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Synthesis and luminescence properties of CdSe:Eu NPs and their surface polymerization of poly(MMA-co-MQ)[☆]

Junfang Gao, Junhong Yang, Shengli Yong, Lijing Liu, Xingwang Liu^{*}

Department of Chemistry, Baotou Teachers College, Baotou 014030, China

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ABSTRACT

CdSe:Eu nanoparticles (NPs) were synthesized using an oil phase method and the substitution of Cd²⁺ with Eu³⁺ was confirmed by XRD, TEM, UV-Vis absorption and fluorescence emission analyses. The CdSe:Eu NPs are monodispersed and uniform spherical particles with a diameter of 3.2 nm, bigger than the pure CdSe NPs (2.3 nm), but with a similar cubic structure as CdSe NPs. Compared with those of pure CdSe NPs, both emission spectrum and absorption spectrum of CdSe:Eu NPs are red-shifted. The CdSe:Eu NPs are incorporated into poly(MMA-co-MQ) to afford poly(MMA-co-MQ)-CdSe:Eu NPs with the cubic structure and particle size (~3–4 nm) similar to those of CdSe:Eu NPs. The TEM imaging suggests that the CdSe:Eu NPs are uniformly dispersed in poly(MMA-co-MQ) without any obvious aggregation. The fluorescent emission peak and absorption peak of poly(MMA-co-MQ)-CdSe:Eu NPs are between those of CdSe:Eu NPs and poly(MMA-co-MQ), possibly due to the energy transfer caused by the interactions of Cd or Eu atoms on the surfaces of CdSe:Eu NPs with the N and O atoms of poly(MMA-co-MQ). These CdSe:Eu and poly(MMA-co-MQ)-CdSe:Eu NPs with tunable photoluminescence properties can be potentially used for the fabrication of optical and optoelectronic devices.

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1. Introduction

In recent years, the lanthanide doped semiconductor NPs have attracted comparative attentions due to their high photostability and strong luminescence.^{1–6} They have been widely used in the components of light emitting diodes (LEDs),⁷ novel optoelectronic devices,^{8,9} and biological labels,¹⁰ etc. Lanthanide ions possess unique properties of sharp spectral lines (4f–4f) in solid phase. The spectral intensities of trivalent lanthanide ions can be fine-tuned by choosing the appropriate embedding medium.¹¹ Various lanthanide ions doped media, especially the lanthanide ions doped semiconductor NPs, have been prepared.^{12–16} The optical properties of these semiconductor NPs can be tuned by doping with various lanthanide ions¹⁷, such as Eu³⁺ doped CdTe,¹⁸ Yb³⁺ doped CdTe,¹⁹ Mn²⁺ and Eu²⁺ co-doped ZnS²⁰ and Eu³⁺ doped ZnSe.²¹ CdSe is highly stable and possesses a good optical transmittance

in the near infrared region. There has been growing interest in various lanthanide ions doped CdSe NPs, such as the Yb doped and Eu doped CdSe NPs, that have been successfully synthesized and exhibit the properties of both lanthanide elements and CdSe.⁵ Although the lanthanide ions doped CdSe NPs possess good luminescent properties, their exposure to the surrounding media, such as oxygen and humidity in air, can cause aggregation and Ostwald ripening, even under ambient conditions,²² which affects the stability of their fluorescence quantum yield and functionalization. To improve the stability and functionalization of the lanthanide doped CdSe NPs, it is necessary to modify the surface of these particles.

Conjugated-polymer/NPs nanocomposites have been extensively studied for their applications in photovoltaic devices.^{23–25} Conjugated polymer photovoltaic devices have many positive properties that may provide the means to overcome the current hurdles toward low-cost photovoltaics.²⁶ Combining the properties of NPs with the intrinsic functionalities of organic or biomolecular systems may yield hybrid materials with novel properties and functions.²⁷ For example, the hydrophobic CdSe-based NPs were successfully transferred to aqueous solutions by encapsulating CdSe NPs with amphiphilic molecules and used as biolabeling agents.²⁸ The introduction of NPs into organic solar cells successfully improved the device performances.²⁵ The most representative

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^{*} Corresponding author.

