ACADEMIC
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Visible and near-IR luminescence via energy transfer in rare earth doped mesoporous titania thin films with nanocrystalline walls

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Abstract

Selected photoluminescence in the wavelength range of 600–1540 nm is generated by energy transfer from a light-gathering mesostructured host lattice to an appropriate rare earth ion. The mesoporous titania thin films, which have a well-ordered pore structure and two-phase walls made of amorphous titania and TiO_2 nanocrystallites, were doped with up to 8 mol% lanthanide ions, and the ordered structure of the material was preserved. Exciting the titania in its band gap results in energy transfer and it is possible to observe photoluminescence from the crystal field states of the rare earth ions. This process is successful for certain rare earth ions (Sm^{3+}, Eu^{3+}, Yb^{3+}, Nd^{3+}, Er^{3+}) and not for others (Tb^{3+}, Tm^{3+}). A mechanism has been proposed to explain this phenomenon, which involves energy transfer through surface states on titania nanocrystals to matching electronic states on the rare earth ions.

1. Introduction

Mesoporous titania has been a long sought after material because of its potential usefulness in applications such as solar energy conversion [1–3], battery applications [4] and photocatalysis [5]. Mesostructured titania powders and thin films have been synthesized by a number of groups using several different approaches over the past few years [6–15]. These approaches include various attempts to slow down the condensation of the highly reactive titanium (IV) precursors such as ligand-assisted templating [16], non-hydrolytic routes [13,14], the addition of chelating agents [17], and high acid concentrations [10,18,19]. In particular, sol–gel derived mesoporous titania thin films developed previously in our group using the latter method have a well-ordered cubic or hexagonal array of nanometer-sized pores, and a wall structure that is mostly crystallized, made of 2–5 nm anatase nanocrystallites, with regions of amorphous titania at the interface [18]. The thermal stability of these films, with maintenance of structural integrity, is preserved up to at least 450°C.

This two-phase structured material has found an interesting application as an excellent host for trivalent europium ions, and we have recently reported efficient energy transfer to the europium ions when light is absorbed by the titania nanocrystallites in the mesoporous matrix [19]. Here, the titania nanocrystallites act as an antenna which absorbs light greater than or equal in energy to its band gap. The energy is then transferred to the europium ions, which exhibit the characteristic red luminescence arising from f–f crystal field transitions [20]. The photoluminescence spectra show completely unresolved, inhomogeneously broadened emission bands, indicating that the europium ions are located in glassy amorphous titania regions near the interface between the anatase nanocrystallites, rather than included as substituted sites in the nanocrystal structure. Another important result of this work was the discovery that even after adding up to 8 mol% europium ions, the well-ordered mesostructure is preserved.

Since it has been shown that the mesoscopic ordering is not disturbed, it may be possible that relatively large

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quantities of ions with different functionalities (luminescent, magnetic, etc.) could be incorporated into these materials. Rare earth ions have been chosen for study as dopants because they are extremely useful in various applications due to their sharp, near-monochromatic emission lines. Furthermore, the *f–f* transitions are fairly insensitive to conditions such as temperature and the surrounding chemical environment [21–23]. Extensive research has been carried out on the luminescence properties of rare earth ions doped in sol–gel and quenched glasses [24–30]. These properties together with the large number of available transitions ranging from the deep UV to the mid-IR make them ideal candidates for optical applications such as phosphors, lasers, displays and amplification systems [31]. The mesoporous titania thin films have proven to have the characteristics of an ideal host matrix: the material is strongly absorbing, transfers energy efficiently to the otherwise weakly absorbing rare earth ions and is stable to environmental conditions such as moisture and temperature.

We have explored the system of doped mesoporous titania thin films further by synthesizing well-ordered cubic mesostructures containing various concentrations of trivalent Nd, Sm, Eu, Tb, Er, Tm, and Yb. Due to the similar chemistry (size and charge) of the trivalent rare earth ions, the two-phase mesostructure can be doped with up to 8 mol% of any rare earth and luminescence as a result of energy transfer can be observed with several of the emitting species. It has been determined that among the doped materials studied, the energy transfer process occurs only in samples containing Nd, Sm, Eu, Er, and Yb. Here we report on the structural and luminescence properties of the doped mesoporous titania thin films that showed successful energy transfer, and propose a model for the mechanism of the energy transfer.

2. Experimental section

The mesoporous titania thin films were synthesized using a sol–gel method reported previously [18]. In short, titanium (IV) tetraethoxide (TEOT) was dissolved in concentrated hydrochloric acid. This was added to a solution containing ethanol, a non-ionic triblock copolymer ((poly ethylene oxide)$_{20}$ (poly propylene oxide)$_{70}$ (poly ethylene oxide)$_{20}$, Pluronic P123), and the rare earth chloride hydrate. Mole ratios (RE:Ti) were varied between 0.01 and 0.10. The films were dip coated at a pulling rate of 1 mm/s and stored at 10–15°C before calcining at 400°C for 4 h.

