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Control of Atomic or Nano-Scale Structure of Functional Metal Oxides for Clean Energy Conversion Systems

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ABSTRACT

In this comprehensive paper, we present an overview of our recent studies in reveal of influences of “atomic- and nano-scale structure” on catalytic and photocatalytic activity or preparation of functional materials for clean energy conversion systems such as water splitting, solar cells, photocatalysts and fuel cells. In the case of atomic scale structures, amorphous and atomic-scale roughed surface structure of RuO_2 and TiO_2 shows high catalytic activity for oxygen evolution reaction. On the other hand, in the case of nano-scale structures, the anodic porous TiO_2 films controlled their crystallinity and pore size can be used as new applications such as flexible dye sensitized solar cells and size selective photocatalysts. The porous Al_2O_3 films can be used as a template for formation of highly durable platelet carbon nanofiber supports of cathode electrode for fuel cells.

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Keywords : Amorphous, Atomic-scale Roughened Surface, Anodic Mesoporous Oxide Films, Porous Templates

1. Introduction

Recently, the attention on clean energy conversion systems such as water splitting, solar cells, photocatalysts and fuel cells has increased due to the limitation of fossil fuels and suppression of the global warming and the environment pollution. For practical use of them, it is quite important to develop the functional metal oxides used as photocatalysts, electrochemical catalysts, substrates for some devices and so on. In general, the performance of them is affected by various factors and one of the most important factors is “atomic- and nano-scale structures” of them. For example, in the case of catalysts, the catalytic activity drastically changes by changing of atomic-scale surface structures such as crystal faces, whereas the chemical composition and crystal geometry of them don't change. Therefore, control of the atomic- and nano-scale structures of the functional metal oxides is promising and interesting approach to achieve the formation of key materials for the clean energy conversion systems.

This review summarizes our recent studies in the development of useful functional metal oxides by controlling of the atomic- or nano-scale structures of them. In section 2, we reported the influence of atomic-scale structures of RuO_2 and TiO_2 on the electrochemical/ photoelectrochemical catalytic activity for an oxygen evolution reaction (OER). On the other hand, in section 3, we reported the application of nano-scale controlled porous TiO_2 and Al_2O_3 to substrates of dye sensitised solar cells (DSSCs), size selective photocatalysts and templates of carbon nanofibers used as supports of platinum catalysts for an oxygen reduction reaction (ORR).

2. Influences of Atomic-scale Structures of Metal Oxides on Catalytic Activity

2.1 Catalytic activity of amorphous RuO_2 for OER¹

Active catalysts for OER play important roles in the overall performance of electrochemical/photoelectrochemical water splitting because of the majority of energy losses occurring at not

hydrogen evolution reaction, but OER. Some researchers reported that the OER activity for oxide catalysts primarily correlates to the electronic states and valence of metal species. On the other hand, the catalytic activity is also strongly dependent on the local surface structure of the electrode, because the stability and reactivity of the reaction intermediate is affected by local structure of the adsorption site and the surrounding surface structure. Actually, many researchers have reported that the Miller index of surface faces or facet faces of electrode affects the electrocatalytic activity. Therefore, it is interesting subject to compare the reaction activity of the amorphous electrode with that of the crystalline one because the property of the surface local structure of the amorphous is different from that of the crystal. In this section, we reported the electrocatalytic activity of amorphous RuO_2 for OER with a focus being placed on the onset potential (U_{onset}), which is strongly related to activation energy for OER.

RuO_2 films were prepared on FTO substrates by an electrochemical method with annealing at 200 and 300°C (denoted as e200- and e300- RuO_2), or a sputtering method without and with annealing at 300°C (denoted as snon- and s300- RuO_2). Figure 1 shows Raman spectra of (a) e200- RuO_2 , (b) snon- RuO_2 , (c) e300- RuO_2 and (d) s300- RuO_2 . The broad peak at 420 cm^{-1} was attributed to hydration water containing in the e200- RuO_2 film.^{2,3} Triple peaks at 521, 634 and 704 cm^{-1} were observed in spectra (c) and (d), whereas those were not observed in spectra (a) and (b). These triple peaks were assigned to E_g , A_{1g} and B_{2g} vibrational modes of rutile RuO_2 crystal,⁴ indicating that e300- RuO_2 and s300- RuO_2 were crystallized, whereas e200- RuO_2 and snon- RuO_2 were amorphous.

