

# Sonochemical Synthesis and Optical Properties of Europium Oxide Nanolayer Coated on Titania

V. G. Pol,<sup>†</sup> R. Reisfeld,<sup>‡</sup> and A. Gedanken<sup>\*,†</sup>

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel, and Department of Inorganic Chemistry, Hebrew University, Jerusalem 91904, Israel

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Submicron-size particles of titania were coated by a nanolayer of europium oxide with the aid of power ultrasound. Ultrasound irradiation of a slurry of titania, europium nitrate, and ammonia in an aqueous medium for 120 min yielded a  $\text{Eu}_2\text{O}_3\text{--TiO}_2$  nanocomposite. The  $\text{Eu}_2\text{O}_3$  nanolayer deposited on the submicron-size  $\text{TiO}_2$  particles was characterized by transmission electron microscopy, high-resolution scanning electron microscopy, high-resolution transmission electron microscopy, energy-dispersive X-ray analysis, and optical X-ray photoelectron spectroscopies.

## Introduction

The optical properties of the rare-earth ions (also known as lanthanides) trapped in host lattices continue to be a research attraction in terms of both their fundamental and technological importance.<sup>1,2</sup> Combining the promising optical properties of rare-earth ions and nanoparticles in the form of coatings or thin films is important in the fabrication of optical devices such as optical amplifiers and microlasers having a submicron dimension.<sup>3</sup> The study of the luminescent properties of the rare-earth (RE) elements hosted in several crystalline matrixes, such as fluoride glass,<sup>4</sup> metal oxides,<sup>5</sup> phosphors,<sup>6</sup> metal–organic complexes,<sup>7</sup> and a variety of semiconductor materials,<sup>8</sup> is strongly motivated because of their technological applications in optoelectronic devices and flat panel displays.<sup>9</sup> The synthetic methods of these materials can be modified to create nanostructured films and nanocomposites. The luminescence efficiency of these materials is often limited by the dynamics of the lanthanide ion, which depends on interactions with the insulating host. The rationale to study nanostructures of lanthanide-doped insulating materials arises because the spectral and dynamic properties of these technologically important materials change when the reduced dimensions affect

the chemistry and physical properties of the host. In a similar manner, the lanthanide dopant can serve as a sensitive probe of the chemistry and structure of its host.<sup>10</sup> Titania is a good candidate to be used as a host material of rare earth because of its good mechanical, thermal, semiconducting, and anticorrosive properties.<sup>11a,b</sup>

Semiconductor photocatalysts have evoked tremendous interest over the past decade for the light-stimulated degradation of aqueous pollutants.<sup>11c</sup> Several oxides exhibit band-gap energies adequate for catalyzing the degradation of organic materials. Among them,  $\text{TiO}_2$  has proven to be the most effective catalyst for detoxification of organic pollutants.  $\text{Eu}_2\text{O}_3$ , as well as other rare-earth oxides, has been doped in  $\text{TiO}_2$ . This composite was used as a photocatalyst for the degradation of a few aromatic and chloroaromatic compounds.<sup>11d</sup> Lanthanide ions are known for their ability to form complexes with various Lewis bases (e.g., acids, amines, alcohols, aldehydes, thiols, etc.) via the interaction of surface functional groups with f orbitals of the lanthanides. This property is used in NMR spectroscopy, where the magnetic features of  $\text{Eu}^{3+}$  or  $\text{Pr}^{3+}$  yield significant chemical shift changes in the protons of the ion-associated organic ligands.<sup>11e</sup> Thus, the incorporation of lanthanide ions in a  $\text{TiO}_2$  matrix could provide a means to concentrate the organic pollutant at the semiconductor surface. Sol–gel is the most widely used technique for the preparation of these composites.<sup>12a,b</sup> However, the sol–gel method enables the synthesis of high surface area  $\text{TiO}_2$  particles and nanometer-size

\* To whom all correspondence should be addressed. Fax: +972-3-5351250. E-mail: gedanken@mail.biu.ac.il.

<sup>†</sup> Bar-Ilan University.

<sup>‡</sup> Hebrew University.

