Chemical Physics Letters 652 (2016) 220–224

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Photodegradation of the electronic structure of PCBM and C_{60} films in air

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ARTICLE INFO

Article history:
Received 14 December 2015
Revised 31 March 2016
In final form 2 April 2016
Available online 26 April 2016

Keywords:
Degradation
Fullerene
Photostability
Photovoltaics
NEXAFS

ABSTRACT

Fullerenes are common electron acceptors in organic solar cells. Here the photostability in air of the electronic structures of spin-coated PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) and evaporated C_{60} films are studied using ultraviolet photoelectron spectroscopy (UPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. After exposing these materials in air to simulated sunlight, the filled and empty molecular orbitals are strongly altered, indicating that the conjugated π-system of the C_{60}-cage has degraded. Even a few minutes in normal lab light induces changes. These results stress the importance of protecting fullerene-based films from light and air during processing, operation, and storage.

1. Introduction

The most common acceptor molecule in polymer-based organic photovoltaics (OPV), is the C_{60}-derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), whose main advantages are its high solubility in organic solvents, its high electron mobility, and its large electron affinity. Provided the lowest unoccupied molecular orbital (LUMO) of PCBM lies below that of the polymer, excitons can dissociate when they meet the donor–acceptor interface. Once free electrons have been generated, they will be transported from the donor–acceptor interface through the blend film to the low work function electrode. The LUMO of PCBM plays an important role in these electron transfer and transport processes. For this reason it is important that the electronic structure of PCBM is well understood and unaffected during device operation. In more general terms, the chemical stability of the molecular materials in the active layer both during fabrication and under device operation is of course a prerequisite for stable device performance.

Stability studies of polymer solar cells have provided understanding of the various contributions to the degradation of the electrical performance, including the electrodes, the active layer morphology, and the light-absorbing material [1–5]. The device stability depends strongly on environmental conditions. Standardisation of the testing conditions, as is for instance provided by the ISOS-protocols, is therefore very valuable for OPV degradation studies [6]. Stable performance requires encapsulation of the devices to protect them from the influence of water and oxygen from the atmosphere.

For poly 3-hexylthiophene (P3HT):PCBM devices intentionally exposed to oxygen, with and without light, both reversible and irreversible device degradation has been observed [7]. The former was assigned to p-doping by oxygen, increasing the number of mobile holes in the donor polymer and/or decreasing the number of mobile electrons in PCBM [8]. The latter was assigned to (photo)chemical oxidation of the polymer or PCBM, resulting in the formation of new C–O bonds [9,10] which was shown to reduce the charge mobility. The photodegradation mechanisms of pure polymer films, such as P3HT, MDMO-PPV, have been studied in great detail [9,11,12]. The effect of oxygen and light on C_{60} has also been investigated, and for instance in field-effect transistors decreased electron mobilities have been reported after oxygen exposure [13,14]. Photooxidation of C_{60} in the presence of oxygen is well known for solutions and films [15–17]. The photodegradation of PCBM is, however, less extensively studied [5,18–20]. Hummelen and Kooistra stated that one of the major degradation processes in organic solar cells involves singlet oxygen formation by quenching of the triplet exited state of the C_{60}- or C_{70}-based fullerenes by oxygen [18,21]. Rivaton et al. have observed the formation of new peaks in the carbonyl region of the Fourier transform infrared (FTIR) spectra for PCBM and C_{60} films exposed to UV–visible light in air, and concluded that in PCBM the carbon-cage moiety degrades faster than the substituent [19]. This was confirmed in a recent FTIR spectroscopy study of the photodegradation of PCPDTBT, PCBM and their blends in pure oxygen, where

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http://dx.doi.org/10.1016/j.cplett.2016.04.003
0009-2614/

three stages of PCBM photooxidation were identified [48]. By MALDI (matrix-assisted laser desorption ionization) mass spectrometry Reese et al. have demonstrated the formation of oxidation products of PCBM upon exposure of P3HT:PCBM blend films to white light for 1000 h, which led to a decreased photoconductance of the blend [20].

NEXAFS spectroscopy at the C1s edge is commonly used to study the electronic structure of organic semiconductors, and in particular PCBM films [22–25]. The absorption resonances of fullerenes are very clear molecular signatures. Pedersen et al. have studied the photodegradation of PCBM, P3HT, and blends of those, under simulated solar light in ambient conditions by NEXAFS spectroscopy [26]. They found, in agreement with Rivaton, that the side chain of PCBM is unchanged, whereas the carbon cage is oxidized. Exposure of C_{60} films to oxygen at increased temperature was found to affect both the unoccupied and the occupied molecular energy levels, as observed by C1s and O1s NEXAFS and UPS spectroscopy, respectively [27,28]. The X-ray absorption spectra at the C- and O-edges, reported by Käämbre et al. for a C_{60} film exposed to O_2 and UV-light for 190 h, were found to be similar to those of the photoreaction product $C_{60}O$ [29].

In contrast, PCBM exposure to light in oxygen- and moisture-free atmosphere, is reported to change its solubility [30] and cause dimerisation [31]. The latter is related to the observation for films of C_{60} that exposure to ultraviolet and visible light in oxygen-free environments results in photopolymerization [32].