Figure 2 shows current density (j) vs. potential (U) curves of (a, b) the amorphous and (c, d) the rutile crystalline RuO_2 measured in 0.1 M HClO_4 aqueous solution. The large anodic current for OER was observed at the potential region over 1.1 V vs. $\text{Ag}/\text{AgCl}/\text{KCl}$ (satd). We can see that the difference in the U_{onset} for OER between the amorphous and crystalline RuO_2 films (there were no influence of hydration water on catalytic activity for OER). The values of the U_{onset} of the amorphous films (e200- RuO_2 and snon- RuO_2), were

Figure 1. (Color online) Raman spectra of (a) e200-RuO₂, (b) snon-RuO₂, (c) e300-RuO₂ and (d) s300-RuO₂. (Reproduced by permission of Elsevier.¹)

Figure 2. (Color online) j - U curves of (a) e200-RuO₂, (b) snon-RuO₂, (c) e300-RuO₂ and (d) s300-RuO₂. The insets are Tafel plots for these lines. (Reproduced by permission of Elsevier.¹)

shifted toward the negative side by about 0.05 V from that of the crystallized ones. These results suggest that the amorphous RuO₂ films were more active for OER than the crystalline ones. Insets of Fig. 2 show Tafel plots of them. The Tafel slope of the amorphous RuO₂ was 30 mV dec⁻¹, whereas that of the crystalline one was 40 mV dec⁻¹, implying that the rate determining step for OER was also affected by the difference of the local structures.

Some researchers reported that the formation of an intermediate state during OER induced the relaxation or distortion of Ru-O bonds on the RuO₂ surface.^{5,6} This indicates that the reaction rate of the OER at the RuO₂ electrode is partially controlled by the activation energy which is determined by the distortion energy of the surface local structure. On the other hand, it is well known that amorphous materials have structural flexibility.^{7–10} Therefore, it is reasonable to consider that the distortion energy needed to form the structural

Figure 3. (Color online) Atomic force micrographs of the (110) rutile TiO₂ surfaces (a) before and (b), (c) after photooxidation reaction under the UV irradiation (0.65 mW/cm²) and models of (110) rutile TiO₂ surfaces. The electric charge passing across the electrode is (b) 1.0 C/cm² and (c) 3.0 C/cm², respectively. (Reproduced by permission of ACS publications.¹¹)

distortion of the amorphous RuO₂ film for OER is much smaller than that of the crystalline ones. Accordingly, the overvoltage of the amorphous film for OER was decreased, and the U_{onset} of the amorphous film was shifted toward the negative side from that of the crystalline ones.

2.2 Photocatalytic activity of rutile TiO₂ single crystals controlled its atomic-scale surface structures¹¹

Many researchers have studied on new photocatalysts for OER based on the properties of their band structure such as the energy level of conduction band (CB) and valence band (VB), and band gap energy. Actually, the relative energy position between the redox potential of oxygen and bottom edge of CB of photocatalyst strongly affect the electron transfer efficiency between the oxygen and the photocatalysts. On the other hand, we should also note that the surface structure of the photocatalyst has also a strong influence on the photocatalytic activity as is the case in electrocatalysts such as RuO₂. However, the influences of the atomic-scale surface structures of TiO₂ on the photocatalytic activity for OER have not been discussed enough. Therefore, in this section, we reported the photocatalytic activity for OER at the atomically-flat and roughened TiO₂.

