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Study of Nanostructured Polymeric Composites and Hybrid Layers Used for Light-Emitting Diodes

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Nanocomposite polymeric thin films of poly(2-methoxy-5-(2'-ethyl hexyloxy)phenylene vinylene) (MEH-PPV) with nano-crystalline titanium oxide (nc-TiO₂) and polycarbazole (PVK) with cadmium selenide (CdSe) were fabricated by spin-coating. A 20-nm-thick nanocrystalline (molybdenum oxide) MoO₃ layer prepared by using thermal oxidation was also spin-coated with a PVK film. A study of photoluminescence (PL) spectra of the polymers and nanocomposites showed an enhancement in the photoluminescence from the nanocomposites. Moreover, MEH-PPV+nc-TiO₂ composites exhibited a blue-shift of the PL spectrum as compared to that of the polymer film. The current-voltage characteristics of the Mo/nc-MoO₃/PVK/Al-Au structures show that a semitransparent metallic coating or a transparent polymer can serve as a cathode in devices with enhanced charge carrier injection.

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Keywords: Polymeric nanocomposite, Photoluminescence, OLED

I. INTRODUCTION

Polymer-based electroluminescent materials have potential for many applications; for instance, organic light-emitting diodes (OLEDs) are now commercialized in display fields [1,3]. Efficient device operation requires optimization of three factors: (i) equalization of the injection rates of positive (hole) and negative (electron) charge carriers, (ii) a combination of the charge carriers to form singlet excitons and (iii) radiative decay of the excitons. Of the two carriers, holes have the lower mobility in general and may limit the current conduction process. By adding a hole transport layer (HTL) to a three-layer device, one can expect equalization of the injection rates of holes and electrons; consequently, a higher electroluminescent efficiency will be obtained for the OLED. However, both the efficiency and the lifetime of OLEDs are still lower in comparison with those of inorganic LEDs. To improve these parameters,

one can use nanostructured polymeric/inorganic composites, instead of standard polymers, for the emitting layer. The aim of this work is to study the photoluminescence of some polymeric nanocomposites, such as poly(2-methoxy-5-(2'-ethyl hexyloxy)phenylene vinylene) (MEH-PPV) with nano-crystalline titanium oxide (nc-TiO₂) and polycarbazole (PVK) with selenium cadmium (CdSe), together with the use of (molybdenum oxide) MoO₃ in PVK/nc-MoO₃ hybrid junctions.

II. EXPERIMENT

The solutions of PVK and MEH-PPV were made by dissolving PVK and MEH-PPV powder, respectively, in pure chloroform and in pure xylene. These solutions were spin-coated onto both glass and tin-indium-oxide (ITO) substrates at spin rates ranging from 1200 rpm to 2000 rpm for 1 to 2 min; the detailed procedure has been described elsewhere [4]. To prepare polymeric nanocomposite films, we added nanoparticle TiO₂ powders and CdSe quantum dots (QDs) to chloroform or

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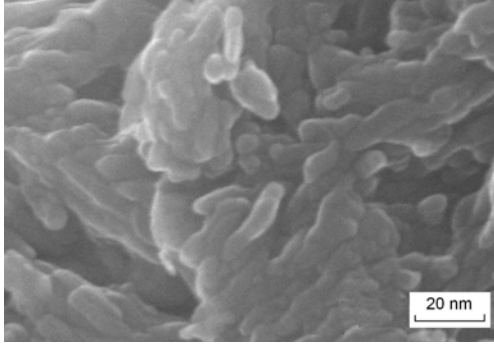


Fig. 1. FE-SEM image of annealed Mo-substrate.

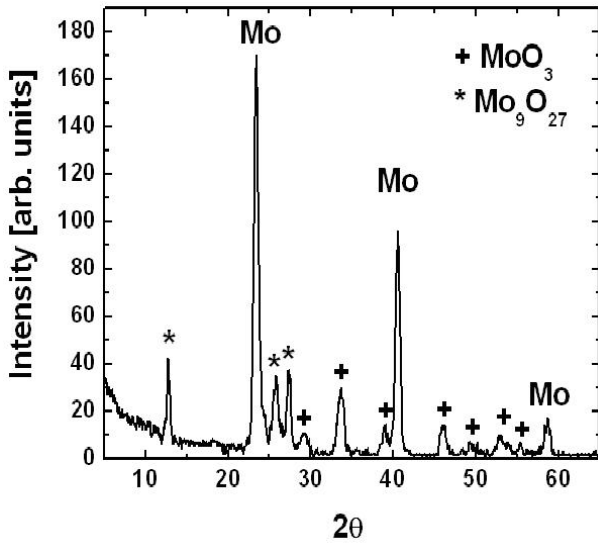


Fig. 2. XRD patterns of annealed Mo-substrate whose FE-SEM image is shown in Figure 1.

xylylene, stirred by using an ultrasonic bath; then, MEH-PPV and PVK were dissolved in these solutions to obtain polymeric nanoparticle solutions. The last were spin-coated on glass and ITO substrates. To prepare the hybrid structure of nc-MoO₃/PVK, we annealed the Mo metallic substrate in ambient air at temperatures ranging from 350 to 550 °C for 1 to 3 hrs to get a nanostructured MoO₃ layer; then, PVK was deposited by spin-coating, followed by vacuum annealing [5]. The surface morphologies and the nanocrystalline structures of MoO₃ were checked, respectively by using scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Photoluminescence spectra (PL) were measured on a FL3-2 spectrophotometer using a Xenon lamp with a power of 450 W for the excitation source; the excitation wavelength was 300 nm. The current-voltage (I-V) characteristics were measured using an Auto-Lab. Potentiostat PGS-30.

