

Photoinduced formation of polythiophene/TiO₂ nano-hybrid heterojunction films for solar cell applications

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The FT-IR spectra of the photoelectrochemically fabricated PBT-BTC/TiO₂ and the electrochemically prepared PBT-FTO were observed to confirm photo-polymerization. Spectroelectrochemical measurements for the TiO₂ films were performed to determine a conduction band edge and a density of electron acceptor states. IPCE spectra for the sensitized type solar cell based on PBT-BTC/TiO₂ were observed.

Experimental Methods

The IR spectra of the PBT-BTC/TiO₂ and the PBT-FTO electrodes were measured by FT-IR spectrometer with an ATR arrangement (Perkin Elmer, Spectrum 100), with the data collection at a resolution of 1 cm⁻¹. The polymer samples were dedoped with a potential application of -0.4 V over long periods.

A density of electron acceptor states (conduction band + surface states)¹ of the TiO₂ film was qualitatively estimated by spectroelectrochemical measurements. The experimental method is similar to those described previously.²⁻⁴ The TiO₂ film electrode was set to a three electrode cell with a quartz window, and placed in an absorption spectrometer (JASCO, V-670). Pt and Ag/AgCl electrodes were employed as counter and reference, respectively. Absorption spectra were observed after bias application into the TiO₂ film in BMITFSI or 0.1 M LiClO₄ in PC for 5 min. The bias was applied from 0 V with -0.1 V steps following the measurement of the reference line after 15 min. stabilization at +0.8 V vs. Ag/AgCl. N₂ gas was employed prior to and during the optical experiments in order to avoid O₂ contamination.

Sandwich type solar cells were fabricated by binding a redox electrolyte with the nanohybrid electrode and the Pt counter electrode.⁵ The electrolyte was prepared by dissolving 0.6 M dimethyl propyl imidazolium iodide (Tomiya Pure Chemical), 0.05 M iodine (99.8%, Wako), 0.1 M lithium iodide (99.995 %, Wako), and 0.5 M *tert*-butylpyridine (99%, Aldrich) in dried acetonitrile (99%, Wako). A Xe lamp with a monochromator (Bunko Keiki, SM-25) was used to characterize IPCE spectra.

An I-V measurement was performed by an AM1.5 solar simulator (100 mW/cm², Yamashita Denso, YSS-50A).

Results

Figure S1 compares the FT-IR spectra of the PBT-BTC/TiO₂ and the PBT-FTO electrodes. These are similar; in particular, a strong absorption band at 790 cm⁻¹ is clearly assigned to the C-H out-of-plane vibration, being typically observed for 2,5-substituted thiophene.^{6,7} Although degraded polythiophene is known to exhibit a C=O group absorption band at 1700 cm⁻¹,⁸ this band was not recognized for the hybrid film. This observation suggests that degradation by the photo-induced polymerization process is negligible. Note that the absorption at <800 cm⁻¹ for the PBT-BTC/TiO₂ is due to the TiO₂ broad absorption.

The density of TiO₂ electron acceptor states including the conduction band and the surface states¹ was qualitatively measured spectroelectrochemically. The absorption difference, measured after the negative bias application, indicates the number of electrons accumulated in the TiO₂ acceptor states,²⁻⁴ thereby enabling us to estimate their relative density. Moreover, these acceptor states correlate their availability for photo-polymerization, since the electronically unconnected states cannot be observed by this method. Thus, a relative density of the acceptor states for the electrons injected from a BTC can be obtained from these measurements. Figure S2 shows absorption change of the TiO₂ electrode observed in BMITFSI and PC with 0.1 M LiClO₄ at 1000 nm. The inset on Figure S2 exhibits absorption difference spectra obtained at the indicated bias application. The absorbance increase measured in BMITFSI is negatively shifted compared to PC, in agreement with the data reported by Fabregat-Santiago et al.⁹ This shift is probably explained by the absence of the potential determining ions such as Li⁺ or H⁺ in BMITFSI.

Figure S3 shows IPCE spectra for the solar cell with the PBT-BTC/TiO₂ electrode. The nanohybrid film was prepared in 0.1 M BT in BMITFSI under light irradiation at various times. The IPCE decreases

within 1 min. and with the excess polymerization time. The inset of Figure S3 shows IPCE changes as a function of charges collected during the photo-induced polymerization. The IPCE at 550 nm clearly shows that the absorbance increase initially contributes to slight IPCE increase.

