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Synthesis of MWNT/PEDOT Composites for the Application of Organic Light Emitting Diodes

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Organic-inorganic composites composed of electrically conducting poly(3,4-ethylenedioxythiophene)/multi-walled carbon nanotube (PEDOT/MWNT) were prepared by in-situ oxidative polymerization of ethylenedioxythiophene (EDOT) in the presence of MWNTs in supercritical carbon dioxide. Prior to the polymerization, MWNTs were surface modified with 3-(trimethoxysilyl) propyl methacrylate in order to improve the dispersibility in CO₂. This approach provides a facile way to develop solvent free composites with nanostructures and uniformity. The resulting composites were analyzed by FT-IR, transmission electron microscopy, field emission scanning electron microscopy, thermogravimetric analysis, X-ray diffraction and UV-visible spectroscopy. In addition, the effect of the ratio of the MWNT to PEDOT on the polymerization was investigated.

Keywords: conjugated polymer; MWNT; silylating agent; supercritical carbon dioxide; surface modification

INTRODUCTION

Organic and polymeric materials are of interest in recent years for their potential applications in the electronic devices such as organic light emitting diodes (OLEDs) and photovoltaic cells [1]. Carbon nanotubes (CNTs) containing unique structural, mechanical, and electronic

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properties have recently attracted considerable interest for their potential applications, such as field emitters [2], nanoelectronic devices [3], probe tips for scanning probe microscopy [4], and nanotube-based composites [5]. Experimentally introducing CNTs into a polymer matrix can improve the mechanical properties and electrical conductivity of the neat polymer matrix [6–9]. According to many reports, besides possibly improving the mechanical and electrical properties of polymers, the formation of polymer/CNT composites is considered a useful approach for incorporating CNTs into the polymer based devices [10–12]. Among these polymer/CNT composites, many studies have been focused on the combination of CNTs and intrinsic conducting polymers, including poly(*p*-phenylene vinylene)/CNT or poly(3-octylthiophene)/CNT for their use in the highly efficient photovoltaic cells [10,11]. Among the various intrinsic conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are relatively new members to the intrinsically conducting polymer family, and are among the most successful and useful conjugated polymers due to their high stability, low band gap, high conductivity and excellent transparency in their doped state [13]. Nanotube dispersion into polymers can be improved by either using surfactants as processing aids, functionalization, or *in situ* polymerization. The ability to combine CNT with conducting matrices such as PEDOT to produce composite materials has stimulated much research interest in organic electronics [14–17]. Diverse chemical methodologies have been developed to synthesize PEDOT/CNT composites. However, processing of polymers generally employs large quantity of organic solvents that are noxious and harmful to the environment. In addition the residual solvents remained in the polymers limited their applications in the organic electronics. Thus, the processing with supercritical fluids offers an attractive alternative to the conventional processing. Among supercritical fluids, supercritical carbon dioxide (scCO₂) is the most popular because it is non-flammable, non-toxic, cheap and easy to obtain. It can dissolve many organic compounds, and carry them into micropores [18]. On the other hand the solubility of scCO₂ or compressed CO₂ in many organic solvents is very high, leading to a reduction in the solvent strength of the organic solvents. The special properties of scCO₂ have been used to fabricate nanomaterials which are difficult to prepare by traditional technique. Recently, Dai and co-workers synthesized carbon nanotube/poly(2,4-hexadiyne-1,6-diol) composites in scCO₂ [19]. More recently, Steinmetz *et al.* showed that scCO₂ can be used to fill nanotubes with various organic molecules and that is possible to polymerize conducting polymers inside carbon nanotubes [20]. Though few studies have been reported, particularly

there has been no report in the literature so far based on the *in-situ* one pot synthesis of conducting polymer/CNT composite in scCO_2 .

In this report, we have demonstrated the synthesis of MWNT/PEDOT composites by *in-situ* oxidative polymerization of EDOT in the presence of surface functionalized nanotubes in scCO_2 . The resulting composites are characterized by various techniques including FT-IR, TEM, TGA, and UV-visible.

EXPERIMENTAL

Materials

Ethylenedioxythiophene (EDOT) (Aldrich) was purified using a column of activated basic alumina. The multi-walled carbon nanotubes (MWNTs) synthesized by a catalytic chemical vapor deposition (CCVD) method were purchased from Aldrich (>90% pure). The MWNTs have a diameter of 10–15 nm and length of 0.1–10 μm . 3-(Trimethoxysilyl) propyl methacrylate (MPS, Aldrich), methanol (Aldrich), ferric chloride (Aldrich) and research-grade CO_2 (Daeyoung Co., 99.99%) were used as received.

