Structure and Photo-Induced Charge Transfer of Pyridine Molecules Adsorbed on $\text{TiO}_2(110)$: A NEXAFS and Core-Hole-Clock Study

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ABSTRACT

The structure and photo-induced charge transfer time of pyridine molecules adsorbed on a rutile $\text{TiO}_2(110)$ surface have been studied by near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, density functional theory (DFT) calculations and core-hole-clock (CHC) spectroscopy. Polarization dependence of NEXAFS spectra and geometrical optimization by the DFT calculations revealed that the pyridine molecules are bound to the TiO_2 surface with an upright configuration where the N atom binds to a surface Ti atom. The CHC results indicate that the charge transfer from the LUMO+2 orbital of pyridine with a π^* symmetry to the conduction band of TiO_2 is quite fast, where the timescale is less than 3 fs.

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1. Introduction

Organic thin films deposited on electrodes are potentially useful for various functional devices such as sensors, electroluminescence devices and dye-sensitized solar cells. The charge transfer from the organic molecules to the electrodes significantly contributes to the electric properties of the devices. Although the geometric and electronic structures of adsorbed molecules should affect the charge transfer behavior, the number of studies on the structure dependence of the charge transfer is limited. One of the reasons for the lack of such studies is that the time scale of the charge transfer from adsorbed molecules to electrodes is extremely fast and typically at the low femtosecond regime.¹ The core-hole clock (CHC) spectroscopy is a powerful technique to estimate charge-transfer time from molecules to electrodes around or below 1 fs through the use of the decay time of a core hole as internal time standard.^{1–9} With this technique, photo-induced charge transfer times have been estimated for several adsorption systems which include $\text{N}_2/\text{graphite}$,² bi-isonicotinic acid/ $\text{TiO}_2(110)$,³ $\text{C}_{60}/\text{Au}(110)$,⁴ copper(II) phthalocyanine (CuPc)/ $\text{Au}(111)$,⁶ self-assembled monolayer (SAM) of thiolate/ $\text{Au}(111)$ ⁷ and $\text{S}/\text{Ru}(0001)$.⁸

The dye-sensitized solar cell, which has been originally developed by Grätzel and co-workers,⁹ consists of TiO_2 nanoparticles (NPs) as a nano-structured electrode, dye molecules bound to the NPs surfaces for photo-absorption and electrolytes for electron carrier as illustrated in Fig. 1(a). The photo-induced charge transfer from the molecules to the electrode as depicted in Fig. 1(b) is one of key factors that determine the efficiency.¹ So far a Ru-bipyridine com-

Figure 1. (Color online) (a) Schematics for a dye-sensitized solar cell using TiO_2 nanoparticles (NPs) and dye molecules adsorbed on the surfaces of TiO_2 NPs. Photo-excited electrons of the molecules transfer to the TiO_2 NPs and flow in an electric circuit and return to the photo-excited molecule via charge transfer of electrolytes. (b) Energy diagram at the surfaces of TiO_2 NPs and schematics for the HOMO-LUMO excitation of the dye molecule via a visible-light absorption and subsequent transfer of the excited electron to the conduction band of TiO_2 .

plex (4,4'-dicarboxy-2,2'-bipyridine) $_2\text{Ru}(\text{NCS})_2$, so-called “N3”, and its derivatives have been used as promising dye molecules.⁹ These dye molecules are bound to the nanostructured TiO_2 electrode surfaces via the carboxylic group in common. The carboxylic oxygen atoms bind to the Ti atom(s) in a M-monodentate or 2M-

bidentate form. The photo-induced charge transfer time through the carboxylic ligand has been studied using bi-isonicotinic acid molecules adsorbed on a rutile $\text{TiO}_2(110)$ surface by the CHC spectroscopy and found to be less than 3 fs.³ It is intriguing how the charge transfer time depends on the structure and the chemical property of functional group that links between the molecule and the electrode, which would be useful information for the development of further efficient sensitizer molecules.

