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## Photoluminescence properties of lamellar aggregates of titania nanosheets accommodating rare earth ions

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Fluorescent semiconductor materials doped with rare earth ions have been synthesized by flocculation of colloidal titania nanosheets,  $\text{Ti}_{0.91}\text{O}_2$ , with  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  ions. The composites had a lamellar structure with a gallery height of 1.06 nm, accommodating rare earth ions between the nanosheets with a doping concentration as high as  $10 \pm 1$  mol %. The composite with  $\text{Eu}^{3+}$  exhibited intense characteristic emission from  $\text{Eu}^{3+}$  either by exciting the  $\text{Ti}_{0.91}\text{O}_2$  host with UV light ( $\lambda < 350$  nm) or by directly exciting  $\text{Eu}^{3+}$  at a longer wavelength where there was no absorption by  $\text{Ti}_{0.91}\text{O}_2$ . This indicates that nonradiative energy transfer from the  $\text{Ti}_{0.91}\text{O}_2$  host to  $\text{Eu}^{3+}$  can take place in this system. In contrast, no energy transfer was observed in the composite with  $\text{Tb}^{3+}$ . © 2004 American Institute of Physics. [DOI: 10.1063/1.1812811]

Rare earth (RE) or lanthanide (Ln) ions have attracted great interest in technological applications such as optoelectronics devices and flat panel displays<sup>1,2</sup> because of their excellent luminescence characteristics with extremely sharp emission bands originating from their  $4f$  electronic transition. It is well known that in rare earth complexes with organic ligands, especially those with  $\beta$ -diketones, the emission from RE ions can be enhanced through the nonradiative energy transfer from the triplet state of the ligands to the crystal field states of the central ions. However, due to their poor thermal stability and weak mechanical properties, these complexes have been excluded from some practical applications such as tunable solid-state laser and phosphor devices. Recently, strenuous efforts have been made to solve this problem by doping RE ions in semiconductor particles such as ZnS, CdS and  $\text{TiO}_2$ , through sol-gel processing or the co-precipitation method.<sup>3-8</sup> The characteristic emission of RE ions has been observed from some of the doped semiconductors. However, Bol, Beek, and Meijerink reported<sup>8</sup> that RE ions are mostly adsorbed at the particle surface in these doped semiconductors and the characteristic emission of RE ions is not due to the energy absorbed by the host but RE ions themselves. In addition, the doping concentration was limited, generally less than 3%. Most recently, on the other hand, Stucky and co-workers<sup>9,10</sup> demonstrated that mesoporous titania thin films with nanocrystalline walls were an excellent host for trivalent europium ions and this material could yield efficient photoluminescence (PL) through energy transfer from the host to the guest.

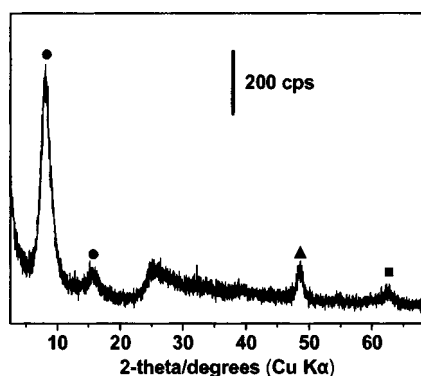
Apart from the mesoporous modification as well as conventional granular forms, a nanosized titanium oxide can be produced as unilamellar crystallites, which have been synthesized by exfoliating a protonic layered titanate  $\text{H}_{0.7}\text{Ti}_{1.825}\text{O}_4 \cdot \text{H}_2\text{O}$  into colloidal single layers.<sup>11</sup> The resulting nanosheet crystallite with the composition of  $\text{Ti}_{0.91}\text{O}_2$ <sup>0,36-</sup> has extremely high two-dimensional anisotropy with a lateral dimension of 0.1–1  $\mu\text{m}$  and a thickness of about 0.75 nm.

This titania nanosheet could be easily re-stacked by flocculation with various positively charged species to yield composite materials with a layered structure.<sup>12,13</sup> One of the advantages of this re-stacking reaction is that we can incorporate guest species into host materials which are difficult to insert through a conventional intercalation process in layered materials.

