

Mechanistic Aspects of Quantum Dot Based Probing of Cu (II) Ions: Role of Dendrimer in Sensor Efficiency

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Abstract Selective quenching of luminescence of quantum dots (QDs) by Cu^{2+} ions vis-à-vis other physiologically relevant cations has been reexamined. In view of the contradiction regarding the mechanism, we have attempted to show why Cu^{2+} ions quench QD-luminescence by taking CdS and CdTe QDs with varying surface groups. A detailed study of the solvent effect and also size dependence on the observed luminescence has been carried out. For a 13% decrease in particle diameter (4.3 nm \rightarrow 3.7 nm), the quenching constant increased by a factor of 20. It is established that instead of surface ligands of QDs, conduction band potential of the core facilitates the photo-induced reduction of Cu (II) to Cu (I) thereby quenching the photoluminescence. Taking the advantage of biocompatibility of dendrimer and its high affinity towards Cu^{2+} ions, we have followed interaction of Cu^{2+} -PAMAM and also dendrimer with the CdTe QDs. Nanomolar concentration of PAMAM dendrimer was found to quench the luminescence of CdTe QDs. In contrast, Cu^{2+} -PAMAM enhanced the fluorescence of CdTe QDs and the effect has been attributed to the binding of Cu^{2+} -PAMAM complex to the CdTe particle surface. The linear portion of the enhancement plot due to Cu^{2+} -PAMAM can be used for determination of Cu^{2+} ions with detection limit of 70 nM.

Keywords CdTe · Nanoparticles · Cu^{2+} ions · PAMAM dendrimer · Photoluminescence (PL)

Introduction

Semiconductor nanoparticles (QDs) have attracted considerable attention as novel luminescent probe in recent years [1–3]. The widespread interest in these QDs is attributed to their high photostability and size tunability of luminescence. They also exhibit narrow emission and broad excitation spectra, allowing excitation of multiple QD with a single wavelength [4, 5]. These superior optical properties surmount the constraints of conventional fluorophores, thereby offering exciting new opportunities for sensing and bio-imaging. In order to develop a fluorescence-based nano-sensor for physiologically important cations, these nanoparticles should have the ability to interact well with these ions. High selectivity and sensitivity is of prime concern for the nanosensor to work efficiently, even in the presence of elevated levels of competing divalent cations. One of the physiologically important metal ions is Cu^{2+} , which plays a key role in the synthesis of hemoglobin, elastin, collagen and cleaning of the organism from the excesses of free radicals and cholesterol [6]. Maintaining an appropriate physiological concentration of Cu^{2+} ions is crucial to normal functioning of biological machinery. A slight deficiency or excess could lead to serious ailments like rheumatoid arthritis, osteoporosis and Wilson disease. Therefore, determination of copper is quite essential to detect an early onset of such diseases.

Luminescence of semiconductor QDs are known to be sensitive to surface states and the binding of analytes onto the nanoparticle-surface affects these electronic states, which, in turn, influences the PL emission of QDs [7, 8].

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In our earlier reports, the binding of amino acid and DNA bases with semiconductor QDs was investigated and a quantitative correlation established therein [9, 10]. The interaction of biologically relevant cations with these QDs has recently been studied [11–13]. However, there are hardly any reports regarding the mechanistic details of these interactions. In the present work, interaction of cysteine capped CdTe QDs with various physiological cations has been extensively investigated and Cu^{2+} ions were found to selectively quench the QD-fluorescence. The insensitivity of CdTe QDs to other ions, particularly, Zn^{2+} is of diagnostic significance since Zn^{2+} and Cu^{2+} elicit an interfering response from fluorescent organic indicator [14–16]. The quenching of CdTe luminescence by Cu^{2+} ions could be utilized for specific and accurate determination of Cu^{2+} ions in micromolar concentration range. In the present study, a novel polymeric ligand, polyamidoamine (PAMAM) dendrimer has been employed in order to further enhance the sensitivity of detection. Polyamidoamine (PAMAM) dendrimers are highly branched macromolecules and possess the solvent filled interior ethylenediamine core (nanoscale container) as well as interior amide groups and exterior surface functionality of amine groups [17, 18]. They are also high capacity chelating agents for metal ions [19, 20] and especially attractive for binding metal ions in aqueous solution due to their controlled size. The influence of PAMAM dendrimer and Cu^{2+} -PAMAM complex on luminescence of CdTe QDs was also investigated. Cu^{2+} -PAMAM complex exhibited a unique enhancement effect, which is in stark contrast to the quenching effect of the two species constituting the complex, PAMAM dendrimer and Cu^{2+} ions. We also show that a lower detection limit for Cu^{2+} ions can be achieved by using PAMAM dendrimer and CdTe QDs together, which is comparable to the one achieved by employing CdTe nanorods [21]. The mechanistic pathways leading to such differential behaviour of the three species has been investigated.

Experimental

Reagents

L-Cysteine hydrochloride, cadmium nitrate tetrahydrate, copper sulfate pentahydrate, zinc sulfate pentahydrate, iron (III) nitrate nonahydrate, sodium chloride, potassium chloride, magnesium chloride hexahydrate, manganese (II) chloride tetrahydrate, calcium chloride dihydrate, glutathione were purchased from Merck, Germany. The starburst dendrimer (PAMAM) of generation 5.0 was obtained from Sigma Aldrich, Germany. Telluric acid (H_2TeO_4 , $2\text{H}_2\text{O}$) and sodium borohydrate (NaBH_4) were purchased from BDH. All the chemicals were of analytical grade or highest

purity available and were used as obtained. Milli-Q water (Millipore) was used as a solvent.

