

Molecular Orientation, Electronic Structures and Charge Transfer Dynamics of PTCDA molecules on TiO₂(110)



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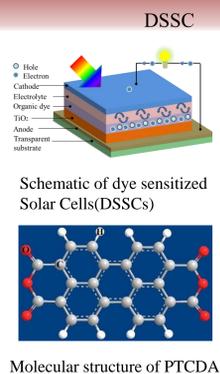
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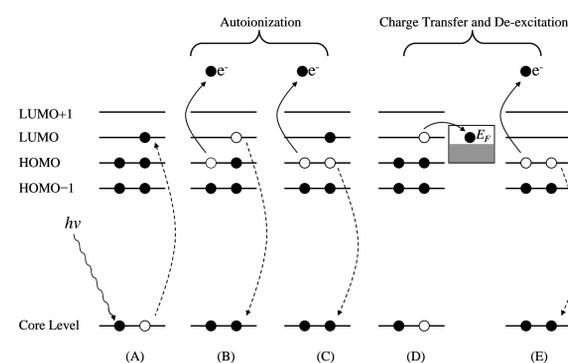
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INTRODUCTION

Titanium dioxide is one of the most intensively studied transition metal oxides because of its excellent properties for numerous applications, in particular in dye sensitized solar cells (DSSCs) as the anode. Charge transfer dynamics at the organic dye/TiO₂ interface largely determine the device performance. In this work, synchrotron based PES, NEXAFS and core-hole clock spectroscopy (RPES) were used to investigate the molecular orientation, electronic structures and charge transfer dynamics at the PTCDA/TiO₂(110) interface.



Resonant PES



Schematic diagram of the core-hole clock spectroscopy. (A) Core level excitation (NEXAFS); (B) Participator decay (Resonant PES; constant binding energy); (C) Spectator decay (Resonant Auger; constant kinetic energy); (D) Interfacial charge transfer (CT); (E) Auger emission.

Charge transfer (D) is competing with the de-excitation of excited state via RPES(B) or resonant Auger(C). The timescale of individual decay process determines which one will dominate. Using core hole lifetime of C/N 1s (~6fs) as a reference, the electron transfer timescales (τ_{ET}) could be calculated by the following equation:

$$\tau = \tau_{CH} \frac{I_{RPES}^{mono} / I_{NEXAFS}^{mono}}{I_{RPES}^{multi} / I_{NEXAFS}^{multi} - I_{RPES}^{mono} / I_{NEXAFS}^{mono}}$$

EXPERIMENTAL

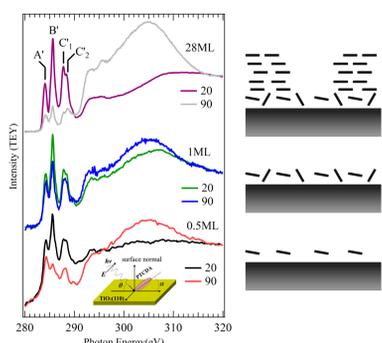
The experiments were carried out at the soft X-ray beam line (SINS) of SSLS. The available photon energy range is from 50 eV to 1200 eV. The base pressure is better than 1×10^{-10} mbar. Nominal energy resolution ($E/\Delta E$) is better than 1000 with flux of 10^{10} photon/s.

The endstation of the SINS beamline consists of three UHV chambers: an XMCD chamber, an analyzing chamber equipped with a Scienta R4000 analyzer, and a preparation chamber.



