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Photoelectrochromism in Chemically Modified Nickel−Titanium Dioxide Nanocomposite Films

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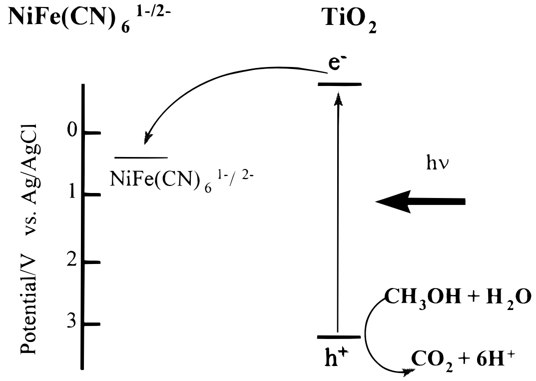
Electrochromic films that change their color in response to an electrical perturbation have attracted considerable recent interest stemming from potential applications in “smart” windows, displays, automobile rearview mirrors, and the like.[1,2] Their photoelectrochromic counterparts have been less widely explored to date. In the photoelectrochromic approach, the coloration → bleaching transition is triggered by initial optical excitation of a semiconductor followed by electron transfer to the chromic component (usually a dye) in the device. The reverse (bleached state → colored state) sequence occurs in the dark. An example of this approach is based on the TiO_2−methylene blue (MB) system.[3,4] On UV excitation of TiO_2, the initially blue MB dye is transformed to the colorless leuco state. The color is restored when the excitation light is turned off.

It is advantageous from a practical perspective to design a photoelectrochromic system of this sort wherein the active components (semiconductor and dye) are confined within a (solid) film. In this vein, recent authors have described composite films containing TiO_2 particles and either polyaniline[5,6] or prussian blue (PB).[7] Semiconductor electrodes coated with PB have also been described.[8,9] Finally, a hybrid device containing a dye-sensitized TiO_2 film and a WO_3 electrochromic counter-electrode has been recently reported.[10]

This paper describes an alternative approach to a photoelectrochromic device based on chemical modification of a nickel−TiO_2 nanocomposite film. Preparation of the latter was described by us recently;[11] these films are comprised of TiO_2 particles that are dispersed in a uniform manner within a continuous nickel matrix. In the present study, we have utilized chemical or electrochemical modification of the nickel component in these nanocomposites to obtain a nickel hexacyanoferrate (NHF)−TiO_2 film that, in turn, forms the basis for a new family of photoelectrochromic devices.

Scheme 1. Energy Diagram Showing Photoelectron Injection from the Occluded TiO_2 Particles to Oxidized NHF Sites within the NHF−TiO_2 Composite Film. The Photogenerated Holes Are Consumed by CH_3OH on the Composite Film Surface



We show below that optical transitions (and thus color changes) in the NHF component can be instigated by initial photoexcitation of the TiO_2 particle followed by electron transfer from it to the adjacent (oxidized) NHF sites within the film (Scheme 1). Concomitantly, the initially yellow film turns blue. This photoelectrochromic transition occurs at open-circuit (i.e., is thermodynamically spontaneous, Scheme 1) as long as hole scavengers (e.g., methanol) are present as illustrated in Scheme 1. The reverse transition (blue → yellow) can be accomplished (in the dark) by electrochemically reoxidizing the Fe(II) sites within the NHF component of the film (see below).

Derivatization of the nickel surface generally followed protocols described by previous authors.[12] In our case, the 0.01 M $K_3Fe(CN)_6$ + 0.1 M $NaNO_3$ medium that was employed for this purpose additionally contained 0.2 M TiO_2 (Degussa, P25). Films containing NHF and occluded TiO_2 thus could be grown either potentiostatically (0.7 V,[13] 5 min) or by simple immersion for several hours in the derivatization medium. In either instance, a surface-bound Prussian blue analogue, $[Ni^{II}(NC)Fe^{II/III}(CN)_5]^{2-/-}$, is generated on the nickel surface.[12] Cyclic voltammetry of the resultant films in 0.1 M

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(1) (a) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, 1995. (b) Granqvist, C. G. *Handbook of Inorganic Electrochromic Materials*; Elsevier: Amsterdam, 1995.

(2) Green, M. *Chem. Ind.* **1996**, *2 Sept*, 641.

(3) Kamat, P. V. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 509.

(4) de Tacconi, N. R.; Carmona, J.; Rajeshwar, K. *J. Electrochem. Soc.* **1997**, *144*, 2486.