Synthesis of cysteine-capped CdTe quantum dots

CdTe and CdS QDs were synthesized following the method as reported earlier [22]. In a typical synthesis, an aqueous solution of Cd^{2+} ion (4.68×10^{-2} M) and L-cysteine (11.70×10^{-2} M) was prepared and pH was adjusted to 11.2–11.8 (using Jenway 3345 ion meter). Then NaHTe solution was added under nitrogen atmosphere. The resultant solution was refluxed at 100 °C and different aliquots were collected various time interval having different size of the QDs. The UV-Vis absorption and photoluminescence (PL) spectra of each of the aliquots were recorded on Shimadzu UV-1601PC and Perkin Elmer LS-55 luminescence spectrometer, respectively.

Synthesis of L-cysteine-capped CdS quantum dots

In a typical synthesis of nanoparticles, an aqueous solution (50 ml) Cd^{2+} ions (2.34×10^{-2} M) and L-cysteine (5.85×10^{-2} M) was prepared. pH of the solution was adjusted to 11.2–11.8 by adding NaOH solution (0.1 M) and argon was bubbled through the solution to remove dissolved oxygen. A saturated aqueous solution of H_2S was added to make the final molar ratio of Cd^{2+} :cysteine: S^{2-} , 1: 2.5: 0.5. The resultant solution was refluxed and different aliquots were collected at various time intervals and its absorption and luminescence spectra were recorded. Following the same method, CdS QDs were prepared with other capping agent, namely, Glutathione.

Synthesis of dendrimer-capped CdS quantum dots

A typical preparation of CdS nanoparticles in Dendrimer matrix with an initial $\text{Cd}^{2+}/\text{S}^{2-}$ molar ration of 1:0.5 was as follows:—5 ml aliquot of Cd^{2+} stock solution was added to 10 ml of dendrimer stock solution at 5°C and vigorously stirred for 2 min. Then freshly prepared aqueous solution of H_2S of known concentration (estimated iodometrically using sodium arsenite) was added in stoichiometric amount to the N_2 purged solution mixture of Cd^{2+} and dendrimer.

Determination of the average particle size

Semiconductor nanoparticles exhibit a blue shift in the absorption spectra as the size is reduced below the characteristic Böhr exciton diameter of the bulk material [1, 2]. The quantitative relationship between absorption spectra and particle size is now well understood [23]. The band gap (E_g) was calculated from absorption onset (λ_{onset}) in the UV-Vis absorption spectra of each nanoparticle

solution using the relation, $E_g = hc/\lambda_{\text{onset}}$, where h is the Planck's constant and c the speed of light. The average size of nanoparticles (d) was obtained using the correlation of band gap shift ($\Delta E_g = E_{g(\text{nanocrystal})} - E_{g(\text{bulk})}$), and particle size deduced by tight-binding approximation [23] (Eq. 1).

$$\Delta E_g = a_1 e^{-d/b_1} + a_2 e^{-d/b_2} \quad (1)$$

The values of the parameters for CdTe nanocrystals are $a_1=5.77$, $b_1=8.45$, $a_2=1.33$ and $b_2=43.73$. The particle size determined by this optical method was found to be in good agreement with the size obtained from TEM measurements [22].

Photoluminescence studies of QDs with Cu^{2+} , PAMAM, Cu^{2+} -PAMAM

The excitation wavelength chosen was 390 nm and the PL intensities at 530 nm were recorded. The as-prepared CdTe QD-solutions were further diluted 10 times with phosphate buffer (pH-7) and a known volume of Cu^{2+} ion as well as other physiological relevant ion was added. Concentration were chosen so that solution absorbance was kept < 0.1 to avoid self-absorbance effects. The aqueous solution of Cu^{2+} , Cu^{2+} -PAMAM with 4.42×10^{-5} M concentration and dendrimer with 3.47×10^{-7} M were prepared and few micro-litres (10–50 μL) of these solutions were added to the different sets of 3 ml solution of CdTe QDs. Here PAMAM dendrimer Generation 5 was used for the interaction with CdTe QDs. Cu^{2+} -PAMAM complex was prepared by using afore mentioned PAMAM dendrimer containing 128 amine end-groups and the complexation was accomplished by adding copper sulphate to a dilute solution of dendrimer in water and metal to ligand ratio was 1:1. The subsequent changes in optical properties arising out of the interaction of CdTe QDs with these molecules were monitored by optical absorption and emission. Fluorescence lifetimes of CdTe QDs in buffer solution (pH 7.0), both in the absence as well as in the presence of Cu^{2+} ions were measured using a time-correlated single-photon-counting (TCSPC) spectrophotometer (Edinburgh) with FWHM (Full width at half maximum) = 1.2 ns and repetition rate of 25 kHz. The details of the set up are described elsewhere [24]. All the CdTe NPs were excited at 390 nm and the decay kinetics were monitored at 530 nm. Luminescence decay in this system displayed bi-exponential kinetics. The fluorescence lifetime data were analyzed by considering reduced chi-square value. The calculation of average lifetime has been done using the formula: $\tau_{\text{av}} = \tau_1 f_1 + \tau_2 f_2$, where τ_{av} is the average life time, τ_1 , τ_2 , two lifetime values and f_1 , f_2 , the corresponding fractional contribution of each decay time to the steady state intensity.

