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# Remote energy storage in $Ni(OH)_2$ with $TiO_2$ photocatalyst

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Oxidative energy generated by UV-irradiated $TiO_2$ photocatalyst was stored in $Ni(OH)_2$ that was 12.5–50 μm apart from the $TiO_2$. It is likely that active oxygen species generated on $TiO_2$ diffused into the gas phase and oxidized $Ni(OH)_2$. Loading the $TiO_2$ with Pt accelerated the remote energy storage by an order of magnitude. It was revealed that the stored energy could be taken out and used chemically or electrochemically. The oxidized $Ni(OH)_2$ was reduced by gaseous formaldehyde, formate, ethanol and $H_2O_2$.

## Introduction

It is known that $TiO_2$ photocatalyst[1–3] exhibits various useful effects under UV light. As electrons in the $TiO_2$ valence band are photo-excited to the conduction band, holes are generated in the valence band, and reduction and oxidation reactions are driven by the excited electrons and the holes, respectively. These reactions lead to attractive effects such as self-cleaning, bactericidal and anti-corrosion effects. So as to retain these effects even after dark, we have developed photocatalysts with energy storage abilities by coupling a redox-active n-type semiconductor, such as $WO_3$[4–7] or $MoO_3$,[8] as an energy storage material with a $TiO_2$ photocatalyst, which is also an n-type semiconductor. We have reported that surplus reductive energy of $TiO_2$ can be stored in $WO_3$ or $MoO_3$ under illumination, and that the stored energy can be used to give rise to anti-corrosion[4] and bactericidal[7] effects even after dark. Oxidative energy can also be stored in $Ni(OH)_2$, a redox-active p-type[9,10] semiconductor, since it can be oxidized by UV-irradiated $TiO_2$, as Kostecki *et al.* have reported.[11] We have revealed that the stored oxidative energy can be used to oxidize various species including alcohols, aldehydes, formate and phenol.[12] For instance, formaldehyde, which causes sick building syndrome,[13] can be removed.

Thus far, in those systems, an energy storage material has been mixed or laminated with $TiO_2$ in order to optimize the efficiency of electron exchange between them. In the present work, $TiO_2$ was separated from an energy storage material $Ni(OH)_2$ by 12.5 or 50 μm, and a remote energy storage system was developed. In the system, some oxidizing species generated on $TiO_2$ photocatalyst may diffuse into the gas phase and oxidize $Ni(OH)_2$ to $NiO_x(OH)_{2-x}$.

Separation of a photocatalyst from an energy storage material would be advantageous from the viewpoints of selectivity and availability. Although the oxidizing ability of UV-irradiated $TiO_2$ is high enough to mineralize most organic compounds to $CO_2$, that of the oxidized $Ni(OH)_2$, $NiO_x(OH)_{2-x}$, is quite moderate. Therefore, if the photocatalytic oxidative energy is stored in $Ni(OH)_2$, it will allow, for instance, selective oxidation of alcohols and aldehydes in an organic solvent such as an ether. In addition, the present system enables us to select oxidation reactions alone from photocatalytic reactions, which involve both oxidation and reduction. In particular, it will be useful in preventing oxidation products from re-reduction. Also, in the present system, energy storage is a dry process using a simple equipment like a black-light or a mercury lamp. Although $Ni(OH)_2$ can also be oxidized by general electrochemical means without photocatalysts, it requires a liquid electrolyte. An additional feature of the present study is to shed light on mechanisms of $TiO_2$ photocatalysis in the gas phase.

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## Experimental

A Pyrex glass plate and an indium tin oxide (ITO) coated glass plate were cleaned by sonication in a detergent solution for 1 h, and further treated with 1 M aqueous NaOH for 1 h.

An anatase $TiO_2$ film was prepared on the Pyrex plate or the ITO coated glass plate from a $TiO_2$ sol (STS-21, Ishihara Sangyo) that had been diluted with water (75 vol%) by a spin-coating technique at 1500 rpm for 10 s, and annealed at 400 °C for 1 h. The thickness of the film, which was measured by scanning electron microscopy (SEM; S-4500, Hitachi), was ~0.9 μm.