In this work, pyridine ($\text{C}_5\text{H}_5\text{N}$) molecules were adsorbed on a rutile $\text{TiO}_2(110)$ single-crystal surface and photo-induced charge transfer from the adsorbed pyridine to the conduction band of TiO_2 has been measured by means of the CHC spectroscopy. Pyridine is one of Lewis-base molecules and can bind to the surface Ti ion via σ -donation of the lone pair to the Ti 3d orbital. Since the photo-induced charge transfer in the TiO_2 -based solar cell usually occurs from the molecule to Ti-3d-derived conduction band, the direct bonding to the Ti ion might enhance the charge transfer. The actual adsorption structure of pyridine on the $\text{TiO}_2(110)$ surface has been studied by polarization dependence of near-edge x-ray absorption fine structure (NEXAFS) and density functional theory (DFT) calculations. The charge transfer time of the pyridine/ $\text{TiO}_2(110)$ system has been estimated by one of the CHC spectroscopy techniques; a combination of NEXAFS and resonant photoemission spectroscopy (RPES) spectra. Although the present NEXAFS and RPES measurements were performed under ultrahigh vacuum (UHV) conditions, the ambient-pressure PES technique¹⁰ will allow us to apply the CHC spectroscopy to charge transfer processes at solid-liquid interfaces under electrochemical environments in future.

2. Experimental

The experiments were performed at soft x-ray beamlines 7A¹¹ and 13A¹² at the Photon Factory of High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan. NEXAFS measurements were carried out using a UHV chamber equipped with an electron energy analyzer (SCIENIA, SES-2002) and a micro-channel-plate detector. RPES measurements were conducted with another UHV chamber equipped with an electron energy analyzer (SPECS, PHOIBOS 100). A rutile $\text{TiO}_2(110)$ surface ($10 \times 10 \times 0.5 \text{ mm}^3$) was cleaned by repeated cycles of Ar^+ sputtering and annealing at 890 K. The cleanliness was checked by X-ray photoelectron spectroscopy (XPS). Pyridine was purified by the freeze-thaw-pumping method and introduced by a variable leak valve. A pyridine monolayer was prepared by exposing the clean TiO_2 surface to gaseous pyridine with 5 L ($1 \text{ L} = 1 \times 10^{-6} \text{ torr s}$) at 250 K.

The NEXAFS measurements were performed by the partial electron yield method with a retarding voltage of -300 V . Polarization dependence was measured with the normal (90°) and the grazing (30°) incidence in a photo-scattering plane along $[001]$ direction. The RPES spectra were measured at a normal emission for a valence energy range from -5 to 20 eV as a function of photon energy ranging from 284 to 290 eV for C K-edge and from 397 to 407 eV for N K-edge. According to a previous temperature programmed desorption study on pyridine/rutile- $\text{TiO}_2(110)$,¹³ the pyridine full monolayer starts to desorb at 230 K , the surface temperature was kept at 200 K during the measurements.

3. Calculation Method

We performed DFT calculations with the program package DMol³ in Materials Studio (version 4.4) of Accelrys Inc. In the DMol³ method,¹⁴ the physical wave functions are expanded in terms of numerical basis sets. We used the double-numeric quality basis set with polarization functions (DNP). The size of DNP basis set is

comparable to Gaussian 6-31 G^{**}, but the DNP is more accurate than the Gaussian basis set of the same size.¹⁵ The core electrons were treated with DFT semi-core pseudopotentials (DSPPs).¹⁶ The gradient-corrected GGA functional, developed by Perdew, Burke, and Ernzerhof (PBE),¹⁷ was employed. A Fermi smearing of 0.002 hartree ($1 \text{ hartree} = 27.2114 \text{ eV}$) and a real-space cutoff of $4.5 \text{ \AA}$ were used to improve computational performance. Periodic surface slabs of nine physical layers' thickness were used, with a $30 \text{ \AA}$ vacuum region between the slabs. For the numerical integration, we used FINE quality mesh size of the program. A $2 \times 4 \times 1$ k-point sampling was used. The adsorbate and all the layers of substrate were allowed to relax in the geometry optimization calculations without symmetry restriction (i.e., using $P1$ symmetry). The tolerances of energy, gradient, and displacement were $2 \times 10^{-5} \text{ hartree}$, $4 \times 10^{-3} \text{ hartree/\AA}$, and $5 \times 10^{-3} \text{ \AA}$, respectively. A (4×1) surface unit cell was chosen to model the adsorption of pyridine. Adsorption energies were computed by subtracting the energies of the gas-phase pyridine molecule and surface from the energy of the adsorption system as shown in Eq. (1).

$$E_{\text{ad}} = E(\text{pyridine/surface}) - E(\text{pyridine}) - E(\text{surface}) \quad (1)$$

With this definition, a negative E_{ad} corresponds to stable adsorption on the surface.

