



Influence of the photoluminescence property of carbon nanodots on the reduction of silver ions

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ARTICLE INFO

Keywords:

Photoluminescence property
Carbon nanodots
Ag NPs
Reduction kinetics
Photoreduction property

ABSTRACT

Carbon nanodots have been demonstrated to be an effective reducing agent in fabricating silver nanoparticles. In this study, the dependence of reduction efficiency of the CDs on the irradiation wavelength and their photoluminescence property is investigated. We find that the CDs excited by short wavelength light shows much higher photoreducibility than those excited by longer wavelength irradiation, although their PL intensity might be about the same. By analyzing the PL and the time-resolved PL property of the formed CDs-Ag NPs composites we find that, when the CDs are excited, there are two kinds of recombination path ways of the carriers contributing to their photoluminescence: the direct excitation of surface states, and the excited electrons from carbonic-core transferred to the surface states; only the electrons originates from the intrinsic carbonic-core excited by short wavelength can reduce the Ag ions, while those originates from the direct excitation of the surface states by long wavelength light are ineffective. The proposed reduction kinetics of Ag ions is significant to understand the photoreduction property of the CDs.

1. Introduction

Since they were firstly discovered in 2004, carbon nanodots (CDs) have attracted considerable attentions due to their great advantages of good biocompatibility, strong photoluminescence (PL) and unique electron transfer behaviors [1–4]. These unique properties make CDs potential application in drug transfer, biological labeling, biosensing and optoelectronic devices [5–8]. Generally, the CD is constituted of a carbonic core with a sub-10 nm size and functional groups on the surface of carbon core [9]. The strong PL of the CDs could be originated from surface functional groups or surface states, due to their strong capturing ability of the excited electron and holes. It has been reported that the photoluminescence of the CDs could be easily quenched by electron donors or electron acceptors molecules in solution, which means that photoexcited CDs can be used as excellent electron acceptors or electron donors. Due to the generous functional groups on the surface of the CDs, photoexcited CDs could exhibit both excellent reducibility and oxidation properties [10].

Noble metal nanoparticles have drawn considerable interest in various fields owing to their unique and considerably changed physical, chemical and biological properties [11–14]. Among the noble metal

nanoparticles, silver nanoparticles (Ag NPs) have been used in some areas such as optoelectronics, biological labeling, photography and catalysis [15–17]. Up to now, many kinds of methods have been reported for the synthesis of Ag-NPs such as chemical reduction, gamma irradiation, ultra-sound processing, microwave processing, ion irradiation and plasma processing [18–23]. Based on the unique photochemical properties of CDs, Hyosung Choi et al. proposed to synthesize Ag NPs with CDs excited by ultraviolet (UV) lamp as the reductant. The prepared carbon-dot-supported silver nanoparticles have been successfully used in polymer optoelectronic devices [24]. In our previous reports, we also fabricated CDs-Ag NPs nanocomposites with the similar strategy and studied the optical nonlinearity of the products [25]. It is generally acknowledged that, the reducibility of the photoexcited CDs is bound up with their PL intensity. However, the relation between the reduction efficiency of the CDs and the irradiation wavelength as well as their photoluminescence (PL) property, especially the photoexcited carrier dynamics in the photoreduction process, is still indistinct and need further investigations.

In this work, Ag NPs were successfully prepared using CDs excited by UV light irradiation as the reductant. The influence of the wavelength of the exciting light on Ag NPs formation by Fluorescence and UV-Vis

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spectroscopy. By analyzing the PL and the time-resolved PL (TRPL) property of the formed CDs and Ag NPs composites, the reduction kinetics of silver ions using photoexcited CDs, as well as the relations between the reducibility of the CDs and their PL behavior were clarified. We found that only the electrons from the excited states of the carbonic-core irradiated by short wavelength light was able to reduce the Ag ions, while those originated from the direct excitation of the surface states excited by long wavelength light was ineffective.

2. Experimental

2.1. Chemicals

Graphite powder and N-Methyl pyrrolidone (NMP) were purchased from Aladdin Chemistry Co., Ltd (China) and Sinopharm Chemical Reagent Co., Ltd (China), respectively.