If necessary, the $TiO_2$ film was loaded with Pt nanoparticles to obtain a Pt–$TiO_2$ film by photocatalytic deposition from 0.05 mM aqueous $H_2PtCl_6$ for 1 h under UV light. For all UV-irradiation experiments, a 200 W Hg–Xe lamp (Luminar Ace, Hayashi Tokei) with a 365 nm band-pass filter (FWHM 44 nm) was used as the light source, and the light intensity was 100 mW $cm^{-2}$, unless otherwise specified.

A $Ni(OH)_2$ film was prepared on a sonicated ITO or the $TiO_2$ coated ITO by cathodic electrodeposition from 0.02 M aqueous $Ni(NO_3)_2$ (pH 7) at 1 mA $cm^{-2}$ for 30 s. The thickness of the film was ~60 nm (measured by SEM). All electrochemical experiments were performed with a digital potentiostat (HZ-3000, Hokuto Denko), a Ag/AgCl reference electrode and a Pt wire counter electrode.

Absorbance changes of the $Ni(OH)_2$ films were measured by using a UV-Vis spectrophotometer (Ubest V-560, JASCO). Charges stored in $Ni(OH)_2$ were measured by constant-current

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electrochemical discharging at 500 nA $cm^{-2}$ in air-saturated 25 mM $NaHCO_3$ buffer (pH 10). The cut-off potential was +0.3 V *vs.* Ag/AgCl. For the present $Ni(OH)_2$ films, the absorbance increase was in proportion to the stored charge. Therefore, the stored charge was calculated from the absorbance increase.

## Results and discussion

### Direct energy storage

The $TiO_2$–$Ni(OH)_2$ bilayer film, which was obtained by electrodeposition of $Ni(OH)_2$ on a $TiO_2$ film, was irradiated with UV light (10 or 100 mW $cm^{-2}$) in the pH 10 carbonate buffer. As a result, the colorless film turned brown (Fig. 1, curves (a) and (b)), indicating that $Ni(OH)_2$ was photocatalytically oxidized (*i.e.*, oxidative energy was stored in $Ni(OH)_2$) as follows.

$$TiO_2 \xrightarrow{UV} TiO_2^*(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$\underset{\text{(colorless)}}{Ni(OH)_2} + xOH^- \leftrightarrow \underset{\text{(brown)}}{NiO_x(OH)_{2-x}} + xH_2O + xe^- \quad (2)$$

The electrons from $Ni(OH)_2$ (eqn (2)) are combined with the holes in $TiO_2$ ($h^+_{VB}$ of eqn (1)). On the other hand, the excited electrons ($e^-_{CB}$) should be consumed by reactions such as $O_2$ reduction (*e.g.*, eqn (3)).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

This color change of $Ni(OH)_2$ was not observed without $TiO_2$.

These have already been reported.[11,12] On the basis of the above-mentioned linear relationship between the absorbance of the oxidized $Ni(OH)_2$ and the stored charge, the apparent quantum yield of the energy storage (= (initial charging rate/rate of photon supply) × 100 (%); *i.e.*, incident photon to *charging* current conversion efficiency) was calculated from the absorbance increase to be $\sim 1.2 \times 10^{-1}$ or $\sim 6.5 \times 10^{-2}$% at light intensity of 10 or 100 mW $cm^{-2}$, respectively.

This oxidative energy storage was possible even in humid air (> 80% relative humidity) (Fig. 1, curve (c)). The apparent quantum yield of energy storage at a light intensity of 100 mW $cm^{-2}$ was *ca.* 20% of that in the pH 10 buffer ($\sim 1.4 \times 10^{-2}$%). This difference in the efficiency is possibly explained in terms of ion mobility. In the course of the energy storage reaction, cations are produced and/or anions are consumed at an oxidation site, at which oxidation reactions like eqn (2) take place, and *vice versa* at a reduction site, at which reduction reactions like eqn (3) take place. Therefore, ions should be transported between the sites to maintain electrostatic neutrality. In the case of the system in air, ions are transported in the adsorbed water layer,[14] in which ion mobility should be smaller than that in the buffer. Thus the lower efficiency of the system in air seems to be reasonable.

