Fluorescence Quenching by Förster Resonance Energy Transfer in Carbon–Cadmium Sulfide Core-Shell Quantum Dots

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ABSTRACT: Carbon quantum dots (QDs) are an active subject of research in many areas of science and engineering for various applications. The present work reports the first occurrence of a carbon–cadmium sulfide core-shell QD prepared by an extremely simplified wet chemical approach where the CdS shell plays the role of a fluorescence quencher to the carbon core. The quenching effect was confirmed by fluorescence spectroscopy (steady-state and lifetime). These QDs stand as a potential candidate for sensing and imaging applications.

INTRODUCTION

The accidental discovery of carbon (C) quantum dots (QDs) in 2004 opened up a new field of exploration in the arena of fluorescent materials.1 These C nanodots display excellent size-dependent optical and electronic properties, which makes them ideal candidates for biosensing, photocatalysis, light-emitting diodes (LED), and energy harvesting. Even after over one and a half decade of active research, the C QD keeps surprising the scientific community with its structure, properties, and an array of applications in various fields. In order to enhance the fluorescence (FL) and photon absorption properties, the C QD has been doped with materials like hydroxyapatite nanorods, nitrogen, and boron.2−7 The C QD has also served as a shell for core semi-conducting nanoparticles such as CdS for various applications such as photocatalysis, photoelectrochemical water splitting, and solar cells.8−10 The fluorescence quenching mechanism of C QD has also been reported with various nitroaromatic compounds such as 2,4,6-trinitrophenol, 2,4-dinitrophenol, p-nitrotoluene, nitrobenzene, etc.11

CdS is a versatile semi-conductor and is favored by materials scientists. Its strong absorption and luminescence, ease of synthesis, and size-tunable nature make it a preferred candidate for LED, lasers, and various optoelectronic devices.12−14 Here, we attempted for the very first time to prepare core-shell-structured C–CdS QDs with C as the core and CdS acting as the shell. The electron lifetime of the C–CdS core-shell QD decreased by 1.95 ns compared to the C QD. The CdS shell played the role of a fluorescence quencher to the carbon core. HR-TEM images revealed a perfectly circular-shaped C QD and C–CdS QD of size ~10 nm.

RESULTS AND DISCUSSION

Optical Studies. The UV−visible absorption spectra of C and C–CdS solutions are shown in Figure 1 with the
additional absorption spectrum of the CdS QD, which was separately prepared under the same experimental conditions as C−CdS. The C QD shows a miniature peak at 326.12 nm and a sharp narrow signature peak at 290.46 nm with another unresolved absorption maximum (λ_max) at 230.56 nm. The singular λ_max of the CdS QD lies at 375.7 nm.

For the C−CdS QD, a strong λ_max appears at the exact position of the CdS QD with two minor uprisings corresponding to the C QD. Considering the possibility that the CdS QD and C QD might be present separately or as a composite in the solution, the absorption intensity of the signature peak of the C QD would not have diminished. Owing to the formation of the core-shell structure, the photon energy would be first absorbed by the CdS shell, leaving only a fraction of energy to reach the carbon core. Further, since the CdS shell is dictating the absorption of photons, it might also have an effect on the emission spectra. The inset of Figure 1 shows the Tauc plot of the QDs whereby the identified band gaps of the C QD, CdS QD, and C−CdS QD were 3.54, 2.96, and 3.05 eV, respectively.

The steady-state FL spectra of the QDs were taken at an excitation wavelength of 290 nm, and the obtained emission characteristics are shown in Figure 2. The C QD shows a single broad emission peak at 432.60 nm, while the C−CdS QD gives an emission peak at 450.50 nm followed by two unresolved emission peaks at 480.36 and 523.26 nm. Further, the emission intensity of C−CdS is significantly lower (~1.4 times) than that of the C QD, which further affirms the fluorescence quenching effect of the CdS shell. Further, as shown in the inset images of Figure 2, upon illumination with 365 nm UV light, the C−CdS QD shows dim yellowish luminescence only at the brim, which suggests that only partial light was able to pass through the solution, while the C QD shows bright blue luminescence. Figure S1 (Supporting Information) shows the difference prominently. This effectively confirms the fluorescence quenching effect of the CdS shell. Furthermore, as reported in the literature, if the core was of CdS and the shell was of C, then enhancement in fluorescence would have been observed. Therefore, the quenching in fluorescence further confirms the presence of C as the core and CdS as the shell.

The phenomenon of fluorescence quenching could occur either due to the electron transfer mechanism or due to the energy transfer mechanism, i.e., Förster resonance energy transfer (FRET). The predominant condition for FRET is that the energy emission spectrum of the donor species should overlap with the energy absorption spectrum of the acceptor species. With the C QD being the donor species here, its emission onset starts as ~350 nm and attains a maximum at ~432 nm (Figure 3). On the other hand, the absorption onset of the CdS QD starts at ~440 nm and attains a maximum at ~375 nm, beyond which its absorption intensity keeps rising (Figure 3). Hence, the energy emitted by the carbon core is majorly absorbed by the CdS shell, leading to fluorescence quenching by the FRET mechanism.

The time-resolved FL spectrum shown in Figure 4 (bi-exponential fitting) conclusively proves the fluorescence quenching effect, courtesy of the CdS shell over the carbon
core. Fluorescence quenching upon addition of metal ions has been reported earlier; however, this is the first demonstration of FL quenching by a semi-conductor shell. The obtained average electron lifetime ($\tau_{\text{avg}}$) of the C QD was 4.66 ns, while that of the C–CdS QD was 2.69 ns. The decrease in the lifetime marks the reduction in FL. The inset of Figure 4 shows the FL intensity in a linear scale.