2.2. Synthesis of CDs

Firstly, femtosecond laser pulse ablation in liquid method was used to prepare the CDs. 0.1 mg graphite powder was dispersed in 50 ml NMP and then processed with ultrasonic treatment for 10 min. The uniform suspension was put into a glass beaker and irradiated using femtosecond pulses from a Ti: sapphire laser for 1 h. The repetition rate of femtosecond laser is 1 kHz, the pulse width is about 100 fs and the central wavelength is about 800 nm. The laser was focused by a 100 mm lens and the focus was located at 5 mm below the liquid surface. In the ablation process, the solution was stirred by a magnetic stirrer to avoid the precipitation of graphite powder. After irradiation, the solution was centrifuged in a centrifuge at 10,000 rpm for 20 min. Finally, large graphite particles were removed and supernatant containing CDs were collected.

2.3. Synthesis of CDs-Ag NPs using photoexcited CDs

Ag NPs supported on CDs were prepared using the CDs as the reductant under UV light irradiation. The mixture of silver nitrate with a concentration of 0.1 mM and 10 ml CDs liquid was poured into a glass beaker and irradiated by UV lamp with different wavelength for 15 min. During irradiation, the color of the mixed solutions changed from yellow to dark brown, indicating that the Ag ions in the solution have been reduced to Ag NPs.

3. Results and discussion

Firstly, we investigated the optical and luminescent properties of the as-prepared CDs using UV-Vis and PL spectroscopies. From Fig. 1(a) we can see that there are two optical absorption peaks. The obvious absorption peak at 283 nm is due to the intrinsic absorption of the carbon core, while the small absorption peaks located at 375 nm with a tail extending to about 420 nm correspond to the abundant surface functional groups of CDs [26]. TEM image of the CDs (Fig. 1(b)) shows that the CDs distribute on the copper grid homogeneously and the mean size of CDs is about 2.30 nm (Fig. S1). The inset of Fig. 1(b) shows the HRTEM picture of CDs. From the figure, we can see that the lattice spacing of CDs is measured to be 0.21 nm, which corresponds to graphite carbon [27]. Besides, the FTIR spectra of the CDs (Fig. 1(c)) confirm that CDs contain C=O bonds, C=C bonds, N-H bonds and C-H bonds, which means that a large number of functional groups are connected onto the surface of CDs. Since the strong PL of the CDs is originated mainly from surface functional groups, the as-prepared CDs can show strong and adjustable fluorescence [25–29]. As shown in Fig. 1(d), excitation-dependent intense fluorescence emissions spectra are observed when the excitation wavelength changes from 340 to 440 nm. The optimal excitation wavelength is 380 nm and the corresponding optimal emission wavelength is about 450 nm.

During the photoreduction process of Ag ions, LEDs with different wavelengths (365 nm, 395 nm, 425 nm, and 450 nm) are used to excite

