

Influence of Pt Nanocrystallinity on Electrochromism of TiO<sub>2</sub>

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The Pt nanocrystals as nanonetwork conductors improved electrochromic properties of TiO<sub>2</sub> such as increased optical modulation and fast response time, compared to pure TiO<sub>2</sub> as well as TiO<sub>2</sub> incorporated by amorphous Pt nanophases. It is likely that an enhancement of cathodic electrochromism in TiO<sub>2</sub>-Pt is due to an improved injection or extraction of electron/proton caused by Pt nanocrystals.

## Introduction

Electrochromism (EC), defined as the reversible change in optical properties under an applied electric field, has been intensively studied because of the potential of variable applications for electrochromic materials.<sup>1–3</sup> In an electrochromic process, electrons are injected or extracted under an applied voltage, and at the same time, ions are moved uniformly into or out of the EC material for the balance of charge neutrality. Accordingly, the mechanism of EC is described in terms of double injection or extraction of electrons and ions. In general, it has been well-known that many transition-metal oxide structures such as tungsten oxide (WO<sub>3</sub>) and nickel oxide (NiO) can be electrochemically switched to a redox state that has an intense electronic absorption band.<sup>4–6</sup> In particular, titanium dioxide (TiO<sub>2</sub>) has been very attractive because of its interesting properties such as excellent photoelectrochemical and photocatalytic activity. Although much research and work has been done on dye-sensitized solar cells and photo catalysts, there have been few reports on electrochromic applications.<sup>7–9</sup>

Recently, since metallic nanophases show size- and structure-dependent effects such as decreased melting point, optical absorbance spectra, and high surface-to-volume ratio, they are of particular interest for many applications including catalysis, photochemistry, and chemical–biological sensors.<sup>10,11</sup> However, the proton-transfer phenomena competitively occur in the nanocomposite electrode consisting of metal and oxide as modifier and electrochromic matrix, respectively, which can be mutually affected under electrochemical potentials. In particular, due to excellent unreactivity of Pt during sputtering at room temperature and proton reduction/oxidation in the potential range of the electrochromic phenomena, such nanocomposite electrodes consisting of noble metal and transition-metal oxide as an electrochromic matrix are attractive.

In this paper, electrochromic properties of TiO<sub>2</sub> modified by platinum nanophases are reported. The Pt-nanophase-incorporated TiO<sub>2</sub> thin-film electrodes (TiO<sub>2</sub>-Pt) were fabricated by means of sputtering deposition method and showed an improved electrochromic phenomenon compared to that of pure TiO<sub>2</sub> without Pt.

