Efficient light-to-current conversion by organic-inorganic interfacial charge-transfer transitions in TiO₂ chemically adsorbed with 2-anthroic acid

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Organic-inorganic interfacial charge-transfer (ICT) transitions provide the concepts that organic-inorganic interfaces serves as a field for light absorption and charge separation directly occurs without energy loss. Here, we report efficient light-to-current conversion due to the ICT transitions in TiO₂ chemically adsorbed with 2-anthroic acid. The incident photon-to-current conversion efficiency (IPCE) surpasses 85%, showing the significant improvement as compared to the reported results. Density functional analysis shows that the ICT absorption arises from strong d_π-π* interactions at the inorganic-organic interface. In addition, we examined the density of states (DOS) of unoccupied surface states on TiO₂ from the absorption and IPCE spectra.

1. Introduction

Organic-inorganic interfacial charge-transfer (ICT) transitions offer the following concepts that organic-inorganic interfaces serve as a field for light absorption and charge separation directly occurs without energy loss. The former feature enables to use low-cost colorless organic compounds that have not been used for light absorption. The latter feature leads to charge separation at the organic-inorganic interface with an internal quantum efficiency of 100% without energy loss. Because of these features, ICT transitions have been expected to be applied to solar-energy conversions such as photovoltaic conversion. So far, organic-inorganic ICT transitions have been reported in TiO₂ nanoparticles chemically adsorbed with organic molecules [1,2] and organic-inorganic hybrid lead-iodide nanowire perovskite [3-6]. For the latter hybrid material, one-dimensional lead-iodide perovskite with organic electron acceptors, methylviologen, has been studied. [3-6] It was demonstrated that the ICT transitions from the lead-iodide nanowire to methylviologen much more efficiently generate photocurrent than intra-wire electronic transitions, revealing the high

potential of the ICT transitions in photoelectric conversion. On the other hand, the former TiO₂ nanoparticles adsorbed with ascorbic acid [7,8] and catechol derivatives [9,10] were applied to photovoltaic cells. Although the incident photon-to-current conversion efficiencies (IPCE) were reported to be quite low (IPCE $\lesssim$ 30%), the experiments first demonstrated photovoltaic conversion due to ICT transitions. Recently, a relatively high IPCE value of ca. 75% was reported with the hybrid material prepared from TiO₂ nanoparticles and tetracyanoquinodimethane (abbreviated to TCNQ). [11] However, the researches of the photovoltaic conversion due to ICT transitions are still quite limited. For successful applications of ICT transitions to photovoltaic conversion, further fundamental studies are required. In this Letter, we report efficient light-to-current conversion by the ICT transitions in TiO₂ chemically adsorbed with 2-anthroic acid (abbreviated to AT-COOH), showing the significant improvement in the IPCE value exceeding 85%. In addition, we have clarified the mechanism of the generation of the ICT absorption and examined the density of states (DOS) of unoccupied surface states on TiO₂ nanoparticles from the absorption and IPCE spectra.

2. Methods

2.1. Experimental methods

Mesoporous TiO₂ electrodes were prepared by screen-printing TiO₂ nanoparticle pastes (Solaronix SA Co., anatase, average diameter: 15-20 nm) on F-doped SnO₂ (FTO) transparent conducting glass substrates (Nippon Sheet Glass Co.) with sheet resistance of 10 Ω per square and sintering them at 773 K for 30 min. The thickness of the TiO₂ electrode was set to ca. 18 μ m. The TiO₂ electrode was immersed in the 1 mM AT-COOH solution (solvent: acetonitrile) for 24 hours at room temperature. AT-COOH was purchased from Tokyo Chemical Industry Co., Ltd. Photovoltaic cells were fabricated using the AT-COOH treated TiO₂ electrode (active area: 4 $\times$ 4 mm²), a Pt-spattered FTO glass counter electrode, I⁻/I₃⁻ redox couple electrolyte (1 M LiI, 0.025M I₂ /acetonitrile), and a polymer spacer film (thickness: 30 μ m). IPCE excitation spectra were measured by means of a Hypermonolight system (Bunkoukeiki Co., SM-250E) with a calibrated silicon photodiode (Bunkoukeiki Co., S1337). Current density-voltage (J - V) curves under the AM 1.5G simulated sunlight at 100 mW/cm² were measured with a potentiostat (Hokutodenko Co., HSV-100) and a solar simulator (Yamashita Denso Co., YSS-50S).

