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Molecular-scale observation of YD2-*o*-C8 self-assembled monolayer on TiO_2 (1 1 0)

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ABSTRACT

The self-assembled monolayer (SAM) on TiO_2 nanocrystal surface plays an important role in the processes of photoelectric conversion in dye sensitized solar cells (DSSCs). The SAM of dye YD2-*o*-C8, which was the best dye for DSSCs, has been observed by scanning tunneling microscope (STM) at molecular scale for the first time. The observation results showed that different morphologies of YD2-*o*-C8 SAM can be formed with or without chenodeoxycholic acid (cheno), which determined their corresponding photovoltaic cell efficiencies. The density functional theory (DFT) calculations explored the reason that was caused by the reduced electron coupling between side-to-side dimers separated by cheno molecules.

1. Introduction

Dye-sensitized solar cells (DSSCs) constitute a promising approach to sustainable and low-cost solar energy conversion [1–5]. In DSSCs, the structures and coverage of self-assembled dye molecules monolayer on surface of wide band-gap nanocrystals (TiO_2) significantly determines light absorption and multi-channel charge-transfer dynamics impacting cell efficiency [6–10]. Many technologies were used to investigate the impact of interface properties on light absorption, electron injection and recombination rate, including laser transient absorbance spectroscopy [11], steady-state and time-resolved fluorescence spectra [7,12–14]. But these technologies cannot observe the morphology of sensitized surface directly.

Scanning tunneling microscope (STM) has been used to observe the interaction between dye molecules and substrate by researchers because of its atomic resolution [15–19]. Small molecules which are stable at evaporation temperature were usually deposited on substrate in UHV chamber [20–22]. But organic metal chelate dye molecules are big molecules with thousands of relative molecular mass. They will decompose before evaporating to gas. Mayor et al. adopted UHV electrospray deposition method to deposit Ru(4,40-dicarboxy-2,20-bipyridine)$_2$(NCS)$_2$ (N3) dye molecules on TiO_2 (1 0 1) crystal surface [17]. This deposition method can effectively avoid crystal surface contaminated by environment. Sasahara et al. chose solution deposition method to deposit ruthenium dye sensitizer on TiO_2 (1 1 0) surface which was covered by a monolayer of pivalate ions prior to being removed from vacuum [23]. But the morphology of dyes by the two means may be different from the results of real DSSC processing. In order to observe the real condition of dye molecules on TiO_2 in DSSCs, Onishi and co-workers immerse TiO_2 (1 1 0) surface into the acetonitrile solution of N3 dye [20] directly in air because they found organic solvents such as methanol, benzene did not destroy the atom step of TiO_2 (1 1 0) crystal surface [24]. And they decrease the soak time to reduce the number of molecules in order to get molecular resolution. However, the morphology of dyes self-assemble monolayer (SAM) in real DSSCs processing has not been investigated, which played the key role to determine the cell efficiency in DSSCs.

Zinc porphyrin has been demonstrated as the best performing sensitizers from viewpoints of efficiency and stability [25]. One of the successful sensitizers used up to now for DSSCs is zinc porphyrin YD2-*o*-C8 dye molecule, which can reach 12.3% co-adsorbed with an organic dye molecule Y123 [26]. Dye molecules co-adsorption with small molecule cheno increased the efficiency of solar cells [27–31]. However, the understanding of the interaction between them is still on the macro-level. Research on the micro morphology is crucial to investigate the interaction mechanism between small molecule and dyes, therefore we used STM to study the effect of cheno on YD2-*o*-C8 SAM as a typical model system.

In real DSSCs processing, the molecules are deposited on the porous TiO_2 nanoparticle layer. But the nanoparticle layer is too rough (in Figure S1) for STM to distinguish the molecule adsorbed on it. In consid-

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eration of that TiO_2 (1 0 1) or TiO_2 (0 0 1) surface is sensitive to adsorb and dissociate water and oxygen from environment, TiO_2 (1 1 0) crystal surface was used as the substrate in our work. We used LT-UHV-STM to observe morphology (in Figure S2) of different concentrations of YD2-*o*-C8 molecules on TiO_2 (1 1 0) surface and investigated the difference between morphology with cheno and without cheno. Side-to-side aggregate along [0 0 1] direction of TiO_2 (1 1 0) surface was observed. Cheno separated YD2-*o*-C8 to amorphous islands and the solar cell corresponding to this morphology achieved the best efficiency. We anticipated that the cheno blocks the intermolecular charge transfer between YD2-*o*-C8.