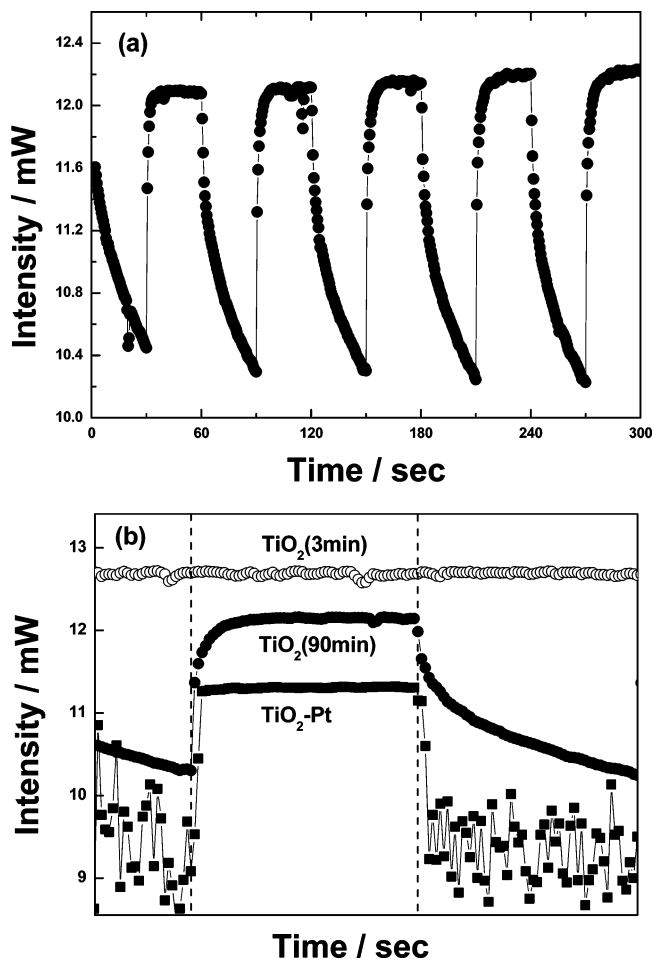
## Experimental Section

The TiO<sub>2</sub>-Pt and TiO<sub>2</sub> thin-film electrodes were prepared using a sputtering system. Indium tin oxide (ITO) coated glass was used as a transparent conducting substrate to observe electrochemical and electrochromic properties. The power of the TiO<sub>2</sub> and Pt sputtering guns was individually manipulated to fabricate the TiO<sub>2</sub>-Pt electrodes. To compare with the EC of TiO<sub>2</sub>-Pt, the TiO<sub>2</sub> thin-

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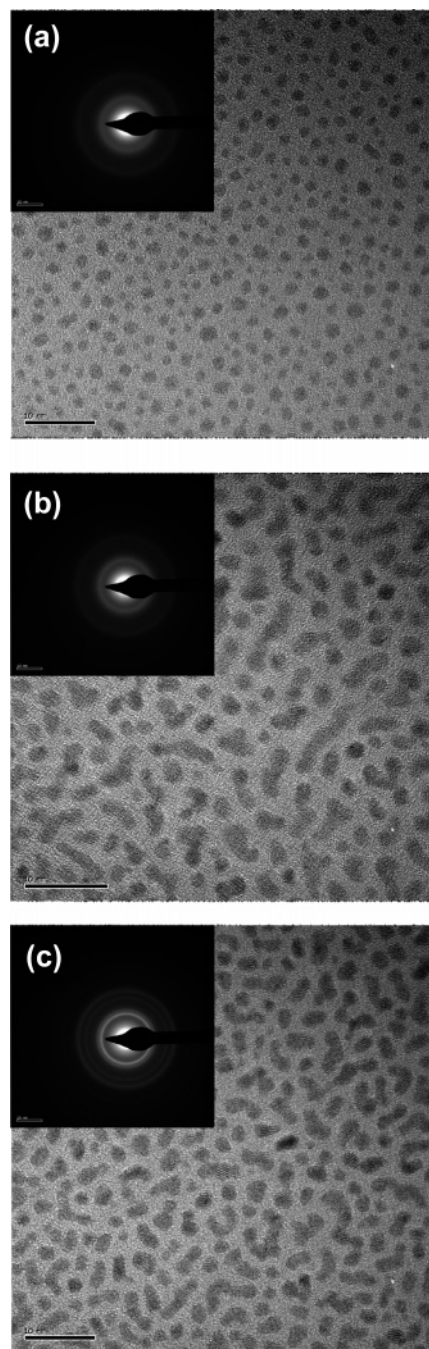
**Figure 1.** (a) Optical intensity modulation of pure  $\text{TiO}_2$  thin-film electrode as a function of electrochemical cell potential of  $-1.0$  to  $+1.5$  V. (b) Comparison of optical modulation of pure  $\text{TiO}_2$  thin-film electrodes sputtered for 3 and 90 min compared to  $\text{TiO}_2$  electrode incorporated by Pt nanocrystals.

film electrode was prepared by means of the  $\text{TiO}_2$  sputtering gun. In particular, the  $\text{TiO}_2$ -Pt electrodes having an amorphous, medium level, or crystal texture of Pt nanophases with almost the same level of Pt amount were fabricated as function of power of the  $\text{TiO}_2$  and Pt sputtering guns. Sputtering was carried out under an atmosphere of Ar gas at room temperature. Cu grids were also used as substrates for analysis by transmission electron microscopy (TEM). The TEM investigation was carried out using a Phillips CM20T/STEM electron microscope at an accelerating voltage of 200 kV.

The electrochemical measurements for the direct observation of EC in the electrodes were carried out in an electrochemical cell with optics consisting of a He-Ne laser as the light source and a power meter for detection of the optical signal modulation. During the electrochemical reaction with respect to the potential, the laser was transmitted through the thin-film electrode and the modulation of the signal intensity was continually detected. The electrochemical cell was comprised of Pt and Ag/AgCl as the counter and reference electrodes, respectively. The electrodes were used as the working electrodes in the electrochemical cell.

