Metal Oxides and Hydroxides as Rechargeable Materials for Photocatalysts with Oxidative Energy Storage Abilities

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ABSTRACT

NiO, Co(OH)₂, Ir oxide, and Ru oxide were combined as rechargeable materials with TiO₂ or Pt-TiO₂ photocatalyst to obtain novel photocatalysts with oxidative energy storage abilities. NiO, which is more stable than the conventional storage material, Ni(OH)₂, showed similar characteristics to those of Ni(OH)₂. The redox potential of Co(OH)₂ was more negative, and those of Ir oxide and Ru oxide were more positive than that of Ni(OH)₂. The photo-electrochemically charged Ir oxide was reduced by acetone, acetic acid, Br⁻, and water. The diversity of energy storage materials was accordingly improved in terms of the reaction potential and stability.

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1. Introduction

TiO₂ is practically used as photocatalysts driven by UV light.^{1,2} Electrons in the TiO₂ valence band are photoexcited to the conduction band, and holes are generated in the valence band, accordingly. The excited electrons and holes are used for reduction and oxidation reactions, respectively, which allow application to, for instance, removal of harmful compounds and bacteria. However, TiO₂ functions as a photocatalyst only under illumination. In order to retain its useful effects even after dark, we have developed photocatalysts with energy storage abilities.^{3–15} They can store surplus charges from photocatalysts in rechargeable materials during the day, and the stored charges are used to carry on redox reactions during the night.

We have combined TiO₂^{3–8} or SrTiO₃⁹ as well as Au-TiO₂,¹⁰ which exhibits photocatalytic activity on the basis of plasmon-induced charge separation,^{16–19} with a rechargeable material such as WO₃,^{3–6,9,10} MoO₃,^{7,10} or H₃PW₁₂O₄₀ (PWA),⁸ which undergoes redox reactions at negative potentials. Those photocatalysts with reductive energy storage abilities retain some photocatalytic effects based on cathodic reactions, such as anti-bacterial⁶ and anti-corrosion³ effects, even after dark. We also used Ni(OH)₂,^{11–14} which undergoes redox reactions at positive potentials, as a rechargeable material to develop photocatalysts with oxidative energy storage abilities [Fig. 1(a)]. They persist even after dark some effects based on oxidative reactions, such as mineralization of formaldehyde to CO₂¹³ and oxidative removal of other harmful organic compounds like phenol.¹¹ However, their oxidation abilities are limited by the redox potential (ca. +0.7 V vs. Ag|AgCl at pH 10) and stability (pH > 7) of Ni(OH)₂. Therefore, here we investigate other redox-active metal oxides and hydroxides as rechargeable materials to combine with photocatalysts, for improvement of the diversity of photocatalysts with energy storage abilities in terms of the reaction potential and stability. Here we employed NiO, which is more stable, Co(OH)₂, which is expected to drive milder oxidative reactions selectively, and Ir oxide and Ru oxide, which are anticipated to be applied to a wider variety of oxidative reactions than Ni(OH)₂.

Figure 1. (Color online) Mechanisms of (a) photocatalysts with oxidative energy storage abilities and (b) remote energy storage.

2. Experimental

An indium tin oxide (ITO)-coated glass plate or a pyrex glass plate was coated with metal oxide films after cleaning by sonication in a surfactant and then in 1 M NaOH. A TiO₂ film (2.5 cm²) was prepared from an anatase TiO₂ sol (STS-21, Ishihara Sangyo) diluted with ultrapure water (v/v = 3:1) by spin-coating at 1500 rpm for 10 s, and annealed at 400°C for 1 h. Pt was deposited photocatalytically on TiO₂ from 0.05 mM aqueous H₂PtCl₆.¹² The substrate was kept under black light at least 12 h before use.

A NiO film (1.0 or 0.8 cm²) was obtained by annealing (300°C,²⁰ 1 h) Ni(OH)₂ electrodeposited from 0.02 M aqueous Ni(NO₃)₂ (pH 7) at 1 mA cm⁻² for 30 s.¹¹ A NiO-TiO₂ mixed film was obtained from a mixture of 1.1 g of NiO (8–20 nm, Alfa Aesar), 5 mL of the diluted TiO₂ sol and 3 mL of ultrapure water by

Figure 2. Cyclic voltammograms of (a) the NiO film in a pH 10 buffer, (b) Co(OH)_2 in a pH 10 buffer, (c) Ir oxide in 0.1 M NaNO_3 , and (d) Ru oxide in 0.1 M NaNO_3 . Scan rate is (a, c, d) 50 mV s^{-1} or (b) 5 mV s^{-1} .

