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Enhanced phosphorescence and electroluminescence in triplet emitters by doping gold into cadmium selenide/zinc sulfide nanoparticles

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Abstract

Gold–cadmium selenide/zinc sulfide (Au–CdSe/ZnS) nanocomposites (NCs) were synthesized and characterized by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, ultraviolet–visible (UV–visible) absorption and photoluminescence (PL) emission spectroscopy. The PL intensity in the Au–CdSe/ZnS NCs system was found to be much greater than that of CdSe/ZnS nanoparticles (NPs) alone, because of the surface-enhanced Raman scattering of Au NPs. Adding Au–CdSe/ZnS NCs to the cyclometalated iridium(III) complex (Ir-complex) greatly enhanced the PL intensity of a triplet emitter. Three double-layered electroluminescence (EL) devices were fabricated where the emitting zone contains the definite mixture of Ir-complex and the NCs [molar concentration of Ir-complex/NCs = 1:0 (Blank, D-**1**), 1:1 (D-**2**) and 1:3 (D-**3**)] and the device D-**2** exhibited optimal EL performances.

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1. Introduction

CdSe quantum dots (QDs) exhibit size-dependent tunable photoluminescence (PL) with broad excitation spectra and narrow emission bandwidths that span the visible spectrum. Therefore, they are potentially useful in a wide range of applications [1–3]. These characteristics of semiconductor CdSe QDs have inspired scientific communities to fabricate hybrid organic light emitting diodes (OLEDs), which combine the diversity of organic materials with the excellent electronic and optical properties of inorganic materials. Coe et al. reported [4] the fabrication of a hybrid OLED, where QDs function exclusively as lumophores. Recently, Chaudhary et al. [5] demonstrated a trilayer polymer-quantum dot OLED which was fabricated by sandwiching a CdSe/ZnS QDs layer between films of polyvinylcarbazole (PVK) and butyl-oxadiazole derivative. The benefit of such a QD-based OLED is that each recombination of a hole and an electron generates a photon, resulting in a possible 100% quantum efficiency at any visible wavelength, since the tuning property of the emission wavelengths depends on the variability of the QDs' size. In most hybrid OLED devices, the ODs themselves act as light emitting centers [4–6]. For the first time, we reported elsewhere [7] that the enhancement of quantum efficiency of a triplet iridium(III) complex (Ir-complex) emitter in the presence of CdSe/ZnS QDs in the emitting layer of OLED.

The nonlinear response of composites of nanoparticles (NPs) with a metal and semiconductor suspended in a nonlinear medium exhibited was several orders of magnitude stronger than that of each of their components [8–11]. A strong surface-enhanced Raman scattering (SERS) effect was observed in Au/semiconductor or Ag/semiconductor colloidal nanocomposites (NCs) [8–12]. Nayak et al.

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generated Au–CdSe NCs [13], although a large fraction of the particles was a mixture of individual gold and CdSe NPs, as indicated by transmission electron microscopy (TEM) micrographs. Enhanced optoelelectronic properties have been extensively reported and have been determined from the SERS activity of Au and Ag metallic NPs [14,15]. These facts motivated the exploration herein of the optical and electronic properties of metallic NPs and CdSe NPs and observations of the effect of these NPs on the PL and electroluminescence (EL) of a triplet emitter. This work reports the syntheses and characterizations of Au–CdSe/ZnS NCs and their applications in enhancing the thin-film PL and EL efficiencies of a triplet iridium(III) emitter when the NCs incorporated into the triplet emitter in the emitting layer of a hybrid OLEDs.

2. Experimental details

2.1. Chemicals and reagents

Hydrogen tetrachloroaurate (III) and tetraoctylammonium bromide were purchased from Acros Chemicals Company. Cadmium oxide (~1 μm, 99.5%), selenium (Se) powder (~100 mesh, 99.5+%), zinc acetate dehydrate (>98%), polyvinylcarbazole (PVK) and sulfur powder (99.8%) were all purchased from Aldrich Chemicals, USA. 1-Hexadecylamine (HDA, 98+%), lithium fluoride (LiF) and aluminum (Al) were obtained from Lancaster. Tri-*n*-butylphosphine (TBP) was obtained from Showa Chemicals Company, Japan. Anhydrous toluene and chloroform were purchased from TEDIA. Bis(4-trifluoro-methyl)-2-phenyl-benzothiazolatoacetylacetonate-iridium(III) (Ir-complex) was synthesized following the method reported in the literature [16].