2.2. Computational details

Optimized structures, vibration spectra, and electronic-excitation spectra of AT-COOH and a model compound of AT-COOH treated TiO₂ were calculated with density functional theory (DFT) [12] and time-dependent DFT (TD-DFT) [13] calculations with the B3LYP functional [14,15] and 6-31G+(d,p) [16,17] basis set, using a Gaussian 09 software [18]. In the TD-DFT calculation, solvation effects in acetonitrile that was used as a solvent in the measurement of the near UV-visible absorption spectra were taken into account with the conductor-like polarizable continuum model (CPCM) [19,20].

3. Results and discussion

In this study, we found that TiO₂ (anatase) nanoporous films are intensely colored bright yellow by immersion in the colorless AT-COOH solution, as shown in Figure 1(a). Figure 1(b) shows near UV-visible absorption spectra of TiO₂ nanoporous films before and after the immersion in the AT-COOH solution and that of the AT-COOH solution. As shown in Figure 1(b), AT-COOH shows a π - π^* absorption band at wavelengths shorter than ca. 400 nm with a vibrational structure ($\Delta E = \text{ca. } 1360 \text{ cm}^{-1}$). This vibrational structure is attributed to the symmetric C=C vibrational mode in the anthracene moiety. [21] TiO₂ nanoporous films before the immersion show inter-band absorption in the near UV region, reflecting the wide band gap of ca. 3.2 eV [1,2]. Since the TiO₂ film consists of TiO₂ particles with an average diameter of ca. 15 - 20 nm, no attenuation peak due to Mie-scattering [22] from the TiO₂ nanoparticles is observed in the visible region. Although AT-COOH and TiO₂ show little light absorption in the visible region, the TiO₂ film treated with AT-COOH shows a broad absorption band in the visible region, as shown in Figure 1(b). The broad absorption gradually rises up around 600 nm and shows no vibrational structure. This result indicates that the broad absorption band does not originate from the intra-molecular electronic transitions in the anthracene moiety and inter-band transitions in TiO₂.

In order to examine the broad absorption band of the AT-COOH treated TiO₂, at first, the adsorption structure of AT-COOH on TiO₂ was examined by FT-IR spectroscopy. FT-IR spectra of AT-COOH, TiO₂, and AT-COOH treated TiO₂ were measured, as shown in Figure 2. AT-COOH shows a strong absorption peak at 1681.7 cm⁻¹ with several weak peaks at the lower-wavenumber region. To identify these peaks, the vibrational absorption spectrum of AT-

COOH was calculated by DFT. As shown by blue vertical lines in Figure 2(a), the calculated spectrum is almost consistent with the experimental result. The most prominent peak is attributed to a localized asymmetric vibrational mode of the carboxylic-acid group (COOH). The other weak peaks at the lower wavenumbers are assigned to C=C vibrational modes in the anthracene ring. As shown in Figure 2(c), TiO₂ exhibits a broad absorption band around 1639 cm⁻¹. This broad absorption band is attributed to water molecules physically adsorbed on TiO₂. [24] On the other hand, for AT-COOH treated TiO₂, although the sharp peaks of the C=C vibrational modes in the anthracene ring and the broad peak of water molecules physically adsorbed on TiO₂ are observed, the strong asymmetric COOH vibrational mode in AT-COOH perfectly vanishes by the adsorption on TiO₂. This result evidently indicates that the carboxylate group chemically adsorbs to the TiO₂ surface. In addition, a new peak appears at 1400.1 cm⁻¹ with two broad bands around 1400 and 1550 cm⁻¹. These vibrational modes were examined using a model compound, [Ti(OH)₃(H₂O)-OOC-AT] (Figure 3(a)), in which the carboxylate group coordinates with a Ti atom by a chelating bidentate ligation. The calculated vibrational spectrum is shown by red vertical lines in Figure 2(b). At first, we can see that the DFT calculations of AT-COOH and [Ti(OH)₃(H₂O)-OOC-AT] well reproduce the overall change in the FT-IR spectrum between AT-COOH and AT-COOH treated TiO₂. In addition, the DFT calculation shows the strong peak at 1400 cm⁻¹, which is consistent with the experimental result. The prominent peak at 1400 cm⁻¹ is attributed to a mixed vibrational mode between the asymmetric vibration of the carboxylate group and C=C vibration. This result reveals that AT-COOH adsorbs on TiO₂ by the **chelating bidentate coordination of the carboxylate group. In addition to the chelating bidentate coordination, a bridging bidentate coordination of the carboxylate group to two adjacent Ti atoms on TiO₂ is considered to be also possible. Unfortunately, it is not possible to examine the bridging bidentate adsorption in our model complex. Hopefully, the bridging bidentate adsorption will be analysed by DFT using TiO₂ nanoclusters [25,26], which will be reported elsewhere. In this work, we analyse the electronic structure and absorption properties of TiO₂-OOC-AT using the model complex with the chelating bidentate adsorption, which is supported by the above DFT calculations. Such a mono-Ti model complex has been widely employed for characterizations of organic-inorganic ICT absorption bands. [9,10,27]**

