Research Article

Preparation of Composite Films of a Conjugated Polymer and C₆₀NWs and Their Photovoltaic Application

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Composite films of conjugated polymers, such as poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and poly(3-hexylthiophene) (P3HT), with C₆₀ nanowhiskers (C₆₀NWs) were prepared. The photoluminescence originating from the conjugated MDMO-PPV polymers was effectively quenched in the composite film, indicating a strong interaction between the conjugated polymer and C₆₀NWs. The photovoltaic devices were fabricated using C₆₀NW (conjugated polymer) composite films, resulting in a power conversion efficiency of ∼0.01% for P3HT with short length thin C₆₀NWs, which is higher than that previously reported for thick C₆₀ nanorods. The present study gives new guidance on the selection of the type of C₆₀NWs and the appropriate polymer for new photovoltaic devices.

1. Introduction

Due to their unique physical and chemical properties, fullerenes have tremendous potential as building blocks for new materials [1]. Recently, fullerene-based supramolecular nanoarchitecture, such as nanowhiskers [2], nanotubes [3], nanorods [4], nanowires [5], and nanosheets [6, 7], has attracted special interest because of their unique chemical and physical properties and their possible application in the fields of materials and medical sciences. Their unique properties are a result of the high symmetry of the nanoarchitecture and the presence of novel π-conjugated systems in supramolecular nanoarchitecture. Very recently, high photosensitivity and excellent electron accepting nature of C₆₀ nanorods were reported by Saran et al. [8]. They also demonstrated that the photosensitivity of the C₆₀ nanorods can be enhanced by organic and inorganic photodoping [8].

Fullerenes form a wide variety of donor-acceptor complexes with different classes of organic and organometallic donors [9]. These complexes possess a wide range of physical properties, including metallic, photoconductive, and unusual magnetic properties. Within this family, we have recently reported the preparation of C₆₀/ferrocene hybrid nanosheets [10, 11] and C₆₀/Co-porphyrin nanosheets [12] by a liquid-liquid interfacial precipitation (LLIP) method. These nanosheets showed very unique optical and charge transport properties.

In various donor molecules, conjugated polymers such as polyphenylenevinylene (PPV) are well known and have been widely studied as photoactive materials in organic thin-film transistors (OTFTs) [13] and organic photovoltaics (OPVs) [14]. To date, various blends of conjugated polymers and fullerene molecules have been reported to fabricate the effective OTFTs and OPVs [15]. In such cases, PCBM (C₆₀ ester derivative) soluble in organic solvents was the most effective one; however, after fabricating the blend films, the molecules were present mostly as aggregates forming the chain structure, through which electrons migrate efficiently [16].

We herein report the preparation of composite films of C₆₀ nanowhiskers (C₆₀NWs), instead of the C₆₀ molecules because the C₆₀NWs are known to exhibit high electron
mobility [17–19]. The observed mobility of well-aligned 1D C$_{60}$ nanocrystals [19] was also much higher than that of PCBM [20]. The C$_{60}$ NWs were then mixed with well-employed conjugated polymers (poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)-1,4-phenylene-vinylene] (MDMO-PPV) and poly(3-hexyliothiophene) (P3HT)). Thus, C$_{60}$ NWs are expected to be efficient new blend components.

The conjugated polymers (MDMO-PPV and P3HT) were employed because these conjugated polymers are well-known photoenergy harvesting polymers with electron donating ability.

In the present study, we found that the photoluminescence originating from MDMO-PPV was effectively quenched in the composite films, indicating a strong interaction between the conjugated polymers and C$_{60}$ NWs. The photovoltaic devices were also fabricated using C$_{60}$ NW (conjugated polymer) composite films; the power conversion efficiency varied with the diameter and length of the C$_{60}$ NWs, in addition to the type of polymer and device structure.