4. Principle of the CHC Experiments using NEXAFS and RPES

The principle to estimate the charge transfer time based on the CHC technique using NEXAFS and RPES is illustrated in Fig. 2. In the normal PES process (a), a valence electron is emitted as a photoelectron, and in the NEXAFS process (b), an electron is excited from a core level to an unoccupied orbital. While in the case of RPES process (c), photo-induced excitation of a core-level electron to an unoccupied orbital is followed by de-excitation of the excited electron to the core level with simultaneous emission of a valence electron. The de-excitation time is the life time of the core hole, typically a few fs for C 1s and N 1s core levels. However, if the transfer of the excited electron to the conduction band of the electrode occurs faster than the de-excitation (d), the RPES process

Figure 2. (Color online) Schematics for relevant photo-induced excitation and de-excitation processes applied to a molecule. (a) photoemission (PES), (b) near-edge x-ray absorption fine structure (NEXAFS), (c) resonant photoemission (RPES). PES provides information on the occupied states and NEXAFS the unoccupied states. RPES monitors the decay of the excited state. (d) If the molecular orbital couples to the substrate density-of-states a charge transfer may be possible that competes with RPES. Depending on the extent that the charge transfer occurs, the RPES is reduced in spectral intensity.

Figure 3. (Color online) Polarization dependence of C K-edge (a) and N K-edge (b) NEXAFS spectra taken for a pyridine monolayer adsorbed on a rutile $\text{TiO}_2(110)$ surface. NI and GI correspond to normal incidence (90° from the surface parallel) and grazing incidence (30° from the surface parallel), respectively.

does not take place, which results in disappearance of the RPES peak. The intensity reduction of the RPES peak is a measure of the extent of the charge transfer.

5. Results and Discussion

First we measured polarization dependence of C K-edge and N K-edge NEXAFS spectra for the pyridine/ $\text{TiO}_2(110)$ surface as shown in Fig. 3. Both for the two edges, a prominent peak is observed at 285.6 eV for C-K and 399.0 eV for N-K, which is associated with excitation to $\pi^*_1(b_1)$ (LUMO),^{18,19} and exhibits clear polarization dependence; it is strongly enhanced at the normal incidence. Note that there is a shoulder structure at 285.0 eV for C K-edge. The splitting into the main and shoulder structures is due to the difference in ionization potential between two carbon atoms directly bound to N and three carbon atoms located apart from N of the pyridine ring. Since the transition moment of the excitation to the $\pi^*_1(b_1)$ orbital is aligned perpendicular to the ring plane, this polarization dependence clearly indicates an upright configuration of the pyridine ring. This is further supported by the absence of polarization dependence for the $\sigma^*(\text{C-H})$ peak at 287.5 eV for C K-edge. At a higher energy by approximately 4 eV from the LUMO peak, another π^* peak is observed both for the two edges and attributed to $\pi^*_2(b_1)$, which corresponds to LUMO+2.¹⁸ Because the energy level of LUMO+1 with a_2 symmetry is lying very closely from the LUMO level,¹⁹ it cannot be clearly distinguished by the present energy resolution.

The upright configuration of the pyridine ring is also confirmed by the DFT calculation ($E_{\text{ad}} = -0.91$ eV). The optimized adsorption structure of pyridine on $\text{TiO}_2(110)$ is shown in Fig. 4. The pyridine

Figure 4. (Color online) Structure model of pyridine molecules adsorbed on the rutile $\text{TiO}_2(110)$ surface optimized by DFT calculations assuming a (4×1) -pyridine structure with a coverage of 0.25 ML. Pyridine molecules are adsorbed on the Ti rows with an upright configuration with the nitrogen atom being located at the atop site of the Ti atom.

ring stands up perpendicular to the surface with the ring plane being parallel to $[110]$ direction. It is noted that the nitrogen atom of pyridine binds to the Ti atom with atop geometry ($\text{Ti-N} = 2.3$ Å). The lone-pair electrons of nitrogen are donated to the $3d_{z^2}$ orbital of Ti with making Ti-N σ bond and the π^* orbitals of pyridine could interact with the Ti $3d_{xz}$ or $3d_{yz}$ orbital.

