

## Research Article

# Preparation of Polyaniline-Doped Fullerene Whiskers

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Fullerene C<sub>60</sub> whiskers (FWs) doped with polyaniline emeraldine base (PANI-EB) were synthesized by mixing PANI-EB/*N*-methyl pyrrolidone (NMP) colloid and FWs suspension based on the nature of the electron acceptor of C<sub>60</sub> and electron donor of PANI-EB. Scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), and ultraviolet-visible (UV-Vis) spectra characterized the morphology and molecular structure of the FWs doped with PANI-EB. SEM observation showed that the smooth surface of FWs was changed to worm-like surface morphology after being doped with PANI-EB. The UV-Vis spectra suggested that charge-transfer (CT) complex of C<sub>60</sub> and PANI-EB was formed as PANI-EB<sup>δ+</sup>-C<sub>60</sub><sup>δ-</sup>. PANI-EB-doped FWs might be useful as a new type of antibacterial and self-cleaning agent as well as multifunctional material to improve the human health and living environment.

## 1. Introduction

Since the discovery of fullerenes (including buckminsterfullerene, C<sub>60</sub>), the physical and chemical properties of this new allotropic carbon form have been investigated extensively [1–3]. Recently, fullerene nanocrystal which is constructed by fullerene C<sub>60</sub> attracts many researchers' attention, because those special crystals not only own the property of fullerene C<sub>60</sub> such as the nature of electron acceptor but also get the special dimension effect [4–8]. Fullerene C<sub>60</sub> whiskers (FWs), among the crystals, catch special attentions and are widely studied in many fields, recognized its potential applications in solar cells, [9] catalysts carriers [10, 11], and so on. Quite recently, FWs have been studied together with other materials. For example, the embedment of potassium atom in fullerene cage could increase the conductivity of FWs dramatically [12]. In biochemical field, joint research of FWs and DNA exhibits potential bioanalytical applications [13].

Polyaniline (PANI), as a conducting polymer, has great potential for modification of molecular structure, undergoes a special proton doping mechanism, and has got enormous attentions since the early 1980s [14]. Excellent antibacterial performance of PANI against *Escherichia coli* and

*Gram*-positive *Staphylococcus aureus* microorganisms has been demonstrated under both dark and visible light conditions [15]. The electrostatic adherence interaction between the PANI molecules and the bacteria may play a very important role in the antibacterial reaction of the PANI. And in this perspective, FWs which are in micron scale could be used in preparing composites materials with large specific surface areas and micron dispersion with better antibacterial effect. Also, previous research reported that PANI-EB doped with fullerene C<sub>60</sub> resulted in charge-transfer (CT) complexes between PANI-EB and C<sub>60</sub> due to the nature of the electron acceptor of C<sub>60</sub> and electron donor of PANI-EB to achieve higher conductivity [16–18]. Practically, due to the special nature of PANI-EB and FWs, PANI-EB-doped FWs might be useful as electromagnetic shielding materials, highly hydrophobic materials, antistatic materials, and a new type of antibacterial agent and self-cleaning as well as multifunctional material for improving the human health and living environment. However, how to integrate PANI-EB and FWs in nanolevel and prepare compatible composites becomes a challenge. Yilmaz and Küçükyavuz studied solution properties of PANI and found that the PANI-EB can be dissolved in *N*-methyl pyrrolidone (NMP) to form