Results and discussion

Cysteine-capped CdTe QDs have been synthesized in aqueous solution following the method reported earlier [22]. The optical absorption and emission spectra of the as-prepared QDs are shown in Fig. 1. The FWHM of the PL spectrum is 36 nm, which suggests narrow size distribution [25]. The average size of the CdTe QDs was found to be ca. 3.0 nm. The interaction of these biofunctionalized QDs with various physiological cations and dendrimer were investigated fluorimetrically as discussed in the following section.

Response to copper

In this work the ability of the CdTe QDs to detect metal ions has been tested in physiological buffer solution (pH 7) by monitoring the changes in their fluorescence spectra in presence of various metal ions. The presence of metal ions in QDs solution is signaled by fluorescence quenching (FQ). The FQ has been determined from the ratio between the maximum fluorescence intensity (solution free from metal ions) and the one after metal ions addition. Figure 2 shows that fluorescence intensity is insensitive to other cations at a level of 10 mM. Much higher concentrations of K(I), Na(I), Ca(II), Mg(II), Mn(II), Ni(II), Zn(II) ions had no effect on the fluorescence and did not significantly compete with the fluorescence response to Cu(II) ions. In case of Fe (III) ions, the small degree of quenching could be attributed to inner filter effect and large absorption coefficient (~ 400 nm) [11]. This is further corroborated by our finding that no FQ was observed on changing the excitation to 450 nm. The highly selective quenching effect produced by Cu^{2+} ions may therefore be utilized for the detection of these cations in the biological as well as in the environmental samples.

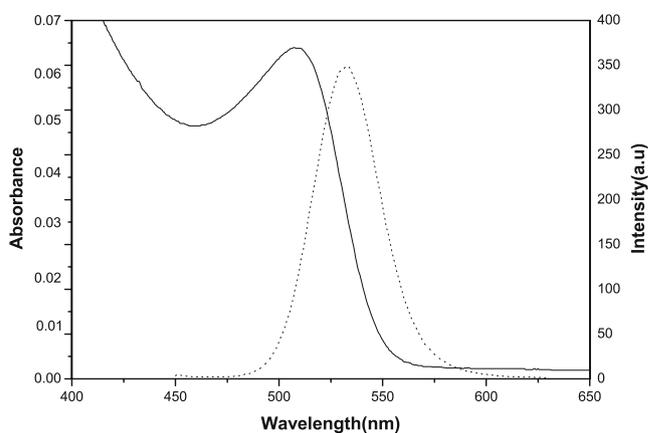


Fig. 1 UV-Vis absorption (—) and photoluminescence (·····) spectra of CdTe QDs (average size 3 nm)

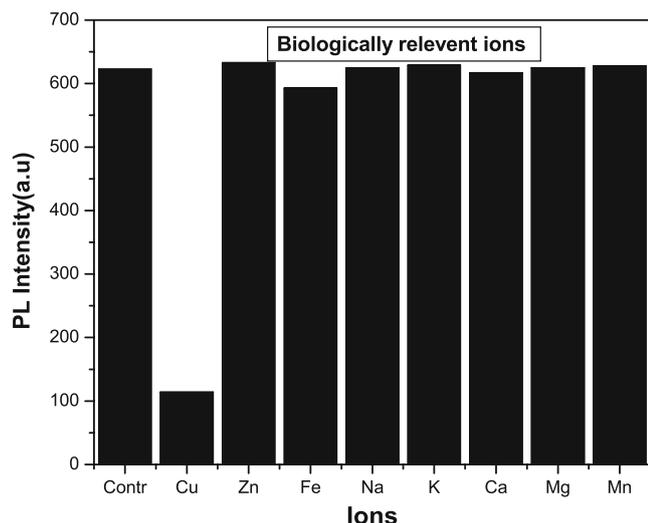


Fig. 2 Effect of various metal ions on the luminescence of CdTe QDs. Concentration of metal ions: 10 mM

Figure 3a displays quenching of CdTe luminescence with increasing concentration of Cu^{2+} to the QDs solution at pH 7. The plot of I_0/I against Cu^{2+} ion concentration is linear in the range of 0.14–2.9 μM (Fig. 3b) where it follows Stern-Volmer equation,

$$I_0/I = 1 + K_{\text{SV}}[\text{Cu}^{2+}] \quad (2)$$

The Stern-Volmer quenching constant (K_{SV}) was determined to be $6.4 \times 10^5 \text{ M}^{-1}$ which is ~54% higher than the K_{SV} obtained for CdTe nanorods [21]. The higher value of slope also implies a better sensitivity of Cu^{2+} determination by CdTe QDs.