In this work, we report the synthesis of re-stacked composites of titania nanosheets and RE ions (europium and terbium) (denoted as ex- $\text{Ti}_{0.91}\text{O}_2/\text{Eu}$  and ex- $\text{Ti}_{0.91}\text{O}_2/\text{Tb}$ , respectively, “ex-” means “exfoliated”) and their PL properties. Both materials had a homogeneous layered structure with a high concentration of RE ions of  $10 \pm 1$  mol %. Upon excitation at a longer wavelength ( $>370$  nm), both samples emitted characteristic line-like spectra from RE ions originated from the energy absorbed by themselves. Furthermore, the composite of ex- $\text{Ti}_{0.91}\text{O}_2/\text{Eu}$  showed strong PL light also through UV irradiation at the absorption range of  $\text{Ti}_{0.91}\text{O}_2$  nanosheets. This suggests that the energy absorbed by  $\text{Ti}_{0.91}\text{O}_2$  can be effectively transferred to  $\text{Eu}^{3+}$  ions. Such energy transfer to  $\text{Tb}^{3+}$  ions was not observed.

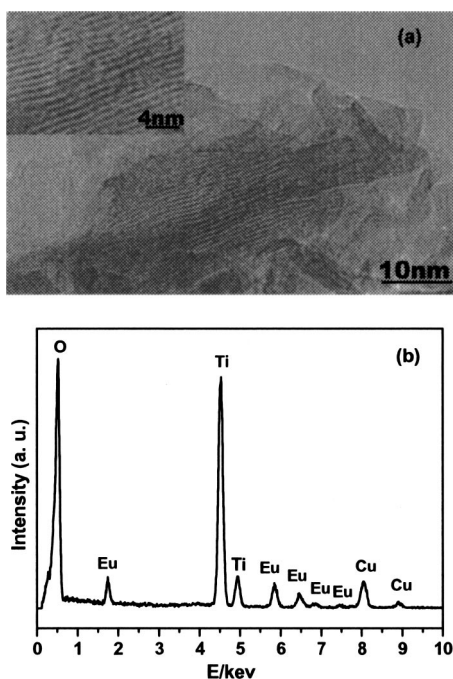
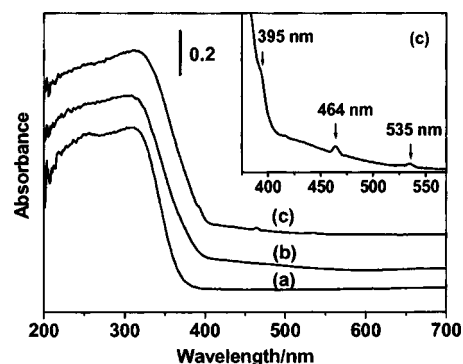
Samples were prepared by slow addition of a colloidal suspension of  $\text{Ti}_{0.91}\text{O}_2$  nanosheets (100  $\text{cm}^3$ , pH = 9, 0.4 wt%) to 100  $\text{cm}^3$  of 0.1  $\text{mol dm}^{-3}$   $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  aqueous solution under stirring at room temperature. The precipitated white product was filtered, washed with ultrapure water and dried in air. X-ray diffraction (XRD) patterns were collected using a Rigaku Rint 2000S powder diffractometer with graphite monochromated  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15405$  nm). UV visible spectroscopy (UV-VIS) absorption spectra were recorded on a Hitachi U-4000 spectrophotometer in the diffuse reflectance mode. PL spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. Transmission electron microscopy (TEM) observations were performed using a high-resolution TEM microscope (JEM-3000F) with energy dispersive x-ray spectrometer (EDS). Two samples, ex- $\text{Ti}_{0.91}\text{O}_2/\text{Tb}$  and ex- $\text{Ti}_{0.91}\text{O}_2/\text{Eu}$ , had very similar chemical analysis results, XRD patterns and TEM images, which should be attributed to the similar size for lanthanide ions. The XRD pattern of ex- $\text{Ti}_{0.91}\text{O}_2/\text{Tb}$  (Fig.

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FIG. 1. XRD pattern of ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb.

