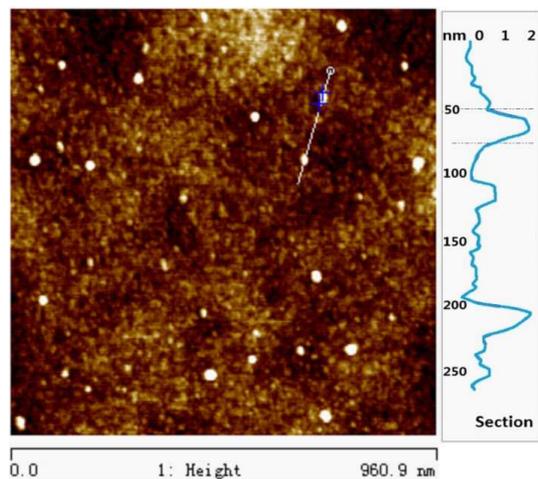
Figure 4. AFM image of the carbon nanodots; the height profile of some nanodots has also been displayed. .

One of the unique characters of carbon nanodots lies in their excitation dependent fluorescent properties. To test the above characteristics of the carbon nanodots in our case, the fluorescence spectra of the carbon nanodot solution under the excitation of a series of wavelengths of a Xeon lamp have been recorded, as indicated in Fig. 6. To distinguish the emission location of the carbon nanodots clearly, in this figure the intensity of each curve has been normalized into unity. It can be seen that the emission of the carbon nanodots is located at around 440 nm under the excitation of the 320 nm line, while it shifts gradually to around 550 nm when the excitation wavelength is increased to 440 nm. The above data confirm the formation of luminescent carbon nanodots.
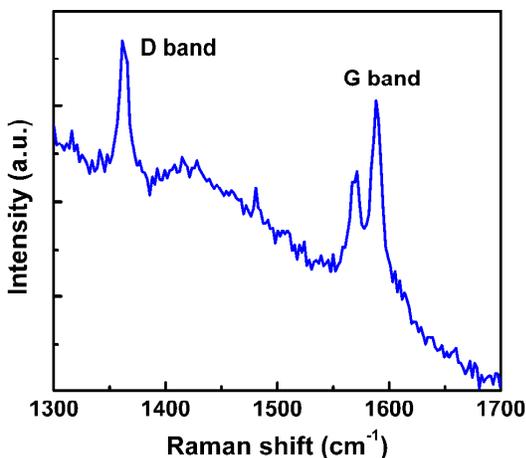
Figure 5. Raman spectrum of the carbon nanodots.

To uncover the interaction between the ZnO QDs and carbon nanodots, the transient fluorescence spectra of the mixed solution have been measured, as illustrated in Fig. 7. Note that the two transient fluorescence spectra shown in Figs. 7(a) and 7(b) were both measured by monitoring the emission peaks of carbon nanodots (456 nm) and ZnO QDs (530nm) under the excitation of 365 nm line of a Xeon lamp. Fig. 7(a) presents the decay curves of the emission at 456 nm for the carbon nanodots and ZnO QDs/carbon nanodots mixed solution. To derive the decay time, the experimental data were fitted using the following single-exponential decay formula:

$$y = y_0 + y_1 \exp(-t / \tau_1)$$
(1)

Where y is the fluorescence intensity, y_0 and y_1 are constants, t means time. The fitting results are labelled in Fig. 7(a), note that the fluorescence intensity has been normalized into unity for the two curves. One can see that the decay time for the carbon nanodot solution is 6.8 ns, while that of the mixed solution is 6.2 ns, that is, the fluorescence lifetime of the carbon nanodots has not been altered much with the introduction of ZnO QDs.
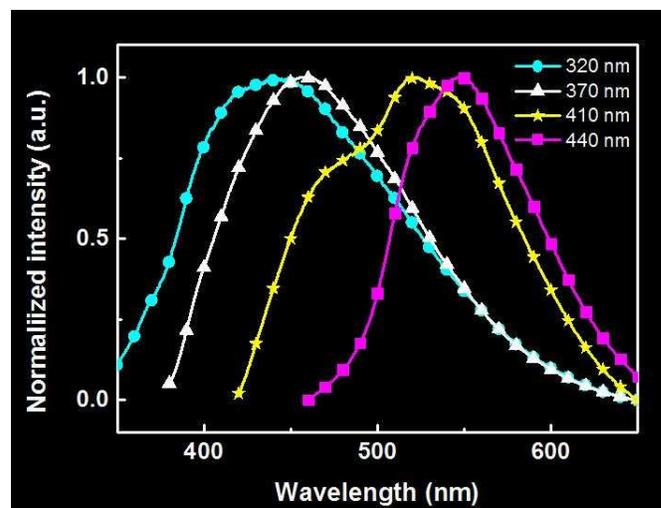
Figure 6. Excitation dependent normalized fluorescence spectra of the carbon nanodots.