To determine the nature of quenching, time-resolved fluorescence spectroscopy was carried out. Figure 4 illustrates luminescence decay profile of CdTe QDs, which follows biexponential decay kinetics. The average lifetimes (τ) were estimated to be $8.56 \pm 0.15 \text{ ns}$ and $20.23 \pm 0.2 \text{ ns}$ for CdTe QDs having average sizes of 2.3 and 3.0 nm, respectively (Table 1). The addition of Cu^{2+} ions to the QDs solution decreases the luminescence intensity, but does not affect lifetime suggesting the quenching to be static one.

Solvent effect on the quenching of QD-luminescence

Solvent polarity and local environment could have profound effect on the interaction of fluorophore and quencher molecules [26]. Hence, quenching of CdTe QDs by Cu^{2+} ions has been studied by changing the composition of the solvent. Solvents of different dielectric constants were prepared by mixing methanol ($\epsilon=33.0$) and water ($\epsilon=80.1$) in different proportions. If electrostatic binding or some sort

of charge transfer process involved in the interaction, the quenching constant should be adversely affected by decreasing polarity of the solvent [27]. As shown in Fig. 5, with decrease in the polarity of mixed solvent, the Stern-Volmer quenching constants decrease sharply. Considering the two extremes of solvents (75% aqueous methanol *vis-à-vis* water), the K_{SV} value increases by 47 times for a nearly 80% increase in dielectric constant (Table 2). The observed trend indicates that charge transfer might have occurred between CdTe QDs and Cu^{2+} ions at the excited state since there is no change in ground state absorption spectrum of CdTe QDs in presence of Cu^{2+} ions. Greater the polarity of the solvent, more stable will be the product and hence more quenching was observed in aqueous solution. In solvent of reduced polarity (methanol),

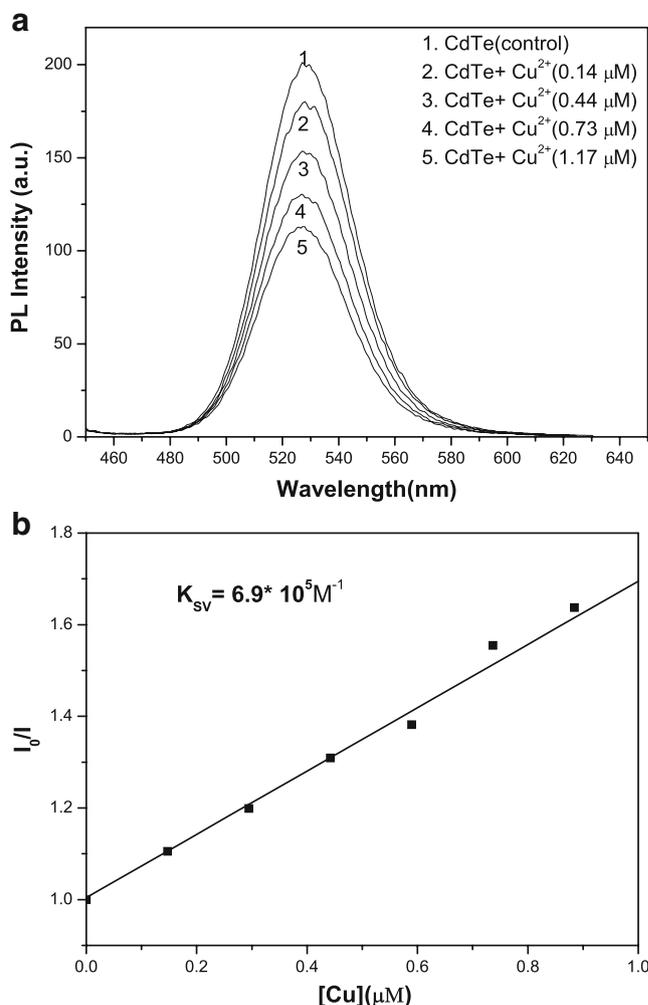


Fig. 3 a PL spectra of CdTe QDs under the influence of Cu^{2+} at various concentrations; b Stern-Volmer plots for the PL quenching of CdTe QDs, (Here, I_0 and I are the PL intensities of the respective CdTe QDs in the absence and presence of Cu^{2+} , respectively). The results are presented as mean values with a minimum of $n=3$ and the error bars are representing the range

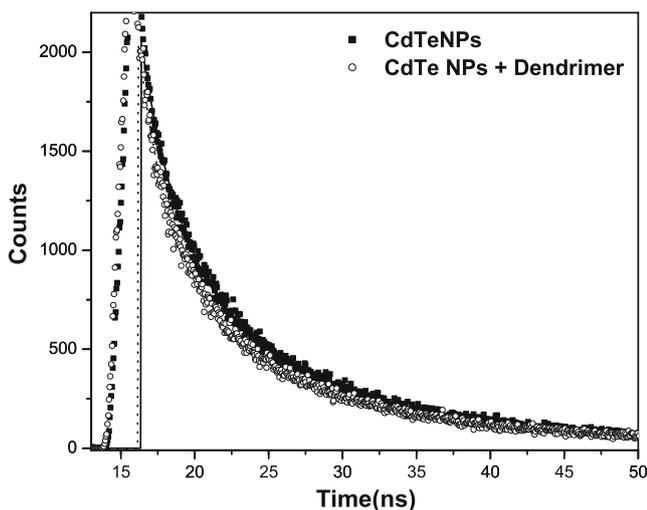


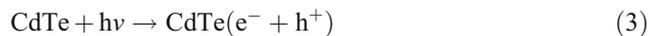
Fig. 4 A typical decay profile of CdTe QDs ($d_{av} = 2.3$ nm) in the absence and in the presence of dendrimer. Bi-exponential fitting of the experimental data were shown with solid line (—) for CdTe QDs and with dotted line (·····) for CdTe QDs in the presence of dendrimer

the charge transfer process gets hampered showing lesser quenching.

