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Physica E 30 (2005) 96–100
PHYSICA E
www.elsevier.com/locate/physe

Large two-photon absorbance of chitosan–ZnS quantum dots nanocomposite film

Xiaohui Wang[a], Yumin Du[a,*], Sha Ding[b], Lihong Fan[a], Xiaowen Shi[a], QuQuan Wang[b,c], Guiguang Xiong[b,c]

[a]*College of Resource and Environmental Science, Wuhan University, Wuhan 430072, China*
[b]*Department of Physics, Wuhan University, Wuhan 430072, China*
[c]*Center of Nanoscience & Nanotechnology Research, Wuhan University, Wuhan 430072, China*

Received 6 June 2005; accepted 14 July 2005
Available online 12 September 2005

Abstract

ZnS semiconductor nanoparticles with average size of 3.4 nm were prepared in situ in chitosan film. TEM, UV–vis spectra and PL spectra show the ZnS nanoparticles in chitosan template were monodispersed and well passivated. The two-photon absorption coefficient (β) of the chitosan–ZnS quantum dots (QDs) nanocomposite film was obtained to be 2.29×10^2 cm/Gw from a standard Z-scan setup with femtosecond laser pusles at 790 nm wavelength. Results show the novel biomacromolecule/QDs nanocomposite film has large third-order optical nonlinear absorption, the mechanism responsible for which was discussed.

PACS: 78.66.−w; 78.66.Sq; 42.70.−a; 42.65.−k

Keywords: ZnS quantum dots; Chitosan; Two-photon absorption; Z-scan

1. Introduction

Recently, fabrication of inorganic nanoparticles in solid polymer matrixes has attracted more and more attention because the combination of inorganic nanoparticle and polymer provide a simple route to stable and processable material integrating the promising properties of both components [1]. Polymers are considered a good choice as host materials, because they can be designed to yield a variety of bulk physical properties, and they normally exhibit long-term stability and possess flexible reprocessability. Interesting optical properties such as fluorescence, electroluminescence and optical nonlinearity have already been observed in these organic–inorganic composites.

Nonlinear optical materials with large third-order nonlinearity are important in future high-speed communication network as all-optical switching, modulating and data processing. Semiconductor quantum dots (QDs) with dimensions close to the Bohr radius of electron–hole pair have received tremendous attention within recent years owing to their unique nonlinear optical properties. Recently, Lin et al. [2] have reported a large optical Kerr coefficient of -8.4×10^{-14} cm^2/W for CdS NCs in poly (methyl methacrylate) (PMMA) with femtosecond laser pulses at 815 nm. He et al. [3] reported a large third-order nonlinearity of CdS NCs embedded in Nafion films. Capped CdS NCs in polydiacetylene [4] and polystyrene [5] were also reported for enhanced nonlinearity in compare with bulk materials.

Chitosan, owing to its unique biocompatibility and bioactivities, attracted great interests in the field of nanotechnology in recent years. Many unique properties of chitosan makes it a suitable matrix to synthesis QDs: firstly, its well-defined polymer chains could prevent QDs from agglomeration during the growth; second, it is easy to be cast into film which imparts favorable bulk mechanical properties to the inorganic nanoparticles; third, its surface functionalization of nanoparticles serves to passivate the

*Corresponding author. Tel.: +86 027 68778501; fax: +86 027 68778501.
E-mail address: duyumin@whu.edu.cn (Y. Du).

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doi:10.1016/j.physe.2005.07.017

QDs' surface and improve their properties. Further, recent work revealed that polysaccharide plays an important role in the biosynthesis of semiconductor sulfide nanoparticles [6]. We have prepared CdS QD chitosan biocomposite using biomimic method [7,8] in the previous work.

In this paper, we report a simple approach to incorporate ZnS nanoparticles into a chitosan network. We make use of the unique microstructure formed in the network due to clustering of chelating groups such as $-NH_2$ as a confined medium to synthesize the nanosized particles. The resultant ZnS–chitosan hybrid composite was a homogeneous transparent film. We investigated the growth and morphology of the nanoparticles and characterized the linear absorption and fluorescence properties of the composites. The nonlinear optical properties of the composites were measured through a *Z*-scan technique at 790 nm. Large two-photon absorbance was observed, and the origins of the observed nonlinear absorbance were discussed.

