



Organic photovoltaic cells with onion-like carbon thin films as hole collection layers



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ABSTRACT

Influence of onion-like carbon (OLC) thin films as insertion layer on the photovoltaic characteristics of soluble zinc phthalocyanine (zinc 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (ZnPc-TB))-based solar cells is investigated. Atmospheric photoelectron yield spectroscopy and ultraviolet-visible absorption spectroscopy reveal that the ionization potential and optical bandgap are 4.84 and 1.70 eV, respectively, for ZnPc-TB and 5.23 and 2.02 eV, respectively, for OLC. The power conversion efficiency of the OLC-inserted solar cell was higher than that of a cell without the OLC interlayer by a factor of 5.3. Improvement in photovoltaic parameters and photocurrent is attributed to an increase in the shunt resistance by a factor of 5.5 due to the OLC thin film which functions as a hole collection layer. The OLC-inserted bulk-heterojunction solar cells comprising ZnPc-TB and [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) achieve the best performance with the power conversion efficiency up to $6.9 \times 10^{-2}\%$ owing to an enhanced contribution of ZnPc-TB to a photocurrent generation. The OLC thin films acting as the hole collection layer provide a new alternative for solution-processed organic solar cells.

1. Introduction

Organic photovoltaic cells have attracted much attention as an efficient renewable energy source owing to their advantages such as, ease in fabrication (solution-based processing techniques), low cost, light weight, and use of flexible substrates [1–6]. For the small molecule-based solar cell [5–11], structure-controlled thin films deposited at molecular level result in high purity owing to their improved crystallinity. Among various small molecules, zinc phthalocyanine (ZnPc) [10–14] has become one of the most researched active materials for organic photovoltaics by virtue of its long exciton diffusion length (30 ± 10 nm) [10], large optical absorption coefficient, high charge generation efficiency and thermal stability at room temperature. ZnPc-based solar cells have been fabricated by vacuum deposition techniques until now [10–14]. ZnPc and fullerene (C₆₀) are recognized as one of the most prospective material combinations for use in heterojunction or bulk-heterojunction type solar cells. High power conversion efficiencies (PCE) of up to 4.9% have been reported in the ZnPc:C₆₀-based bulk-heterojunction solar cells using various kinds of hole/electron transport layers [5,11]. In regard to fullerene-free, phthalocyanine-based cells, a higher conversion efficiency of 8.4% has been obtained by exploiting long-range exciton energy transfer [6]. In view of the recent progress

achieved in solution-processed organo-lead halide perovskites [15,16] and polymer solar cells [1–4], solution-processed, small-molecule organic materials show great promise for development as the next-generation thin film photovoltaic materials considering their flexibility for low-cost production. Soluble phthalocyanines [17–21] have been mainly used in dye-sensitized solar cells consisting of micrometer-thick titanium dioxide (TiO₂) layers; here, the TiO₂ layers often require a high-temperature (~500 °C) treatment [17,18]. In view of the application to the low-temperature processed, thin film photovoltaics, the solution-processed phthalocyanine offers an attractive alternative for low-temperature thin film photovoltaics by overcoming these challenges. However, the power conversion efficiency of the solar cell with solution-processed phthalocyanine layer [17–21] is still low.

Meanwhile, carbon materials such as C₆₀ (fullerene) as well as its derivatives, including [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) [1–4], carbon nanotubes [22–25] and graphene [26–30] have been extensively used as electron acceptors or as transparent electrodes in organic solar cells. In donor/acceptor-blended films, an aggregation of planar and spherical molecules can form charge carrier transport paths. Moreover, since the spherical molecules such as the C₆₀ derivatives have three-dimensional π -electron conjugation systems, a favorable π - π orbital overlap occurs between the adjacent molecules.

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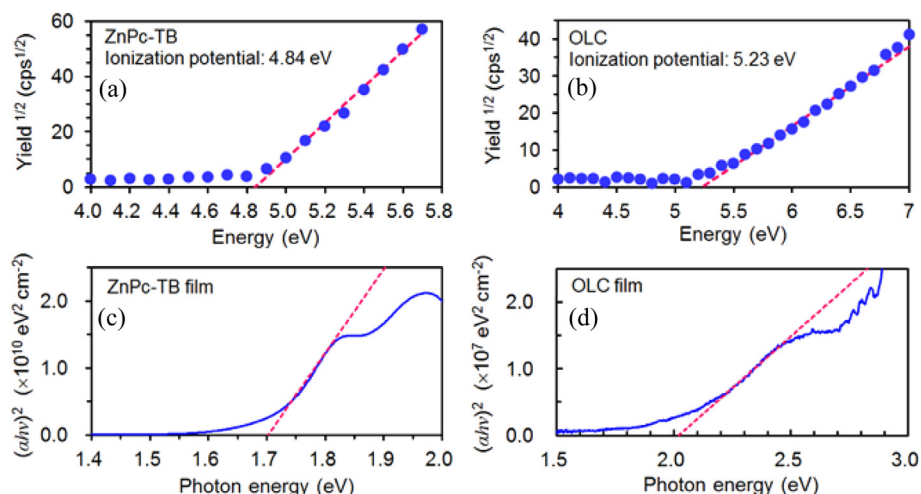


Fig. 1. Photoelectron yield spectra obtained for: (a) soluble ZnPc (ZnPc-TB), and (b) onion-like carbon (OLC) powder. The lower panels show the dependence of $(ah\nu)^2$ on photon energy $h\nu$ for: (c) ZnPc-TB, and (d) OLC. The linear portion is extrapolated to yield the optical bandgap (intercept on the abscissa).