The electronic structure and absorption properties of the AT-COOH treated TiO₂ (abbreviated to TiO₂-OOC-AT) were examined by DFT and TD-DFT calculations, using the mentioned model compound. The electronic distributions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are shown in Figure 3(a). The HOMO is localized on the anthracene ring. In contrast, the LUMO is delocalized on both the

anthracene ring and titanium atom. This electronic hybridization in the LUMO is caused by the bonding interaction between the $3d_{zx}$ orbital of the titanium atom and LUMO (π^*) of the anthracene ring, as shown in Figure 3(b). Figure 3(c) shows the calculated electronic-excitation spectrum of $[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})\text{-OOC-AT}]$ together with that of AT-COOH. As compared to the calculated intra-molecular absorption band at 419.3 nm in AT-COOH, the absorption band is red-shifted to 430.1 nm in $[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})\text{-OOC-AT}]$. The calculated lowest absorption band in AT-COOH and $[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})\text{-OOC-AT}]$ are predominantly assigned to the HOMO→LUMO transition. The red-shift is attributed to the much larger stabilization (0.06 eV) of the LUMO due to the mentioned bonding $d_{zx}\text{-}\pi^*$ interaction with the Ti atom than that (0.01 eV) of the HOMO. The red-shift of the calculated absorption band is consistent with the experimental result in Figure 1 (b). This result indicates that the broad absorption band in Figure 1(b) has the nature of ICT absorption. On the other hand, the ICT absorption band rises up at the much longer wavelength (ca. 600 nm) in the experimental absorption spectrum, as shown in Figure 1(b). The difference in the onset wavelength between the TD-DFT calculation and experimental result is attributed to the use of the mono-Ti model complex. By replacing the mono-Ti complex with a TiO_2 cluster, further red-shift of the ICT band is expected.

Photovoltaic cells were fabricated with the mesoporous $\text{TiO}_2\text{-OOC-AT}$ photoelectrode (Figure 1(a)) and iodide electrolyte (1M LiI, 0.025 M I_2 /acetonitrile), as shown in Figure 4(a). Figure 4(b) shows IPCE spectra of the photovoltaic cells based on TiO_2 (blank) and $\text{TiO}_2\text{-OOC-AT}$. In the IPCE spectrum of the TiO_2 photovoltaic cell, photovoltaic conversion due to the internal electronic transitions in TiO_2 is observed around 350 nm. On the other hand, the IPCE spectrum of the $\text{TiO}_2\text{-OOC-AT}$ photovoltaic cell shows photovoltaic conversion due to the ICT absorption in the visible region with a maximal IPCE value of 87% at 450 nm. It is noteworthy that this value is much higher than the reported results [7-10, 11]. Therefore, the result demonstrates that efficient light-to-current conversion is possible for ICT transitions. From the J - V curve in Figure 4(c), the power conversion efficiency under simulated solar illumination (AM1.5G, 100 mW/cm^2) for the $\text{TiO}_2\text{-OOC-AT}$ photovoltaic cell was obtained as 2.2% with a short-circuit current density (J_{SC}) of 6.6 mA/cm^2 , an open-circuit voltage (V_{OC}) of 0.50 V, and a fill factor (FF) of 0.66. As compared to the photovoltaic properties ($J_{\text{SC}} = 0.57 \text{ mA}/\text{cm}^2$, $V_{\text{OC}} = 0.39$, $FF = 0.76$, $PCE = 0.17\%$) of the untreated TiO_2 photovoltaic cell, the photocurrent and photovoltage were significantly enhanced by the ICT absorption in $\text{TiO}_2\text{-OOC-AT}$. Furthermore, we examined photovoltaic properties of the photovoltaic cell based on a TiO_2 treated with anthracene (AT) without carboxylic acid groups instead of AT-COOH. As shown in Figures S1(a) and S1(b) in the supporting information, no remarkable increases in the IPCE and photocurrent in relation to AT were observed. Therefore, the

above-mentioned high IPCE and enhanced photocurrent are attributed to the chemical adsorption of AT-COOH via the carboxylate group, supporting the FT-IR result.

