4990 *Chem. Mater.* **2006,** *18,* 4990−4992

Novel Fluorescent Polymer/Zinc Oxide Hybrid Particles: Synthesis and Application as a Luminescence Converter for White Light-Emitting Diodes

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Received April 25, 2006
Revised Manuscript Received August 3, 2006

A series of fluorescent polymer−zinc oxide (ZnO) hybrid materials were synthesized, in which a polymer core was capped with different amounts of ZnO on the surface. The fluorescent core consisted of a spherical polymer particle with a mean diameter ranging from ∼500 to 700 nm. The fluorescence emission efficiency of the polymer was significantly increased by the incorporation of the ZnO nanoparticles. Hybrid light-emitting diodes (LEDs) were fabricated, using a commercial blue LED (GaN, 460 nm) and the fluorescent hybrid material as a primary pumping source and luminescence converter (LUCO), respectively. The hybrid LED yielded a white light with very high efficiency when this fluorescent hybrid material was employed.

Recently, white LEDs have attracted a great deal of attention, as a result of their tremendous potential in lighting and backlight applications, and various strategies have been utilized to fabricate them.[1−3] One of the approaches consists of making a hybrid LED, in which a primary light source provides the short wavelength component and, simultaneously, serves as a pump for the excitation of the LUCO materials to obtain a longer wavelength component.[4,5] When the primary light emitter provides a blue light, the reemitted (converted) light can be yellow or yellow-orange, depending upon the LUCO materials. The combination of the blue light from the pump and the converted yellow or yellow-orange light can produce white light. GaN-based blue and green LEDs are now commercially available. The LUCO material can be either an organic or inorganic compound.[6] The most representative inorganic LUCO material is a yellow light-emitting phosphor (YAG:Ce, Nichia Chemical Industries). However, the use of organic LUCO materials, especially fluorescent polymers, seems to be advantageous, in terms of their cost, fabrication, and color tuning. Furthermore, the self-absorption by the LUCO materials can be minimized, as a result of their large Stokes shifts.

Heeger et al.[4] obtained white light emission from InGaN/conjugated polymer hybrid LEDs, where the InGaN-based LED provides the blue component and simultaneously serves as a primary light source to excite the photoluminescence (PL) of the polymer double layer films. The polymers employed in their research were poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (red-emitting, MEH-PPV) and poly(2-butyl-5-(2′-ethylhexyl)-1,4-phenylene vinylene) (green-emitting, BuEH-PPV). In particular, the color tuning of the hybrid LEDs was readily achieved, by choosing an appropriate polymer and adjusting the film thickness. Zhang and Heeger[7] also obtained pure white light emission from an InGaN/single layer of conjugated polymers, or copolymers, such as poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene) and poly(MEH-PPV-*co*-BuEH-PPV). When the polymers were properly encapsulated, the operating lifetimes of the hybrid LEDs were comparable to those of commercial blue LEDs.

The stability of organic LUCO materials against photooxidation largely depends on their chemical structures. The output luminosity of a hybrid LED (or LUCO LED) is limited by the PL quantum efficiency (Φ_{PL}) of the LUCO materials. However, two different approaches can be used to overcome the problems associated with LUCO materials: their poor stability and low PL quantum efficiency. The first strategy is to synthesize new organic LUCO materials with a high quantum yield and high resistance against photo-oxidation. The second strategy is to prepare organic−inorganic hybrid materials. One example of this is the use of core−shell nanoparticles, which can effectively protect the dye molecules from photo-oxidation and simultaneously improve their fluorescence efficiency, due to the caging effects.[8,9]

ZnO is mostly an n-type semiconductor and exhibits many attractive features, due to its unique electrical and optical properties. Typically, the PL spectra of ZnO particles consist of an excitonic emission in the near UV region and a deep level (DL) emission which is situated mostly in the green region, with some yellow and red spectral regions. The DL emission strongly reflects the polycrystalline structure of ZnO, which results from its high density of native defects, such as oxygen vacancies and Zn interstitials.[10−12] The selective synthesis of a fully defected form of ZnO was