spin-coating at 1500 rpm for 10 s and annealing at 450°C for 1 h. A Co(OH)_2 film (1.0 or 0.8 cm^2) was electrodeposited from 0.02 M aqueous $\text{Co(NO}_3)_2$ (pH 7) at 1 mA cm^{-2} for 30 s. An Ir oxide film (1.5 cm^2) was obtained from 0.5 M aqueous IrCl_3 by spin-coating at 1000 rpm for 10 s and annealing at 250°C for 1 h.^{21,22} A Ru oxide film (1.0 or 0.8 cm^2) was electrodeposited from 0.02 M aqueous RuCl_3 at 1 mA cm^{-2} for 60 s.²³

Electrochemical measurements were performed in a pH 10 sodium carbonate buffer or 0.1 M aqueous NaNO_3 . A Hg-Xe lamp (Luminar Ace, Hayashi Watch-Works) with a 365 nm band-pass filter (FWHM 44 nm) was employed for UV-irradiation (100 mW cm^{-2}). Remote energy storage¹² was carried out in air at $>80\%$ relative humidity (RH) by using polyimide films for adjusting the gap between Pt-TiO₂ and a metal oxide film.

3. Results and Discussion

3.1 Oxidative energy storage abilities of NiO

In cyclic voltammetry (CV) of NiO at pH 10, redox waves were observed at around $+0.7 \text{ V}$ vs. Ag/AgCl [Fig. 2(a)]. Photoelectrochemical charging of the NiO film was examined by the remote energy storage system,¹² in which a rechargeable material apart from a photocatalyst is oxidized on the basis of photocatalytic remote oxidation [Fig. 1(b)],^{24–26} because it is less affected by the film thickness and electron conductivity. In the photocatalytic remote oxidation, oxygen is reduced at the photocatalyst surface to hydrogen peroxide, which diffuses in the gas phase.²⁷ The diffused hydrogen peroxide is photocleaved into hydroxyl radicals, which oxidizes a target material.²⁶ Remote oxidation is therefore accelerated by decreasing the gap between the photocatalyst and the target.²⁵ The Pt-TiO₂ film was faced to the NiO film (gap = $12.5 \mu\text{m}$) and irradiated with UV light for 1.5 h. However, no significant change in absorbance or potential of the film was observed, suggesting that it was not oxidized because of its lower redox activity than Ni(OH)_2 .

Then we prepared a NiO film on a TiO₂ film to examine direct photoelectrochemical charging¹¹ under UV light. Although the NiO film was not charged in air ($>80\%$ RH), an increase in absorbance, which suggested oxidation of NiO, was observed in a pH 10 carbonate buffer, although the rate was 10-fold lower than that for Ni(OH)_2 . Ion transport between anodic and cathodic sites is necessary in any electrochemical systems. In the present system, the

Figure 3. (Color online) Electrochemical discharging curves at 500 nA cm^{-2} for (a) the Co(OH)_2 film after electrochemical oxidation at $+1 \text{ V}$ for 60 s in a pH 10 buffer and (b) Ru oxide and Ir oxide films after electrochemical oxidation at $+1.2 \text{ V}$ for 60 s and 15 s, respectively, in 0.1 M NaNO_3 . (Inset in a) The Co(OH)_2 film (A) before and (B) after photoelectrochemical oxidation.

ion transport in the adsorbed water layer [Fig. 1(a)] may not be sufficiently fast. So as to accelerate the ion transport and thereby oxidation of NiO, the NiO-TiO₂ mixed film was prepared for minimizing the distance between the anodic and cathodic sites. As a result, we found that the photoelectrochemical charging of the mixed film is possible even in dry air ($<20\%$ RH). We therefore expect that NiO, which is more stable than Ni(OH)_2 , can also work as a rechargeable material.

3.2 Oxidative energy storage abilities of Co(OH)_2

The Co(OH)_2 film exhibited redox waves at around $+0.5 \text{ V}$ in CV at pH 10 [Fig. 2(b)]. Color of the film changed from pale blue to pale brown in the first cycle. In the following cycles, the film exhibited reversible electrochromic behavior between pale brown (reduced) and greenish brown (oxidized). The Co(OH)_2 film was anodically charged by polarization at $+1.0 \text{ V}$ for 60 s at pH 10, and discharging curve was obtained at 500 nA cm^{-2} [Fig. 3(a)]. Although the potential during the discharging ($+0.4$ – $+0.5 \text{ V}$) was more negative than that of Ni(OH)_2 ($+0.5$ – $+0.6 \text{ V}$),^{11,12} Co(OH)_2 can also store oxidative energy. Then photocatalytic remote energy storage (gap = $12.5 \mu\text{m}$) in Co(OH)_2 was examined (6 h). As a result, the film turned to greenish brown, suggesting that the film was oxidized [Fig. 3(a), inset]. It is therefore expected that Co(OH)_2 can selectively drive oxidative reactions that take place at milder potentials.

