Effect of Phosphonate-Functionalized Surface Modification on Nanocrystalline TiO_2 Film Electrode

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Since the pioneering works of Grätzel's group for dye-sensitized solar cells (DSSC),[1] nanocrystalline semiconductor film electrodes have been intensively investigated.[2] In DSSC, the interfacial charge transfer between the surface of the film and the solution electrolyte is very important. Especially, the effect of surface complexation on the rate of interfacial electron transfer reaction is known to be crucial. In the Grätzel's DSSC, the light-absorbing ruthenium complexes were adsorbed on the surface of TiO_2 through the carboxylate chelation. The strong electronic coupling between π orbital of the ligand and 3d orbital of the conduction band of TiO_2 rendered the very rapid electron transfer from the metal-to-ligand charge transfer state to the conduction band feasible and the rate of recombination between the conduction band and Ru(III) was retarded by the high driving force in the Marcus inverted region and the spacer ligand. In the result, about 80% incident photon-to-current conversion efficiency in a certain wavelength region was achieved in those cells.[1e]

Recent studies showed that a phosphonate group instead of a carboxylate group was also strongly adsorbed on the surface of nanocrystalline TiO_2 film and an efficient electron transfer between them occurred.[3] Using the metal bisphosphonate multiplayer technique,[4] we have also demonstrated that the redox couple multiplayers of bisphosphonate derivatives were constructed on the surface of a nanocrystalline TiO_2 film.[5] Whereas a carboxylate compound was sensitive to pH of an electrolyte solution and was desorbed from the surface of TiO_2 at the pH higher than 4, a phosphonate compound was less sensitive to the solution pH and remains on the surface until pH 9.[3c] To elucidate the surface sites and the surface complexation effect of nanocrystalline TiO_2 (NT) film electrode, here we briefly report the effect of surface chelation of two different types of phosphonate-functionalized compounds on the interfacial electron transfer of NT film electrode for water oxidation: one is electron-donating and the other is electron-accepting.

VP and DBPA were both adsorbed directly on the surface of NT electrode by a simple immersion in aqueous and ethanolic solutions, respectively. After the immersion for an hour, the electrodes were thoroughly washed with copious amounts of water and ethanol. The adsorption of DBPA on the surface of TiO_2 film could be confirmed from CH-stretching mode (at 2919 and 2851 cm^{-1}) in the IR spectra of DBPA-treated TiO_2 that is not shown here, although the amount of the adsorbed DBPA could not be estimated quantitatively. The cyclic voltammograms of NT electrodes prepared here are shown in Figure 1. For the bare NT electrode, the cathodic current appeared at potentials negative than flat band potential (E_{fb}) and increased as the applied potential increased. Since there was no appreciable faraday component except solvent water, the current can be assigned to the capacitive current that can be due to the complex capacitance such as Helmholtz layer, double layer and space charge layer capacitance, if space charge layer exists, etc.[6]

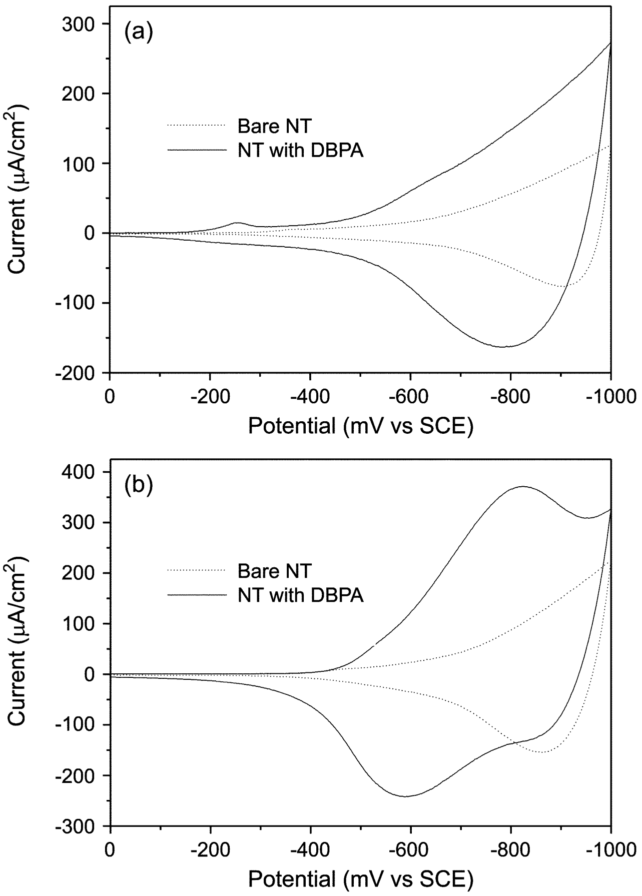

Figure 1. Cyclic voltamograms of (a) DBPA-adsorbed and (b) VP-adsorbed NT electrode compared with that of bare NT electrode in 0.1 M KCl solution. (scan rate: 20 mV/s)