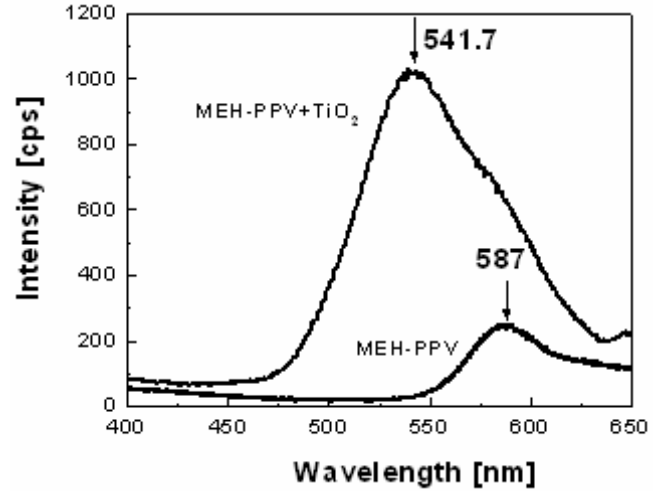


Fig. 3. Photoluminescence spectra of MEH-PPV and MEH-PPV + nc-TiO₂.

III. RESULTS AND DISCUSSION

1. Morphology and Crystalline Structure of the MoO₃ Layer

The thickness of the annealed Mo substrate layers was found to depend on the annealing conditions, such as temperature and time. The samples used for devices were chosen from those annealed at 500 °C for 2 h. The bright-field micrograph of a sample is shown in Figure 1. The films are not perfectly uniform; for the MoO₃ phase, the average grain is ~ 7 nm in diameter and ~ 15 nm in length. The structure of the films was checked by performing an X-ray incident beam experiment. For thin annealed layers, the three XRD peaks of the Mo substrate are obtained with a strong intensity (denoted by Mo-peaks in Figure 2), indicating the bulk Mo crystalline structure of the substrate. The three other sharp peaks denoted by stars in Figure 2 characterize the crystalline structure of Mo₉O₂₇ formed upon annealing. In the XRD diagram, there are seven diffraction peaks corresponding MoO₃. The fact that the peak width is rather large shows that the MoO₃ layer was formed by nanocrystalline grains. To obtain the grain size, τ , we used the Scherrer formula:

$$\tau = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where λ is the X-ray wavelength, β is the full width at half maximum in radians and θ is the Bragg angle of the considered diffraction peak [6]. The values of β were found to range from 0.008 to 0.010; consequently, the average size of the grains was determined as $\tau \approx 7 - 10$ nm. This result is in good agreement with the data obtained from the SEM data for the average size of the grains. The MoO₃ layer was further spin-coated with PVK to get a heterojunction of PVK/nc-MoO₃.

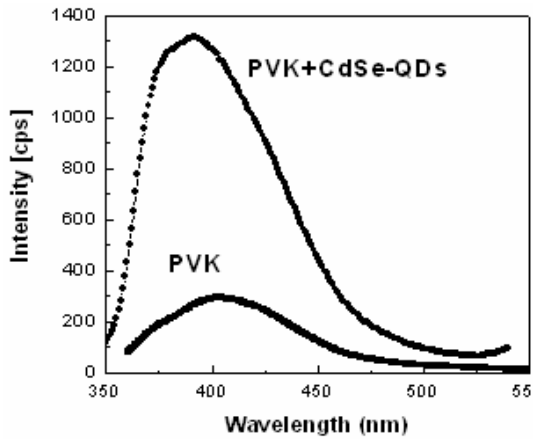


Fig. 4. Photoluminescence spectra of PVK and of the PPV+ CdSe-QDs composite.

2. Photoluminescence of Polymeric Composites

The photoluminescence spectra for polymeric nanocomposites of MEH-PVK+nc-TiO₂ and PVK+CdSe-QDs are presented in Figure 3 and Figure 4, respectively. In both cases, the photoluminescence intensity is enhanced compared to that in the bare polymer films, although the sizes of the TiO₂ nanoparticles and the CdSe quantum dots are different.