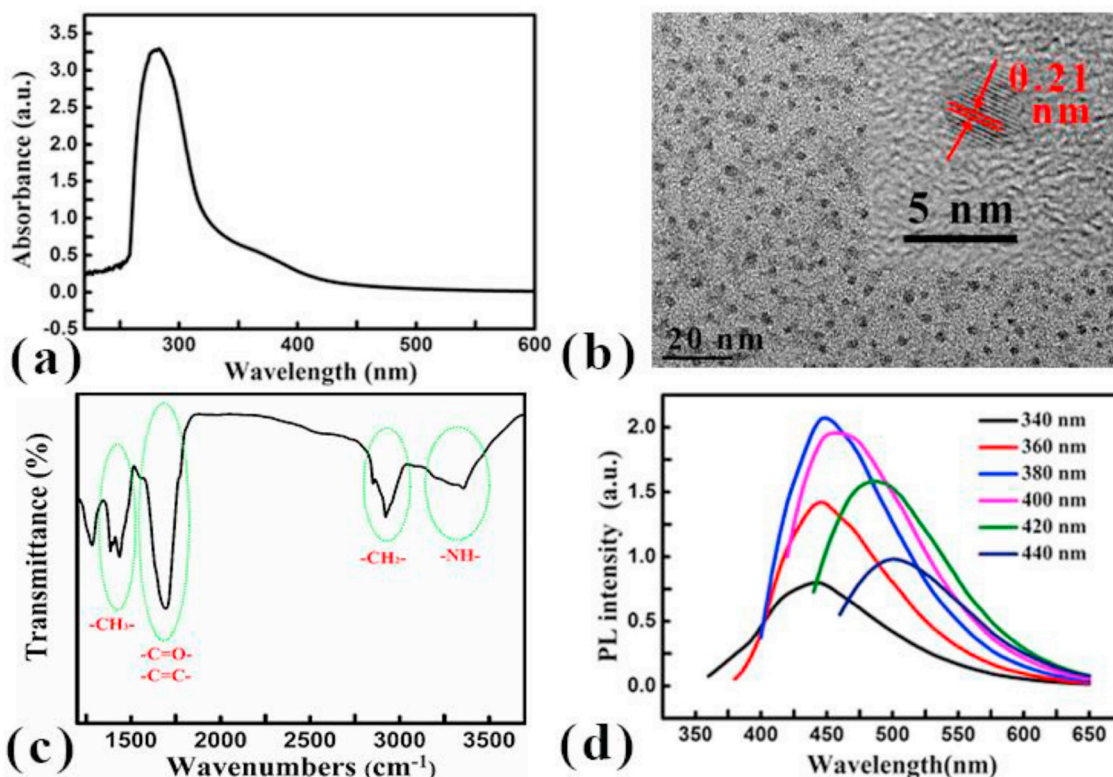


Fig. 1. (a) UV-Vis spectra of CDs, (b) TEM images of the as prepared CDs, (c) FT-IR spectra of CDs, (d) Fluorescence spectra of CDs.

the CDs. In order to confirm the existence of Ag NPs, we measured the absorption spectra of the mixed solutions after irradiation with different wavelength. As shown by the UV-Vis spectra in Fig. 2 (a), when the mixed solutions were irradiated at short wavelength, such as 365 and 395 nm, there is an obvious absorption peak near 420 nm caused by surface plasmon resonance (SPR) of Ag NPs. While under long wavelength irradiation, such as 425 and 450 nm, the characteristic absorption peaks of Ag NPs can hardly be observed. In addition, Ag ions solution was irradiated using different wavelength light without the presence of CDs, and the results indicated that UV light irradiation alone had no effect on the reduction of Ag ions. TEM image of the as-prepared Ag-CDs (Fig. 2(b)) shows that the Ag-CDs distribute on the copper grid homogeneously, and the mean size is about 3.84 nm (Fig. S2). The inset of Fig. 2(b) is the HRTEM picture of Ag-CDs. From the HRTEM image we can see that there are two different lattice spacing stripes, the lattice spacing distance of 0.21 nm is in close match with the (100) lattice spacing of graphite carbon and that of 0.235 nm is correspond to (111) plane of Ag [30]. Besides, EDS analysis also proved that the prepared nanoparticles contained silver element (Fig. S3). These results indicate that CDs excited by UV light can act as effective reductant to synthesis the Ag NPs.

However, the reducibility difference of the CDs under various excitation wavelengths is out of our expectation. According to the PL behavior of the CDs given in Fig. 1 (b), light at 365 nm and 425 nm could excite the fluorescence of CDs with the similar intensity, but the former is effective to reduce the Ag ions while the latter is ineffective. Hence, we speculate that the reducibility of the photoexcited CDs has no direct correlation with their PL intensity. In our previous reports, we have demonstrated that, fluorescence of CDs prepared using laser ablation methods are mainly originated from functional groups on the surface [31]. As shown by Fig. 3(a), when CDs are irradiated by excitation light, both carbon core and surface functional groups could be excited. When the carbon core is excited, the excited electrons generated will relax to the surface functional groups, and then to the ground state through radiative recombination, which is correspond to Process (I) in the figure. When the surface states are excited, the generated electrons will directly relax to the ground state through fluorescence emission, which is correspond to Process (II). Since both carbon core and surface functional groups can be excited at short wavelength excitation, and only surface functional groups can be excited at long wavelength excitation, we speculate that only the excited electrons from the carbonic core are effective in the reduction of the silver ions, although both the excitation of the carbonic core and the surface states could attribute to the fluorescence of the CDs.