2.2. Preparation of Au NPs

The Au NPs were synthesized according to the method reported in the literature [17]. A 25 ml aqueous solution of $HAuCl_4$ (0.3 mmol) was added to an 80 ml toluene solution of tetraoctylammonium bromide (1.8 mmol). The transfer of the Au metal salt to the toluene phase was clearly visualized within a few seconds. 25 ml of 0.25 M $NaBH_4$ solution was then added to the stirred mixture, resulting immediately to reduction. The toluene phase was then saved and the water phase was removed.

2.3. Preparation of Au–CdSe/ZnS NCs

A mixture of Au and CdSe/ZnS NPs with 0.02:1 in molar ratio was prepared as follows. CdO (0.6 mmol) and HDA (9 mmol) were dissolved in 20 ml of tributlyphosphine (TBP). The reaction mixture was then heated at 260 °C for 2 h under nitrogen atmosphere. 4 ml of Au NPs (3×10^{-3} M) was injected into the reaction mixture. The prepared Se solution (0.7 mmol of Se in 5 ml TBP solution) was immediately injected into the reaction mixture, which was kept at the desired temperature (160–260 °C) for 1 min. Then, zinc acetate (0.1 mmol) and sulfur (0.12 mmol) were dissolved in 5 ml of TBP, and injected into the reaction mixture. The temperature of the reaction mixture was maintained at 120 °C for 0.5 h. Toluene was injected into the reaction vessel. Other nanocomposites of Au and CdSe/ZnS NPs with different stoichiometries have been prepared following the method described above and all of the samples were dispersed and stored in toluene.

2.4. Instrumentations

Raman scattering spectra were obtained using a Jobin Yvon HR 800 spectrometer and a He–Ne laser as a light source. A Jeol JEM-4000EX TEM operated at 200 kV was used to determine the microstructure of QDs and their composition was analyzed using energy dispersive X-ray (EDX) analysis. PL excitation and ambient temperature emission spectra were measured using a Jobin Yvon Spex Fluorolog 3 spectrofluorometer with a monochromatized Xe light source (300 W). The emission spectra of various NCs were obtained at an excitation wavelength (λ_{ex}) of 367 nm. Ultraviolet–visible (UV–visible) absorption spectra of NCs were measured using a Hitachi U-3010 UV–visible spectrophotometer. The concentration of the samples for PL and UV–visible measurements was maintained at the concentration of 1×10^{-4} M in toluene. The fluorescence decay lifetimes were obtained by time-correlated single photon counting (TCSPC; Fluo Time 200, Pico-Quant) and the samples were excited by using a short pulse diode laser (LDH-P-C 375, Pico-Quant) at 375 nm.

2.5. Fabrication of thin films and EL devices

By spinning from concentrated dispersions in chloroform (3 ml) on flat quartz substrate (i.e., Ir-complex:Au–CdSe/ZnS = 1:0 to 1:5), we have fabricated several uniform thin films comprising a fixed number of moles of Ir-complex with various molar concentrations of Au–CdSe/ZnS NCs in a fixed amount of Au–CdSe/ZnS PVK matrix. The 1:1 mixture of Ir-complex and Au–CdSe/ZnS NCs (Au:CdSe/ZnS = 0.001:1) were prepared as follows. 1 ml of Ir-complex (1.6×10^{-6} M) was mixed with 0.016 ml of Au–CdSe/ZnS (1×10^{-4} M) in chloroform. Similarly, we have prepared other Ir-complex and Au–CdSe/ZnS NCs mixture solutions proportionately. Then, 30 mg of PVK was added to each of the mixtures and the total volume was kept constant to 3 ml by adding chloroform. The thicknesses of the thin films were measured by the alpha-stepper method at various arbitrary points (8 ± 0.5 nm).

A series of double-layered EL device with structure represented in Fig. 1 were designed and fabricated. These devices mainly contain green-emitting Au–CdSe/ZnS NCs doped with the orange-emitting iridium(III) triplet emitter in