Synthesis of PEDOT/MWNT Composite

In a typical experiment, 0.03 g of MPS modified MWNTs was dispersed into 1 g of EDOT under sonication for 30 minutes to form a suspension, and then the black suspension was moved into a 40 mL high-pressure reactor vessel. A required amount of ferric chloride dissolved in small amount of methanol was added into the vessel. The reactor was sealed, and the compressed CO_2 was introduced using a syringe pump at 40°C and 103 bar. The *in-situ* polymerization was carried out with the stirring speed of 600 rpm for about 3–4 h, and then the vessel was cooled to room temperature. The resulting precipitate was collected and repeatedly washed with methanol and distilled water to remove the oxidant. Finally, the sample was dried at 80°C for 24 h in a vacuum oven.

Characterization

Microscopic images of composites were obtained by a Hitachi S-2400 field emission scanning electron microscope (FESEM). TEM images were obtained on a transmission electron microscope (JEOL, JEM-2010) operated with an accelerating voltage of 200 kV. FT-IR characterizations were performed using a BOMEM Hartman & Braun spectrometer. The XRD patterns were collected on a powder X-ray diffractometer (Philips, X'Pert-MPD) with Cu K α radiation. Thermal stability was

investigated by thermal gravimetric analyzer (Perkin Elmer, TGA-7) under a nitrogen flow (35 mL/min). The heating rate was 10°C/min. UV-visible spectra of the diluted composite dispersions in the 200–1000 nm range are obtained using a Perkin Elmer instrument.

RESULTS AND DISCUSSION

The principle procedure involved in the synthesis of PEDOT/MWNT composite consists of two steps: the surface modification of MWNT with MPS in order to disperse well in scCO_2 , which is due to the favorable interaction between MPS molecules and CO_2 [21]. The surface modification of MWNTs was carried out according to the procedure given in the literature [22]. The PEDOT/MWNT composite was synthesized by chemical oxidative polymerization of monomer EDOT in the presence of surface modified MWNT in scCO_2 . The composites with different weight fraction of MWNT (1% and 3%) with respect to EDOT were also carried out.

Typical FT-IR spectra of PEDOT and PEDOT/MWNT 3 wt% composite are shown in Figure 1. It is clear that PEDOT and the composite showed very similar spectra. In the spectrum of PEDOT bulk powder the vibrations at 1334 and 1512 cm^{-1} are due to the C–C or C=C stretching of the quinoidal structure of thiophene ring and the ring stretching of thiophene ring, respectively. The peaks originating from the stretching in the alkylendioxo group are observed at 1183, 1142, and 1050 cm^{-1} . The peaks assigned to C–S bond stretching in the thiophene ring are also observed at 977, 832, and 680 cm^{-1} [23]. As expected, the spectrum of PEDOT/MWNT composite clearly exhibited the similar adsorption bands. However, the corresponding peaks were broadened and shifted to lower wavenumber in the spectrum of composite, which might result from the interaction of PEDOT with MWNTs.

The surface morphologies of MWNTs, PEDOT and PEDOT/MWNT 3 wt% composite were examined using FESEM. From Figure 2(a), it is clear that the bulk PEDOT, synthesized without MWNT, showed a typical morphology. The pristine MWNT morphology was also displayed in Figure 2(b) as endless, tangled, hollow ropes with smooth surface and the diameter of each nanotube is about 10–15 nm. In Figure 2(c), PEDOT is tightly coated onto the surface of each nanotube and many neighboring MWNTs were joined together with the conducting polymer PEDOT at a variety of angles. Figure 3 shows the typical TEM image of PEDOT/MWNT 3 wt% composite. The apparent physical nature of PEDOT changed remarkably after composite formation and is shown in Figure 3(a). From the close inspection of composite (Fig. 3(b)), a tubular layer of PEDOT film is coated on the surface of

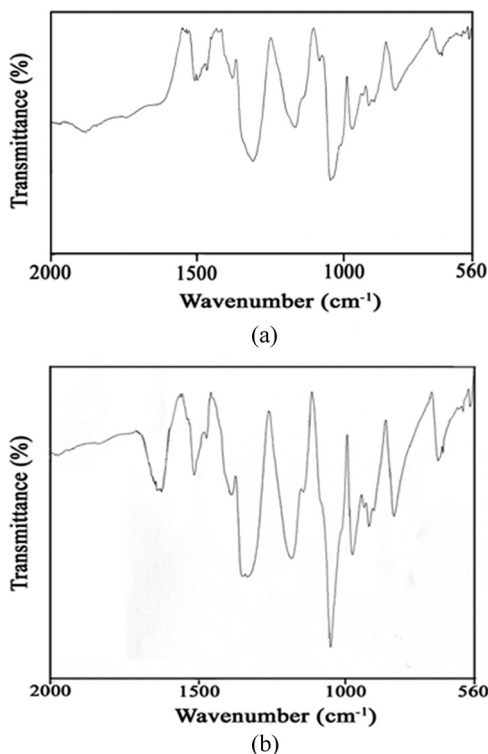


FIGURE 1 FT-IR spectra of (a) PEDOT and (b) PEDOT/MWNT 3 wt% composite.