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semiconductor colloids.<sup>12c</sup> Nanophase europium oxide polycrystalline thin films were deposited on Si(100) substrates by nebulization of a 0.01 M solution of europium acetylacetonate in a 50% ethanol/water mixture followed by pulse ultrasonic spray pyrolysis<sup>13</sup> in flowing air.

Recently, sonochemical processing has been proven to be a useful technique for generating novel materials with unusual properties. The ability of the power ultrasound to effect chemical changes arises from the cavitation phenomena involving the formation, growth, and collapse of bubbles in liquid.<sup>14a</sup> The implosive collapse of bubbles generates localized hot spots through adiabatic compression within the gas phase of the collapsing bubble. The conditions formed in these hot spots have been experimentally determined, with transient temperatures of about 5000 K, pressures of 1800 atm, and cooling rates in excess of 108 K/s. With the continuing interest in the controlled synthesis and characterization of ceramic and metal–ceramic nanoparticles, we have explored the effect of power ultrasound on ceramic materials, such as silica microbeads and alumina gel,<sup>14b</sup> and the deposition of various nanoparticles, such as CdS,<sup>14c</sup> iron/iron oxides,<sup>14d</sup> and silver.<sup>14e</sup> A few papers have recently reported on the coating of europium oxide nanoparticles on silica<sup>14f</sup> or alumina<sup>14g</sup> by the ultrasound method. In this paper we report on the ultrasound-driven synthesis, morphological characterization, and optical properties of an europium oxide nanolayer deposited on the surface of titania.

## Experimental Section

**Sonochemical Deposition of Europium Oxide Nanolayer.** Titanium(IV) oxide (99.99%) predominantly rutile, europium(III) nitrate pentahydrate (99.9%), and ammonium hydroxide (99.99%) were purchased from Aldrich Chemical Co. and used as received. Doubly distilled water was used for the sonication.

A total of 400 mg of the as-received titania was sonicated for 10 min in order to disperse all particles in 100 mL of distilled water in a sonication cell. A total of 50 mg of europium(III) nitrate pentahydrate was added to the above solution, and the cell was attached to the sonicator horn. The sonication of the slurry with the high-intensity ultrasound radiation was conducted for 120 min by employing direct immersion of the titanium horn (Sonics and Materials VCX 600 sonifier, 20 kHz, 40 W/cm<sup>2</sup>) in a sonication cell. A total of 7–10 mL of 24% (by weight) aqueous ammonia was added in drops during the sonication. The sonication cell was placed in an acetone cooling bath, with a temperature of 15–20 °C maintained during the sonication. The gray-colored product was centrifuged at 10 000 rpm, washed thoroughly twice with doubly distilled water and finally with ethanol, and dried in a vacuum. The separated dry product synthesized by the sonochemical method is termed the “as-prepared” sample. Calcination of the as-prepared sample was carried out at 700 °C, under air for 4 h. An additional control reaction was carried

out with vigorous mixing of the reactants in an aqueous medium but without sonication, leading to the formation of uncoated Eu<sub>2</sub>O<sub>3</sub> particles.

**Characterization.** The powder X-ray diffraction (XRD) patterns of the product were measured with a Bruker AXS D\* Advance powder X-ray diffractometer (using Cu K $\alpha$  = 1.5418 Å radiation). The particle size, morphology, and nature of europium adherence to titania were studied by transmission electron microscopy (TEM) employing a JEOL-JEM 100 SX microscope working at 100 kV. Samples for the TEM experiments were prepared by suspending the dried sample in absolute ethanol in a sonication bath for 20 min. A drop of the sample suspension was allowed to dry on a copper grid (400 mesh; Electro Microscopy Sciences) coated with a carbon film. High-resolution scanning electron microscopy (HR-SEM) images were obtained using a LEO Gemini 982 field emission gun SEM (FEG-SEM) operating at a 4 kV accelerating voltage. High-resolution transmission electron micrographs (HR-TEM) were obtained using a JEOL-3010 set to a 300 kV accelerating voltage. A conventional CCD video camera, with a spatial resolution of 768 × 512 pixels, was used to digitize the micrographs, which were then processed using Digital Micrograph software. The elemental composition of the material was analyzed by energy-dispersive X-ray analysis (EDAX; JEOL-JSM 840 scanning electron microscope). X-ray photoelectron spectroscopy (XPS) was recorded using an AXIS, HIS 165, ULTRA (Kratos Analytical). The Ar<sup>+</sup> sputtering was carried out for 15 min at an energy of 4 keV and a current density of 0.5  $\mu$ A/cm<sup>2</sup>. Under these conditions the estimated surface removal depth was 10–15 Å. The excitation and emission spectra of Eu<sup>3+</sup> ions coated on the titania were measured on a Jasco FP 750 spectrometer.