1) shows basal reflections at a  $2\theta$  value of 8.2 and 15° as indicated by circles. This indicates the re-stacking of Ti<sub>0.91</sub>O<sub>2</sub> nanosheets to form a uniform layered structure with a gallery height of 1.06 nm, the dimension of which may be reasonable for the accommodation of hydrated RE ions. The two peaks at  $2\theta=48.5$  and 62.6° (triangle and square in Fig. 1) are diagnostic of two-dimensional architecture of Ti<sub>0.91</sub>O<sub>2</sub> nanosheet.<sup>11</sup> The TEM image (Fig. 2) clearly shows the lamellar feature of the materials. The incorporation of RE ions in the flocculated sample is confirmed by EDS analysis, giving its content of 10±1 mol %. This composition is roughly consistent with the charge balance between Ti<sub>0.91</sub>O<sub>2</sub><sup>0.36-</sup> and Ln<sup>3+</sup>. It should be noted that the exfoliation-re-stacking route is essential to achieve this high content of RE ions. Such high level of doping cannot be attained by the conventional ion-exchange reaction of the parent layered titanate.

Figure 3 depicts UV-VIS absorption spectra for the flocculated samples. The data for a re-stacked sample of ex-Ti<sub>0.91</sub>O<sub>2</sub>/H prepared using 0.1 mol dm<sup>-3</sup> HCl solution as a flocculation agent is included for comparison. This sample of ex-Ti<sub>0.91</sub>O<sub>2</sub>/H showed strong UV-VIS absorption with a

FIG. 2. TEM (a) and energy dispersive x-ray (b) of the composite ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu.FIG. 3. UV-VIS absorption spectra of ex-Ti<sub>0.91</sub>O<sub>2</sub>/H (a), ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb (b), and ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu (c). Inset: the enlarged spectrum of ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu at a wavelength range of 360–550 nm.

steep onset around 380 nm. This is similar to its parent titanate H<sub>0.7</sub>Ti<sub>1.825</sub>O<sub>4</sub>·H<sub>2</sub>O, the absorption of which corresponds to the band gap of the titanate (3.24 eV).<sup>14</sup> For ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu, sharp peaks (Fig. 3, inset) were detectable at 395, 464, and 535 nm, apart from the huge absorption from the titania nanosheet similar to ex-Ti<sub>0.91</sub>O<sub>2</sub>/H. These three peaks are assignable to the intraconfigurational 4f<sup>m</sup>→4f<sup>m</sup> transition of Eu<sup>3+</sup> as is usually observed.<sup>7</sup> In contrast, such features were not observed for ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb. The 4f-4f transitions of Tb<sup>3+</sup> are located at the wavelength range of 200–380 nm, which is overlapped with the strong absorption of Ti<sub>0.91</sub>O<sub>2</sub>. Thus, the absorption by Tb<sup>3+</sup> ions may be quenched. This result may be consistent with the fact that RE ions are located in-between the nanosheets rather than merely adsorbed at the surface.

The PL spectra (both excitation and emission) of the three samples measured under identical conditions are shown in Fig. 4. The excitation spectra were measured by monitoring the emission peak wavelength at 395, 544 and 612 nm for ex-Ti<sub>0.91</sub>O<sub>2</sub>/H, ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb and ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu, respectively. The sample of ex-Ti<sub>0.91</sub>O<sub>2</sub>/H showed relatively weak emission with a main peak at 395 nm, which is similar to our previous report on PL of Ti<sub>0.91</sub>O<sub>2</sub> nanosheets.<sup>14</sup> This feature may be originated from defect states of Ti<sub>0.91</sub>O<sub>2</sub>. The composite sample of ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb exhibited emission characteristics very similar to those for Ti<sub>0.91</sub>O<sub>2</sub>/H throughout almost all the absorption range of Ti<sub>0.91</sub>O<sub>2</sub>. Even at the excitation wavelength of 274 nm where Tb<sup>3+</sup> ions have the strongest absorption, no emission from Tb<sup>3+</sup> ions was detected. On the other hand, excitation at the wavelength of 378 nm, where absorption by Ti<sub>0.91</sub>O<sub>2</sub> is relatively weak, yielded characteristic lines from Tb<sup>3+</sup> ions. The four main peaks at 489, 544, 582 and 618 nm correspond to <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>j</sub> (j=3–6) transitions,<sup>15</sup> respectively, indicating that the emission bands arise from the absorption of Tb<sup>3+</sup> ion itself, not the host. These results revealed that no energy transfer took place between the host of Ti<sub>0.91</sub>O<sub>2</sub> nanosheets and Tb<sup>3+</sup> ions. It is notable that the intensity of emission from Tb<sup>3+</sup> ions was very weak, and was lower than that from the host excited at 250 nm. The weak absorption should be responsible for this behavior. As mentioned above, the absorption by Tb<sup>3+</sup> ions could not be detected by the UV-VIS measurement.

