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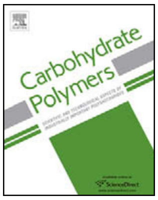

A novel method for fabricating hybrid biobased nanocomposites film with stable fluorescence containing CdTe quantum dots and montmorillonite-chitosan nanosheets

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ABSTRACT

A method was presented for fabricating the fluorescent nanocomposites containing CdTe quantum dots (QDs) and montmorillonite (MMT)-chitosan (CS). MMT-CS/CdTe QDs nanocomposites were prepared via a simple, versatile and robust approach combination of covalent and electrostatic assembly methods (Scheme 1). The negatively charged MMT was initially modified with positively charged CS through electrostatic assembly, followed by incorporation of CdTe-QDs into the MMT-CS nanosheets by covalent connections between the amino groups of CS and the carboxylic acid groups of thioglycollic acid (TGA). The X-ray diffraction (XRD), High resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and the FTIR were used to prove the QDs have intercalated into the MMT-CS matrix. The fluorescence emission spectra showed that the MMT-CS/CdTe QDs nanocomposites had the best fluorescence intensity compared with the bare CdTe QDs and CS-QDs.

1. Introduction

Chitosan is the principle de-acetylated derivative of chitin which is the second most abundant natural biopolymer after cellulose. Chitosan is a cationic copolymer composed of randomly distributed *N*-acetyl glucosamine and D-glucosamine, which exhibits some advantages such as nontoxicity, biodegradability and biocompatibility (Pan, Wu, Bao, & Li, 2011). Chitosan can interact with bio-macromolecules without degrading them. Moreover, chitosan is a positively charged, naturally occurring polysaccharide (Samal et al., 2012). For this reason, chitosan can interact strongly with negatively charged entities, including many lipids and proteins. Owing to the unique characters mentioned above, chitosan has been extensively investigated for several decades for drug delivery, tissue engineering, water engineering, and so on (Chen, Chen, Bai, & Li, 2013; Croisier & Jérôme, 2013; Zhang, Chan, & Leong, 2013).

On the other hand, the development of bio-hybrid nanostructured materials has received more attention in recent years (El Kadib & Bousmina, 2012; Ruiz-Hitzky et al., 2013). Inorganic nanostructured composites have unique mechanical, thermal, electronic or photic performance compared with the organic ones. A current trend in materials science involves the development of materials with special structure and character based on the combination of natural polymers with inorganic composites. The inorganic filler materials including clay minerals (Darder et al., 2006), layered double hydroxide (Wei et al., 2012), metal nanoparticles (Nandanan, Jana, & Ying, 2008), metal oxide nanoparticles (Petkova et al., 2014), carbon nanotube (Pan, Bao, & Li, 2011), graphene (Fan et al., 2010) and graphene oxide (Lin et al., 2012) have been employed to fabricate the hybrid nanostructured materials with natural polymers. What's more, semiconductor quantum dots (QDs) also have attracted considerable attention due to their unique properties including size-dependent optical properties, high photo-stability and narrow emission spectra compared with the conventional organic dyes (Kim, Woo, Jeong, & Han, 2011; Liang et al., 2013; Liang et al., 2014; Liu, Shi, Yu, Yang, & Zuo, 2010). QDs have been widely used in the fields of fluorescent materials(Zhang & Chen, 2014), optical bioimaging (Li & Zhu, 2013; Luo et al., 2013; Wu & Yan, 2013), photovoltaic devices (Chuang, Brown, Bulović, & Bawendi,

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2014; Kamat, 2013) and light-emitting diodes (Dai et al., 2014). Among various QDs materials, CdTe QDs possess unique fluorescence property. However CdTe QDs displayed a strong tendency towards oxidization and agglomeration due to its nanosize effects, especially in polymers (Xu et al., 2013). So, it is desirable to improve the compatibility and stability of these nanocomposites in biopolymers.

In this work, a novel method was employed to fabricate stable MMT-CS/CdTe hybrid nanocomposites. In this process, chitosan was first intercalated into montmorillonite to get MMT-CS hybrid composites, and then the CdTe QDs were in situ intercalated into MMT-CS to obtain MMT-CS/CdTe hybrid nanocomposites. The as-synthesized composites can show excellent fluorescence property in aqueous solution. Moreover, a film containing MMT-CS/CdTe with artificial nacre-like structure can also be produced by simple filtration. Importantly, the multilayer hybrid films of MMT-CS/CdTe obtained by a simple filtration method also present strong and stable fluorescence, which have potential use in optical or electronic applications.