References

- (1) We are fully aware that currently controversy exists over the assignment of the accumulated electrons to conduction band filling, surface states trapping or trapping in the lattice. We therefore refer to the term "electron acceptor states" for the states filled by the electrons during the negative bias application.
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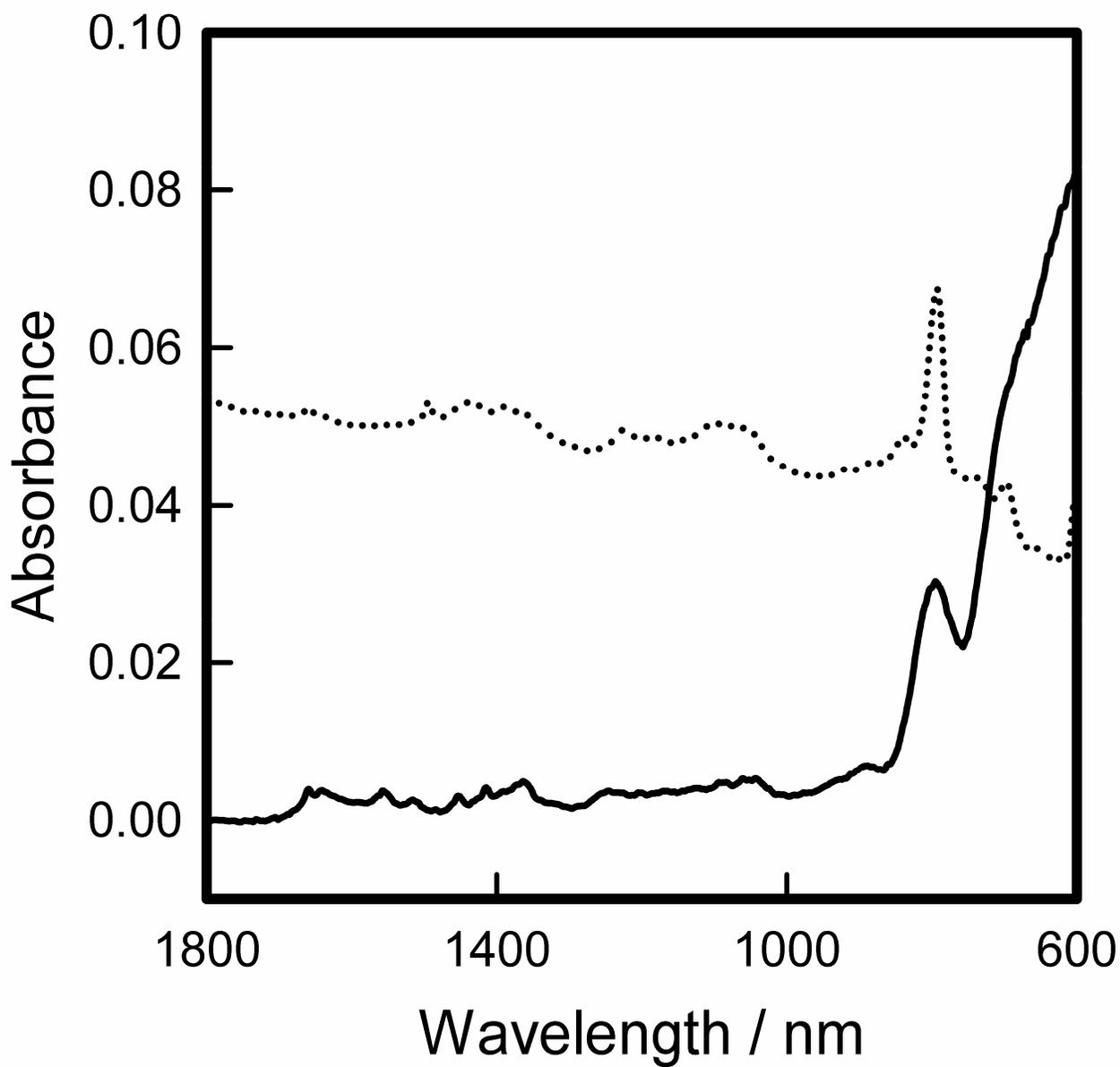


Figure S1. FT-IR spectra of the photoelectrochemically fabricated PBT-BTC/TiO₂ (solid line) and the electrochemically prepared PBT-FTO (dotted line).