Mechanism of quenching

On having a closer look at the electron transfer involved in the quenching process, it appears that photo excited CdTe QDs might give up the electron to Cu^{2+} ions, thereby by reducing them Cu^+ ions. The absorption of sufficient light

energy causes excitation of electrons from valence band (highest occupied molecular orbital, HOMO) to the conduction band (lowest unoccupied molecular orbital, LUMO).



Such charge separation leads to formation of reactive electron-hole pair, which may migrate to the particle surface and get de-excited, transferring the energy to the quencher molecules. In quantitative terms, for the electron transfer to be feasible, the redox potential of the conduction band edge should be more negative than that of the redox couple of the quencher species. The redox potential of Cu^{2+}/Cu^+ is 0.1682 V whereas the redox potential of the conduction band edge in CdTe particles ($d_{av} \leq 3.5$ nm) lies in the range of -1.9 to -2.7 V [28]. Therefore, thermodynamic data favor the reduction Cu^{2+} ions by photo-excited CdTe QDs. These new-formed non-radiative channels for electron annihilation effectively compete with the radiative electron-hole recombination within the QDs giving rise to FQ.

In order to check the presence of Cu (I) ions, another set of experiment was performed by addition of potassium iodide and Cu^{2+} ions to the QD-solution. Upon excitation of the solution with 3.2 eV photons, a thick brownish white precipitate of CuI was formed which dissolved in excess KI. It should also be mentioned that the control sets, containing potassium iodide and Cu^{2+} ions, did not produce any precipitate in the absence of either CdTe QDs or the

Table 1 Effect of additives on fluorescence lifetime of CdTe QDs ($\lambda_{ex} = 390$ nm; $\lambda_{em} = 530$ nm)

Sample	Additives	Fluorescence lifetime				I_0/I	τ_0/τ
		τ_1 (ns) (f_1)	τ_2 (ns) (f_2)	τ_{av} (ns) ^a	χ^2		
CdTe-I (2.3 nm)	Nil	2.43 (21.60)	10.25 (78.4)	8.56	1.16	–	–
	Cu^{2+}						
	a) 1.5 μ M	2.20 (19.76)	9.50 (80.24)	8.05	1.1	1.94	1.06
	b) 2.5 μ M	2.20 (19.41)	9.48 (80.59)	8.0	1.16	2.62	1.07
	Dendrimer						
	a) 3nM	2.2 (21.17)	9.41 (78.83)	7.88	0.96	1.09	1.08
b) 5nM	1.90 (20.95)	9.01 (79.05)	7.58	0.97	1.15	1.13	
	Cu-Dendrimer Complex	2.47 (22.20)	10.08 (77.80)	8.39	0.99	–	–
CdTe-II (3.0 nm)	Nil	10.23 (42.02)	27.50 (57.98)	20.03	1.2	–	–
	Cu^{2+}						
	1.5 μ M	9.79 (41.77)	27.60 (58.23)	20.16	1.01	1.94	1.0
	Dendrimer						
	5.7 nM	1.81 (36.4)	24.42 (56.59)	17.33	1.08	1.19	1.18

^a $\tau_{av} = \tau_1 f_1 + \tau_2 f_2$

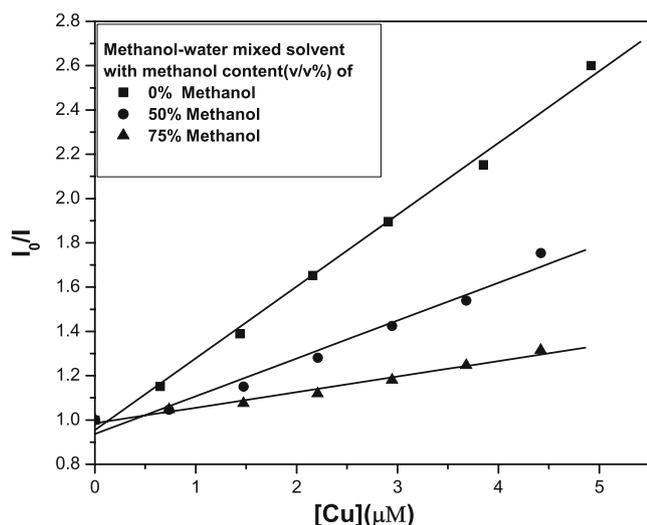


Fig. 5 Effect of solvent polarity on the PL quenching of CdTe QDs by Cu^{2+} ions (methanol-water mixture with following methanol content (v/v): 0%, (■), 50% (●), 75% (▲))

photons of required energy. This observation confirms that the quenching of CdTe luminescence involves photoinduced reduction of Cu^{2+} to Cu^+ .

