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Study on the interaction between CdSe quantum dots and chitosan by scattering spectra

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ABSTRACT

Two different stabilizing agents thioglycolic acid (TGA) and L-cysteine (L-Cys) capped CdSe QDs with the diameter of 2 nm were synthesized, large amounts of stabilizing agents connected to CdSe QDs surface through Cd–S bond. The interaction between chitosan and QDs had been investigated, respectively. The interaction lead to the remarkable enhancement of RRS, RNLS and the enchantments were in proportional to the concentration of chitosan in a certain range. Under the optimal conditions, compared with TGA–CdSe QDs, the interaction between L-Cys–CdSe QDs with chitosan owned more broad linear range 0.042–3.0 μg mL^{-1} and lower detect limits 1.2 ng mL^{-1}. The influences of factors on the interaction between chitosan with QDs and some foreign substances were all examined, which showed that the methods had a good sensitivity and selectivity. Based on this, it is hoped to build a method for the determination of chitosan using CdSe QDs as probes. Through Fourier transform infrared spectroscopy (FTIR) transmission electron microscopy (TEM), it was speculated that CdSe QDs interacted with chitosan to form a network structure aggregates through electrostatic attraction and hydrophobic forces. The reasons for the enhancement of RRS intensity were assumed as follows: resonance enhanced Rayleigh scattering effect, increase of the molecular volume, and hydrophobic effect.

1. Introduction

During the last two decades, there was an intense scientific and technological interest in making II–VI colloidal semiconductor nanoparticles also called quantum dots (QDs) for different applications [1–8] because of theirs unique excellent optical properties, such as wide absorption and narrow emission spectra, large extinct coefficients, resistance to photobleaching, long fluorescence lifetime, and size-tunable emission [9]. Up to now, there are a number of methods for the preparation of CdSe QDs, such as the sonochemical method [10,11], the microwave irradiation method [12], the organometallic precursor method [13,14], and so on [15]. The organometallic precursor method is the most popular route for the synthesis of high quality CdSe QDs. Compared with the organometallic routes, aqueous synthesis is more reproducible, cheaper, less toxic and the as-prepared samples have high aqueous stability and biological compatibility without any post-preparation [14].

Resonance Rayleigh scattering (RRS) is a special elastic scattering produced when the wavelength of Rayleigh scattering (RS) is located at or close to the molecular absorption band. In this case, the frequency of the electromagnetic wave absorbed by the electron is equal to its scattering frequency. Because of the intensive absorption of light energy of the electron, rescattering takes place [16]. RRS and RNLS including second-order scattering (SOS) and frequency doubling scattering (FDS) have been applied successfully to the study of aggregation of chromophores on biological macromolecules [17,18] and applied to the determination of biological macromolecules such as nucleic acids [19], proteins [20], inorganic ions [21], pharmaceuticals [22]. In particular, with the rapid development of nanotechnology, great attention has been focused on the using of nanoparticles as the RRS probes. For example, Au nanoparticles [23–28], Ag nanoparticles [29] and core–shell of Au–Ag nanoparticles [30], however, QDs have unique light scattering signals, and they are likely to be used as effective light scattering emission probes, while presently they were seldom used as RRS probes [31].

Chitosan, a fully or partially deacetylated product of its parent polysaccharide chitin, has attracted significant interest in the broad range of scientific research, including biomedical, agriculture, and environmental protection fields, because of its biodegradability, biocompatibility, and bioactivities [32–34], it is being considered in various countries as a dietary supplement of human consumption [35]. Its cationic nature leads to a strong interaction with CdSe QDs having an opposite charge. Based on this, it is hoped to build a method for the determination of chitosan using CdSe QDs as probes.

In this work, it was found that positively charged chitosan could bind with CdSe QDs to form a network structure aggregates via

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electrostatic attraction and hydrophobic forces in pH 4.5–7.5 Britton–Robinson (BR) buffer solution. Which caused a stronger RRS signal and the enhanced intensities of RRS were proportional to the concentration of chitosan in the certain range. Based on it, chitosan can be sensitively detected. The effective factors and optimum conditions of the reaction have been investigated. The sensitivity, selectivity, and the linear range for the determination of chitosan by RRS are reported. The reasons of RRS enhancement were investigated by FTIR, TEM and UV, and influential factors on the variation of RRS have been tentatively investigated.

2. Materials and methods

2.1. Materials

A Hitachi F-2500 spectrofluorophotometer (Hitachi Company, Japan) was used to record the RRS, SOS and FDS spectra and measure the scattering intensities. A UV-8500 spectrophotometer (Tianmei Corporation, Shanghai) was applied to record the absorption spectra. TECNAI-10 transmission electron microscopy (TEM) (Philips Company, Holland) was used to observe the appearance and size of nanoparticles. A PHS-3C pH meter (Leici, Shanghai) was used to adjust pH.

$CdCl_2{\cdot}2.5H_2O$ (Shanghai Chemicals Reagent Co., Shanghai), Se powder (Sinopharm chemical Reagent Co., Shanghai), thioglycolic acid (TGA, Sinopharm chemical Reagent Co., Shanghai), $NaBH_4$ (Tianjin Huanwei Fine Chemical Co., Tianjin), L-cysteine (Kangda chemical Reagent Co., Shanghai), Britton–Robinson buffer solution was used to control the acidity of the aqueous medium. All reagents were analytical grade without further purification and ultrapure water was used throughout.

2.2. Methods

Aqueous colloids of CdSe QDs solution was prepared according to previously published method [36]. Briefly, under N_2 atmosphere, Se powder (0.0200 g) and excessive sodium borohydride were added into absolute ethanol solution (10.0 mL) under magnetic stirring at room temperature, the colorless ethanol solution of NaHSe was prepared (step 1).

