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Photochemical and Photoelectrochemical Behavior of a Novel $TiO_2/Ni(OH)_2$ Electrode

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ABSTRACT

Transparent $Ni(OH)_2$ films were electrochemically deposited onto TiO_2 layers which had been formed on conductive glass. This optically transparent composite electrode exhibited strong, reversible photochromic and electrochromic properties when either illuminated by a 75 W Xe lamp at open circuit or anodically polarized in 1.0 M aqueous NaOH electrolyte. The extent of electrode darkening depended on the intensity of UV light, exposure time, and applied potential. Electrochemical and optical-absorption measurements indicated that UV-photogenerated holes in the TiO_2 valence band recombined with electrons from the electrochromic $Ni(OH)_2$ layer, which consequently oxidized the $Ni(OH)_2$ to NiOOH and darkened the composite electrode. Because the darkening process occurred only on the specific electrode areas which were exposed to light, nonuniform illumination produced a patterned optical state of the electrode.

Introduction

The NiOOH-$Ni(OH)_2$ electrode is under consideration for use in electrochromic devices,[1-5] which are being developed for architecture, aerospace, and vehicle applications. The transparency change from clear to opaque (black) that accompanies the Ni^{2+} to Ni^{3+} oxidation reaction represents an advantage over electrochromic oxides which are strongly colored. Although significant knowledge about the electrochemical behavior of NiOOH-$Ni(OH)_2$ films has arisen from studies of nickel electrodes used in rechargeable alkaline batteries,[6,7] there remain several challenges related to the electrochemistry of the nickel electrode which affect its electrochromic properties. The crystalline structure, morphology, and porosity of the NiOOH-$Ni(OH)_2$ film, the character of adjacent sublayers and overlayers, and the electrolyte composition all determine the durability and reversibility of the electrochromic film. A thin $Ni(OH)_2$ film can be fabricated by a wide range of processes, including anodic oxidation, chemical and cathodic precipitation, sol-gel techniques, vacuum evaporation, etc. Electrochemical precipitation produces $Ni(OH)_2$ films that exhibit some of the best electrochemical as well as electrochromic properties.

The NiOOH-$Ni(OH)_2$ electrode is not photosensitive under natural illumination, therefore in an electrochromic device it must be used in combination with a photosensitive material. Semiconductor powders and thin films have been studied as effective photocatalysts for the conversion and chemical storage of light energy.[8-10] The interfacial charge-transfer processes in semiconductor-mediated photocatalytic reactions involve photogenerated free-charge carriers from conduction and/or valence bands. Photochemical properties of numerous metal oxides and metal chalcogenides have been studied for this purpose. Several approaches have been used to prevent photogenerated pair recombination and to enhance the efficiency of charge separation, thereby improving the photocatalytic activity. Examples include semiconductor doping,[11] deposition of a noble metal[12,13] or a second semiconductor[14-16] on the semiconductor surface, and coupling a semiconductor with redox mediators.[17,18]

Of particular relevance to the present work are recent studies of electrochromic and photosensitive oxide-electrode combinations. It was found that a suspension of WO_3 oxide particles in contact with TiO_2 acquire a deep blue color upon irradiation in the presence of water as a result of electron transfer from TiO_2 to $WO_3 \cdot H_2O$.[19] Bericher et al.[20] demonstrated the idea of a self-powered "smart" electrochromic window which combines two separate photosensitive electrodes: a dye-sensitized semiconductor TiO_2 electrode which drives a WO_3 electrode to change from transparent to dark blue. However, the authors ascribed the electrochromic effect of this composite system entirely to electronic charge transfer between the electrodes through an external circuit, neglecting the possibility of direct electron transfer between the two electrodes. The results of the present work show that direct electron transfer is responsible for spatially resolved coloration when only part of the composite electrode is illuminated. The photoelectrochromic effect in WO_3 colloids with steady-state UV photolysis in the presence of oxalic acid as a hole scavenger was studied in Ref. 21 and 22. DeBerry and Viehbeck[23] described the photoelectrochromic characteristics of thin prussian blue (PB) layers on both single-crystal and polycrystalline TiO_2 electrodes. It was found that illumination of the composite electrode led to the oxidation of the colorless prussian white (PW) film to PB at potentials at least 500 mV lower than the PW/PB redox potential for a modified Pt electrode. Tacconi et al.[24] reported photoelectrochromic bleaching and recoloration of methylene blue in aqueous or methanolic slurry suspensions of TiO_2.