X-ray diffraction patterns were recorded on a SMART diffractometer using Mo$K\alpha$ radiation, and recorded using a CCD camera. Transmission electron microscopy (TEM) with energy dispersive X-ray (EDX)

measurements were carried out using a JEOL 2000FX electron microscope operating with an accelerating voltage of 200 kV. Samples for TEM were prepared by removing the films from the substrate, crushing them, suspending them in ethanol and depositing on a copper grid with a carbon film.

UV-visible absorption spectra were taken on an OLIS Cary-14 Spectrometer. Visible photoluminescence emission and excitation measurements were taken on a Cary Eclipse Spectrophotometer. Near-infrared emission spectra were acquired by phase sensitive detection using a liquid nitrogen cooled germanium detector from Edinburg Instruments and a Liconix helium cadmium laser (325 nm) modulated at 100 Hz with an optical chopper. The emission light was separated using a 600 l/mm grating with a 1.25 μm blaze. PL lifetime for the visible luminescence was taken using the 337 nm line of a 1 ns pulsed nitrogen laser and analyzed using an oscilloscope and a monochromator.

3. Results and discussion

3.1. Structural characterization

The nanocrystalline walls in the mesoporous titania films have been characterized by wide angle powder X-ray diffraction (Fig. 1). The powder pattern of an undoped cubic mesostructured TiO$_2$ film heat treated at 400°C for 4 h shows peaks from both anatase and rutile. The peaks in the mesoporous titania pattern have been deconvoluted using Gaussians and are broadened due to the small size of the nanocrystallites, with the rutile peaks being more severely broadened than the anatase peaks. The size of each type of nanocrystallite was calculated from the Scherrer formula: the average
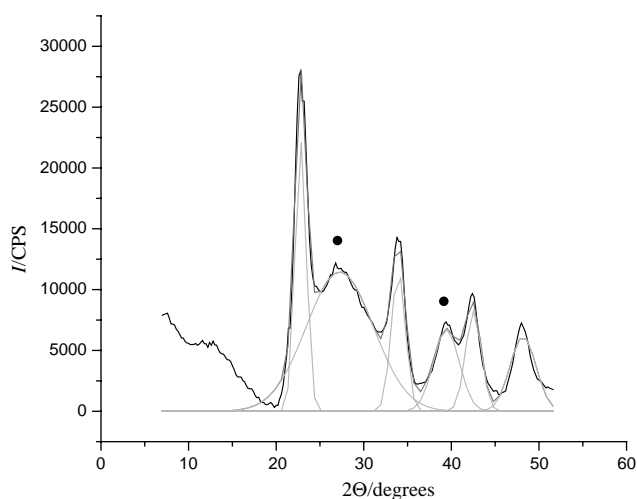

Fig. 1. X-ray diffraction pattern of nanocrystalline mesoporous titania film. Peaks marked with ● represent rutile, and umarked peaks represent anatase.

anatase crystallite size is 6 nm and those of rutile are 1 nm, which is in accordance with the crystallization temperatures of the two materials (anatase 415°C, rutile 680°C). These calculated crystallite sizes corroborate high-resolution TEM images of the titania nanocrystallites reported previously [18].

Table 1 lists the five rare earth ions that exhibited luminescence upon excitation of the titania nanocrystalline matrix. The percentage of each ion listed corresponds to the maximum amount of dopant that could be incorporated without a decrease in the signal of the luminescence spectra, or in other words, before some type of quenching occurred. The mechanism for this quenching is the subject of current study. In Fig. 2, TEM micrographs of the samples listed in Table 1 show that the rare earth doped mesoporous titania films which showed successful energy transfer also have well-ordered cubic mesostructures. We have observed in general that the order of the mesoporous films actually seems to improve slightly upon increasing the percentage of the rare earth ion incorporated into the films. Rare earth ions have been used by other groups as stabilizing agents to slow down condensation during the synthesis of mesoporous materials [11,32]. Slower condensation between individual titania precursors on the molecular scale could lead to better order in our material.

3.2. Photophysical characterization

UV-visible absorption spectra of the doped and undoped films are shown in Fig. 3. The band edge of each film appears at approximately 360–365 nm, which is shifted with respect to the band gap of bulk anatase (382 nm). None of the absorption peaks for any of the rare earth ions can be observed in the spectra due to the weak absorption cross section of the parity forbidden nature of the f–f transitions in all of the rare earths in combination with the small thickness of the films (<500 nm). Since the band edge shift, which is a result of the small size of the nanocrystallites, is independent of the doping level (0–8%), it can be concluded that the nucleation and growth of the nanocrystallites is not affected by the addition of the rare earth ions to the