(5) Kuwabata, S.; Takahashi, N.; Hirao, S.; Yoneyama, H. *Chem. Mater.* **1993**, *5*, 437.

(6) Yoneyama, H.; Tokuda, M.; Kuwabata, S. *Electrochim. Acta* **1994**, *39*, 1315.

(7) Nishizawa, M.; Kuwabata, S.; Yoneyama, H. *J. Electrochem. Soc.* **1996**, *143*, 3462.

(8) (a) Viehbeck, A.; DeBerry, D. W. *J. Electrochem. Soc.* **1985**, *132*, 1369. (b) DeBerry, D. W.; Viehbeck, A. *Ibid.* **1983**, *130*, 249.

(9) Ziegler, J. P.; Hemminger, J. C. *J. Electrochem. Soc.* **1987**, *134*, 358.

(10) Bechinger, C.; Ferrere, S.; Zaban, A.; Sprague, J.; Gregg, B. A. *Nature* **1996**, *383*, 608.

(11) (a) Zhou, M.; Lin, W.-Y.; de Tacconi, N. R.; Rajeshwar, K. *J. Electroanal. Chem.* **1996**, *402*, 221. (b) Zhou, M.; de Tacconi, N. R.; Rajeshwar, K. *Ibid.* **1997**, *421*, 111.

(12) (a) Bocarsly, A. B.; Sinha, S. *J. Electroanal. Chem.* **1982**, *137*, 157. (b) Bocarsly, A. B.; Sinha, S. *Ibid.* **1982**, *140*, 167. (c) Sinha, S.; Humphrey, B. D.; Bocarsly, A. B. *Inorg. Chem.* **1984**, *23*, 203. (d) Schneemeyer, L. F.; Spengler, S. E.; Murphy, D. W. *Ibid.* **1985**, *24*, 3044.

(13) A conventional three-electrode, single-compartment electrochemical cell was used for both anodic film growth and voltammetry. A Pt sheet was used as the auxiliary electrode, and Ag/AgCl/3 M KCl was used as reference. All potentials in this work are quoted with respect to this reference electrode.

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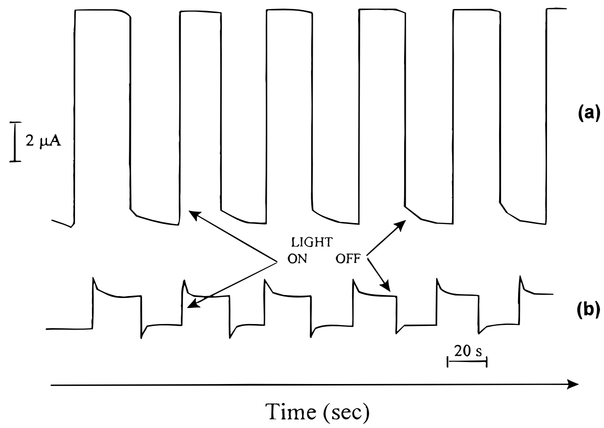

Figure 1. Photocurrent transients for a NHF−TiO_2 composite film in 0.1 M $NaNO_3$ at 0.6 V (a) and at 0.1 V (b). At 0.6 V, the NHF sites are in the oxidized state [Fe(III)] and at 0.1 V, the NHF component is electrochemically reduced [Fe(II)].

$NaNO_3$[14] exhibited the Fe(II) → Fe(III) redox signature at ca. 0.35 V with no interference from the TiO_2 component. The NHF−TiO_2 composite films grown either at open-circuit (i.e., chemically) or anodically, behaved in a similar manner such that no distinction is drawn between the two types of films in what follows below.

Figure 1 contains photocurrent transients[15] for a Ni-supported NHF−TiO_2 film potentiostated at 0.6 V (Figure 1a) and 0.1 V (Figure 1b) in 0.1 M $NaNO_3$. These two profiles correspond to the NHF component of the film in the oxidized and reduced states, respectively. Both the magnitudes of the photocurrents and the transient shapes are strikingly different in the two cases. The higher photocurrents and the plateau nature of the transients for the NHF film in the oxidized state (Figure 1a) are diagnostic of its facile reduction by the photogenerated electrons from TiO_2 as per Scheme 1. On the other hand, photooxidation of reduced NHF sites (by the photogenerated holes from TiO_2) is a sluggish process that does not compete very well with e^-−h^+ pair recombination. This is indicated by the spiked nature of the photocurrent transients in Figure 1b. Presumably, the photogenerated holes are also not transferred efficiently at the film surface under the electrostatic conditions existing at 0.1 V.