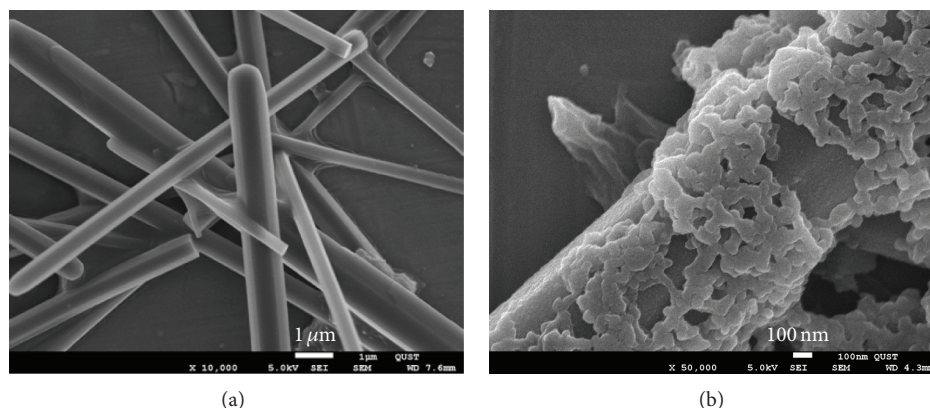


FIGURE 1: SEM images of (a) FWs and (b) PANI-EB-doped FWs.

PANI-NMP colloid [19]. A well mixture of PANI-EB-NMP colloid and FWs in suspension is likely to cause interaction between  $C_{60}$  and imine groups of PANI-EB at molecule level.

In this work, we aimed at preparation of PANI-EB-doped FWs by using ultrasound treatment and NMP as medium solvent. Scanning electron microscopy (SEM), Fourier transformation infrared (FT-IR) and ultraviolet-visible (UV-Vis) spectra characterized the composite product of FWs, PANI-EB and their interaction.

## 2. Experimental

**2.1. Synthesis of FWs.** FWs were prepared using the liquid-liquid interfacial precipitation method [20]. Firstly, a powder of  $C_{60}$  fullerene (30 mg, 99.95% purity, MTR Ltd., USA) was dissolved in 10 mL toluene to prepare a toluene solution with saturated  $C_{60}$ . Secondly, the  $C_{60}$ -toluene solution was ultrasonically stirred in a bath of water for 10 min at 8°C (40 kHz, 50 W, KQ-50DA, Kun Shan Ultrasonic Instruments Co., Ltd.). After ultrasound treatment, the  $C_{60}$ -toluene solution was filtered to remove the excessive  $C_{60}$  powder. Next, 5 mL isopropyl alcohol (IPA) was slowly added to the 5 mL  $C_{60}$ -toluene saturated solution to form a liquid-liquid interface between IPA and  $C_{60}$  solution. The 10 mL  $C_{60}$ -toluene-IPA solution was named “mother solution.” Dark-brown cluster FWs were suspended in the mother solution after stored at 8°C for 3 days. Thirdly, in order to quantify the product of FWs, 10 mL mother solution was filtered by filter paper. After vacuum drying and weighing, 10.8 mg of FWs was deposited on the screen and the yield of the FWs is estimated to be about 72%.

**2.2. Synthesis of PANI-EB.** Firstly, 1.8 mL of aniline and 1.14 g of ammonium persulphate (APS) were added to 100 mL 1 M aqueous of hydrochloric acid (HCl) in beaker, respectively. The mixed HCl solution was stirred for 1 min and then kept at 4°C for 12 h to carry out aniline polymerization. Then, the dark green resulting product-PANI emeraldine salt (PANI-ES) was filtrated and the precipitate was washed several times with distilled water. Secondly, the PANI-ES was soaked by 45 mL aqueous of 3 wt% ammonium at 60°C in a 15 cm

evaporating dish for 72 h and then blue nonconductive PANI emeraldine base (PANI-EB) was obtained.

**2.3. Synthesis of PANI-EB-Doped FWs.** The PANI-EB powder was grinded and mixed with NMP to make 10 mg/mL PANI-EB/NMP colloid. PANI-EB/NMP colloid was ultrasonicated for 30 min at 4°C to ensure homogeneity and filtered to remove undissolved PANI-EB particles. 3 mL of PANI-EB/NMP colloid filtrate was added to the mother solution prepared in Section 2.1. The mixed solution was stirred by ultrasound for 30 min. After ultrasonic treatment, the mixed solution was kept at 4°C for 48 h and then FWs were well enwrapped by PANI-EB; that is, PANI-EB-doped FWs were obtained.