Finally, we examine the tail structure of the IPCE spectrum. As shown in Figure 4(b), the IPCE spectrum shows a long tail at wavelengths longer than 550 nm. Such a long tail is characteristic of ICT absorption. [1,2,7-11] Since the tail is too long for the Urbach tail originating from electron-lattice interactions, [4] the IPCE tail is attributed to ICT transitions to unoccupied surface-states on TiO₂ below the conduction band edge. We tentatively plotted the IPCE spectrum with a vertical logarithmic axis. As shown by red solid circles in Figure 5, interestingly, the IPCE value decreases exponentially with photon energies. In general, the photon-energy dependence of IPCE is given by the product of the quantum efficiencies of light absorption, charge separation and charge collection (Φ_{abs} , Φ_{cs} and $\Phi_{\text{collection}}$, respectively). $\Phi_{\text{abs}}(E)$ is governed by the absorbance (Abs) with the equation of $\Phi_{\text{abs}} = 1 - 10^{-Abs}$. In the case that Abs is much less than 1, Φ_{abs} is proportional to Abs . Since Abs is proportional to the DOS of unoccupied surface states ($D(E)$) on TiO₂ and transition dipole moment ($\mu(E)$), IPCE is proportional to $D(E)$. Therefore, the IPCE tail suggests the exponential distribution of unoccupied orbitals on TiO₂ below the conduction band edge, as shown in the inset in Figure 5. As shown by blue open squares in Figure 5, the ICT absorbance of TiO₂-OOC-AT in Figure 1(b) decays exponentially with decreasing photon energies, well agreeing with the IPCE tail. This result would reveal the exponential distribution of surface unoccupied states on TiO₂, supporting the assignment of the ICT band.

4. Conclusion

In this study, we demonstrated efficient light-to-current conversion due to ICT transitions with the TiO₂-OOC-AT system. By DFT calculations, it was found that the ICT absorption is generated by the electronic hybridization due to the strong $d_{\text{ZK}}-\pi^*$ interaction at the inorganic-organic interface. In addition, the analysis of the tail of the absorption and IPCE spectra directly revealed the exponential distribution of the unoccupied surface states on TiO₂ below the conduction band edge, supporting the assignment of the ICT band.

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Figures

Figure 1. (a) Coloration of a nanoporous TiO_2 film (area: $4 \times 4 \text{ mm}^2$) by immersion in the 1 mM AT-COOH solution (solvent: acetonitrile) and (b) near UV-visible absorption spectra of thin nanoporous TiO_2 films in acetonitrile before and after immersion in the AT-COOH solution and that of the AT-COOH solution.

Figure 2. FT-IR spectra of (a) AT-COOH, (b) $\text{TiO}_2\text{-OOC-AT}$, and (c) TiO_2 together with DFT-calculated line spectra of AT-COOH (blue vertical lines) and $[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})\text{-OOC-AT}]$ (red vertical lines) in vacuum. Calculated wavenumbers are corrected with a scaling factor of 0.9613^[23].

Figure 3. (a) DFT optimized structure and calculated electronic distributions of HOMO and LUMO ($|\text{isovalue}|=0.02$) of $[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})\text{-OOC-AT}]$. Gray: carbon, red: oxygen, small white: hydrogen, and large white: titanium atom. Green and red isosurfaces stand for opposite signs in amplitude. (b) Schematic picture of $d_{zx}\text{-}\pi^*$ interaction. (c) TD-DFT calculated absorption spectra of $[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})\text{-OOC-AT}]$ (red lines) and AT-COOH (blue lines). H: HOMO, L: LUMO, and f : oscillator strength.

Figure 4. (a) Device structure (cross section) of a $\text{TiO}_2\text{-OOC-AT}$ photovoltaic cell with iodide electrolyte (1M LiI, 0.025 M I_2 /acetonitrile) and (b) IPCE spectra and (c) $J-V$ curves of the photovoltaic cells based on $\text{TiO}_2\text{-OOC-AT}$ (solid curve) and TiO_2 (blank, dashed curve) under simulated solar illumination (AM1.5G, $100\text{mW}/\text{cm}^2$).

Figure 5. Tails of the IPCE spectrum (red solid circles) of the TiO₂-OOC-AT photovoltaic cell and absorption spectrum (blue open squares) of TiO₂-OOC-AT. Inset: schematic picture of the exponential distribution of unoccupied surface states on TiO₂. DOS: density of states, CBE: conduction band edge.

Graphical abstract