In such semiconductor-catalyzed photo-reduction, redox potential of the conduction band edge is crucial in determining the feasibility of the process. On considering the band edge positions of other cadmium chalcogenide, it appears that the CdS nanoparticles should also be able to catalyze the reduction of Cu^{2+} in a similar manner. To verify this, cysteine-capped CdS nanoparticles ($d_{\text{av}} = 3$ nm) were prepared and the effect of Cu^{2+} ions on the luminescence of CdS QDs was investigated. As shown in Fig. 6a, the Cu^{2+} ion induced FQ was indeed observed. However, the Stern-Volmer constant ($7.8 \times 10^4 \text{ M}^{-1}$) was much lower than that of CdTe QDs of similar size (Fig. 6b). This result is in stark contrast to the earlier report by Chen et al [9], where no FQ was observed for cysteine-capped CdS QDs on addition of Cu^{2+} ions. However, they did observe the FQ on changing the capping ligand to thioglycerol, which led them to conclude the reduction of Cu^{2+} to be mediated by the surface ligand. We also note that substantial quenching was observed for polyphosphate capped CdS QDs in the same work, for which no

Table 2 Effect of solvent polarity on Stern-Volmer (K_{sv}) constant for Cu^{2+} ions

Solvent	Dielectric Constant	$K_{\text{sv}} 10^4 (\text{M}^{-1})$
Water	80.1	32.8 ± 0.01
50% aq. methanol	57.1	1.7 ± 0.04
75% aq. methanol	44.9	0.7 ± 0.06

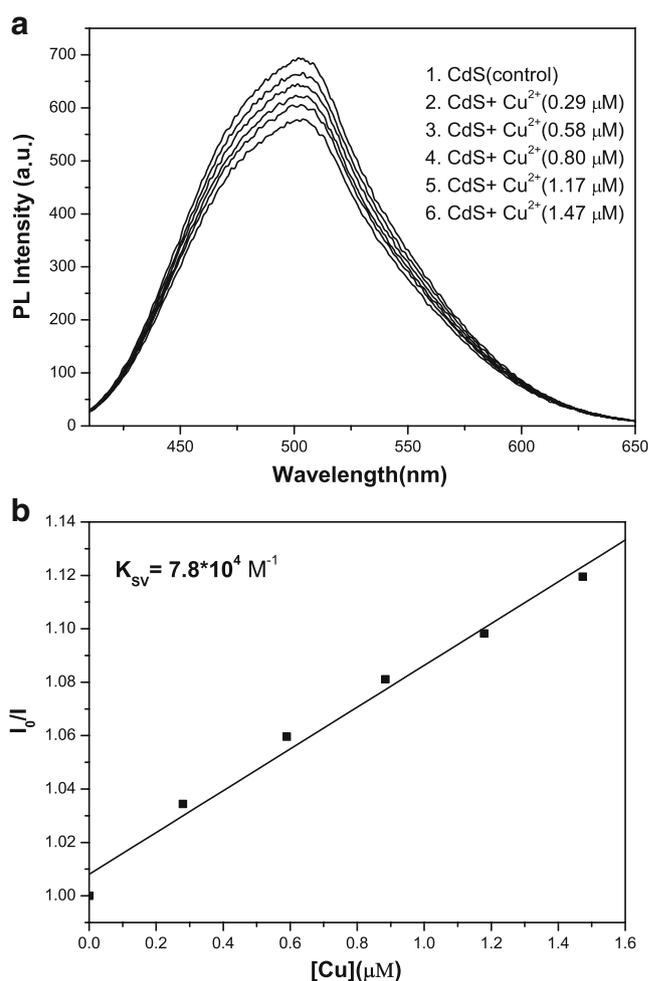


Fig. 6 **a** PL spectra of CdS QDs under the influence of Cu^{2+} at various concentrations; **b** Stern-Volmer plots for the PL quenching of CdS QDs, (Here, I_0 and I are the PL intensities of the respective CdS QDs in absence and presence of Cu^{2+} , respectively)

explanation was offered. In our view, it is the CdS core that is responsible for reduction of Cu^{2+} and the capping agent might have little role to play.

To further substantiate the proposed mechanism, the capping agents for CdS QDs were varied in two ways. Glutathione (GSH), a tripeptide containing cysteine, was taken for one set and dendrimer, a molecule entirely different from cysteine or thiols, was taken for another set. It is worth noticing that quenching of QD-fluorescence was prominently observed in both the cases in presence of Cu^{2+} ions [$K_{\text{SV}} (\text{CdS-GSH}) = 4 \times 10^4 \text{ M}^{-1}$, $K_{\text{SV}} (\text{CdS-Dendrimer}) = 1.8 \times 10^5 \text{ M}^{-1}$]. Further, it is important to note that, in the absence of semiconductor particles, no reduction was observed in Cu^{2+} -cysteine solution as well as in other systems (Cu^{2+} -GSH, Cu^{2+} -Dendrimer). However, on addition of CdS or CdTe QDs to the above solutions and excitation with 3.2 eV photons, brownish white precipitate of CuI was obtained. This finding further lends credence to