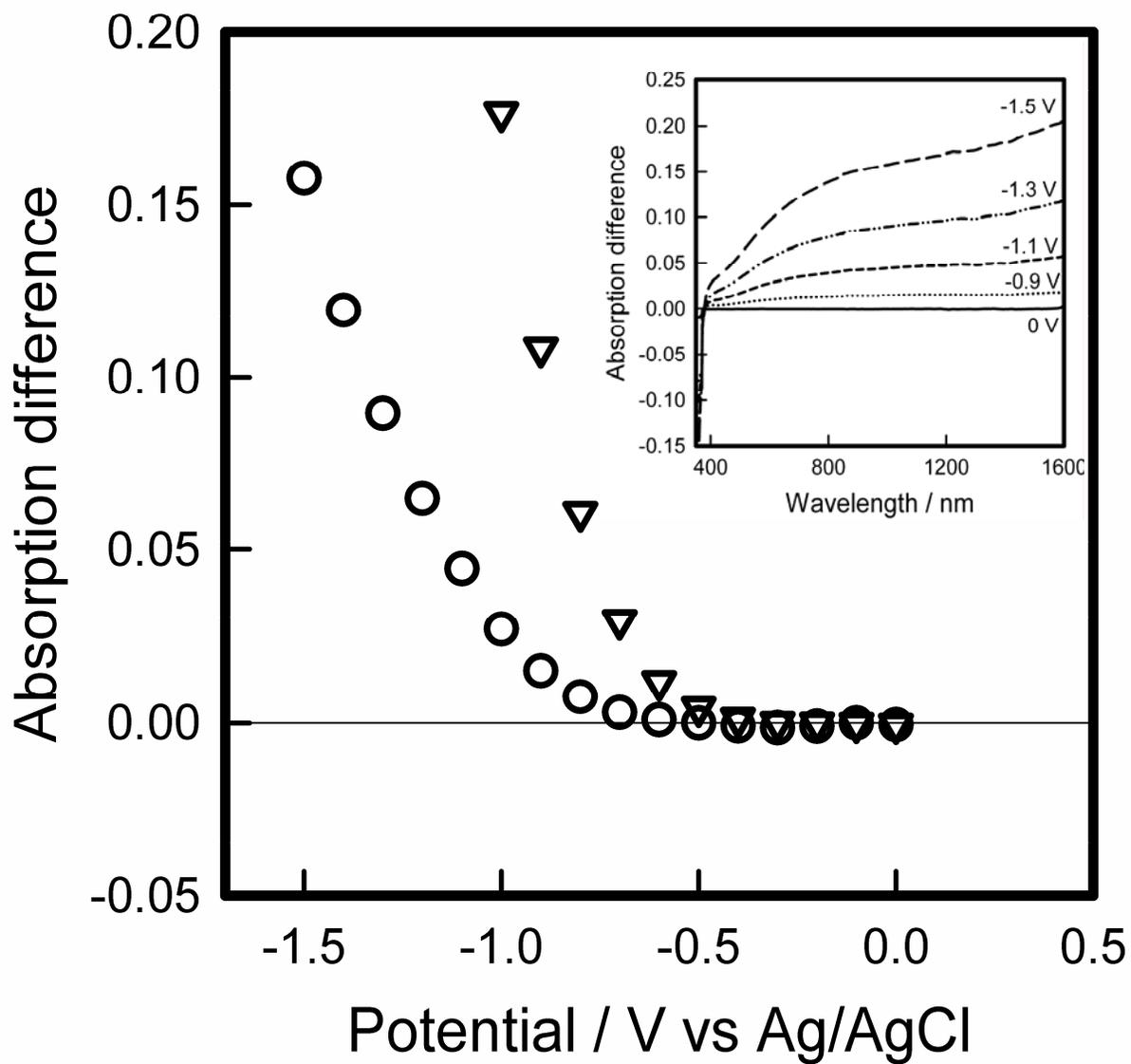


Figure S2. Absorbance change of a TiO₂ film in BMITFSI (circle) and in PC with 0.1 M LiClO₄ (triangle) at 1000 nm. The inset shows the corresponding absorption spectra after each bias application.