### Remote energy storage

We also prepared $TiO_2$ and $Ni(OH)_2$ films independently. The former was placed on the latter and irradiated with UV light (100 mW $cm^{-2}$) for 1.5 h in air. As a result, the $Ni(OH)_2$ film was oxidized and turned brown (Fig. 2, curve (a)). The apparent quantum yield of the oxidative energy storage was estimated from the absorbance increase to be $\sim 1.4 \times 10^{-3}$% (Table 1). Although this value was *ca.* 10% of that of the bilayer film, we found that the oxidative energy storage is possible even in the separated system. Poorer contact between $TiO_2$ and $Ni(OH)_2$ in the separated system than in the bilayer system is probably responsible for the lower efficiency. Because of the poor contact, oxidation of $Ni(OH)_2$ by the holes in $TiO_2$ is decelerated and depletion of the holes is accelerated by recombination with the excited electrons and/or oxidation of adsorbed water.

Next, the $TiO_2$ film was positioned to face the $Ni(OH)_2$ film with an intervening gap (12.5 μm, controlled by using polyimide films, as shown in the inset of Fig. 2) and irradiated with UV light (100 mW $cm^{-2}$) for 1.5 h. The $Ni(OH)_2$ film consequently turned brown, indicating that oxidative energy can be stored even in the remote system (Fig. 2, curve (b)), although

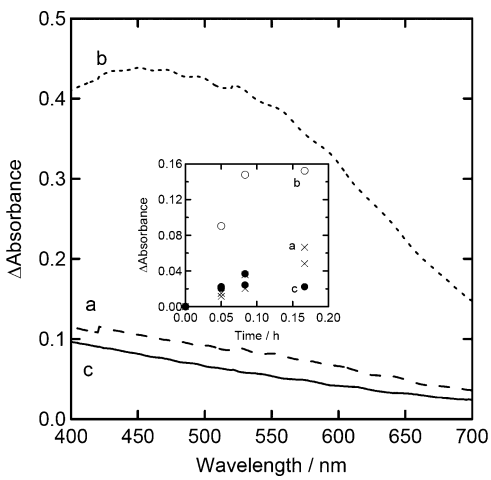


**Fig. 1** Typical differential absorption spectra of $TiO_2$–$Ni(OH)_2$ bilayer films after UV irradiation (10 (a) or 100 (b, c) mW $cm^{-2}$), in pH 10 buffer (a), (b) or in air (c) for 5 min. Initial time courses at 700 nm are also shown (inset).

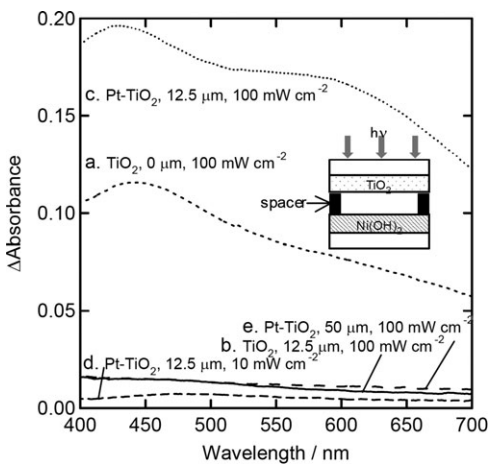


**Fig. 2** Typical differential absorption spectra of $Ni(OH)_2$ films that were faced to $TiO_2$ (a, b) or Pt–$TiO_2$ (c, d, e) with an intervening gap (0 (a), 12.5 (b, c, d) or 50 (e) μm) after UV irradiation (100 (a, b, c, e) or 10 (d) mW $cm^{-2}$) for 1.5 h in air. Inset shows the experimental setup.