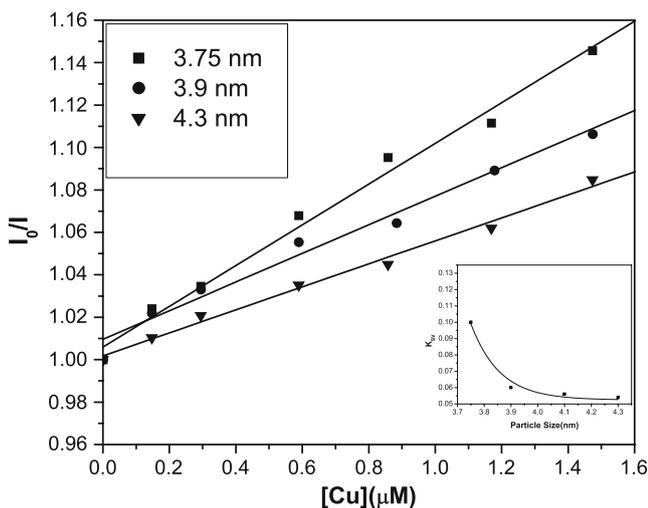


Fig. 7 Size dependence of PL quenching of CdTe QDs by Cu²⁺ ions, d_{av}: 3.7 nm (■), 3.9 nm (●), 4.3 nm (▲). Inset: A plot of Stern-Volmer constants (K_{SV} values) against average particle size

the hypothesis that the Cu²⁺/Cu⁺ reduction is photocatalyzed by semiconductor particles.

Size dependence of CdTe quenching

To study the size dependence of quenching, CdTe QDs of different sizes were prepared by varying the reflux time as reported earlier [22], the average sizes being in the range of 3.0–4.3 nm. Interestingly, the interaction of CdTe QDs with Cu²⁺ ions exhibited strong size dependence. As shown in Fig. 7, Stern-Volmer constants were found to decrease with increasing particle size. For a 13% decrease in particle diameter (4.3 nm → 3.7 nm), the quenching constant increased by a factor of 20. As the size of the nanoparticles decreases, the energy of the conduction band shifts to

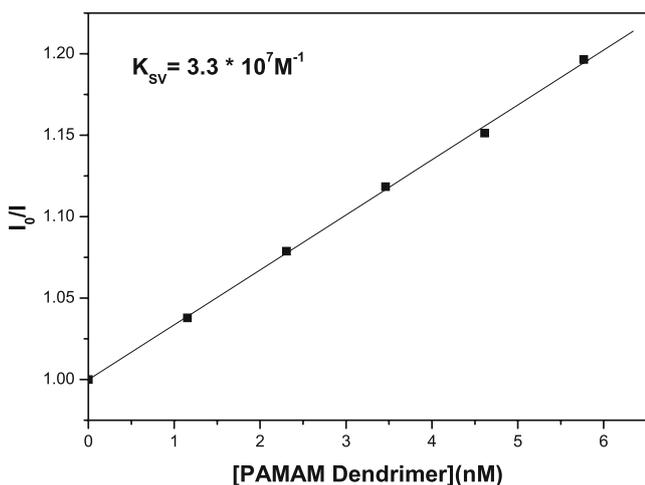


Fig. 8 Stern-Volmer plots for the PL quenching of CdTe QDs by PAMAM dendrimer (Here, I₀ and I are the PL intensities of the CdTe QDs in the absence and presence of dendrimer, respectively)

higher energy due to the quantum confinement effect. Redox potentials of the conduction band become more negative [29, 30] thereby enhancing the reducing power with a decrease in particle size. Due to higher surface to volume ratio in smaller nanoparticles, most of the constituent atoms reside on the surface of the particles [31] and can have more efficient transfer of electrons to the suitable species adsorbed on the surface, reducing the chances of radiative recombination of (e⁻ + h⁺) pairs. So, enhanced reducing power and higher ratio of surface to core atoms could account for the observed increase in the value of Stern-Volmer constants with decreasing particle size.

Effect of PAMAM dendrimer

In similar manner fluorescence quenching of CdTe QDs by PAMAM dendrimer was also studied. The fluorescence intensity of the QDs was found to be quenched by even nanomolar concentrations of dendrimer at pH 7. As shown

