An Interactive Quantum Dot and Carbon Dot Conjugate for pH-Sensitive and Ratiometric Cu$^{2+}$ Sensing


Herein we report the photoinduced electron transfer from Mn$^{2+}$-doped ZnS quantum dots (Qdots) to carbon dots (Cdots) in an aqueous dispersion. We also report that the electron transfer was observed for low pH values, at which the oppositely charged nanoparticles (NPs) interacted with each other. Conversely, at higher pH values the NPs were both negatively charged and thus not in contact with each other, so the electron transfer was absent. Steady-state and time-resolved photoluminescence studies revealed that interacting particle conjugates were responsible for the electron transfer. The phenomenon could be used to detect the presence of Cu$^{2+}$ ions, which preferentially, ratiometrically, and efficiently quenched the luminescence of the Qdots.

1. Introduction

The growing importance of quantum dots (Qdots)[1–4] and the relatively new entrant, carbon dots (Cdots),[5] in the context of technological applications, is apparent from the extensive literature that continues to grow at a rapid pace. The ease of synthesis and functionalization of colloidal Qdots, in conjunction with their optoelectronic properties and chemical and photochemical reactivity, have helped to make a plethora of model devices. Furthermore, a fundamental understanding of the process of action of the key elements helps to achieve improved efficiency. For example, electron transfer between Qdots and metal nanoparticles, metal ions, or organic molecules is useful for solar cells, light-emitting diodes and logic operation.[6–9] The rate of charge transfer is key to the efficiency of the device performance, which depends on the driving force between donor and acceptor, the position of energy levels, the distance and energy landscapes between donor and acceptor, and the dielectric environment.[10, 11]

Additionally, similar devices are being developed based on environmentally friendly Cdots, with their unique optical and electronic properties, particularly for applications in bioimaging, biosensing, photonics, optoelectronics, and catalysis.[12–15] Cdots, with their highly luminescent and photo-electrochemical properties,[12, 16] can act as good electron donors or acceptors,[17] which leads to various opportunities in light-energy conversion, light-emitting diodes, and white-light emission, photoreduction, and related photocatalytic reactions.[17–20] The carbon-based nanomaterials, along with graphene quantum dots and their metal-nanoparticle-based nanocomposites, have been successfully applied for the efficient detection of metal ions, such as Ag$^{+}$, Fe$^{3+}$, and Hg$^{2+}$, and also biologically relevant molecules, such as glutathione and hydrogen peroxide, in both aqueous media and biological samples.[21–25]

Therefore, it would be worthwhile to pursue applications in which a combination of the properties of both materials is utilized. This can be based on interactions between Qdots and Cdots, in which electron or energy transfer from the excited state of one species to the other would lead to new properties that would be particularly applicable, for example, as analyte sensors. Although Cdots have been used with Qdots to construct energy-transfer systems for the efficient detection of biological molecules,[26] to our knowledge, no progress has been made on using Cdots and Qdots to study the detailed origin of the electron-transfer mechanism and to use this conjugate in possible applications.

Given the high extinction coefficient and easily tunable quantum efficiency of Qdots, the fabrication of a device that involves energy or electron transfer from Qdots to Cdots would be favorable. Photoluminescence (PL) quenching in Qdots could take place through dynamic quenching (by charge transfer, energy transfer, exciplex formation, or photochemical reactions) or by ground-state complex formation (static quenching). For efficient energy transfer, there should be an appropriate spectral overlap between the donor emission spectrum and the absorption spectrum of the acceptor.
These requirements are not there for electron transfer; however, the two species must necessarily interact with each other. We report herein the pH-dependent electron transfer between interactive photoexcited Mn-doped ZnS Qdots and Cdots in an aqueous medium. Based on the results from a combination of steady-state and time-resolved spectroscopic techniques and by varying the pH of the medium, we concluded that the emission from the excited state of Mn-doped ZnS Qdots was indeed quenched by the presence of Cdots. More importantly, we have demonstrated conclusively that the quenching of the Qdots was due to charge transfer, particularly transfer of photoexcited electrons from the Qdots to Cdots, as compared with the previously observed energy-transfer mechanism that is easily discernible from absorption and photoluminescence spectroscopic measurements. We also used the phenomenon in the ratiometric detection of Cu²⁺ ions with high efficiency, owing to the enhanced sensitivity and distinct visual responses as compared with first-generation intensity probes.

