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Luminescent nanocomposites of conducting polymers and *in-situ* grown CdS quantum dots

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Abstract. Luminescent PVK:CdS and P3HT:CdS nanocomposites with enhanced electrooptical properties have been synthesized. The nucleation and growth of CdS nanoparticles have been obtained by the thermolysis of a single Cd and S precursor dispersed in the polymers. The size distribution and morphology of the nanoparticles have been studied by TEM analyses. Monodispersive and very small nanoparticles of diameter below 3 nm in PVK and 2 nm in P3HT, have been obtained. The application of such nanocomposites as emitting layers in OLED devices is discussed.

Keywords: Nanocomposites, CdS nanoparticles, conducting polymers, electroluminescence **PACS:** 82.35Np, 81.07b, 78.67Sc

INTRODUCTION

Nanocomposites obtained by combining conducting polymers and semiconductor nanoparticles have so far attracted much interest for manifold applications such as tuneable luminous sources for field emission displays and electroluminescent devices [1]. Nanocomposites have several advantages with respect to fully organic or fully inorganic systems [2]. As an example, polymers embedding semiconducting nanoparticles combine their good processability, high transparency, digital printing flexibility also on a large scale with the unique optical properties of the nanoparticles. In particular the incorporation of II–VI nanocrystals (or quantum dots) in conjugated polymers has been found to enhance the electroluminescence properties of these materials [3] and to improve the long term stability, colour tunability and quantum efficiencies of electroluminescent devices based on such nanocomposites.

Conventionally nanocomposites of nanocrystals and conjugated polymers are obtained by mixing a given polymer with nanocrystals in presence of surfactants to prevent the growth of larger crystals. However the presence of surface ligands may reduce the charge transfer between the polymer matrix and the nanocrystals [4].

This work presents the realization of conducting and luminescent hybrid nanocomposite materials by nucleation and growth of CdS nanoparticles directly in two organic polymers, Polyvinylcarbazole (PVK) and Poly (3-Hexylthiophene) (P3HT). The purpose of our research is to improve the optoelectronic properties of the polymers, by enhancing the luminescence intensity or tuning the emission wavelength. CdS nanoparticles have been synthesised in-situ within the polymers by thermolysis of a cadmium bis(thiolate) precursor avoiding the use of any surfactant or other stabilizing agents.

The size of CdS nanoparticles was controlled by varying the annealing conditions. The nanoparticle morphology and dimensions were investigated by TEM analyses.

The P3HT based nanocomposites have been used for the realization of a single layer OLED device with structure ITO/P3HT:CdS/LiF/Al which transport and emission properties have been compared to the analogous pure polymer device.

RESULTS AND DISCUSSION

 $Cd(SC_{12}H_{25})_2$ cadmium dodecylthiolate has been used as Cd and S precursor. The polymers P3HT and PVK have been dissolved in chlorobenzene at a concentration of 25mg/mL. The precursor has been successively added to this solution at 20% wt. A bulk foil has been obtained by casting and annealed at different temperatures under vacuum.

Previous studies on the nucleation and growth of CdS nanoparticles by thermolysis have shown that the formation of the nanoparticles starts at temperatures of about 170°C in a thermoplastic copolymer [5]. However the choice of the annealing temperatures depends also on the glass transition of the polymers. Therefore the annealing processes have been conducted at temperatures higher than their Tg to allow a better diffusion and distribution of the Cd dodecylthiolate in the polymeric matrix. The annealing in PVK (Tg=226°C) have been carried on at 250, 265 and 275 °C while the annealing in P3HT (Tg<-3°C) have been carried on at 200 and 240 °C.

TEM analyses of the samples, realised by a TEM TECNAI G2 F30, have confirmed the formation of CdS nanoparticles. The samples for TEM have been prepared by dropping few μ L of the precursor polymer solution on Cu grids. Spherical and very small nanoparticles are present in both polymers, as shown in Fig. 1a for P3HT:CdS. The HRTEM image in the inset shows regular lattice fringes at a distance of about 0.31 nm. Statistical analysis over about 100 nanoparticles (see istogram in Fig. 1b) has given a narrow nanoparticles size distribution peaked at about 2 nm for the nanocomposite annealed at 240 °C. The results obtained in the case of PVK:CdS indicate nanoparticles of about 3 and 5 nm upon annealing at 265°C and at 275°C, respectively.



FIGURE 1. (a) Bright Field TEM image of CdS nanocrystals in P3HT matrix after annealing at 240 °C; (b) Statistical distribution of the nanoparticle size evaluated from sampling about 100 nanoparticles.

The P3HT:CdS prepared at 240°C of Fig. 1 have been employed to prepare simple OLED devices ITO/P3HT:CdS/LiF/Al. The nanocomposite solution was spin coated (2000 rpm) on a patterned ITO/glass substrate used as anode electrode and covered by a LiF/Al electrode (100 nm thick) obtained by evaporation. Current-voltage characteristics (Fig. 2a) and electroluminescence at V ~ 8.5Volts (Fig. 2b) are reported for the device including the nanoparticles and compared with the device of P3HT only. The current-voltage characteristics show a decrease of the turn-on voltage from the pure polymer (5.8V) to the P3HT:CdS (5.4V). The electroluminescence of P3HT is characterized by a double peak between 550 and 800 nm due to π - π * transitions [6]. The introduction of the CdS nanoparticles induces a strong enhancement of the electroluminescence signal with loss of the double structure of the P3HT electroluminescence signal. The study of the nanoparticles influence on the electroluminescence mechanism of P3HT:CdS in currently under study together with possible effects of the annealing process on the morphology and transport properties of P3HT [7]. To this scope, additional devices will be realised using P3HT:CdS at 200°C and the PVK related nanocomposites.



FIGURE 2. Current-voltage characteristics (a) and electroluminescence at V~8.5Volts (b) on ITO/P3HT/LiF/Al and ITO/P3HT:CdS/LiF/Al where P3HT:CdS has been obtained after annealing at 240°C.

CONCLUSIONS

Luminescent PVK and P3HT nanocomposites containing CdS nanoparticles have been synthesized by in-situ thermolisis of a cadmium bis(tiolate). This synthetic approach allows the use of a single, air stable and easy to prepare precursor for both Cd and S. Moreover the nucleation and growth of CdS nanoparticles directly in the polymer avoids the use of surfactants. The CdS nanoparticles obtained are very small (few nm) and present a narrow size distribution in both polymers as shown by TEM analysis of the samples.

P3HT nanocomposites have been used to prepare simple OLED devices ITO/P3HT:CdS/LiF/Al whose electric and electrooptical properties have been measured. A strong increase of electrooptical signal has been obtained in the case of the nanocomposite at 240°C with respect to pure P3HT.

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