Next RPES spectra were measured as a function of photon energy at around C K-edge and N K-edge as shown in Fig. 5. The O 2p-derived valence band of TiO_2 is observed broadly at 5–10 eV. A lower binding-energy peak in the C K-edge RPES spectra, which shifts from 3 to -3 eV with increasing photon energy, is due to C1s photoemission from pyridine excited by the 2nd-order harmonics of the incident X ray. Pyridine MO-derived features appear at 12 eV and 16 eV depending on the photon energy. The intensity of the photoemission peak from the occupied pyridine MOs is corresponding to excitation probability from the 1s level to unoccupied pyridine MOs if the charge transfer to the substrate is neglected. In such a case, the RPES intensity plot as a function of photon energy (i.e. RPES-yield spectrum) should be in accordance with NEXAFS. While if contribution from the charge transfer is significant, the RPES intensity could be decreased. By comparing the NEXAFS spectrum with the RPES yield spectrum, we can estimate the charge transfer time τ_T using the equation (2):

$$\tau_T = \tau_C \left(\frac{I_{\text{RPES}}/I_{\text{NEX}}}{C - I_{\text{RPES}}/I_{\text{NEX}}} \right), \quad (2)$$

where τ_C is the life time of core hole (~ 6 fs for N1s), C is a constant ($\approx 1/3$), I_{NEX} and I_{RPES} are the peak intensities at the same photon energy in NEXAFS and RPES, respectively.³ To obtain the RPES-yield spectrum, the RPES peak intensities from the pyridine MOs were estimated by curve-fitting analysis at each photon energy to eliminate contribution from a broad Auger-derived band; three Gaussian functions representing two pyridine MO-derived features at 12 eV and 16 eV and the tail of the broad Auger-derived band were involved in the curve-fitting analysis by the least-square method.

Figure 5. (Color online) Resonant photoemission spectra taken for the pyridine/TiO₂(110) surface as a function of photon energy at around C K-edge (a) and N K-edge (b).

Figure 6. (Color online) RPES-yield spectra as a function of photon energy and NEXAFS spectra taken at C K-edge (a) and N K-edge (b) with an incidence angle of 55° from the surface parallel for a pyridine monolayer adsorbed on the TiO₂(110) surface.

The RPES-yield spectra are compared with the NEXAFS spectra as shown in Fig. 6. Here both the RPES and NEXAFS spectra are normalized by the intensity of the $\pi^*_1(b_1)$ (LUMO) peak, because the LUMO level is lower than the bottom of the conduction band of TiO₂ resulting in that no charge transfer takes place from the LUMO and hence the corresponding intensities of NEXAFS and RPES-yield spectra should be the same.³ Comparison between the NEXAFS and RPES spectra shows that the $\pi^*_2(b_1)$ peak disappears in the RPES spectra both for C K-edge and N K-edge. The disappearance of the $\pi^*_2(b_1)$ peak clearly indicates that the excited electron into the $\pi^*_2(b_1)$ orbital delocalizes faster than the core-hole decay via charge transfer to the conduction band. Considering above equation and the signal to noise ratio of the spectra, the charge transfer time τ_T for the $\pi^*_2(b_1)$ orbital is estimated to be shorter than 3 fs. This fast charge transfer would be realized by significant overlap between the $\pi^*_2(b_1)$ orbital and the Ti-3d orbitals that form the conduction band. It should be noted that the $\sigma^*(\text{C-H})$ peak in the RPES-yield spectrum [Fig. 6(a)] shows no apparent reduction. This observation suggests that the charge transfer from the $\sigma^*(\text{C-H})$ orbital is relatively slow ($\tau_T > \sim 30$ fs, assuming ~ 6 fs for C1s⁷ and $C \approx 1$). This might be explained by less overlap between the $\sigma^*(\text{C-H})$ orbital and the Ti-3d orbitals due to the upright configuration of the pyridine ring.

