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Study on Interaction between Chitosan and CdS Quantum Dots *via* Photoluminescence Spectra

Zhan LI, Yu Min DU*, Yan WEN

Department of Environmental Science, Wuhan University, Wuhan 430072.

Abstract: The interaction between CdS quantum dots and amino polysaccharide chitosan in aqueous solution was studied *via* photoluminescence (PL) spectra. The surface binding of chitosan with different molecular weight (MW) quenched the luminescence of QDs due to the elimination of radioactive anion vacancy centers. This process fits well with the Perrin model; lower MW chitosan exhibits higher quenching efficiency due to better availability to the surface.

Keywords: CdS, quantum dots, chitosan, interaction, photoluminescence.

Semiconductor nanoparticles, also known as quantum dots (QDs), have been extensively studied in the past two decades[1]. Recently, intense interest in QDs focuses on their biological applications as robust luminescent probes[2]. Generally the fluorescence of QDs is attributed to the recombination of charge carriers generated by light absorption and the surface state of QDs is very important to this photoluminescence (PL), it is also believed that anion vacancies play an important role, as the fluorescence is stronger in the presence of excess Cd^{2+} ions[3]. In fact, the use of QDs in a biological context is potentially more problematic because the high surface area and its interaction with bio-macromolecules might lead to reduced luminescence efficiency and photochemical degradation.

As a major kind of bio-macromolecules polysaccharide acts as bio-membrane component of most cells. The outer polysaccharide part usually protrudes up to 30 or more nanometers into the cell surrounding[4]. The polysaccharide is, therefore, most likely responsible for the first stage of short-range interaction between QDs and the cell. Thus, to investigate the effect of interaction with polysaccharide on the PL of QDs is necessary for their bio-applications; however, to the best of our knowledge there is still no such report. In this letter we examine the changes of PL spectroscopy of CdS QDs through polysaccharide surface binding, we choose low molecular weight (LMW) chitosan to mimic the outer polysaccharide part of the cell, that is because chitosan, (1, 4)-2-amino-2-deoxy-β-D-glucan, is a linear polysaccharide and the amino groups on chitosan backbone have strong chelating ability, these amino groups can act as hole-acceptors to modify the QDs surface state, which can be reflected by the PL spectra.

* E-mail: duyumin@whu.edu.cn

Experimental

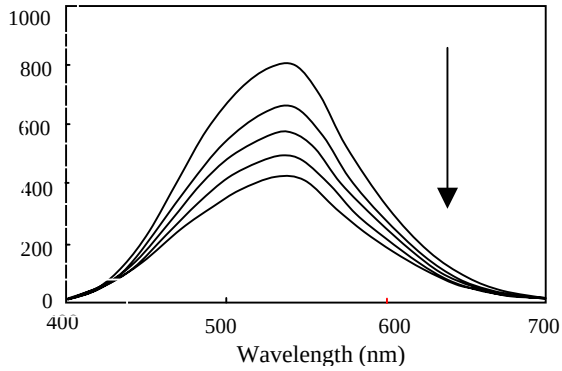
LMW chitosan was prepared by enzymatic degradation[5], followed with ultra filtration (PallFiltron Corporation, USA) to get three fractions of the sample. The molecular weight of the samples was measured by gel permeation chromatography (GPC) to be 864(CS-1), 2104(CS-2) and 8260(CS-3), respectively.

Luminescent CdS aqueous solution was prepared with sodium polyphosphate as stabilizer[6]: a 500 mL solution containing 6×10^{-4} mol/L $Cd(OAc)_2$ and 6×10^{-4} mol/L $Na(PO_3)_n$ was added dropwise with 1 mol/L Na_2S solution under stirring to get yellowish CdS aqueous solution. To enhance the luminescence intensity excess amount of Cd(Ⅱ) salts was used ($[Cd^{2+}]/[S^{2-}]=1.5$). The resulting CdS concentration was 4×10^{-4} mol/L. the UV-spectrum showed that the absorption onset of CdS QDs located at about 480 nm, indicating the resulting QDs diameter was about 5 nm according to the well-established calibration curve[3].

LMW chitosan samples were dissolved in double-distilled water to obtain 1 mg/mL solutions. 50 μL aliquots were added to 50 mL CdS solution every 10 minutes under stirring, PL spectra were recorded before each addition. Measurements of luminescence intensity as a function of chitosan concentration were carried out in the region 400-700 nm on a Shimadzu RF-5301 PC instrument.

