3524 *Chem. Mater.* **2004,** *16,* 3524–3532

Enhanced Mesostructural Order and Changes to Optical and Electrochemical Properties Induced by the Addition of Cerium(III) to Mesoporous Titania Thin Films

Karen L. Frindell, Jing Tang, John H. Harreld, and Galen D. Stucky*

Department of Chemistry and Biochemistry, University of California,
Santa Barbara, California 93106-9510

Received March 26, 2003. Revised Manuscript Received February 18, 2004

The addition of up to 10 mol % cerium(III) during the synthesis of cubic mesoporous titania thin films significantly increases the degree of mesostructural order in the final material. Photocurrent measurements, cyclic voltammetry, and spectroelectrochemistry show that the addition of cerium introduces a large number of interfacial states into the mesoporous material, which act as electron traps. Electron trapping by individual cerium ions also causes changes in the electrochemical properties of the mesoporous films. The mesoporous cerium-doped titania films show an increased electrochromic response that is indicated by an increase in absorbance at 550 nm with respect to pure titania. This effect is counter to the behavior of sol–gel ceria–titania films, which generally show a loss of electrochromism compared to pure titania.

Introduction

Mesoporous titania has been extensively researched mainly because of its potential use in applications such as photovoltaics[1–3] and photocatalysis.[4,5] In the past few years, several groups have successfully synthesized ordered mesoporous titania powders[6–12] and thin films.[13–16] Recently, it has been shown that well-ordered cubic mesoporous thin films with nanocrystalline walls can act as a sensitizing host matrix for luminescent rare-earth ions.[17,18] In particular, visible and near-IR luminescence from Eu(III), Sm (III), Nd(III), Yb(III), and Er(III) have been observed by exciting the band gap of the mesoporous titania thin films, suggesting energy transfer between nanocrystallites in the titania matrix and rare earth ions.

Besides enhancing the optical properties of mesoporous titania, the addition of rare earth ions also affect the stability and order of the mesostructure. For example, in the synthesis of wormlike mesoporous titania and alumina powders, trivalent lanthanum and cerium additives have been used to improve the temperature stability of the mesostructure.[9,19] This effect has been attributed to the ability of the lanthanide ions to repress crystallization of the oxide matrix,[20–22] which would otherwise cause densification of the walls and a loss of mesoscopic features. In the case of the ordered mesoporous titania thin films synthesized in our group, structural studies reported previously suggest that the doping of rare earth ions into the cubic mesostructure at loadings between 1 and 8 mol % improves the order in the film after calcination.[17]

While the structural properties of mesoporous materials have been studied extensively, the optical and electronic properties have been investigated to a much lesser degree. The study of the properties of mesoporous materials with enhanced or unusual optical and electronic functionality could lead to their use in new applications and devices. These studies are also important in the research of fundamental differences between mesoporous and bulk materials. One notable example

---

* To whom correspondence should be addressed. Fax: (805) 893-4120. E-mail: stucky@chem.ucsb.edu.

(1) Hagfeldt, A.; Graztel, M. *Acc. Chem. Res.* **2000**, *33*, 269–277.
(2) Gratzel, M. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 314–321.
(3) Gratzel, M. *Prog. Photovoltaics* **2000**, *8*, 171–185.
(4) Dai, Q.; Shi, L. Y.; Luo, Y. G.; Blin, J. L.; Li, D.; Yuan, C. W.; Su, B. L. *J. Photochem. Photobiol., A* **2002**, *148*, 295–301.
(5) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69–96.
(6) Wang, Y.; Tang, X.; Yin, L.; Huang, W.; Hacohen, Y.; Gedanken, A. *Adv. Mater.* **2000**, *12*, 1183–1186.
(7) Wang, Y.; Chen, S.; Tang, X.; Palchik, O.; Zaban, A.; Koltypin, Y.; Gedanken, A. *J. Mater. Chem.* **2001**, *11*, 521–526.
(8) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature (London)* **1998**, *396*, 152–155.
(9) Yue, Y.; Gao, Z. *Chem. Commun.* **2000**, 1755–1756.
(10) Yang, P.; Zhao, D.; Margolese, D.; Chemlka, B.; Stucky, G. *Chem. Mater.* **1999**, *11*, 2813–2826.
(11) Soler-Illia, G.; Louis, A.; Sanchez, C. *Chem. Mater.* **2002**, *14*, 750–759.
(12) Antonelli, D. *Microporous Mesoporous Mater.* **1999**, *30*, 315–319.
(13) Alberius, P. C. A.; Frindell, K. L.; Hayward, R. C.; Kramer, E. J.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **2002**, *14*, 3284–3294.
(14) Grosso, D.; Soler-Illia, G.; Babonneau, F.; Sanchez, C.; Albouy, P. A.; Brunet-Bruneau, A.; Balkenende, A. R. *Adv. Mater.* **2001**, *13*, 1085–1090.
(15) Hwang, Y. K.; Lee, K. C.; Kwon, Y. U. *Chem. Commun.* **2001**, 1738–1739.
(16) Yun, H. S.; Miyazawa, K.; Zhou, H. S.; Honma, I.; Kuwabara, M. *Adv. Mater.* **2001**, *13*, 1377–1380.
(17) Frindell, K. L.; Bartl, M. H.; Robinson, M. R.; Bazan, G. C.; Popitsch, A.; Stucky, G. D. *J. Solid State Chem.* **2003**, *171*, 81–88.
(18) Frindell, K. L.; Bartl, M. H.; Popitsch, A.; Stucky, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 959–962.
(19) Zhang, W. Z.; Pinnavaia, T. J. *Chem. Commun.* **1998**, 1185–1186.
(20) Masui, T.; Fukuhara, K.; Imanaka, N.; Sakata, T.; Mori, H.; Adachi, G. *Chem. Lett.* **2002**, 474–475.
(21) Francisco, M. S. P.; Mastelaro, V. R. *Chem. Mater.* **2002**, *14*, 2514–2518.
(22) Sibu, C. P.; Kumar, S. R.; Mukundan, P.; Warrier, K. G. K. *Chem. Mater.* **2002**, *14*, 2876–2881.