6. Conclusion

We studied the adsorption structure of pyridine molecules on a

rutile TiO₂(110) surface and photo-induced charge transfer time from the pyridine to the substrate. From the polarized NEXAFS measurements and the DFT calculations the pyridine molecules are found to be adsorbed with an upright configuration and with the N atom being located at the on-top site of the Ti atom. The combined measurements of NEXAFS and RPES revealed that the charge transfer from the $\pi^*_2(b_1)$ orbital of the adsorbed pyridine to the conduction band of TiO₂ is fast ($\tau_T < 3$ fs). This charge transfer timescale is comparable to that for bi-isonicotinic acid/TiO₂(110) where the molecule is bound to the surface via Ti-carboxylate bonds. Although pyridine itself exhibits no visible-light absorption, it may be potentially useful for a linking moiety between chromophore and TiO₂ electrode. The CHC spectroscopy used here is powerful to estimate the photo-induced charge transfer time for each unoccupied molecular orbital.

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References

1. L. Wang, W. Chen, and A. T. S. Wee, *Surf. Sci. Rep.*, **63**, 465 (2008).
2. O. Björneholm, A. Nilsson, A. Sandell, B. Hernnas, and N. Mårtensson, *Phys. Rev. Lett.*, **68**, 1892 (1992).
3. J. Schnadt, P. A. Brühwiler, L. Patthey, J. N. O'Shea, S. Södergren, M. Odelius, R. Ahuja, O. Karis, M. Bässler, P. Persson, H. Siegbahn, S. Lunell, and N. Mårtensson, *Nature*, **418**, 620 (2002).
4. P. A. Brühwiler, O. Karis, and N. Mårtensson, *Rev. Mod. Phys.*, **74**, 703 (2002).
5. D. Menzel, *Chem. Soc. Rev.*, **37**, 2212 (2008).
6. W. Chen, L. Wang, D. C. Qi, S. Chen, X. Y. Gao, and A. T. S. Wee, *Appl. Phys. Lett.*, **88**, 184102 (2006).
7. W. Chen, L. Wang, C. Huang, T. T. Lin, X. Y. Gao, K. P. Loh, Z. K. Chen, and A. T. S. Wee, *J. Am. Chem. Soc.*, **128**, 935 (2006); L. Wang, L. Liu, W. Chen, Y. P. Feng, and A. T. S. Wee, *J. Am. Chem. Soc.*, **128**, 8003 (2006).
8. A. Föhlisch, P. Feulner, F. Hennies, A. Fink, D. Menzel, D. Sanchez-Portal, P. M. Echenique, and W. Wurth, *Nature*, **436**, 373 (2005).
9. B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991); U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel, *Nature*, **395**, 583 (1998); A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, **33**, 269 (2000); M. Grätzel, *Nature*, **414**, 338 (2001).
10. B. S. Mun, H. Kondoh, Z. Liu, and Phil N. Ross Jr., and Z. Hussain, *Current Trends of Surface Science and Catalysis* (Ed. J. Y. Park), Springer, New York, Chapter 9 (2013).
11. K. Amemiya, H. Kondoh, T. Yokoyama, and T. Ohta, *J. Electron Spectrosc. Relat. Phenom.*, **124**, 151 (2002).
12. A. Toyoshima, T. Kikuchi, H. Tanaka, K. Mase, K. Amemiya, and K. Ozawa, *J. Phys.: Conf. Ser.*, **425**, 152019 (2013).
13. S. Suzuki, Y. Yamaguchi, H. Onishi, T. Sasaki, K. Fukui, and Y. Iwasawa, *J. Chem. Soc., Faraday Trans.*, **94**, 161 (1998).
14. B. Delley, *J. Chem. Phys.*, **92**, 508 (1990); B. Delley, *J. Phys. Chem.*, **100**, 6107 (1996); B. Delley, *J. Chem. Phys.*, **113**, 7756 (2000).
15. Y. Inada and H. Orita, *J. Comput. Chem.*, **29**, 225 (2008).
16. B. Delley, *Phys. Rev. B*, **66**, 155125 (2002).
17. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996).
18. I. Nennert and G. J. Schulz, *J. Chem. Phys.*, **62**, 1747 (1975).
19. M. Bader, J. Haase, K.-H. Frank, A. Puschmann, and A. Otto, *Phys. Rev. Lett.*, **56**, 1921 (1986).