The atomically-flat rutile (110) TiO₂ surfaces were obtained by the “HF etching and annealing” procedure.^{12–14} On the other hand, the roughened surface was obtained from the atomically-flat surface by photooxidation reaction at the applied potential of +1.5 V vs. Ag/AgCl/KCl (satd) under the UV irradiation (0.65 mW/cm²).¹¹ Figure 3 shows AFM images of the (110) rutile TiO₂ surfaces before and after the photooxidation. In the case of the TiO₂ surfaces before photooxidation, we can see that the single steps extended in the [001] direction on the surface, suggesting that the surface is atomically-flat. On the other hand, the TiO₂ surfaces after the photooxidation have a lot of small pits, indicating that the surfaces are roughened, and they have much steps and kinks. The roughness factors of the TiO₂ surfaces after the photooxidation with the passing electric charge of 1.0 and 3.0 C/cm² were 0.197 and 0.488 nm, whereas those before photooxidation reaction were 0.101 nm. Therefore, considering the fact that the single-step height of the (110) TiO₂ surface are 0.35 nm,^{15,16} the degree of the surface roughness induced by photooxidation was quite small (i.e. atomic-scale roughening).

Figure 4 shows the j - U curves of the atomically-flat and roughened (110) TiO₂ electrodes measured in 0.1 M HClO₄ aqueous

Figure 4. (Color online) Photocurrent density (j) vs. potential (U) curves of (a) the atomically-flat (110) and (b) roughened (110) TiO₂ electrodres (with the passing electric charge of 1.0 C/cm²) measured in 0.1 M HClO₄ aqueous solution under the UV irradiation (0.65 mW/cm²). The insets are Mott-Schottky plot of each electrode surface. (Reproduced by permission of ACS publications.¹¹)

Scheme 1. Reaction Scheme for Oxygen Photoevolution Reaction on Rutile TiO₂ in an Acidic Solution. (Reproduced by permission of ACS publications.¹¹)

solution under UV irradiation. We can see that the photocurrent for OER was observed at the potential region over 0.1 V vs. Ag/AgCl/KCl (satd). The most important feature is the difference in the U_{onset} for oxygen photoevolution between the flat and roughened TiO_2 electrodes. The U_{onset} values of the roughened TiO_2 electrodes were shifted toward the negative side by about 0.20 V from that of the flat ones. These results suggest that the overvoltage for oxygen photoevolution at the roughened TiO_2 electrode was smaller than that at the flat TiO_2 electrode. On the other hand, from Mott-Schottky plots, the flat band potential (U_{fb}) of the flat and the roughened (110) surface were almost the same with each other. Although the U_{onset} of semiconductor generally corresponds to the U_{fb} , the difference in the U_{onset} between the roughened and the flat (110) TiO_2 was much larger than that in the U_{fb} , indicating that the negative shift of the U_{onset} after the surface roughening was mainly caused by not the negative shift of the U_{fb} , but other factors such as the surface recombination rate of the photogenerated carriers and the activation energy of the active sites for oxygen photoevolution.

The oxygen photoevolution mechanism at TiO_2 suggested in our previous report also supported the difference of catalytic activity between the atomically-flat and roughened surfaces.^{12-14,17} In these reports, the oxygen photoevolution reaction is not initiated by the oxidation of surface Ti-OH but by a nucleophilic attack of an H_2O molecule to a surface-trapped hole (Scheme 1). The hole trapped at the bridging oxygen site is attacked by H_2O molecule, followed by the formation of peroxide species (intermediate species). In this

mechanism, the rate of the water photooxidation reaction strongly depends on the relaxation energy against the distortion of the surface lattice which is induced by the formation of the intermediates (i.e. TiOOTi) for OER. Thus, the surface local structure is of key importance for catalytic activity for oxygen photoevolution at TiO_2 surface, because the relaxation energy of the lattice depends on the surface local structure. Therefore, in the present case, it is reasonable to consider that the negative shift of the U_{onset} by the surface roughening was mainly attributed to the decrease of the activation energy at the active sites.

