



# Multicolor and Fast Electrochromic P(DTB-EDOT)/ZnO Nanocomposite Film

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In this work, uniform and controllable size of ZnO nanoparticles were fabricated via solution-phase approach, and the copolymer based on the monomers of 1,4-di(thiophen-3-yl)benzene (DTB) and 3,4-ethylenedioxythiophene (EDOT) was successfully synthesized with electrochemical polymerization. A new P(DTB-EDOT)/ZnO nanocomposite film was obtained via situ preparation. Cyclic voltammogram and spectroelectrochemical characterization showed that the composite film had a stable and well-defined reversible redox process as well as electrochromic behavior. Besides, the composite film exhibited fast switching time (1 s at 746 nm), significant optical contrast and a variety of colors (red, ochre, green and blue) under different potentials.

**Keywords:** Conjugated Polymer, ZnO Nanoparticles, Nanocomposite Film, Electrochromism.

## 1. INTRODUCTION

Organic-inorganic composites have attracted much attention, especially for composite materials consisting of conducting conjugated polymers and inorganic nanomaterials since they can combine the advantages of both components and may offer special properties through the reinforcement or modification of each other.<sup>1-3</sup> Conjugated polymers have been widely investigated by virtue of their advantageous properties such as excellent conductivity, low fabrication cost and dynamic, color-tunable smart windows.<sup>4-6</sup> Inorganic nanomaterials have excellent thermal stability, high charge transport rate, large surface area and tunable micro-structure.<sup>7-9</sup> The composite film between the two materials tend to bring significant improvement in the performance.<sup>10,11</sup> As well to known, a lot of transition oxide-conducting polymer electrochromic composite films, such as NiO/PPY,<sup>12</sup> IrO<sub>2</sub>/PANI,<sup>13</sup> TiO<sub>2</sub>/PEDOT,<sup>7</sup> have been exploited and the improved electrochromic performances have been found in these composite systems. It is therefore anticipated that the composites based on conjugated polymers and inorganic nanomaterials would present a charming electrochromic performance, such as high coloration efficiency, faster response time and an outstanding operation lifetime.<sup>14-17</sup>

In this article, ZnO nanoparticles were prepared via solution-phase approach. Crystalline structure and morphology characterization were investigated by XRD and TEM. ZnO nanoparticles film was prepared by spin-coating

method and characterized by SEM. Then the copolymer based on the monomers of 1,4-di(thiophen-3-yl)benzene (DTB) and 3,4-ethylenedioxy-thiophene (EDOT) was electrochemically incorporated with ZnO nanoparticles film. The SEM photographs of the composite film were presented; the electrochromic properties such as spectroelectrochemical spectra, switching time were also investigated herein.

## 2. EXPERIMENTAL DETAILS

### 2.1. Preparation of ZnO Nanoparticles and Film

Zinc acetate dihydrate and a certain amount of water were added to ethylene glycol (EG). This solution was heated under reflux for one hour. Then, the precipitates were separated by centrifugation and washed with deionized water. The centrifugation and washing procedure were performed three times. Finally, the collected powders were dried in an electric oven at 100 °C for 24 h.

ZnO powders were ultrasonically dispersed in the ethanol solution. This solution was spin-coated (1000 rpm, 30 s) five times to deposit ZnO nanoparticles on the ITO glass substrate. The samples were dried in ambient conditions at 70 °C. After that, transparent and even ZnO film was obtained from the ITO glass sheet.

### 2.2. Preparation of Composite Film

The copolymer was electrochemically synthesized from a reaction medium containing 3 mM DTB, 3 mM EDOT

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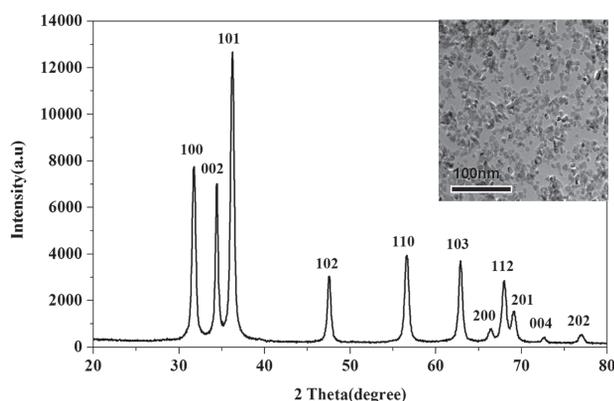
and 0.1 M tetrabutylammonium perchlorate (TBAP) in  $\text{CH}_2\text{Cl}_2$  solution. The redox behavior of copolymer was investigated by cyclic voltammogram (CV) using a three compartment electrolysis cell.<sup>18</sup> ITO conductive glass with ZnO nanoparticles film was used as working electrode. The counter electrode was made from a platinum sheet, and a double-junction Ag/AgCl electrode (silver wire coated with AgCl in saturated KCl solution), 0.1 M TBAP in  $\text{CH}_2\text{Cl}_2$  solution as the second junction was applied as the reference electrode. Electrochemistry experiments were carried out at room temperature.