10.1021/cm0341989 CCC: $27.50

of the comparison of electronic properties in mesoporous and bulk materials is the investigation of the electrochromic properties of mesoporous WO_3 thin films by Cheng et al., who found that the films displayed enhanced electrochromic properties when compared to their sol−gel WO_3 counterparts.[23]

In this paper, we report on ordered mesoporous titania thin films which have been doped with varying amounts of cerium ions. This system has been investigated using photocurrent measurements, cyclic voltammetry, and spectroelectrochemistry. The possible role of the cerium ions in the electrochemical properties and electronic band structure of the mesoporous titania is described.

Experimental Section

Film Synthesis. In a typical synthesis of a mesoporous titania film, 3.88 mL of titanium(IV) ethoxide was added to 2.7 mL of concentrated hydrochloric acid and stirred for 5 min. In a separate beaker, 1 g of block copolymer (Pluronic P123, BASF) and 0−3 g (0−30 mol %) of $CeCl_3 \cdot 7H_2O$ were dissolved in 12 g of ethanol. The two solutions were mixed and stirred for 10 min. Sol−gel films were prepared in the same manner without any block copolymer added to the solution. The solution was aged for 10 min before dip-coating the films onto glass or $F:SnO_2$-coated (Libby Owens Ford, TEK-15) substrates. The films were then aged at 10 °C for 2−5 h and then calcined at 400 °C for 4 h.

Structural Characterization. Small-angle X-ray diffraction measurements were carried out on a Scintag X2 powder diffractometer with Cu Kα radiation. TEM measurements were taken on a JEOL 2000 transmission electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by removing the calcined films from the substrate using a razor blade. The powders were ground and dispersed in ethanol and a drop of the solution was placed on a copper TEM grid and allowed to dry.

Electrochemical Measurements. Photocurrent measurements were taken in a two-electrode cell with the TiO_2 or Ce−TiO_2 film on $F:SnO_2$-coated glass as the working electrode and a platinum mesh counter electrode. The measurements were carried out under the illumination from a 150-W Xe lamp. The electrolyte was a 0.1 M aqueous solution of sodium acetate. The data were collected using an ammeter under zero bias while the sample was illuminated with chopped light.

Cyclic voltammetry (CV) measurements were carried out using a three-electrode configuration using a TiO_2 or CeO_2−TiO_2 thin film on $F:SnO_2$-coated glass as the working electrode, a platinum counter electrode, and a saturated Ag/AgCl reference electrode. The electrolyte was a 1 M solution of $LiClO_4$ in propylene carbonate. The data were collected on an EG&G M273 potentiostat between 1.5 and −2.5 V vs Ag/AgCl at a scan rate of 1 or 10 mV/s. Spectroelectrochemistry measurements were carried out using the same three-electrode configuration in an optical cuvette inside of a CARY-14 OLIS spectrophotometer.

Results

Structural Characterization. TEM images show typical cubic pore structures present in the mesoporous titania and ceria−titania thin films (Figure 1). In previous work, the space group of this mesostructure has been assigned as body-centered cubic, $Im3m$.[13] The addition of cerium does not appear to affect the space group of the mesoporous titania. The pure and cerium-doped titania films show mesostructural domains oriented along the [100] and [111] directions. It was evident from the TEM analysis that the ordered domains are slightly larger in the cerium-doped samples.

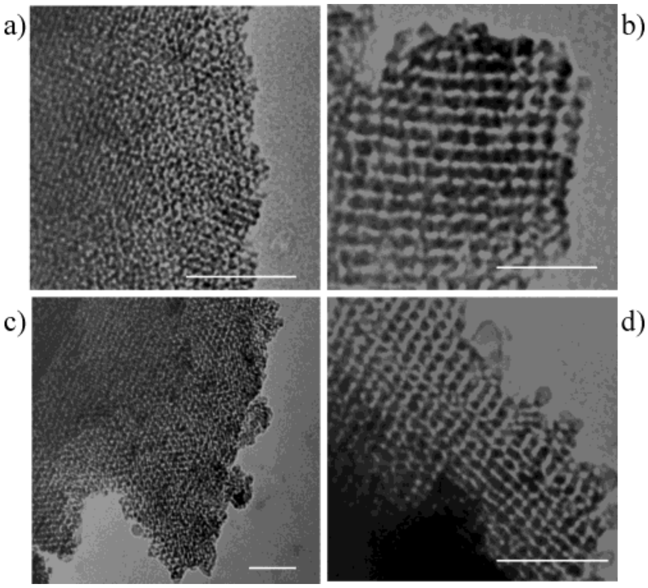

Figure 1. Typical TEM images of mesoporous thin films. (a) Pure TiO_2 along [111] zone axis, scale bar = 100 nm. (b) Pure TiO_2 along [100] zone axis, scale bar = 50 nm. (c) 8 mol % Ce−TiO_2 along [111] zone axis, scale bar = 100 nm. (d) 8 mol % Ce−TiO_2 along [100] zone axis, scale bar = 100 nm.

Small-angle X-ray diffraction was used to probe the degree of mesostructural order in the mesoporous thin films. After calcination of the oriented mesoporous TiO_2 or Ce−TiO_2 thin films, the [200] peak is present at a d spacing of 45 Å. A more intense and narrow X-ray peak at this d spacing is consistent with a more well-ordered mesostructure with larger domain sizes. The diffraction patterns for films doped with 0, 1, 4, 8, and 10% cerium ions show an increase in mesostructural order with increasing cerium content (Figure 2a). The lack of order in the undoped mesoporous titania sample can be explained by the fact that the films were aged at 10 °C for approximately 3 h, which is not enough time for the undoped mesoporous titania sample to obtain a high degree of ordering.[13] Another way to quantify the degree of order is by the decrease in the full width at half maximum (fwhm) of the X-ray diffraction peak; a smaller fwhm represents a more narrow distribution of pore and wall sizes and a larger domain size. The fwhm of the X-ray peak drops steeply with increasing cerium content (Figure 2b).

Photocurrent Properties. It has been suggested that a well-ordered mesoporous titania thin film may be a good candidate to improve the performance of extensively studied nanocrystalline dye-sensitized solar cells due to the large accessible surface area and uniform pore size in these materials.[3] Thus, it is especially important to investigate the effect of adding order-improving dopants on the photoconductivity of the titania matrix. While the addition of cerium to the titania mesostructure improves the ordering of the mesoporous titania thin films, it also affects the photocurrent substantially.

The photoresponse of the mesoporous titania thin films decreases dramatically with the addition of even a small concentration of cerium ion dopants (Figure 3).