As has been proposed by Yuri Choi et al., when silver ions are added into the CDs solution, they could be adsorbed on the surface of the CDs by electrostatic force generated by generous surface functional groups [32]. M. Liu et al. have examined the change of the surface functional

groups using FTIR spectroscopy, and found that some groups, especially oxygenated functional groups decreased significantly after the formation of Ag NPs, demonstrating their importance on the reduction of silver ions [30]. As shown by Fig. 3(b), when the Ag ions are adsorbed on the CDs, free electrons generated by photoexcited carbon core can be transferred to the silver ions on their surface to reduce them to Ag atoms. Then the large number of Ag atoms will condense into nucleation and eventually form Ag NPs.

To confirm our speculations, we examined the PL difference of the CDs and the CDs-Ag NPs composites under different wavelength excitations (as shown in Fig. 4). For more intuitive presentation, we also take the picture of the fluorescence emissions of the photoexcited CDs with and without Ag NPs under ultraviolet lamp with different wavelength. As shown by Fig. 4, the PL of CDs is obviously quenched with the formation of Ag NPs when excited by 360 nm and 400 nm light. When excited by longer wavelength light, however, the quenching effect of Ag NPs becomes weaker. From the recorded fluorescence emissions pictures we can also see that, the emission of the CDs-Ag NPs composites changes from blue to yellow under 365 nm and 395 nm excitation, but changes little under 425 and 450 nm excitations. It's easy to understand the quenching effect of the Ag NPs on the photoluminescence of the photoexcited CDs. Due to the existence of Ag NPs on their surface, the electrons generated from photoexcited CDs would preferentially transfer to Ag NPs, which would lead to the decreases of radiation recombination of electron-hole pairs. However, more discussions are needed to explain the invalidation of the quenching effect of the Ag NPs on the PL excited by long wavelength light.

According to the fluorescence mechanism described in Fig. 3, the fluorescence decay of CDs consists of two processes: (I) excitation of the carbonic-core and carrier relaxation to the surface states followed with a radiative recombination; and (II) direct excitation-recombination of carriers from the surface states (as illustrated by the left inset of Fig. 5 (a)). When the CDs-Ag NPs composites are excited under short wavelength light, both surface states and the carbonic-core might be excited by short wavelength light. Because the excited electrons from the carbonic core tend to transfer to the Ag NPs, the contribution of the process (II) to the PL of the CDs is diminished, causing the quenching of the PL of CDs (as illustrated by the right inset of Fig. 5(a)). While under the long wavelength excitation only the surface states are able to be excited. As shown by Fig. 4(d), Ag NPs has little influence on the PL excited by 440 nm light. Hence, we can conclude that, the excited electrons on the surface states would recombine through fluorescence radiation instead of being transferred to the metal. In other words, only the electrons generated on the carbonic core are effective in the photoreduction process of the Ag ions using CDs, while those generated on the surface states are ineffective.

Besides, temporal behavior of the fluorescence of the CDs and CDs-Ag NPs with different excitations are compared to support our

