

Layer-by-Layer Assembled TiO₂ Nanoparticle/PEDOT-PSS Composite Films for Switching of Electric Conductivity in Response to Ultraviolet and Visible Light

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The sequential layer-by-layer adsorption of oppositely charged polyelectrolytes is one of the most promising ways of fabricating multilayer thin films with precisely controlled composition, thickness, and architecture on a nanometer scale.¹ The components for the multilayer assemblies using this method range from polyelectrolytes to inorganic nanoscale materials.^{2–7} The integration of organic and inorganic materials with different functions is also interesting from both fundamental and practical points of view. The present paper describes the layer-by-layer assembly of two different components, an n-type inorganic semiconductor (TiO₂ nanoparticles) and a p-type semiconducting polymer (PEDOT-PSS), and how their electric conductivity responds to the excitation light of each component.

Since the Honda–Fujishima effect on the photolysis of water at TiO₂ semiconductor electrodes was reported in 1972,⁸ semiconductor photocatalysts have been extensively investigated. Electronic excitation of TiO₂ or related materials produces photoexcited electrons and holes, causing reduction and oxidation reactions, respectively. These materials have drawn much attention because of their potential applications, such as environmental cleaning and solar-to-chemical energy conversion.⁹

Since the discovery of polymeric organic conductors in 1977,¹⁰ on the other hand, extensive efforts have been made

for their synthesis and characterization. Among them, poly(3,4-ethylenedioxythiophene) doped by poly(4-styrenesulfonate) (PEDOT-PSS) is one of the most promising conducting polymers and has been intensively studied because of its good film-forming properties, high conductivity, high visible light transmissivity, and excellent stability.¹¹ The fields of application have extended to include optoelectronic devices such as light-emitting diodes, solar cells, and thin-film transistors, as well as other devices, including sensors, smart windows, lithium batteries, and capacitors.¹²

The tuning of electric conductivity is one of the important keys in the field of organic-based optoelectronics.¹³ Although the chemical and electrochemical tunings of the electric conductivity of PEDOT have been reported by several groups,¹⁴ there have been no reports on conductivity tuning by light irradiation at different wavelengths. In the present paper, we show the layer-by-layer assembly of PEDOT-PSS/TiO₂ nanoparticle composite films and how their electric conductivity can be tuned by the excitation light of each component.

The charge of TiO₂ is dependent on the pH of the suspension because of its amphoteric nature.¹⁵ Because TiO₂ nanoparticles are positively charged at pH 1.5, negatively charged PEDOT-PSS can be employed as a counterpart for layer-by-layer assembly. The film assembly on a quartz substrate could be followed by UV–vis absorption spectra. Figure 1 shows the UV–vis absorption spectra as a function of the number of TiO₂ nanoparticle/PEDOT-PSS bilayers deposited on a quartz glass substrate. The absorption at $\lambda < 350$ nm is characteristic of TiO₂ nanoparticles. Its band-gap

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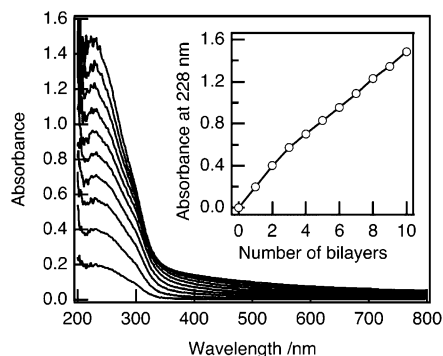


Figure 1. UV-vis absorption spectra for multilayer films of $(\text{TiO}_2/\text{PEDOT-PSS})_n$ on a quartz glass substrate. Inset shows the dependence of the observed absorbance at 228 nm on the number of deposition cycles.

energy, which seems wider than that of bulk anatase, may not be attributable to the size-quantization effect of nanoparticles.¹⁶ The concentration of embedded TiO_2 nanoparticles may be too low to yield the absorption signal in this wavelength range. In practice, the original colloidal solution showed the spectrum comparable to that for bulk anatase. The progressive enhancement in absorbance with an increasing number of layer pairs supports the successful multilayer buildup, as shown in the inset of Figure 1. The absorbance enhancement rate is very similar to our previous results on the multilayer assembly of TiO_2 nanoparticles/PSS films.^{6c} The optical absorption of PEDOT-PSS lies in the visible light region but is very weak and invisible in this scale.