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In this paper we report observations of reversible photochromism in an irradiated two-layer electrode, consisting of an electrochemically active $Ni(OH)_2$ layer deposited on a thin film of polycrystalline TiO_2. The evidence we present demonstrates that the observed photochromism arises from direct charge transfer between $Ni(OH)_2$ and photogenerated carriers within the space-charge layer in TiO_2. These initial results not only suggest the development of new class of electrochromic and optical devices, but also represent an interesting example of photocatalysis applied to an electrochemical system.

Experimental

Microporous nanocrystalline TiO_2 films were prepared on a 25 × 38 mm piece of indium-tin oxide (ITO) conducting glass (Donnelly Corporation) according to the coating procedure given in Ref. 25. The coating solution consisted of Ti(iso-$OC_3H_7)_4$ dissolved in ethanol mixed with isopropyl alcohol and hydrochloric acid. A detailed description of the solution composition and preparation method can be found in Ref. 25, 26. The glass substrate was spin-coated with the solution and dried in air under ambient conditions for 1 h. Finally, the coated film was heat-treated at 773 K for 1 h and cooled to room temperature in a dry N_2 atmosphere.

Nickel hydroxide films were deposited by galvanostatic cathodic precipitation onto freshly prepared TiO_2 or ITO glass substrates from an aqueous solution of 0.01 M $Ni(NO_3)_2$ as described elsewhere.[27] The films were deposited at ca. -14.3 mA/cm^2 for 20 s which corresponds to a charge capacity of 286 mC/cm^2 and films from 1 to 1.4 μm thick. The electrodes were rinsed thoroughly with distilled water and dried under ambient conditions for 4 h.

All measurements were performed in 1.0 M NaOH solution in a quartz cuvette. The optically transparent working electrode was inserted into the cuvette so that its transmittance changes could be recorded during electrochemical measurements. The counter electrode consisted of a Pt grid with a central hole to allow light passage, and all electrode potentials were measured and are quoted vs. a Hg/HgO/1 M NaOH reference electrode. All solutions were prepared using twice-distilled water and reagent-grade chemicals, and all measurements were performed at room temperature (298 K). Where necessary, the electrolyte was deaerated and kept under Ar gas.

Electrochemical measurements were made using an EG&G Princeton Applied Research (PAR) 362 scanning potentiostat coupled with a multichannel PC-controlled data-acquisition system, employing Keithley DAS20 hardware. For the photoelectrochemical measurements light from a 75 W xenon lamp (Osram) set in an Oriel housing model 6137 was transmitted through a 250-380 nm bandpass filter before irradiating the electrode. The light beam was focused uniformly into a 1 cm diam spot on the surface of the electrode, which was placed close to the wall of the quartz cell. The UV irradiation intensity was 30 mW/cm^2 at the electrode surface. Light-transmittance characteristics of the electrode were measured with an ISA Hr-320 single monochromator equipped with a 1024 channel EG&G PAR 1420 intensified photodiode array cooled to 253 K. This device was controlled by an EG&G OMA III optical multichannel analyzer, wherein collected data were initially processed. The entrance slit of the monochromator was placed behind the cell and was aligned with the Xe lamp optical axis. The transmittance of the electrode was monitored in the spectral range 515 to 552 nm, using the residual signal of the filtered Xe lamp. By using this arrangement, the Xe lamp provided a simple and convenient means to not only irradiate the electrode with near-UV light, but also measure transmittance changes in the visible region. For non-UV illuminated electrode transmittance measurements an additional 500 nm edge filter was used to remove the shorter (UV) wavelengths from the lamp spectrum. Near-UV and visible transmittance spectra of the $TiO_2/Ni(OH)_2$ films were obtained with a Perkin Elmer Lambda 9 spectrometer.

Ex situ AFM images were obtained with a molecular imaging (MI) scanning probe microscope coupled with a Park Scientific Instruments (PSI) electronic controller. For the AFM measurements PSI MLCT-AUNM microlevers (0.05 N/m) were used.

Results

Topographic AFM images (without numerical image processing) of the freshly prepared TiO_2 and $TiO_2/Ni(OH)_2$ electrodes are shown in Fig. 1. The TiO_2 film exhibits a compact surface structure, and the average thickness of a fired film after a single coating was found to be 115 nm.[25] The surface appears to be relatively uniform except for the presence of large TiO_2 aggregates of planar size ~200 nm. The existence of deep cracks and pores at grain boundaries may also be expected. This type of structure was characteristic for all TiO_2 films deposited under similar conditions. The electrochemical precipitation of $Ni(OH)_2$ produced a mostly featureless surface with rms roughness of ~3.5 Å. The thickness of the $Ni(OH)_2$ film was estimated to lie in the range from 1.0 to 1.4 μm, which is sufficiently large that the TiO_2 film morphology had no effect on the $Ni(OH)_2$ film surface texture. Indeed, the surface of the $Ni(OH)_2$ film is substantially smoother than the TiO_2 substrate. The uniform nanocrystalline $Ni(OH)_2$ film without large grains of crystallized material is expected to provide good adhesion to the TiO_2 substrate.