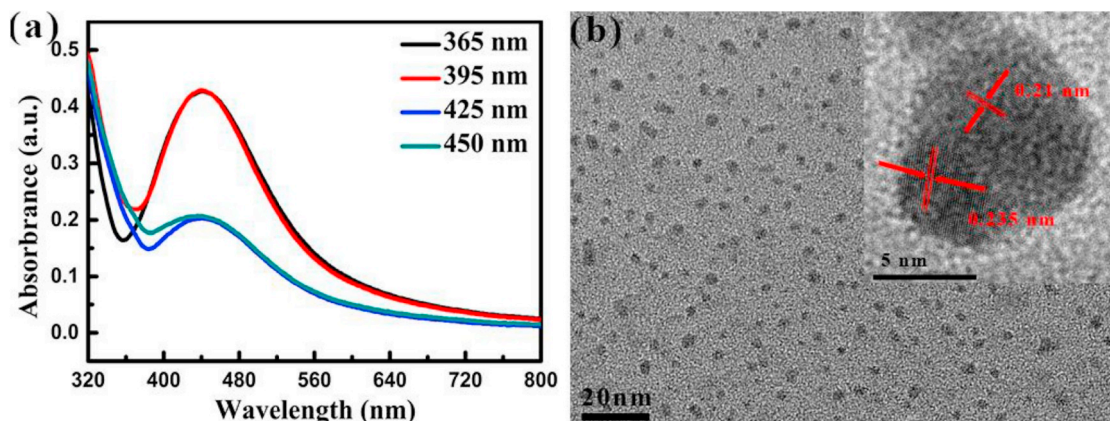


Fig. 2. (a) UV-Vis spectra of Ag synthesized with different UV lamp wavelength, (b) TEM images of the as prepared Ag-CDs.

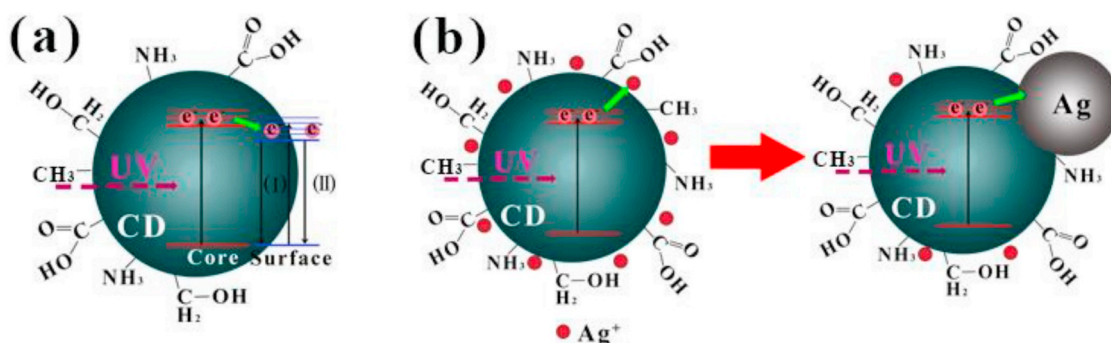


Fig. 3. (a) Schematic illustration of the synthesis process of Ag NPs, (b) Schematic illustration of the fluorescence mechanism of CDs.

