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Fabrication of chitosan–CdSe/CdS/ZnS multilayer films by electrostatic self-assembly method

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ABSTRACT

The L-cysteine-modified CdSe/CdS/ZnS nanocrystals were synthesized in aqueous solution by using L-cysteine as stabilizer. The chitosan–CdSe/CdS/ZnS ultrathin multilayer films were fabricated on the pretreated quartz substrate by layer-by-layer electrostatic self-assembly method. The CdSe/CdS/ZnS nanocrystals were characterized by X-ray power diffraction (XRD), fluorescence spectrum and UV–vis spectrum. The UV–vis spectrum, fluorescence spectrum, IR spectrum, contact angle analysis and atomic force microscope analysis were used to characterize the chitosan–CdSe/CdS/ZnS ultrathin multilayer films. The results indicate that chitosan and CdSe/CdS/ZnS nanocrystals are alternatively deposited on the quartz surface, resulting in the buildup of a high quality chitosan–CdSe/CdS/ZnS multilayer films. The prepared ultrathin films of chitosan–CdSe/CdS/ZnS show good fluorescent property, which have potential application in biosensor.

1. Introduction

II–VI semiconductor nanocrystals (NCs) have received wide attention in the past decade due to their unique physical and chemical properties [1–6]. Comparing with conventional organic fluorophores, the semiconductor nanocrystals have better spectral characteristics, such as having a broad, continuous excitation spectrum and a narrow, tunable, symmetric emission spectrum. Besides, they are brighter, more stable against photobleaching, and do not suffer from blinking [4,5]. So the semiconductor nanocrystals have been extensively exploited in optoelectronic devices and biosensor [4–6].

The layer-by-layer electrostatic self-assembly method has been proved to be a very simple approach to assemble nanoparticles or functional molecules into ultrathin films with favorable stability [7]. By this technique, it is possible to control the thickness, composition and surface structure of the multilayer films. Fascinated by the advantages of this method, researchers have employed it to construct all kinds of films by self-assembling nanocrystals with active component and corresponding polyelectrolytes [8]. The fabrications of CdTe-PDDA [9,10] and CdSe-PPV [11,12] multilayer ultrathin films were reported by researches with the layer-by-layer electrostatic self-assembly method. However, there are only a few reports of using biopolymer chitosan as film forming materials [13].

Chitosan (CS) is a natural linear biopolyaminosaccharide derived from alkaline deacetylation of chitin, which has been found to be the second most abundant biopolymer in nature behind only cellulose. As a functional biomaterial, chitosan possesses many favorable qualities, such as having hydrophile, biocompatibility and biodegradability. The chemical structure of chitosan is shown in Fig. 1. The chitosan chains have plenty of free primary amino groups and hydroxyl groups, whose protonated amino groups stay positively charged under weakly acidic conditions, which make it possible to electrostatic self-assembly with anion. The more importantly, because of its semirigid macromolecule backbone, excellent film forming ability and non-toxic, the films made from chitosan possess favorable properties for their use in biosensor.

The synthesis of L-cysteine-modified CdSe/CdS/ZnS nanocrystals with favorable water solubility, stability and biocompatibility was reported by our research group [14]. The carboxyl groups of the L-cysteine modified on the surface of CdSe/CdS/ZnS provide a negative charge surface density, which make it possible for electrostatic interaction between CdSe/CdS/ZnS and the polycations. The fluorescent intensity of the CdSe/CdS/ZnS core/shell/shell nanocrystals has been proved to be stronger and more stable than that of single core CdSe and CdSe/CdS core/shell nanocrystals in water solution in our experiment [14]. Therefore, the negatively charged CdSe/CdS/ZnS core/shell/shell nanocrystals are used for interacting with positively charged chitosan on the pretreated quartz substrate to fabricate electrostatic self-assembly ultrathin films. To the best of our knowledge, there has been no report on the fabrication of multilayer films of chitosan–CdSe/CdS/ZnS by electrostatic self-assembly methods. The UV–vis spectrum,

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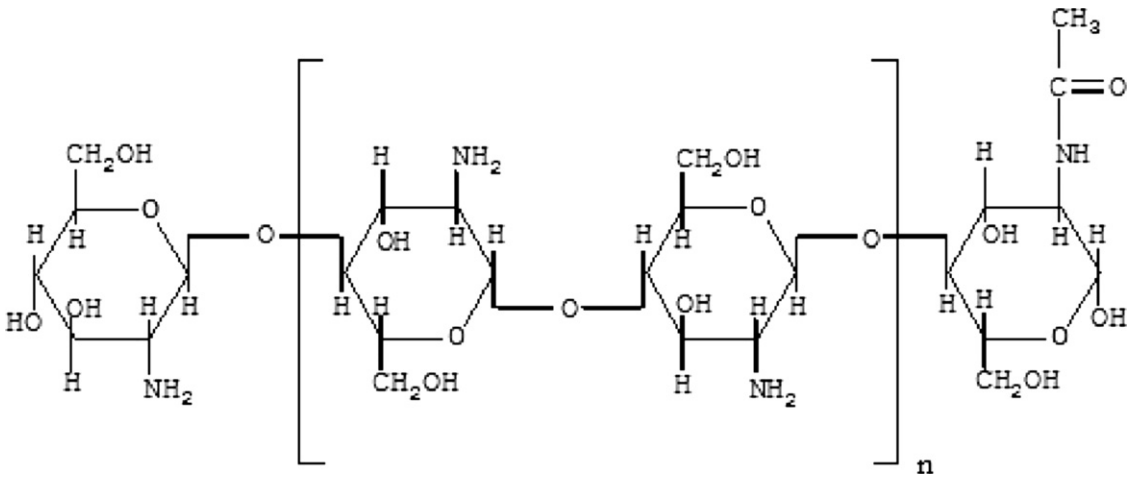