The photoelectrochemical properties of the TiO_2 electrode are represented by two cyclic voltammograms (CVs) recorded in Ar-saturated 1 M aqueous NaOH solution in the dark and under near-UV illumination (Fig. 2). Both curves exhibit behavior characteristic of n-type semiconductor electrodes. The slight cathodic current on the polycrystalline TiO_2 electrode in the dark corresponds to the water reduction reaction and/or the surface reduction of TiO_2,[6] which may be formulated as

$$(Ti^{4+})_4(O^{2-})_8 + nH_2O + ne^- \rightleftarrows (H^+)_n(Ti^{4+})_{4-n}(Ti^{3+})_n(O^{2-})_8 + nOH^- \quad [1]$$

Illumination of the TiO_2 electrode led to a rise of anodic photocurrent at potentials above -0.8 V due to the photooxidation of water. Photogenerated peroxo species present at the surface of the TiO_2 particles and also dissolved photogenerated oxygen are very good targets for the conduction

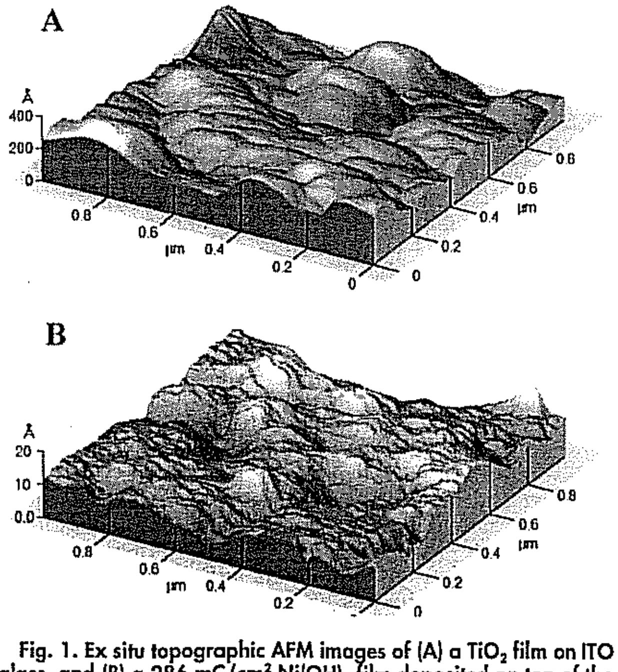

Fig. 1. Ex situ topographic AFM images of (A) a TiO_2 film on ITO glass, and (B) a 286 mC/cm^2 $Ni(OH)_2$ film deposited on top of the ITO/TiO_2 electrode.

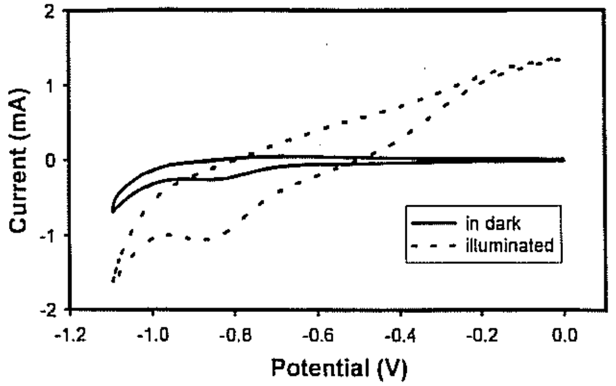

Fig. 2. Cyclic voltammograms of the ITO/TiO_2 electrode recorded in Ar-saturated 1.0 M aqueous NaOH solution in the dark and under near-UV illumination. Scans performed at 50 mV/s.

band electrons,[28-30] and consequently are reduced at potentials more negative than −0.5 V during the cathodic scan.