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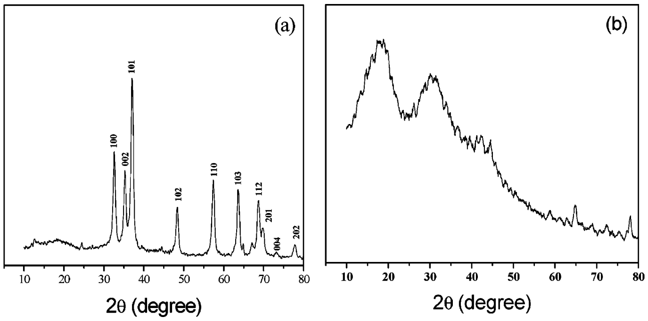

Figure 1. XRD patterns of (a) pure ZnO and (b) FTBT−ZnO20 particles dispersed in the PMMA matrix.

reported through chemical bath deposition at low temperature, without using a base.[13]

Recently, we synthesized various yellow light-emitting polymers bearing fluorescein dye units and employed one of them (see Supporting Information) in the construction of a white hybrid LED.[14,15] The quantum efficiency of the polymer, poly(fluoresceinyl terephthalate-*co*-bisphenol A terephthalate) (FTBT), was estimated to be 0.57, which is comparable to those of PPV derivatives.[16] However, it is still not high enough. In this research, we attempted to prepare FTBT−ZnO hybrid particles, to improve the emission quantum efficiency of the polymer, FTBT. The experimental details are provided in Supporting Information.

Figure 1 shows the X-ray diffraction (XRD) patterns of the pure ZnO particles prepared in this experiment and the FTBT−ZnO20 particles dispersed in the poly(methylmethacrylate) (PMMA) matrix. The pure ZnO particles display very sharp XRD peaks, which correspond to the JCPDS file of ZnO (JCPDS 36-1451; wurtzite-type crystalline, space group $P6_3mc$).[13] On the other hand, pure FTBT and the PMMA matrix are totally amorphous in nature and cannot give a sharp XRD peak (see Supporting Information). However, the FTBT−ZnO20 particles and other hybrids clearly showed sharp XRD peaks which were characteristic of the ZnO particles. This observation indicates that the crystalline ZnO particles were incorporated onto the FTBT particle surfaces.

The scanning electron microscopy (SEM) images revealed that the pure FTBT particles are spheres with a smooth surface, as shown in Figure 2a. The diameter of the pure FTBT particles was mostly in the range of 500−700 nm. However, the FTBT−ZnO particles appeared to be very rough, even though their overall shape was spherical, as illustrated in Figure 2b. The pure ZnO particles prepared under the same conditions were less than 20 nm in diameter, as shown in Figure 2c. The inset in Figure 2d shows the selected electron diffraction pattern, which consists of clear electron diffraction circles and bright spots, indicating the presence of the crystalline ZnO particles on the FTBT particles (see Supporting Information).[17] These SEM and transmission electron microscopy (TEM) images clearly confirmed that the poly-

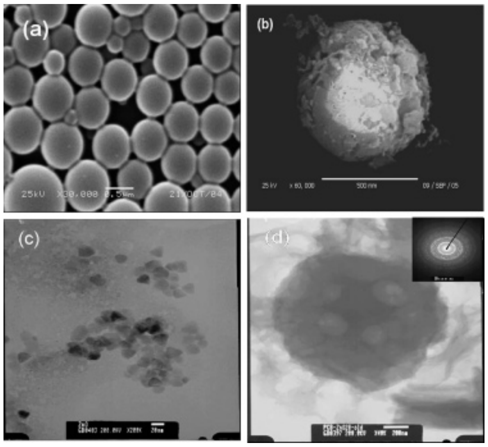

Figure 2. SEM micrographs of (a) pure FTBT and (b) FTBT−ZnO20 and TEM images of (c) pure ZnO and (d) FTBT−ZnO20. Inset: selected area electron diffraction pattern.

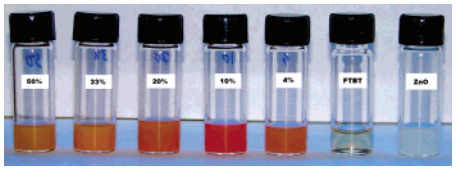

Figure 3. Photographs of FTBT−ZnO hybrids: 1 wt % suspension in THF, under UV light.