---

(23) Cheng, W.; Baudrin, E.; Dunn, B.; Zink, J. I. *J. Mater. Chem.* **2001**, *11*, 92−97.

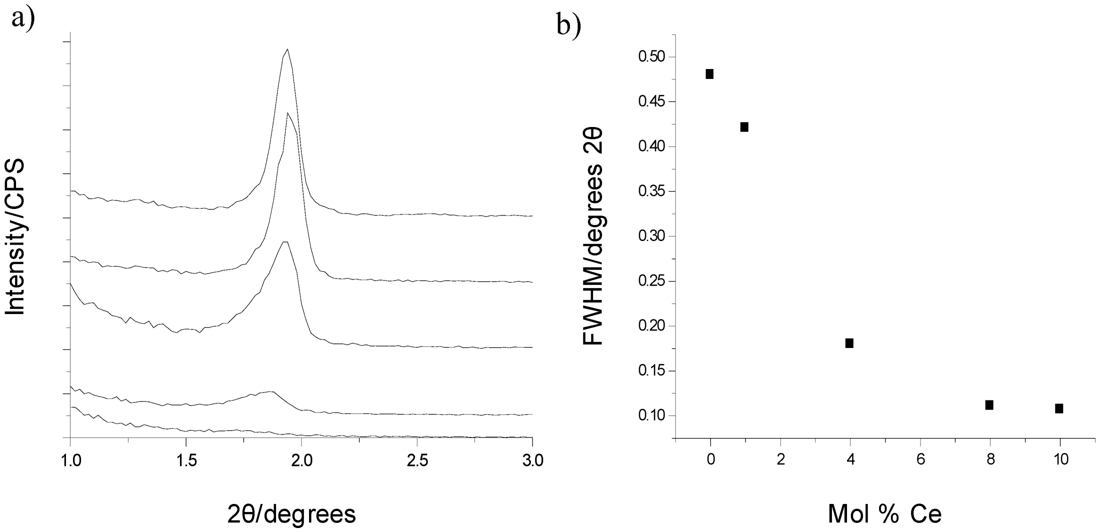

Figure 2. (a) Small-angle X-ray diffraction patterns of mesoporous TiO_2 and Ce−TiO_2 thin films. From bottom to top: Pure TiO_2, 1% Ce, 4% Ce, 8% Ce, and 10% Ce. (b) Plot of full width at half maximum of XRD peak as a function of mole fraction of Ce.

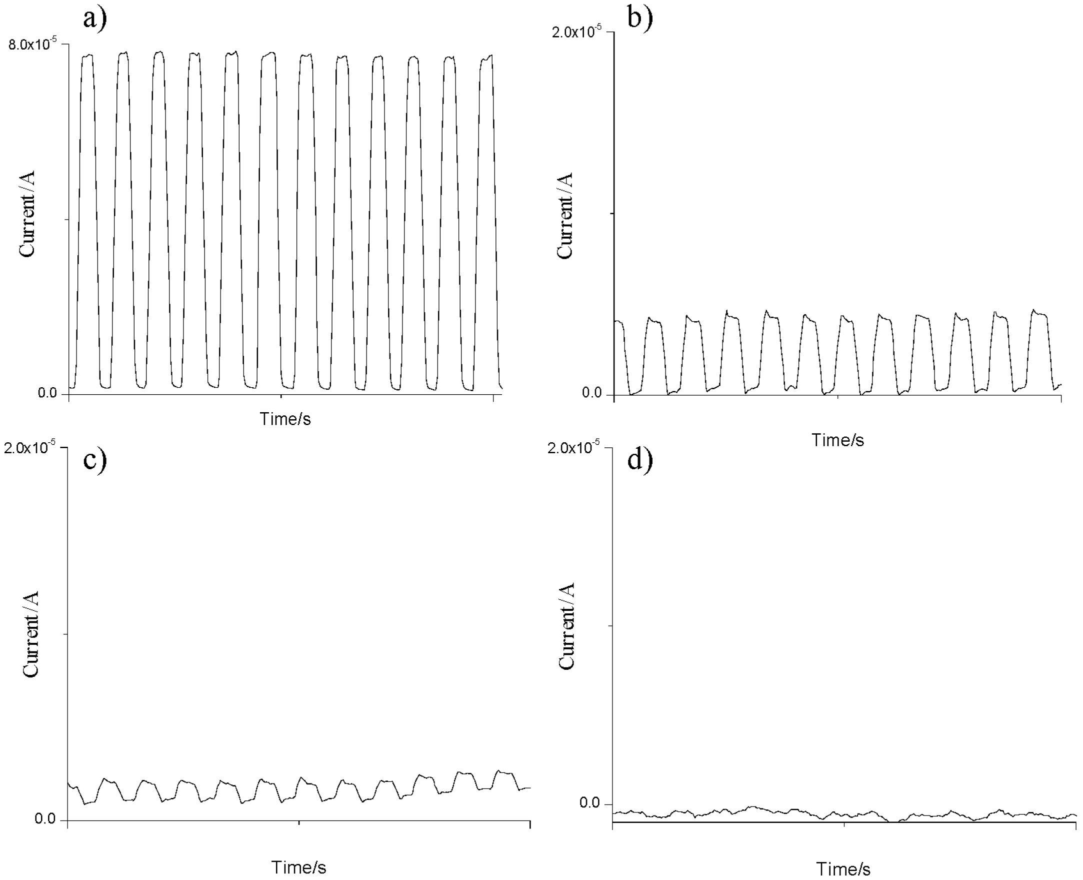

Figure 3. Photocurrent response for (a) pure mesoporous TiO_2, (b) mesoporous 2% Ce−TiO_2, (c) mesoporous 4% Ce−TiO_2, and (d) mesoporous 10% Ce−TiO_2 thin films. Peaks represent photocurrent and troughs represent dark current.

The measured response drops from about 30 to 2 μA/cm^2 with the addition of 2 mol % cerium ions to the film. Doubling the loading of cerium to 4% decreases the photocurrent by a factor of 5, and the photocurrent is completely deactivated when 10% cerium ions are added.