Figure 3 shows a cyclic voltammogram of a freshly electroprecipitated $Ni(OH)_2$ electrode on an ITO glass substrate carried out in 1.0 M aqueous NaOH. The redox couple located at ~0.41 V is associated with the well-known reaction usually written as

$$Ni(OH)_2 + OH^- \rightleftarrows NiOOH + H_2O + e^- \quad [2]$$

The oxidation peak at 0.46 V and the reduction peak at 0.36 V correspond to the darkening and bleaching processes, respectively. The visible spectral characteristics of $Ni(OH)_2$ films depend on the film thickness and film preparation method, however, in the reduced state they do not exhibit significant absorption bands in the visible range. This property renders them nearly transparent in the reduced state, whereas the spectra of the black NiOOH films show strong and broad absorption in the 300 to 700 nm range.[4,31] Illumination of the NiOOH electrodes with UV light neither altered the shape of the voltammogram nor induced visible photoeffects in the thin film. The active (oxidized) nickel material present in the thin film can be described as a mixed p-n conductor in which n-type conductivity normally predominates,[32] thus spontaneous photochromism is not expected.

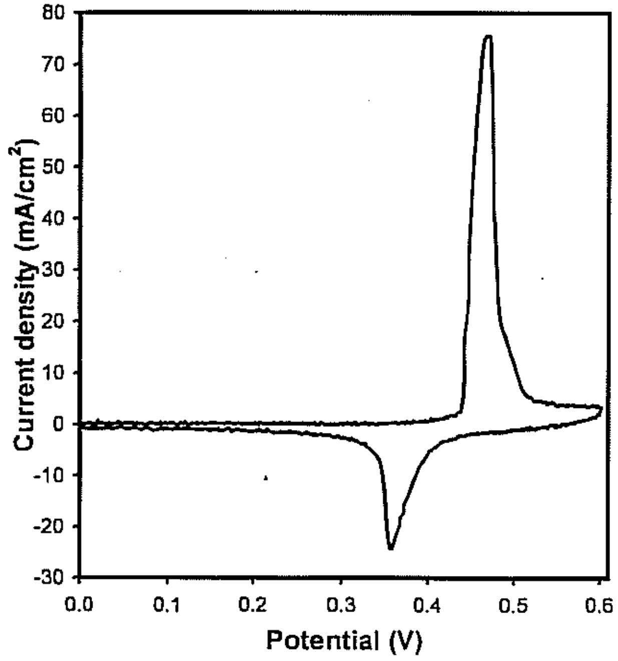

Fig. 3. Cyclic voltammogram of a 286 mC/cm² $Ni(OH)_2$ layer electroprecipitated onto a glass/ITO substrate in 1.0 M NaOH solution. Scan performed at 10 mV/s.

Illumination of the composite TiO_2-$Ni(OH)_2$ structure led to a gray-black appearance of the light-exposed area of the electrochromic material, even when the electrode was held at open circuit. The unexposed part of the electrode remained in its bleached state whereas the illuminated part became dark. At open circuit without illumination, the potential of the electrode varied between −0.2 and −0.4 V. Light absorption by the electrode material resulted in a substantial negative shift of the electrode potential to −0.8 to −0.9 V. In order to quantify the electrochromic behavior of the composite TiO_2-$Ni(OH)_2$ electrode, in situ absorption measurements were carried out during irradiation and/or polarization of the electrode. Figure 4 shows the electrode light-absorption (1 minus transmittance) change within the spectral range 515-552 nm vs. time of irradiation/bleaching. The darkening process at open circuit (A) began immediately upon irradiation, and its extent was a direct function of light intensity and light exposure time. After 18 min exposure the electrode transmittance decreased by 8%. When a UV filter ($\lambda < 500$ nm) was then interposed, the electrode returned to its original bleached state, thereby demonstrating that the origin of the photoeffect is TiO_2 bandgap excitation. Bleaching was accompanied by a spontaneous return of the electrode potential to its initial value in the bleached state, i.e., −0.3 to −0.4 V. Recovery to the reduced state after the UV light was blocked was ~5% slower than the darkening process. The effect was clearly reversible under these conditions and could be repeated for at least 40 times. The reversible photochromism of the TiO_2-$Ni(OH)_2$ electrode under open-circuit conditions represents a new observation, which may be found in other similarly prepared composite electrodes.[14-20,23,24]