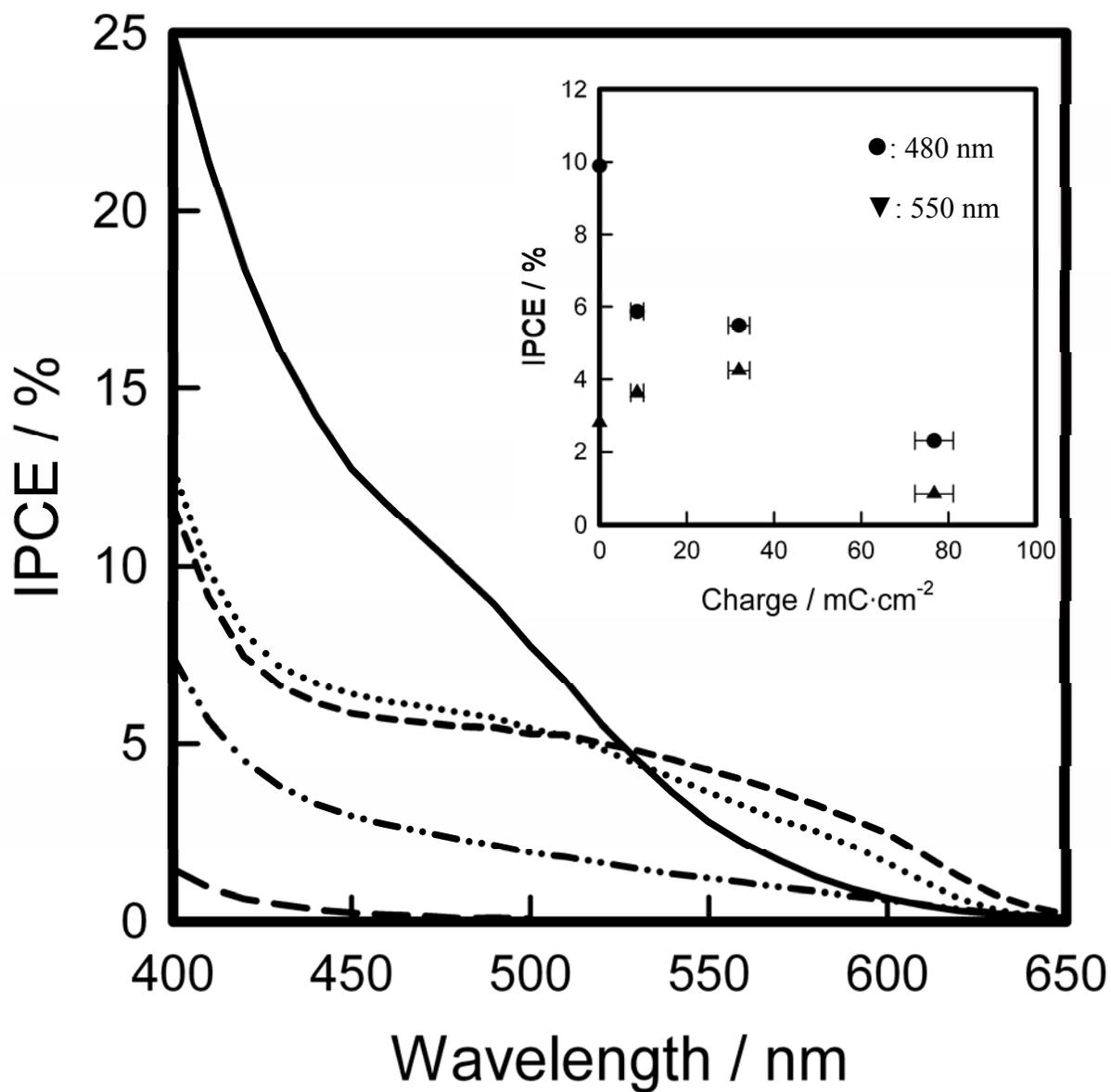


Figure S3. IPCE spectra observed for the sensitized type solar cell based on PBT-BTC/TiO₂. The PBT was photo-polymerized for 0 (—), 1 (·····), 10 (---) and 30 (-·-·-·-) min. The IPCE obtained for the TiO₂ alone is also shown (- - -). The inset shows IPCE changes of the PBT-BTC/TiO₂ solar cell as a function of charges collected during the photo-induced polymerization, monitored at 480 (circle) and 550 (triangle) nm.