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**Table 1** Absorbance increases and apparent quantum yields ($\Phi$) of the remote energy storage in the $Ni(OH)_2$ film

| Photo-catalyst | Light intensity/ mW $cm^{-2}$ | Gap[a]/ μm | ΔAbs.[b] | $\Phi$[d] (%) |
|---|---|---|---|---|
| $TiO_2$ | 100 | 0 | $0.0559 \pm 0.0132$[c] | $\sim 1.4 \times 10^{-3}$ |
| | 100 | 12.5 | $0.0089 \pm 0.0004$ | $> 2.1 \times 10^{-4}$ |
| Pt–$TiO_2$ | 100 | 12.5 | $0.1254 \pm 0.0141$[c] | $\sim 3.0 \times 10^{-3}$ |
| | 10 | 12.5 | $0.0022 \pm 0.0008$ | $> 5.4 \times 10^{-4}$ |
| | 100 | 50 | $0.0026 \pm 0.0016$ | $> 6.4 \times 10^{-5}$ |

[a] Gap between the photocatalyst and the $Ni(OH)_2$ film. [b] Absorbance increase at 700 nm in the initial 1.5 h. Mean ± standard error ($n = 3$). [c] ΔAbs. in the subsequent 1.5 h was nearly equal to that in the initial 1.5 h. [d] Estimated from the absorbance increase in the initial 1.5 h.

the absorbance increase was smaller than that in the contact system. The apparent quantum yield was $> 2.1 \times 10^{-4}$% (Table 1). On the basis of this result, we can conclude that indirect energy storage mediated by a diffusing redox species is possible at least in air.

It has been reported that the active oxygen species that is generated on UV-irradiated $TiO_2$ and desorbed to the gas phase causes photocatalytic remote oxidation of surfaces of organic films, gold, silver, copper, silicon and diamond.[15–17] There is a possibility that the present remote energy storage system involves similar processes.

### Acceleration of remote energy storage

It is known that photocatalytic remote oxidation,[18] as well as conventional photocatalysis,[19] can be accelerated by loading a photocatalyst with metal nanoparticles such as Pt or Ag.[18] This has been explained in terms of promoted charge separation and facilitated generation and desorption of active oxygen species. Of these metal nanoparticles, Pt is known to be the most effective in accelerating the remote oxidation.[18] Although the mechanism of the present remote energy storage is unknown, there is a possibility that this process is also accelerated by loading $TiO_2$ with Pt. Thus, remote energy storage with a Pt-loaded $TiO_2$ (Pt–$TiO_2$) film was examined.

Pt was deposited on a $TiO_2$ film from 0.05 mM aqueous $H_2PtCl_6$ by photocatalytic reduction. The Pt–$TiO_2$ film faced a $Ni(OH)_2$ film with an intervening gap of 12.5 μm and irradiated with UV light (100 mW $cm^{-2}$) for 1.5 h. A typical UV-Vis spectrum obtained after the irradiation is shown in Fig. 2 (curve (c)). The apparent quantum yield was $\sim 3.0 \times 10^{-3}$%; the efficiency was improved by an order of magnitude by loading $TiO_2$ with Pt (Table 1). It was even larger than that in the energy storage by using $TiO_2$ with no intervening gap. Incidentally, the amount of Pt was optimized by changing the concentration of the aqueous $H_2PtCl_6$ from 0.02 to 0.5 mM.

The remote energy storage was possible even at 10 times lower light intensity, 10 mW $cm^{-2}$ (Fig. 2, curve (d)). However, the apparent quantum yield decreased (Table 1), whereas it increases with decreasing light intensity in general photocatalytic systems. The efficiency decrease is possibly explained in terms of a loss of the mediator due to degradation and/or convective dissipation. Decreasing the light intensity slows the production, desorption and accumulation of the mediator and thereby retards the oxidation of $Ni(OH)_2$. As a result, the relative rate of the loss is increased and consequently the overall efficiencies are lowered.