Table 1
Composition of rare earth-doped mesostructured titania films

Element	Mol% (RE/Ti)
Sm	2
Er	2
Yb	2
Nd	4
Eu	8

The percentage listed corresponds to the maximum percentage of lanthanide ions incorporated into mesostructured titania thin films without quenching of the photoluminescence.
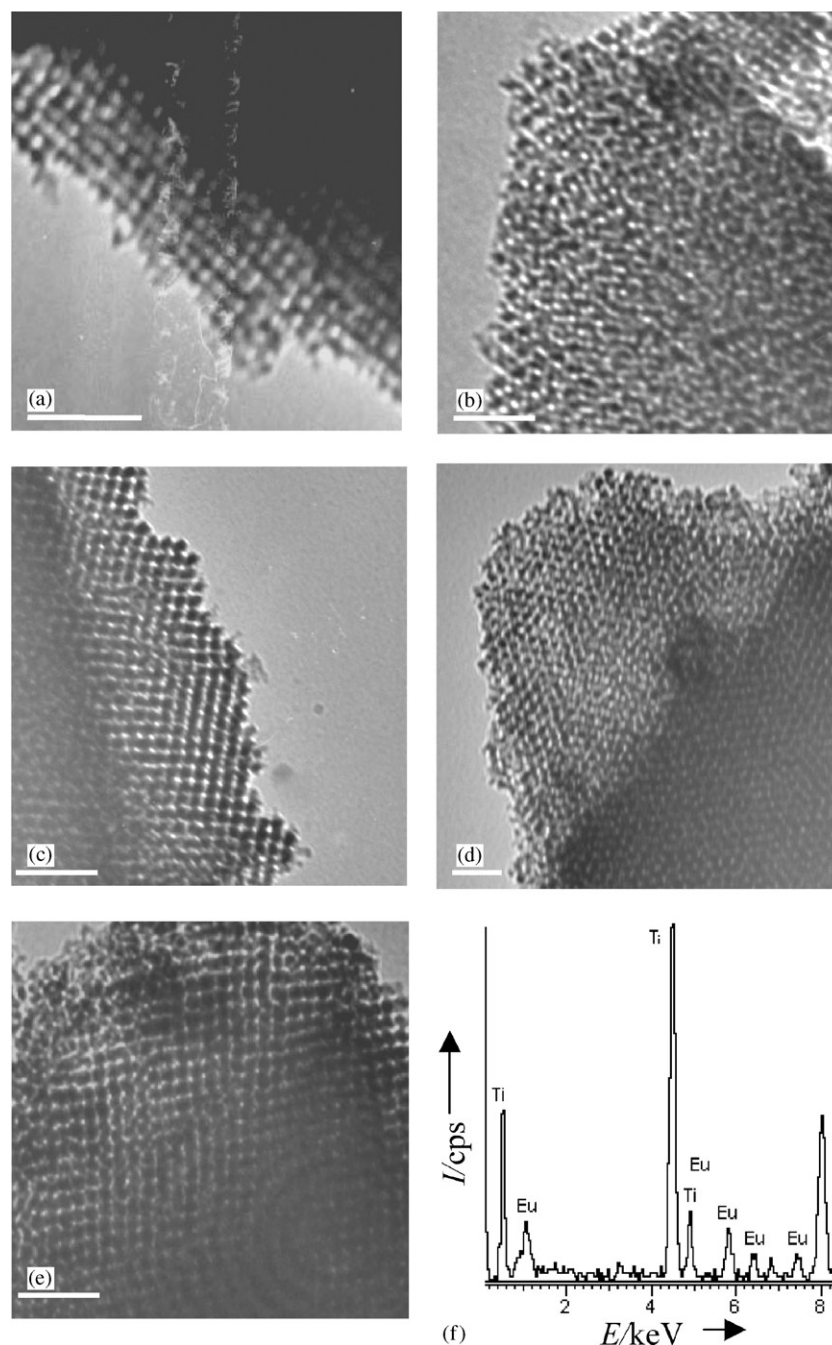
mesoporous material. Also shown is the location of the band edge of bulk titania. The films are highly transparent, and any absorbance that appears at energies below the band gap energy is a result of interference fringes, and due to the high index of refraction of the titania with respect to the glass substrate.

3.2.1. Europium doped films

Fig. 4a shows the emission spectrum of an 8 mol% europium doped TiO_2 film after an excitation of 330 nm. The transitions between the Russell–Saunders multiplets $^5D_0$ to ^7F_J show completely unresolved inhomogeneous broadening as a result of the location of the europium atoms in the amorphous titania regions. The most intense transition, the $^5D_0$ to $^7F_2$, is observed at 614 nm. The excitation spectrum of this emission at 614 nm (also Fig. 4a) clearly reflects the band gap of the titania as the main contribution to the excitation. Additionally, the europium emission is bright enough to be seen with the naked eye when excited under the 302 nm excitation of a UV lamp [19].

Photoluminescence lifetimes of europium were measured for 1, 2, 4, 8, and 10 mol% in the titania. Table 2 shows that within experimental error, all of the lifetimes are basically the same, with an average value of 500 μs up to 10% where then lifetime drops off to 330 μs. The lifetime curve is actually made up of two components: in addition to the 500 μs contribution from the europium $^5D_0$ to $^7F_4$ transition, a short component with a lifetime of 100 ns is observed, which can be associated with luminescence from defect states in the titania [20]. The two lifetime curves are shown in Fig. 6.