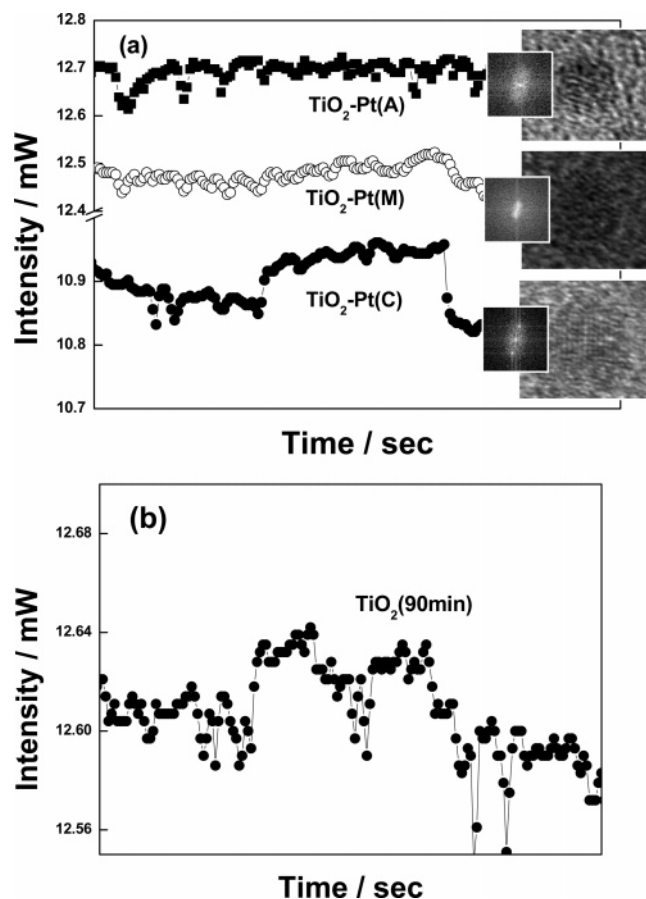
## Results and Discussion

Figure 1 shows a variation of optical transmittance in electrodes ( $\text{TiO}_2$  and  $\text{TiO}_2$ -Pt) with respect to an applied potential. As shown in Figure 1a, an optical signal intensity of the  $\text{TiO}_2$  thin film deposited for 90 min ( $\text{TiO}_2(90\text{min})$ )



**Figure 2.** TEM images of  $\text{TiO}_2$  electrodes incorporated by (a) amorphous, (b) medium level, and (c) crystalline Pt nanophases. (The insets correspond to transmission electron diffraction patterns of the  $\text{TiO}_2$ -Pt electrodes.)

would be reduced at negative potential of  $-1.0$  V vs normal hydrogen electrode (NHE) and increased at positive potential of  $+1.5$  V vs NHE in parallel with the potential of the electrochemical cell. Accordingly, the  $\text{TiO}_2$  thin film exhibits a typical cathodic coloration in EC. In Figure 1b, the  $\text{TiO}_2$ -Pt shows the same EC properties as those of the  $\text{TiO}_2(90\text{min})$  as a function of an applied potential, while the  $\text{TiO}_2$  deposited for 3 min with the same thickness as the  $\text{TiO}_2$ -Pt shows almost no change in optical intensity. It is likely that the  $\text{TiO}_2(3\text{min})$  electrode with several nanometers in thickness has no sufficient electron/proton conductivity to produce an electrochemical motion and shows no electrochromic proper-



**Figure 3.** (a) Comparison of optical modulation of  $\text{TiO}_2$  electrodes incorporated by amorphous, medium level, and crystalline Pt nanophases. (The insets correspond to high-resolution TEM images and Fourier-transformed diffraction patterns of the  $\text{TiO}_2$ -Pt electrodes.) (b) Optical modulation of the  $\text{TiO}_2$  electrode sputtered for 90 min under applied pulse potentials of  $-0.3$  and  $+0.9$  V.

ties. However, the  $\text{TiO}_2$ -Pt electrode with the same thickness as the  $\text{TiO}_2(3\text{min})$  displays an EC of cathodic coloration materials. This infers that an increased electronic conduction in  $\text{TiO}_2$ -Pt caused by Pt conductors would enhance cathodic electrochromic properties of  $\text{TiO}_2$ . As shown in the Figure 1b, some signal fluctuations of  $\text{TiO}_2$ -Pt appear at the negative potential because of hydrogen evolution. However, it was surprisingly found that  $\text{TiO}_2$ -Pt has two improved EC properties: almost the same variation of intensity, i.e., transmittance, as that of the  $\text{TiO}_2(90\text{min})$  and even much faster response time during transition of negative to positive potential. Originally, since the thickness of electrochemical electrodes indicates capacity for electrochemical reactions, it is very interesting that  $\text{TiO}_2$ -Pt with only 10 nm in thickness shows almost the same variation of intensity as the  $\text{TiO}_2(90\text{min})$  with about 200 nm in thickness, as confirmed by scanning electron microscopy. In addition, in the case of the  $\text{TiO}_2$ -Pt, the time to reach maximum intensity at positive potential, i.e., response time, is only 2 s, while a response time of the  $\text{TiO}_2(90\text{min})$  is over 10 s. It is likely that the increased optical modulation and fast response of the  $\text{TiO}_2$ -Pt in the EC are caused by improved electronic/protonic motion by Pt nanophases.