Fig. 1. The chemical structure of chitosan.

fluorescence spectrum, infrared spectrum, contact angle analysis and atomic force microscope (AFM) analysis were used to characterize the chitosan–CdSe/CdS/ZnS ultrathin films. And the growth uniformity, fluorescence property and surface morphology of the multilayer films were investigated.

2. Experimental

2.1. Chemicals and instruments

The XRD pattern was obtained on an X'pert-MPD X-ray power diffractometer (Philips, USA). The ultraviolet–visible (UV/vis) absorption spectra were recorded on a CARY50 UV/vis spectrophotometer (Varian, USA). The fluorescence spectra were performed on a F-1000 spectrofluorometer (Hitachi, Japan) with a quartz cell (1 cm × 1 cm). Infrared spectra were acquired on an AVATAR 360 FTIR spectrometer (Nicolet, USA). Contact angle analysis was performed on SL200B contact angle instrument (Suolun, China). AFM analysis was conducted on a Veeco di NanoScope IIIa atomic force microscope (Veeco di, USA).

All the chemicals including cadmium chloride, sodium sulfide, sodium hydroxide, selenium, sodium borohydride, zinc acetate, acetic acid, L-cysteine, chitosan (CS, the degree of deacetylation was 92.5%) and other routine chemicals were purchased from Shanghai Chemical Co., China. All reagents were of analytical reagent grade and were used without further purification. Double-deionized water was used throughout the experiment. A 2.5×10^{-3} mol/L NaHSe solution was prepared from the reaction between Se and $NaBH_4$ in water solution according to the procedure from literature [15].

2.2. Synthesis of L-cysteine-modified CdSe/CdS/ZnS core/shell/shell nanocrystals

The water-soluble CdSe/CdS/ZnS nanocrystals were prepared according to our report [14] as follows:

First, under a N_2 atmosphere, 30.2 mg of L-cysteine was added to 25 mL of pH 9.2 Tris–HCl buffer solution in a three-necked flask with magnetic stirring, and 25 mL of 2.5×10^{-3} mol/L cadmium chloride solution was added dropwise into above solution. Under moderate stirring, 18 mL of a freshly prepared nitrogen-saturated 2.5×10^{-3} mol/L NaHSe solution was quickly added into above reaction mixture. The transparent yellow solution was heated and incubated at 40 °C in a water bath with a slow N_2 flow for 1.0 h. The water-soluble nano-CdSe modified with L-cysteine colloidal solution was acquired.

Then, 35 mL of 2.5×10^{-3} mol/L cadmium chloride solution and 35 mL of 2.5×10^{-3} mol/L sodium sulfide solution were dropwise added alternatedly into L-cysteine-modified CdSe solution under a N_2 atmosphere. The solution was heated and incubated at 40 °C in a water bath with a slow N_2 flow for 1.0 h to acquire a yellow, transparent L-cysteine-modified nano-CdSe/CdS core/shell colloidal solution.

Finally, 35 mL of 2.5×10^{-3} mol/L zinc acetate solution and 35 mL of 2.5×10^{-3} mol/L sodium sulfide solution were slowly added alternatedly into the CdSe/CdS solutions at 40 °C with a slow nitrogen flow for 1.0 h to acquire a yellow, transparent L-cysteine-modified CdSe/CdS/ZnS core/shell/shell colloidal solution. The crude solution was concentrated by a rotary evaporator. The purified CdSe/CdS/ZnS nanocrystals powder was obtained through the ethanol precipitation procedure [16,17].

2.3. Preparation of chitosan–CdSe/CdS/ZnS multilayer films

The CS was dissolved in 2% acetic acid solution at a concentration of 2 mg/mL, and the solution was filtered by one-off pinhead strainer for subsequent use. The quartz substrate was treated according as literature [18] to produce a negatively charged surface. Immobilization of chitosan–CdSe/CdS/ZnS film was performed as follows. The freshly cleaned substrate was alternately immersed in aqueous solutions of positively charged chitosan for 20 min, then immersed in a aqueous solutions of negatively charged CdSe/CdS/ZnS nanocrystals for 20 min. Each immersion was followed by washing with distilled water and drying with a stream of nitrogen. This procedure was shown in Fig. 2. For each deposition cycle, a bilayer film of chitosan/nanocrystals was formed. This cycle was repeated *n* times to obtain a film of n bilayers.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the as-prepared CdSe, CdSe/CdS and CdSe/CdS/ZnS nanocrystals are shown in Fig. 3. In the pattern, the

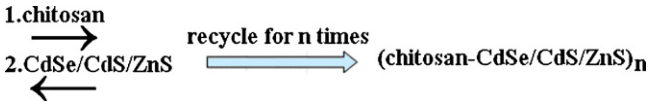

Fig. 2. Schematic representation of the fabrication of chitosan–CdSe/CdS/ZnS multilayer films.