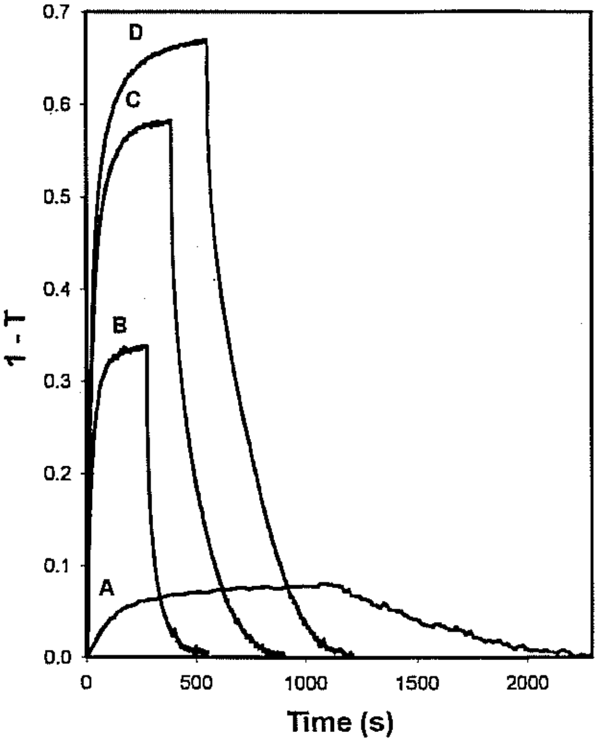

Fig. 4. Difference of integrated optical transmittance at $515 < \lambda < 552$ nm of a ITO/TiO_2/$Ni(OH)_2$ electrode measured as a function of UV irradiation/bleaching time and applied potential in 1.0 M NaOH solution. The electrode was irradiated at open-circuit potential (A) for 1053 s, then the UV light was blocked. Curves (B), (C), and (D) correspond to the electrode irradiated at −0.5, −0.3, and 0.0 V for 276, 389, and 550 s, respectively, and after the UV light was blocked and the potential was stepped to −1.1 V.

The electrochromic behavior of the composite electrode was investigated by recording light-absorbance changes vs. time at applied potentials between −1.1 and 0.0 V. Both cathodic and anodic electrode polarization had substantial effects on the darkening/bleaching rate. The absorbance reached 33, 58, and 67% at −0.5 (B), −0.3 (C), and 0.0 V (D), respectively (Fig. 4). The time required to complete the darkening process was ranged from 280 s at −0.5 V to 550 s at 0.0 V. Subsequent cathodic polarization at −1.1 V drove the electrode back to its bleached state whether or not UV light illuminated the electrode. The time required to bleach the electrode at −1.1 V was nearly identical to the corresponding time of coloration at each anodic potential.

Cyclic voltammetry results for the ITO/TiO_2/$Ni(OH)_2$ electrode in 1.0 M NaOH electrolyte are shown in Fig. 5. In the dark, no oxidation reaction was observed unless the anodic scan was extended above the potential of Ni^{2+} to Ni^{3+} oxidation. At potentials higher than 0.43 V, direct electrochemical oxidation of the $Ni(OH)_2$ layer is accompanied by darkening of the entire electrode surface (the scan shown in Fig. 5 was extended to 0.65 V, but the large anodic current is not shown in order to preserve the clarity of presentation). On the reverse scan, the NiOOH reduction peak at 0.32 V was followed by a large cathodic plateau at about −0.7 V. The charge associated with the reduction process was significantly lower than that of the anodic process. Consistent with this charge imbalance, the black color of the oxidized film remained when the potential was swept to −1.2 V. The film returned to its initial transparent state only after a 5 min cathodic polarization at −1.2 V. The voltammogram of the illuminated composite electrode (Fig. 5, dashed curve) shows differences in appearance compared to that of the single-layer TiO_2 electrode (Fig. 2), which suggests the presence of different photogenerated species. The darkening of the electrode and the shift of the cathodic peak toward higher potentials confirm this hypothesis.

The electrochromic behavior of the ITO/TiO_2/$Ni(OH)_2$ electrode was characterized by recording ex situ transmittance spectra of darkened and bleached electrodes (Fig. 6). The electrode was irradiated at 0.0 V in 1.0 M NaOH for 5 min, removed from the cell, rinsed with distilled water, dried in a stream of N_2, and then placed in the spectrometer. After the spectrum was recorded, the electrode was returned to the cell and polarized cathodically at −1.1 V for 5 min. The same procedure was then repeated to record another spectrum. The black coloration of the electrode typically persisted for 2 days in air; therefore we presume that changes which occurred during the electrode preparation and spectrum measurement are negligible. The spectrum of the oxidized electrode (solid curve, Fig. 6) exhibits a broad maximum centered around 480 nm, which is evident when viewed in comparison to the spectrum of ITO glass. The spectrum of the reduced film (dotted curve, Fig. 6) shows an absorption band shape very similar to that of the darkened film, however it is much more transparent. These results are in good agreement with previous optical studies of the nickel electrode.[4,31] The strong absorption band was shown to be responsible for the gray-black color of the sample and was assigned to charge transfer from high-valence nickel sites to oxygen. In contrast, the visible spectra of $Ni(OH)_2$ films in the reduced state show no significant absorption bands. The spectrum of the reduced electrode therefore corresponds to an intermediate stage of charge of the $Ni(OH)_2$ layer and indicates that the film was not fully reduced. Both spectra exhibit a strong absorption band in the UV region which extends to 420 nm and has been assigned to the bandgap absorption of TiO_2. The shape of the band at short wavelengths <350 nm may be somewhat distorted by the baseline correction process, because of significant light absorption by the ITO-coated glass in the UV region.