Figure 2 contains diffuse reflectance spectra for a NHF−TiO_2 composite film supported on nickel.[16] The spectra are shown before and after photoexcitation of the TiO_2 component in the film at open-circuit and are corrected for the background absorption of TiO_2. The two spectra correspond to the oxidized and reduced redox states of NHF respectively, or equivalently, to the two colored states of the photoelectrochromic device. The transition between the two states is stable and reversible. In the particular experiments in Figure 2, methanol was used as the hole scavenger. The reverse transition in the dark can be induced by pulsing the film from open-circuit to 0.7 V for a few minutes to reoxidize the Fe(II) sites within the NHF component. On the basis of previous studies on NHF, we presume that the spectral transitions seen in Figure 2 arise from ligand-field transitions located on Ni(II) and Fe(II) centers.[17]

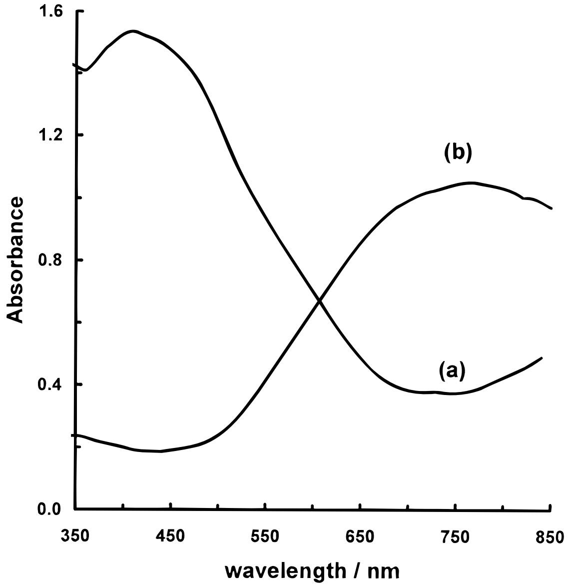

Figure 2. Diffuse reflectance spectra for a NHF−TiO_2 composite film before (a) and after (b) photoexcitation of TiO_2 particles occluded within the film. The NHF component was in its oxidized state and the film was yellow prior to illumination with the xenon arc lamp.

Finally, one can also envision an *electrochromic* system based solely on NHF.[17] In contrast, the present study shows that by combining NHF with TiO_2 in a composite film, a *photoelectrochromic* device can be realized wherein the transition is triggered in one direction by light, and the reverse sequence proceeds in the dark. For many applications, however, the time scales of these processes (several seconds to minutes) may be unacceptably slow. Another potential problem with active components such as NHF and PB relates to the intrinsic asymmetry of the redox transition in them in the two directions. This is because changes in the oxidation states within the film dictate counterion transport that can become rate-limiting under non-steady-state conditions.[12,17] Some of these issues are being addressed in experiments in progress.

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[14] These experiments were performed at potential scan rates ranging from 20 to 80 mV/s. The peak currents scaled linearly with the scan rate, and the peak separation at low scan rates approached zero, consistent with the behavior expected from a surface-confined redox system. See also: de Tacconi, N. R.; Carmona, J.; Rajeshwar, K. *J. Phys. Chem.*, in press, for further details.

[15] An Oriel 75 W xenon arc lamp was used for electrode illumination. The light was chopped at ~0.4 Hz at constant potential. The incident light flux was ca. 2.2 mW cm^{-2} over the range from 250 to 400 nm. This quoted value is not corrected for reflection/scattering losses.

[16] The reflectance spectra were acquired on a Perkin-Elmer Lambda 6 spectrophotometer using barium sulfate as reference.

[17] (a) Humphrey, B. D.; Sinha, S.; Bocarsly, A. B. *J. Phys. Chem.* **1984**, *88*, 736. (b) Sinha, S.; Humphrey, B. D.; Fu, E.; Bocarsly, A. *J. Electroanal. Chem.* **1984**, *162*, 351. (c) Arent, D. J.; Rubin, H. D.; Chen, Y.; Bocarsly, A. B. *J. Electrochem. Soc.* **1992**, *139*, 2705. (d) Arent, D. J.; Hidalgo-Luangdilok, C.; Chum, J. K. M.; Bocarsly, A. B.; Woods, R. E. *J. Electroanal. Chem.* **1992**, *328*, 295.