

In situ synthesis and characterization of lead sulfide nanocrystallites in the modified hyperbranched polyester by gamma-ray irradiation

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Received 16 December 2004; received in revised form 11 January 2005; accepted 13 February 2005

Abstract

Lead sulfide (PbS) nanocrystallites in the modified hyperbranched polyester matrix were prepared in situ by ^{60}Co gamma-ray irradiation with sodium thiosulfate at room temperature, and characterized with Fourier transform infrared, X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence (PL). The average diameter of PbS nanocrystallites was estimated to be 7.8 nm on the basis of analysis of the TEM image and dispersed homogeneously within the modified hyperbranched polyester matrix. The possible formation mechanism of the PbS nanocrystallites under irradiation was discussed.

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Keywords: Nanoparticle; Hyperbranched polyester; Gamma-ray irradiation; Lead sulfide

1. Introduction

In recent years, it has been of great research interest that semiconductor nanocrystallites exhibit electronic, magnetic, optical, photochemical and photophysical properties greatly differing from those observed in the corresponding bulk materials due to quantum size effects, resulting from the predominant number of surface atoms in nanoscale materials [1]. Among these materials, lead sulfide (PbS) is an important IV–VI semiconductor with a narrow band gap (0.41 eV) and large exciton Bohr radius (18 nm), and widely used for potential photonic materials and Pb^{2+} ion-selective sensors. Many methods have been developed to fabricate PbS nanoparticles, such as micelle [2], microwave heating [3], photochemical reaction [4], hydrothermal process [5], gamma-ray irradiation [6], etc.

The application of dendimers polymers has opened a new way for producing nanomaterials with small size and narrow distribution because of their unique three-dimensional architectures [7]. For example, Zhao et al. reported a template-synthesis strategy for preparing metal nanoclusters with

dendimers as “nanoreactors” [8]. As we all know, the preparation of dendimers with a well defined and perfectly branching structure is usually complicated, while hyperbranched polymers with an imperfect branched structure can be easily produced in large amount by so called “one-step” approach preparation. Furthermore, hyperbranched polymers still maintain many of the architectural features of dendimers. Therefore, recently developed hyperbranched polymers are more attractive because of their simple synthesis routes, their unique highly branched molecular structures, and their large number of functional end groups in comparison with traditional linear polymers [9]. It is surprising, however, that reports on the preparation of nanoparticles in hyperbranched polymer are still less [10]. For instance, Zhai et al. prepared the self-assembly film with hyperbranched conjugated poly(phenylene vinylene) used as a template to deposit CdS nanoparticles in situ [11]. In our previous work, PbS/hyperbranched polyester nanocomposite hollow spheres through coordination and organometallic chemistry method were prepared [12].

In this study, a novel method for in situ preparation of PbS nanoparticles in the modified hyperbranched polyester were presented by ^{60}Co gamma-ray irradiation in the field

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of a 2.59×10^{15} Bq at room temperature. The metalion-containing hyperbranched ionomer was firstly synthesized and then in situ transformed to form PbS nanocrystallites by gamma-ray irradiation. The obtained PbS nanoparticles were characterized with Fourier transform infrared (FTIR), X-ray diffraction (XRD), transmission electron microscopy and photoluminescence (PL). Furthermore, the possible formation mechanism of PbS nanocrystallites was also proposed.

2. Experimental

All the reactants and solvents were analytical grade except for 1,4-dioxane, which was dried over potassium hydroxide and then freshly vacuum distilled before use. Hyperbranched polyester BoltornTM H20 was supplied by perstorp AB, Sweden, having an average of 16 hydroxyl groups per molecule. The modified BoltornTM H20 (MHP) was acquired using succinic anhydride to esterify end hydroxyl groups of polyester chains [13]. In a typical preparation, the modified BoltornTM H20 (0.435 g) solution in acetone (30 ml) was slowly dropped into a saturated aqueous lead nitrate (0.0015 mol) solution under stirring at room temperature. When the reaction mixture became milk-white, Na₂S₂O₃ (0.006 mol) aqueous solution (10 ml) and isopropanol (2 ml) were slowly dropped into above reaction vessel, and stirred for 10 min. The mixture was then irradiated in a 2.59×10^{15} Bq ⁶⁰Co gamma-ray source with a dose of 30 kGy. Finally, PbS powder was precipitated from the irradiated suspension colloids, then collected, washed with acetone and distilled water, and dried in vacuum at room temperature for 24 h.

