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Synthesis and fluorescent properties investigation of CdSe quantum dots embedded in a biopolymer based on poly((2-dimethylaminoethyl) methacrylate) grafted onto κ-Carrageenan

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ABSTRACT

In this work, CdSe quantum dots (CdSe QDs) were successfully synthesized and embedded in a biopolymer based on poly((2-dimethylaminoethyl) methacrylate) grafted onto kappa-Carrageenan (κC) via a facile process. The synthesized samples were studied by transmission electron microscopy (TEM) and it showed that the CdSe quantum dots have an average size of around 3.5 nm which were dispersed in the biopolymer matrix. Fourier transform infrared spectrum (FT-IR) was used to characterize the functional groups on the surface of QDs and the structure of biopolymer samples. UV–vis and FL spectra were employed to study the optical properties of QDs before and after ligand exchange with modified κ-Carrageenan biopolymers. The obtained samples showed significant improvement in their thermal behavior as indicated by thermo gravimetric analysis (TGA). Lastly, the effect of some factors on the fluorescent properties of CdSe quantum dots has been investigated to obtain QDs with highest fluorescent intensities.

1. Introduction

Semiconductor nanocrystals (NCs) also referred as quantum dots (QDs), have attained great attention because of their broad excitation wavelength, tunable emission wavelength, bright fluorescence (FL), and high stability against photobleaching and chemicals [1–7]. Especially, QDs such as CdSe and CdTe have attracted much attention because they exhibit size dependent FL in the visible to red spectral region [8–13]. This feature makes them very attractive for various biological applications such as optical sensing, tracing, and imaging of biomolecules. Since aqueous synthesis is simpler, cheaper, less toxic, and the “as-prepared” samples are more water-soluble and biocompatible in comparison with non-aqueous routes, water-based synthesis of QDs has been developed as a promising alternative. In order to improve properties of QDs such as water solubility, redispersion capability, chemical stability, and non-specific binding property, many aqueous synthetic methods, as well as chemical methods were applied [14–19].

Recently, the incorporation of QDs into polymer matrices via synthetic routes or ligand exchange process has been shown to be promising alternative method for incorporation of QDs in water for different applications [20–22]. In this method, the polymer not only acts as a stabilizer to keep inherently metastable QDs kinetically stabilized but also provides inorganic QDs with growth controllability, flexibility, solubility, and processability. It is worth noting that the prerequisite for the development of this method with desirable properties is the achievement of good dispersion of QDs in polymer matrices, since the occurrence of QDs aggregation and phase separation in the polymer matrices can result in diminished or quenched fluorescence of QDs [23–26] such as FL behavior of QDs in organic dendrons [27], linear or hyperbranched polymers [28], chemically modified proteins [29], and amphiphilic polymers [30,31]. Furthermore, most of these works need high temperature, high pressure, and inert atmosphere protection. Therefore, it remains a challenge to produce high fluorescent, stable and water-soluble QDs via simple and economical methods.

kappa-Carrageenan (κC) is a kind of water-soluble and totally eco-friend polysaccharide which can be extracted from different species of marine red algae with a primary structure based on an alternating disaccharide repeating unit of α-(1–3)-D-galactose-4-sulphate and β-(1–4) 3,6-anydro-D-galactose (Fig. 1) [32–40]. Herein, we introduce a natural multidentate biopolymer based on poly((2-dimethylaminoethyl) methacrylate) grafted onto kappa-Carrageenan (κC) for preparation of CdSe QDs with reasonable optical properties and high stability.

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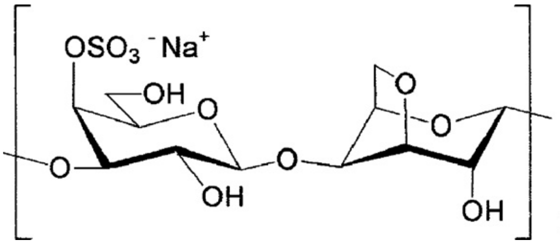


Fig. 1. The general structure of κC units.

2. Experimental

2.1. Materials

κC was obtained from Condinson, Denmark (2-dimethylaminoethyl) methacrylate (DMA) (98%), cadmium sulfate ($CdSO_4{\cdot}8H_2O$, 99%), selenium (Se, 97%), thioglycolic acid (TGCA) (99%), and sodium borohydride ($NaBH_4$, 99%), were purchased from Merck, Germany. Ammonium persulfate (APS) (99%) were obtained from Fluka and used without further purification. The solvents were analytical grade and used as received. Double distilled water was used for synthesis and sample preparation.