The remote energy storage (at 100 mW $cm^{-2}$) was also possible even with a 4 times larger intervening gap, 50 μm (Fig. 2, curve (e)), whereas no significant coloration of $Ni(OH)_2$ was observed with the gap of 125 μm. The apparent quantum yield decreased as the gap increased (Table 1). This can be explained again in terms of the loss of the mediators. Increasing the gap also slows the accumulation of the mediator in the gap and thereby decelerates the oxidation.

### The use of stored oxidative energy

We have reported that the oxidative energy stored in the $TiO_2$–$Ni(OH)_2$ bilayer film can be used to oxidize various species such as alcohols, aldehydes, formate, phenol, $H_2O_2$ and $I^-$ in aqueous solutions.[12] Oxidation reactions of these substrates by electrochemically oxidized $Ni(OH)_2$ (eqn (4)) have also been reported.[20–22]

$$NiO_x(OH)_{2-x} + \text{substances} \rightarrow Ni(OH)_2 + \text{products} \quad (4)$$

A $Ni(OH)_2$ film oxidized and colored by the UV-irradiated Pt–$TiO_2$ film (gap, 12.5 μm; light intensity, 100 mW $cm^{-2}$; irradiation time, 1.5 h) could also be reduced and bleached rapidly (<30 s) by exposure to gaseous $H_2O_2$, ethanol, formaldehyde and formate. This suggests that the oxidative energy stored in $Ni(OH)_2$ by remote storage can be used to oxidize those species in the gas phase. The chemically reduced $Ni(OH)_2$ film could be photocatalytically oxidized again. Thus, the present system would be applied to the oxidation reactions, such as oxidative removal of formaldehyde, which is one of the causative agents of sick building syndrome.[13]

The stored oxidative energy can also be discharged electrochemically. After the irradiation, the $TiO_2$-coated glass plate and spacers were removed and the $Ni(OH)_2$-coated ITO electrode was transferred to the pH 10 buffer. The open-circuit potential of the electrode was 0 to +0.1 V and +0.4 to +0.6 V *vs.* Ag/AgCl before and after the photocatalytic oxidation, respectively. During the electrochemical discharging of the photocatalytically oxidized $Ni(OH)_2$ at 670 nA $cm^{-2}$, the potential was +0.45 to +0.50 V *vs.* Ag/AgCl (Fig. 3).

### Mechanisms of the remote energy storage

In our previous work on the $TiO_2$–$Ni(OH)_2$ bilayer film,[12] it was unknown whether the electron transfer from $Ni(OH)_2$ to $TiO_2$ was direct or indirect. In the present work, however, it was revealed that the oxidative indirect energy storage can take place due to the electron transfer mediated by an airborne redox species. It is known that active oxygen species such as $^{\bullet}OH$, $H_2O_2$, $O_2^{-\bullet}/HO_2^{\bullet}$ and $^1O_2$ are produced from $O_2$ and/or $H_2O$ on UV-irradiated $TiO_2$. Although the generation of $O_3$ has not been reported,[23] its possibility cannot be ruled out. It is likely that one of the active oxygen species acts as the mediator. Actually, it was confirmed that the remote oxidation of $Ni(OH)_2$ was not observed in an $N_2$ atmosphere; the remote energy storage requires $O_2$. With regard to the remote

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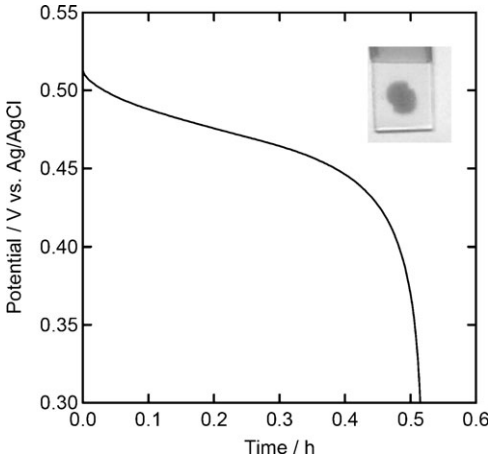


