PHOTOINDUCED ELECTRON ACCUMULATION OF TITANIUM DIOXIDE NANOPARTICLES MODIFIED ELECTRODES

HIROKAZU MIYOSHI

Radioisotope Research Center, The University of Tokushima, 3-18-15 Kuromoto-cho, Tokushima 770-8503, Japan
hmiyoshi@ri.tokushima-u.ac.jp

KENSHO SAKAMOTO, MASARU KURASHINA and EIJI KANEZAKI*

Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, 2-1 Minami Josanjima-cho, Tokushima 770-8506, Japan
**kanezaki@chem.tokushima-u.ac.jp*

Titanium dioxide (TiO_2) nanoparticles (Nps) were prepared by the hydrolysis of titanium tetraisopropoxide (TTIP) in 2-propanol with different water contents (0.5 vol% to 7.2 vol%) at 45 °C. The diameter of the Nps was estimated to be 1.5 ± 0.5 nm (L- TiO_2) and 3.0 ± 0.6 nm (S- TiO_2) from the onset wavelength in the absorption spectra and by transmission electron microscopy (TEM). A modified Pt electrode with a three-layered sandwich structure was prepared; the outermost and innermost layers were composed of S- TiO_2 and L- TiO_2 , respectively, and the middle layer contained 1, 1'-dimethyl-4,4'-bipyridyl (MV^{2+})/Nafion®. Irradiation by a 500 W superhigh-pressure mercury lamp produced electrons in the conduction band of TiO_2 . An anodic current was observed after turning off the light. The mechanism by which anodic current is generated after turning off the radiation involves the reduction of MV^{2+} to $\text{MV}^{+\cdot}$ by photogenerated electrons on the Nps and the diffusion of $\text{MV}^{+\cdot}$ in the middle layer. After turning off the irradiation, $\text{MV}^{+\cdot}$ transferred an electron to the Pt electrode via holes in the innermost layer or the conduction band of S- TiO_2 coincidentally localized on the Pt electrode, resulting in the generation of the anodic current. The generation of $\text{MV}^{+\cdot}$ was confirmed by the absorption spectra of $\text{MV}^{+\cdot}$. As a sacrificial reagent, 2-propanol (0.1 M) was used.

Keywords: TiO_2 nanoparticle; electron accumulation; methylviologen

1. Introduction

Titanium dioxide (TiO_2) nanoparticles (Nps) are a well-known photocatalyst¹ and have been used in dye-sensitized solar cells². Generally, TiO_2 Nps of various sizes can be prepared by a sol-gel method while controlling the titanium tetraisopropoxide (TTIP) content, reaction time, and temperature³. The size of TiO_2 Nps is related to their band gap energy⁴. A simple preparation of TiO_2 Nps with a capsule structure has also been reported⁵. Miyoshi et al. reported that photogenerated electrons that had accumulated on encapsulated 1,1'-dimethyl-4,4'-bipyridyl (MV^{2+}) molecules in TiO_2 nanocapsules were detected as $\text{MV}^{+\cdot}$ radicals and that their electrons were released as an anodic current after turning off the light used for photogeneration⁶. However, in the preparation of the nanocapsules, Au Nps were used as a core. However, Au Nps are expensive and poisonous NaCN was used to dissolve the Au Nps to form the nanocapsules. For this

reason, a layered structure, which was composed of a Nafion® layer containing MV^{2+} and layers of TiO_2 Nps with different sizes, was used in this study instead of the capsule structure. The deposition of MV^{2+} in Nafion® films on SnO_2 electrodes and their electrochemical properties have also been reported⁷. The advantages of the layered structure are twofold. One is the control of the diffusion distance for MV^{2+} , which depends on the thickness of the Nafion® layer, and the other is the ability to control the potentials at the conduction band edges by changing the size of the TiO_2 Nps in contact with the Nafion® layer. These advantages will make it possible to prepare a simple electron capacitor to accumulate photogenerated electrons and to release them as an anodic current in the dark. Such a system will increase the likelihood of TiO_2 Nps in a dye-sensitized solar cell acting as a photocapacitor. Recently, Wang et al. have reported a water-assisted synthesis method for anatase TiO_2 nanocrystals⁸.