Cyclic Voltammetry Studies. The study of Li insertion by cyclic voltammetry was used as a probe to determine the effect cerium has on the electronic properties of the mesoporous titania thin films. The reaction that occurs during lithium insertion into the titania can be described as

$$n\mathrm{Li}^+ + n\mathrm{e}^- + \mathrm{TiO_2} \rightleftarrows \mathrm{Li}_n\mathrm{TiO_2} \qquad (1)$$

Previous work on Li insertion into nanotextured anatase done by Kavan et al. has revealed that titania systems that are made up of a mixture of crystalline and amorphous phases show distinct features in the CVs that result from the large number of interfacial sites present in this type of structure.[24] Their data show current responses resulting from lithium insertion into

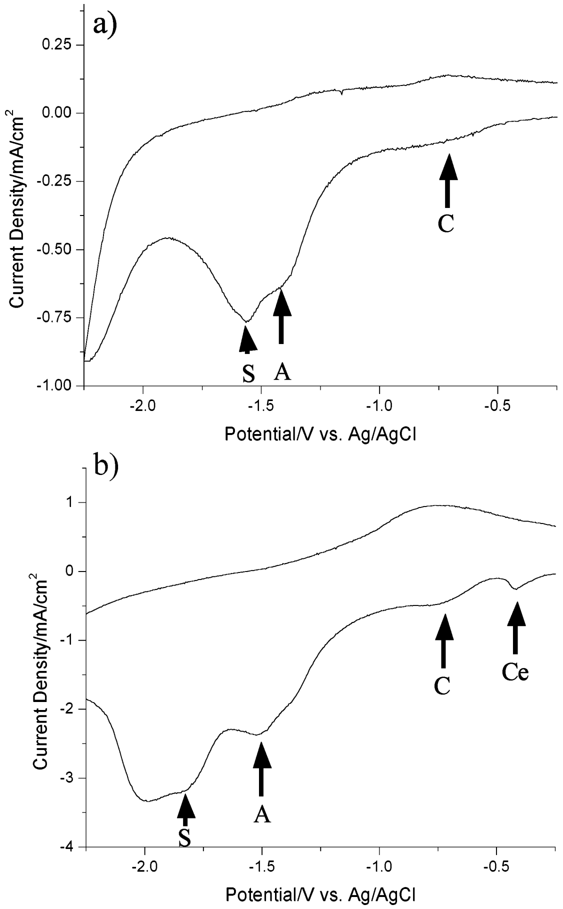

Figure 4. Cyclic voltammograms for (a) pure mesoporous TiO_2 and (b) mesoporous 2% Ce$-$$TiO_2$ thin films. Scan rate = 10 mV/s.

anatase crystals (A bands) and interfacial sites (S bands). These findings concur with the results for the cubic mesoporous titania thin films in the present work.

Typical CVs obtained at a scan rate of 10 mV/s for an undoped and a 2% cerium-doped mesoporous titania thin film show significant differences in their features (Figure 4). In a pure mesoporous titania film, the cathodic peak corresponding to Li insertion into anatase appears at about -1.4 V vs Ag/AgCl, and the cathodic peak resulting from surface or interfacial states appears at approximately -1.55 V vs Ag/AgCl. Both the A and S bands appear in the cerium-doped material as well, along with several new features. A cathodic peak that corresponds to the reduction of Ce^{4+} to Ce^{3+} appears at -0.5 V vs Ag/AgCl, and the S bands appear to be shifted to more negative potential (from -1.55 V to between -1.75 and -2 V). In both samples, a broad shoulder-like cathodic peak can be seen between -0.5 and -1 V vs Ag/AgCl. This peak has been assigned to capacitative or space charge effects at the surface of the titania film and the electrolyte and has been observed previously in nanocrystalline titania films.[25]

General trends in the lithium insertion properties occur with increasing amounts of cerium doped into the mesoporous titania thin films. Figure 5 shows selected cyclic voltammograms for mesoporous films containing 4%, 8%, and 25% cerium ions. The most noticeable trend is the shift of the Ce^{4+} reduction peak toward more negative potential as well as an increase in integral area, which is quantified for a number of samples with varying amounts of cerium added in Figure 5d. The peak corresponding to insertion of lithium into anatase (A band) decreases in intensity with respect to the surface state peak as the cerium content is increased. Also, the peak corresponding to lithium insertion into surface states (S band) exhibits a marked broadening and shift to more negative potential. These phenomena can be explained in terms of the changing nanotexture of the films as cerium is added, a model for which is presented in the Discussion section.

Repeated cycling of the potential sweeps in Ce$-$$TiO_2$ mesoporous thin films gives information about the reversibility of the Li insertion into this material (Figure 6). This type of information can be useful for evaluating the system for device applications. Reversibility is measured by the percentage of lithium that can be extracted from the material after one voltage cycle. In a sample doped with 8% cerium ions, it appears that there are sites with varying degrees of reversibility in the material. After the first cycle, the cerium ions have become irreversibly reduced from Ce^{4+} to Ce^{3+}, as can be seen from the disappearance of the peak at -0.5 V vs Ag/AgCl. Also, approximately half of the interfacial surface states trap lithium ions during the first cycle, and the remainder of them trap lithium ions during the second cycle. This irreversible step is in conjunction with the decrease and eventual disappearance of the peak at approximately -1.6 V vs Ag/AgCl. The third and fourth cycles show the Li insertion sites in the matrix that appear to be reversible to a greater degree than the insertion into anatase nanocrystallites.

Spectroelectrochemistry. Titanium dioxide is a known electrochromic material that turns from colorless to dark blue or black under cathodic bias potential.[25] EPR studies have shown that the coloration (usually blue, gray, or black) is the result of titanium(III) ions that are formed by the insertion of electrons and lithium ions into the titania.[26] Examining changes in the optical absorption spectrum of the mesoporous films as electrons are injected into the material provides information about its electronic structure.

A typical spectroelectrochemical profile for a pure mesoporous titania thin film shows two characteristic decreases in transmittance near 710 and 425 nm that appear as the voltage is decreased stepwise from 0 to -2.5 V vs Ag/AgCl (Figure 7). In previous literature reports, Kang et al. have described these broad bands as corresponding to various types of surface states in the titania. The spectroelectrochemical profile of a mesoporous 15% Ce$-$$TiO_2$ film shows a different spectroelectrochemical profile than that of pure titania (Figure 8a). The most prominent difference is the decrease in transmittance near 550 nm; the Ce$-$$TiO_2$ films show as much decrease at 550 nm as at 450 and 710 nm, while the pure titania films retain a relatively high transmittance in this region. The spectroelectrochemical profile of a 15% Ce$-$$TiO_2$ sol$-$gel sample shows significantly less decrease in transmittance throughout the

---

(24) Kavan, L.; Rathousky, J.; Gratzel, M.; Shklover, V.; Zukal, A. *J. Phys. Chem. B* **2000**, *104*, 12012$-$12020.

