



High luminescence, organic–inorganic nanocomposite films with covalently linked 8-hydroxyquinoline anchored to ZnS nanoparticles

Yongli Shi^a, Yuqin Fu^b, Changli Lü^{a,*}, Li Hui^a, Zhongmin Su^a

^aInstitute of Chemistry, Northeast Normal University, Changchun 130024, PR China

^bCollege of Life Sciences, Jilin Agricultural University, Changchun 130118, PR China

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ABSTRACT

A series of transparent, highly fluorescent, organic–inorganic nanocomposite films were prepared by incorporating mercaptoethanol-capped ZnS nanoparticles into a copolymer of trialkoxysilane-capped poly(MMA-co-Hq-CH₂-HEMA) carrying an 8-hydroxyquinoline (Hq) unit, followed by ligand exchange and sol–gel processing. Electron microscopy revealed that the ZnS nanoparticles were uniformly dispersed in the organic–inorganic hybrid matrix regardless of the content and matrix composition. The hybrid nanocomposites had good optical transparency in the visible region. The nanocomposites that contained the ZnS nanoparticles were stable and displayed high fluorescence emission at 500 nm, which differed from that of hybrid materials obtained by simply blending the zinc ions or bis(8-hydroxyquinoline) zinc compound with the copolymer matrix. Thermogravimetric analysis indicated that the nanocomposite materials had high thermal stability.

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1. Introduction

Since the first, efficient, low-voltage-driven, organic light-emitting diodes (OLEDs) based on tris(8-hydroxyquinoline) aluminium (Alq₃) were reported by Tang and co-workers in 1987 [1], 8-hydroxyquinoline (Hq) and its metalloquinolates have attracted great interest because their high thermal stability and good electroluminescence properties make them important prototypical electron transport and emitting materials for OLED devices [2–4]. Among the metalloquinolates, Alq₃ and zinc(II)-bis(8-hydroxyquinoline) (Znq₂) are typical representatives. The emission properties of the metalloquinolates can be tuned by the electronic nature of the arylethynyl substituents on the Hq ligand or by introducing optically inactive spacer molecules into their crystalline networks [5–9]. Generally, fabrication of device films for metal-quinoline chelates is carried out using vacuum-deposition [8,10] and, therefore, it is desirable to develop low-cost solution-processing techniques, such as spin-coating or ink-jet printing, for the large-scale fabrication of such devices [11–13].

The design and fabrication of novel organic–inorganic hybrids have been the focus of research for a long time [14–18]. Nowadays, most hybrid materials are synthesized using conventional chemistry

and combine the properties of organic and inorganic components [18]. However, with the rapid development of nanoscience and nanotechnology, functional organic–inorganic hybrids of innovative multiscale and hierarchically organized structures offer potential application as photovoltaic and fuel cells, smart and bionic materials, catalysts and sensors as well as the next generation of optical and photoelectronic systems [18,19]. In this context, fluorescent components such as rare earth complexes [20–22], dyes [16,23], Alq₃ [24] and semiconductor quantum dots (QDs) [25] have been incorporated into hybrid systems using a sol–gel route to secure materials with high stability, excellent thermal stability and ease of processing.

This study concerns a facile route for the preparation of highly fluorescent hybrid nanocomposites from trialkoxysilane-capped poly(MMA-co-Hq-CH₂-HEMA) and mercaptoethanol (ME)-capped ZnS nanoparticles (NPs) via ligand exchange and sol–gel process. The novelty of this strategy is that the Hq molecules are used to attach to the surface of semiconductor NPs for the first time to fabricate the fluorescence organic–inorganic nanocomposites with Hq-containing copolymers through ligand exchange. The interaction between NPs and the metalloquinolates formed on the NPs surface may mainly contribute to the interesting highly photoluminescence properties. By using the design of the copolymer of trialkoxysilane-capped poly(MMA-co-Hq-CH₂-HEMA) in this paper, the integration of the luminescent function within the stable and processible organic–inorganic hybrids can be achieved by the sol–gel process.

* Corresponding author. Fax: +86 431 85098768.

E-mail addresses: lucl055@nenu.edu.cn (C. Lü), zmsu@nenu.edu.cn (Z. Su).

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) and 3-(trimethoxysilyl) propyl methacrylate (MSMA) were distilled under reduced pressure before use. Azodiisobutyronitrile (AIBN) was recrystallized in ethanol. 5-(2-Methacryloyloxyethyl)oxymethyl)-8-quinolinol (Hq-CH₂-HEMA) was synthesized as reported previously [13]. Tetrahydrofuran (THF) was dried by refluxing over metal sodium before use. 2-Mercaptoethanol (ME), zinc acetate dihydrate, thiourea and N, N-dimethylformamide (DMF) were all analytical grade reagents and were used without further purification. Bis(8-hydroxyquinoline) zinc (Znq₂) was synthesized according to the reported method [26].

2.2. Characterization

FTIR spectra were recorded on a Magna 560 FTIR spectrometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene standards were employed for the GPC calibration. Transmission electron microscopy (TEM) was carried out on a JEOL-2021 microscope. UV–vis spectra were recorded on a Vary 500 UV-vis-NIR spectrometer in the range of 200–800 nm. Photoluminescence spectra were measured on a Cary Eclipse fluorescence spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-2 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 20 °C min⁻¹.