Fig. 7(b) shows the transient fluorescence curves of the ZnO QDs and ZnO QD/carbon nanodot mixed solution, and all the experimental data can be well fitted using a bi-exponential decay expression, the fitting results of which are listed in Table 1. Here τ_1 may come from the deep-level recombination inside the ZnO QDs, while τ_2 from the surface defects. It is noteworthy that the decay times of the ZnO QDs are 34.3 ns and 605.4 ns, respectively, while for the mixed solution with ZnO QDs/carbon nanodots mole ratio of 125, the decay times are 6.6 ns and 28.9 ns. Note that for different ZnO/carbon ratios, the decay times are similar, confirming the credibility of the data, as listed in Table. I. One can see from the above results

that the decay times have been decreased significantly with the introduction of carbon nanodots into the ZnO QD solution, indicating that the carbon nanodots not only enhance the fluorescence intensity of the ZnO QDs, but also decreases the fluorescence lifetime of the QDs greatly.
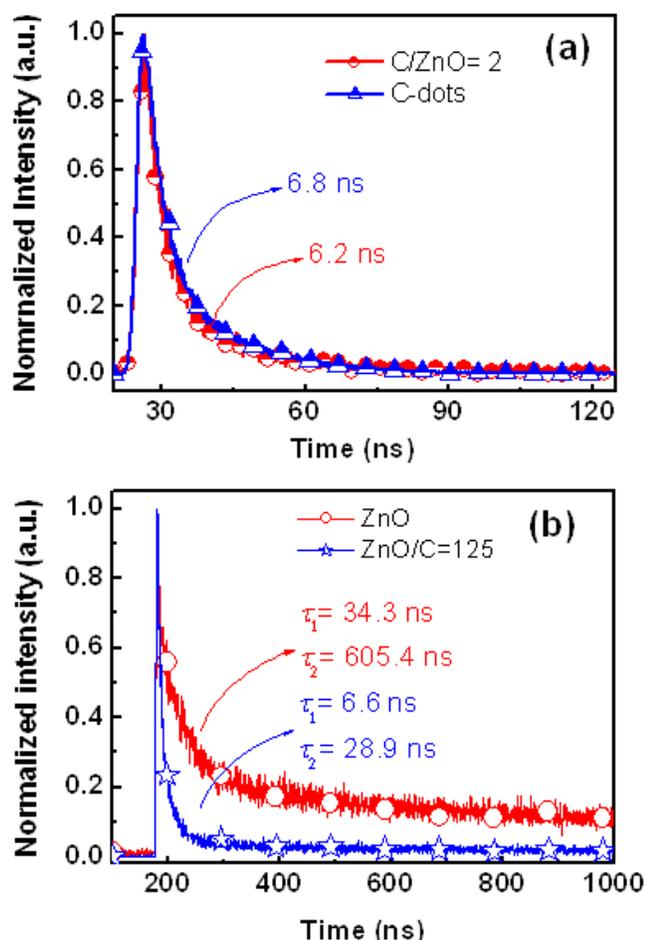
Figure 7. (a) Transient fluorescence spectra of the emission at 456 nm from carbon nanodots and ZnO QDs/carbon nanodots mixed solution; (b) Transient fluorescence spectra of the emission at 530 nm from ZnO QDs and ZnO QDs/carbon nanodot mixed solution with the ratio of 125.