(25) van de Krol, R.; Goossens, A. *J. Appl. Phys.* **2001**, *90*, 2235$-$2242.

(26) Cao, F.; Oskam, G.; Searson, P. C.; Stipkala, J. M.; Heimer, T. A.; Farzad, F.; Meyer, G. J. *J. Phys. Chem.* **1995**, *99*, 11974$-$11980.

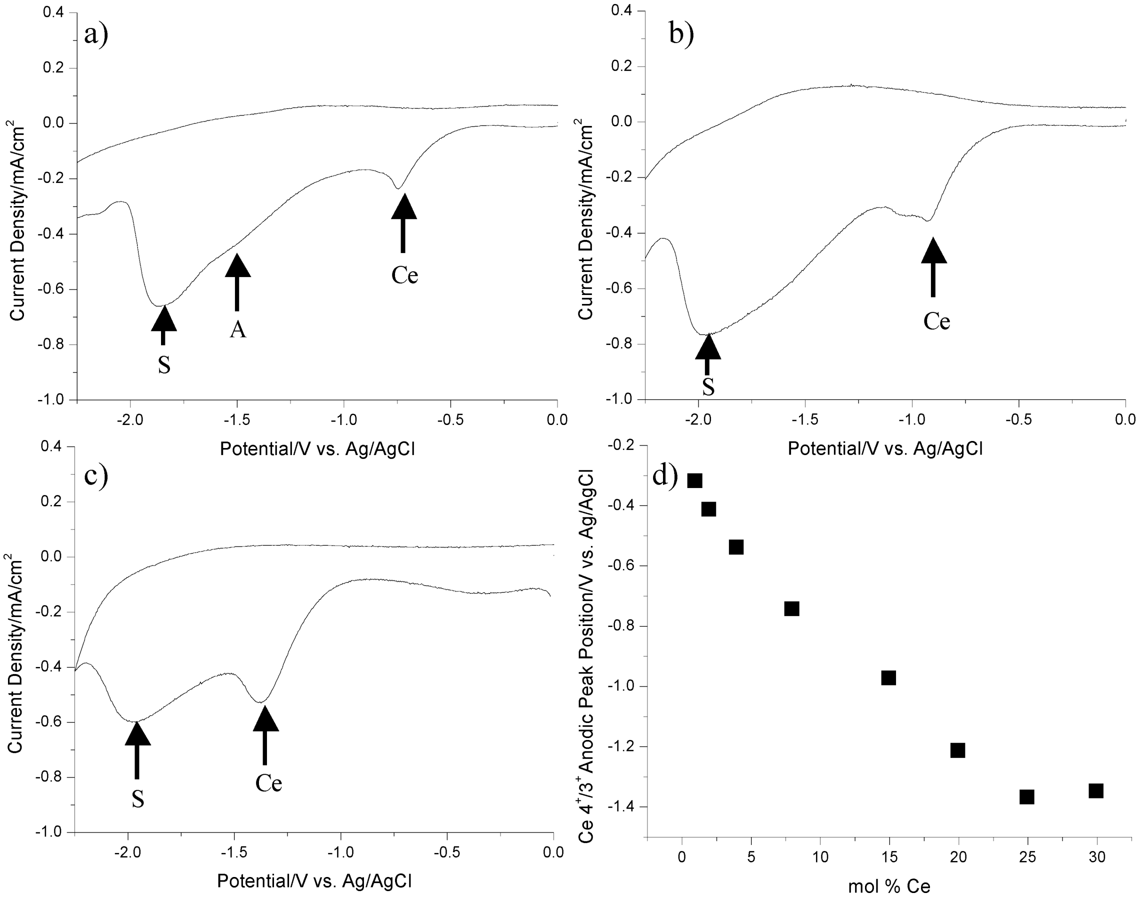

Figure 5. Cyclic voltammograms for selected compositions of Ce−TiO$_2$ thin films. Mol % Ce: (a) 4%, (b) 8%, and (c) 25%. Surface state peak is denoted by S, anatase peak by A, and Ce^{4+} → Ce^{3+} by Ce. (d) Position of Ce^{4+} reduction peak as a function of mol % Ce.