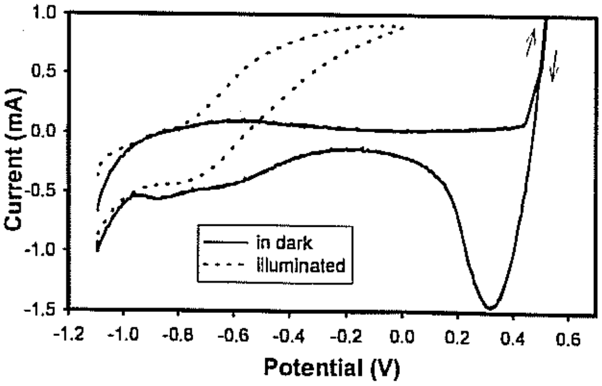

Fig. 5. Cyclic voltammograms of the ITO/TiO_2/$Ni(OH)_2$ electrode in 1.0 M NaOH electrolyte, with and without illumination. The potential sweep rate was 50 mV/s.

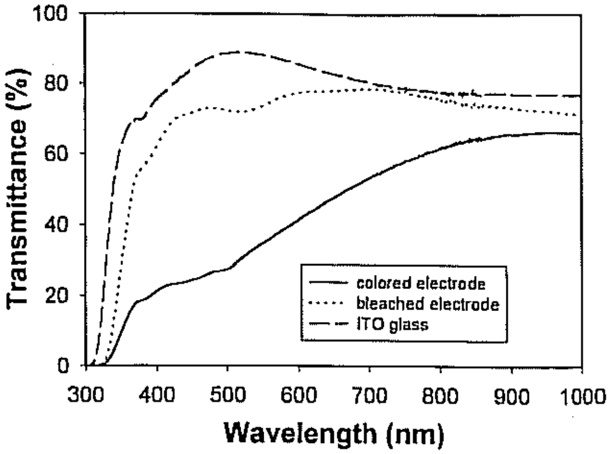

Fig. 6. Ex situ transmittance spectra of bare ITO glass, an ITO/TiO_2/$Ni(OH)_2$ electrode UV-irradiated in 1.0 M NaOH for 5 min, and a bleached electrode after electrochemical reduction at −1.1 V for 5 min in 1.0 M NaOH solution.

The contrast between the darkened area and transparent background was visibly sharp and exhibited good lateral resolution. The images shown in Fig. 7 were produced

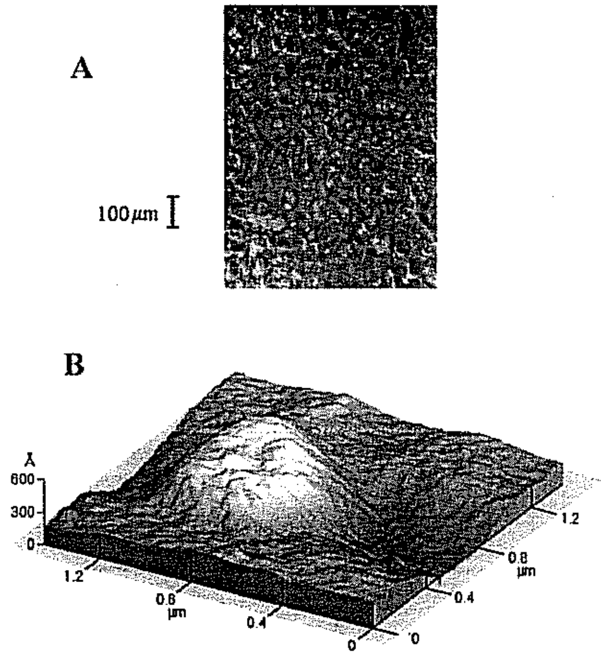

Fig. 7. Ex situ images of an ITO/TiO_2/$Ni(OH)_2$ electrode subjected to UV irradiation for 5 min in 1.0 M NaOH. (A) Photograph, (B) ex situ AFM topographic image.