Excited at a wavelength (>380 nm) longer than the absorption edge of the Ti<sub>0.91</sub>O<sub>2</sub> host, the composite of ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu exhibited intense characteristic light origi-

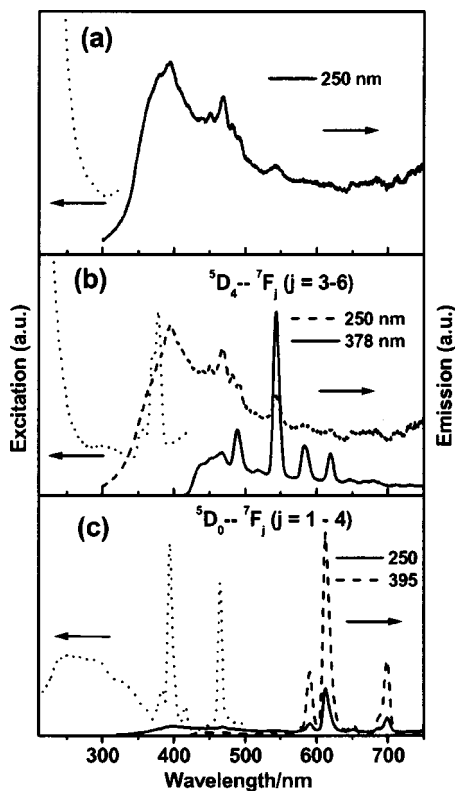


FIG. 4. PL excitation and emission spectra of ex-Ti<sub>0.91</sub>O<sub>2</sub>/H (a), ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb (b) and ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu (c). The excitation spectra were measured by monitoring the emission peak wavelength at 395, 544 and 612 nm for ex-Ti<sub>0.91</sub>O<sub>2</sub>/H, ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb and ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu, respectively. The excitation wavelengths are also shown.

nated from Eu<sup>3+</sup> [Fig. 4(c)]. Four main peaks at 590, 612, 653 and 693 nm can be attributed to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>j</sub> (j = 1–4) transition, respectively. Obviously, this emission is due to the absorption of Eu<sup>3+</sup> ions as confirmed by the excitation spectrum, which shows a feature similar to that in UV-VIS absorption data. The two main peaks at 395 and 464 nm in the excitation spectrum can be attributed to the <sup>7</sup>F<sub>0</sub> → <sup>5</sup>L<sub>6</sub> and <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>2</sub> transitions (for clarity, the profile at higher wavelength is omitted). When excited at a wavelength of 220–380 nm, ex-Ti<sub>0.91</sub>O<sub>2</sub>/Eu emitted light both from the Ti<sub>0.91</sub>O<sub>2</sub> host and Eu<sup>3+</sup> ions, and the excitation peak at this range coincided very well with the absorption band of Ti<sub>0.91</sub>O<sub>2</sub> nanosheet [Fig. 3(c)], indicating that Eu<sup>3+</sup> ions could be excited via the Ti<sub>0.91</sub>O<sub>2</sub> host. The emission intensity from Eu<sup>3+</sup> was clearly stronger than that from the host, confirming the efficient nonradiative energy transfer from Ti<sub>0.91</sub>O<sub>2</sub> nanosheet to Eu<sup>3+</sup> ions. In both cases, a bright red light due to the strongest emission at 612 nm could be seen by the naked eye.

The energy transfer mechanism between Ti<sub>0.91</sub>O<sub>2</sub> nanosheets and RE ions can be explained by a difference in energy position of excited levels (Fig. 5). As has been proposed by Stucky *et al.*<sup>10</sup> for the Eu-doped mesoporous titania films, PL via the energy transfer would take place if the defect state levels of titania were equal to or greater than the

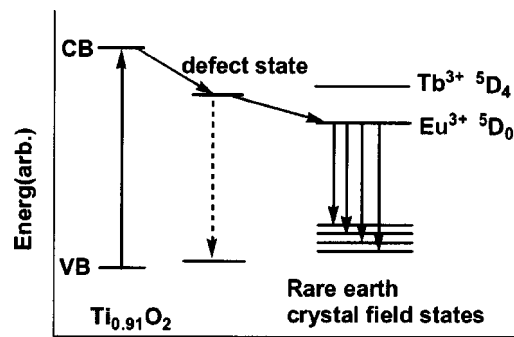


FIG. 5. Plausible model for the energy diagram to explain PL behavior.

