Capturing transiently charged states at the $C_{60}/TiO_2(110)$ interface by time-resolved soft X-ray photoelectron spectroscopy

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ABSTRACT

Time-resolved soft X-ray photoelectron spectroscopy is utilized to determine an energy level alignment and the photoexcited carrier dynamics at a $C_{60}/TiO_2(110)$ interface. The interface electronic structure is characterized by a type II junction, which favors an injection of photoexcited electrons from C_{60} to TiO_2. Ultraviolet (UV) laser pulse irradiation induces transient shifts of both C 1s and Ti 2p core levels towards the higher binding energies. These energy shifts are caused by a laser-induced charge transfer between the C_{60} layer and the $TiO_2(110)$ surface. Upon UV absorption, valence electrons of C_{60} are promoted to unoccupied levels, followed by a resonant transfer to TiO_2, leaving C_{60} in a cationized state. On the $TiO_2(110)$ side, the electrons are injected into the conduction band to raise the carrier density so that downward bending of the TiO_2 band is induced. The UV-excited states of C_{60} and TiO_2 have sufficiently longer lifetime than the lifetime of the electron−hole pairs in solid C_{60}. The $C_{60}/TiO_2(110)$ interface is, thus, proved to be efficient for separating the electron−hole pairs generated within the C_{60} layer.

1. Introduction

One of key technologies for realizing sustainable society is an efficient conversion of the sunlight into chemical and electrical energies. Titanium dioxide (TiO_2) exhibits a high photocatalytic activity for water splitting to produce a zero-emission fuel, H_2 [1]. TiO_2 is also used as a transparent electrode in photovoltaic cells [2]. One of the extensively studied TiO_2-based photovoltaic cells is a dye-sensitized organic cell [3−5], in which visible-light sensitive dye molecules or polymers are loaded onto the TiO_2 electrodes. The TiO_2 electrode collects photoexcited electrons from the light absorbing layer to facilitate electron−hole separation. In such a photovoltaic cell, a charge transfer across the interface is an important elemental step to define the overall performance of the cell.

Many theoretical and experimental studies have been devoted to elucidate the interface electronic structure of model photovoltaic cells, because one can predict the charge transfer efficiency by assessing electron- and hole-injection barriers at the interface [6−8]. On the other hand, real-time observations of the carrier dynamics across the interface have been limited [9−11], unfortunately, so that the relation between the interface electronic structure and the charge transfer time has not been established yet.

The time-resolved soft X-ray photoelectron spectroscopy (TRPES) utilizing a pump-probe method has been proved to be a powerful tool to simultaneously determine the electronic structure and the dynamics of the photoexcited carriers at semiconductor surfaces such as silicon [12−14], GaAs [9], ZnO [10,14,15] and TiO_2 [16] as well as at a semiconductor−semiconductor interface [9,10]. In these studies, transient changes of the surface photovoltage (SPV) effect are determined by following temporal binding-energy (BE) shifts of the core-level and/or valence-band photoemission spectra of the semiconductor surfaces.

In the present study, we apply TRPES to the $C_{60}/TiO_2(110)$ heterojunction in order to elucidate how the excited carriers behave at the junction. C_{60} is an important component of dye-sensitized photovoltaic cells, where the C_{60} layer is used as an electron acceptor or as an electron transport layer [17,18]. C_{60} also serves to enhance photocatalytic activity of TiO_2 by promoting the

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separation of the photoexcited electron–hole pairs [19,20]. We show that the electronic structure of the C_{60}/TiO_2(110) interface is characterized by a type II junction, which favors an electron transfer from C_{60} to TiO_2, and that an efficient $C_{60} \rightarrow TiO_2$ electron transfer actually occurs upon ultraviolet (UV) light irradiation.

2. Experimental details

A single crystal of rutile TiO_2 with (110) orientation (Earth Chemical Co.) was used as a substrate. The sample surface was cleaned in an ultrahigh vacuum (UHV) chamber by cycles of Ar^+ sputtering (1 kV) and annealing at 950 K in Ref. 1×10^{-4} Pa until a sharp (1×1) low energy electron diffraction pattern was obtained. No carbon-related peak was detected in the photoemission spectra of the clean surface. C_{60} (> 99% purity, Kanto Chemical Co.) was deposited on TiO_2(110) using a home-made evaporation cell, consisted of a quart crucible around which a tungsten wire for resistive heating and a thermocouple for temperature monitoring were wound. Thoroughly out-gassed C_{60} was sublimated at 680 K while keeping the substrate at room temperature. An average thickness of the deposited C_{60} overlayer, estimated from intensity attenuation of

the Ti 2p core-level peak (Fig. 1b), was 0.57 nm [21], which is ~ 70% of a monolayer thickness of the C_{60} layer on TiO_2(110) [22].