2. Materials and Methods

2.1. Materials. The C$_{60}$ NWs used in this study were prepared by a liquid–liquid interfacial precipitation (LLIP) method in which C$_{60}$ NWs were formed at an interface between the C$_{60}$-containing benzene and isopropyl alcohol (IPA). In a typical preparation, 4 mL of C$_{60}$-saturated benzene was placed into a glass bottle in an ice bath. To this solution, 8 mL of IPA was added slowly, and the resulting two-layer mixture was vigorously shaken and subjected to ultrasonication for 1 min. The resulting mixture was stored at 5°C for 24 h to grow C$_{60}$ NWs.

2.2. Optical Measurements. Optical microscopy images were observed with an Olympus BX51. UV-Vis-NIR spectra of the films were measured by UV-Vis-NIR spectrometer (V-570, JASCO, Japan) equipped with an integrating sphere in the reflection geometry. Photoluminescence spectra were measured by fluorescence spectroscopy (FP-6600, JASCO, Japan).

2.3. Preparation and Characterization of Photovoltaic Devices. Photovoltaic devices based on C$_{60}$ NWs were prepared as follows. A film of poly(3,4-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was deposited onto prepatterned ITO electrodes by spin-coating (HC Stark), followed by annealing at 100°C for 1 h. C$_{60}$ NWs film was prepared on the ITO electrodes by casting C$_{60}$ NW solution. The solution of conjugated polymers (5 mg/mL) was spin-coated onto the C$_{60}$ NW film. After annealing at 80°C for 8 h under vacuum, LiF (∼0.5 nm) and Al (∼100 nm) were deposited under vacuum to completely fabricate the devices; ITO/PEDOT:PSS/C$_{60}$ NWs-polymer/LiF/Al, which contained poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and poly(3-hexyliothiophene) (P3HT), were employed as polymers.

The devices were characterized using Ivium CompactStat (Ivium Technologies) under an AM 1.5 G (1 sun 100 mW/cm$^2$) illumination from an OTENTO-SUN-III (Bunkoukeiki, Japan) solar simulator after annealing at 150°C for 20 min under Ar atmosphere.

3. Results and Discussion

In 2007, the preparation of nanoporous C$_{60}$ NWs by the LLIP method at the interface between the C$_{60}$-containing benzene and isopropyl alcohol (IPA) was reported in our group [21]. The formation of pores has been confirmed by the observed higher specific surface area of 376 m$^2$/g, whereas the specific surface area of pristine C$_{60}$ powder is 20 m$^2$/g. The fine pores on the wall surface of C$_{60}$ NWs were also observed by TEM [21]. Recently, we used nanoporous C$_{60}$ NWs to prepare C$_{60}$ NWs modified onto glassy carbon (GC) electrodes to study the electrochemical reduction of oxygen, suggesting that nanoporous C$_{60}$ NWs are electrochemically active materials [22]. Therefore, in the present study, we also used these nanoporous C$_{60}$ NWs to prepare C$_{60}$ NW-MDMO-PPV composite films. We prepared the C$_{60}$ NW-MDMO-PPV composite films by casting a cyclohexanone solution of MDMO-PPV onto C$_{60}$ NW films on a glass plate. Figure 1 shows the optical microscope images of the (a) C$_{60}$ NWs and (b) C$_{60}$ NW-MDMO-PPV composite films. The photographs of three films are also shown in Figure 1.

The C$_{60}$ NW film in Figure 1(a) was prepared by casting a benzene/IPA solution of C$_{60}$ NWs onto a glass plate, in which most of the C$_{60}$ NWs had diameters less than 100 nm and some C$_{60}$ NWs had larger diameters (∼1 μm). The lengths of C$_{60}$ NWs ranged from 100 μm to 1000 μm. The representative image in Figure 1(b) shows that the one-dimensional morphology of C$_{60}$ NWs was retained even after the formation of the composite film and that the larger diameters of C$_{60}$ NW-MDMO-PPV composite became prominent and hid smaller ones under the polymer film. The interface between C$_{60}$ NWs and MDMO-PPV was not as clear, indicating that C$_{60}$ NWs and MDMO-PPV fused together at the interface. This can be related to the increase in diameter of the C$_{60}$ NW-MDMO-PPV composite. Furthermore, fattening of C$_{60}$ NWs would be expected with polymer wear, and advances in the aggregation of the C$_{60}$ NWs with the cyclohexanone solution containing MDMO-PPV would also be anticipated.