MWNTs. The diameter of the composite (around 50 nm) becomes larger than that of pristine MWNTs after *in-situ* polymerization. Together with the FESEM images, we conclude that MWNTs are well dispersed in the polymer matrix.

Thermal stability of PEDOT/MWNT 3 wt% composite was analyzed by TGA in nitrogen, and the result was compared with pure PEDOT as shown in Figure 4. All the samples followed the similar decomposition trend with exhibiting a gradual weight loss. It can be seen that MWNTs were stable and did not show a dramatic decomposition in the tested temperature range. The as prepared PEDOT was stable up to the temperature of 250°C. From 250°C a continuous degradation occurs until major decomposition obtained in the region between 350–450°C [23]. However, it was found that the thermal stability of composite is higher than that of pure PEDOT which was obviously related to the existence of thermally stable MWNTs.

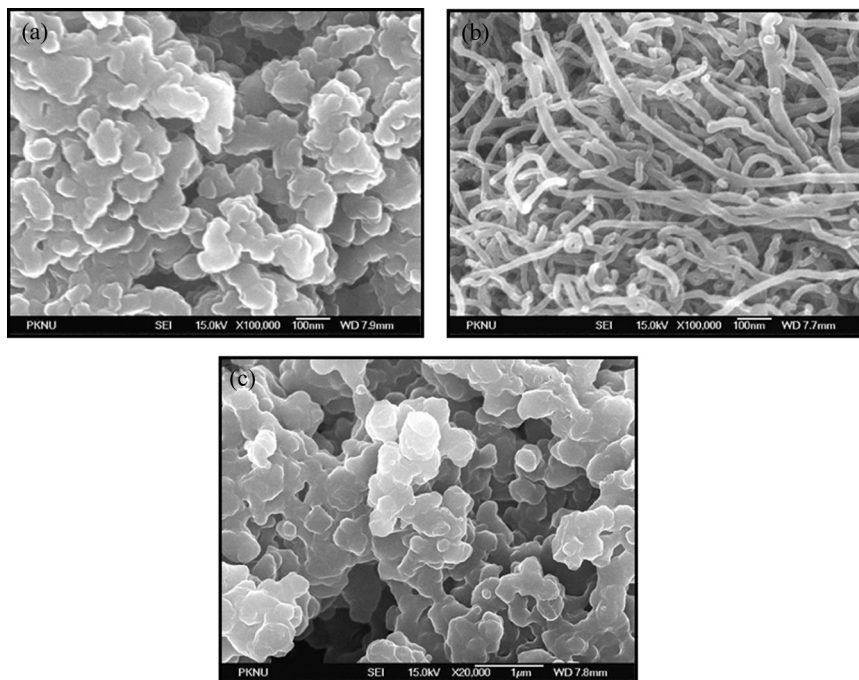


FIGURE 2 FESEM images of (a) PEDOT, (b) MWNTs, and (c) PEDOT/MWNT 3 wt% composite.

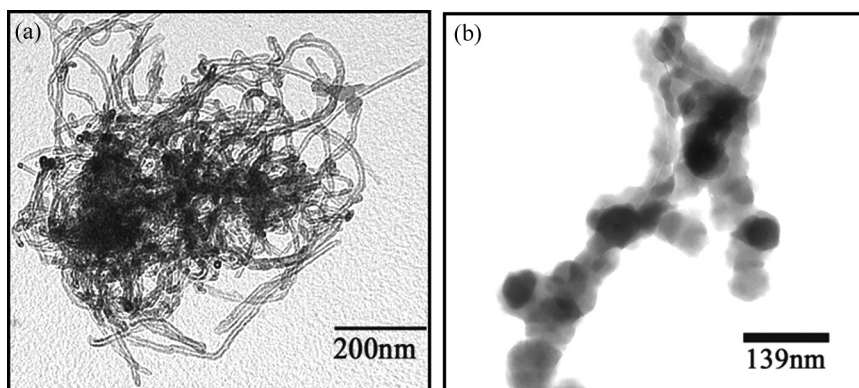


FIGURE 3 TEM images of (a) PEDOT/MWNT 3 wt% composite and (b) close inspection.