2.3. Synthesis of trialkoxysilane-capped poly(MMA-co-Hq-CH₂-HEMA) copolymer

A mixture of MMA (4.0 g), MSMA (0.95 g), HEMA-CH₂-Hq (0.05 g), AIBN (0.03 g) and anhydrous THF (25 mL) was placed in a 100 mL three-neck round bottom flask fitted with a magnetic stirrer and a reflux condenser under nitrogen atmosphere. The reaction solution was kept at 60 °C for 20 h with stirring. A THF solution of the copolymer with a solid content of 28 wt% was obtained. The copolymer was precipitated several times by using ether and a white powder was obtained. The number-average molecular weight (M_n) of this copolymer was determined to be 31 800 [polydispersity index, $M_w/M_n = 1.52$] by the GPC. The copolymer of p(MMA-MSMA) with a weight ratio of 80:20 for MMA to MSMA was synthesized through a similar process as mentioned above. The M_n and M_w/M_n of this copolymer are 48 500 and 2.53, respectively. Fig. 1 is the synthetic routes for these copolymers.

2.4. Preparation of mercaptoethanol (ME) capped ZnS (ME-ZnS) NPs

ME-ZnS nanoparticles (NPs) were prepared in DMF solution using the similar method reported earlier [27]. In a typical experiment, zinc acetate dihydrate (16.5 g, 75.3 mmol), thiourea (5.2 g, 68.3 mmol) and ME (8.7 g, 111.4 mmol) were dissolved in 150 mL DMF. The solution was stirred at 155–160 °C for 10 h under nitrogen atmosphere. The reaction solution was concentrated to about 50 mL at a reduced pressure, and then the resulting solution was poured into 200 mL ethanol and the formed white precipitate was collected by centrifugation. The white powder was thoroughly washed several times with methanol and then dried in vacuum.

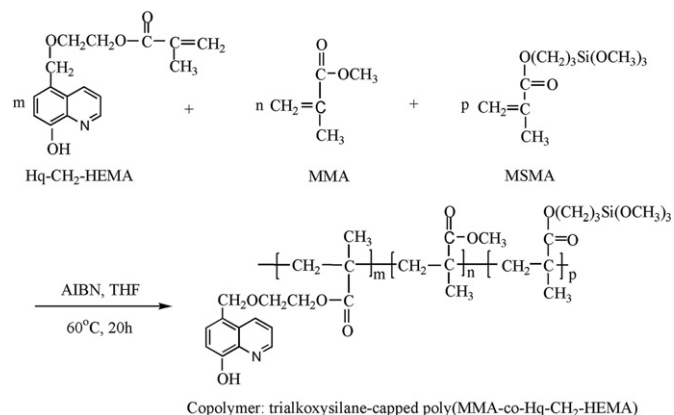


Fig. 1. Synthetic scheme for the copolymer of trialkoxysilane-capped poly (MMA-co-Hq-CH₂-HEMA).

2.5. Preparation of polymer nanocomposite films

For p-ZnSX-SiY samples, ZnS NPs dispersed in DMF were added into the copolymer solution of trialkoxysilane-capped poly(MMA-co-Hq-CH₂-HEMA). After the mixture solution was kept under ultrasonic vibration for 5 min, TEOS and water was added (the molar ratio of -Si-OR in copolymer and TEOS to H₂O is 0.625:1). The reaction solution was stirred for 8 h at room temperature, and then the solution was spin-coated on a quartz wafer at 3000 rpm for 30 s. The quartz wafer was pretreated with sulfuric acid and hydrogen peroxide. The solid content of the coating solution is about 5 wt%. The films were cured at 60 °C for 3 h, 80 °C for 1 h, 100 °C for 1 h, 120 °C for 1 h and 100 °C under vacuum for 1 h. For p-ZnS samples, except without use of TEOS, all the other conditions are similar to that of the synthesis for p-ZnSX-SiY samples. The zinc ion (acetate dihydrate as zinc salt) was also introduced into the sol-gel systems to prepare the hybrid samples of p-Zn²⁺(2:1), p-Zn²⁺(1:1) and p-Zn²⁺-Si20 (see Table 1). Here, the molar ratio of Hq-CH₂-HEMA units in the copolymer to Zn ions is 2:1 and 1:1 respectively, and the SiO₂ weight content in the resulting hybrids is fixed at 20 wt%. The p-Znq₂ hybrid sample was also prepared by blending Znq₂ complex with the copolymer of poly(MMA-MSMA) in THF solution, followed by the same procedure mentioned above. The weight content of Znq₂ complex in hybrid is similar to that of p-Zn²⁺(2:1) (0.61 wt%). The thickness of the above hybrid films was controlled at about 1.0 μm.

Table 1
Some properties of the organic–inorganic hybrid nanocomposite films.

Sample ^a	λ_{ex} ^b (nm)	λ_{em} ^c (nm)	T (%) ^d	T _d (°C) ^e	Residue (wt%) ^f
P(copolymer)	–	–	99.2	294	15.1(4.6)
p-ZnS1	370	495	96.4	292	27.5(23.0)
p-ZnS3	373	500	98.2	281	20.4(12.3)
p-ZnS10	369	500	98.4	249	19.2(7.2)
p-Zn ²⁺ (1:1)	370	501	–	–	–
p-Zn ²⁺ (2:1)	370	492	–	227	17.8(4.7)
p-Znq ₂	378	515	–	227	16.0(4.8)
p-ZnS3-Si10	372	499	98.1	307	24.5(21.0)
p-ZnS3-Si40	372	500	98.8	301	57.0(47.2)

^a P-ZnSX-SiY is defined as a nanocomposite with X weight percent of Hq unit in copolymers to ZnS NPs and Y weight percent of silica in nanocomposites.

^b Maximum excitation wavelength.

^c Maximum emission peak positions.

^d Transmittance at 450 nm.

^e 5 wt% decomposition temperatures.

^f Char yield at 785 °C after TGA (Theoretical char yield).

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