3.2.2. Samarium doped films

Fig. 4d shows the photoluminescence spectrum of a film doped with 2% samarium excited at 330 nm. The $^4G_{5/2}$ to ^6H_J transitions are observed, and like the europium, the unresolved broad peaks indicate a glassy environment for the samarium ions. The excitation spectrum (Fig. 4c) of the most intense emission at 601 nm ($^4G_{5/2}$ to $^6H_{7/2}$) reflects the titania band gap as the main contribution to the excitation. Additionally, it is possible to observe this red luminescence of the samarium ions when the sample is excited with a UV lamp.

3.2.3. Near-infrared luminescent films

Fig. 5 shows the photoluminescence spectra of the three near-IR emitting species Nd^{3+}, Yb^{3+}, and Er^{3+} upon excitation of the titania at 325 nm. The neodymium-doped films exhibit characteristic near-IR luminescence bands at 880 ($^4F_{3/2}$ to $^4I_{9/2}$) and 1054 nm ($^4F_{3/2}$ to $^4I_{11/2}$). The ytterbium-doped sample shows a broad, split luminescence peak centered around 980 nm, which corresponds to the $^2F_{5/2}$ to $^2F_{7/2}$ transition. The

Fig. 2. TEM images of rare earth-doped mesoporous titania thin films with doping levels corresponding to Table 1. (a) Er–TiO$_2$, (b) Sm–TiO$_2$, (c) Nd–TiO$_2$, (d) Yb–TiO$_2$, (e) Eu–TiO$_2$, (f) EDX spectrum of an 8 mol% Eu–TiO$_2$ film. All of the films have a cubic mesostructure and the TEM images show images along either the [100] ((a), (c), (e)) or [111] ((b), (d)) zone axes. Each scale bar represents 100 nm.

spectrum arising from the sample containing erbium shows the $^4I_{13/2}$ to $^4I_{15/2}$ transition at 1540 nm as the most intense peak, which is important because this is the wavelength used for optical communications.

The mesoporous titania films did not exhibit energy transfer to terbium or thulium. However, when the rare earth ions in the films are excited directly, a weak fluorescence is observed. The presence of this weak fluorescence indicates that while the ions are indeed present in the films, no energy transfer takes place.

3.3. Proposed energy transfer mechanism

We propose a model for the energy transfer in this system, which involves relaxation to defect states on titania before the energy is transferred to the lanthanide
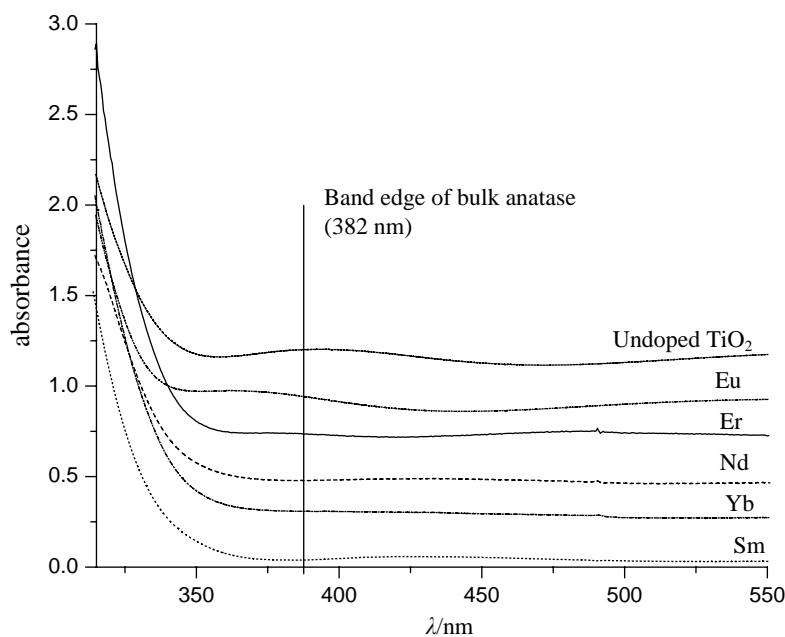
Fig. 3. UV-visible absorption spectra of rare earth doped and undoped mesoporous titania thin films. The mole fractions of each rare earth doped sample correspond to Table 1. It should be noted that each absorption spectrum in this figure is offset vertically by 0.2 absorbance units above the previous spectrum for clarity.
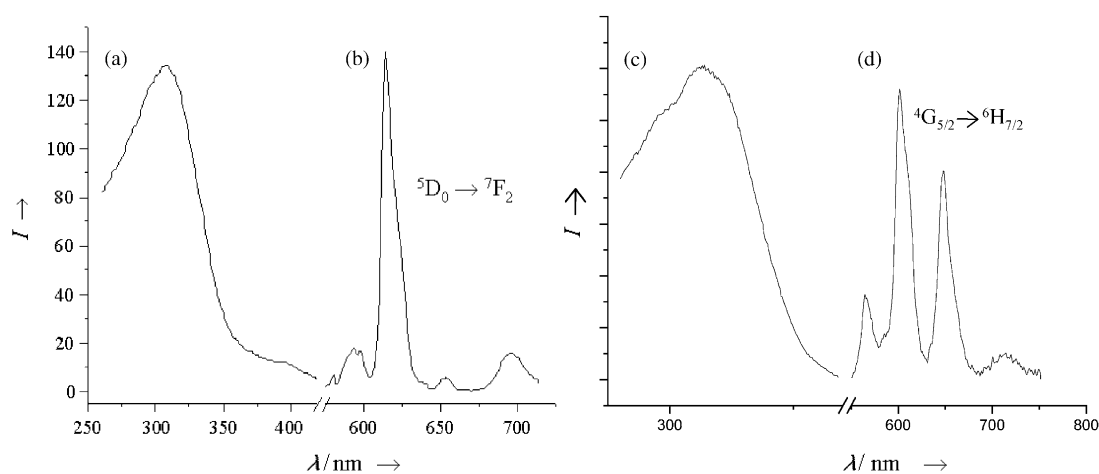