## Results and Discussion

**EDAX.** The presence of titanium, europium, and oxygen in the coated materials was examined by EDAX measurements. The EDAX measurement is also useful to obtain a quantitative estimate of the Ti and Eu/Ti ratio. For the light elements such as oxygen, only a rough estimate could be obtained. Therefore, the Eu/O or Ti/O ratio could not be estimated from EDAX spectra. The europium, titanium, and Eu/Ti ratios in all of the samples were identical (for both nonheated and heated samples as well). The europium content in all of the samples was about 6% (by weight). This value is close to the molar ratio of EuNO<sub>3</sub>/TiO<sub>2</sub> in the starting solution.

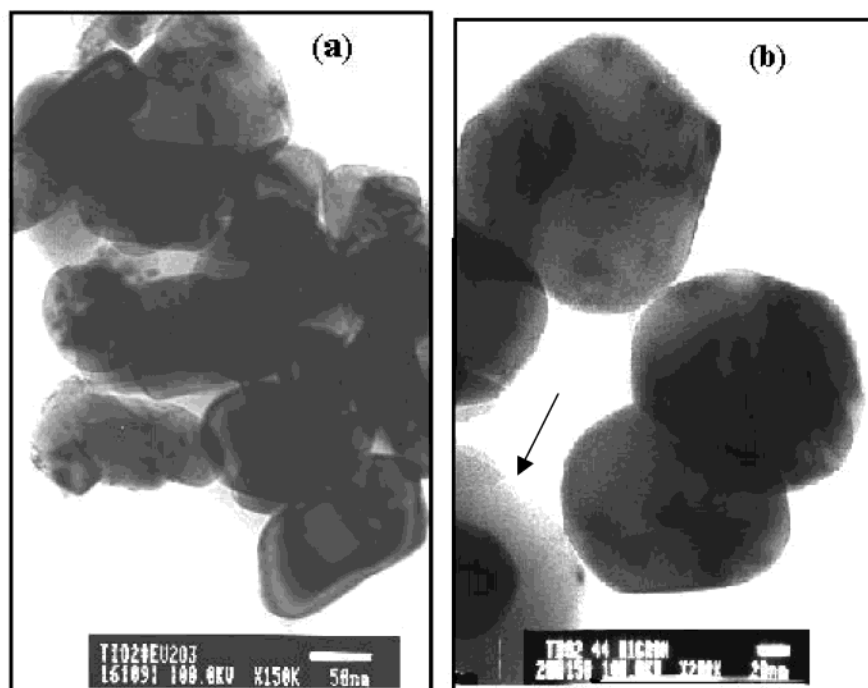
The XRD patterns of the host titania, the as-prepared coated sample, and calcinated samples are studied. The crystalline nature of the product is demonstrated by the presence of diffraction peaks of rutile titania. The XRD results of the titania, titania coated with Eu<sub>2</sub>O<sub>3</sub>, and calcinated samples are the same and match the XRD (not shown here) data of titania (rutile) (PDF No. 21-1276). We could not detect the XRD pattern of Eu<sub>2</sub>O<sub>3</sub> because the Eu<sub>2</sub>O<sub>3</sub> coating is perhaps less than the detection limit of the instrument. Shen et al.<sup>15</sup> reported in the study of structural and acid/base properties of supported europium oxides that samples containing less than 500  $\mu$ mol of europium do not appear in the XRD pattern.