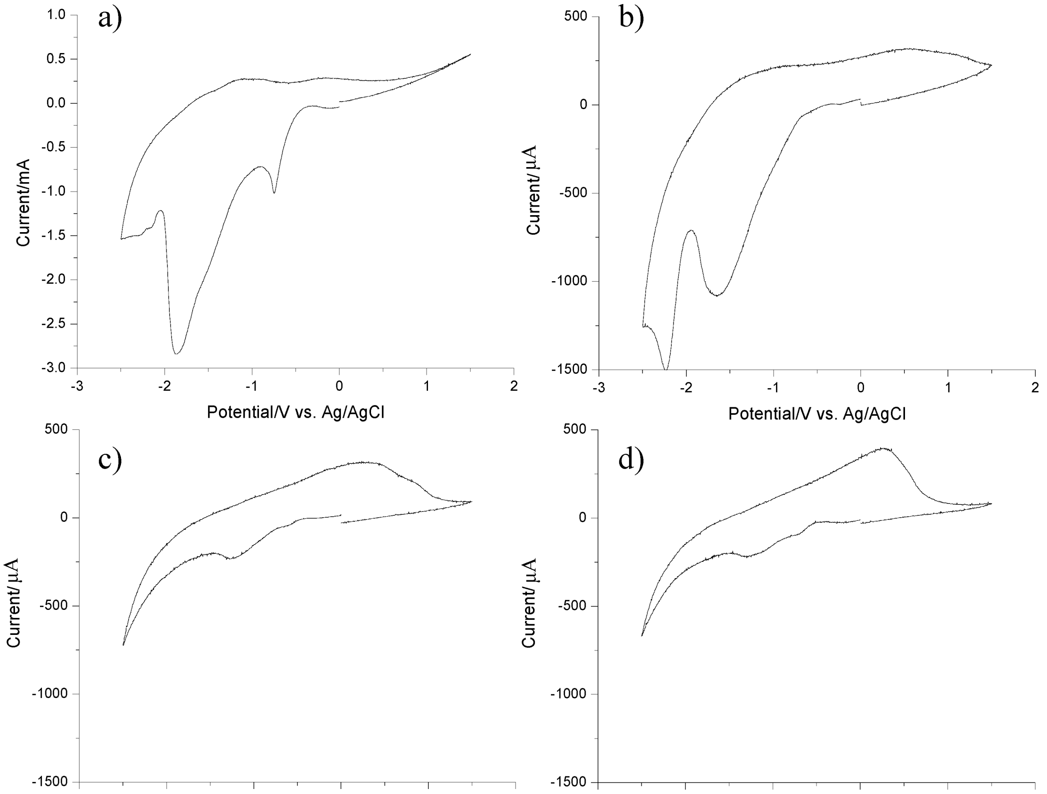

Figure 6. Cyclic voltammograms from four consecutive Li insertion and deinsertion cycles on a mesoporous 8% Ce−TiO$_2$ thin film. (a) First cycle, (b) second cycle, (c) third cycle, and (d) fourth cycle.

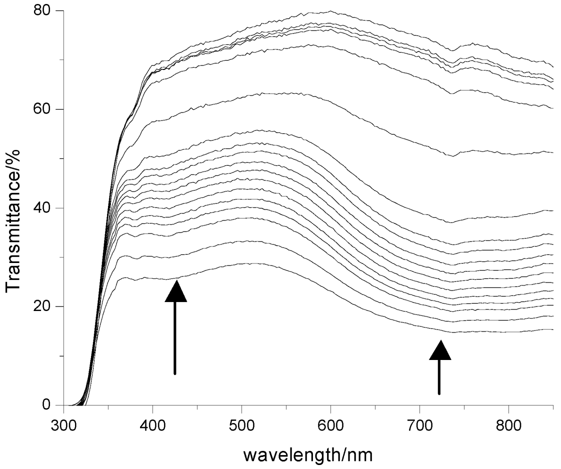

Figure 7. Spectroelectrochemistry of a pure mesoporous TiO_2 thin film for applied potentials between 0 V (top) and −2.5 V (bottom) vs Ag/AgCl. The voltage step increments are 0.25 V between 0 and −1.0 V, 0.05 V between −1.0 and −1.5 V, 0.25 V between −1.5 and −2.0, and 0.5 V between −2.0 and 2.5 V. Arrows denote areas of decreased transmittance.

same wavelength range while the voltage is decreased from 0 to −2.5 V (Figure 8b). In fact, the film turns a pale gray color rather than the characteristic deep blue of the titania.

The coloration efficiency (CE) is one way to quantify and compare differences in electrochromism between materials.[23,27] This figure can be calculated using the formula

$$\mathrm{CE} = \ln(T_{\mathrm{bl}}/T_{\mathrm{col}})/\Delta Q \qquad (2)$$

where T is the transmittance at a given wavelength in the bleached (0 V vs Ag/AgCl) or colored (−2.25 V vs Ag/AgCl) state and Q is the charge inserted into the material. In all samples, the coloration efficiency was measured at 550 nm. The pure mesoporous titania exhibited a CE of 9.5 cm²/C. For sol−gel samples synthesized in this work, the CE was 14 cm²/C for pure titania and decreases to 6 cm²/C when 15 mol % cerium(III) ions were added. In sputtered samples reported by Kullman et al., the CE at 550 nm decreased from 16 to 6 cm²/C when the amount of cerium in the sample was increased from 0 to 15 mol %.[27] The mesoporous samples showed a dramatically different effect; the 15% Ce−TiO_2 sample showed an *increase* in CE from 9.5 to 12 cm²/C. These results are summarized in Table 1. The reversal in trend for the electrochromic properties of the mesoporous materials is consistent with the differences in the cyclic voltammograms between the mesoporous and the sol−gel samples with 15 mol % cerium (Figure 8c,d). As mentioned previously, the band in the CV corresponding to the interfacial sites in the mesoporous titania broadens significantly with the addition of 15 mol % cerium ions. The 15 mol % Ce−TiO_2 sol−gel sample does not show peaks in the CV resulting from interfacial sites.

Table 1. Coloration Efficiency Data (cm²/C) for Several TiO_2 and Ce−TiO_2 Thin Films

	pure TiO_2	15% Ce−TiO_2
sputtered[a]	16	6
sol−gel	14	6
mesoporous	9.5	12

[a] See ref 30.

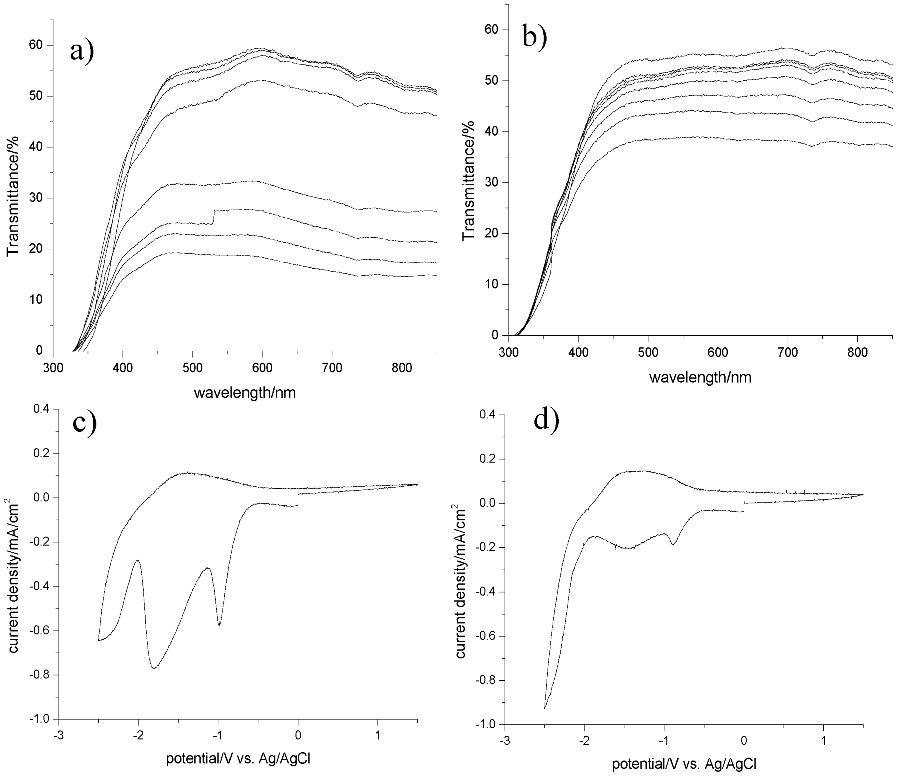

Figure 8. Spectroelectrochemical profiles and cyclic voltammograms of 15% Ce−TiO_2 films (a), (c) mesoporous, (b), (d) sol−gel. For (a) and (b), applied potentials are between 0 V (top) and −2.25 V (bottom). Voltage step increments are 0.5 V between 0 and −1.0 V and 0.25 V between −1.0 and −2.25 V.