We measured the electric conductivity of the films fabricated on an interdigitated Pt electrode printed on a quartz glass substrate. The width of the electrode and the gaps between electrodes are 10 and 5 μm , respectively. Because the height of the electrode is 120 nm, the layer-by-layer assembled films may be formed inside the space surrounded by the quartz glass substrate and two electrodes. A constant current was flowed under a biased voltage of 1 mV. UV light ($\lambda = 300\text{--}400$ nm) irradiation for 30 s decreased the current to approximately one-tenth of its original value (Figure 2a). The current gradually reverted to its original value when the UV light was switched off, although it took much longer (~ 1000 s) than the time taken for the conductivity to decrease by UV light irradiation. Because the action spectrum, which is plotted between the decrease rate of the current and the incident wavelength of monochromatized light, was closely overlapped with the absorption spectral profile of TiO_2 nanoparticles, the excitation of TiO_2 nanoparticle plays an important role in the conductivity decrease. The alternate procedure of UV light irradiation (30 s) and subsequent storage in the dark (30 min) showed a quasireversible switching of the conductivity, although the maximum current gradually decreased (Figure 2b).

We also examined the effect of visible light ($\lambda = 400\text{--}700$ nm) irradiation on the conductivity change. Alternate irradiation of UV (30 s) and visible (60 s) light decreased and increased the current, respectively (Figure 3). The low-conductivity films induced by UV light irradiation returned

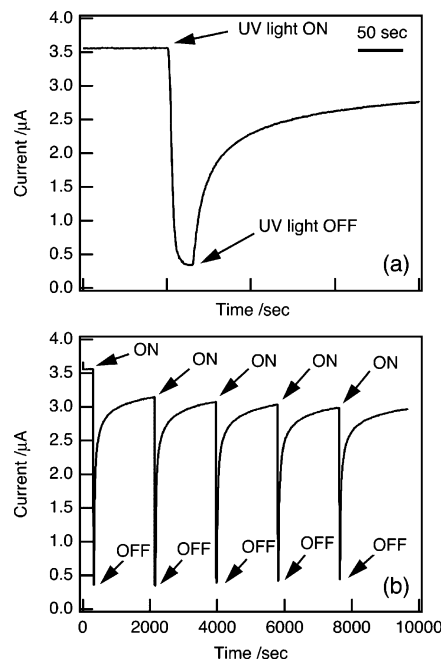


Figure 2. (a) Change in current under UV light irradiation and subsequent storage in the dark. The current was measured at a constant voltage of 1.0 mV. The light intensity was 6.7 mW cm^{-2} . (b) Reversible change in current upon UV light irradiation and dark storage.

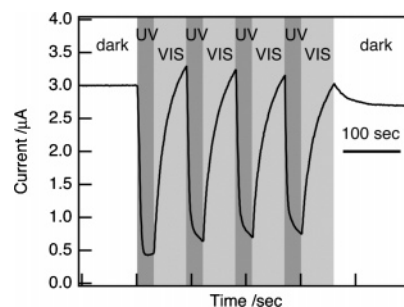


Figure 3. Reversible change in current under alternate irradiation of UV and visible light. The current was measured at a constant voltage of 1.0 mV. The intensities were 6.7 and 130 mW cm^{-2} for UV and visible light, respectively.

to their original conductivity upon exposure to visible light for 60 s, which is much faster than the time taken for conductivity to increase for those stored in the dark, as shown in Figure 2b. Thus the conductivity of the films could be controlled by light irradiation with different wavelengths.

Next, the mechanism of the conductivity change under UV and visible light irradiation and in the dark is discussed. Because the previously reported films of TiO_2 nanoparticle/PSS^{6c} did not show such a conductivity change under UV and visible light irradiation, the conductivity of the present composite films is derived from the carriers of PEDOT, which are holes, because PEDOT is a p-type semiconductor. The excitation of a TiO_2 nanoparticle by UV light irradiation produces excited holes and electrons, causing oxidation and reduction reactions, respectively. The phenomena observed suggest that the electrons are injected into the valence band of PEDOT-PSS, which decreases the carrier number of the PEDOT-PSS and, consequently, lowers the conductivity of the composite films. On the other hand, the holes may oxidize the adsorbed water or PEDOT-PSS. In the dark, the injected electrons are possibly trapped by electron acceptors such as

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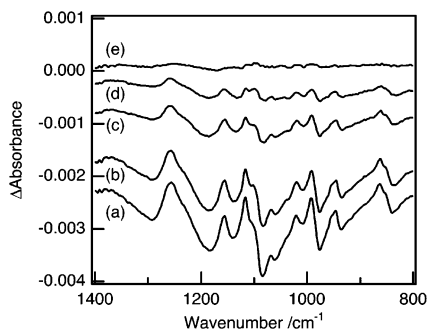


Figure 4. FT-IR difference spectra for $(\text{TiO}_2/\text{PEDOT-PSS})_{10}$ on a Si wafer chip (a) under in situ UV light irradiation, and subsequent storage in the dark for (b) 0, (c) 5, (d) 10, and (e) 20 min. The baseline was obtained with the films before UV light irradiation. The acquisition of spectra was started after preirradiation of UV light for 30 s. The values on the vertical axis are the absolute ones without offsets.¹⁹

oxygen in the air, and the carrier density of the PEDOT-PSS increases, which results in the enhancement of conductivity. Because the band-gap energy of the p-type semiconducting polymer, PEDOT-PSS, is 1.6 eV,¹⁷ the PEDOT-PSS can be excited by visible light. The visible light irradiation excites the electrons in the valence band of PEDOT-PSS into the conduction band, producing the holes as a carrier. The excited electrons may be transferred to electron acceptors, e.g., oxygen molecules in the air.