**Electron Microscopy Analysis.** The HR-TEM images revealed a perfectly circular-shaped carbon QD scattered periodically on the grid as shown in Figure 5A with red arrows. The average particle size obtained from 30 particles was $\sim$10.92 nm. Two magnified images are shown in Figure 5, where Figure 5B clearly shows the circular-shaped particles, while in Figure 5C, partial lattice fringes of a single particle are visible. The calculated $d$-spacing was $\sim$0.34 nm, which matches well with the reported value of the C QD. A dark field image of the C QD is shown in Figure S2 (Supporting Information) where the white dots correspond to the QD.

Figure 6A shows the predominantly circular-shaped C–CdS QD, which are scattered almost uniformly across the grid.

![Figure 5](image1.png)

**Figure 5.** HR-TEM images of the C QD at various resolutions: (A) 200 nm, (B) 50 nm, and (C) 5 nm.

![Figure 6](image2.png)

**Figure 6.** HR-TEM images of the C–CdS QD at various resolutions: (A) 200 nm, (B) 20 nm, (C) 20 nm, and (D) 5 nm.

Figure 6B conclusively shows the core-shell-structured C–CdS QD. The shown core-shell particle has a C core with a diameter of 9.88 nm with a CdS shell with an average width of 3.08 nm; the maximum shell width stands at 4.3 nm, while the minimum is of 1.86 nm. Further, there are also particles present having multiple C cores assembled together within a single CdS shell as shown in Figure 6C. The smallest C core has a diameter of 10.40 nm with a CdS shell thickness of 8.73 nm. Figure 6D shows the lattice fringes of the core-shell particle. The fringes can be observed both over the particle and by the edges. Figure S3 (Supporting Information) shows fringes present in a vertical position with a width of 0.3 nm and in a slanted position with a width of 0.2 nm, which correspond to the 111 and 220 planes, respectively, of the CdS shell. 

The selected-area electron diffraction pattern (SAED) of the QDs is shown in the Supporting Information (Figure S4). The bright center spot with a halo is indicative of the amorphous nature of the C QD (Figure S4A), while the partial rings appearing in the C–CdS QD (Figure S4B) are due to the semi-crystalline nature of CdS.
**X-ray Diffraction Analysis.** The XRD patterns of the C QD and C–CdS QD are shown in Figure 7 along with the XRD of the CdS QD for comparison. Three prominent peaks of C QD appear at 2θ angles of 26.42, 28.34, and 30.95°. The peak at 26.42° is also common for the CdS QD and thus appears as a broad hump in C–CdS. The major broad peak of C–CdS appearing at ~20.48° is not present in either C QD or CdS; hence, it must have resulted due to the formation of the core-shell structure. Further, if the resultant core-shell structure was CdS–C (instead of C–CdS), then the peak at 20.48° would not be present. In the XRD pattern of the C–CdS QD, the C QD peak appearing at 30.95° is shifted slightly toward lower 2θ, while the CdS peak at 47.52° appears shifted slightly toward higher 2θ. It must be noted that the XRD pattern of the C QD reported in almost every literature is different, possibly due to formation of QDs of different sizes and compositions. However, the diffraction pattern obtained for our sample does match closely with one of the reported patterns. Since formation of the C-CdS QD has not been reported earlier, comparison is not possible.

**CONCLUSIONS**

The carbon QD of size ~10 nm has been prepared successfully by a hydrothermal method. The C QD aqueous solution served as the medium for formation of CdS, ultimately resulting in a core-shell-structured C–CdS QD. The formation of the CdS shell over the C core led to the fluorescence quenching effect by the FRET mechanism, which was conclusively proven by UV–vis absorption and steady-state FL spectroscopy. The time-resolved FL spectra revealed a decrease in the FL lifetime of the C–CdS QD compared to that of the C QD. Finally, HR-TEM revealed the distinctly visible semi-crystalline core-shell-structured C–CdS QD. The excellent FL quenching mechanism effect of the core-shell C–CdS QD should prove useful in its application for sensing and imaging. Further optimization of the core-shell structure and its application are underway.

**EXPERIMENTAL DETAILS**

The synthesis of the C QD was carried out by the hydrothermal method. Citric acid (carbon source) and uric acid (nitrogen source) were taken in the ratio 1:5 and mixed together in double-distilled (DD) water while maintaining a pH level of 7. The solution was transferred to a Teflon-coated stainless-steel container for hydrothermal treatment at 180 °C for 20 h. The obtained C QD solution was filtered twice, and 25 mL of the same was used as a solvent for mixing 77 mg of Cd(NO₃)₂ and heated at ~55 °C. Na₂S (39 mg) was dissolved in 10 mL of DD water separately. Further, 225 µL of 2-mercaptoethanol (β-Me) was added in the Cd precursor solution followed by the addition of Na₂S solution, resulting in a final temperature of 50 °C. The prepared solution was finally filtered with a Whatman filter paper (cat no. 1001-125) and stored for further characterization. The details of the characterization techniques are given in the Supporting Information.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04529.

Details of the employed characterization techniques, C QD and C–CdS QD under 365 nm UV light in a quartz cuvette (Figure S1), dark field TEM image of the C QD (Figure S2), HR-TEM image showing the fringes of the C–CdS QD (Figure S3), and SAED patterns of the C QD and C–CdS QD (Figure S4) (PDF)

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**Author Contributions**

K.S. contributed in conceptualization, data curation, formal analysis, software, methodology, resources, visualization, and writing (original draft). B.B. contributed in investigation, project administration, supervision, validation, visualization, and writing (review and editing).

**Notes**

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