The TRPES measurements employing a pump-probe method were carried out at SPring-8 BL07LSU [23]. For the pump light, a second harmonic of an amplified Ti:sapphire laser pulse was used. The pulse duration and a repetition rate were 35 fs and 1 kHz, respectively. The photon energy was set at 3.06 eV, which exceeds both the band gap of rutile TiO_2 (3.0 eV) [24] and the energy difference between the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level of C_{60} (2.3 eV) [25,26].

For the probe light, synchrotron radiation (SR) lights with the energies of 253 eV and 600 eV were used to measure valence-band spectra and Ti 2p and C 1s core-level spectra, respectively. The SR lights were provided by a single bunch and a 11/29-filling bunch train of an H-mode operation. SR pulses from the single bunches were used for the pump-probe measurements. A width of the pulse was 50 ps, and a time interval between the pulses was 4.79 μs. A time-of-flight electron energy analyzer (VG Scienta ARTOF 10 k) was used to acquire photoelectron spectra. The BEs of the photoelectron spectra were referenced to the Au $4f_{7/2}$ core-level peak
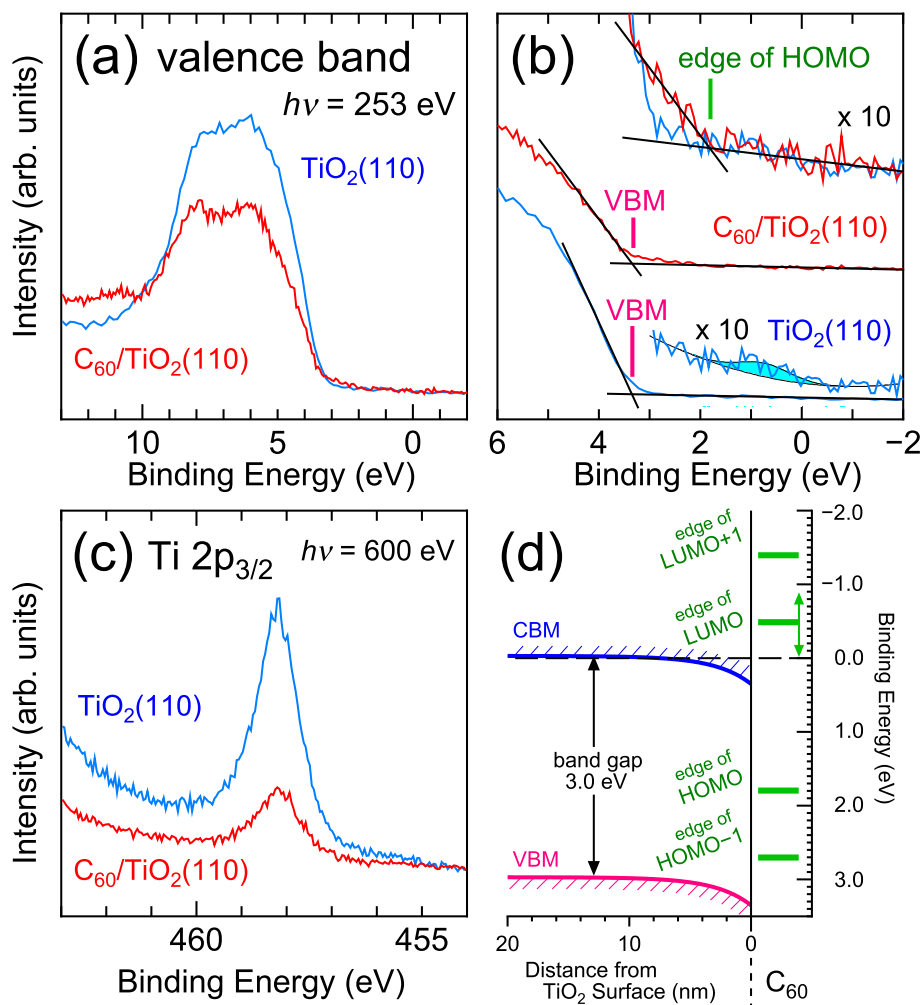
Figure 1. (a) Valence-band spectra of the clean and C_{60}-covered TiO_2(110) surfaces. (b) A magnified view of the spectra in the band gap region and the VBM region. The spectra in the band gap region are displayed with intensities magnified by 10 times. In the spectrum of the clean TiO_2 surface, an O-vacancy induced state, whose lineshape is reproduced by a Gaussian peak on a polynomial background, is observed at just below the Fermi level. The VBM positions of TiO_2 and the leading edge of the HOMO level of C_{60}, which are determined by extrapolating the leading edges to the base lines, are indicated by thick vertical bars. (c) Ti $2p_{3/2}$ spectra of the clean and C_{60}-covered TiO_2(110) surfaces. The intensity is reduced to 27% of that of the clean surface by C_{60} deposition. (d) An energy level diagram of the C_{60}/TiO_2 heterojunction. The energy positions of C_{60} are the upper and lower edges of the HOMO and LUMO levels, respectively.