For the MEH-PPV+nc-TiO₂ composites, where the sizes of the TiO₂ particles are much larger (*e.g.*, 70 – 100 nm) than the quantum dots, the mechanism of the photoluminescence enhancement effect can be explained as follows: Here, the boundaries of the nanocrystalline oxide particles and the polymer play a role more important than the quantum size does. At these boundaries, charge-space regions are expected to be formed due to the charge distribution difference between the oxide and the polymer. Under excitation of the laser beam, electrons from the valence band of TiO₂ can jump to the conduction band, creating holes in the first band and resulting in a decrease in the Schottky barrier height in the second band. Then, these electrons and holes of TiO₂, respectively, diffuse to the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of the polymer. The generation of new excitons in the emitting layer occurs, leading to an increase in the photoluminescence intensity. The blue shift of the photoluminescence peak of MEH-PPV+nc-TiO₂ cannot be clearly understood at this stage. Similar results have been obtained in poly(phenylene vinylene)/oxide nanocomposites [7] and was explained by a reduction in the polymer conjugation chain length. However, the obtained results suggest a potential application as a photonic microcavity based on polymeric nanocomposites.

For the PVK+CdSe-QDs composites, where CdSe nanoparticles have the same size as a quantum dot, the mechanism of the photoluminescence enhancement is be-

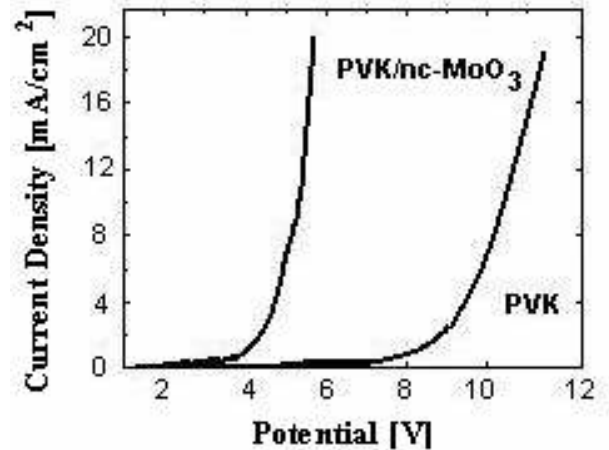


Fig. 5. Current-voltage characteristics of ITO/PVK/Al and Mo/nc-MoO₃/PVK/Al device.

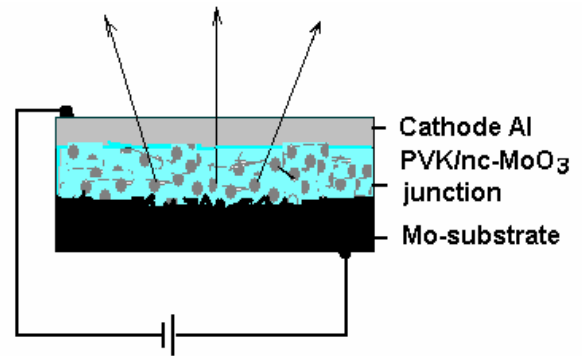


Fig. 6. Schema of the Ag/Mo/nc-MoO₃/PVK/Al device.

ing argued. To elucidate these phenomena is our aim in future work.

3. Photoluminescence and Electrical Properties of the Hybrid Structures

For a hybrid layer of PVK/nc-MoO₃ the photoluminescence enhancement was also observed. Although the way to prepare this layer is different from that used for the PPV+CdSe-QDs film, one can see that the hybrid layer was formed with a microstructure comparable to that of the PVK+CdSe-QDs composite. Since the size of MoO₃ grains is as small as 7 nm, the photoluminescence enhancement can be understood as the effect of the quantum size of the large bandgap MoO₃ in the polymeric composite. Additionally, the current-voltage characteristics of Ag/Mo/nc-MoO₃/PVK/Al and Ag/ITO/PVK/Al (Figure 5) show that the onset voltage of the first junction is lower than that of the second junction. This may be explained by (i) the workfunction of nc-MoO₃ being higher than that of ITO and (ii) the Mo substrate being metallic; thus, the

Ag/Mo contact is more ohmic than the Ag/ITO contact. These results may be applied to the structure of devices in which a semi-transparent metal coating or a transparent conducting polymer is used for the cathode (Figure 6). We shall focus our forthcoming research work on the electroluminescence properties of these structures.

IV. CONCLUSIONS

MEH-PPV+nc-TiO₂ and PVK+CdSe-QDs nanocomposite polymeric thin films were prepared, respectively, by embedding nanocrystalline TiO₂ particles in MEH-PPV and CdSe quantum dots in PVK, followed by spin coating on ITO-coated glasses. A thin nanocrystalline MoO₃ layer thermally grown on Mo was also spin-coated with a PVK film and an Al-Au alloy was evaporated onto the last to form heterojunctions of Mo/nc-MoO₃/PVK/Al-Au. By excitation of a short wavelength of 300 nm, the PL intensity of the nanocomposite films was increased greatly in comparison with the pure polymers. For MEH-PPV + nc-TiO₂ composites, the blue shift of the peak in the PL spectrum was attributed to a reduction in the polymer conjugation chain length caused by embedding the nc-TiO₂ particles. In such a laminar device of Mo/nc-MoO₃/PVK/Al-Au junctions, nc-MoO₃ being a hole transport layer made the onset voltage of the device lower. This suggests an application of the laminar device in OLEDs by using a semitransparent metallic

and/or a transparent polymeric cathode.

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