To investigate the origin of such modified EC properties in the  $\text{TiO}_2$ -Pt, the  $\text{TiO}_2$ -Pt electrodes having an amor-

phous, medium level, or crystal texture of Pt metal were fabricated as function of power of the  $\text{TiO}_2$  and Pt sputtering guns. The possible origin of the formation of the Pt nanostructures within an oxide matrix may be as follows: (1) thermodynamically stable phase separation between metal and oxide and (2) prevention of migration of deposited metal adatoms by oxide matrix. Accordingly, if the power ratio of Pt to  $\text{TiO}_2$  sputtering guns is so small, an amorphous structure can be obtained preventing nanocrystallization of platinum by titanium oxide, while the Pt crystal structure can be formed at comparatively large sputtering power ratio. As can be seen in the TEM image of the  $\text{TiO}_2$ -Pt electrodes in Figure 2, the electrodes ( $\text{TiO}_2$ -Pt(A),  $\text{TiO}_2$ -Pt(M) and  $\text{TiO}_2$ -Pt(C)) consist of amorphous (Figure 2a), medium level (Figure 2b), and crystal (Figure 2c) Pt nanostructures in titanium oxides, respectively. The diffraction patterns in the inset of Figure 2 indicate the formation of Pt nanostructures with amorphousness, medium level, or crystallinity. Compared to the diffused ring pattern in Figure 2a, the several rings in Figure 2c correspond to indexing for face-centered-cubic crystal planes, whereas Figure 2b shows a transition state between amorphous and crystal structure.

Figure 3 shows a variation of optical transmittance in the  $\text{TiO}_2$ -Pt electrodes with respect to applied pulse potentials of  $-0.3$  and  $+0.9$  V vs NHE. As shown in the inset of Figure 3a, high-resolution TEM images and Fourier-transformed diffraction patterns are clear evidences of formation of an amorphous, medium level, and crystalline Pt nanophases within the  $\text{TiO}_2$ . The optical modulation of  $\text{TiO}_2$ -Pt(C) is varied as a function of potentials, while  $\text{TiO}_2$ -Pt(A) and  $\text{TiO}_2$ -Pt(M) show no clear reaction with applied potentials. Compared to such cathodic EC of  $\text{TiO}_2$  by Pt nanocrystals with only 10 nm, the  $\text{TiO}_2(90\text{min})$  (Figure 3b) as a cathodic coloration material shows extremely reduced EC properties under applied pulse potentials of  $-0.3$  and  $+0.9$  V. It is likely that such an improved optical modulation in  $\text{TiO}_2$ -Pt(C) is dominantly caused by nanonetwork conduction, which results from well-dispersion of the Pt crystalline nanophase in the electrode. According to EC, electrons are injected or extracted under applied potentials, and at the same time, ions are moved into or out of the EC material in terms of double injection or extraction of electrons and ions. However, at the given potentials, the  $\text{TiO}_2(90\text{min})$  electrode provides no sufficient electron/proton conducting motion to produce an electrochemical reaction and thus shows no clear electrochromic properties. On the other hand, the  $\text{TiO}_2$ -Pt(C) electrode displays an EC of cathodic coloration materials. This indicates that, in the case of  $\text{TiO}_2$ -Pt(C), an electrochemical behavior for an EC is definitely affected by Pt nanocrystals. The cathodic EC would be enhanced by continuous electron/proton motion of Pt nanophases in the potential range of  $-0.3$  and  $+0.9$  V.

## Conclusions

We found that electrochromic properties of  $\text{TiO}_2$  were improved by Pt nanocrystals in contrast to those of pure  $\text{TiO}_2$

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and  $\text{TiO}_2$  incorporated by amorphous or medium level Pt crystalline nanophases. The origin of enhancement of cathodic EC in the  $\text{TiO}_2$ -Pt is considered to be improved electrochemical motion caused by Pt nanocrystals, thus enhancing proton-transfer phenomenon of  $\text{TiO}_2$ .

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