2. Experimental

Chitosan/ZnS NCs nanocomposite film was prepared using a biomineral method as follows: firstly, chitosan with molecular weight of 200 kDa and degree of deacetylation of 95% was purified before use. Chitosan dilute acetate solution with concentration of 2%(w/v) was prepared. Under the protection of N_2 and with stirring, chitosan formed complexes with Zn^{2+} ions through the reaction with zinc acetate salts for 12 h. Then the solution was cast on clean glass slides, which was afterward dried in vacuum. After drying, the film was immersed in fresh Na_2S solution for certain time. With the formation of ZnS QD, the color of the films was transferred from transparent to whitish. Then the film was washed using saturated NaCl solution, and dried under N_2 to get a smooth transparent white nanocomposite film.

In our experiment, UV–vis and PL spectra have been obtained on a Shimadzu UV-1601 spectrometer and a Hitachi F-4500 PC fluorometer, respectively. TEM observations were performed on JEOL JEM2010 TEM and JEM 2010FEF HRTEM with electron-energy loss spectroscopy (EELS) and Gatan CCD cameras, respectively, operated at 200 kV. The two-photon absorption of the composite film was measured by using femtosecond time-resolved pump probe. The laser pulse used was generated by a mode-locked Ti: sapphire laser (Tsunami, Spectra-Physics), operating at a repetition rate of 76 MHz with a pulse duration of 150 fs and a wavelength of 790 nm.

3. Results and discussion

Fig. 1 showed the molecular structure of of chitosan, which had highly regular structure and was soluble in acid environment. The orderly sited $-NH_2$ groups, provided a major contribution to the well dispersion of ZnS nanocrystals. And the molecular chain and electrostatic repulsion could prevent the aggregation of the nanoparticles during their growth. Thus a stable biopolymer/ZnS NCs composite was obtained.

TEM image of the chitosan/ZnS nanoparticle composite was shown in Fig. 2(a). Nearly monodisperse ZnS particles were obtained with average size of 3.4 nm. Fig. 2(b) was the HRTEM image of one single ZnS nanocrystal, which was of high crystalline properties. It was shown that the lattice fringes of ZnS QD capped by CS were regular and disciplinary indicating lacking of surface defects.

Light absorption leads to an electron in the conduction band and a positive hole in the valence band. In small particles they are confined to potential wells of small lateral dimension, and this leads to a quantization of their energy levels. The phenomena arise when the size of a colloidal particle becomes comparable to the de Broglie wavelength of a charge carrier [9]. Fig. 3 displays the absorption onset of ZnS QDs synthesized in chitosan film to be at 356 nm, blue shifted with bulk ZnS material indication of quantum confinement effect. And the corresponding average particle size was 3.9 nm, which reconfirmed the result of TEM.

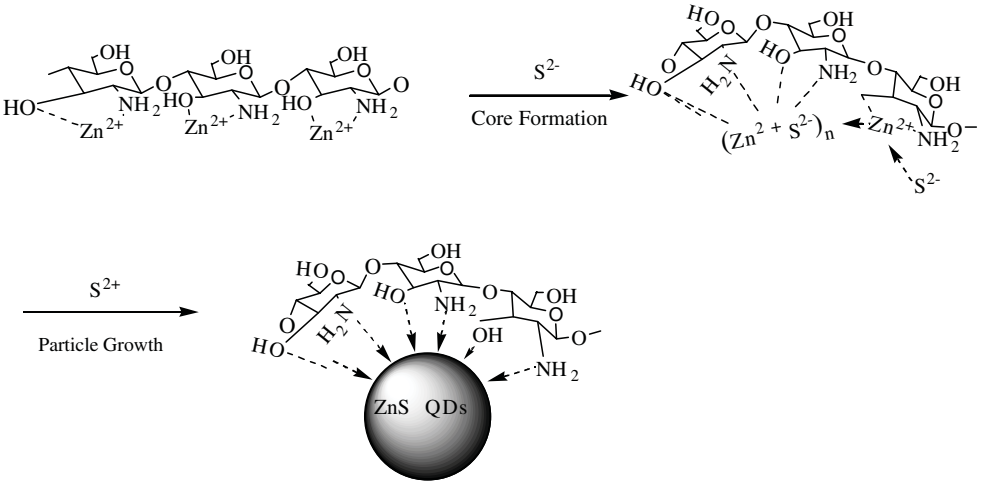

Fig. 1. Schematic presentation of the formation of ZnS QDs in chitosan matrix.