RESULTS

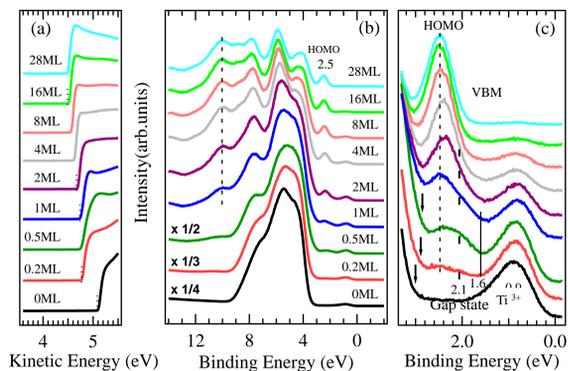
1. Molecular orientation



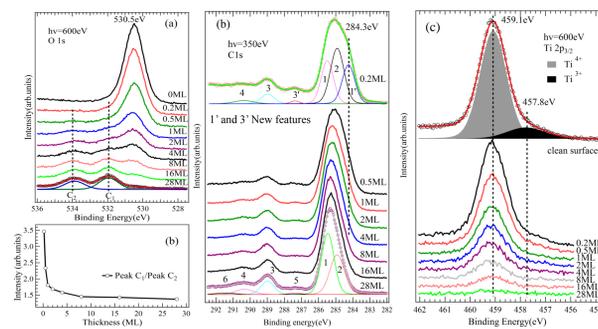
Left: Angular dependent C K-edge NEXAFS spectra of PTCDA submonolayer (0.5ML), monolayer and multilayers (28ML) on TiO₂(110). The inset shows the measurement geometry. **Right:** Schematic diagram of the molecular orientations at different coverages.

The first 2ML PTCDA molecules are strongly bounded to the TiO₂(110) surface through the chemical reaction between the perylene core of molecules and the substrate O atoms. The slightly tilted orientation of PTCDA molecules in monolayer coverage is due to the interfacial chemical reaction, which becomes less significant as coverage increases.

2. Electronic structure

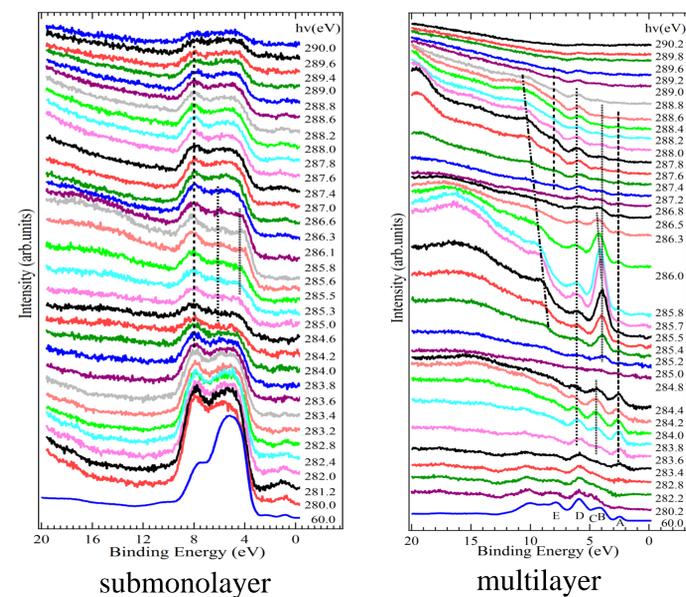


The secondary electron cut-off (a), valence band (b) and the close-up of the valence band features near the Fermi energy (c) of PTCDA on TiO₂(110) with increasing thicknesses ($h\nu=60$ eV, normal emission).



O 1s (a), C 1s(b) and Ti 2p_{3/2}(c) core level spectra as a function of PTCDA thickness.

3. Charge transfer dynamics



RPES spectra of PTCDA molecules on TiO₂(110) surface with incident photon energy ranging from 280 eV to 290 eV across the C K-edge. Less pronounced resonant structures are observed for the submonolayer coverage except for weak resonant structures located at 4.3eV, 6.1eV and 8.0eV (dashed lines). It suggests that the excited electrons within PTCDA molecules are transferred to the TiO₂ conduction band within an ultrafast timescale shorter than the core-hole lifetime (~6fs). In contrast, for multilayer PTCDA, several resonant features are clearly resolved, indicating the excited electrons remain localized in the molecular layers.

CONCLUSIONS

1. Thickness dependent molecular orientation.
2. Strong chemical interaction at PTCDA/TiO₂(110) interface.
3. Ultrafast electron transfer dynamics.

REFERENCE

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