The FT-IR study provides insight into the aforementioned mechanism of conductivity change under UV light irradiation and in the dark. Difference FT-IR spectra of the layer-by-layer assembled TiO_2 nanoparticle/PEDOT-PSS films on a Si wafer chip were acquired using the data before UV light irradiation as a baseline. As shown in Figure 4a, absorption peaks at 800–1400 cm^{-1} were found to decrease under in situ UV light irradiation. The IR bands at 1303, 1187, 1085, 978, and 834 cm^{-1} are derived from the PEDOT.¹⁸ The IR bands at 1142 and 1034 cm^{-1} are assigned to SO_3^- of the PSS.^{6b} The peak at 1008 cm^{-1} is attributable to a bending mode of C–H on aromatic rings of the PSS.^{6b} Spectra b–e were acquired at 0, 5, 10, and 20 min, respectively, after the UV light was switched off.¹⁹ The decreased absorbance gradually increased in the dark and recovered to its original state within 20 min. The behavior with this time scale is in good accord with that of the conductivity change under UV light irradiation and subsequent storage in the dark, as shown in Figure 2b. It is reported that the electrochemical oxidation of PEDOT enhances the absorbance in the IR region.¹⁸ In the present case, therefore, the decrease in absorbance under UV light irradiation suggests the reduction of PEDOT by the electron injection via the excitation of TiO_2 . The increase in absorbance in the dark corresponds to the oxidation of reduced PEDOT.

The slight decrease in the maximum current (Figure 2b) is probably due to photocatalytic decomposition of PEDOT-PSS by the photogenerated holes of TiO_2 nanoparticles. This

change, however, is very small compared to the conductivity decrease under UV light irradiation; most of the PEDOT-PSS is not decomposed in this short period of UV light irradiation. Because a number of stabilized states can exist in the oxidized PEDOT because of its π -conjugation in a long range, the PEDOT may be slightly oxidized by the photogenerated holes of TiO_2 . Accordingly, the holes preferentially oxidize water molecules and/or hydrocarbons adsorbed on the films.

Recently, Hiroi and co-workers reported the tuning of the conductivity of PEDOT-PSS films deposited on a Nb-doped strontium titanate perovskite.²⁰ The excitation of SrTiO_3 via UV light irradiation or the excitation of PEDOT via visible light irradiation enhances the conductivity of PEDOT-PSS films. The effect of UV light irradiation on the conductivity change is contrary to the present work. The energy levels of the conduction and the valence band for TiO_2 and SrTiO_3 are similar to each other. It is possible that the photoexcited electrons and holes are injected into the conduction and valence bands of PEDOT unless the bands of both semiconductors are bending, because the conduction and valence band edges of PEDOT are lower and higher than those of TiO_2 or SrTiO_3 , respectively (see Supporting Information, Scheme S1). In the case of $\text{SrTiO}_3/\text{PEDOT-PSS}$ films, it is considered that the increase in conductivity is derived from the hole injection from the valence band of SrTiO_3 into PEDOT, which results in the increase in carrier number. Because SrTiO_3 and PEDOT-PSS in this case have dimensions in the bulk regime, the excited electrons in the conduction band of SrTiO_3 cannot be injected into PEDOT, because of the Schottky barrier formed at the interface between SrTiO_3 and PEDOT. In contrast, TiO_2 nanoparticles and PEDOT-PSS in the present case are several nanometers in size, and thus, the band bending should be small. Although both of the photoexcited carriers generated in TiO_2 are able to be injected into PEDOT, the electrons may be preferably captured by PEDOT in the present case.

In conclusion, we have achieved the photoinduced tuning of electric conductivity of PEDOT-PSS/ TiO_2 nanoparticle composite films via the layer-by-layer assembly fabrication of these components in a nanometer scale. We have shown a new method for the conductivity tuning of PEDOT other than the chemical and electrochemical methods.¹⁴ FT-IR spectra of the films suggested that the reduction of PEDOT by photogenerated electrons of TiO_2 induces the conductivity decrease under UV irradiation and the reoxidation of PEDOT recovers the conductivity in the dark. Visible light irradiation promotes the oxidation of PEDOT. These materials should contribute to the development of organic-based optoelectronics.

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Supporting Information Available: Experimental details and possible energy diagram for TiO_2 and PEDOT (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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