**Electron Microscopic Studies.** Electronic microscopy is a technique widely used in structural and chemical characterizations of materials. It provides information about morphology, grain size, chemical

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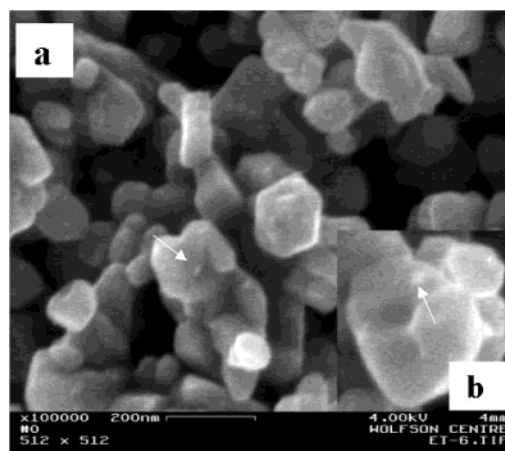
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**Figure 1.** TEM of (a) the bare substrate rutile titania submicroparticles and (b) europium oxide nanolayer coated on titania submicroparticles. A few particles are coated with more than 5 nm size, indicated by an arrow.

composition, crystallinity, and identification of the phases in the coated materials. This technique allows the quantitative analysis, structural studies by high-resolution microscopy, and spectroscopic analysis by electron energy loss. TEM and HR-SEM techniques were used to study the bare titania submicroparticles and europium oxide nanolayer coated on titania substrate. HR-TEM micrographs of these samples have provided details about crystallographic information, the arrangement of atoms in the specimen, their degree of order, and detection of atomic-scale defects in areas of a few nanometers in diameter. Figure 1a shows the TEM of as-received rutile titania substrates which were used in this study. The titania substrate particles have a diameter size distribution in the range of 75–200 nm. The low-resolution TEM (LR-TEM) micrographs of the titania nanoparticle deposited with an amorphous layer of europia are shown in Figure 1b. In this case, the titania nanoparticles were coated with an amorphous layer of europium oxide (prior to the annealing process). The thickness of the europium oxide layer on titania nanoparticles was in the range from 2 to 5 nm. Most of the titania nanoparticles are coated with a 2 nm size nanolayer. Only a few titania particles were coated with a thickness of more than 5 nm (indicated by an arrow). The amount of europium used for deposition was increased in an attempt to see the effect of an excess amount of europium oxide. When that was done, a nonuniform deposition of europium oxide was observed in the SEM and TEM pictures. The HR-SEM micrograph of the sample is shown in Figure 2. Because of the confines of the resolution, only large (approximate diameter of 10 nm) europium oxide nanoparticles can be seen on the surface of titania, indicated by an arrow.

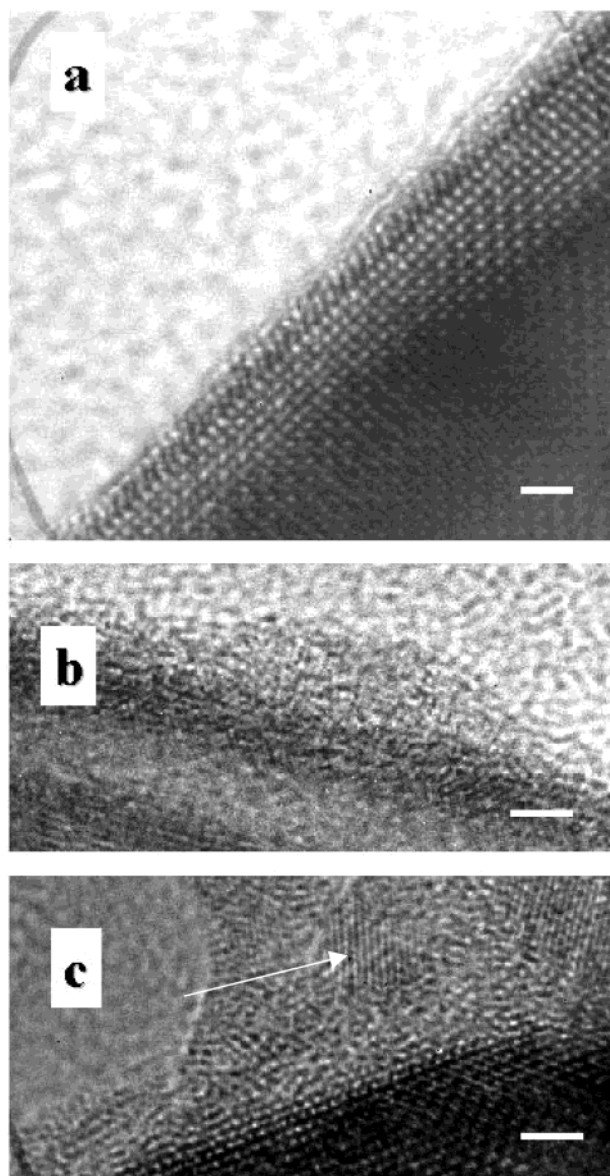
To obtain better evidence of the organization of europium oxide on the titania surface and because of the limitations of the SEM and the LR-TEM, we applied HR-TEM measurements. To distinguish between coated