In this study, TiO_2 Nps of two different sizes were simply prepared by changing the water content during synthesis, and their sizes were estimated from their absorption spectra and by transmission electron microscopy (TEM). Electrodes modified by the TiO_2 Nps indicated that a photoanodic current was generated and that electrons accumulated in MV^{2+} simultaneously. The accumulation of electrons on the TiO_2 Nps- MV^{2+} /Nafion® modified electrode was investigated by observing the anodic current after turning off the light used for photogeneration. The mechanisms of the electron accumulation and release are discussed.

2. Experimental

2.1. Chemicals

TTIP and Nafion® 117 (5 wt% Nafion in alcoholic solution) were purchased from Aldrich Co., Ltd. 2-propanol, MV^{2+} , potassium chloride, and sodium sulfate were purchased from Wako Pure Chemicals Co., Ltd., and were used without further purification.

2.2. Preparation of TiO_2 Nps

TTIP (20 μ l) was mixed in 10 ml of 2-propanol, and the solution was heated at 45 °C using a hot stirrer, after which 49 μ l, 74 μ l, 148 μ l, 360 μ l, or 720 μ l of distilled water was poured into the solution. Then, the solution was stirred for 30 min using a stirrer. To remove unreacted reagents, ultrafiltration equipment (Millipore Stirred Ultrafiltration Cell) with a membrane filter (Millipore YM-100) was used. Next, the solution was washed with 2-propanol seven times to obtain 5 ml of TiO_2 NPs dispersed in 2-propanol solution. L- TiO_2 and S- TiO_2 refer to the Nps obtained with the addition of 74 μ l and 720 μ l distilled water, respectively. Their absorption spectra were measured using a UV-vis spectrometer (Shimadzu, UV-1700). TEM (Hitachi, H-800) observation was performed for L- TiO_2 and S- TiO_2 after their solutions were added dropwise onto a copper grid and then dried.

2.3. Photoelectrochemical experiments

A typical TiO_2 Nps- MV^{2+} /Nafion® modified electrode was prepared as follows. Three

hundred microliters of L- TiO_2 was coated on a 1.5-cm-diameter Pt plate and then dried. Then, 200 μl of MV^{2+} (0.138 M) / 0.5 vol% Nafion® alcohol solution, which had been diluted tenfold by water (1:1), was added dropwise and dried. After that, 300 μl of S- TiO_2 was added and dried. Finally, 200 μl of 0.5 vol% Nafion® alcohol solution, which had been diluted tenfold by water, was coated on the top. A TiO_2 Nps-Nafion® modified electrode that contained no MV^{2+} was also prepared. Photoelectrochemical experiments were performed using a 500 W superhigh-pressure mercury lamp (Ushio, UI-501C) and a potentiostat (ALS/DY2323 Bi-Potentiostat). The irradiated area on the electrode was 0.63 cm^2 and a water filter was used to remove wavelengths of less than 300 nm.

FE-SEM (Hitachi, S-4700) observation of a cross section of the TiO_2 Nps- MV^{2+} /Nafion® modified electrode was performed by preparing a TiO_2 Nps- MV^{2+} /Nafion® modified rectangular glass plate (1 cm^2) by the same procedure as above.

3. Results and Discussion

Figure 1 shows absorption spectra of TiO_2 Nps prepared by the addition of different water contents (49 μl , 74 μl , 148 μl , 360 μl , and 720 μl). The onset wavelength underwent a redshift with increasing water content.

Fig. 1. Absorption spectra of TiO_2 Nps dispersed in 2-propanol. Water contents: 49 μl (—), 74 μl (---), 148 μl (— · —), 360 μl (— · · —), and 720 μl (— · · · —).