by exposing the ITO/TiO_2/$Ni(OH)_2$ electrode in 1.0 M NaOH to filtered light from the Xe lamp at an electrode potential of 0.0 V for 3 min. The electrode was removed from the cell, rinsed in distilled water, and dried under ambient conditions for 30 min. The optical pattern on the dried electrode was stable and persisted in air for several days. The photograph of the electrode shows ~50 mm grains of predominantly NiOOH (dark areas) and $Ni(OH)_2$ (light areas), and indicates that the electrode surface is extensively cracked. This morphology could be a result of drying, however significant differences in the densities of the $Ni(OH)_2$ and NiOOH phases could result in such a morphology by creating mechanical stresses and consequent localized ruptures within the film. These observations are consistent with AFM studies of $Ni(OH)_2$ film microstructure modifications induced by aging and/or changes in the film oxidation state.[33,34] The AFM image (Fig. 7B) of the darkened electrode surface reveals a large feature ~800 nm in diameter and ~60 nm high. The photograph (Fig. 7A) recorded at much lower magnification showed that these micrograins are randomly distributed over a flat and featureless surface, and are identical to those seen on the original $Ni(OH)_2$ film.

Discussion

The spectroelectrochemical experiments described above highlight the photochromic and electrochromic behavior of the composite TiO_2/$Ni(OH)_2$ film. Our results indicate that the photochromism of the TiO_2/$Ni(OH)_2$ electrode originates from the bandgap absorption of TiO_2 in the near-UV region (<400 nm). It has been reported[35-37] that TiO_2 powders suspended in deaerated solvents develop a blue-gray color upon exposure to intense UV excitation. The mechanism of reversible photochromism in TiO_2 was assigned to light-induced trapping of electrons at Ti^{3+} sites in the presence of a solution-phase hole scavenger. This coloration was characterized by a quasi-continuous featureless absorption of the UV-irradiated TiO_2 from 430 to 1000 nm. The photoformed Ti^{3+} species are usually unstable and are easily quenched in the presence of O_2, except for the case when a very high-intensity UV laser was used and the blue color persisted in air for several months.[11] Our UV-vis spectra of the darkened and bleached composite TiO_2/$Ni(OH)_2$ electrodes (Fig. 6) revealed that the black-gray color of the UV-irradiated sample corresponds to the presence of Ni^{3+}, however the long tail which extends to ~1000 nm suggests the possible contribution from photogenerated Ti^{3+} sites.[11,35-37]

Because single films of either TiO_2 or $Ni(OH)_2$ deposited on ITO glass do not exhibit photochromism by themselves in the present experimental conditions,[8,25,26,29] the mechanism of the photochromic reaction in the TiO_2/$Ni(OH)_2$ electrode may be formulated as follows. Illumination of the composite electrode TiO_2/$Ni(OH)_2$ leads to the generation of electron-hole pairs in the conduction and valence bands, respectively, of TiO_2

$$TiO_2 + h\nu \rightarrow h^+ + e^- \qquad [3]$$

The holes migrate toward the TiO_2 surface because of the presence of an electric field induced by the space charge. Direct electron transfer from the $Ni(OH)_2$ phase to the TiO_2 layer proceeds because of the presence of photogenerated holes in the valence band (or hole-occupied surface states) of the TiO_2, which is thereby poised at a potential more positive than that of the Ni^{2+}/Ni^{3+} redox couple[4]

$$Ni(OH)_2 + h^+ \rightarrow NiOOH + H^+ \qquad [4]$$

Oxidation of the $Ni(OH)_2$ to NiOOH leads to the darkening of the electrochromic film from nearly transparent to gray or even black, depending on the light intensity and exposure time. The photogenerated electrons injected into the TiO_2 conduction band can diffuse toward the bulk region of the TiO_2 film, recombine with holes, or become trapped in the surface reduction of TiO_2. The formation of stable Ti^{3+} sites may contribute to the coloration of the electrode upon illumination. Importantly, the presence of trapped Ti^{3+} species decreases the efficiency of further photoinduced charge separation in TiO_2, [11] and thereby decreases the photochromic process efficiency. Moreover, an increasing concentration of majority charge carriers (i.e., electrons) in the space-charge layer will lead to the formation of an accumulation layer in the TiO_2 and a consequent negative shift in the conduction bandedge at the TiO_2 film surface. The excess of electrons in the TiO_2 phase is reflected by the remarkable negative 0.5-0.6 V shift of the electrode rest potential.