**Figure 2.** (a) HR-SEM of the amorphous layer of europium oxide coated on titania nanoparticles. (b) Higher resolution SEM image.

and uncoated titania surfaces, we have carried out HR-TEM measurements of both of the samples. Figure 3a shows the HR-TEM image of the bare titania [the image was taken at the [110] zone axis of rutile, and the interplanar distance of the corresponding atomic planes is equal to 0.325 nm, which is in an agreement with XRD data (PDF No. 21-1276)]. It appears as a regular crystalline lattice superimposed on an amorphous coating in contrast from the carbon support. It is observed that on the surface of the rutile particle a very thin (<0.5 nm) amorphous  $\text{TiO}_2$  layer is present. The images taken from the coated samples are shown in parts b and c of Figure 3 (as-prepared and calcinated samples, respectively). In the unheated sample, an amorphous coating of europium oxide with a different thickness in the range of 2–5 nm was observed. It is also in agreement with LR-TEM that a few particles are covered with a 5 nm size europium oxide nanolayer. This layer is totally amorphous, and that may be the

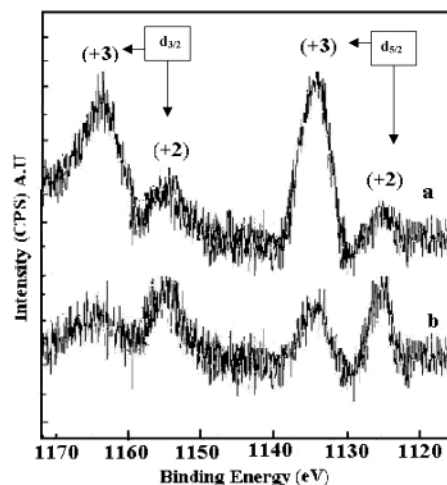




**Figure 3.** HR-TEM micrographs of (a) the bare titania (bar equal to 1 nm; the image was taken at the [110] zone axis of rutile titania), (b) amorphous coating of europium oxide on titania (bar equal to 2 nm), and (c) semicrystalline coating of europium oxide on a titania surface (bar equal to 3 nm).

reason that it cannot be detected by XRD. In the calcinated sample (see Figure 3c), some of the amorphous layer is still found, but additionally small crystallites (diameter  $\sim 2\text{--}3\text{ nm}$ ) were observed to be surrounded by an amorphous layer [the particle marked by an arrow has an orientation of [400] and interplanar distance of 0.272 nm, which is in agreement with the PDF database for europium oxide (PDF No. 34-0392)]. Because of the very small size and very small quantity of these crystallites of europium oxide ( $<6\text{ wt } \%$  because part of the europium oxide is amorphous) relative to titania, it cannot be detected by XRD. On the other hand, a surface analysis method like XPS detects this europium oxide layer easily.