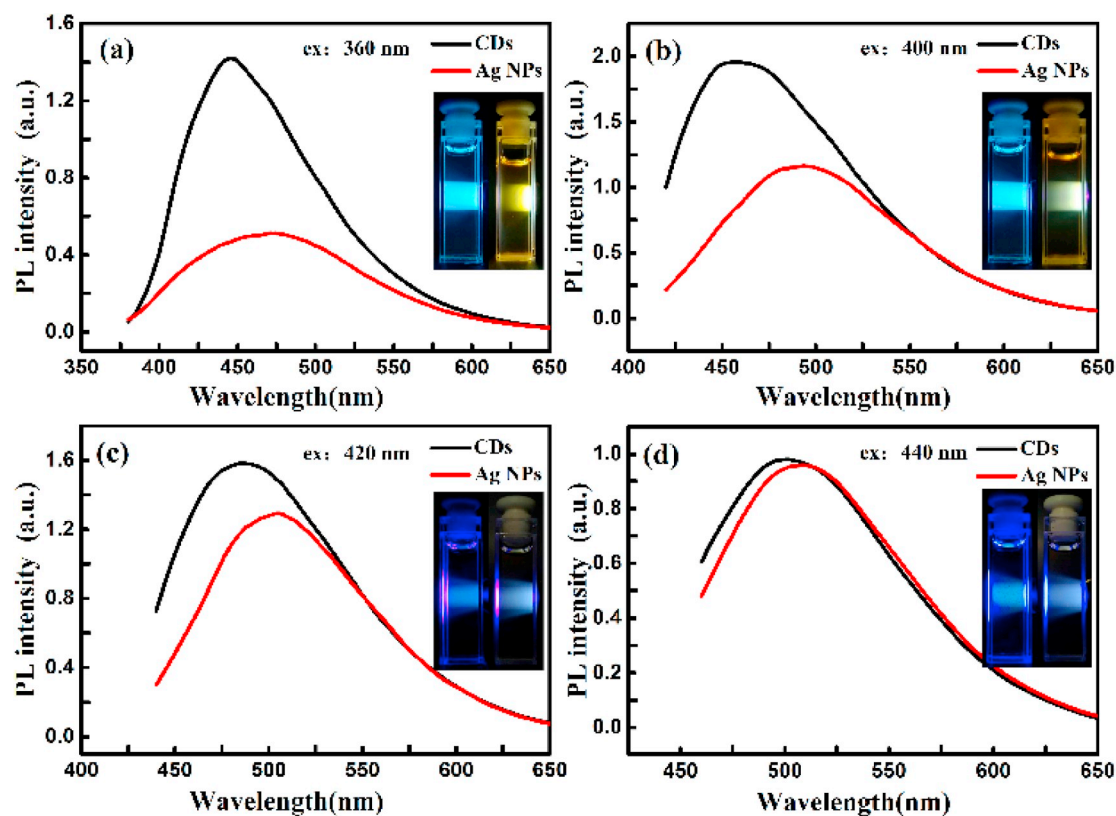


Fig. 4. PL spectra of CDs and CDs-Ag NPs at (a) 360 nm, (b) 400 nm, (c) 420 nm, (d) 440 nm excitation. The insets indicate the picture of the fluorescence color of photoexcited CDs with and without Ag NPs under ultraviolet lamp with different wavelength.

conclusions. The results are given in Fig. 5(b)–(d). Generally, the PL kinetics of the CDs exhibit two different relaxation time scales, a slow decay (about 8 ns) corresponding to Process (I) and a fast decay (about 1 ns) corresponding to Process (II) as mentioned in Fig. 5(a). It can be seen from the figure that at the same excitation wavelength, the lifetime of the composites decreases obviously. Table 1 summarizes the ratio change of the slow and fast components in the decay process of the PL in CDs-Ag NPs under different wavelength light excitation (The fitting equation and specific fitting parameters are included in Supporting Information). When the excitation wavelength increases from 343.6 nm to 369 nm and finally to 405 nm, the variation of slow decays is 23.3%, 15.14%, 9.3%, respectively. The ratio of slow decays is reduced as the excitation wavelength increases, and what's more, the variable of slow decays is also decrease.

Under short wavelength light excitation, the slow decay, i.e., excitation of the carbonic-core and carrier relaxation to the surface states followed with a radiative recombination, plays a dominant role in the PL

process of pure CDs. When they are combined with Ag NPs, this process is blocked and the PL is quenched, and the ratio of slow component in the time-resolved PL is decreased accordingly. With increasing the excitation wavelength, the PL of CDs is more likely originated from the excitation of the surface states with a fast decay process, and the ratio of the slow components changes faintly. These experimental results are consistent with our inferences well.

4. Conclusions

In summary, we propose a hypothesis to explain the mechanism of Ag NPs formation with the CDs as the reductant under the ultraviolet light-assisted. Both the UV-Vis spectra of the mixed solutions after LED irradiation with different wavelength and the image of the fluorescence color of photoexcited CDs without and with Ag NPs under different excitation wavelength proved that only the short-wavelength UV lamps can synthesize Ag NPs, while long wavelengths cannot. This