2. Material and methods

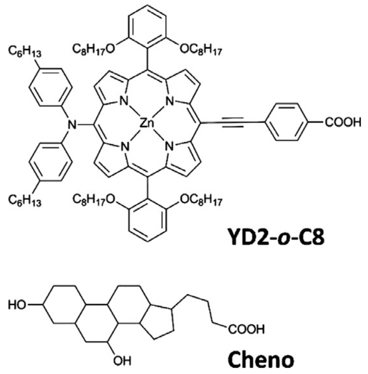
2.1. UHV-LT-STM image measurement

The atomically flat TiO_2 (1 1 0) surface was prepared in an ultra-high vacuum [32] and was confirmed with STM(UNISOKU LT SPM 1200) observation. The TiO_2 (1 1 0) wafer ($5\times5\times1\,mm^3$, Princeton) was sputtered with argon ion beams and annealed in vacuum (below 3×10^{-10} torr) at 650 °C. The TiO_2 (1 1 0) surface prepared in ultra-high vacuum (UHV) was immersed in 200 µmol/L YD2-*o*-C8/Ethanol solution for 18 h (enough long time to make sure the substrate was fully covered by dye molecules). The TiO_2 (1 1 0) surface is exposed to air for less than 5 min during the process. Before transported into load-lock chamber, the TiO_2 (1 1 0)/YD2-*o*-C8 wafer was rinsed by vast chromatographically pure THF solution to remove the dye molecules without adhesion to TiO_2 surface and dried with flow N_2. After pumping the wafer in UHV chamber overnight, transfer the wafer to LT-STM chamber to get image at LN_2 temperature. The slight heating was achieved by using e-beam heater to heat the substrate 30 min with 1 mA emission current. After annealing, the wafer was transferred to LT chamber immediately to avoid small molecules adsorbed on the surface again when the wafer cool down. The TiO_2 (1 1 0) substrate can be reused when we change the concentrate of dye solution. The dye molecules absorbed on the TiO_2 (1 1 0) can be removed by soaking it in 6 mol/L sulfuric acid solution for 2 h. Empty-state STM images were obtained in a constant-current mode at LN_2 temperature in the dark using an electrochemically etched tungsten tip. The images are presented without filtering.

The glass vessel used during preparing the dye solution was cleaned with piranha solution and rinsed with distilled water and absolute ethyl alcohol three times, respectively.

2.2. Solar cell device fabrication

The TiO_2 nanoparticles and their paste were prepared using a previously reported procedure [33]. The obtained paste was spread on the fluorine-doped tin oxide (FTO, TCO-15, 14 ohm/square, 2.2-mm-thick, NSG, Japan) by screen printing to form a TiO_2 electrode. The transparent film thickness was 10-µm-thick by the number of screen printing cycles, after a 5-µm-thick scattering layer (WER-2, 400 nm diameter, Dyesol, Australia) was deposited on the transparent film. The TiO_2 layers were further followed by sintering at 325 °C for 10 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 30 min. After cooling to 100 °C, the TiO_2 electrodes were immersed into a solution of YD2-*o*-C8 dye (0.2 mM in 9:1 (v/v) mixture of ethanol and tetrahydrofuran with or without 1 mM chenodeoxycholic acid) for 18 h at room temperature. Then the TiO_2 photoanodes were rinsed with ethanol and assembled using a thermally platinized FTO counter electrode to fabricated DSSC. The sensitized TiO_2 electrodes and counter electrodes were sealed with a hot-melt ionomer film Bynel (50 µm, Dupont). The redox electrolyte consists 0.165 M $[Co(bpy)_3](B(CN)_4)_2$, 0.045 M $[Co(bpy)_3](B(CN)_4)_3$, 0.8 M tert-butyl pyridine (TBP) and 0.1 M $LiClO_4$ in acetonitrile [26]. Finally, the electrolyte was injected into the interspace between the photoanode and counter electrodes by using a vacuum pump, and then sealed with a Bynel sheet and a thin glass cover by heating. The DSSC with an active area of 0.16 cm^2 were used for photovoltaic performance tests.



Scheme 1. Chemical structure of YD2-*o*-C8 dye molecule and cheno.

3. Theoretical calculations

The geometry of the isolated dye in the ground state was optimized by using B3LYP/6–31 G (d, p) level implanted in a Gaussian 09 software. For calculating the single point energies of different dimers, 6–311 G (d, p) basis set with B3LYP hybrid functional was used. The electronic coupling (V_{RP}) was evaluated with energy splitting in dimer method based on Koopmans' theorem [34]:

$$V_{RP} = \frac{\varepsilon_{\mathrm{LUMO+1}} - \varepsilon_{\mathrm{LUMO}}}{2}$$

where $\varepsilon_{\mathrm{LUMO}}$ and $\varepsilon_{\mathrm{LUMO+1}}$ are the levels of two lowest unoccupied molecular orbitals. Long-chain alkane substituent was simplified as methyl group in the theoretical studies.

4. Results and discussion

Chemical structures of YD2-*o*-C8 dye and small molecule cheno are illustrated in Scheme 1. The carboxylate anchoring groups of YD2-*o*-C8 and cheno are more easily connected with two adjacent five-fold coordinated Ti atoms in the form of bidentate Ti-O bonding as previous reports [35–37]. YD2-*o*-C8 adsorbed on the TiO_2 (1 1 0) substrate along titanium chain closely forming bright line (in Fig. 1a) which means YD2-*o*-C8 adsorbed side to side closely along *oa* [0 0 1] direction illustrated in Fig. 2a and c. Each bright spot in the bright line is about 3 nm diameter (Fig. 1b) which is the same with actual size of one dye molecule. The molecules in each adjacent bright line were face-to-face (in Fig. 2b). We got the minimum space between two adjacent bright line is about 5 nm from Fig. 1c.

The attractive interact (π–π interaction) of adjacent zinc porphyrin rings has been proposed to cause dimerization [16]. In DSSCs, the charge transfer between dye molecules will certainly go against the process of electron injection from dye to TiO_2. The electronic coupling is one of the critical factors in determining intermolecular charge transfer, for which the high value will lead to quick transfer. According to the absorption morphology on the TiO_2 (1 1 0) surface, the electronic couplings (V_{RP}) between YD2-*o*-C8 molecules have been theoretically investigated (Table 1). The theoretical results for face-to-face dimers, namely 0a2b, 0a3b and 0a4b, revealed that the electronic couplings of the dimers along $(1\bar{1}0)$ direction reduced obviously, especially when the distance increased to 4 times *ob*. It means that the charge transfer almost never happens between face-to-face molecules respectively adsorbing on the penta-coordinate titanium chains with the spacing of 2.60 nm. The side-to-side dimers (5a0b, 6a0b, 7a0b, 8a0b) show the same change trend for electronic couplings, but their coupling interactions are much stronger than the ones of face-to-face dimers at the similar distance. When the distance is around 2.0 nm, for instance, V_{RP} of 0a3b is 0.003 eV, and