Fig. 4. Excitation and photoluminescence spectra of 8% europium (a, b) and 2% samarium (c, d) doped mesoporous titania films.

Table 2
Photoluminescence lifetimes of europium doped films with increasing europium content

Mol % Eu	Lifetime (µs)
1	550
3	520
5	470
8	500
10	330

ion. Fig. 7 shows an energy level diagram which shows UV light being absorbed in the band gap of the titania, subsequent relaxation to the defect states, followed by energy transfer to the crystal field states of the rare earth ion. Various types of defect states have been shown to play an important role in energy transfer between other semiconductors such as the III-V and Si and rare earth ions [33]. Surface states, or traps have been observed in titania by several groups [34–36] and are assigned to coordinatively unsaturated titanium ions at the surface of the titania crystals. In our material, this coordinatively unsaturated site would be at the interface between the nanocrystallite and the amorphous matrix. The excited state created by absorption in the titania band gap relaxes to these traps on the surface of the crystals.

As mentioned previously, the radii of the rare earth ions are too large to allow them to replace titania in an anatase crystal, and the unresolved PL spectra are
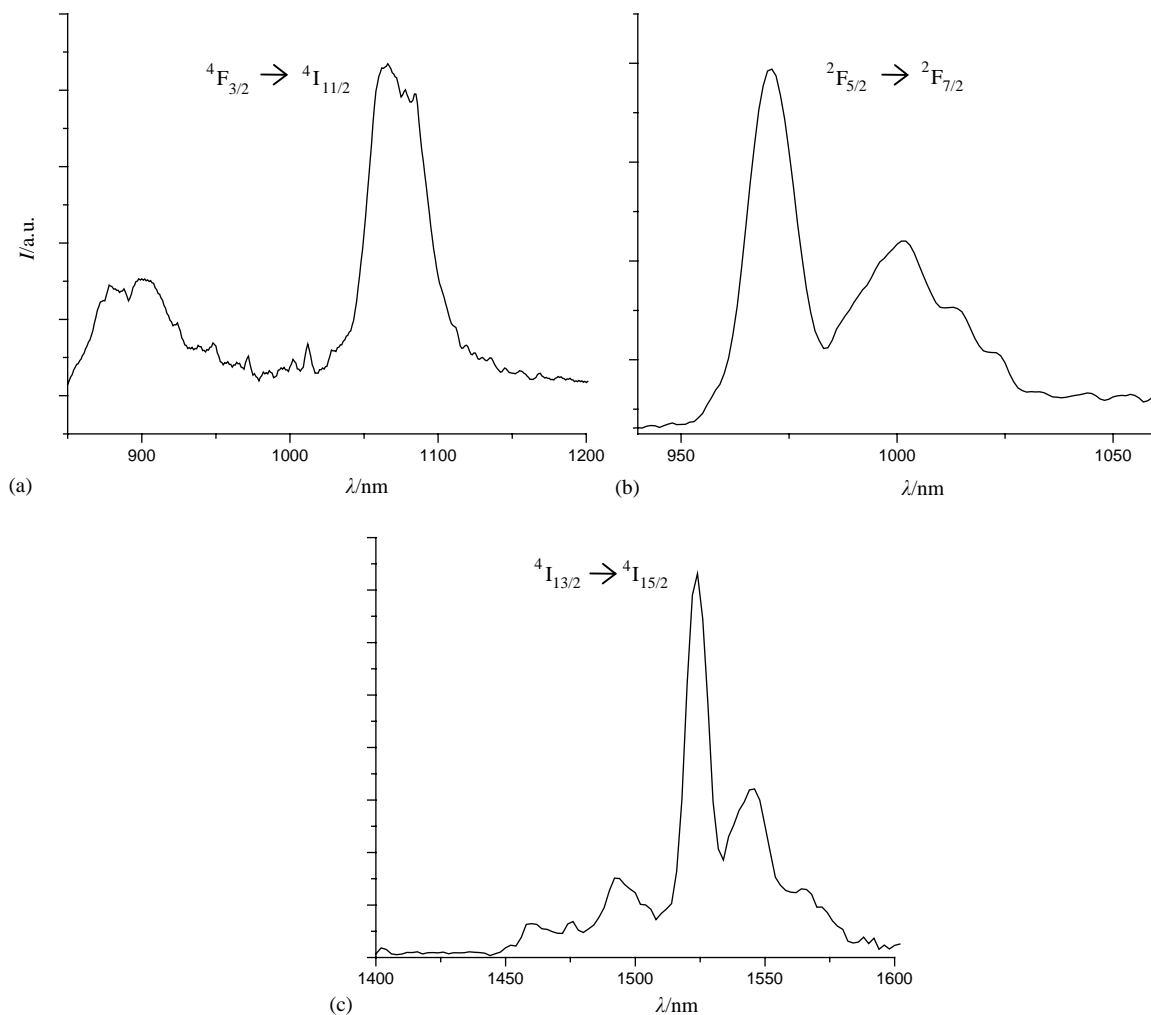
Fig. 5. Near-infrared photoluminescence spectra from (a) 4% neodymium, (b) 2% ytterbium, and (c) 2% erbium doped mesoporous titania thin films.