### 2.3. Instrumentation

All electrochemical experiments were performed on CHI660a electrochemical working station (CHI, Chenhua, Shanghai, China). Spectroelectrochemical studies were carried out on a UV 1800 spectrophotometer. Surface morphologies of composite film were investigated by a Hitachi S-4800 scanning electron microscope. Size and size distribution of nanoparticles were investigated by High Resolution-Transmission Electronic Microscope (HR-TEM, Tecnai G2 F30 S-Twin, Philips-FET). Crystalline structure and particles size were characterized by X-ray diffraction (XRD, X'Pert Pro, PANalytical B.V.)

## 3. RESULTS AND DISCUSSION

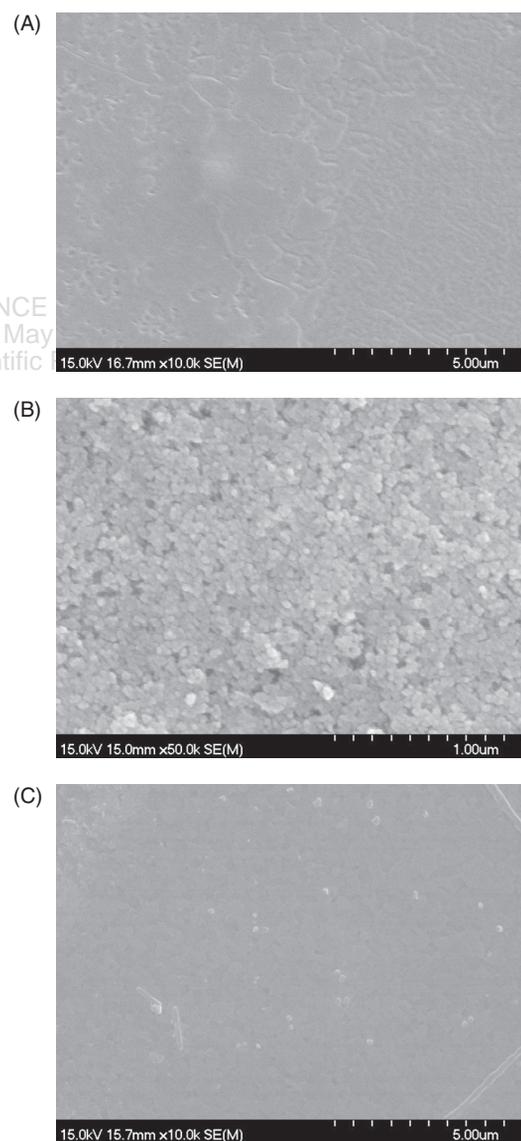
Figure 1 showed the XRD pattern of synthesized ZnO nanoparticles by solution method. The XRD peaks indicated that ZnO nanoparticles had wurtzite structure well matched with standard ZnO according to the Joint Committee on Powder Diffraction Standard (JCPDS) card number 36-1451. The average crystallite size calculated from the XRD pattern was about 15–20 nm according to the Debye-Scherrer formula.<sup>19</sup> The inset of Figure 1 presented TEM image of ZnO nanoparticles, showing that ZnO nanoparticles were nearly spherical in shape and the average size of the particles was about 20 nm, which was similar with the result of XRD pattern. The well-dispersed



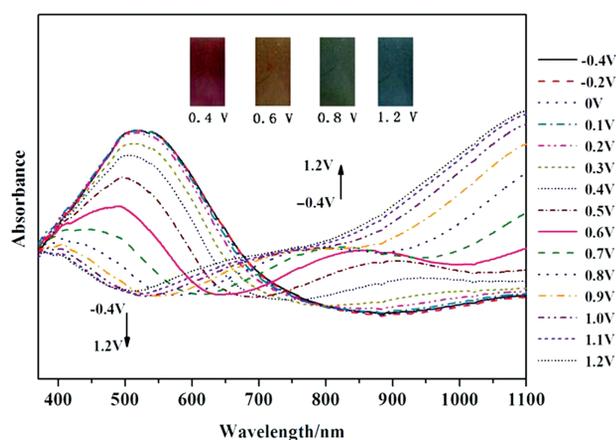
**Fig. 1.** XRD pattern of ZnO nanoparticles (inset: TEM image).

and uniform ZnO nanoparticles were also seen from the TEM image, which could promote the electropolymerization smoothly and obtain stable performance.