E-mail address: 66090@btcc.edu.cn (X. Liu).

work is a simple poly (methyl methacrylate) (PMMA) coated, and core/shell structured CdSe/ZnSe NPs with ultra-dispersion stability and a high fluorescence quantum yield of above 80%. The NPs were able to prevent chemical degradation, such as aggregation and Ostwald ripening.²⁹ However, the PMMA coating is a complicated and less compatible method due to the selective polymerization.

8-hydroxyquinoline (HQ) and its derivatives have been extensively studied in analytical chemistry, biochemistry, and organic materials because they can facilitate form stable complexes with metal cations.³⁰ HQ-metal complexes are the representative small organic molecules of luminescent materials. In 1987, Tang and his collaborators reported a highly efficient 8-HQ aluminum (Alq₃) based electroluminescent device as a light emitting layer.³¹ It is known that semiconductor NPs such as ZnS and CdSe have a great number of surface metal atoms that can coordinate with HQ to form stable fluorescent complexes on the surface of NPs. The inherent luminescent emission of semiconductor NPs may interact with that of the HQ-metal complexes formed on the NP surface. Therefore, here we are interested in knowing whether the optical properties of the poly(MMA-co-MQ)-CdSe:Eu NPs composites can be tailored by the interaction between the functional ligand (poly(MMA-co-MQ)) and semiconductor CdSe:Eu NPs when poly(MMA-co-MQ) is anchored to the semiconductor NPs. However, to our knowledge, there is no report on this aspect. In this paper, 5-(2-methacryloylolethylloxymethyl)-8-quinolinol (MQ) and methylmethacrylate (MMA) were copolymerized and selected as functional ligand because double bonds of MQ can copolymerize with MMA to form stable covalent polymer nanocomposites as illustrated in Scheme 1. The synthesis of Eu³⁺-doped CdSe (CdSe:Eu) NPs with high quantum yields (YQs) firstly were carried out via an organic phase route. To realize the functionalization of the CdSe:Eu NPs, poly(MMA-co-MQ) were conjugated to the surface of the CdSe:Eu NPs through a ligand-exchange process to obtain the surface polymerization of poly(MMA-co-MQ)-CdSe:Eu NPs and an excellent luminescence properties. We discussed the Eu³⁺ incorporation in CdSe, the effect of the functional ligand poly(MMA-co-MQ) and luminescence mechanism of poly (MMA-co-MQ) surface functionalized CdSe:Eu.

2. Experimental

2.1. Synthesis of CdSe:Eu NPs

CdSe:Eu NPs with the Se:Cd:Eu molar ratio of 1:1:0.05 was prepared as follows.

Solution A (Se precursor): 4 mmol Se powder was dissolved in 20 mL octadecylene, degassed at room temperature, and stirred at

200 °C under a nitrogen atmosphere for 3 h until the powder was completely dissolved.

Solution B (Cd precursor): 2 mmol CdO was dissolved in the mixture of 3 mL oleic acid and 17 mL octadecylene, degassed at room temperature, and heated at 160 °C under a nitrogen atmosphere for 30 min until the powder was completely dissolved.

Solution C (Eu³⁺ precursor): 0.025 mmol Eu₂O₃ was added to 3 mL glacial acetic acid and stirred at 130 °C until completely dissolved. The Eu₂O₃ solution was then dried at 160 °C, re-dissolved in the mixture of 0.6 mL oleic acid and 4 mL octadecylene, degassed at room temperature, and heated at 160 °C under a nitrogen atmosphere until the solution became clear.