Discussion

Mesostructural Ordering. It is evident through the TEM and X-ray diffraction data that the addition of cerium ions to mesoporous titania thin films improves the mesoscopic order of the final calcined material by increasing the domain size and thereby narrowing the XRD reflections. It is known that lanthanide ions are not as reactive as the titania precursor species, and the ability of the lanthanides to interfere with the condensation and crystallization of the titanium oxide matrix has been used to explain an increase in thermal stability in wormlike mesoporous materials[9,19] as well as an inhibition of the growth of titania nanocrystals.[22]

This interruption of the network is also likely to be the reason for an increase in mesostructural order. In the case of the mesoporous titania thin films, it has been determined that the successful synthesis of an ordered cubic phase depends greatly on controlling the size of the initial building blocks.[11,13,14] If the hydrolyzed titania building blocks are allowed to condense into larger species, the order of the final material is decreased. The presence of lanthanide ions in the film precursor solution and in the precalcined film may result in decreased condensation activity, thus preserving mesoscopic order. Additionally, rapid and widespread crystallization of the titania matrix is another cause of disorder in the final material. The cerium ions have the ability to limit crystal intergrowth of the titania nanocrystallites, thus delaying or preventing widespread crystallization of the mesoporous film.

Photocurrent Properties. The deleterious effect on the photoresponse caused by the cerium ions added to the films can be explained by considering that the cerium ions are sitting at the edges of titania nanocrystallites embedded in the semicrystalline framework of the mesoporous titania thin films.[17,18] During the calcination process, it is known that approximately half of the cerium(III) ions are oxidized to cerium(IV). Cerium(IV) ions can act as electron-trapping centers by interrupting the band structure of the titania. When a photoinduced conduction band electron in the titania is transferred to a cerium(IV) ion, it is reduced to cerium(III). Increasing the cerium concentration will intensify this trapping phenomenon, which ultimately decreases the carrier mobility in the film (Figure 3). In addition to electron trapping, reduced titania crystallinity and smaller grain size caused by the presence of cerium may also contribute to the loss of photocurrent.

Cyclic Voltammetry Studies. The trends in the cyclic voltammograms provide insight into the effect cerium has on the electronic structure of mesoporous titania. The most noticeable trend is the voltage shift and increase in integral area of the cerium(IV) reduction peak with increasing cerium content. The increase in area corresponds to an increase in the amount of cerium ions, which results in more accessible sites for reduction. The shift of this peak toward more negative potential can be explained by the fact that an increase in the percentage of cerium in the mesoporous titania thin film causes the growth of cerium oxide nanocrystallites which increase in size as more cerium is added.[28] The insertion of lithium ions into the larger nanocrystals may become more difficult, thus requiring a higher potential.

Two additional effects of adding cerium to the titania thin films appear as changes to lithium insertion sites in the titania. The first of these changes is the disappearance of the anatase peak with increasing cerium content, which is consistent with an increased crystallization temperature and a decrease in crystallite size of anatase caused by the addition of cerium ions. The effect rare earth ions have on titania crystal growth has been documented by others in the case of titania colloids doped with lanthanum and cerium.[21,22] It is proposed that the relative inertness of the rare earth ions reduces the overall lability of the oxide matrix at high temperatures, thereby delaying crystallization. Since all of the films in this study were calcined at 400 °C, the growth of the titania crystallites in the cerium doped films is expected to be inhibited.

The other prominent change in the cerium-doped titania cyclic voltammograms is the marked broadening of the peak that corresponds to the interfacial sites or S bands in the titania. The peak, which starts out at approximately 1.6 V vs Ag/AgCl in the undoped sample broadens and its center shifts toward −2 V vs Ag/AgCl. The broadening of the peak can be attributed to new surface states that are created by cerium ions at the edge of the anatase nanocrystallites. The nature of surface states in titania has been discussed in the literature, and they are commonly described as coordinatively unsaturated titanium(IV) ions at the surface of the particle.[29−31] In these unique mesostructured titania thin films, the nanocrystallites have surface states that likely result from grain boundaries between the nanocrystallites and the amorphous titania matrix. Adding cerium ions to the structure creates new types of grain boundaries with different energies, such as that of a titanium ion at the surface of a nanocrystallite with cerium ions as its next nearest neighbor. As the cathodic peak corresponding to the reduction of cerium(IV) ions shifts to a more negative potential; the broadening surface state peak also shifts likewise. A larger number of surface states with varying energies are created in the mesoporous titania thin films when the cerium content is increased due to more grain boundaries and smaller crystallite size. At cerium levels above 20 mol %, the cathodic peak corresponding to the surface states begins to decrease in area, although it still broadens. This effect is attributed to the fact that the cerium content is so high that fewer titania surface sites are accessible.

The results for the repeated cycling of a mesoporous cerium-doped titania thin film suggest that advantages of the high surface area afforded by an ordered mesoporous film may be compromised by the fact that the surface states between the nanocrystallites provide some irreversible trapping sites for lithium ions. Re-

---

(27) Kullman, L.; Azens, A.; Granqvist, C. G. *J. Appl. Phys.* **1997**, *81*, 8002−8010.

(28) Keomany, D.; Petit, J. P.; Deroo, D. *Sol. Energy Mater. Sol. Cells* **1995**, *36*, 397−408.

(29) Zhu, C. Z.; Ding, C. X. *J. Solid State Chem.* **1999**, *145*, 711−715.

(30) Zhu, Y.; Ding, C.; Ma, G.; Du, Z. *J. Solid State Chem.* **1998**, *139*, 124−127.

(31) Kumar, R. M.; Badrinarayanan, S.; Sastry, M. *Thin Solid Films* **2000**, *358*, 122−130.

versibility of lithium insertion may depend on variables such as the electrolyte and lithium ion concentration and the system could most likely be further optimized. The data suggest that, in its present state, this type of mesoporous material exhibits some characteristic Li^+ trapping at crystallite interfaces.