3.3 Oxidative energy storage abilities of Ir oxide and Ru oxide

The major component of the prepared Ir oxide was identified by XPS analysis as $\text{Ir(III)(OH)}_x\text{Cl}_{3-x}\text{H}_2\text{O}$.^{28–30} Similarly, the prepared Ru oxide was suggested to be a mixture of Ru(III) oxide and hydroxide (i.e. $\text{Ru(III)O}_x(\text{OH})_{3-2x}$).²⁸ The redox waves in CV in 0.1 M aqueous NaNO_3 of the Ir oxide at around $+1.0 \text{ V}$ and Ru oxide at around $+0.9 \text{ V}$ were assigned to Ir(III/IV)^{31,32} and Ru(III/IV),³³ respectively [Fig. 2(c), (d)]. The films were electrochemically charged at $+1.2 \text{ V}$ for 60 s (Ir oxide) or 15 s (Ru oxide),

Figure 4. Time course of normalized absorbance of a photoelectrochemically oxidized Ir oxide film in dry air (<20% RH) and that in humid air (>80% RH). The temporary absorbance increase in humid air reflects a decrease in scattering due to condensation of water vapor.

and discharged at 500 nA cm^{-2} [Fig. 3(b)]. Although a plateau region is observed for the Ru oxide at $\sim +0.9 \text{ V}$, the Ir oxide behaves more like a capacitor. In either event, the charged oxides are expected to induce oxidative reactions that cannot be driven by the charged Ni(OH)_2 .

Then we examined remote energy storage (gap = $7.5 \mu\text{m}$). The Ir oxide film turned from pale yellow to blue, which is the color of Ir(IV) oxide³² after 15 h irradiation. Open circuit potential (in 0.1 M aqueous NaNO_3 , in dark) of the Ir oxide-coated electrode shifted positively from $\sim +0.4 \text{ V}$ to $\sim +0.9 \text{ V}$ after the storage. In subsequent discharging at 500 nA cm^{-2} (cutoff potential = $+0.4 \text{ V}$), $\sim 0.5 \text{ mC cm}^{-2}$ of charges were taken from the film. In the case of the Ru oxide film, although no significant color change was observed even after irradiation for 36 h because the as-prepared Ru oxide film looked dark brown, the open circuit potential shifted positively from $\sim +0.4 \text{ V}$ to $\sim +0.7 \text{ V}$. We therefore conclude that both Ir oxide and Ru oxide function as rechargeable materials.

3.4 Oxidation reactions driven by the charges stored in Ir oxide

Oxidation reactions that can be induced by the photoelectrochemically oxidized Ir oxide film were investigated and monitored by measuring the reductive bleaching of charged Ir oxide. Although no significant bleaching was observed in the case of exposure to 1 M aqueous KCl, the film was immediately bleached by 1 M aqueous KBr, acetic acid, and acetone. These results suggest that the charged Ir oxide can rapidly oxidize those substances, which are slowly or hardly oxidized by the oxidized Ni(OH)_2 .¹¹ In dry air (<20% RH), the bleaching ratio was less than 10% at least for 24 h in dark. In contrast, vaporized acetone bleached the charged Ir oxide within 1 min. In addition, the film was almost completely bleached in a humid air at >80% RH in 10 h (Fig. 4), suggesting that water oxidation is possible while the reaction is slow. It is reasonable because an IrO_2 electrode is reported to oxidize water to oxygen at $+1.1 \text{ V}$ vs. Ag|AgCl in 0.1 M aqueous KNO_3 (pH 6.3).³⁴ It was confirmed that the Ir oxide film bleached by water vapor can be reoxidized photoelectrochemically.

4. Conclusions

NiO , Co(OH)_2 , Ir oxide, and Ru oxide can be used as rechargeable materials for photocatalysts with oxidative energy storage abilities. NiO , which is more stable than Ni(OH)_2 , exhibits similar characteristics to those of Ni(OH)_2 . Co(OH)_2 , discharging potential of which is more negative than that of Ni(OH)_2 , is expected to drive milder oxidation reactions selectively. Ir oxide and Ru oxide exhibit more positive discharging potentials. The photoelectrochemically charged Ir oxide would oxidize acetone, acetic acid, Br^- , and water even after dark. The diversity of photocatalysts with energy storage abilities was improved in terms of the reaction potential and stability.

