A new fluorescent composite based on CdS quantum dots immobilized on the multidentate biopolymer matrix is prepared through the graft copolymerization of the acrylamide onto kappa-Carrageenan. A variety of techniques like thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR) was used to confirm the structure of the obtained samples. To investigate the spectrofluorometric properties, fluorescence spectroscopy of the obtained quantum dots was studied.

1. Introduction

Semiconductor quantum dots (QDs), also called nanocrystals (NCs), have gained increasing attention in the past decade [1–3]. They have been widely investigated because of their potential use in sensors [4], laser materials [5], thin-film light-emitting devices (LEDs) [6–8], and biological labels. Among numerous possible applications of QDs, biological labeling will be pointed out [9, 10]. QDs exhibit larger photostability than organic dyes used routinely, since narrow excitation spectra of conventional dye molecules make difficult simultaneous excitation in most cases. However, QDs display size-dependent tunable florescence (FL) with broad excitation spectra and narrow emission band widths, which span the visible spectrum. This property of QDs allows simultaneous excitation of several particle sizes at a single wavelength, and therefore they facilitate multicolor experiments [11–14]. In addition, QDs have high photochemical stability, excellent resistance to chemical degradation and photodegradation, and good fluorescence quantum yields.

For most biological applications of QDs, their water solubility is indispensable. Three different approaches can be used to prepare water-soluble semiconductor QDs: ligand exchange [15, 16], encapsulation into a water-soluble shell (i.e., the silica or phospholipids) [17, 18], and surface coating with polymers [19, 20]. In comparison, silica encapsulation produces good stability but with larger sizes which are about tens of nanometers to several micrometers [21]. In ligand exchange, the stability of the nanocrystals is limited by the stability of ligands on the QD surfaces. The proper choice of ligand is therefore crucial in order to achieve functionality and retain the optical properties of the QDs, and it usually limits the final application range of the QDs [22]. In this context, polymers may be used as suitable substitutes for the small organic ligand molecules due to their good stability on the surface of QDs [23].

A number of strategies were developed to obtain polymer-coated QDs: (1) the surface coating of amphiphilic polymers on the QDs surface by hydrophobic interactions between the surface ligands of nanocrystals and polymers [24]; (2) the attachment of multidentate polymeric ligands directly onto the QD surface via multiple or single bonds [25]; (3) the polymerization of polymeric chains directly from the QD surfaces [26]. However, most synthesized polymers in
literatures are difficult to biodegrade and be further functionalized, which cannot meet the requirements of making low-cost, low-toxicity, and multifunctional water-soluble quantum dots.

Herein, we introduce a multidentate and natural biopolymer based on kappa-Carrageenan (κC) for preparation of CdS QDs with reasonable optical properties and high stability. κC is a kind of sulfated polysaccharides extracted from red marine algae. It is widely utilized in the industry because it can form reasonably stiff and thermoreversible gels in the presence of so-called gel-promoting salts at room temperature [27]. This polysaccharide is linear polymer consisting of chains of (1 → 3)-linked β-D-galactose and (1 → 4)-linked α-D-galactose units which are variously substituted and modified to the 3,6-anhydro derivative, depending on the source and extraction conditions [28–33]. Moreover, it is highly flexible molecules, which, at higher concentrations, wind around each other to form double-helical structures. A particular advantage is that they are thixotropic [34, 35], that is, they thin under shear stress and recover their viscosity once the stress is removed. Due to the strong ionic nature, it exhibits a high degree of reactivity. This material has been used in the field of drug delivery [36, 37], which creates the potential for their use as drug delivery systems in tissue engineering. In view of this, it was chosen as a base for producing biopolymer derivatives (Figure 1).

2. Materials and Methods

2.1. Materials. Commercial grade cadmium sulfate (CdSO₄·8H₂O, 99%), sodium thiosulfate (Na₂S₂O₃·5H₂O, 98%), thioglycerol (TG, 98%), acrylamide (AAm, 98%), and ammonium persulfate (APS) were purchased from Merck. κ-Carrageenan (κC) was obtained from Condinos, Denmark. All chemicals and solvents were used without further purification. Double-distilled water was used for synthesis and optical measurements.