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The DBPA-adsorbed NT electrode also shows that there was no appreciable faraday current except very small reductive peak at -0.25 V and only the background capacitive current increased almost as twice as that of the bare electrode. The origin of the small reductive peak might be due to the oxygen that was trapped in the pores of the film and could not be removed by nitrogen purging through the electrolyte solution. The increase of the capacitive current could be due to the increase of Helmholtz layer capacitance by the adsorption of DBPA on the TiO_2 surface.

For the VP-adsorbed electrode, there appeared the quasi-reversible redox peaks in the cyclic voltammogram as shown in Figure 1(b). When the potential was swept more negative than -0.5 V *vs* SCE, the color of the electrode changed purple from white, which is a characteristic color of the reduced viologen. The visible absorption spectrum of the VP-modified electrode at -0.8V *vs* SCE was shown in the previous study.[5] This electrochromic effect was very reversible when the potential was cycled. The estimated formal potential of VP on the TiO_2 film was about -0.6 V *vs* SCE and consistent with that of VP in solution. The redox peaks in the voltammogram slightly decreased after 10 cycles of the potential sweep and therefore, the reversibility was confirmed. From the integration of the reduction peak after background correction, we have estimated the amount of VP on the electrode as 3.9×10^{-8} moles. The baseline capacitive current also increased as in the DBPA-adsorbed electrode. The heterogeneous electron transfer from the substrate ITO of NT electrode to VP occurs ideally via the conduction band of TiO_2 film. VP will be reduced when the electrode potential is more negative than the flat band potential of TiO_2 film. Since E_{fb} of the NT electrode was estimated as -0.44 V *vs* SCE at pH 6 in our other report,[6] the assumed electron pathway is plausible. Fitzmaurice *et al.* similarly showed that a (salicylic acid)-functionalized viologen compound was adsorbed on a transparent polycrystalline TiO_2 film and the heterogeneous electron transfer from the conduction band of TiO_2 to the compound occurred.[7]

When the NT electrode was illuminated by UV light, the photocurrent was observed from the water oxidation by photogenerated valence band holes.[6] Figure 2 shows photocurrent-potential characteristics of the NT electrodes that was modified and unmodified with VP and DBPA. The observed photocurrents at the unmodified electrodes were due to the water oxidation since there was no oxidizable species at the potential of photogenerated hole except solvent water. The photocurrent onset potential followed roughly the flat band potential of the NT electrode as mentioned above. The dramatic effects were observed when the NT electrode was modified with DBPA and VP compounds as shown in Figure 2. The electrode modified with DBPA showed that saturation photocurrent increased as about three times as in bare NT electrode, whereas the photocurrent for the electrode with VP decreased to about one fifth of that for bare NT electrode. In order to confirm that VP did not absorb the exciting light, the irradiation light from Xe lamp was cut off by a glass filter with water and the wavelengths longer than 330 nm where VP did not absorb but the TiO_2 film absorbed somewhat were used.[8] This opposite effect of VP and DBPA on photocurrent may be explained by the existence of intraband surface states and the electron trapping into the surface states. In a semiconductor electrode, the photocurrent efficiency is mainly dominated by charge recombination of electron-hole pairs that are generated by band-gap excitation. The surface charge recombination through the trapping of electrons into surface states is especially an important factor governing the efficiency.[9] Redmond *et al*. showed the existence of intraband surface states below the conduction band edge that was associated with incompletely coordinated Ti atoms of nanocrystalline TiO_2 film from a transient absorption spectroscopy.[10] They demonstrated that the surface modification of TiO_2 with pyrocatechol molecules that had two hydroxy groups prevented the electron trapping in these surface states and promoted electrons into the conduction band above the surface states. For the DBPA-modified electrode, the enhancement of photocurrent could be ascribed to preventing the trapping of photo-excited electrons into the surface states by DBPA molecules that is electron-donating and occupied the surface states. For the VP-modified electrode, the reduced photocurrent means that VP molecule played the opposite