2. Results and Discussion

The Qdots and Cdots were found to be spherical with nearly uniform shape for all particles, which is in good agreement with previous reports. The optical absorption and luminescence and FTIR spectroscopy, transmission electron microscopy (TEM), electron spin resonance (ESR) spectroscopy, and X-ray diffraction (XRD) results of the as-synthesized Qdots and Cdots were also consistent with previous reports (Figures S1–S5 in the Supporting Information). The Qdots exhibited an absorption maximum at $\lambda = 320$ nm, whereas the absorption spectrum of the Cdots showed a maximum at $\lambda = 340$ nm (Figure S1). When excited by light of $\lambda = 320$ nm, the Qdots showed an emission with a maximum at $\lambda = 590$ nm (due to the $4T_1$–$6A_1$ transition in Mn), whereas the emission spectrum of the Cdots showed a maximum at $\lambda = 440$ nm. The band-edge emission assigned to pristine Qdots, which appears at $\lambda = 450$ nm, was absent because the dominant emissive species was due to the $4T_1$–$2A_1$ transition of Mn²⁺. It is also known that, in the presence of an excess of Mn in the Qdots, the band-edge emission diminishes significantly.

Interestingly, when an aqueous dispersion of Cdots was systematically added to a fixed amount of a Qdots dispersion (with an absorbance value of 0.1 at $\lambda = 320$ nm), quenching of the $\lambda = 590$ nm peak was observed (Figure 1). The reduction in the intensity of emission assigned to the Mn transition could be due to a redox reaction between the Cdots and the Qdots. A similar reaction between potassium peroxodisulphate and Mn-doped ZnS Qdots that leads to a loss of luminescence was observed previously. However, addition of NaBH₄ to the above mixture did not lead to any recovery of the lost intensity (Figure 2), which thus discounts the possibility of the oxidation of Mn²⁺ ions present in the Qdots. An ESR spectroscopy study revealed that the oxidation state of the Mn²⁺ ions in the Qdots was not affected in the presence of the Cdots (Figure 3). This was apparent from the observation that there was no significant change in the characteristic six peaks assigned to a $M_s = 1/2$ to $M_s = -1/2$ transition, with splitting due to a hyperfine interaction with the Mn²⁺ nucleus ($M_I = 5/2$) in the sample prepared from a mixture of Qdot and Cdots dispersions (as compared with Qdots only), which further supports the
above-mentioned observation. In other words, the Mn-doped ZnS Qdots were not oxidized in the presence of Cdots. However, the loss of luminescence of the doped Qdots could be attributed to static or dynamic quenching, based on energy or electron transfer in the presence of Cdots. Time-resolved photoluminescence studies revealed a systematic change in the excited-state lifetime of the $^4T_1$-$^6A_1$ transition of Mn$^{2+}$ (in the Qdots) in the presence of Cdots. Therefore, a dynamic quenching mechanism could be involved in the reduction of the luminescence of the Qdots in the presence of Cdots. A detailed discussion in this regard is presented below.

As described above, Figure S1 shows the absorption and photoluminescence spectra of Cdots and Qdots. The Qdots have a narrow emission peak at $\lambda = 590$ nm whereas the Cdots have a sharp absorption maximum at $\lambda = 340$ nm. As is clear from Figure S1, there is a negligible overlap between the absorption band of the Cdots and the emission of the Qdots (due to the $^4T_1$-$^6A_1$ transition in Mn). Therefore, the possibility of a resonance energy transfer from the Qdot (donor) to the Cdot (acceptor) can be ruled out. The other possibility for the loss of luminescence of the Qdots is through electron transfer from the photoexcited state to the Cdots.$^{[32]}$ The size and morphology of Qdots and Cdots before and after the interaction, as observed from TEM images, remained the same, which is consistent with the pH reversibility test that resulted in the switching of emission between acidic and basic conditions, as discussed below (Figure S3c, d, and e). Furthermore, there was almost no shift in the peak of the absorption spectrum of the Qdots (Figure S6) upon successive addition of Cdots, which confirmed that Qdots did not undergo aggregation upon addition of Cdots.

The Stern–Volmer plot of the steady-state luminescence quenching of Qdots by Cdots is shown in Figure S7 (see the Supporting Information for details). The straight-line graph through the Cdot concentrations (even at considerably higher concentrations) indicated the role of a collisional quenching mechanism in the reduction of the emission intensity. The absorption measurements are also consistent with a collisional quenching mechanism because both components are mutually dependent on each other. The surface-exposed Mn$^{2+}$ ions are affected more than the lattice-bound Mn$^{2+}$ ions because the Qdots and Cdots interact through the electrostatic mode, as described below, which is supported by faster decay ($\tau_1$) and an almost 100% contribution from the faster component ($\alpha_1$). The photoinduced electron transfer from the singlet CB of the Qdots to the singlet CB of the Cdots is spin-allowed, which is thermodynamically more favorable than electron transfer from the $^4T_1$ energy level of Mn$^{2+}$ in the Qdots, as discussed below. The electron transfer from the $^4T_1$ energy level of Mn$^{2+}$ in the Qdots to the singlet $E_{CB}$ of the Cdots would also take longer because of a spin-forbidden transition, which should result in either longer lifetime components or a new longer lifetime component.