2.2. Instrumental analysis

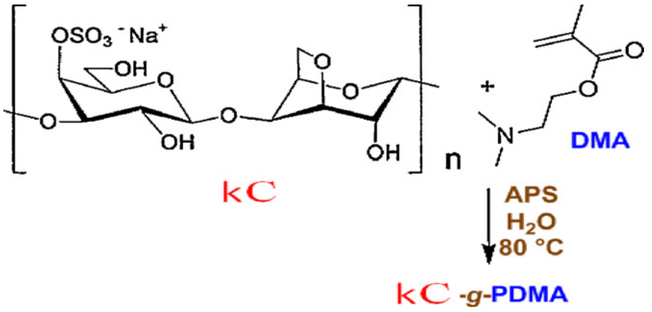
FT-IR spectra of samples in the form of KBr pellets were recorded using a Jasco 4200 FT-IR spectrophotometer. A Shimadzu UV-visible 1650 PC spectrophotometer was used for recording absorption spectra in solution. Fluorescence (FL) spectra were measured using SCINCO's fluorescence spectrometer FluoroMate 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 thermo-gravimetric analyzer (TGA). All tests were conducted under N_2 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. Preparation of CdSe-TGCA QDs

CdSe QDs were synthesized in water according to the previously reported method [41–44]. Typically, freshly prepared aqueous NaHSe solution (50 mL, 40 mM) was injected into N_2 saturated $CdSO_4{\cdot}8H_2O$ (150 mL, 25 mM) solution in the presence of thioglycolic acid (TGCA) (5 mL, 100 mM) to form the QDs precursors at pH = 5. The resultant precursor solution was refluxed at 100 °C for 10 min to prepare CdSe QDs.

2.4. Graft copolymerization of (2-dimethylaminoethyl) methacrylate onto κ-Carrageenan

In general, 1.0 g of κC was added to H_2O (30 mL) in a three-neck reactor equipped with a mechanical stirrer while stirring (200 rpm). The reactor was immersed in a thermo-stated water bath preset at 80 °C. After homogenizing the mixture, four different amounts of DMA monomers (0, 1, 2 and 3 mL (0–18 mmol)) were added to the reaction mixture and stirred for further 20 min. Then, APS (0.09 g (0.4 mmol)) in H_2O (5.0 mL) was added and the reaction was started. After 30 min, a viscous solution was formed (Scheme 1). In order to dewater the product and remove un-reacted monomers and homo-polymers, the product was kept in ethanol (200 mL) for 24 h. We denote all samples by their composition followed by a trailing to indicate how much DMA monomer in mL have been used to prepare the graft copolymers (e.g. κC-g-poly((2-dimethylaminoethyl) methacrylate)-2 or κC-g-PDMA-2 means a graft copolymer sample which is prepared by mixing 1.0 g κC and 2 mL of DMA).



Scheme 1. General route for the graft copolymerization of poly((2-dimethylaminoethyl) methacrylate) onto κC.

2.5. Embedment of CdSe QDs onto κC-g-PDMA biopolymers

The synthesized CdSe-TGCA QDs was added to transparent homogeneous solutions of κC-g-PDMA-0, κC-g-PDMA-1, κC-g-PDMA-2, and κC-g-PDMA-3 biopolymers. 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 via UV and fluorescence (FL) measurements at different time intervals. After that, the ethanol was added to the solution, centrifuged and the residue was collected for further experiments.

3. Results and discussion

3.1. Mechanism aspect for the synthesis of κC-g-PDMA

Radical polymerization is induced by an initiation step in which radicals are formed. Radicals are usually generated by decomposition of an initiator (frequently also called the catalyst). The radicals so formed then react successively with the monomer molecules in the propagation step leading to growing radicals (macroradicals) which are finally deactivated by chain transfer or termination.

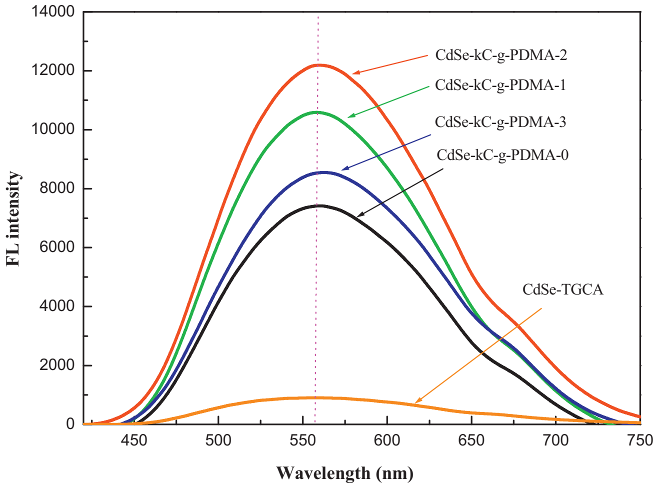


Fig. 2. Comparison of FL spectra of CdSe-κC-g-PDMA-0, CdSe-κC-g-PDMA-1, CdSe-κC-g-PDMA-2, CdSe-κC-g-PDMA-3, and CdSe-TGCA after 5 min stirring (λ_{ex} for emission spectra = 380 nm) at 25 °C.