The above results indicate that there exists an interaction between ZnO QDs and carbon nanodots that leads to the fluorescence intensity enhancement and lifetime decrement of the ZnO QDs. There are three possible mechanisms underlying the phenomenon: Photon excitation, fluorescence resonance energy transfer (FRET), and surface plasmonic resonance. Firstly, according to Fig. 2, both of the two emission bands of ZnO QDs (at around 370 nm and 530 nm) have been enhanced, but the photon emitted from carbon nanodots (440 nm) cannot excite the emission at 370 nm of ZnO for its smaller energy. Thus the fluorescence enhancement at 530 nm cannot come from the excitation of ZnO QDs by the emission from carbon nanodots. Secondly, according to the FRET theory, the donor of the transfer definitely suffers a decline of lifetime while the

acceptor has an increase of lifetime.[49] However, the lifetime of the carbon nanodots donor do not suffer any obvious decrease, and that of the ZnO QDs acceptor decreases greatly, as shown in Fig. 7, contrary to the FRET theory, thus the enhancement caused by FRET can be ruled out. As for the surface plasmon resonance, it has been widely reported to have the ability to improve the fluorescence by decreasing the non-radiative recombination possibility of carriers,[50,51] and since the lifetime of surface plasmons is much smaller than that of electrons and holes,[19] there is always a decline of fluorescence lifetime along with the fluorescence enhancement, which accords well with the phenomena observed in our case, thus the florescence enhancement of the ZnO QDs with the introduction of carbon nanodots may be due to the surface plasmon effect of the carbon nanodots.

Table I. Decay time of the ZnO QDs mixed with carbon nanodots with different mole ratios.

Sample	τ_1 (ns)	τ_2 (ns)
ZnO	34.3	605.4
ZnO/C=5000	6.4	50.1
ZnO/C=2500	7.2	42.8
ZnO/C=500	6.1	31.5
ZnO/C=250	6.2	29.8
ZnO/C=125	6.6	28.9

Actually, it has been demonstrated that both graphene nanodisks and carbon nanotubes can offer a platform for surface plasmonic resonance, and the resonance frequency can be tuned by the adjusting the diameters of the nanodisks.[32-35,52-54] The surface plasmon frequency of graphite structure can be expressed by the following formula:[57-60]

$$\omega(q) = \left[\frac{n_e e^2}{\varepsilon_0 (1+\varepsilon_m) m^*} q + \frac{3}{4} v_F^2 q^2 \right]^{1/2} \qquad (2)$$

Where ω is the plasmon frequency, n_e is electrons density, ε_0 is the permittivity in vacuum, ε_m is the background dielectric constant, m^* is the effective mass of the graphite electrons, and v_F is the Fermi velocity. In our case, the background dielectric constant is 24.5 for the ethanol solvent, and q equals to $2\pi/d$, where d is the diameter of the carbon nanodots. The calculated results reveal that the surface plasmon resonance frequency is located at 357 nm when the diameter of the nanodots is 8 nm, while the frequency is 621 nm when the diameter is 15 nm. That is, the plasmon frequency of the carbon nanodots in our case can cover the range from 357 nm to 621 nm, which overlaps well with the fluorescence spectrum of the ZnO QDs. Note that it has been frequently reported that the plasmon resonance frequency of carbon nanostructures can cover a large

spectrum range by either tuning the size, doping concentration, or bias applied onto the structures.[32-35] The calculated wide plasmon frequency of the carbon nanodots confirms the rationality that the fluorescence of the ZnO QDs can be enhanced by the surface plasmon of the carbon nanodots in our case.

Conclusions

In summary, the introduction of carbon nanodots leads to a remarkable fluorescence enhancement of ZnO QDs along with a significant decrement of the fluorescence lifetime; this enhancement can be attributed to the surface plasmon resonance of carbon nanodot. The calculation confirms that enhancement at different wavelengths depends on the size of the carbon nanodots involved. Considering that none report on the surface plasmon of carbon nanodots can be found before, the results in this paper may find another promising area for carbon nanodots, and trigger much attention in the field of both surface plasmon and carbon nanodots.

Acknowledgements

Notes and references
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