2.2. Instrumental Analysis. FT-IR spectra of samples in the form of KBr pellets were recorded using a Jasco 4200 FTIR spectrophotometer. A Shimadzu UV-visible 1650 PC spectrophotometer was used for recording absorption spectra in solution. Fluorescence spectra were measured using SCINCO’s Fluorescence Spectrometer FluoroMate FS-2. All samples were placed in a 1.00 cm quartz cuvette either for UV or fluorescence measurements. The dynamic weight loss tests were conducted on a TA instrument 2050 thermogravimetric analyzer (TGA). All tests were conducted under N₂ atmosphere (25 mL/min) using sample weights of 5–10 mg over a temperature range of 25–750 °C at a scan rate of 20 °C/min. The mass of the sample pan was continuously recorded as a function of temperature. Transmission electron microscopy (TEM) was taken on a Zeiss TEM at an acceleration voltage of 80 kV. Samples for TEM were prepared by putting a drop of solution on a carbon-coated copper grid.

2.3. Sample Preparation. CdS QDs with maximum emission at 560 nm were synthesized using CdSO₄·8H₂O and Na₂S₂O₃·5H₂O as the precursors and thioglycerol (TG) as the capping agent, according to a known procedure with some modifications [38, 39]. CdS QDs were thermally grown, and colloidal solutions were formed. In a typical procedure, 100 mL aqueous solution of the reactants and the capping agent was prepared while the concentrations of

![Figure 1: Chemical structure of kappa-carrageenan.](image1)

![Figure 2: Comparison of (a) absorption, and (b) FL spectra of CdS-κC-g-PAAm-0, CdS-κC-g-PAAm-2, CdS-κC-g-PAAm-3, CdS-κC-g-PAAm-4, and CdS-TG after 5 minutes stirring (λ_ex for emission spectra = 380 nm) at room temperature.](image2)
CdSO₄·8H₂O, Na₂S₂O₃·5H₂O and thioglycerol were 5, 30, and 400 mM, respectively. The pH was adjusted 8 by adding appropriate amounts of NH₄OH solution. The reaction mixture was then heated at 100°C in an oil bath for 1 h. For preparation of κ-Carrageenan grafted onto polyacrylamide (κC-g-PAAm), 1 g of κC was added to H₂O (30 mL) in a three-neck reactor equipped with a mechanical stirrer while stirring (200 rpm). The reactor was immersed in a thermostated water bath preset at 80°C. After homogenizing the mixture, three different amounts of AAm monomers (3, 4, and 5 g) were added to the reaction mixture and stirred for further 20 min. Then, APS (0.15 g) in H₂O (5.0 mL) was added and the reaction was started. After 30 min, a viscous solution was formed. Then, synthesized CdS QDs was added to a transparent homogeneous solution of κC, polyacrylamide (PAAm), κC-g-PAAm-3 (means a graft copolymer sample which is prepared by mixing 1.0 g κC and 3 g PAAm), κC-g-PAAm-4 (means a graft copolymer sample which is prepared by mixing 1.0 g κC and 4 g PAAm), and κC-g-PAAm-5 (means a graft copolymer sample which is prepared by mixing 1.0 g κC and 5 g PAAm). The solutions were stirred for 30 min at room temperature to ensure homogeneous and extensive diffusion of the QDs into the polymer chains. Meanwhile, the optical properties of the solution were studied through UV and FL measurements at different times. After that, the ethanol was added to the solution, centrifuged, and the remainder was collected for further experiments.

3. Results and Discussion

The absorption and FL spectra of CdS QDs, as taken from their reaction mixture with different ligands after 5 minutes stirring, are reported in Figure 2. Both spectra were obtained at room temperature. The absorption spectrum shows a main peak, ascribed to the first optically allowed transition between quantum confined state in conduction and valence band. The FL spectrum is dominated by a broad emission in the 400–700 nm region which can be attributed to different particle sizes of QDs. As shown in both absorption and FL spectra of Figure 2, the biopolymer influence the CdS QDs optical properties. Recent measurements indicate the important role of functional groups of polymer chains which interact with the surface of CdS QDs and increase the optical properties of CdS QDs [20, 21].