Figures 1(c)–1(e) show photographs of the C$_{60}$ NWs, MDMO-PPV, and the C$_{60}$ NW-MDMO-PPV composite films on glass plates. Although the C$_{60}$ powders appeared black in color, the C$_{60}$ thin film had a yellow ocher color on the glass plate, as shown in Figure 1(c). The orange color of the C$_{60}$ NW-MDMO-PPV composite film became darker compared to the bright reddish orange color of the MDMO-PPV film, supporting the formation of the C$_{60}$ NW-MDMO-PPV composite.

Figure 2 shows the UV-Vis-NIR spectra of the C$_{60}$ NWs, MDMO-PPV, and the C$_{60}$ NW-MDMO-PPV composite film. The UV-Vis-NIR spectrum of the C$_{60}$ NW film contained the main bands at 307 and 440 nm with broadening due to weak interactions among the C$_{60}$ molecules in the C$_{60}$ NWs. The diffuse reflectance spectrum of MDMO-PPV contained peaks at 420 and 580 nm with a sharp cut-off at 600 nm. The diffuse reflectance spectrum of the C$_{60}$ NW-MDMO-PPV composite film clearly showed a superposition of the C$_{60}$ NWs and
MDMO-PPV films. Near 700 nm, a new broad absorption tail appeared, suggesting a weak interaction between the components. From Figure 1(b), because the verges of the C<sub>60</sub>NWs were clearly observed at micrometer optical resolution, appreciable adsorption of the MDMO-PPV occurred on the C<sub>60</sub>NWs, which may be related to this absorption tail.

Figure 3 shows the photoluminescence spectra of the composite film of C<sub>60</sub>NWs and MDMO-PPV. The photoluminescence originating from MDMO-PPV decreased to 10% in the composite film, suggesting an appreciable interaction between MDMO-PPV and the C<sub>60</sub>NWs in the excited state; the ground state interaction may also contribute to the emission quenching, as suggested by the absorption tailing near 700 nm in Figure 2. From Figure 1(b), the verges of the C<sub>60</sub>NWs are clearly shown at micrometer optical resolution; appreciable adsorption of MDMO-PPV on the C<sub>60</sub>NWs could also be a source of the fluorescence quenching.

Until now, the various blends of conjugated polymers such as PPV and P3HT have been used as active materials as a pair of fullerenes in the organic photovoltaics (OPVs), imparting high solar energy conversion. This inspires us to fabricate new OPVs using the C<sub>60</sub>NW-polymer composite films as active materials. Figure 4 shows the current-voltage characteristics of a device made from the C<sub>60</sub>NW-MDMO-PPV composite film. The device structure consisted of ITO/PEDOT:PSS/C<sub>60</sub>NWs-MDMO-PPV/LiF/Al. The short-circuit current (I<sub>SC</sub>) and open-circuit voltage (V<sub>OC</sub>) under AM 1.5 G 1 sun illumination were 0.20 mA/cm<sup>2</sup> and 0.73 V, respectively; the fill factor (FF) was 0.23, and the power conversion efficiency (PCE) was 0.033%, as listed in Table 1.

In polymer-PCBM OPVs, the carrier mobility is higher in P3HT-PCBM blends compared to that in MDMO-PPV-PCBM [23]. Therefore, we fabricated OPVs using P3HT as a conjugated polymer to construct the device structure of ITO/PEDOT:PSS/C<sub>60</sub>NWs-P3HT/LiF/Al. The C<sub>60</sub>NW-P3HT composite film was prepared by spin-coating a toluene solution of P3HT onto the C<sub>60</sub>NW films. The optical microscope image and diffuse reflectance spectrum of the C<sub>60</sub>NW-P3HT composite film are shown in Figures S1 and S2 in Supplementary Material available online at http://dx.doi.org/10.1155/2016/2895850. The properties of the
Table 1: Properties of C₆₀NW (C₆₀ nanorod) OPVs.

