

CdS Nanoparticles as Efficient Fluorescence Resonance Energy Transfer Donors for Various Organic Dyes in an Aqueous Solution

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CdS nanoparticles (NPs) were synthesized in an aqueous phase in order to investigate their spectral behaviors as efficient fluorescence resonance energy transfer (FRET) donors for various organic dye acceptors. Our prepared CdS NPs exhibiting strong and broad emission spectra between 480-520 nm were able to transfer energy in a wide wavelength region from green to red fluorescence dyes. Rhodamine 6G (Rh6G), rhodamine B (RhB), and sulforhodamine 101 acid (Texas red) were tested as acceptors of the energy transfer from the CdS NPs. The three dyes and synthesized CdS NPs exhibited good FRET behaviors as acceptors and donors, respectively. Energy transfers from the CdS NPs and organic Cy3 dye were compared to the same acceptor Texas red dye at different concentrations. Our prepared CdS NPs appeared to exhibit better FRET behaviors comparable to those of the Cy3 dye. These CdS NPs in an aqueous solution may be efficient FRET donors for various organic dyes in a wide wavelength range between green and red colors.

Key Words : Nanoparticles, Organic dyes, CdS, Fluorescence resonance energy transfer, Donor-acceptor

Introduction

In the past decade, research on the biological applications of semiconductor nanoparticles (NPs) has attracted great interest due to numerous potential applications in areas such as luminescence tagging, medical diagnostics, and biosensors.¹ Among these potential applications still in the design-phase, further fundamental research in the field of NP-based fluorescence resonance energy transfer (FRET) remains a challenge due to the toxicity of semiconductor NPs.² However, due to their superior spectral qualities, semiconductor NPs are regarded as ideal for FRET-based devices.³

FRET has been commonly used in biological research to measure molecular distances or donor-to-acceptor proximity.^{4,5} Although fluorescent organic dyes are popular materials generally used in FRET,^{6,7} the resonance energy transfer between dye molecules and NPs has recently been of increasing interest in order to broaden the potential application in the materials science area.^{8,9} Since FRET rates usually depend on the overlap between donor emission and acceptor absorption spectra, the spectral overlap should be significant for a given donor-acceptor system.

Among many fluorescence dyes, cyanine-based molecules are popular probes for cellular organelles and lipid and protein dynamics due to their high specificity and aqueous solubility.^{10,11} The Cy3 dye appeared to be a good donor to an acceptor molecule. Recently, the cadmium-based NP FRET behaviors with organic dyes have been studied using spectroscopic tools.¹²⁻¹⁵ Although there have been numerous FRET studies, the wavelength of the acceptor dye was rather limited to a green region using a CdS donor. In this study, our CdS NPs may reach an energy shift toward a further redshifted wavelength region due to the broad bandwidths. Despite prevalent tri-*n*-octylphosphine oxide-based organic

phase synthesis,¹⁶ CdS NPs were also synthesized in an aqueous phase.¹⁷ In this work, we study the FRET behavior of our CdS NPs that were synthesized in an aqueous solution with several commonly used fluorescence dyes. Due to their broad bandwidths, our CdS NPs appeared to work as an efficient donor to various fluorescence dye acceptors. The FRET efficiencies of the CdS NPs were found better than those of the Cy3 dyes.

Experimental Section

CdS NPs were synthesized in an aqueous solution with a modified procedure.^{17,18} A quantity of 8.0 μL of mercaptoacetic acid was added to a solution of CdCl_2 (1.12×10^4 mol) in triply distilled water (100 mL). The pH was adjusted to 11.0 by dropwise addition of concentrated 0.5 M NaOH. Under nitrogen, a solution of Na_2S (7.5×10^5 mol) in water (50 mL) was slowly added to the resulting alkaline solution with rapid stirring. The reaction mixture was stirred overnight at room temperature. We did not add any polyethyleneimines (PEIs) for these experiments. Rh6G, RhB, and Texas red were purchased from Sigma-Aldrich. Cy3 was purchased from Genechem (Daejeon, Korea). UV-vis and photoluminescence spectra were obtained using Mecasys 3220 absorption and Scinco FS-2 spectrometers, respectively. An excitation wavelength of 370 nm was used to obtain the photoluminescence (PL) spectra. The emission spectra were recorded from 400 to 600 nm. The excitation and emission slit widths were both set to 10 nm. Samples were contained in a 1-cm quartz cell for PL measurement.