energy of the emitting state of RE ions. No sensitized fluorescence in ex-Ti<sub>0.91</sub>O<sub>2</sub>/Tb suggests that the <sup>5</sup>D<sub>4</sub> energy level of Tb<sup>3+</sup> ions is higher than the defect state levels of the Ti<sub>0.91</sub>O<sub>2</sub> nanosheet. The efficient energy transfer between Ti<sub>0.91</sub>O<sub>2</sub> nanosheet and Eu<sup>3+</sup> ions can be explained by a higher position of the defect energy levels of the host than the <sup>5</sup>D<sub>0</sub> energy level of Eu<sup>3+</sup>.

In summary, titania based nanosized fluorescent materials were synthesized by the simple flocculation method involving mixing of colloidal Ti<sub>0.91</sub>O<sub>2</sub> nanosheets with aqueous RE ions. The materials had a homogeneous layered structure accommodating RE ions at a high content of 10 mol %. Efficient nonradiative energy transfer was observed between Ti<sub>0.91</sub>O<sub>2</sub> nanosheets and Eu<sup>3+</sup> ions. Bright red light could be observed by exciting the Ti<sub>0.91</sub>O<sub>2</sub> host and directly exciting the Eu<sup>3+</sup> ions at wavelength beyond the Ti<sub>0.91</sub>O<sub>2</sub> absorption range, which suggests that this material could be useful in optoelectronic devices.

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- <sup>1</sup>J. Kido and Y. Okamoto, Chem. Rev. (Washington, D.C.) **102**, 2357 (2002).
- <sup>2</sup>H. Xin, M. Shi, X. M. Zhang, F. Y. Li, Z. Q. Bian, K. Ibrahim, F. Q. Liu, and C. H. Huang, Chem. Mater. **15**, 3728 (2003).
- <sup>3</sup>A. Conde-Gallardo, M. Garcia-Rocha, I. Hernández-Calderón, and R. Palomino-Merino, Appl. Phys. Lett. **78**, 3436 (2001).
- <sup>4</sup>R. S. Kane, R. E. Cohen, and R. Silbey, Chem. Mater. **11**, 90 (1999).
- <sup>5</sup>W. Chen, J.-O. Malm, W. Zwiller, Y. Huang, S. Liu, R. Wallenberg, J.-O. Bovin, and L. Samuelson, Phys. Rev. B **61**, 11021 (2000).
- <sup>6</sup>S. J. Xu, S. J. Chua, B. Liu, L. M. Gan, C. H. Chew, and G. Q. Xu, Appl. Phys. Lett. **73**, 478 (1998).
- <sup>7</sup>S. Jeon and P. V. Braun, Chem. Mater. **15**, 1256 (2003).
- <sup>8</sup>A. A. Bol, R. V. Beek, and A. Meijerink, Chem. Mater. **14**, 1121 (2002).
- <sup>9</sup>K. L. Frindell, M. H. Bartl, A. Popitsch, and G. D. Stucky, Angew. Chem., Int. Ed. **41**, 959 (2002).
- <sup>10</sup>K. L. Frindell, M. H. Bartl, M. R. Robinson, G. C. Bazan, A. Popitsch, and G. D. Stucky, J. Solid State Chem. **172**, 81 (2003).
- <sup>11</sup>T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, and H. Nakazawa, J. Am. Chem. Soc. **118**, 8329 (1996).
- <sup>12</sup>F. Kooli, T. Sasaki, and M. Watanabe, Chem. Commun. (Cambridge) **1999**, 211.
- <sup>13</sup>T. Sasaki, Y. Ebina, T. Tanaka, M. Harada, M. Watanabe, and G. Decher, Chem. Mater. **13**, 4661 (2001).
- <sup>14</sup>T. Sasaki and M. Watanabe, J. Phys. Chem. B **101**, 10159 (1997).
- <sup>15</sup>H. Xin, F. Y. Li, M. Shi, Z. Q. Bian, and C. H. Huang, J. Am. Chem. Soc. **125**, 7166 (2003).