In this work we study the effect of white light exposure in air on the electronic structure of spin-coated thin-films of PCBM and, for comparison, evaporated thin-films of C_{60}. The electronic structure of the materials was monitored through C1s NEXAFS and valence band (VB) photoemission spectroscopies. The spectra revealed strong changes in the unoccupied and occupied orbitals, indicating photodegradation of the conjugated system of the molecules at the surface of the films. After less than 20 h of illumination, the spectroscopic fingerprints of C_{60} and PCBM were completely altered implying a drastic modification of the carbon-cage.

2. Materials and methods

2.1. Sample preparation

PCBM (99.5% purity from Solenne BV, The Netherlands) and C_{60} (99.98% purity from Term, USA) were used as received. Thin films of PCBM were spin-coated on top of silicon substrates at 3000 rpm/60 s from a 12 mg/ml solution in chloroform at room temperature. The solution had been previously heated to 50–60 °C for ca. 3 h. C_{60} films were deposited on silicon substrates by thermal evaporation (from a quartz crucible in an effusion cell) at a pressure of 10^{-6} mbar. The silicon wafers were n-type with (0 0 1) orientation and a resistivity of 0.001–0.003 Ω cm. They were cleaned according to the standard RCA method without the final HF-etching step, preserving a hydrophilic surface [33]. The films were prepared under dark room conditions (the only light source was a dark room red photo lamp, from DR Fisher, Germany). Exposure to white light was avoided during all stages of preparation, storage, transport and mounting for measurement. For comparison, a sample where the PCBM film was spin-coated under ambient light (less than 5 min under illumination from a standard white fluorescent tube) and stored in the dark until measurement was also prepared. Controlled light exposure was performed with a Xenon-based solar simulator (Sol2A, model 94022A, from Oriel Instruments, USA) at 100 mW/cm^2 irradiation (AM1.5) for 30 min and for 19 h, in air, excluding all other light sources. Another set of samples was exposed to the light from a standard white fluorescent tube (DULUX L 55W/840 from Osram, Germany) for 30 min and for 19 h, also in air, at a distance of ~1.5 m from the source.

2.2. NEXAFS measurements

C1s NEXAFS spectra were recorded at beamline D1011 of the synchrotron storage ring MAX II at MAX-Lab in Lund, Sweden, equipped with a multi-channel plate detector for partial electron yield (PEY) measurements. For the PEY-NEXAFS a retarding voltage of −150 V applied to the entrance grid of the detector was used to suppress low energy electron contributions to the signal. This gives PEY spectra their higher surface sensitivity, compared to the total electron yield (TEY) spectra. TEY NEXAFS spectra were collected by measuring the sample drain current. PEY and TEY were measured at the magic angle (55° angle measured from the sample surface) and collected simultaneously for each sample. Subsequent measurements showed no noticeable radiation damage. The spectra were divided by the corresponding spectrum of a gold film on mica (cleaned in-situ by sputtering with argon), and then normalized in the high photon energy region [34,35]. Energy calibration was done by using the exciton peak at 291.65 eV of highly oriented pyrolytic graphite (HOPG) as a reference [36].

2.3. VB measurements

VB spectra were measured on the same samples in the same vacuum system at the D1011 beamline, which is equipped with a SCIENTA SES200 electron-energy analyzer, which was operated at an energy resolution of 0.1 eV. Spectra were collected in normal emission geometry at a photon energy of 150 eV (15 meV energy spread). The position of the Fermi level was ascertained by measuring on Au, cleaned in situ by argon sputtering.

3. Results and discussion

The TEY- and PEY-NEXAFS spectra of unexposed PCBM are shown in Fig. 1. The main characteristic resonance peaks are found at 284.5 eV (1), 285.8 eV (2), 286.2 eV (3), 288.4 eV (4), 290.8 eV (5), 292.7 eV (6) and 295.3 eV (7). These match well with previously reported values [23–25]. Most of the resonance features in the NEXAFS spectrum of PCBM are very similar to those found in C_{60} spectra [37] – see unexposed spectra in Fig. 2. The main differences between the spectra of unexposed C_{60} and PCBM lie in the existence of a shoulder **S** at the higher photon energy side of the main π^*-resonance peak (285.0 eV), which is absent in the C_{60} spectrum, and the opposite intensity relation between peaks 2 and 3. While the shoulder **S** has previously been assigned to the presence of the phenyl side group [22,24,25,38], we have recently reported that this shoulder contains contributions from specific transitions from the phenyl carbon atom closest to the cage as well as from most of the carbon atoms in the fullerene cage (with the exception of the carbons involved in the side chain bonding) [23]. The change in the intensity ratio of peaks 2 and 3, which arise mainly from the fullerene cage, is likely linked to the fact that the conjugated system in PCBM is disrupted by the presence of the side group [23]. The PCBM spectra collected in TEY (Fig. 1a) and in PEY (Fig. 1b) modes show some differences, which are, given the higher surface sensitivity of PEY relative to TEY, due to surface effects, confirming earlier assignments of shoulder **S** [23]. We note that there is a significant decrease in intensity of the π^*-resonances in the PEY spectrum, compared to the TEY, which is indicative of a decrease in the number of unsaturated bonds in the molecules at the surface of the film. A difference in the intensity of the first π^*-resonance (peak 1) had also been noted by Watts et al. when