**XPS.** XPS is known to probe only the surface of the particles. The analysis of low-energy electrons, which are strongly scattered in materials and consequently have a small escape depth, enables information to be obtained from the top few atomic layers of a surface. In

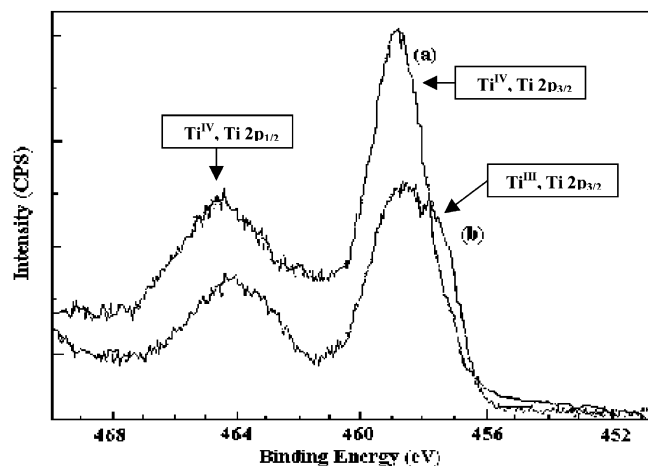


**Figure 4.** XPS of the Eu(3d) level in the same sample showing the coexistence of two oxidation states: (a) before sputtering; (b) after argon sputtering.

XPS, excitation by X-rays allows core atomic levels to be probed, and the resultant chemical shift provides an indication of the oxidation state of the material on the surface. In addition, XPS techniques are useful in conjunction with the removal of surface layers using ion sputtering to produce compositional depth profiles through the surface layer. Carbon is always present in XPS as a result of hydrocarbon deposits in air and/or vacuum, which is commonly used as an internal energy calibrant at 285.0 eV binding energy. The XPS spectra of the  $\text{Eu}_2\text{O}_3$  nanolayer coated on titania particles, recorded in the energy region of the Eu(3d) transition, are presented in Figure 4a,b. The spectra are rich because they contain the  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ionic states, each of which splits because of the spin-orbit coupling. On the basis of the published Eu(3d) spectra of  $\text{Eu}_2\text{O}_3$ ,  $\text{EuF}_3$ , and  $\text{EuCl}_3$ ,<sup>16</sup> we can assign the prominent peak around 1134 eV to a  $\text{Eu}^{3+}_{5/2}(3d4f^6)$  configuration. The other small peak around 1125 eV is attributed to a  $\text{Eu}^{2+}_{5/2}(3d4f^7)$  configuration. The other spin-orbit component, the 3/2, appears at 1165 and 1156 eV for +3 and +2, respectively. The existence of the divalent peak is found also by others, and in fact it always accompanies the XPS of  $\text{Eu}^{3+}$  ions. Its appearance may be due to the following possible reasons. The first possibility is that the divalent component comes from the surface layers, whose ground state is different from the bulk because of different geometric environments.<sup>16</sup> This phenomenon of the so-called “surface valence transition” has been observed before<sup>17a-d</sup> in many rare-earth metallic compounds including europium. The other possibility is that ground states of these commonly believed trivalent compounds are actually mixed valent, with both bivalent and trivalent components coexisting in the bulk ground state.<sup>17e</sup>

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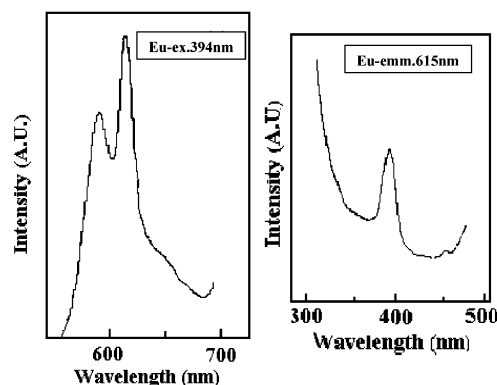


**Figure 5.** XPS spectrum of the Ti(2p) level in Eu-coated TiO<sub>2</sub> (a) before and (b) after sputtering.

We have also probed the Eu<sup>3+</sup> concentration in inner layers by removing surface layers using Ar<sup>+</sup> sputtering. After Ar<sup>+</sup> sputtering, the relative peak intensities of Eu<sup>3+</sup> and Eu<sup>2+</sup> are drastically changed. The intensities of Eu<sup>2+</sup> peaks were increased after the Ar<sup>+</sup> sputtering, while those of Eu<sup>3+</sup> have decreased. This increase in the peak intensity of Eu<sup>2+</sup> is explained as a result of the reduction of Eu<sub>2</sub>O<sub>3</sub> by the Ar<sup>+</sup> ions. These results are in good agreement with other published data.<sup>18</sup> Their results suggest that the Eu diffusion phenomena can be directly correlated with the presence in depth of europium in the +2 oxidation state.