When the illumination of the electrode is blocked, the opposite process takes place. Electrons accumulated in the TiO_2 conduction band and/or trapped in Ti^{3+} sites become available for direct interfacial charge transfer (or through the surface states) to the NiOOH-$Ni(OH)_2$ layer and thereby reduce NiOOH to $Ni(OH)_2$. The electrochromic film then changes its appearance from gray-black to transparent. The bleaching process occurs somewhat more slowly than the darkening process, possibly due to the insulating properties of $Ni(OH)_2$ which inhibit electron transfer from the TiO_2 to unreduced parts of the electrochromic layer.[4] In addition, NiOOH film bleaching can occur due to the thermodynamic instability of nickel higher oxides with respect to the water oxidation reaction.[6]

The most striking aspect of this photochromic-electrochromic phenomenon is the extent of the photocatalytic effect. The oxidation of $Ni(OH)_2$ to NiOOH proceeded at potentials 1.3 V more negative than the Ni^{2+}/Ni^{3+} redox potential in 1.0 M aqueous NaOH. Moreover, photo-oxidation of $Ni(OH)_2$ to NiOOH caused the electrode potential to shift toward lower potentials, which is contrary to what is observed in dark electrochemistry. The energy bandgap and the photogenerated overpotential of the TiO_2 electrode surface are sufficiently large that despite its poor catalytic activity toward electron-transfer reactions, TiO_2 is an excellent photoelectrocatalyst. A composite catalyst consisting of two semiconductor materials is expected to exhibit enhanced catalytic activity, which is usually attributed to enhanced charge separation and altered relative band positions.[14,15,19] Similar photochromic behavior was observed for WO_3 in contact with TiO_2 irradiated in the presence of water, where a deep blue color developed as a result of direct electron transfer from TiO_2 to WO_3. [19]

The photochromic effect in the TiO_2/$Ni(OH)_2$ film was significantly enhanced when the electrode was polarized. At potentials more positive than −0.8 V, holes photogenerated in the space-charge region of the TiO_2 particles are scavenged by the adjacent $Ni(OH)_2$ film and drive the electrochromic reaction Ni^{2+}/Ni^{3+}, and electrons from the conduction band are collected by the positively charged conductive ITO sublayer and flow toward the counter electrode through the external circuit. Cations migrate from the electrochromic film to the counter electrode to complete the circuit. A slight positive polarization above −0.85 V enhanced substantially the efficiency and rate of the photoelectrochromic process. The dark color of the electrode could be preserved for several hours at positive bias after irradiation. As discussed earlier, similar photoelectrochromic behavior was reported by DeBerry and Viehbeck[23] for PB-modified TiO_2 electrodes, however those electrodes did not display photochromism under open-circuit conditions.

When the TiO_2/$Ni(OH)_2$ electrode was slightly polarized in the positive direction under dark conditions, the electrochromic reaction did not proceed because of the absence of light-generated charge carriers. However, at an anodic potential close to Ni^{2+}/Ni^{3+} redox potential, i.e., ~0.46 V, electrochemical oxidation of the electrochromic layer may occur through the micropores in the TiO_2 layer and direct electron transfer from the conducting substrate to the $Ni(OH)_2$ layer. This creates an additional mode of electrode control, which is usually employed in classical electrochromic devices wherein coloration/darkening can be achieved electrochemically without illumination. In such a case, the darkening of the electrochromic film occurs on the entire surface of the electrode and its intensity depends on the amount of charge passed through the system.

In order to drive the electrode back to its bleached state, a negative polarization is required for either an electrochemically or a photoelectrochemically oxidized electrode. In the negative polarization state, the majority charge carriers (electrons) migrate through the electrochromic film and drive the electrochromic reaction in the opposite direction. This purely electrochemical process reduced the black NiOOH to transparent $Ni(OH)_2$. The potential onset at which the reduction reaction occurred depended on whether the electrode was illuminated or not as well as on the concentration ratio of $Ni(OH)_2$/NiOOH in the electrochromic layer. However, the position of the reduction peak at −0.9 V during the cathodic scan remained fixed, independent of the experimental conditions.

Conclusions

This work describes photochromic properties of a novel composite $TiO_2/Ni(OH)_2$ electrode at open circuit and its electrochromic behavior in 1.0 M aqueous NaOH electrolyte upon illumination by a 75 W Xe lamp. The reversible transparent to black-gray coloration of the electrode observed upon UV illumination was a result of the Ni^{2+}/Ni^{3+} redox reaction driven by photogenerated charge carriers formed in the TiO_2 layer. Direct charge transfer between the photovoltaic TiO_2 film and the electrochromic $Ni(OH)_2$ film proceeds at potentials 1.3 V more negative than the standard potential of the $Ni(OH)_2$/NiOOH couple. The rate and efficiency of the composite electrode coloration were strongly enhanced by anodic polarization. Nonuniform illumination produced a patterned optical state of the electrode which could be preserved by positive polarization or erased by negative polarization.

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