<table>
<thead>
<tr>
<th>Source</th>
<th>I_sc/mA</th>
<th>V_oc/V</th>
<th>FF</th>
<th>PEC/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PEDOT: PSS/C₆₀NWs-MDMO-PPV/LiF/Al</td>
<td>0.20</td>
<td>0.73</td>
<td>0.23</td>
<td>0.033</td>
</tr>
<tr>
<td>ITO/PEDOT: PSS/C₆₀NWs-P3HT/LiF/Al</td>
<td>0.56</td>
<td>0.36</td>
<td>0.38</td>
<td>0.075</td>
</tr>
<tr>
<td>ITO/PEDOT: PSS/P3HT/s-C₆₀NWs-P3HT/LiF/Al</td>
<td>0.46</td>
<td>0.51</td>
<td>0.42</td>
<td>0.097</td>
</tr>
<tr>
<td>n-Si/P3OT-C₆₀ nanorod/Au</td>
<td>0.0098</td>
<td>0.155</td>
<td>0.1485</td>
<td>0.0002</td>
</tr>
<tr>
<td>ITO/PEDOT: PSS/P3HT:C₆₀ nanorods/Al</td>
<td>0.091</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

I_sc: short-circuit current; V_oc: open-circuit voltage; FF: fill factor; and PCE: power conversion efficiency. Under AM1.5G 1 sun illumination. NA: not available.

C₆₀NW-P3HT OPVs are also summarized in Table 1. Compared to MDMO-PPV as a partner of C₆₀NWs, the OPV device performance was improved by P3HT (PCE = 0.075%).

We also fabricated OPVs employing short-C₆₀NWs (s-C₆₀NWs) prepared by sonication of C₆₀NW solutions. The device structure consisted of ITO/PEDOT:PSS/P3HT/s-C₆₀NWs-P3HT/LiF/Al. In this device, s-C₆₀NWs were used to prepare thinner C₆₀NW films, and we also inserted a new P3HT layer to inhibit contact between the s-C₆₀NWs and ITO. As shown in Figure 5, I_sc and V_oc under AM 1.5 G 1 sun illumination were 0.46 mA/cm² and 0.51 V, respectively, and the PCE increased up to 0.097%. There are two previous reports on the fabrication of OPVs using C₆₀ nanorods with larger diameters (500–1000 nm [24] and 215 nm [25]) than our C₆₀NWs (~100 nm). Compared to these reported values, we demonstrated an improvement in the device performance. Furthermore, our C₆₀NWs prepared with benzene and an IPA interface were porous (our C₆₀NWs have a much higher specific surface area than either pristine C₆₀ powder or other ID C₆₀ nanocrystals [21, 26, 27]), which may be beneficial for stronger interactions between the C₆₀NWs and conjugated polymers. Our results indicate that the physical properties (high surface area and small diameter) of C₆₀NWs are important for C₆₀NW OPVs.

4. Conclusion

We prepared composite films of conjugated polymers, MDMO-PPV and P3HT, with C₆₀NWs prepared from benzene and an IPA interface with the LIIP method. The photoluminescence originating from the polymers (e.g., MDMO-PPV) was effectively quenched in the composite films, indicating strong interactions between MDMO-PPV and the C₆₀NWs. The applicability of polymer-C₆₀NW composite films in photovoltaic devices was also successfully demonstrated. The physical properties (high surface area and small diameter) of the C₆₀NWs played an important role in improving the OPVs. In addition, selection of conjugated polymers as a pair of C₆₀NWs is also crucial.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


