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Jinhan Cho $^{\rm a}$, Kookheon Char $^{\rm a}$, Jong-Dal Hong $^{\rm b}$ & Dongyoung Kim $^{\rm c}$

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^a School of Chemical Engineering, Seoul National University, Seoul, 151-741, Korea

^b Department of Chemistry, University of Inchon, Inchon, 402-749, Korea

^c Polymer Materials lab, KIST, Seoul, 130-650, Korea

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Electronic Characteristics of Self-Assembled Hybrid Devices Based on PPV and CdS Nanoparticles

JINHAN CHO^a, KOOKHEON CHAR^{a*}, JONG-DAL HONG^b and DONGYOUNG KIM^c

^aSchool of Chemical Engineering, Seoul National University, Seoul 151–741, Korea, ^bDepartment of Chemistry, University of Inchon, Inchon 402–749, Korea and ^cPolymer Materials lab, KIST, Seoul 130–650, Korea

Electronic characteristics of organic/inorganic hybrid devices based on CdS nanoparticles, poly(p-phenylene vinylene) (PPV) and poly(sodium styrene sulfonate) (PSS) were investigated. The average diameter of anionic CdS nanoparticles was measured to be 4 nm as judged from TEM and optical spectral characterization. The Quantum efficiency of the ITO/(PPV/PSS)₁₅(PPV/CdS)₅/Al device was significantly improved in comparison with that of the ITO/(PPV/PSS)₂₀/Al device. The performance improvement of the ITO/(PPV/PSS)₁₅(PPV/CdS)₅/Al device is believed to be due to the low energy barrier of CdS nanoparticles for the electron injection from Al electrode.

Keywords: CdS; poly(p-phenylene vinylene) (PPV); hybrid device; electroluminescence (EL); nanoparticles

INTRODUCTION

Semiconductor nanoparticles such as CdS exhibit interesting sizetunable optical properties due to the confinement of electronic wave functions [1]. Up to date, several groups have reported the use of semiconductor nanoparticles, such as CdSe, in combination with

^{*} To whom correspondence should be addressed

conjugated polymers in the manufacturing of LEDs [2,3]. Recently, organic/inorganic hybrid devices have been fabricated by self-assembly (SA) method using the electrostatic interaction between oppositely charged species [4].

In the present paper, anionic CdS nanoparticles carrying carboxlic groups on the surface were prepared with an aim to obtain multilayer films in combination with cationic PPV precursor. Main interest is focused on the investigation of the electronic characteristics of hybrid devices prepared with CdS nanoparticles.

EXPERIMENTS

PPV precursor was prepared by polymerization of a bis-sulphonium salt of p-xylene. PSS $(M_w = 70K)$ was purchased from Aldrich Chemical.

Anionic CdS nanoparticles were prepared by treating Cd^{2+} ions with Na_2S in the presence of mercaptoacetic acid [5]. The average particle was measured to be 4 nm from TEM observation. Mole concentration of PPV precursor, PSS and CdS aqueous solution was adjusted to 0.01, 0.01 and $3x10^{-4}$ M, respectively.

In order to obtain multilayer film, the PPV precursor was initially deposited onto a negatively charged substrate as described previously [6]. The substrate was alternately dipped in the cationic PPV precursor solution and then into the anionic solution of either CdS or PSS for 20 minutes, respectively. The multilayer film was prepared from the repeated adsorption step. The film thickness before and after thermal conversion was determined with an ellipsometer (Auto EL-II).

The fabrication of a self-assembled film on ITO glass is identical to the procedure described above. After thermal conversion of the PPV precursor to a conjugated form of PPV, aluminum electrode was evaporated onto the PPV multilayer films.

RESULTS AND DISSCUSSION

It was proven by the UV/VIS spectra that the organic/inorganic hybrid films could be successfully fabricated using the self-assembly method. Figure 1 shows the uniform increase of UV/VIS absorbance of a hybrid film with increasing the number of (PPV precursor/CdS nanoparticle) bilayers, indicating the typical absorption of CdS

nanoparticles in the wavelength range from 300 to 400 nm [7]. The linear relation between the absorbance and the number of bilayers shown in the inset of Figure 1 also implies that the adsorbed amount per bilayer is little changed. In order to better understand the peculiar properties of CdS nanoparticles, we investigated the electronic characteristics of organic/inorganic hybrid devices based on CdS nanoparticles and PPV. According to the Brus model for the excited electronic states of semiconductor nanoparticles, the approximate values for the energy bandgap and the conduction band of the CdS quantum dots having a diameter of 4 nm was estimated to be 3 eV and 3.7eV, respectively [8]. In contrast to the energy barrier of 1.8 eV for the electron injection into PPV from Al electrode, the energy barrier into CdS nanoparticles from Al electrode has a quite low value of 0.6 eV [2].

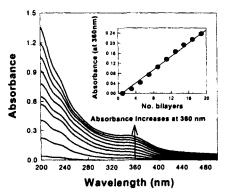


FIGURE 1 UV/VIS absorption spectra of a hybrid film carrying cationic PPV precursor layer and anionic CdS nanoparticle layer alternately. Inset shows the UV/VIS absorbance of the hybrid film measured at 360 nm as a function of the number of bilayer.

Figure 2 shows the relative quantum efficiencies of three EL devices prepared differently. It is noted that the quantum efficiency of (PPV/CdS)₂₀ device is slightly improved compared with that of (PPV/PSS)₂₀. In the case where (PPV/CdS)₅ were inserted at the interface between (PPV/PSS)₁₅ bilayers and the Al electrode, we observed that the quantum efficiency of the hybrid device was significantly improved as can be seen in Figure 2. We attribute the increased quantum efficiency to the lower energy barrier of CdS nanoparticles for the electron injection from Al electrode. This implies

that the insertion of the (PPV/CdS) bilayer has the propensity of transporting electrons much more easily from the Al electrode than the (PPV/PSS) bilayer.

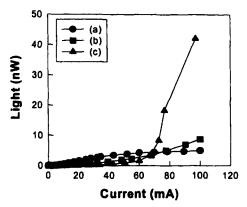


FIGURE 2 Relative quantum efficiencies of EL devices: (a) ITO/(PPV/PSS)₂₀/Al, (b) ITO/(PPV/CdS)₂₀/Al, (c) ITO/(PPV/PSS)₁₉/(PPV/CdS)₉/Al. The film thicknesses were measured to be (a) 12 nm, (b) 10.3 nm and (c) 11.5 nm

In summary, it is demonstrated that CdS nanoparticles can be utilized as an electron transport layer in an EL device with multilayer film prepared with self-assembly method. The details of electronic characteristics of the hybrid multilayer film involving CdS nanoparticles and its connection with film morphology are the topics of future publication.

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