The onset wavelength of each TiO_2 Np is related to the band gap energy^{1,4}, and the particle size can be estimated from its relationship with the band gap energy⁹.

Table 1. Onset wavelength, band gap energy, and particle size for different water contents.

Water content	Onset wavelength	Band gap energy	Particle size
/μl	/nm	/eV	/nm
49	303	4.09	0.94
74	304	4.08	0.94
148	349	3.55	1.4
360	395	3.14	3.4
720	380	3.26	2.2

Table 1 shows the onset wavelength, band gap energy, and particle size for different water contents. The results in Table 1 indicate that the particle size and band gap depended on the water content during the preparation. The band gap energy increased

and the particle size decreased with decreasing water content except for the case of 720 μl of water. L-TiO₂, with 74 μl of water, and S-TiO₂, with 720 μl of water, were used in the photoelectrochemical experiments. The L-TiO₂ Nps had a size of 1.5 ± 0.5 nm and the potential at the conduction band edge was estimated to be -0.643 V vs SCE⁹ at pH 6.3. The S-TiO₂ Nps had a size of 3.0 ± 0.6 nm and the potential at the conduction band edge was estimated to be -0.706 V vs SCE⁹ at pH 6.3. The redox potential (-0.64 V vs SCE) of $\text{MV}^{2+}/\text{MV}^{+}$ was equal to or lower than the potentials of the conduction band edges of S-TiO₂ and L-TiO₂, respectively. Therefore, electron accumulation will occur when using MV^{2+} in a Nafion® layer as a capacitor.

Fig. 2. FE-SEM cross-section image of S-TiO₂-MV²⁺/Nafion®-L-TiO₂

Then an S-TiO₂-MV²⁺/Nafion®-L-TiO₂ modified electrode was fabricated by coating a Pt plate with L-TiO₂, then with MV²⁺/Nafion®, and finally with S-TiO₂, as shown in Figure 2. Both L-TiO₂ and S-TiO₂ donate photogenerated electrons to MV²⁺. L-TiO₂ was used to prevent the direct flow of electrons from MV²⁺ to the Pt electrode owing to the higher potential at the conduction band edge. Part of the S-TiO₂ may be localized on the Pt plate electrode. This S-TiO₂ on the Pt plate electrode accepted electrons from MV²⁺, which flowed to the Pt plate electrode. This modified electrode demonstrates a model of photocharging, that is, upon photocharge separation on the TiO₂ Nps, electrons are stored in MV²⁺ and MV⁺, then, after the light used for photocharging is turned off, the stored electrons are released. In this case, some of the S-TiO₂ attached to the Pt electrode directly, and during light irradiation electrons localized on the particles, giving them a negative charge and preventing electron transfer from MV²⁺.

Fig. 3. Plot of accumulated charge for TiO₂ Nps-MV²⁺/Nafion® (●) and TiO₂ NPs-Nafion® (▲) modified electrode vs irradiation time.

The validity of this model was investigated using the modified electrode by measuring the photocharge and discharge.