References

1. A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
2. A. Fujishima, K. Hashimoto, and T. Watanabe, *TiO₂ Photocatalysis. Fundamentals and Applications*, BKC (1999).
3. T. Tatsuma, S. Saitoh, Y. Ohko, and A. Fujishima, *Chem. Mater.*, **13**, 2838 (2001).
4. T. Tatsuma, S. Saitoh, P. Ngaotrakanwivat, Y. Ohko, and A. Fujishima, *Langmuir*, **18**, 7777 (2002).
5. P. Ngaotrakanwivat, T. Tatsuma, S. Saitoh, Y. Ohko, and A. Fujishima, *Phys. Chem. Chem. Phys.*, **5**, 3234 (2003).
6. T. Tatsuma, S. Takeda, S. Saitoh, Y. Ohko, and A. Fujishima, *Electrochem. Commun.*, **5**, 793 (2003).
7. Y. Takahashi, P. Ngaotrakanwivat, and T. Tatsuma, *Electrochim. Acta*, **49**, 2025 (2004).
8. P. Ngaotrakanwivat, S. Saitoh, Y. Ohko, T. Tatsuma, and A. Fujishima, *J. Electrochem. Soc.*, **150**, A1405 (2003).
9. Y. Ohko, S. Saitoh, T. Tatsuma, and A. Fujishima, *Electrochemistry*, **70**, 460 (2002).
10. Y. Takahashi and T. Tatsuma, *Electrochem. Commun.*, **10**, 1404 (2008).
11. Y. Takahashi and T. Tatsuma, *Langmuir*, **21**, 12357 (2005).
12. Y. Takahashi and T. Tatsuma, *Phys. Chem. Chem. Phys.*, **8**, 2716 (2006).
13. F. Yang, Y. Takahashi, N. Sakai, and T. Tatsuma, *Phys. Chem. Chem. Phys.*, **12**, 5166 (2010).
14. F. Yang, Y. Takahashi, N. Sakai, and T. Tatsuma, *J. Mater. Chem.*, **21**, 2288 (2011).
15. Y. Takahashi, S. Yamada, and T. Tatsuma, *Electrochemistry*, **82**, 726 (2014).
16. Y. Tian and T. Tatsuma, *J. Am. Chem. Soc.*, **127**, 7632 (2005).
17. Y. Takahashi and T. Tatsuma, *Appl. Phys. Lett.*, **99**, 182110 (2011).
18. E. Kazuma and T. Tatsuma, *Adv. Mater. Interfaces*, **1**, 1400066 (2014).
19. T. Tatsuma, *Bull. Chem. Soc. Jpn.*, **86**, 1 (2013).
20. F. Zhang, Y. Zhou, and H. Li, *Mater. Chem. Phys.*, **83**, 260 (2004).
21. R. K. Kwar, P. S. Chigare, and P. S. Patil, *Appl. Surf. Sci.*, **206**, 90 (2003).
22. P. S. Patil, R. K. Kwar, and S. B. Sadale, *Electrochim. Acta*, **50**, 2527 (2005).
23. B.-O. Park, C. D. Lokhande, H.-S. Park, K.-D. Jung, and O.-S. Joo, *Mater. Chem. Phys.*, **87**, 59 (2004).
24. T. Tatsuma, S. Tachibana, and A. Fujishima, *J. Phys. Chem. B*, **105**, 6987 (2001).
25. W. Kubo, T. Tatsuma, A. Fujishima, and H. Kobayashi, *J. Phys. Chem. B*, **108**, 3005 (2004).
26. W. Kubo and T. Tatsuma, *J. Am. Chem. Soc.*, **128**, 16034 (2006).
27. W. Kubo and T. Tatsuma, *Anal. Sci.*, **20**, 591 (2004).
28. C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics Industries, Eden Prairie, MN (1983).
29. R. Kotz, H. Neff, and S. Stucki, *J. Electrochem. Soc.*, **131**, 72 (1984).
30. C.-C. Hu and K.-H. Chang, *J. Power Sources*, **112**, 401 (2002).
31. J. Juodkazyte, B. Sebek, I. Valsiunas, and K. Juodkazis, *Electroanalysis*, **17**, 947 (2005).
32. W. C. Dautremont-Smith, *Displays*, **3**, 67 (1982).
33. V. V. Panic, A. Dekanski, S. K. Milonjic, R. T. Atanasoski, and B. Z. Nikolic, *Colloids Surf., A*, **157**, 269 (1999).
34. M. Yagi, E. Tomita, and T. Kuwabara, *J. Electroanal. Chem.*, **579**, 83 (2005).