3. Formation of Nano-scale Porous Metal Oxide Films and Their Applications

3.1 Mesoporous TiO₂ films anodized in hot phosphate/glycerol electrolytes^{18–21}

Recently, TiO_2 nanotubular and nanoporous films prepared by anodizing of titanium specimens have much attention due to such unique structures, high surface area^{22,23} and superior electron transport to that of TiO_2 nanoparticle films.^{24,25} The TiO_2 nanotubular films have been formed by anodizing in organic electrolytes containing fluoride ions.^{22–25} However, such anodic TiO_2 nanotubular films are highly contaminated with fluoride and carbon species derived from the electrolyte, leading to amorphous structures. Therefore, post-annealing of the anodized specimens at more than 450°C is indispensable for removing such impurities and crystallization of TiO_2 nanotubes. On the other hand, more recently, we reported the formation of mesoporous TiO_2 films by anodizing of titanium in phosphate/glycerol electrolytes at 160°C .^{18–21} The resultant films showed some interesting features. For example, Fig. 5 shows XRD patterns and the pore size distributions of the film anodized in a hot phosphate/glycerol electrolyte at 3 V and 20 V (denoted as P3 and P20), together with that in a fluoride/ethylene glycol electrolyte at 60 V with post-annealing at 450°C (denoted as F60). From Fig. 5(a), the XRD pattern of the P3 showed only broad diffraction halo between 20 and 30° , apart from the intense substrate peaks, indicating that the P3 film was amorphous. In contrast, the sharp peaks due to the presence of anatase crystal appeared in the pattern of the P20, even though the film was not annealed after anodizing. This result suggests that increasing of the formation voltage promoted crystallization of TiO_2 films in the hot phosphate/glycerol electrolyte, whereas it was known that crystallization in the fluoride-containing organic and aqueous electrolytes was not promoted. Meanwhile, from Fig. 5(b), we can see that the peak pore diameter of the P3 and P20 was as small as ~ 10 nm which is “meso” size, whereas that of F60 was more than 50 nm.

As mentioned above, the P20 film can be crystallized even without post-annealing at high temperature. Therefore, the P20 film is of potential interest for fabricating flexible dye-sensitized solar cells (DSSCs) which were formed on the heat-labile materials such as ITO thin films and plastic sheets. Figure 6(a) shows the photographs of sputtered titanium thin films on ITO/glasses after anodizing. The films gradually became transparent from the edges of the specimen (30 and 50 s) and completely transparent after anodizing for ~60 s, suggesting that the TiO₂ films can be formed from the sputtered titanium thin films during the anodizing. Therefore, DSSCs shown Fig. 6(b) were prepared by using the P20/ITO for 60 s and F60/ITO. Figure 6(c) shows the *j*-*U* curve of each DSSC. We can see that the DSSC using the P20/ITO shows higher performance than that using the F60/ITO. In addition, the photocurrent density of the DSSC using the P20/ITO was remarkably reduced by post-annealing at 450°C, suggesting that the high performance of the DSSC using the P20/ITO was caused by impressing high electric resistance of ITO with post-annealing at elevated temperature.

Figure 5. (Color online) (a) X-ray diffraction patterns of the P3 and P20 films, together with the F60 film annealed at 450°C in air for 3 h. (b) Pore size distributions in the P3 and P20 and F60 films. The distributions were obtained from nitrogen adsorption isotherms at -196°C . Each film thickness is 5 μm . (Reproduced by permission of Elsevier.¹⁸)

Figure 6. (Color online) Photographs of (a) the Ti/ITO after anodizing in the hot phosphate/glycerol electrolyte at 20 V for 30–80 s and the DSSC using TiO_2/ITO anodized at 20 V for 60 s. (c) Photocurrent density (j) vs. potential (U) curves of the DSSCs using the P20 without and with the post-annealing and the F60 with the post-annealing at 450°C. Each TiO_2 film thickness is 500 nm. (Reproduced by permission of Elsevier and The Institute of Electrostatics Japan.^{19,20})