Results and Discussion

Photos and Emission Color of CdS. Figure 1 shows

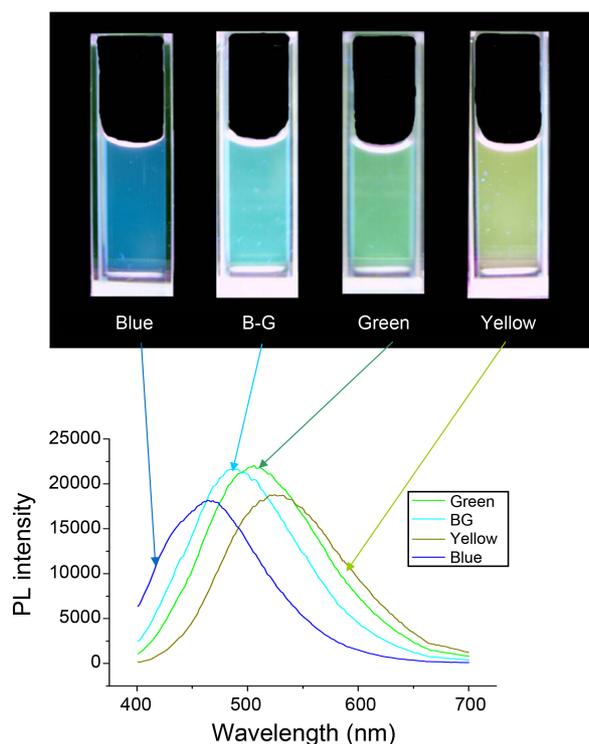


Figure 1. Emission colors of the synthesized CdS NPs. The corresponding fluorescence spectra are also illustrated. “B-G” stands for blue-green color. “PL” stands for photoluminescence.

fluorescent images of CdS NPs depending on their sizes and resulting emission spectra. The fluorescence maxima of CdS NPs were found at 480–520 nm, exhibiting different colors, depending on their annealing time and resulting sizes. Although not shown here, the size of the CdS NPs was estimated to be ~ 2.5 nm.^{17,18} The NP emission spectrum is nearly symmetrical and broad in peak width while its excitation profile is broad and continuous, meaning that NPs can be efficiently excited at any wavelength shorter than ~ 500 nm. Moreover, a FRET device is possible over a wide wavelength region from green to red. We have tested the three organic fluorescence dyes, Rh6G, RhB, and Texas red whose absorption spectra are within the range of the emission spectrum of the CdS NPs.

Excitation and Emission Spectra of CdS and Fluorescence Dyes. The CdS NPs emitting at the maximum of approximately 480 nm was used for the present FRET study. Figure 2(a) displays the absorption and normalized photoluminescence (PL) spectra of CdS NPs. We found that the absorbance maximum was observed at approximately 350 nm as shown in Figure 2(a). The extinction and emission spectra of organic fluorescence dyes of Rh6G, RhB, and Texas red were also compared in Figure 2(b). The fluorescence maxima of Rh6G, RhB, and Texas red were found at 553, 579, and 615 nm, respectively, and each exhibited their own different colors. Their positions in maxima, as summarized in Table 1, were consistent with the previous reports.^{19,20} As shown in Figure 2(b), the absorption maxima of the dyes at 525 to 590 nm overlaps with the emission

