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Impurity-related degradation in a prototype organic photovoltaic material: A first-principles study

G. Volonakis [a,*], L. Tsetseris [b], S. Logothetidis [a]

[a] *Department of Physics, Laboratory for Thin Films Nanosystems and Nanometrology – LTFN, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*
[b] *Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece*

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ABSTRACT

The phenyl-C61-butyric acid methyl ester (PCBM) fullerene derivative is among the most widely used acceptor materials in organic photovoltaics (OPVs). Similar to the case of several other organic semiconductors and systems, experimental data show that the performance of OPV blends of PCBM with a polythiophene polymer degrades when the system is exposed to ambient molecules, such as O_2 and H_2O. Here we use first-principles calculations to identify physical mechanisms that can give rise to this type of degradation. We find that oxygen impurities can be incorporated in PCBM crystals and form several different types of configurations that range from intact molecules in crystalline voids to oxidized PCBM molecules. A number of O-related impurity structures generate states within the energy band gap of the PCBM crystal, creating thus shallow and deep carrier traps. Likewise, incorporation of H_2O molecules gives rise to a shallow acceptor-like trap. The results are consistent with pertinent experimental observations of degradation paths for air-exposed PCBM samples and can aid in the optimization of PCBM-based OPV blends.

1. Introduction

The power conversion efficiency of organic photovoltaic (OPV) devices continue to rise, surpassing recently the value of 10% [1]. One of the most efficient and commonly used acceptor materials in bulk heterojunction OPV devices [2–7] is the organic semiconductor phenyl-C61-butyric acid methyl ester (PCBM), a fullerene derivative composed by a C_{60} core and a functional tail. Further advances in the PCBM-based OPV field, however, require the resolution of fundamental questions regarding the dependence of the electronic properties of PCBM samples on factors such as blend morphology, defects, and impurities. It is well-known, for example, that the insertion of extrinsic species in inorganic [9,10] and organic [8,11–17] semiconductors, either during crystal growth, or during long-term operation of related devices, introduces significant changes in the physical characteristics of the host systems. In recent years, the role of oxygen- and water-related impurities has been highlighted also with respect to charge transport properties of the active layer in organic photovoltaic systems [18–25].

Experiments find that when fullerene-based materials are exposed to oxygen or water, related devices show an increase of shallow and deep charge trap densities [26–33]. In particular, exposure of C_{60} samples to oxygen has been associated with the reduction of the electron mobility, even by several orders of magnitude [31]. It has also been shown [34,35] that illumination of C_{60} films in the presence of O_2 may lead to the formation of deep carrier traps with energies close to the middle of the gap. Both intercalated and chemically attached oxygen molecules seem to be responsible for the effect [34,35]. Similar observations apply to PCBM-based systems; when they are exposed to oxygen they show a decrease of the mobility and an increase of the density of deep traps [21]. On the other hand, theoretical works have probed the modification of the properties of C_{60} species, either in molecular [36] or fullerite crystalline form

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* Corresponding author. Tel.: +30 2310 998239.
E-mail address: gvolo@physics.auth.gr (G. Volonakis).

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[37], by oxygen and water impurities. These studies identified energetically favorable configurations and their role in the creation of levels within the fullerite gap, in close agreement with experimental observations [37].

In contrast, impurity effects in PCBM samples have received far less attention in theoretical studies. The attachment of oxygen species on an isolated molecule was recently investigated [38], by DFT based calculations, as a possible cause for the creation of deep traps inside the PCBM domains. However, the atomic-scale details of O- and H_2O-related degradation in the solid phase of PCBM remain largely unknown.

In this paper, we use extensive first-principles quantum-mechanical calculations to describe processes that control the modification of the electronic properties of PCBM samples in the presence of oxygen and water species. We find that both physisorbed and chemisorbed oxygen configurations are possible. Similar to the fullerite case [37], these configurations may form, depending on temperature and oxygen pressure, on successive stages of oxygen incorporation. The most important aspect of oxygen insertion is that certain structures give rise to a multitude of levels within the band gap of a simple cubic PCBM crystal [39]. Water molecules, on the other hand, remain in intact physisorbed geometries within the PCBM crystal voids and and create states above the valence band maximum.