The spectrum of Ti(2p<sub>1/2,3/2</sub>) before sputtering (Figure 5b) shows two well-resolved peaks. One of them is centered at 458.6 eV with a full width at half-maximum (fwhm) of 2.2 eV binding energy. The other is centered at 464.8 eV with 2.9 eV fwhm binding energy. The peaks are due to the Ti<sup>IV</sup> ions in titania<sup>19</sup> assigned to Ti(2p<sub>3/2</sub>) and Ti(2p<sub>1/2</sub>) states, respectively. The fwhm values are wider than those reported in the literature<sup>19</sup> [fwhm: 1.5 eV for Ti(2p<sub>3/2</sub>) and 2.5 eV for Ti(2p<sub>1/2</sub>)]. We attribute the large width to a size effect, where our 75–200 nm TiO<sub>2</sub> nanoparticles show wider peaks than the bulk material. The spectrum of Ti(2p<sub>1/2,3/2</sub>) after Ar<sup>+</sup> sputtering also shows two well-resolved peaks. Here, one additional peak (marked by an arrow) at 457.5 eV is observed, and it is probably due to the 2p<sub>3/2</sub> of Ti<sup>III</sup> in Ti<sub>2</sub>O<sub>3</sub>. Our results are in good agreement with the results of Choudhury et al.,<sup>19</sup> with their reduction of titanium oxide by a low-energy ion bombardment study. The binding energy value found for Ti(2p) also matches the data of Hofmann and Sanz.<sup>20</sup> They have also shown a similar reduction of TiO<sub>2</sub> after sputtering.

During the ultrasonic irradiation of liquid–powder aqueous slurries, cavitation and shock waves are created, which can accelerate to europium oxide solid particles to move very high velocities<sup>21</sup> toward the titania surface. The extremely high temperatures (~5000



**Figure 6.** Fluorescent and excitation spectra of the europium oxide nanolayer coated on the titania surface. Excited wavelength = 394 nm.

K) attained during acoustic cavitation lead to the formation of microjets. These microjets accelerate the solid particles to very high speeds and thus lead to sintering of the particles. Because of the orientation of these ultrasonic microjets, the very short lifetime (microseconds) of cavitation bubbles<sup>14a,21</sup> and possible inter-particle collisions between TiO<sub>2</sub> and Eu<sub>2</sub>O<sub>3</sub> change the surface morphology and reactivity,<sup>14a</sup> which finally resulted in binding or nanolayer coating. On the other hand, the slurry of titania, europium nitrate, and ammonia in an aqueous medium mixed with a magnetic stirrer for 120 min yielded a Eu<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> nanocomposite. This reaction resulted in uncoated Eu<sub>2</sub>O<sub>3</sub> polydispersed particles having a diameter of more than 100 nm, confirmed by TEM measurements.

**Photoluminescence Study.** The fluorescent and excitation spectra of the europium oxide nanolayer coated on titania nanoparticles are shown in Figure 6. The absorption and emission spectra of rare-earth ions arise from transitions within the 4f shell. The excitation spectrum is observed as an intense band peaking at 394 nm, and the strong emission spectrum consisted of two main lines related to red emission at 591 nm (<sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub>) and 615 nm (<sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub>) based on an Eu<sup>3+</sup> electronic transition. These results match the published results of Jin et al.<sup>12</sup>

## Conclusions

In this work, we have presented the results of a Eu<sub>2</sub>O<sub>3</sub> nanolayer coated on submicron-size titania particles with the aid of power ultrasound. TEM, HR-SEM, and HR-TEM analyses show a 2–5 nm nanolayer of europium oxide coated on titania nanoparticles. The presence of Eu ions on the surface is also confirmed by photoluminescence and XPS studies. On the other hand, the XRD studies do not provide evidence for its existence because of concentration detection limits.

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