**2.4. Characterizations.** The morphologies of FWs and PANI-EB-doped FWs were characterized by using SEM (JEOL JSM-6700F). For the purpose of electron microscopic measurement, the specimens were placed on aluminum foil as substrate. FT-IR spectroscopy was performed for the specimen dried at room temperature and a FT-IR apparatus (Bruker Vertex 70) was used to analyze the constituents of FWs, PANI-EB powder, and PANI-EB-doped FWs. UV-Vis spectroscope (Shimadzu, UV-2450) was used to analyze the formation mechanism of PANI-EB-doped FWs.

## 3. Results and Discussion

Figure 1(a) shows that FWs were obtained and the diameters of FWs ranged from a few hundred nanometers to a micrometer. The length of the FWs was in order of microns. The highly anisotropic nature of these crystal seeds formed after IPA was injected into  $C_{60}$ -toluene solution is generally accepted as the explanation of the formation of the one-dimensional (1D) structure [21]. The growth direction is confined to [110] direction resulting in the 1D structure shown in Figure 1. [22, 23] The surfaces of the FWs were quite smooth and flat compared with PANI-EB-doped FWs which were coated with PANI-EB as shown in Figure 1(b). Meanwhile, it was speculated that the uniform attachment may be due

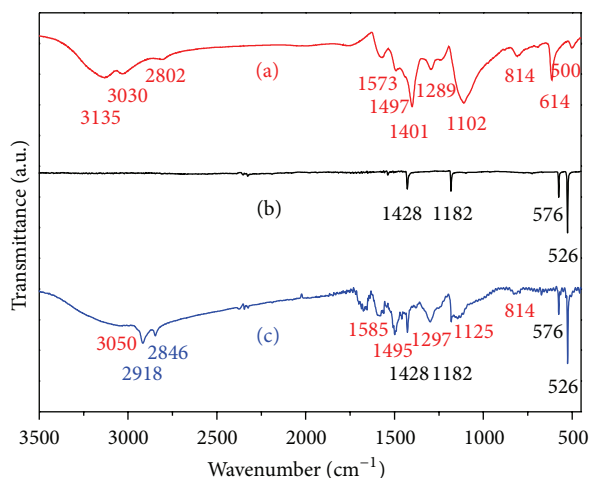


FIGURE 2: FT-IR spectra of (a) FWs, (b) PANI-EB powder, and (c) PANI-EB-doped FWs.

to the formation of CT complex between  $C_{60}$  and PANI-EB [16, 17, 24].

Figure 2 shows FT-IR spectra of FWs, PANI-EB powder, and PANI-EB-doped FWs, respectively. In Figure 2(a), the four characteristic peaks of  $526\text{ cm}^{-1}$ ,  $576\text{ cm}^{-1}$ ,  $1182\text{ cm}^{-1}$ , and  $1428\text{ cm}^{-1}$  indicate that the FWs constitute  $C_{60}$  [25]. As shown in Figure 2(b), the IR absorption peaks at  $500\text{ cm}^{-1}$ ,  $814\text{ cm}^{-1}$ , and  $1102\text{ cm}^{-1}$  observed in PANI-EB powder are the results of bending and plane vibration of aromatic ring. The absorption peaks of Ar-N vibration appeared at  $1401\text{ cm}^{-1}$  and  $1289\text{ cm}^{-1}$ . The absorptions at  $1497\text{ cm}^{-1}$  and  $1573\text{ cm}^{-1}$  reflect the existence of N-B-N and N=Q=N.  $2802\text{ cm}^{-1}$  and  $3030\text{ cm}^{-1}$  are the vibration of C-H in benzene ring with different chemical environment. The absorption of stretching vibration of -N-H is  $3135\text{ cm}^{-1}$ . The ten characteristic peaks as shown in Figure 2(b) agreed with IR spectrum of PANI-EB reported in [26]. Figure 2(c) shows the FT-IR spectra of PANI-EB-doped FWs. Apparently, the peaks constituted the peaks of PANI-EB, such as  $814\text{ cm}^{-1}$ ,  $1125\text{ cm}^{-1}$ , and so forth, and four characteristic peaks of  $526\text{ cm}^{-1}$ ,  $576\text{ cm}^{-1}$ ,  $1182\text{ cm}^{-1}$ , and  $1428\text{ cm}^{-1}$  of  $C_{60}$ . However, to the peaks of PANI-EB in composite material, many peaks have shifted probably due to the interaction between PANI-EB and  $C_{60}$ ; especially the disappearance of absorption of stretching vibration of -N-H indicates that  $C_{60}$  may have taken the place of H atom which means the formation of the CT complex of PANI-EB $^{\delta+}$ - $C_{60}^{\delta-}$  structure [24].

