Capped carbon nanotube photovoltaic cells: Influence of distribution of the five-membered rings on the efficiency

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ABSTRACT

Electronic structure and energy conversion efficiency η for a photovoltaic organic solar cell of single-walled carbon nanotubes (CNTs) with various end-cap geometries facing Zn-phtalocyanine are studied based on density functional theory. Accumulation of the 5566 clusters, composed of two five-membered rings and two six-membered rings, at the cap raises the energy of the localized state, which plays a key role in improving the magnitude of η, whereas both the rotational symmetry around the axis and the chirality of the tube seem to be less important in determining the magnitude of η. These properties are explained by a charge transfer from the CNT to the cap.

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1. Introduction

Since the successful synthesis of carbon nanotubes (CNTs) by S. Iijima [1], CNTs have opened doors to low-dimensional physics and technological applications due to its electrical and thermal properties. Several techniques for producing single-walled CNTs exist, including arc discharge [2], laser ablation [3], thermal plasma [4], chemical vapor deposition (CVD) using transition-metal catalytic particles on a substrate [5,6], super-growth CVD method [7,8], and so forth.

The end of the CNT synthesized by the above methods is usually closed by a cap that consists of five- and six-membered rings.[1] There have been also first-principles theoretical studies on the growth of single-walled CNTs concerning also the initial formation of the cap on transition-metal catalytic particles [10,11]. Reich et al. [12], have reported that the geometric structure of a cap uniquely determines the chirality of the nanotube that is attached to it, implying a possibility for chirality selective growth of single-walled CNTs by CVD method. The cap may be considered as a defect because it breaks the translational periodicity of the CNT, which brings about *localized states* near the cap. The effect of the presence of the cap on the electronic structure has been investigated both experimentally and theoretically. With the use of the scanning tunneling spectroscopy, the sharp resonance states in the

local density of states have been observed near the valence band edge [13]. The resonance states have been interpreted by the localized state, in which the electron localizes at the cap. Theoretically, Tamura and Tsukada [14] studied electronic states of the cap structure in CNTs in a simple tight-binding model. Tuning of the work function of a few capped CNTs by electric fields [15] and alkali-metal adsorption on a cap [16] has been studied by density functional calculations.

The capped CNTs have a peculiar property because the CNT behaves as a good conductor or semiconductor according to its chirality, while the cap behaves as a fullerene with the large electron affinity. Therefore, they are expected to behave as a good acceptor electrode. In such an application, the lowest unoccupied molecular orbital (LUMO) with a large amplitude on the cap, which we will call the cap LUMO or the acceptor LUMO, plays an important role and the position of its energy level becomes an important quantity. On the other hand, the highest occupied molecular orbital (HOMO) with a large amplitude on the cap, which we will call the cap HOMO or the acceptor HOMO, is usually not important. If we put a donor molecule such as a Zn-phthalocyanine (ZnPc) facing the cap (Fig. 1), the character of the molecular orbital can be decomposed into three types: the first type strongly localizes to the ZnPc, the second one is distributed along the tube, and the last one localizes to the cap (i.e., the acceptor LUMO or HOMO). Since the last type is caused by a breakdown of the translational periodicity along the tube axis, the amplitude decays drastically as it goes from the cap to the tube region. In this heterojunction, the photo-induced charge separation may take place [17]. Using the capped CNT as the acceptor-type conducting electrode, one may realize an efficient photovoltaic

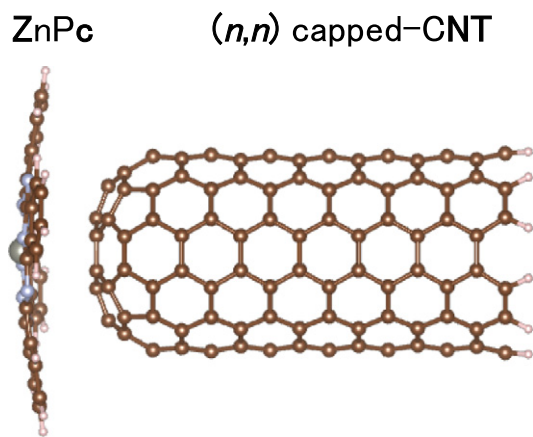## ZnPc   (n,n) capped−CNT

Fig. 1. Heterojunction geometry of a capped CNT and a ZnPc molecule.