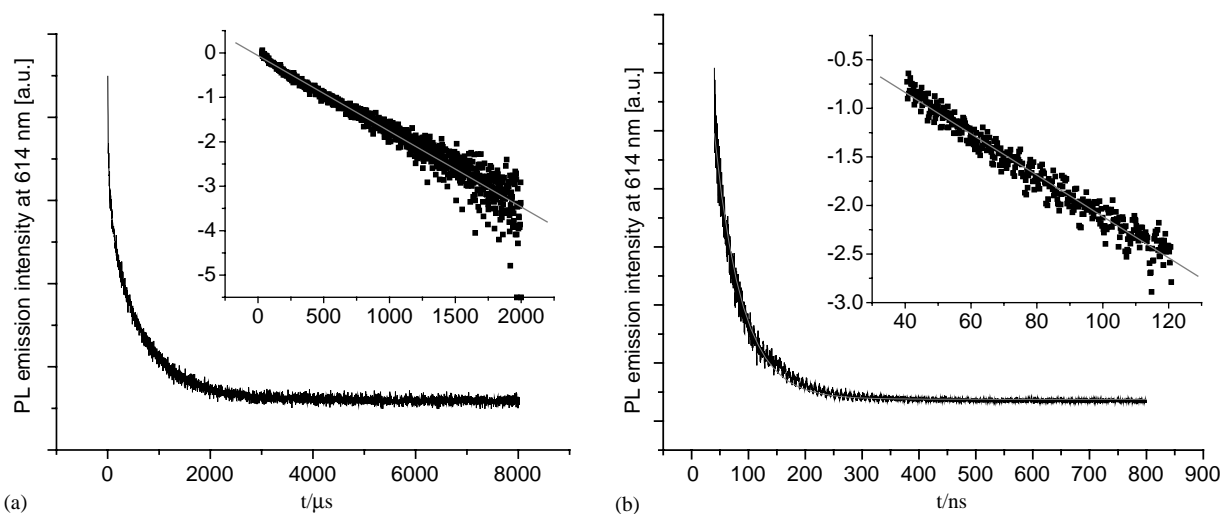

Fig. 6. Lifetime curves for 8 mol% europium doped mesostructured titania thin films. (a) Long component of the lifetime resulting from luminescence of europium ions ($\tau = 500\,\mu s$). (b) Short component of lifetime from luminescence of titania defect states ($\tau = 100\,ns$).

consistent with rare earths in a glass-like environment. These facts indicate that the rare earth ions are located at the edge of the nanocrystallites, or in close proximity to these surface defects. Because of the small size and large number of nanocrystallites in these materials, there are a great number of the surface states available to transfer energy to the crystal field states of the rare earth ions. The energy level of these surface defects is critical to the energy transfer process because if it is lower in

energy than the emitting state of the rare earth ion, no sensitized luminescence can be observed.

By using the well-known energies of the emitting states of the lanthanides [37] it is possible to verify the lower limit for the energy level of the trap states in the titania that transfer energy to the ions (see Fig. 8). The energy level of the emitting state of samarium ($^4G_{5/2}$) approximately $19,000\,cm^{-1}$ and this is the highest state that showed energy transfer for the rare earths studied here. It can therefore be proposed that the energy of the surface states of the titania is not below this value.