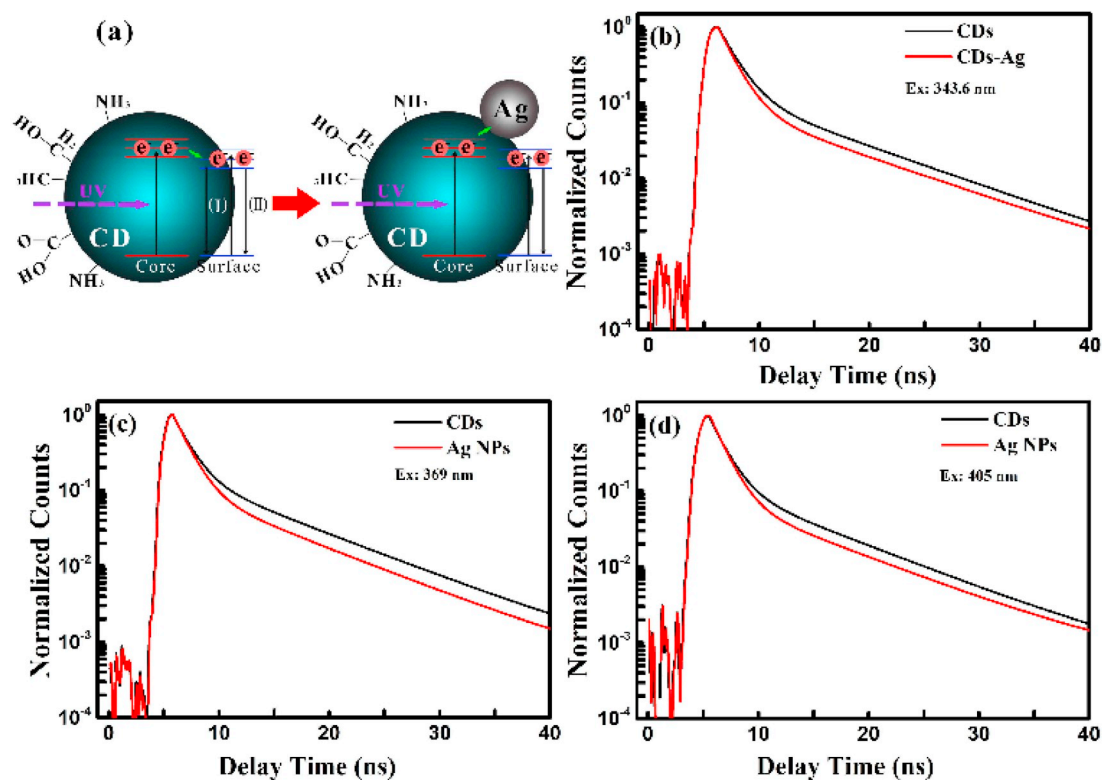


Fig. 5. (a) Excitation-recombination of carriers of the CDs without and with Ag NPs and the fluorescence lifetime of the CDs and CDs-Ag NPs at (b) 343.6 nm, (c) 369 nm (d) 405 nm excitation.

Table 1

The ratio change of the slow and fast components in the decay process of the PL in CDs and CDs-Ag NPs under different wavelength light excitation.

Exciting light	CDs			CDs-Ag NPs		
	Ratio of fast decay	Ratio of slow decay	Average lifetime	Ratio of fast decay	Ratio of slow decay	Average lifetime
343 nm	38.96%	61.04%	5.8 ns	62.22%	37.78%	3.9 ns
369 nm	48.83%	51.17%	4.6 ns	64.27%	35.73%	3.6 ns
405 nm	57.37%	42.63%	4.0 ns	66.68%	33.32%	3.4 ns

phenomenon indicates that it is the excitation-recombination pathway who plays a key role in the formation of Ag NPs by reducing silver ions. The PL intensity and the fluorescence lifetime of the CDs and the CDs-Ag NPs after the UV irradiation under different excitations further confirmed that only the electrons originates from the carbonic-core can reduce the silver ions to form the Ag atoms, while the electrons originates from the surface states will relax to the ground state and release fluorescence.

Declaration of competing interest

There are no conflicts to declare.

Acknowledgements

This work was supported by National R&D Program of China (2017YFA0207400), and the National Natural Science Foundation of China (Grant No. 11674260, and 61690221), the Key research and development program of Shaanxi province (Grant No. 2017ZDXM-GY-120), and the Fundamental Research Funds for the Central Universities (No. xjj2017189), and the collaborative Innovation Center of Suzhou Nano Science and Technology. The TEM work was performed at the

International Center for Dielectric Research (ICDR), Xi'an Jiaotong University, Xi'an, China. The authors also thank Mr. Ma and Ms. Lu for their help in using TEM.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2019.116804>.

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