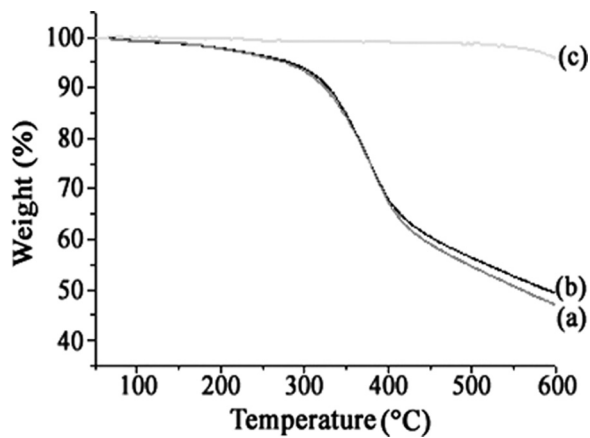


FIGURE 4 TGA curves of (a) PEDOT, (b) PEDOT/MWNT 3 wt% composite, and (c) MWNTs in nitrogen.

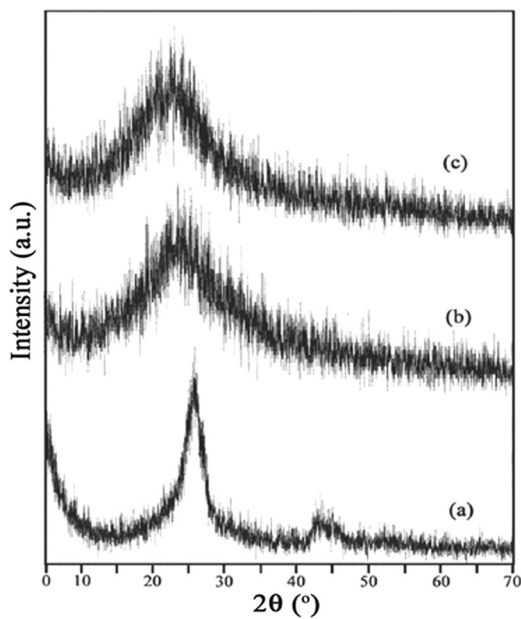


FIGURE 5 XRD patterns of (a) MWNTs, (b) PEDOT/MWNT 3 wt% composite, and (c) PEDOT.

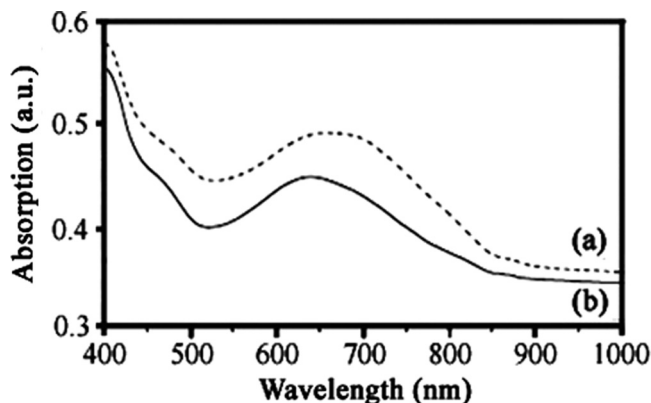


FIGURE 6 UV-visible absorption spectrum of (a) PEDOT/MWNT composite and (b) PEDOT.

Figure 5 shows the XRD patterns of MWNTs, PEDOT, and PEDOT/MWNT 3 wt% composite. Two peaks were observed at 2θ values of 25.8° and 43.3° in the spectrum of MWNTs, which were attributed to a graphite-like structure [24]. In contrast, no peaks were observed in the spectrum of PEDOT, suggesting that the polymer prepared in the absence of MWNTs is amorphous. The XRD pattern of composite was very similar to that of PEDOT, indicating that no additional crystalline order had been introduced. The results revealed that a layer of very thin film was formed on the surface of MWNTs in the polymerization process; the outer layer of the composite was thus similar to PEDOT. While the appearance of a small peak at 2θ value of 25.6° suggested the existence of MWNTs in the composite.

The UV-visible absorption spectrum of PEDOT/MWNT composite is shown in the Figure 6. As expected like PEDOT [25], two features were observed for composite in the range between 200–1000 nm. The absorption peak around 500 is assigned to $\pi-\pi^*$ electronic transition of the polymer. A broad peak starting near 600 nm and centered at 890 nm has been attributed to the polaron or bipolaron state, a charge-carrying energy state between the valence and conduction bands.

CONCLUSION

In summary, we have described a facile route for the synthesis of composites composed of MWNT and PEDOT by scCO_2 mediated *in-situ* chemical oxidative polymerization method. *In-situ* polymerization allows the monomer to interact with the CNT surface, producing an

enclosed nanotube wrapped and stabilized by polymer. TEM and FESEM analysis showed that a tubular layer of coated PEDOT film is present on the surface of MWNTs. By comparing with pure PEDOT, the PEDOT/MWNT composite showed enhanced thermal stability. The UV-visible absorption spectra of the diluted colloidal dispersion of PEDOT/MWNT composites were similar to those of the PEDOT. The analytical results showed the feasibility of the PEDOT/MWNT composites in various applications, such as diodes, photovoltaic cells and other devices.

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