**Fig. 3** Typical electrochemical discharging curve (at 670 nA $cm^{-2}$) of the $Ni(OH)_2$ film in which oxidative energy was stored by UV-irradiated Pt–$TiO_2$ (gap, 12.5 μm; light intensity, 100 mW $cm^{-2}$; irradiation time, 1.5 h). Inset shows the oxidized $Ni(OH)_2$ film.

oxidation of alkyl chains, the following mechanism has been proposed; $H_2O_2$ generated on the photocatalyst is transported in air, then photocleaved into $^{\bullet}OH$ by UV light in the vicinity of the organic substrate, and the $^{\bullet}OH$ attacks the substrate (double excitation mechanism).[15–17]

In the present system, the possibility of direct oxidation of $Ni(OH)_2$ by $H_2O_2$ is excluded because $NiO_x(OH)_{2-x}$ is rapidly reduced by gaseous or aqueous $H_2O_2$ (eqn (5)) as mentioned above.

$$NiO_x(OH)_{2-x} + x/2H_2O_2 \rightarrow Ni(OH)_2 + x/2O_2 \qquad (5)$$

Indeed, a $Ni(OH)_2$ film was not darkened by exposure to $H_2O_2$.

However, there is a possibility that $Ni(OH)_2$ is oxidized by $^{\bullet}OH$ (eqn (6)), which is either produced *via* $H_2O_2$ or generated directly on $TiO_2$.

$$Ni(OH)_2 + x^{\bullet}OH \rightarrow NiO_x(OH)_{2-x} + xH_2O \qquad (6)$$

However, the oxidation was not observed when a $Ni(OH)_2$ film was exposed to $H_2O_2$ vapor under UV light ($H_2O_2$ + UV → $2^{\bullet}OH$). Even if $^{\bullet}OH$ oxidizes $Ni(OH)_2$, ambient $H_2O_2$ would reduce the oxidized form to $Ni(OH)_2$ immediately. The contribution of $^{\bullet}OH$ as well as $O_2^{-\bullet}/HO_2^{\bullet}$ is thus difficult to examine because $H_2O_2$ is used as a source of these species in general (*e.g.*, $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+}$, $H_2O_2 + Ce^{4+} \rightarrow O_2^{-\bullet} + 2H^+ + Ce^{3+}$).

On the other hand, $^1O_2$ can be produced from $O_2$ by using a dye, such as methylene blue or rose bengal, as a sensitizer ($^3O_2$ + vis → $^1O_2$).[24] Instead of a photocatalyst, a frosted glass coated with methylene blue (~1 μmol $cm^{-2}$) was positioned facing a $Ni(OH)_2$ film and irradiated with visible light (*ca.* 800 mW $cm^{-2}$) for 1.5 h. However, the $Ni(OH)_2$ film was not darkened. Hence, it seems unlikely that $^1O_2$ functions as a mediator in the remote energy storage system, at least by itself.

Since $Ni(OH)_2$ is known to be oxidized by $O_3$,[25] it is expected to function as a mediator (eqn (7)) if it is generated on $TiO_2$.

$$Ni(OH)_2 + x/2O_3 \rightarrow NiO_x(OH)_{2-x} + x/2H_2O + x/2O_2 \quad (7)$$

However, there has been no evidence of $O_3$ generation on UV-irradiated $TiO_2$.[23]

On the basis of these discussions, it is possible that $^{\bullet}OH$, $HO_2^{\bullet}$ or $O_3$ contributes to the remote energy storage as a mediator.

## Conclusions

Oxidative energy, which was generated on UV-irradiated $TiO_2$, was successfully stored in $Ni(OH)_2$ that was 12.5 μm apart from $TiO_2$, in air (> 80% RH). Loading the $TiO_2$ with Pt accelerated the remote energy storage. It was revealed that indirect energy storage mediated by a diffusing species is possible, at least in the gas phase. The stored oxidative energy could be used to oxidize gaseous $H_2O_2$, ethanol, formaldehyde and formate.

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