Although the diameter of C_{60} is only about 0.7 nm [25], closed-shell molecules with larger diameter are expected to offer more successive carrier transport paths in the active layer owing to molecular aggregation. This results in multi-shell fullerenes, generally known as onion-like carbon (OLC), with potential for use as an alternative material to the C_{60} derivatives [31–37]. The OLC can serve as a low-cost organic material in comparison to the conventional C_{60} derivative-based photovoltaic devices. Ugarte [31] first reported the formation of OLC in 1992 by demonstrating the curling and closure of graphitic networks under electron-beam irradiation. Since then, the physical and electronic properties of OLC have been investigated in detail by several researchers for tribological behavior of OLC composites [34–37]. Giordani et al. [38] performed cellular imaging by utilizing functionalized OLCs linked with organic molecules. However, no device development studies involving OLC as an electronic material have been reported yet. The relatively unexplored research areas in regard to their functionality motivated us to compile experimental data of the properties and utility of OLCs in organic photovoltaic cells. Here, using direct experimental evidence, we demonstrate the enhancement in PCE of a solution-processed ZnPc-based solar cell in conjunction with an OLC thin film.

2. Experimental details

OLCs were used, synthesized by heat treatment of fine diamond particles at 1400 °C by Shinko Seiki Co., Ltd. The OLC powder was first ground thoroughly with mortar and pestle. The OLC suspension was prepared by dispersion in *N,N*-dimethylformamide (DMF) (4 mg/mL) using high-frequency ultrasonification (40% intensity, 20 kHz, Vibra Cell VCX 500, Sonics & Materials, Inc.). The OLC thin film was deposited by spin-coating the suspension at 500 rpm for 200 s on a pre-cleaned indium tin oxide (ITO) (pre-deposited on a glass substrate) substrate. The ITO film thickness and sheet resistance were ~ 150 nm and $\sim 10 \Omega/\square$, respectively. For the measurement of highest occupied molecular orbital (HOMO) level (defined as equivalent to ionization potential) in OLC, atmospheric photoelectron yield spectroscopy (AC-3, Riken Keiki Co.) was performed. The optical bandgap (E_g) was estimated by depositing the OLC thin film on a quartz substrate. Surface morphologies of the organic thin films were studied using atomic force microscopy (AFM) (Nano Navi probe station and an S-image unit, SII Nano Technology Inc.). The cross-section of the OLC-inserted solar cell was examined by scanning transmission electron microscopy (STEM) in a HITACHI HD-2700 equipment operated at an acceleration voltage of 120 kV.

Zinc 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (ZnPc-TB) (soluble ZnPc) [21,39] was purchased from Sigma-Aldrich Co. Ltd. Recrystallization of ZnPc-TB was performed three times using chloroform (CF). The recrystallized ZnPc-TB was dissolved in a solvent mixture of CF and chlorobenzene (CB) (volume ratio 3:1) (1.27×10^{-2} mol/L). The solution was stirred for 24 h at room temperature. The ZnPc-TB solution was spin-coated (the final film thickness of ~ 140 nm) at 500 rpm for 200 s on the OLC thin film, or on the ITO substrate. We estimated the thickness of ZnPc-TB from the optical absorption intensity. 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI) [40,41] was used as an acceptor molecule, which was first synthesized according to a published procedure [40,41] and then deposited as a 50-nm thick film on the ZnPc-TB layer. To complete the photovoltaic device fabrication, indium (In) (20 nm) and aluminum (Al) (30 nm) electrodes were successively deposited by vacuum evaporation on the PTCBI film to form the desired structure (ITO/ZnPc-TB/PTCBI/In/Al or ITO/OLC/ZnPc-TB/PTCBI/In/Al). The vacuum evaporation of PTCBI, In and Al was performed at a pressure of 4.0×10^{-4} Pa. In the preparation of OLC/PTCBI heterojunction solar cells, the 50-nm thick PTCBI layer was deposited by the vacuum evaporation on the OLC thin film. In case of fabricating the bulk-heterojunction-type solar cells, a ZnPc-TB:PCBM blended film was prepared by spin-coating (500 rpm for 200 s) a CF solution containing ZnPc-TB and PCBM at a 1:1 molar ratio on the OLC thin film. This PCBM was purchased from Sigma-Aldrich Co. Ltd. and used as received. The device architecture of ITO/OLC/ZnPc-TB:PCBM/In (20 nm)/Al (30 nm) was designed to investigate the influence of the donor-acceptor blended film on the photocurrent response. For all photovoltaic devices, we used ITO as anode and Al as cathode. While the evaporation rates employed were 0.1 Å/s (in the thickness range from 0 to 10 Å) and 1.0 Å/s (from 10 to 500 Å) for PTCBI, the rates were 0.1 Å/s (0–10 Å) and 0.3 Å/s (10–200 Å) for In and ~ 4.0 Å/s (0–300 Å) for Al. These deposition rates were controlled by a quartz crystal oscillator (ULVAC Inc., CRTM-6000G). Current density (J)-voltage (V) curves were measured under white light illumination (100 mW/cm², simulated solar spectrum AM1.5). The photocurrent action spectra were obtained by irradiating the fabricated photovoltaic devices with monochromatic light.

3. Results and discussion

Photoelectron yield spectra obtained for ZnPc-TB and OLC powders are shown in Fig. 1(a) and (b) (blue solid circles). The ionization potentials of ZnPc-TB and OLC were determined as 4.84 eV and 5.23 eV, respectively, by extrapolating the straight line from the linear portion of

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