Figure 3 shows the UV-Vis spectra of FWs, PANI-EB powder, and PANI-EB-doped FWs, respectively. The FWs give four absorption peaks at 240, 322, 420, and 680 nm, which are characteristic peaks of  $C_{60}$  molecule [27]. As shown in Figure 3(b), the absorption at 286 nm is reckoned as the  $n-\pi^*$  transition, and 370 nm and 680 nm correspond to the excitation of benzene and quinoid structure [28]. The peaks at 440 nm and 546 nm are speculated the result of residual salts. Figure 3(c) is the UV-Vis spectrum of PANI-EB-doped FWs. Apparently, the peaks of Figure 3(c) are not a simple superposition of the former two peaks which means the

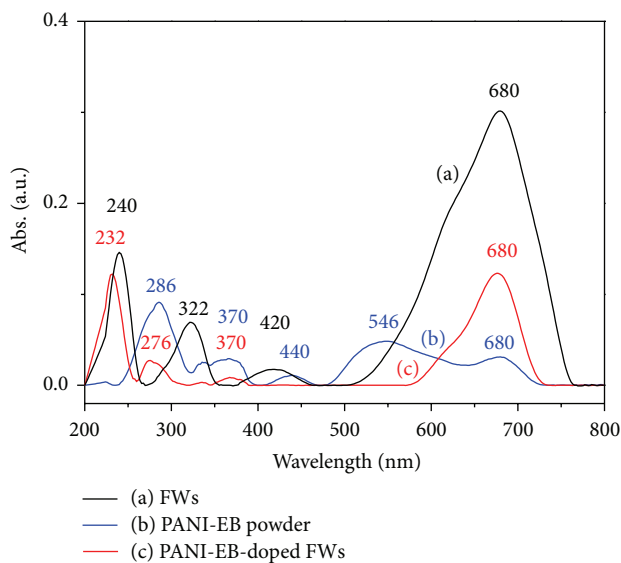


FIGURE 3: UV-Vis absorption spectra of (a) FWs, (b) PANI-EB powder, and (c) PANI-EB-doped FWs.

interaction happens between  $C_{60}$  and PANI-EB. Blue shift happened for FWs and PANI-EB from 240 nm to 223 nm and from 286 nm to 276 nm, respectively, indicating the formation of PANI-EB $^{\delta+}$ - $C_{60}^{\delta-}$  CT structure is confirmed.

#### 4. Conclusions

A new method of preparation of PANI-EB-doped FWs by ultrasonating the mixture of PANI-EB/NMP colloid and FWs suspension was demonstrated. The interaction between PANI-EB and FWs in PANI-EB-doped FWs was confirmed by FT-IR and UV-Vis spectra and it is suggested that CT complex of  $C_{60}$  and PANI-EB was formed as PANI-EB $^{\delta+}$ - $C_{60}^{\delta-}$ .

#### Conflict of Interests

The authors declare that they have no conflict of interests.

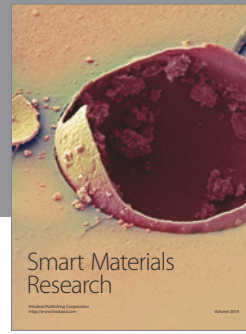
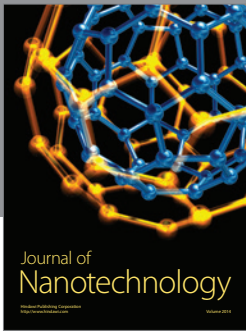
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