Eu³⁺ doped CdSe NPs: Solutions B and C were added to three flasks, degassed, and heated at 230 °C under a nitrogen atmosphere. A solution of 10 mL A was quickly injected into the flasks containing solutions B and C. The reaction mixture was sampled and measured for fluorescence intensity at specific time intervals. The final reaction solution was precipitated with excess acetone and carrene, centrifuged and dissolved in hexane. The precipitation was repeated 3 times, and the precipitate was dried at 40 °C to afford CdSe:Eu NPs.

2.2. Preparation of poly(MMA-co-MQ)-CdSe:Eu NPs

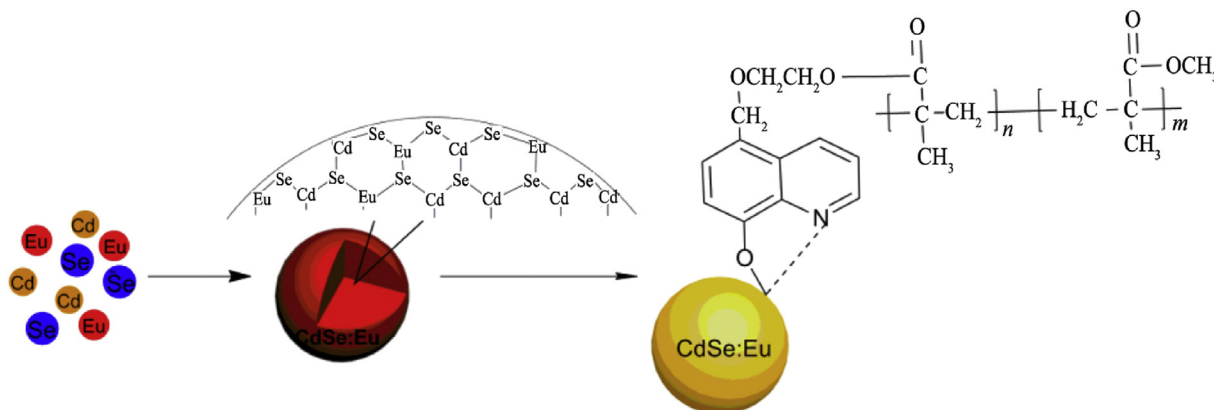
Poly(methylmethacrylate-co-5-(2-methacryloylolethylloxymethyl)-8-quinolinol)-CdSe:Eu NPs (poly(MMA-co-MQ)-CdSe:Eu NPs) were synthesized at the mass ratios of poly(MMA-co-MQ):CdSe:Eu of 1:0.01, 1:0.05 and 1:0.1, respectively. The typical synthesis process is as follows.

Poly(MMA-co-MQ): MQ was synthesized as reported by Du et al.³² MQ (2 mmol, 0.5 g), MMA (80 mmol, 8 g), and azodiisobutyronitrile (AIBN) (0.6 mmol, 0.1 g) were dissolved in 15 mL toluene, heated at 80 °C under a nitrogen atmosphere for 6 h, and precipitated with methanol to afford poly(MMA-co-MQ).

Poly(MMA-co-MQ)-CdSe:Eu: 1 g poly(MMA-co-MQ) and 0.05 g CdSe:Eu NPs were mixed in toluene, heated at 50 °C for 12 h under a nitrogen atmosphere, precipitated with methanol, and suction filtered. The filter cake was dissolved in toluene and precipitated with methanol. The precipitation was repeated 3 times, and the final precipitate was vacuum dried at 40 °C to afford poly(MMA-co-MQ)-CdSe:Eu NPs.

2.3. Characterization

UV-visible (UV-Vis) absorption spectra were measured with a PE Lambda 950 spectrophotometer. Emission spectra were collected on a Horiba JY FluoroLog-3 spectrophotometer using a Xe lamp as



Scheme 1. Synthesis of CdSe:Eu NPs via oil phase and fabrication of surface polymerization CdSe:Eu NPs with poly(MMA-co-MQ).

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