Results and Discussion

Figure 1 Effect of increasing CS-1 addition on the PL spectra of CdS QDs.



The final chitosan concentrations expressed on molar amino group are: (from up to down) 0; 6; 12; 18; 24×10^{-5}mol/L.

The as-prepared CdS solution exhibits strong PL with the emission peak at 536 nm, due to excess Cd^{2+} resulting in large amount of anion vacancies on QDs surface. With the incremental addition of CS-1 solution the PL quenched markedly, as shown in **Figure 1** Controls were done with addition of equal volume of water and did not

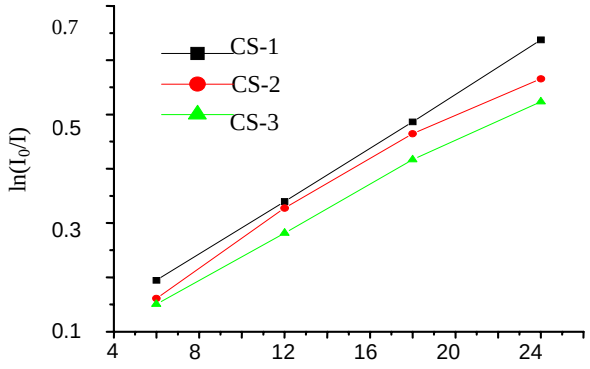
exhibit any noticeable change in PL spectra. Sample CS-2 and CS-3 exhibited similar quenching effect. This quenching therefore is viewed as a firm evidence of the role of chitosan in influencing the surface of CdS QDs. The amino groups of chitosan could coordinate with Cd^{2+} sites on the QDs surface, which are responsible for observed emission spectra. The elimination of these radiative centers resulted in PL quenching.

Attempts to fit changes in chitosan-induced CdS QDs emission intensity to a Perrin relationship gave satisfactory results, which was similar to those results observed in DNA-QDs interaction[7]. The Perrin model is valid for energy transfer between donor-acceptor components unable to change spatial positions with regard to one another on the time scale of the quenching process[8]. Since we did not observe any fluctuation in quenched spectra during this process, we therefore assume that this surface binding is irreversible. The Perrin relationship is given in the following equation:

$$\ln(I_0/I) = VN_0[Q]$$

Where I_0 and I are emission intensities in the absence and presence of chitosan, respectively. V is the volume of quenching sphere and N_0 is Avagadro's number, and [Q] is molar concentration of quencher, in this case the quencher refers to the amino group of chitosan. A plot of $\ln(I_0/I)$ *versus* [Q] should demonstrate linear behavior with a slope equal to VN_0. **Figure 2** illustrates the linear or near-linear behavior of $\ln(I_0/I)$ for CdS QDs emission after addition of three chitosan samples.

Figure 2 Perrin relationship for the quenching of the PL spectra of CdS QDs with chitosan of different molecular weight. Quencher concentration refers to [NH_2].



The similar slope of three curves indicated the chitosan samples have almost the same volume of the effective quenching sphere, which means that the electron transfer moods of these chitosan molecules were almost same with CdS QDs, *i.e*, the Cd^{2+} coordinated with amino groups and their interaction sites located on the particle surface. The curves for CS-2 and CS-3 demonstrate somewhat downward curvature at higher concentration of chitosan; it is easy to understand since at higher concentration the absorbed chitosan chains could bring difficulty for sorption, with the consideration of

larger spatial volume for higher MW chitosan chain this hindering effect become more obvious, in the result that the quenching efficiency is lowered for higher MW chitosan at higher concentration. We can also find in **Figure 2** that the samples with lower MW exhibits higher quenching efficiency. Since the adsorption of individual monomer within a polymer chain is cooperative[9]. *i.e*. adsorbed monomers facilitate the sorption of their neighbors by increasing their collision probability with the solid surface, the lower MW chitosan chain consist of less monomers has smaller energy barrier to overcome for conformational change, resulting in better availability and higher quenching efficiency to the QDs surface.

In summary, luminescence in CdS QDs surface can be quenched by the addition of chitosan; the quenching process fits well to a Perrin-model. The lower molecular weight chitosan exhibits higher quenching efficiency due to better availability to the QDs surface. This study will be helpful to understand the short-range interaction between luminescent QDs with outer polysaccharide of the cell in biological applications. Further, since the size of QDs (4-5 nm) is similar to those of globular protein, this investigation can also be regarded as a model of non-specific polysaccharide-protein interaction.

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