The upper limit for the energy level of the trap states is a more complicated matter, and depends on the type of energy transfer taking place. However, if a Dexter-type mechanism for energy transfer is assumed, or in other words, a mechanism involving wavefunction overlap between the donor and acceptor, then it can be proposed that if the trap levels were equal to or greater than the energy of the emitting state, luminescence via energy transfer would take place [38,39]. Since sensitized luminescence is not observed for terbium, which has the next highest luminescence excited state above samarium, our model would imply that the trap levels on the titania nanocrystals lie somewhere between these two states. This corresponds to an energy of the surface states in our titania nanocrystallites somewhere between $19,000$ and $21,000\,cm^{-1}$ ($2.35–2.59\,eV$, $475–525\,nm$). The proposed values for this defect state energy are in close agreement with energies of titania surface defects reported by other groups [34,36]. Fig. 8 shows a schematic which summarizes this proposed mechanism. The luminescent state of each rare earth is indicated in relation to the proposed level of the titania defect states.
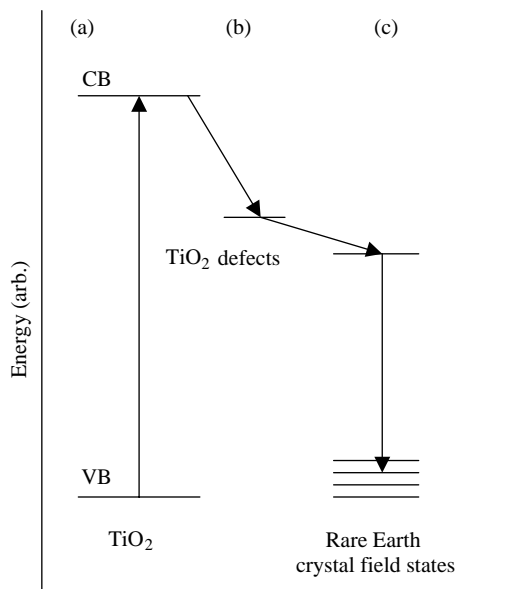

Fig. 7. Schematic showing proposed energy transfer mechanism. (a) UV light is absorbed within the titania band gap, (b) relaxation to titania defect states occurs, and (c) there is energy transfer to the crystal field states of the rare earth ion, which exhibits photoluminescence.

4. Conclusions

Rare earth ions have been doped into highly absorbing nanocrystalline, mesoporous titania thin films, which retain their mesoscopically ordered structure despite the addition of large amounts of dopants. Photoluminescence as a result of energy transfer was observed from samples doped with Nd^{3+}, Sm^{3+}, Eu^{3+}, Er^{3+}, and Yb^{3+}. A mechanism for the energy transfer process has been proposed such that the excited matrix undergoes relaxation to the defect levels and the energy is transferred to the rare earth ions. The proposed energy transfer mechanism allows us to determine that in our material, the defect levels have an energy of approximately $19,000–21,000\,cm^{-1}$. The remaining rare earths that were studied (Tb^{3+} and Tm^{3+}) did not show any energy transfer at all due to the relatively high energy of their luminescence excited states.

The unique structure of these mesoporous titania thin films has proven to be a robust host matrix. The completely inorganic framework of the material is
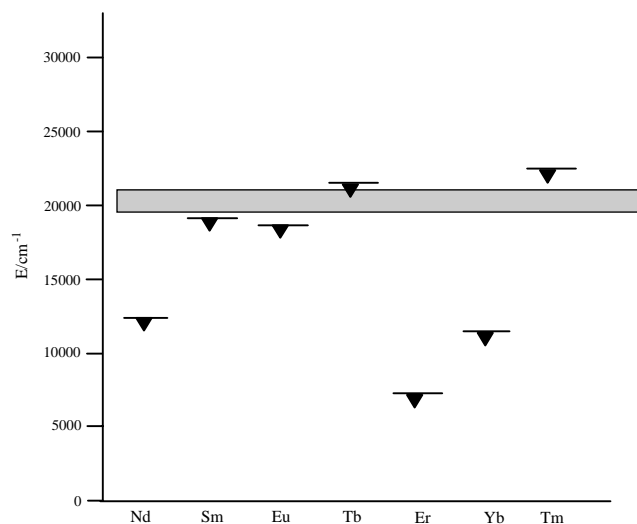

Fig. 8. Luminescence excited states of the lanthanide ions studied, indicated by ▼. The shaded area represents the proposed energy level of the titania defect states.

environmentally stable, and it has a structure which supports the stability of rare earth ions in a glass environment, as well as the requirement for energy transfer which must come from the ions being in close proximity to the anatase nanocrystallites. The doped materials presented here could have potential for use in phosphors, amplifiers or other optical applications. Additionally, this work suggests the potential of these mesoporous titania materials to be doped with ions of diverse functionality to created nanostructures that can be integrated into various types of devices. It is our aim to further explore this energy transfer system and elucidate the mechanism for the apparent concentration quenching, as well as verify the mechanism proposed here.