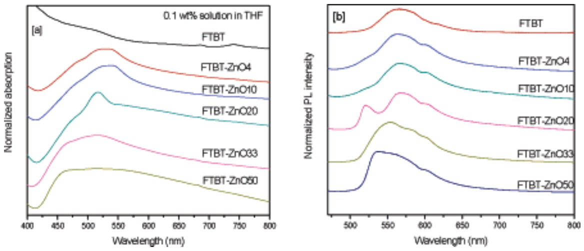

Figure 4. (a) UV−vis absorption and (b) PL spectra of pure FTBT solution and the FTBT−ZnO hybrid suspension (0.1 wt % in THF).

crystalline ZnO nanoparticles were irregularly dispersed on the FTBT particle surfaces.

The physical appearances of the FTBT−ZnO suspensions in tetrahydrofuran (THF) are shown in Figure 3. Hybrid materials with different shades were obtained, depending on the ZnO content. The pure FTBT was pale yellow in color. Interestingly, the color of the hybrid materials changed to reddish orange when the ZnO content was low but turned to bright yellowish orange when the ZnO content was increased. A similar color shade trend was also observed in solid materials. In fact, the pure polymer was completely dissolved in THF. However, the FTBT−ZnO particles did not dissolve well, which indirectly confirmed the presence of the ZnO nanoparticles on the surface of the FTBT particles, because the deposited ZnO can suppress the solubility of the polymer in organic solvents.

The absorption spectra of the pure FTBT solution and FTBT−ZnO suspension in THF (0.1 wt %) are presented in Figure 4a. The absorption maximum of the pure FTBT was near 430 nm, whereas those of the FTBT−ZnO suspensions were red-shifted to some extent and broadened. Coherently, the absorption intensity of the FTBT−ZnO suspensions

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increased with increasing ZnO content. Figure 4b shows the corresponding PL spectra of the pure FTBT and FTBT−ZnO suspensions in THF. Up to 10 wt % of ZnO, the PL spectra were similar to that of pure FTBT, except for a small shoulder at 603 nm. However, at 20 wt % of ZnO, a wider PL spectrum with an additional shoulder at ~520 nm was obtained. At 33 and 50 wt % of ZnO, the emission spectra were blue-shifted, and the shoulder at ~520 nm disappeared. These results were attributed to incorporation of higher carrier property ZnO materials on the surface of the FTBT (see Supporting Information).[11]

The PL quantum yield of the pure FTBT particles dispersed in epoxy films was estimated to be 0.57, using DCM2 as a standard, while that of FTBT−ZnO20 was 0.86. The main reason for the enhancement of quantum yield in hybrid polymer/ZnO materials is due to the formation "caging effect", which protects the fluorescent dye molecules in the core.[8,9] Here, the ZnO nanomaterials that were deposited on the surface of the polymer might have immobilized the polymer moieties within their confined space. The fluorescent FTBT polymer moieties were significantly immobilized by the ZnO nanomaterials on the surface and may cause an increase in emission quantum yield by suppressing radiationless (internal conversion and/or intersystem crossing) decay mechanisms of the photoexcited state. The schematic representation for immobilized FTBT molecules in FTBT−ZnO20 hybrids is shown (Supporting Information). In fact, the total energy losses (due the radiationless decay) between the absorption and emission of pure FTBT and FTBT−ZnO20 hybrids were calculated to be 0.71 and 0.29 eV, respectively, from the figures in Supporting Information. It indicates that the pure FTBT polymer was losing most of its energy in the form of heat, and when compared to the FTBT−ZnO20 hybrid, it means that the difference in energy of ~0.42 eV between pure FTBT and the FTBT−ZnO20 hybrid ($0.71 - 0.29 = 0.42$ eV) was utilized to enhance their emission in FTBT−ZnO20 hybrid.[8] In addition to that, the interactions between the pure polymer molecules can quench their emission intensity due to the formation of excimer at high concentration. However, in FTBT−ZnO20 hybrids, the deposited ZnO nanomaterials might act as the shield, to avoid the interactions among the polymer molecules, and will ultimately enhance their emission intensity leading to the higher quantum yield, when compared to the pure counterpart. On the basis of the above arguments, we speculate that the ZnO particles can hinder some vibration motions of the FTBT chains, which may suppress the internal conversion or intersystem crossing in the excited states, leading to PL emission being blue-shifted and of higher intensity. The high PL intensity was also attributed to the "caging effect" of the ZnO shell, which can reduce the self-quenching of the FTBT molecules in the core.[8,9]