If we assume that the decay of an electron from the excited state of a Qdot is only by direct transfer to a Cdot, the electron-transfer rate can be given as Equation (1):$^{[35]}

$$
k_{et} = 1/t_{Qdot-Cdot} - 1/t_{Qdot}
$$

in which $k_{et}$ is the rate of electron transfer and $t_{Qdot}$ and $t_{Qdot-Cdot}$ are the average lifetimes of a Qdot and a Qdot–Cdot mixture, respectively. From the average lifetime of the Qdot–Cdot system and the intrinsic lifetime of the Qdot, the estimated electron-transfer rate was calculated to be $0.044 \mu s^{-1}$, which gives an electron injection time of $22.92 \mu s$. The slow electron

![Figure 4. Time-resolved photoluminescence spectra of Qdots after the addition of different concentrations of Cdots (0–3.22 µg mL$^{-1}$) at an excitation wavelength of $\lambda = 320$ nm.](image-url)
injection time, as calculated, is comparable to the previously reported slow electron transfer between PbS quantum dots and TiO₂ nanoparticles. Transient absorption spectroscopy is generally used to get deeper insights into the electron-transfer mechanism, but unfortunately such transient absorption measurements on Qdots was unsuccessful here due to poor signal-to-noise ratio.

We also studied the effect of Qdots on the emission and lifetime of Cdots by successive addition of Qdots to Cdots. We observed that the emission of the Cdots decreased slightly on addition of Qdots (Figure S9a), which was attributed to competitive absorption between Cdots and Qdots because the concentration of Qdots was greater than the Cdots. The lifetime of the Cdots remained unaltered upon the addition of Qdots (Figure S9b and Table S2), which supported the assumption of competitive absorption between Cdots and Qdots. Furthermore, it is important to mention here that the excited-state lifetime of the Cdots remained unaltered even following electron transfer from the Qdots. This is because the electron injection time from the Qdots to the Cdots was 22.92 μs, whereas the lifetime of the Cdots was that of the order of nanoseconds.

The thermodynamic driving force, ΔGₜₐₚ, in terms of the energy difference between donor (D) and acceptor (A), for the photoinduced electron transfer between Qdots and Cdots can be verified from the Rehm–Weller expression [Eq. (2)]:

\[ \Delta G_{\text{et}} = E_D^0(D^{-}/D) - E_A^0(A^+/A) - \Delta E_{\text{et}}^{*} - \frac{e^2}{4\pi\epsilon_0r} \]  

in which e is the charge of an electron; \( E_D^0(D^{-}/D) \) is the reduction potential of the donor, that is, the Qdot (−1.91 V); \( E_A^0(A^+/A) \) is the reduction potential of the acceptor, that is, the Cdot (−1.02 V); \( \epsilon \) is the dielectric constant of the solvent; \( r \) is the distance between the charges; and \( \Delta E_{\text{et}}^{*} \) is the excited-state energy of the donor (Qdot), which is 2.10 eV (estimated from the luminescence maximum due to the \( ^1T_1 \rightarrow ^1A_1 \) transition in Mn). Because the solvent used is polar in nature, the Coulombic term in the above expression (\( e^2/\epsilon_0r \)) can be neglected. The calculated ΔGₑₜ value was −2.99 eV, and thus the process is thermodynamically favorable. However, if we assume the excited-state energy of the Qdot (\( \Delta E_{\text{et}}^{*} \)) is 2.95 eV (estimated from the luminescence maximum of the ZnS host, which corresponds to λ = 420 nm), a ΔGₑₜ value of −3.84 eV is obtained, which indicates the thermodynamic feasibility of electron transfer from the conduction band of the ZnS host, in addition to the \( ^4T_1 \) energy level of the dopant (Mn²⁺), as is also supported by the lifetime decay measurements.

To investigate the mode of interaction between Qdots and Cdots further, the zeta potentials for a Qdot, a Cdot, and a Qdot–Cdot mixture were measured (Table S3) and gave values of 12.5, −10.6, and 5.17 mV, respectively, at pH 7. For electron transfer to occur, it is necessary that the two species must interact with each other, which is possible when they are oppositely charged. Thus the addition of a negatively charged Cdot to a positively charged Qdot might have resulted in the formation of a Qdot–Cdot complex through an electrostatic interaction.