To test the influence of the κC-g-PAAm-3/CdS ratio on the optical properties of CdS-κC-g-PAAm-3, we kept all other experimental variables constant, and different amounts of KC-g-PAAm-3 were added while the κC-g-PAAm-3/CdS molar ratio was adjusted to 0.5:1, 1:1, 1.5:1, 2:1, 2.5:1, 3:1, 3.5:1, 4:1, and 4.5:1. The temporal evolution of maximum FL intensity under different κC-g-PAAm-3/CdS ratio is shown in Figure 3. As one can see in Figure 3, the FL intensity increased monotonically to a maximum and then gradually fixed with the blue-shift of maximum FL intensity wavelength. At lower κC-g-PAAm-3/CdS ratio (0.5 : 1–1.5 : 1), the maximum FL intensity is located at a longer wavelengths while in the case of higher κC-g-PAAm-3/CdS ratio (2 : 1–4.5 : 1), the maximum FL intensity is located at the shorter wavelengths. That is to say of higher κC-g-PAAm-3/CdS ratio favors the QDs with shorter
emission wavelengths; while lower κC-g-PAAm-3/CdS ratio favors for the QDs with longer emission wavelengths. The mechanism of the influence of κC-g-PAAm-3/CdS ratio on the optical properties of CdS QDs can be explained by aggregation of CdS QDs in lower κC-g-PAAm-3/CdS ratio and uniformly distribution of CdS QDs on κC-g-PAAm-3 matrix in higher κC-g-PAAm-3/CdS ratio.

Due to the sensitivity of the CdS QDs on processes occurring at the QDs surface, the stability of the FL became a very important parameter for the application of QDs in optoelectronic devices or luminescent labels. The study of temporal stability of FL intensity suggested that our synthesized CdS-κC-g-PAAm-3 has a decline in optical properties over time (as shown in Figure 4). Nevertheless, while the CdS-κC-g-PAAm-3 had almost a strong FL intensity after 18 h, the FL of CdS-TG quenched during this period. It is caused by the increasing the concentration of hydroxyl/amide groups on the surface of CdS QDs.

Figure 5 shows the transmission electron microscopy (TEM) image of CdS-κC-g-PAAm-3 along with its particle size histogram, which indicates a good dispersion of CdS QDs in κC-g-PAAm-3 matrix. According to this histogram, the CdS QDs has different particle sizes (mean size is about 4.2 nm).

In order to verify the presence of CdS QDs in κC-g-PAAm-3, the thermogravimetric analysis (TGA) of CdS-κC-g-PAAm-3 was compared with κC-g-PAAm-3 (Figure 6). Three degradation step appearing in the curve of CdS-κC-g-PAAm-3 is same to the curve of κC-g-PAAm-3, which means that CdS-κC-g-PAAm-3 are produced. About 40 wt. % of the CdS-κC-g-PAAm-3 sample begins to decompose at 600°C, higher than the decomposing of κC-g-PAAm-3 (20% at 600°C), denoting the formation of robust bonding between κC-g-PAAm-3 and CdS QDs. The actual content of CdS QDs in polymer matrix is calculated about 20 wt. %.

Figure 7 shows the FT-IR spectra of (a) κC, (b) κC-g-PAAm-3, (c) CdS-κC-g-PAAm-3, and (d) CdS-TG. The bands observed at 841, 912, 1016, and 1220 cm$^{-1}$ can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycoside linkage and ester sulfate stretching of κC, respectively (Figure 7(a)). The broad band at 3200–3400 cm$^{-1}$ is due to stretching of OH groups in the polysaccharide substrate.
The product, κC-g-PAAm-3 comprises a κC backbone with side chains that carry on carbonyl functional groups (from amide groups) which are evidenced by a broad doublet peak around 1660 cm⁻¹ (Figure 7(b)). Figure 7(c) shows the FT-IR spectra of CdS-κC-g-PAAm-3 after ligand exchange process. It is clear that all main signals of κC-g-PAAm-3, copolymer (OH and amide stretching vibrations) are presented in Figure 7(c) which demonstrates the presence of biopolymers around the CdS QDs. The occurrence of a little shift in some signals of FT-IR spectrum in Figure 7(c) can be attributed to the chelating of the biopolymer functional groups on the surface of QDs. A representative FT-IR spectrum of the CdS-TG is illustrated in Figure 7(d). There is obvious difference between the FT-IR spectra of CdS-TG and the CdS-κC-g-PAAm-3. This indicates the formation of polymeric shell around CdS QDs.

4. Conclusion

In the present study, we report the synthesis of CdS-κC-g-PAAm-3 with facile process at ambient temperature in water. It was observed that the FL intensity of CdS QDs was increased after embedment of CdS QDs into κC-g-PAAm-3 biopolymer-based matrix. It is worth to mention that the entailed biopolymer-conjugated QDs has high stability and marked optical properties besides being more eco-friendly.

References