Acknowledgments

References

[1] M. Gratzel, Prog. Photovoltaics 8 (2000) 171–185.

[2] M. Gratzel, Curr. Opin. Colloid 4 (1999) 314–321.

[3] A. Hagfeldt, M. Graztel, Acc. Chem. Res. 33 (2000) 269–277.

[4] L. Kavan, A. Attia, F. Lenzmann, S.H. Elder, M. Gratzel, J. Electrochem. Soc. 147 (2000) 2897–2902.

[5] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. (Washington, DC) 95 (1995) 69–96.

[6] D. Antonelli, J. Ying, Angew. Chem. Int. Ed. 34 (1995) 2014.

[7] D. Antonelli, Micropor. Mesopor. Mater. 30 (1999) 315–319.

[8] Y.K. Hwang, K.C. Lee, Y.U. Kwon, Chem. Commun. 18 (2001) 1738–1739.

[9] D. Grosso, G. Soler-Iliia, F. Babonneau, C. Sanchez, P. Albouy, A. Bruneau, A. Balkenende, Adv. Mater. 13 (2001) 1085–1090.

[10] G. Soler-Illia, A. Louis, C. Sanchez, Chem. Mater. 14 (2002) 750–759.

[11] Y. Yue, Z. Gao, Chem. Commun. 18 (2000) 1755–1756.

[12] Y. Wang, S. Chen, X. Tang, O. Palchik, A. Zaban, Y.A. Gedanken, J. Mater. Chem. 11 (2001) 521–526.

[13] P. Yang, D. Zhao, D. Margolese, B. Chemlka, G. Stucky, Chem. Mater. 11 (1999) 2813–2826.

[14] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, Nature (London) 396 (1998) 152–155.

[15] Y. Wang, X. Tang, L. Yin, W. Huang, Y. Hacohen, A. Gedanken, Adv. Mater. 12 (2000) 1183–1186.

[16] D. Khushalani, G.A. Ozin, A. Kuperman, J. Mater. Chem. 9 (1999) 1491–1500.

[17] H.S. Yun, K. Miyazawa, H.S. Zhou, I. Honma, M. Kuwabara, Adv. Mater. 13 (2001) 1377–1380.

[18] P. Alberius-Henning, K. Frindell, R. Hayward, E. Kramer, B. Kramer Chmelka, G. Stucky, Chem. Mater. 14 (2002) 3284–3294.

[19] K.L. Frindell, M.H. Bartl, A. Popitsch, G.D. Stucky, Angew. Chem. Int. Ed. 41 (2002) 959.

[20] A. Conde-Gallardo, M. Garcia-Rocha, I. Hernandez-Calderon, Appl. Phys. Lett. 78 (2001) 3436–3438.

[21] J. Ballato, J.S. Lewis, P. Holloway, MRS Bull. 24 (1999) 51–56.

[22] S. Hufner, Optical Spectra of Transparent Rare Earth Compounds, Academic Press, New York, 1978.

[23] R.G. Denning, J. Mater. Chem. 11 (2001) 19–28.

[24] M.F. Hazenkamp, G. Blasse, Chem. Mater. 2 (1990) 105–110.

[25] D. Levy, R. Reisfeld, D. Avnir, Chem. Phys. Lett. 109 (1984) 593–597.

[26] R. Reisfeld, Struct. Bonding 13 (1973) 53–98.

[27] R. Reisfeld, Struct. Bonding 22 (1975) 123–175.

[28] R. Reisfeld, Struct. Bonding 30 (1976) 65–97.

[29] B.T. Stone, K.L. Bray, J. Non-Cryst. Solids 197 (1996) 136–144.

[30] G. Pucker, K. Gatterer, H.P. Fritzer, M. Bettinelli, M.G. Ferrari, Phys. Rev. B 53 (1996) 6225–6234.

[31] H. Maas, A. Currao, G. Calzaferri, Angew. Chem. Int. Ed. 41 (2002) 2495–2497.

[32] W.Z. Zhang, T.J. Pinnavaia, Chem. Commun. 11 (1998) 1185–1186.

[33] T. Gregorkiewicz, D.T.X. Thao, J.M. Langer, Phys. Status Solidi B 210 (1998) 737–745.

[34] R.M. Kumar, S. Badrinarayanan, M. Sastry, Thin Solid Films 358 (2000) 122–130.

[35] Y. Zhu, C. Ding, G. Ma, Z. Du, J. Solid State Chem. 139 (1998) 124–127.

[36] Y.C. Zhu, C.X. Ding, J. Solid State Chem. 145 (1999) 711–715.

[37] W.T. Carnall, H. Crosswhite, H.M. Crosswhite, Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF3, Argonne National Lab, Argonne, IL, Springfield, VA, 1977.

[38] S. Sato, M. Wada, Bull. Chem. Soc. Jpn. 43 (1970) 1955–1962.

[39] G.A. Crosby, R.E. Whan, R.M. Alire, J. Chem. Phys. 34 (1961) 743–748.