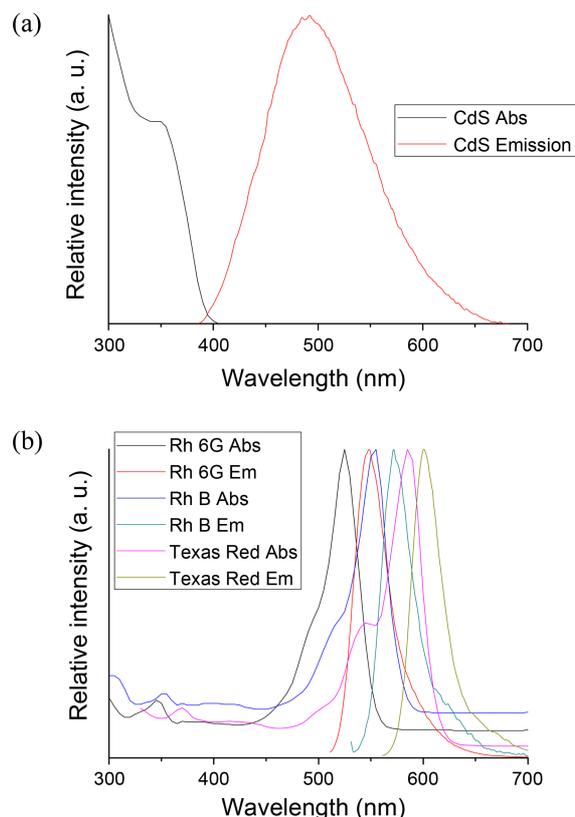


Figure 2. Excitation and emission profiles of (a) CdS NPs and (b) organic fluorescence dyes Rh6G, RhB, and Texas red. The synthesized CdS NPs emitting at ~ 480 nm was used for a FRET study.

Table 1. Absorption and emission maxima of CdS NPs and organic dyes^a

Dyes and NPs	Absorption Maximum	Emission Maximum
Rh6G	525	553
RhB	555	579
Cy3	550	570
Texas red	590	615
CdS	370	480–520

^aUnit in nm.

spectrum of CdS NPs. To further investigate the FRET characteristics in detail, we performed fluorescence measurements depending on the three dyes.

Dyes and Energy Transfer. Energy transfer from the CdS donor to the Rh6G and RhB acceptor (1×10^{-6} M) was checked first. As shown in Figure 3, the quenching of the CdS emission along with the increasing emission of Rh6G and RhB were observed at the excitation of approximately 370 nm for the CdS NPs. It was observed that RhB exhibited a greater increase in the PL intensity with a less decrease of the CdS emission compared with Rh6G. This may be caused by different spectral overlap and the dissimilar adsorption characteristics of the organic dyes. Because the molecular structures of Rh6G and RhB are different, their adsorption behaviors on CdS NPs could be dissimilar. Both of

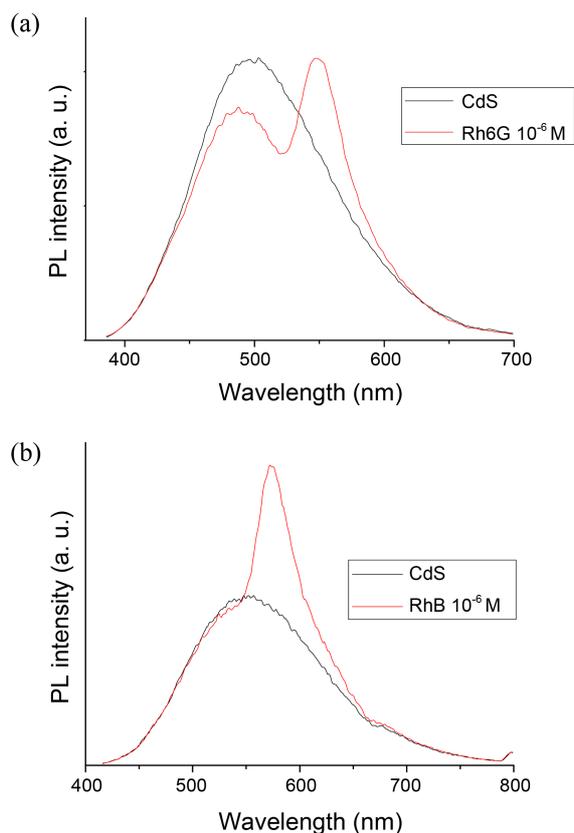


Figure 3. Energy transfer from the CdS donor to the (a) Rh6G and (b) RhB acceptor at an acceptor concentration of ($\sim 10^{-6}$ M).

the two dyes contain the nitrogen groups that can bind to NP surfaces. It is noteworthy that RhB has a carboxylic acid group that can chemically interact with NP surfaces. We expected that RhB's adsorption characteristics should differ from those of Rh6G. Due to the different absorption and emission peak positions of RhB at 555 and 579 nm from those of 525 and 553 nm, respectively, the spectral overlap and energy transfer should also be dissimilar.