In a typical device fabrication, a certain percentage of pure FTBT or FTBT−ZnO particles were uniformly dispersed in either epoxy or PMMA, and the resulting mixture was dropped into the reflector cup of blue GaN LEDs (Optoway, 460 nm), where the blue chips were situated and the epoxy or PMMA was cured at 120 or 75 °C, respectively. The fabricated hybrid LEDs were characterized, using a high-speed LED test & measurement system with a Keithley current source. The blue LEDs exhibited Commission Internationale de l'Eclairage (CIE) coordinate (x, y) values of less than 0.15. The CIE chromaticity diagrams and related data are presented in Figure 5. In this experiment, the quantity of polymeric material required to convert a portion of the blue light into yellow emission to obtain white light is an important factor. A concentration of 10 wt % of pure FTBT in epoxy was required for white light to be observed. However, only 2 wt % FTBT−ZnO20 in epoxy was sufficient to achieve white light (0.30, 0.36) with much higher brightness. The white light luminosities of the hybrid LEDs fabricated using FTBT and FTBT−ZnO20 were measured to be 1.56 and 1.81 lm, respectively, at a constant operating current of 20 mA. For the sake of comparison, the luminosity of a poly(phenylene vinylene) derivative containing cholestanoxy substituents was reported to be 1.7 lm at 25 mA.[7] This improved result is mainly due to the higher PL quantum yield of the hybrid material (2 wt % in epoxy, $\Phi_{PL} = 0.86$), compared to that of pure FTBT (10 wt % in epoxy, $\Phi_{PL} = 0.57$).

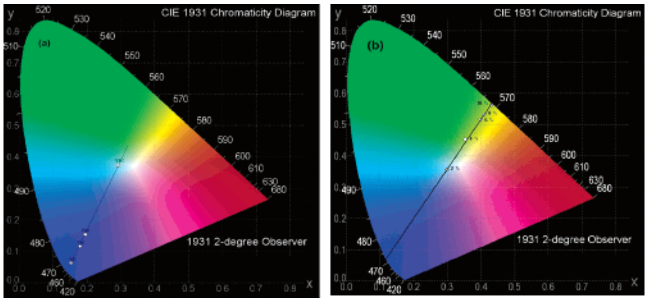

Figure 5. CIE coordinates of hybrid LEDs, fabricated from a commercial blue LED (460 nm) and (a) pure FTBT or (b) FTBT−ZnO20. The contents of pure FTBT and FTBT−ZnO20 in the epoxy matrix were 10 and 2 wt %, respectively.

In summary, polymer−ZnO hybrids were successfully prepared using a chemical bath deposition method at a very low temperature. The formation of ZnO nanoparticles and their deposition on the surface of the FTBT particles were confirmed by XRD, SEM, and TEM. The PL quantum yield of the hybrid was greater than that of the pure polymer. The hybrid LED fabricated from a commercial blue LED and FTBT−ZnO20 yielded a white light with improved efficiency, as compared to the hybrid LED, fabricated from the same blue LED and FTBT. The stability and lifetime of hybrid LED devices that consist of FTBT−ZnO20 showed twofold improvements, which can be further improved by proper encapsulation, while fabricating LED devices. The other detailed mechanism underlying the enhanced PL quantum yield of the hybrid materials is currently under investigation.

Acknowledgment. This work was financially supported by Korea Research Foundation Grant funded by the Korean Government (MOEHRD), KRF-2005-005-J07502.

Supporting Information Available: Experimental technique and methods, hybrid LED fabrication, XRD diffraction of pure FTBT and the PMMA matrix, SAD images of pure FTBT and FTBT−ZnO20 hybrid, PL spectra of pure ZnO, and preliminary lifetime test results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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