$CdCl_2{\cdot}2.5H_2O$ (0.0752 g) were dissolved in 100 mL ultrapure water, and 55 μL TGA stabilizer were added under stirring, then adjusted the pH to 11 by dropwising addition of 1 mol L^{-1} NaOH solution. Under stirring, H_2Se gas generated by the reaction of NaHSe with diluted H_2SO_4 solution (50 mmol L^{-1}) (step 2) was passed through the oxygen-free original solution together with a slow nitrogen flow for 30 min. CdSe QDs precursors were formed at this stage. The molar ratio of Cd^{2+}/TGA/HSe^- was fixed at 1:2.4:0.5. Then the resulting mixture was subjected to reflux for a certain time under N_2 condition with condenser, the salmon pink TGA–CdSe QDs solution was obtained.

The synthetical method of L-Cys–CdSe QDs was similar to TGA–CdSe QDs, the differences were list as follows: In step 1 the colorless water solution of NaHSe was prepared. Stabilizing agents thioglycolic acid were substituted by L-Cys, the molar ratio of Cd^{2+}/L-Cys/HSe^- was fixed at 1:2.5:0.25, the resulting mixture was subjected to reflux at 80 °C and adjusted the pH to 9 by dropwise adding of 1 mol L^{-1} NaOH solution in step 2.

CdSe QDs (1.0 mL), appropriate amount of buffer solution and chitosan were added into a 10 mL volumetric flask, then diluted with ultrapure water to the mark and mixed thoroughly with gentle shake. After incubation for 10 min, the RRS spectra of solution were examined. The relative RRS intensity (ΔI_{RRS}) of CdSe QDs and CdSe QDs–chitosan system was represented as $\Delta I_{RRS} = I_{RRS} - I^0_{RRS}$. Here I_{RRS} and I^0_{RRS} are the RRS intensity of system in the presence and absence of chitosan, respectively.

The intensities of SOS and FDS were measured at $\lambda_{ex} = 1/2\lambda_{em}$ and $\lambda_{ex} = 2\lambda_{em}$ under different incident light by the spectrofluorophotometer. The SOS and FDS spectra were obtained by constructing the wavelength incident light versus I_{SOS} and I_{FDS}. The SOS intensity (I_{SOS}) and FDS intensity (I_{FDS}) were measured for the reaction product, I^0_{SOS} and I^0_{FDS} for the chitosan blank were measured at maximum peaks of SOS and FDS.

3. Results and discussion

3.1. TEM images

Fig. 1 TEM images of TGA–CdSe QDs in the absence and presence of chitosan. The average diameter of CdSe QDs (a) was about 2 nm, it can be seen from (a) that the CdSe QDs were homogeneously distributed and not aggregated. When chitosan was added into the CdSe QDs solution, many irregular aggregates were observed from (b) that CdSe QDs interact with chitosan.

3.2. Spectral characteristics

3.2.1. L-Cys–CdSe QDs–chitosan RRS spectra

Fig. 2 shows the RRS spectra of L-Cys–CdSe QDs–chitosan. It can be seen that: (1) the RRS intensity of chitosan solution is very weak; (2) CdSe QDs has certain RRS intensities and the maximum scattering peak is located at 340 nm, and (3) when CdSe QDs reacted with Chitosan solution to form larger network structure aggregation, the RRS intensity of the solution can be greatly enhanced and a new RRS spectrum appears, and the maximum scattering peak is locked at 370 nm. At the same time, the

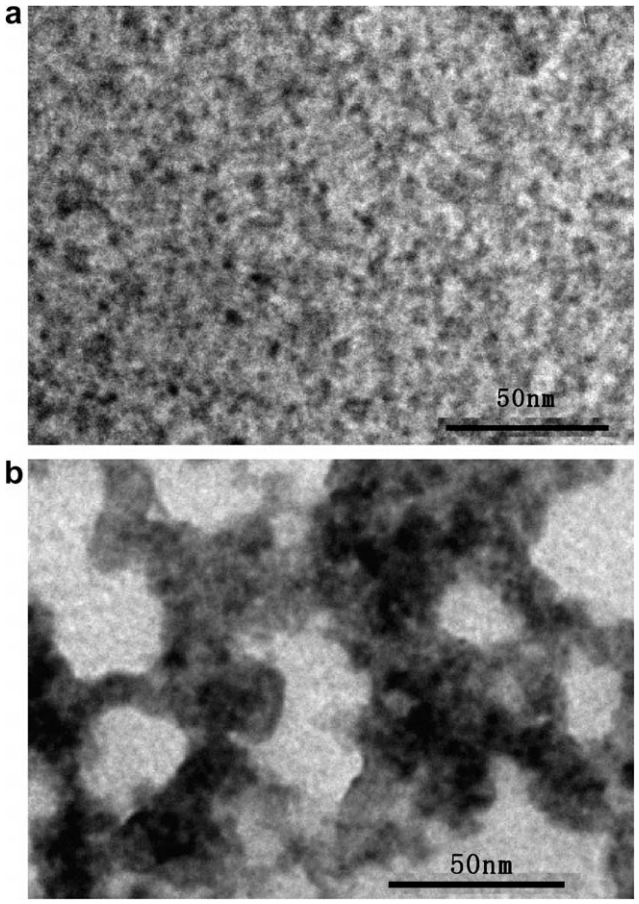

Fig. 1. TEM images of TGA–CdSe QDs (a) and presence of chitosan (b).