The X-ray powder diffraction pattern was obtained with a Rigaku (Japan) D/max-γA X-ray diffractometer equipped with graphite monochromated high-intensity Cu Kα radiation ($\lambda = 0.154178$ nm). The accelerating voltage was set at 40 kV with a 100 mA flux. The scanning rate was 0.06°/s in the 2θ range of 10–70°. The IR spectrum was recorded with a Nicolet MAGNA-IR 750 Fourier transform infrared spectrometer using a KBr disk. The transmission electron microscopy (TEM) studies were carried out with a Hitachi Model H-800 (Japan), transmission electron microscope with an accelerating voltage of 200 kV. Photoluminescence spectrum was recorded on a Hitachi 850-fluorescence spectrophotometer with a Xe lamp of 300 nm excitation wavelengths at room temperature.

3. Results and discussion

3.1. Characterization

The corresponding XRD pattern of the obtained powder compared with that of BoltornTM H20 is shown in Fig. 1. All the diffraction peaks are indexed as cubic PbS (JCPDS Card File no. 5-592). The average crystalline size, which

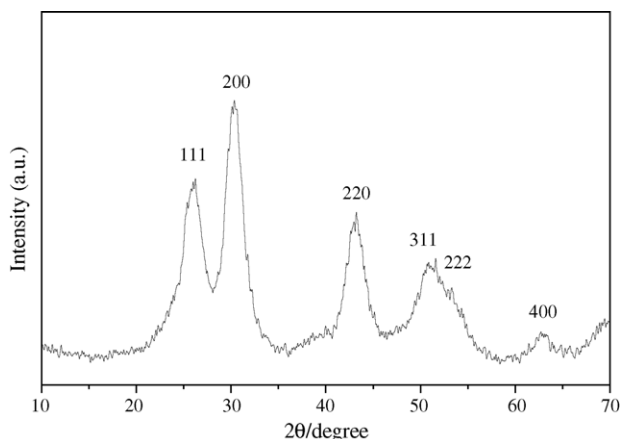


Fig. 1. XRD patterns of the product.

was determined from the half-width of diffraction peak using the Debye–Scherrer equation, was approximately 6.7 nm [14]. However, the crystalline diffraction peaks for modified BoltornTM H20 are not observed. Hyperbranched polymers exist generally in an amorphous because of their highly branched architectures, which make the molecules very hard to stack compactly [15].

Plotted in Fig. 2 are FTIR spectra of the modified hyperbranched polyester with and without the loading of Pb²⁺ ions or PbS. The characteristic peaks at 3445, 1733 and 1162 cm⁻¹ in the IR spectrum of the powder are assigned to –OH, ester C=O and C–O groups [13], respectively, for the modified hyperbranched polyester. And then, a new absorption peak at 1563 cm⁻¹ shows up when the modified hyperbranched polyester is loaded with Pb²⁺ ions. This peak can be attributed to formation of carboxylic lead group in the modified hyperbranched polyester–Pb²⁺ ions (curve b). The peak disappears basically after the sample is irradiated. Moreover, an extra weak peak was detected at 835 cm⁻¹, corresponding to Pb–S band, as shown in curve c [16].

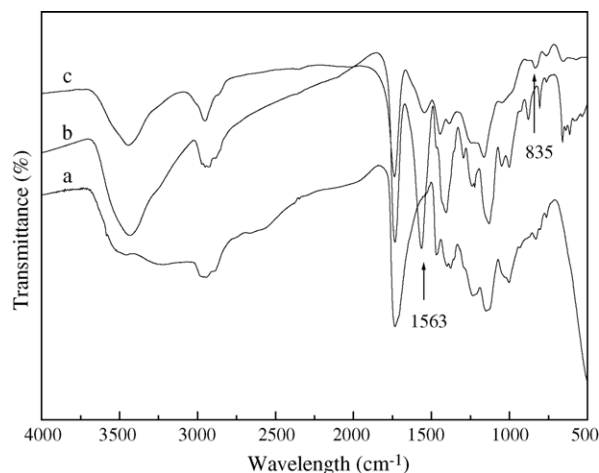


Fig. 2. FTIR spectrum of the modified BoltornTM H20 (curve a), the modified BoltornTM H20–Pb²⁺ ionomers (curve b) and the modified BoltornTM H20–PbS (curve c).

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