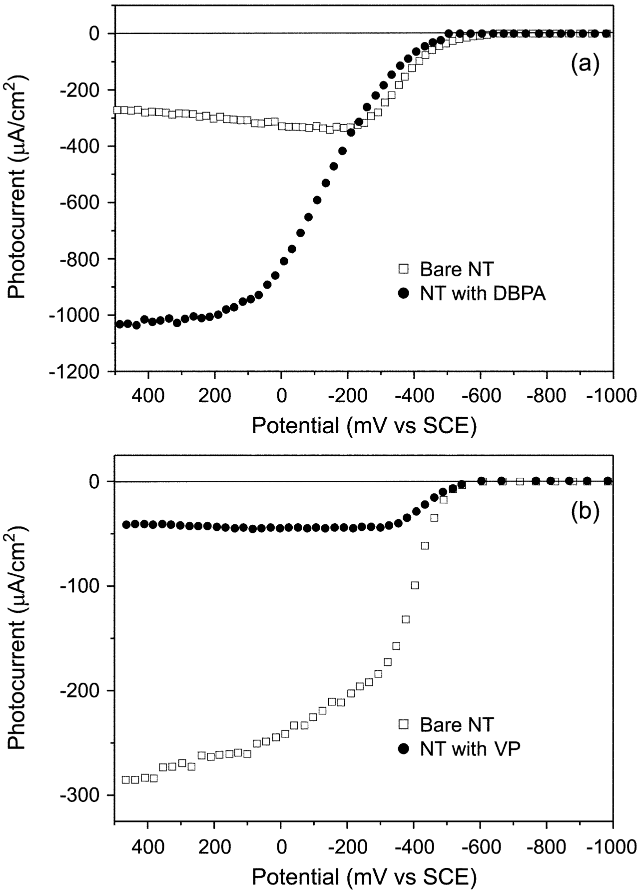

Figure 2. Photocurrent-potential characteristics of (a) DBPA-adsorbed and (b) VP-adsorbed NT electrode compared with that of bare NT electrode in 0.1 M KCl solution (light intensity: 166 mW/cm^2, wavelength >330 nm)

role compared with DBPA molecule. Since VP is an efficient electron acceptor, the photo-excited electrons can be trapped into VP molecules through surface states if the states are higher than the formal potential of VP and can be directly transferred to the molecule. The reduction of a viologen molecule by photo-excited colloidal TiO_2 particles was well known whether a viologen was adsorbed on the surface of TiO_2 or in solution.[11] In a positively biased electrode, the direct injection of photo-excited electrons into VP will compete with the generation of photocurrent. In that case, the photocurrent will depend on the bias potential. However, such dependence was not observed as shown in Figure 2(b). Therefore, the decreased photocurrent could be due to the acceleration of electron trapping into surface states by the surface-anchored VP. The density of surface states in a NT electrode that consisted of the smaller TiO_2 particles than that of our NT electrode was determined as $3 \times 10^{12}/\text{cm}^2$ from spectroelectrochemical method.[12] Considering the reported surface area of the NT film from BET measurement as $40.2\ \text{m}^2/\text{g}$,[13] the surface concentration of VP on the NT electrode could be estimated about 1.4×10^{-10} moles/cm^2 from the amounts of the adsorbed VP and TiO_2 film. Therefore, the VP molecules on the NT electrode are enough to cover the surface states on the electrode.

In summary, we have demonstrated the very efficient surface-anchoring of the phosphonate-functionalized molecules, which controlled oppositely the photocurrent efficiency of water oxidation in the nanocrystalline TiO_2 film electrode, depending on the anchored molecules. This implies that the chelation of the phosphonate-functionalized compounds on the surface defect sites can play a key role on controlling the trapping of photogenerated electrons in NT film electrode. The more detailed investigation of this surface modification effect is in progress.

Experimetal Section

The NT electrode was prepared with commercially available Degussa P25 TiO_2. The details are described elsewhere.[6] The geometrical area of the electrode that was exposed to the electrolyte solution was 1.5 cm^2. The thickness of the TiO_2 film was estimated to be about 5 μm from scanning electron microscopic image. N,N'-Bis(ethylphosphonic acid)-bipyridinium (VP) chloride was synthesized from the substitution reaction of 4,4'-bipyridine and diethyl 2-bromoethyl phosphonate and the subsequent hydrolysis of the resulting phosphonate.[14] 1,10-decanediylbisphosphonic acid (DBPA) was synthesized by Michaelis-Arbuzov reaction of 1,10-dibromodecane and triethylphosphite as a literature method.[15] The cyclic voltammograms were measured in a standard three-electrode cell with a PAR 263A potentiostat. Pt counter, SCE reference electrode and 0.1 M KCl electrolyte solution were used in an aqueous solution for all measurements. The electrolyte solutions were purged with N_2 or Ar gas for 20 min before measurement. Photocurrent measurements were performed in a three-electrode cell with a flat quartz window, using the potentiostat and Xe arc lamp (150W, Oriel) with water and glass filter. The photocurrent was discriminated by an optical chopper (Scitec) at the frequency of 15 Hz.

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