The P20 film also has quite small size pores. Therefore, size-selective photocatalytic decomposition was achieved by using the P20 films. In the case of mesoporous TiO_2 films anodized in the hot phosphate/glycerol electrolyte, the porous structures can be controlled by changing the basicity of the electrolyte, i.e., the more regular mesoporous developed with increasing basicity of the electrolyte by changing the mixing ratio of containing phosphates such as of K_3PO_4 , K_2HPO_4 , and KH_2PO_4 . Figure 7 shows the UV-vis spectra of a mixture of methylene blue (MB, MW 319.85, $1.4\text{ nm} \times 0.6\text{ nm}$, the molecular sizes were calculated using ChemBio3D software) and direct red 80 (DR, MW 1373.05, $3.8\text{ nm} \times 1.2\text{ nm}$) under UV irradiation for 120 min on the P20A, which have the most regular mesopores, and F60 film. In both the films, the two main peaks at 682 and 508 nm were attributed to the MB and DR molecules respectively. The insets in Fig. 7 show a comparison of the photocatalytic decomposition rates of MB

($\lambda_{\text{max}} = 682\text{ nm}$) and DR ($\lambda_{\text{max}} = 508\text{ nm}$) with the P20A and F60 films. In the case of the F60 film, the amount of MB and DR decreased with the UV-irradiation time, suggesting that both molecules could be decomposed on TiO_2 films. On other hand, in the case of the P20 film, the rate of decomposition of DR was relatively slow while that of MB was comparatively faster on the F60 film because of the higher surface area. In most cases, photo-generated holes on TiO_2 reacted with either the surface OH groups or H_2O molecules and generate active hydroxyl radicals, which are usually nonselective oxidants of organic molecules. However, in the case of mesoporous TiO_2 with pore sizes in the range 3–7 nm, Shiraishi et al. reported that the diffusion distance of the hydroxyl radicals formed inside the pores was 1.3–2.4 nm.²⁶ Therefore, in the case of mesoporous TiO_2 films, only the molecular which through into the pores could be decomposed by photo-generated hydroxyl radicals.

Figure 7. (Color online) Time-dependent UV-Vis spectra of methylene blue (MB) and direct red 80 (DR) mixture during UV irradiation on (a) P20A film, and (b) F60 film for 120 min. Insets on the right-hand-sides show scanning electron micrographs of P20A and F60 films. The left-hand-side insets show kinetic data for MB ($\lambda_{\max} = 682$ nm) and DR ($\lambda_{\max} = 508$ nm). (Reproduced by permission of Elsevier.²¹)

3.2 Porous Al_2O_3 templates for platelet carbon nanofibers for ORR catalysts²⁷

In general, platinum or platinum alloy nanoparticles supported on carbon (Pt/C) are used as cathode ORR catalysts of the polymer electrolyte fuel cells.^{28,29} However, for practical applications, it is necessary to improve the durability of the Pt/C. The structures of carbon supports used for ORR, such as carbon blacks, graphene sheets, carbon nanotubes and other carbon nanofibers (CNFs), strongly affect their activity and durability. The liquid phase carbonization using anodic porous Al_2O_3 templates is powerful method to control the structure of CNFs.^{30,31} Recently, we have also prepared platelet CNFs (p-CNFs) by the liquid phase carbonization of polymer powders in the pores of porous anodic Al_2O_3 templates.^{32,33} The platelet structure is developed even at temperatures as low as 600°C, with the degree of graphitization increasing with the heat-treatment temperature.³³ Therefore, it is expected that the p-CNFs thus prepared allow us to systematically examine the influence of the degree of graphitization of p-CNFs on the platinum particle dispersion, ORR activity, and durability. In this section, platinum-supported p-CNF catalysts heat-treated at various temperatures were prepared and their ORR durability was investigated.