Spectroelectrochemistry. The results for the mesoporous titania thin films are consistent with spectroelectrochemical data found in the literature for nanocrystalline TiO_2 made from sintered colloidal particles. The absorption bands at 450 and 710 nm that represent the filling of two types of surface states with conduction band electrons have been assigned by Kang et al., who determined the positions of these trap levels by fluorescence measurements of the nanocrystalline titania in its colored state.[32] The 710-nm band appears at less negative potential and has been assigned to shallow traps or surface defects roughly 0.1−0.6 eV below the titania conduction band. The 450-nm band appears at more negative potential and has been assigned to deep surface states with an energy 1.2 eV below the conduction band. A similar situation appears to occur in the data shown in Figure 7; the broad band near 710 nm appears under less applied negative potential than the band near 425 nm. This corresponds to the filling of two interband surface states.

As has been demonstrated thus far, the electrochemical properties of bulk titania are significantly altered by the addition of cerium ions. According to literature reports, the addition of 15 mol % cerium ions to the titania thin films is expected to decrease the electrochromism of the titania[27] In fact, it has been previously established that the addition of a critical amount of cerium (~20 mol %) to bulk TiO_2 thin films eliminates the electrochromic effect of the titania altogether.[27,33,34] Sol−gel titania films synthesized in this work and doped with 15 mol % cerium ions showed a loss in electrochromism that is consistent with these literature reports. Under cathodic bias potential, the sol−gel films turned pale gray, rather than the deep blue associated with pure titania. The cause of the vanishing electrochromism effect in ceria−titania has been attributed to the reduction of cerium(IV) in place of titanium(IV),[27] which occurs without a color change.

In contrast, the cerium-doped mesoporous titania thin films in this study show an effect opposite to the vanishing electrochromism reported for sputtered and sol−gel cerium-doped titania films. The mesoporous samples doped with 15% cerium showed an increase in electrochromism as quantified by an increase in coloration efficiency measured near 550 nm. The changes in the absorbance spectrum of titania that occur during coloration have been used in conjunction with cyclic voltammetry to create a model of electronic structure of the material.

The mesoporous titania sample doped with 15% cerium shows a decrease in transmittance near 710 nm similar to the one that occurs in the pure mesoporous titania sample (Figure 8a). Although it is not as pronounced as in the pure mesoporous titania sample, it indicates that there are titanium atoms that are still accessible to the lithium ions and electrons. Another effect visible in this sample is that the decrease in transmittance appears to be uniform across the visible region with the exception of the small band at 710 nm. In other words, the sample turns deep blue-black rather than the usual blue color observed for pure mesoporous titania. The fact that the transmittance at 550 nm decreases much more for the cerium-doped mesoporous sample compared with pure mesoporous titania is consistent with the increase in coloration efficiency for this wavelength.

These variations in electrochromic behavior can be accounted for by examining the mechanism involved in coloration of the material. The deep blue color of the titania is attributed to the absorption of light by the titanium(III) ions and has been described as polarons hopping between neighboring titanium ions.[27] A more uniform decrease in transmittance indicates the presence of titanium(III) species that absorb light over an extremely broad range of energies, which implies that the environment around those titanium ions is more diverse. This diversity of sites could be introduced by the large number of surface states in the material, each with many its own proximity to cerium ions. If cerium(IV) ions take part in polaron absorption, it is also reasonable to expect that polarons are hopping between titanium and cerium ions.

Since the sol−gel samples densify to a much greater extent upon heating than do the mesoporous samples, there is a lower concentration of titanium sites that are available to be reduced during the lithium insertion than there is in the mesoporous structure. Also, fewer cerium sites appear to be accessible for reduction, as can be seen by the diminished size of the peak corresponding to the reduction of cerium.[18,29,30,35]

Conclusion

Structural, optical, and electrochemical properties of mesoporous titania thin films doped with ceria were investigated in this study and compared to pure mesoporous titania as well as bulk sol−gel materials. It was found that the addition of cerium ions to the mesoporous titania structure increased the degree of mesoscopic ordering because of the reduction in lability of the oxide matrix and the repression of the crystallization of anatase in the walls. The photocurrent response of the mesoporous thin films dropped dramatically as the amount of added cerium was increased. The loss in photocurrent can be explained by the fact that the cerium−titanium oxide films have smaller anatase nanocrystallites and also that cerium ions trap photogenerated electrons.

Electrochemical characterization revealed several effects of increasing the content of cerium in the mesostructure and presented significant differences between mesoporous and bulk (sol−gel or sputtered) cerium-doped titania materials. The large number of interfacial surface states is the greatest structural difference between the mesoscopically ordered thin films and the more dense sol−gel films. The presence of these surface

---

(32) Kang, T.; Kim, D. H.; Kim, K. *J. Electrochem. Soc.* **1998**, *145*, 1982−1986.

(33) Azens, A.; Kullman, L.; Ragan, D. D.; Granqvist, C. G. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 85−91.

(34) Mattsson, M. S.; Azens, A.; Niklasson, G. A.; Granqvist, C. G.; Purans, J. *J. Appl. Phys.* **1997**, *81*, 6432−6437.

(35) Liu, Y.; Claus, R. O. *J. Am. Chem. Soc.* **1997**, *119*, 5273−5274.

states results in the gain rather than loss of electrochromic behavior upon adding cerium to the titania samples. This surface state model was validated by the cyclic voltammetry study, which shows an increase in the surface state peak as more cerium is added.

The ordered porous networks, high surface area, and surface accessible porosity associated with this type of mesoporous thin film suggests great potential for their use in device applications such as solar cells, electrochromic devices, and batteries. The electrochemical evaluation of these mesoporous titania films has revealed another important point. A more highly ordered network was achieved at least partially by repressing crystallization through the incorporation of cerium ions, which had a negative effect on the photoconductivity of the material. The mesoscopic ordering and the conductivity of this material should be simultaneously optimized to realize its potential.

Acknowledgment. The authors thank Thomas Jaramillo for assistance with photocurrent measurements and Professor Eric McFarland for the use of equipment. This work was supported by the U.S. National Science Foundation under Grants DMR 00-80034, DMR 96-34396, and DMR 02-33728.

CM0341989