With the ZnO nanoparticles film as the working electrode, a copolymer P(DTB-EDOT) was synthesized via the electrochemical polymerization. The FESEM images of copolymer film, ZnO nanoparticles film and as-prepared composite film were investigated as shown in Figure 2. Compared to the rough P(DTB-EDOT) film (Fig. 2(A)) and loose porous ZnO nanoparticles film (Fig. 2(B)), the successful polymerization of P(DTB-EDOT) was confirmed by the obvious deposition layer on the surface of ZnO nanoparticles (Fig. 2(C)). The smooth surface morphology of the composite film was essential and offered the possibility for the preparation of electrochromic devices.



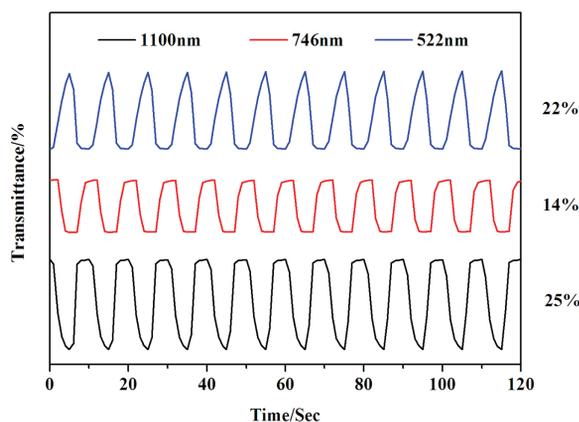
**Fig. 2.** SEM images of (A) P(DTB-EDOT), (B) ZnO nanoparticles, (C) P(DTB-EDOT)/ZnO nanocomposite film.



**Fig. 3.** Spectroelectrochemical spectra and colors of P(DTB-EDOT)/ZnO nanocomposite film at different potentials.

Figure 3 depicted the spectroelectrochemical spectra of the composite film at different potentials ranging from  $-0.4$  V to  $1.2$  V. A well-defined maximum absorption band at  $522$  nm was observed due to the  $\pi-\pi^*$  transition of the neutral state copolymer backbone, and it decreased with the increasing of the potential. The appearance of charge carrier bands (at around  $746$  nm and  $> 1100$  nm) could be attributed to the evolution of polaron and bipolaron bands.<sup>20</sup> In addition, P(DTB-EDOT)/ZnO composite film displayed four different colors (red, ochre, green and blue) at various potentials, which was corresponding to various doped and neutral states. The composite between polymer and inorganic nanomaterial may lead to an increasing in the doping state, and therefore result in the multicolor property of composites.

Electrochromic switching time and optical contrast ( $\Delta T\%$ ) are the two most important characteristics for EC materials. The switching characteristics of the P(DTB-EDOT)/ZnO composite film were analyzed by monitoring the change in transmittance at different wavelengths. The studies were performed by continuously stepping the



**Fig. 4.** Electrochromic switching, optical contrast of P(DTB-EDOT)/ZnO nanocomposites in  $0.1$  M TBAP/ $\text{CH}_2\text{Cl}_2$  between  $-0.6$  and  $1.2$  V with a residence time of  $5$  s at  $522$ ,  $746$  and  $1100$  nm respectively.

voltages between  $-0.6$  V and  $1.2$  V with a  $5$  s delay at each potential (In this case, the switching time was defined as the time required for a system to reach  $95\%$  of its full response<sup>21</sup>). Electrochromic switching response of the composite film was presented in Figure 4. The percentage transmittance changes ( $\Delta T\%$ ) between the neutral and oxidized states were  $22\%$  for  $522$  nm,  $14\%$  for  $746$  nm and  $25\%$  for  $1100$  nm. And the switching times were  $1.6$  s at  $522$  nm,  $1$  s at  $746$  nm and  $2$  s at  $1100$  nm. Therefore, the composite film showed significant optical contrast of  $25\%$  in  $1100$  nm and fast switching time ( $1.0$  s at  $746$  nm). The good stability of the  $\Delta T\%$  in time, fast switching time and high contrast ratio made this composite film a promising material for EC devices and its multicolor and fast electrochromic property possessed potential applications in smart windows or displays.

#### 4. CONCLUSION

A new electrochromic composite material P(DTB-EDOT)/ZnO was successfully synthesized via electrochemical method. At different potentials, the composite film exhibited four hues (from red to blue) with reversible color changes. Spectroelectrochemical studies and electrochromic characterization demonstrated that the composite film had an excellent electrochromic performance such as fast switching time of  $1.0$  s at  $746$  nm and high optical contrast of  $25\%$  at  $1100$  nm.

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