Figure 3 shows that the accumulated charge of the $\text{S-TiO}_2\text{-MV}^{2+}/\text{Nafion}^\circ\text{-L-TiO}_2$ modified electrode depends on the irradiation time. That is, the photogenerated electrons that were transferred to MV^{2+} and MV^{+} in the middle layer accumulated. Then, after the light was turned off, the electrons of MV^{+} transferred via S-TiO_2 to the Pt electrode. This led to the accumulation of charge due to the formation of an anodic current. The observed accumulated charge for $\text{S-TiO}_2\text{-Nafion}^\circ\text{-L-TiO}_2$ increased from 58 μC after 150 s irradiation to 95 μC after 600 s irradiation. However, the accumulated charge did not increase linearly, because dissolved O_2 could react easily with the MV^{+} . The observed long retention time for the anode current after turning off the light may be due to the diffusion of MV^{+} in the Nafion $^\circ$ layer. That is, MV^{2+} diffuses in the layer, and when it becomes attached on the photoirradiated L-TiO_2 , it accepts an electron and diffuses. Then, MV^{+} becomes attached to S-TiO_2 and the electron is transferred to S-TiO_2 and the Pt electrode. However, in the presence of O_2 , the stored electron in MV^{+} will transfer to O_2 and disappear. The absorption spectra of MV^{+} after light irradiation are shown in Figure 4, which indicates that MV^{+} was produced in this $\text{S-TiO}_2\text{-MV}^{2+}/\text{Nafion}^\circ\text{-L-TiO}_2$ system. The lifetime of MV^{+} corresponding to a 10% decrease in absorbance was 54 s, compared with 29.4 min for TiO_2 nanocapsules⁶, indicating that the Nafion $^\circ$ layer was not protected from O_2 in the solution and that O_2 rapidly reacted with MV^{+} .

Fig. 4. Plot of absorbance of MV^{2+} at 396 nm for TiO_2 Nps- $\text{MV}^{2+}/\text{Nafion}^\circ$ coated on glass plate in an aqueous solution under air. Light irradiation: 500 W superhigh-pressure mercury lamp. Inset: Absorption spectra of MV^{2+} at 280 s (—), and 540 s (---).

Fig. 5. Plot of charges stored in MV^{2+} (white) and charges released from MV^{2+} (black) for TiO_2 Nps- $\text{MV}^{2+}/\text{Nafion}^\circ$ under N_2 purging and air. Inset: charge-time curves during light irradiation and after turning off the light for TiO_2 Nps- $\text{MV}^{2+}/\text{Nafion}^\circ$ (—) and TiO_2 Nps/ Nafion° (-----).

The evaluation of the accumulated charge in this system was also performed in the presence of a sacrificial reagent without O_2 . Figure 5 shows a plot of charges stored in MV^{2+} and charges released from MV^{+*} for TiO_2 Nps- MV^{2+} /Nafion® under N_2 purging and air. N_2 purging and the sacrificial reagent resulted in increases in charge accumulation and the observed retention time for S- TiO_2 - MV^{2+} -L- TiO_2 but not for S- TiO_2 -L- TiO_2 as shown in the inset figures, indicating that MV^{2+} acted as a capacitor for the electrons. That is, N_2 purging led to the prevention of quenching of MV^{+*} by O_2 . The efficiency of the use of the charges stored in MV^{2+} after turning off the light increased from 14% under air to 45% under N_2 purging, as shown in Figure 5, and the loss of charge may have been due to the decomposition of MV^{+*} . Finally, the observed retention time of the anodic current after turning off the light also increased from 470 ± 200 s under air to 1340 ± 420 s under N_2 purging as shown in the inset figures.

4. Conclusion

L- TiO_2 and S- TiO_2 were selected on the basis of their potential at the conduction band edge compared with the redox potential of MV^{2+} , where the L- TiO_2 Nps had a size of 1.5 ± 0.5 nm and the potential at the conduction band edge was estimated to be -0.643 V vs SCE at pH 6.3, whereas the S- TiO_2 Nps had a size of 3.0 ± 0.6 nm and the potential at the conduction band edge was estimated to be -0.706 V vs SCE at pH 6.3. Electrodes modified by TiO_2 Nps with an MV^{2+} /Nafion® interlayer were prepared. The photogenerated electrons transferred to MV^{2+} , and after turning off the light used for photogeneration an anodic current was observed. The accumulated charge depended on the irradiation time, the presence of O_2 , and the use of a sacrificial reagent. The efficiency of the use of the charges stored in MV^{2+} after turning off the light increased from 14% under air to 45% under N_2 purging. The observed retention time of the anodic current after turning off the light increased from 470 ± 200 s under air to 1340 ± 420 s under N_2 purging. The proposed system acts as a simple capacitor that accumulates photogenerated electrons on the modified electrode itself.

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