The surface charge on the Qdot thus plays a major role in the interaction that leads to quenching by a Cdot. This was further confirmed by performing PL measurements and following changes in the pH of the Qdot medium (Figure 5a). At neutral pH the zeta potential of the Qdot was positive, which led to PL quenching by the negatively charged Cdot through an electrostatic interaction. But at higher pH (pH 11) the Qdots became negatively charged, which led to no PL quenching upon addition of negatively charged Cdots (Figure 5b). The pH-reversible PL quenching experiments were also explored by varying the pH of the Qdots between 4 and 11, which changed the surface charge of the Qdots (Table S3), which further proved that the surface charge played a major role in the interaction. Overall, the Qdot–Cdot system exhibited pH-sensitive PL quenching through electron transfer from the Qdots to the Cdots, which ran reversibly between pH 4 and 11. By using the pH-dependent interaction between Qdots and Cdots, we have successfully demonstrated a visual pH sensor that operates between pH 5 and 10 (Figure 5c). The distinct change in the color of the Qdot–Cdot system from blue at pH 5 to orange at pH 10 under UV light can be used to detect the pH of the solution reversibly without the need to record an absorption or emission spectrum.

Finally, the Qdot–Cdot electron-transfer (ET) system was also applied for the efficient and ratiometric detection of Cu²⁺ ions (Figure 6a), an essential trace element in various biological systems. The Cu²⁺ ions preferentially bound to the Qdot surfaces rather than Cdots, which resulted in gradual quenching of Qdot emission but left the Cdot emission nearly intact. The very low solubility product of CuS (\( K_{sp} = 6 \times 10^{-19} \)) compared with ZnS (\( K_{sp} = 3 \times 10^{-22} \)) and K₂(zinc blend) = 2 × 10⁻¹⁰ and the similar ionic radius of Cu²⁺ and Zn²⁺ could facilitate the chemical displacement of surface Zn²⁺ ions by Cu²⁺. The Cu²⁺ ions possibly displaced the surface Zn²⁺ ions to form nonfluorescent CuS due to the lower solubility product, which led to quenching of the Qdot emission through surface annihilation. Along with the formation of CuS, electron transfer from the Qdots to Cu²⁺ is also possible, as suggested by the reduction potential of Cu²⁺ (0.3419 V), which lies below the reduction potential of the Qdots. The Stern–Volmer binding constant was found to be 8.73 × 10⁻⁵ M⁻¹ (Figure S10), which is comparable to earlier reported methods. The detection limit for Cu²⁺ ions was found to be 33.1 nM, which is far lower than the prescribed limit of 20 μM in drinking water given by the U.S. Environmental Protection Agency (EPA). Furthermore, the effect of Cu²⁺ in the presence of the Qdot–Cdot ET system showed enhanced quenching of the Qdot emission as compared with bare Qdots (Figure S11). The enhanced quenching of the Qdot emission in the Qdot–Cdot ET system could be based on two plausible mechanisms. First, the formation of CuS on the surface of the Qdots would reduce the emission quantum yield. Second, the formation of complexes between the surface functional groups of Cdots and Cu²⁺ is possible. This may contribute to an enhanced electron-transfer efficiency from the Qdots to the Cdots to make the combined system...
more efficient. The selectivity of the Qdot–Cdot ET system was also studied and was found to be the most sensitive to Cu$^{2+}$ ions (Figure S12). Furthermore, a discernible color change in the emission of the Qdot–Cdot system induced by Cu$^{2+}$ may also be used for the visual identification of Cu$^{2+}$ (Figure 6b).

### 3. Conclusion

We have been able to demonstrate the luminescence quenching of doped Qdots by Cdots through an electrostatic interaction between them. The positively charged Qdots interacted strongly with the negatively charged Cdots at lower pH, which led to a loss of luminescence. Conversely, at higher pH both the species were negatively charged, which led to the formation of independent species in the dispersion medium. This led to the observation of a lack of luminescence quenching. The pH-dependent luminescence quenching led to the development of a facile method for the visual detection of Cu$^{2+}$ ions with high sensitivity. The Coulombic interaction between the two luminescent species, which could be controlled by the pH of the medium, led to luminescence quenching and may also lead to important developments based on interacting nanoscale luminophores.
Experimental Section

Qdots and Cdots were prepared by using previously reported methods. The details of the experimental procedures are available in the Supporting Information.

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Figure 6. a) The photoluminescence emission spectra of the Qdot–Cdot ET system upon successive addition of Cu^{2+} (0–17.25 μM) at pH 6.0. b) Digital images of the photoluminescent Qdot–Cdot system upon successive addition of Cu^{2+}. Conditions: λ_{ex} = 320 nm for a) and b). The ratiometric probe was constructed by adding Cdots (1 μg mL^{−1}) to a Qdot dispersion (3 mL, with an absorbance value of 0.2 at λ = 320 nm).


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Join the dots to see! The interaction between luminescent quantum dots and carbon dots in an aqueous medium leads to pH-sensitive Cu$^{2+}$ ion detection.