To further understand the quenching process, a longer wavelength, Texas red, was used to measure fluorescence intensity with varying quencher (dye) concentrations. Quenching of the photoluminescence (PL) emission of NPs with increasing the dye (acceptor) concentrations was observed at 0–2.6 mM of Texas red dye. A gradual quenching of the fluorescence intensity of NPs with increasing the concentration of dye (quencher) is shown in Figure 4(a). We found that the PL intensity of the CdS NPs decreases when the Texas red dye concentration increases. A comparison with conventional Cy3 dye is provided in Figure 4(b). As summarized in Table 1, the excitation to emission bands of Cy3 are similar to those of RhB. Figure 5 plots the PL changes depending on the concentrations of acceptor (Texas red) dye, which indicate that our prepared CdS NPs should exhibit FRET behaviors comparable with the organic Cy3 dye. As shown in Figure 5(b), the increase in the acceptor's emission appeared to occur at a lower concentration for CdS than Cy3. This result may indicate that CdS may act as a more

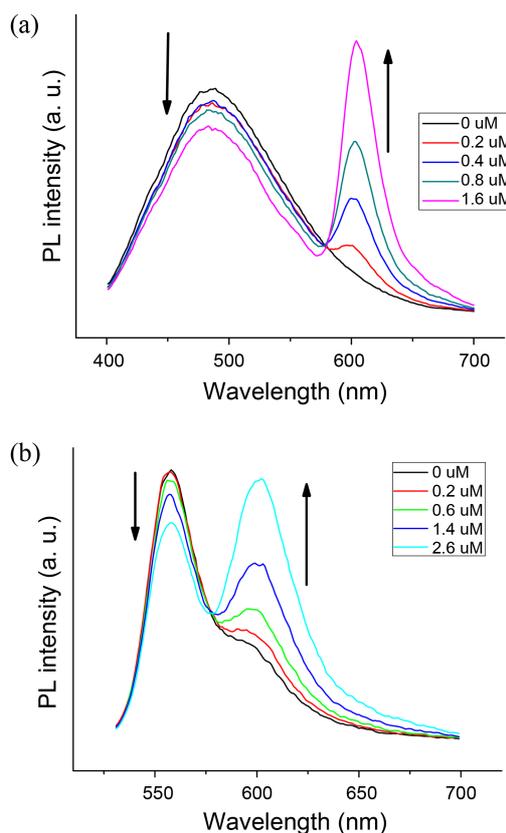


Figure 4. Energy transfer between (a) CdS and (b) Cy3 donor and the Texas red acceptor depending on the acceptor concentrations of Texas red. The arrows indicate a decrease in the donor emission and an increase in the acceptor emission.

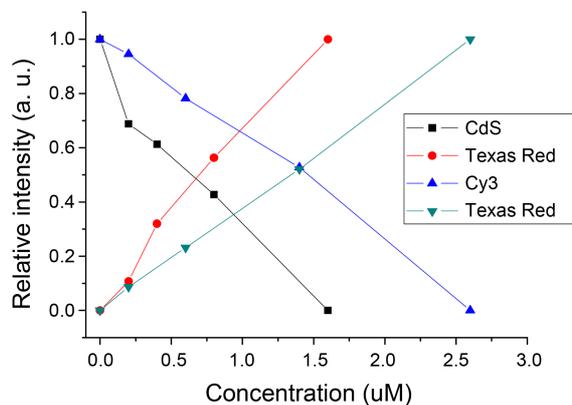


Figure 5. Plot of the Cy3 and CdS donor decrease and Texas red acceptor increase in fluorescence intensities depending on the acceptor concentrations of Texas red.

efficient donor than Cy3.

Conclusions

CdS NPs synthesized in an aqueous phase exhibiting strong and broad emission spectra between 480–520 nm were able to transfer energy in a wide wavelength region from green and red fluorescence dyes. Rh6G, RhB, and Texas red were tested as acceptors of the energy transfer

from the CdS NPs. The three dyes and synthesized CdS NPs exhibited good FRET behaviors. The energy transfer for a donor-acceptor system was compared depending on the concentrations of the acceptor Texas red dye. The prepared CdS NPs appeared to exhibit comparable FRET behaviors with an organic Cy3 dye. Our CdS NPs in an aqueous solution may be efficient FRET donors for organic dyes in a wide wavelength range between green and red colors.

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