2. Experiment

2.1. Materials

Sodium montmorillonite (Na-MMT, G105-PGW) nanoclays (particle size = 16–22 μm; aspect ratio = 200–400) were purchased from NANOCOR. Chitosan (≥95% deacetylate; viscosity$_{2\%}$ = 100–200 mPa.s), thioglycolic acid (TGA, AR, 90%) and $CdCl_2{\cdot}2.5H_2O$ (99.95%) were purchased from Aladdin. $NaBH_4$ (96%), tellurium (Te) power, acetic acid (AR, ≥99.5%) and NaOH (AR, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. The water used in this work was deionized water.

2.2. Preparation of MMT-chitosan nanosheets

MMT-chitosan nanosheets were prepared as follows (Yao, Tan, Fang, & Yu, 2010). 0.5 g MMT was dispersed in 100 mL of deionized water under vigorous stirring for two days and then the solution was stayed for 24 h and took the liquid supernatant for subsequent use. Solid content of the supernatant was 0.42 wt% and the pH was 10.14. 100 mL of 2 wt% chitosan (2 wt% of chitosan were prepared by dissolving chitosan in an aqueous solution of 2 wt% acetic acid for 24 h before use) were added into 100 mL liquid supernatant of the MMT solution and stirred for 6 h to form MMT-CS mixed solution. The mixture was centrifuged and washed with deionized water to remove the unabsorbed chitosan. Then we dissolved the MMT-CS into 100 mL deionized water for further use (solid content = 1.02%, pH 4.02).

2.3. CdTe QDs fabrication on the structure of MMT-CS nanosheets

100 mL re-dispersion MMT-CS solution and 80 mg $CdCl_2{\cdot}2.5H_2O$ were added into a three-neck bottle. After stirring for 3 h under N_2 atmosphere at room temperature, 72 μL TGA was added into the mixture and the pH of the mixture was adjusted to 9 using 1 mol/L NaOH (Li et al., 2013). After that, a freshly prepared NaHTe (Cao, 2012) solution (1.085 μL, 0.2 mol/L) was added into above mixed solution. Several reactions were carried out at 135 °C for different reflux time (1 h, 2 h, 3 h, 4 h) to synthesize negatively charged CdTe QDs solutions. The method to synthesis CdTe QDs aqueous solutions without MMT-CS was almost the same with that of MMT-CS/QDs. The only difference was that we used 100 mL deionized water instead of 100 mL re-dispersion MMT-CS solution.

2.4. Fabrication of multilayer films of MMT-CS/QDs

The multilayer films of MMT-CS/QDs were fabricated by a one-step layer-by-layer (LBL) (Han et al., 2011; Podsiadlo et al., 2007; Yao, Fang, Tan, Wu, & Yu, 2010) assembly method. A 15 mL aliquot of the MTM-CS/CdTe QDs nanosheets suspension was vacuum filtrated by a cellulose acetate filter membrane (0.22 μm, Jinteng) set on a sand core (4#, $\phi = 50$ mm) funnel. The wet hybrid film was rinsed gently with deionized water and dried at 40 °C by nitrogen flow. Consequently, the film with average thickness of 0.04 mm can be easily peeled off from the filter membrane.

3. Characterization

3.1. X-ray diffraction (XRD)

The X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffraction spectrometer using Cu-$K\alpha$ radiation at 80 kV and 40 mA. The scanning rate was 4°/min and the scanning scope of 2θ was 5–50° at room temperature.

3.2. Fourier-transform infrared (FTIR)

Fourier-transform infrared (FTIR) spectra of the samples were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher) in the frequency range of 4000–400 cm^{-1}. The specimens were prepared by the KBr disk method.

3.3. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was performed using an H-7650 Hitachi transmission electron microscope operating at 160 kV. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns were carried out using a FEI Tecnai G2 F30 S-Twin transmission electron microscope operating at 200 kV. All the samples were diluted 20 times in water and then dried on the carbon-coated copper grid for the TEM measurements.

3.4. Scanning electron microscope (SEM)

The morphology of films was investigated by using a scanning electron microscope (SEM Hitachi S-4800) equipped with an energy dispersive spectroscopy (EDS) attachment (EMAX), and the accelerating voltage applied was 20 kV. The films were cooled in liquid nitrogen and then broken, and the fracture surfaces were vacuum coated with gold for SEM.

3.5. Ultraviolet absorption and fluorescence emission

UV–vis absorption spectra were recorded on a Hitachi U-4100 spectrometer. Fluorescence spectra were recorded using a Hitachi F-4600 spectrometer at room temperature with excitation wavelength at 360 nm. All the solutions were diluted 50 times and all the films were cut into strip-type and fixed on a special fixture before UV–vis and fluorescence measurements.

3.6. Thermo gravimetric analysis (TGA)

Thermal properties of films were measured with a thermo gravimetric analyzer (Shimadzu, model DTG-60, Kyoto, Japan). The sample was heated from 25 °C to 600 °C with a heating rate of 10 °C/min in a nitrogen flow (30 mL/min) to avoid thermo-oxidative degradation.