2. Methodology

All results presented in this work were obtained with the density functional theory (DFT) code VASP [40]. Two sets of calculations were performed using two different approaches. First, we used ultra-soft pseudo-potentials [41] to describe interactions between valence electrons and the ionic cores. We took into account exchange–correlation (xc) effects through a local-density (LDA) approximation [42] functional. Similar methodology has been employed in previous studies on the properties of various carbon-based systems [13,43,44], including those of defective fullerene crystals [37,45]. The energy cutoff for expansion of wavefunctions in a plane-wave basis was set at 400 eV and Γ-point sampling was used for the calculation of total-energy differences. The force (energy) criterion for the relaxation of the ionic (electronic) degrees of freedom was set at 0.01 eV/Å^2 (10^{-5} eV). In addition, we allowed spin polarization and the reported stable configurations have no spin polarization, unless stated otherwise.

In the second set of calculations we employed the so-called DFT-D2 method [46], using projector-augmented waves [47] combined with the PBE [48] generalized gradient approximation (GGA) functional. This approach aims to take into account in a semi-empirical fashion the van der Waals (vdWs) interactions. The energy cutoff for the DFT-D2 calculations was set at 550 eV, while the convergence criteria were kept the same as the ones for the LDA studies. Below we present results based on the DFT-D2 approach, unless stated otherwise. The electronic density of states (DOS) calculations employed the tetrahedron method and a larger $2 \times 2 \times 3$ grid for sampling of reciprocal space.

In the following we assess the stability of different defective structures through a suitable binding energy (E_b), defined as the absolute difference between the energy of the defective crystal, the energy of the pristine crystal structure and the energy of the relevant molecule (i.e. O_2 or H_2O) in vacuum. The higher the reported E_b the more stable is the defective structure. The crystalline structure of PCBM was taken as simple cubic, based on pertinent *ab initio* studies [39]. Large $2 \times 2 \times 1$ supercells with four PCBM molecules per cell and more than 350 atoms in total were employed to simulate the effect of isolated impurities. We explored a large number of possible structures by creating corresponding physisorbed or chemisorbed configurations, which were subsequently fully relaxed.

3. Results and discussion

Insertion of molecular oxygen in a PCBM crystal may first lead to the configuration depicted in Fig. 1a. In this physisorbed structure the molecule resides intact and no C–O bonds between the O_2 entity and the PCBM matrix are formed. We should note here that the O_2 molecule in the void remains in the triplet state. The configuration of Fig. 1a has a small binding energy E_b of 0.15 eV (0.10 eV) according to DFT-D2 (LDA) calculations. Table 1 summarizes the binding energies (DFT-D2 and LDA) and structural details for the most important configurations. Similar configurations with O_2 molecules within crystalline voids have been reported [37] in the case of C_{60} fullerites, albeit with a slightly higher E_b of 0.23 eV [37]. The presence of the functional tail of PCBM, restricts the space that is available for the incorporation of an O_2 molecule. Because of the steric constraint, the insertion energy E_b is lowered. Nonetheless, the lack of a substantial incorporation energy penalty indicates that annealing in an oxygen atmosphere will result in the absorption of a significant number of O_2 molecules. In fact, reorientation of an O_2 species can increase somewhat the LDA binding energy to 0.15 eV through the formation of the structure shown in Fig. 1b. In this geometry, the O–O bond is stretched to 1.48 Å, while a new C–O bond with a length of 1.44 Å is created between the impurity and the host material. We should note, however, that the structure of Fig. 1b is stable only in the case of LDA calculations. Use of the DFT-D2 method always leads to its spontaneous dissociation to atomic species.

When the stretched O_2 molecule re-organizes so that both its oxygen atoms form C–O bonds with a PCBM entity, then the binding energy decreases further. Two such configurations are shown in Fig. 1c and d. In particular, in Fig. 1c the oxygen molecule chemisorbs over a so-called 6-6 bond, i.e. a C–C bond between two neighboring hexagons of the fullerene moiety of a PCBM molecule. The energy gained in this type of chemisorption is 0.20 eV (0.90 eV in LDA). Fig. 1d depicts another, less favorable possibility, wherein the oxygen molecule adsorbs over a 6-5 bond, i.e. a bond between a pentagon and a hexagon of the C_{60} cage. The 6-5 structure of Fig. 1d is not favorable within the DFT-D2, and within the LDA, E_b is significantly smaller at 0.20 eV. Certain structural details are common in the configurations of Fig. 1c and d. The O–O and C–O