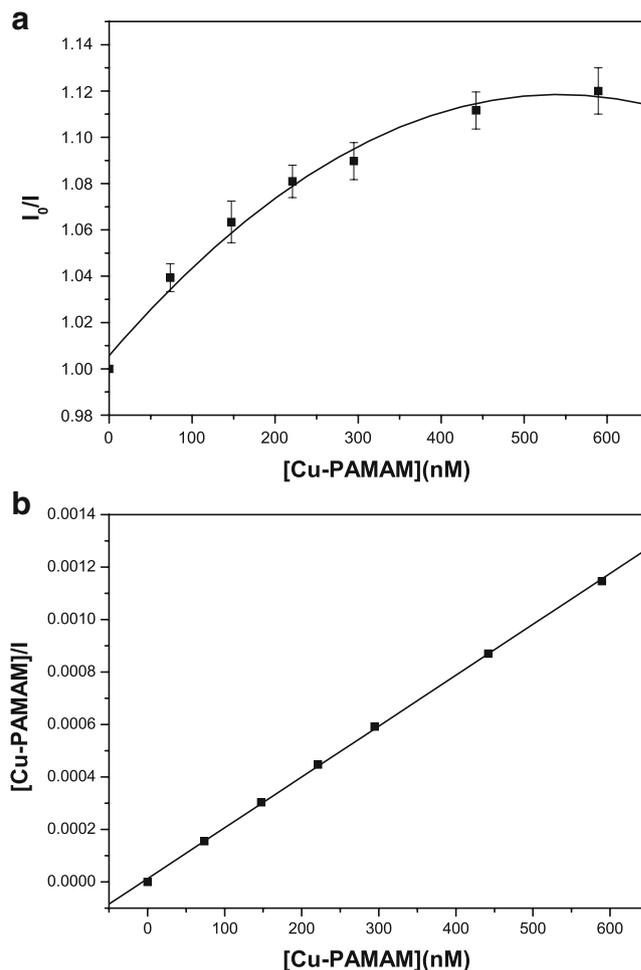


Fig. 9 a Effect of Cu²⁺-PAMAM on the luminescence of CdTe QDs showing increasing PL intensity with increasing complex concentration; b Langmuir binding isotherm

in the Fig. 8 the plot of I_0/I against dendrimer concentration in the range of 0–6 nM follows Stern-Volmer equation and the quenching constant (K_{SV}) was determined to be $3.3 \times 10^7 \text{ M}^{-1}$. To establish the nature of quenching, the fluorescence lifetime measurement was carried out on a single photon counting set up. It is quite evident from Fig. 4 that the luminescence decay kinetics of the QDs undergoes a change in the presence of dendrimer. The average lifetime (τ) of CdTe QDs decreased on addition of dendrimer and the ratio of lifetimes (τ_0/τ) equaled that of PL intensities (I_0/I) (Table 1). This confirms the quenching to be dynamic in nature. Therefore, the quenching process involves the energy dissipation through collisions between two dimensionally similar species, CdTe QDs (ca.3.0 nm) and dendrimer (5.4 nm).

Effect of Cu-PAMAM dendrimer complex

In contrast to the effects of Cu (II) and PAMAM dendrimer, Cu^{2+} -PAMAM complex caused a PL enhancement of CdTe QDs. As displayed in Fig. 9a, there is consistent rise in PL intensity up to the Cu^{2+} -PAMAM concentration of 880 nM. For further increase in concentration of the complex, the emission of CdTe QDs remained constant. This enhancement could be attributed to the passivation of trap states on the nanoparticle surface due to binding of Cu^{2+} -PAMAM molecules. As more of such molecules are added, more of surface traps get passivated. But at a certain concentration (880 nM), the surface gets saturated and no more Cu^{2+} -PAMAM molecules could be accommodated. Therefore, further addition does not cause any PL enhancement.

To get an idea about the nature of the interaction of CdTe QDs with Cu^{2+} -PAMAM complex, the effect of ionic strength on the enhancement of luminescence was investigated. If the interaction between QDs and Cu^{2+} -PAMAM is mainly due to electrostatic forces, the ionic strength should have some effect on the interaction [32]. The fluorescence intensity remained unchanged with a gradual increase in KCl concentration, which suggests that the nature of interaction is covalent in nature. Furthermore, the average lifetime (τ) of CdTe QDs in the presence of Cu^{2+} -PAMAM remained unaffected (Table 1).

The concentration dependence of the luminescence intensity follows the binding of Cu^{2+} -PAMAM complex to the surface of the CdTe QDs and is effectively described by a Langmuir-type binding isotherm [33]. According to the theories, the equation could be established as following:

$$C/I = (1/B I_{\max}) + (1/I_{\max})C \quad (4)$$

Where B is the binding constant, I and I_{\max} represent luminescence intensity of CdTe QDs at Cu^{2+} -PAMAM concentration of C and the observed maximum intensity,

respectively. Accordingly, if the Langmuir description of the binding of Cu^{2+} -PAMAM on the surface of the CdTe QDs is correct, a plot of C/I as a function of C should be linear. Figure 9b show that a good linearity between C/I and C is observed throughout the entire range of Cu^{2+} -PAMAM concentrations. Interestingly, Zn^{2+} -PAMAM complex did not influence the fluorescence of CdTe QDs suggesting the specificity of Cu^{2+} -PAMAM complex. The linear range of the enhancement plot can be used for the determination of Cu^{2+} ions, making it possible to detect Cu^{2+} ions as low as 70 nM.

Conclusion

The present study has demonstrated that CdS and CdTe QDs irrespective of surface ligands exhibit quenching effect by Cu^{2+} ions. The observed results suggest that quenching is primarily caused by the electron transfer from the semiconductor core to the metal ions. The PL enhancement caused by Cu^{2+} -PAMAM complex was found to be quite in contrast to the individual response of its constituents, Cu^{2+} and PAMAM dendrimer. The mechanistic insights into all these interactions have also been obtained and the three species seem to follow different pathways. Cu^{2+} ions undergo QD-mediated photoreduction, whereas collisional quenching mechanism operates in the case of dendrimer. The PL enhancement effect of Cu^{2+} -PAMAM complex appears to be caused by adsorption of the complex onto the particle surface. The linear range of enhancement plot could be utilized for determination Cu^{2+} ions. Thus, the detection limit can be achieved as low as 70 nM, simply by adding PAMAM into the analytes. It underscores the role of PAMAM in enhancing efficiency of nanoparticle-based ion probes.

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