Figure 8(a)(b) shows the SEM images of the porous anodic Al_2O_3 template and p-CNFs prepared at 1400°C (denoted as p-CNF1400). We can see that the Al_2O_3 template has regular pores, with a diameter of about 50 nm and the formed p-CNFs have a high aspect ratio and their diameters are approximately in agreement with the pore diameters of the templates. Figure 8(c)(d) shows the TEM images of p-CNF and Pt/p-CNF prepared at 1400°C. The lattice fringes of the (002) plane could be observed clearly, and the selected area diffraction patterns also revealed the presence of the preferred texture with the {001} plane being normal to the fiber axis. After deposition of platinum nanoparticles, much more thickly dispersed platinum nanoparticles are found in the Pt/p-CNFs. The sizes of

Figure 8. Scanning electron micrographs of (a) the anodic alumina template (cross-section) and (b) p-CNF1400, and Transmission electron micrographs of (c) Pt/p-CNF1400 and (d) Pt/p-CNF140. The inset of (c) is the respective selected area diffraction pattern. (Reproduced by permission of Elsevier.²⁷)

the platinum nanoparticles are also uniform, about ~3 nm. On the other hand, the platinum nanoparticles are thinly dispersed on the commercial Ketjen black (KB) carbon supports and their size distribution is also relatively large (1–5 nm, not shown). In addition, the platelet structures developed on increasing the heat-treatment temperature, leading to a thick and even deposition of platinum nanoparticles.

Figure 9. (Color online) Change of (a) ECSA and (b) ORR activity (current density at 0.78 V vs. RHE) of the Pt/p-CNF600, Pt/p-CNF1000, Pt/p-CNF1400, and Pt/KB during the accelerated durability test for 200 and 1000 cycles. The values of ECSA and current density were normalized by the respective initial values. (Reproduced by permission of Elsevier.²⁷)

The durability of the Pt/p-CNFs and the Pt/KB was also examined by the accelerated durability test by a continuous potential cycling between 0.5 and 1.5 V vs. RHE in the argon-saturated H_2SO_4 aqueous solution. Figure 9 shows the change in the electrochemically active surface area (ECSA) and ORR activity of the Pt/p-CNFs and Pt/KB during the potential cycling for 200 and 1000 cycles. The ORR activity was evaluated from the current density at 0.78 V vs. RHE. The values of ECSA and current density were normalized by their respective initial values. The ECSA and ORR activity of the Pt/KB decreased markedly to less than 20% after 200 cycles. However, the degradation of the ECSA and ORR activity for the Pt/p-CNFs is much suppressed compared with that of the Pt/KB. In particular, the degradation becomes less significant for the p-CNFs formed at higher temperatures. The ECSA of the Pt/p-CNF1400 increases from 0 to 400 cycles, and then, decreases gradually with the number of potential cycles. Similar phenomena have been reported previously,^{34,35} and explained by the delay in wetting the platinum catalysts sufficiently or by the surface rearrangement of platinum atoms to more stable and active conformations.³⁴ The ORR activity of the Pt/p-CNF1400 shows more than 90% of the initial value after potential cycling for 200 cycles. Furthermore, after 1000 cycles, the ECSA value and current density at 0.78 V vs. RHE maintain more than 60% of their initial values.

The present study demonstrates that platinum nanoparticles are deposited more uniformly on the p-CNFs heat-treated at higher temperatures. Even if graphitization is increased, p-CNFs should provide many active sites of carbon edges at the side walls of CNFs for the adsorption of platinum nanoparticles. Furthermore, it is likely that carbon corrosion on CNFs is suppressed due to inhibited platinum migration. This inhibition increases with increasing degree of graphitization, probably due to the increased platinum-carbon support interaction. Thus, the p-CNFs with the increased degree of graphitization are suitable and promising carbon supports with improved durability for ORR.

4. Conclusions

This comprehensive article presents an overview of recent our studies about the influences of atomic or nano-scale structure on the functional metal oxides for clean energy conversion systems such as water splitting, solar cells, photocatalysts and fuel cells. These findings are of much interest in that it opens a new possibility that the design of the new electrochemical/photoelectrochemical catalysts, the substrates of DSSCs and the supports of catalysts.

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