organic solar cell. The principle of power generation is decomposed into three steps: (i) photon absorption by ZnPc induces electron excitation from the donor (ZnPc) HOMO to the donor (ZnPc) LUMO, leaving a hole behind, (ii) the excited electron moves to the acceptor (cap) LUMO, i.e., a lower empty state localized near the cap of CNT, and (iii) the electron moves freely along the tube axis, going around the circuit, and finally recombining with the hole at ZnPc, which generates an electric current. The energy diagram of such a molecular heterojunction is illustrated in Fig. 2. There are two important quantities: one is the energy gap E_g between the donor LUMO and the donor HOMO, i.e., the LUMO and HOMO having large amplitudes at the donor molecule. The other is the energy loss ΔE, which is the energy difference between the donor LUMO and the acceptor LUMO. In our previous study [17], we reported that the heterojunction of a capped metallic (5,5) CNT and ZnPc has E_g = 1.49 eV and ΔE = 0.26 eV, yielding the energy conversion efficiency of η = 25.1%, which approaches the upper limit of single-junction inorganic photovoltaic cells of the Schockley–Queisser limit [18]. Although this enhancement of the efficiency could be attributed to the end-cap geometry dependence of the energy of the localized state, our investigation was not enough to derive any conclusive relationship between them, because we studied the most symmetrical cap structure only to reduce a huge number of possible choices of the end-cap geometry. From a mathematical point of view, Brinkmann et al. [19], have shown, using a graph-theoretical method, that the number of end-cap geometry of the CNTs grows as a power of $(n^2 + nm + m^2)$ where n and m are integer that defines the chiral vector. For example, while the (10,0) CNT has only seven unique caps, the (15,0) CNT has 1963 unique caps. Recently, Robinson et al. [20], have proposed that a method to solve the Thomson problem describing the uniform distribution of point charges on a sphere

is useful for the geometrical optimization of the end-cap geometry with less numerical cost.

From a physical point of view, it is natural to pose a question: Is there a correlation between the end-cap geometry and the physical properties of the capped-CNTs? As a first step toward a unified understanding, it is necessary to investigate the electron energy of the localized state. Since six five-membered rings should be distributed in the cap, one may consider that the electron energy would be determined by two factors: the global and the local structure of the cap. Since the global distribution of the five-membered rings is closely related to the rotational symmetry around the tube axis, it might affect the energy of the localized states. On the other hand, the local distribution of the five-membered rings is relevant to the single and double bond distributions in the carbon network of the cap. It is thus desirable to investigate the energy level of the localized states as a function of how the five-membered rings are distributed in the cap.

In this paper, we consider various metallic (n,n) armchair CNTs with a cap facing a ZnPc molecule and explore the relationship between the distribution of the five-membered rings and the energy conversion efficiency η as well as the energy level of the acceptor (cap) LUMO, using density functional theory. It is noteworthy that the end-cap geometry is similar to the geometry of fullerenes and higher fullerenes. In most of fullerenes and higher fullerenes, five-membered rings are single bonds typically less than or equal to 1.40 Å, while five bonds shared by two six-membered rings and radially connected to a five-membered ring have a tendency to become double bonds typically longer than or equal to 1.43 Å. There is a typical structure composed of two six-membered rings and two five-membered rings illustrated in Fig. 3, which we will call the 5566 cluster or simply the cluster. In this cluster the center bond shared by two six-membered rings is a clear double bond of a bond length ~1.44 Å. Accumulation of the 5566 clusters is the origin of the large electron affinity of fullerenes. We find that the energy of the localized state and the value of η strongly depend on the running number of the 5566 clusters in the cap while they are almost insensitive to the rotational symmetry around the tube axis.

Our paper is organized as follows. The computational details are described in Section 2. In Section 3, 25 different capped CNTs are studied and analyzed from the aspect of global and local structures of the cap. Finally, summary and conclusion are given in Section 4.

2. Computational details

First-principles calculations were carried out based on the density functional theory (DFT) implemented in the DMol³ package [21,22]. The local density approximation (LDA) of Perdew and Wang [23] was used for all calculations. Although this approach (DFT–LDA) underestimates
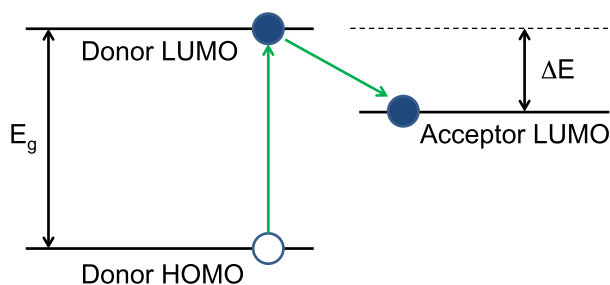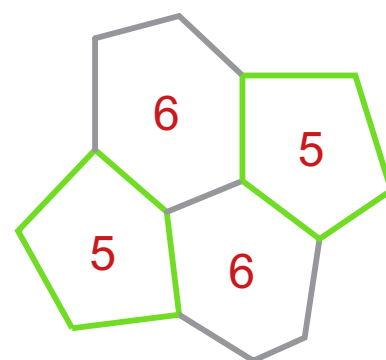

Fig. 2. Energy diagram of the photovoltaic organic solar cell. The photoexcited charge transfers from the donor LUMO level to the acceptor LUMO one by losing the energy ΔE.

Fig. 3. Schematic illustration of the 5566 cluster composed of two six-membered rings and two five-membered rings.