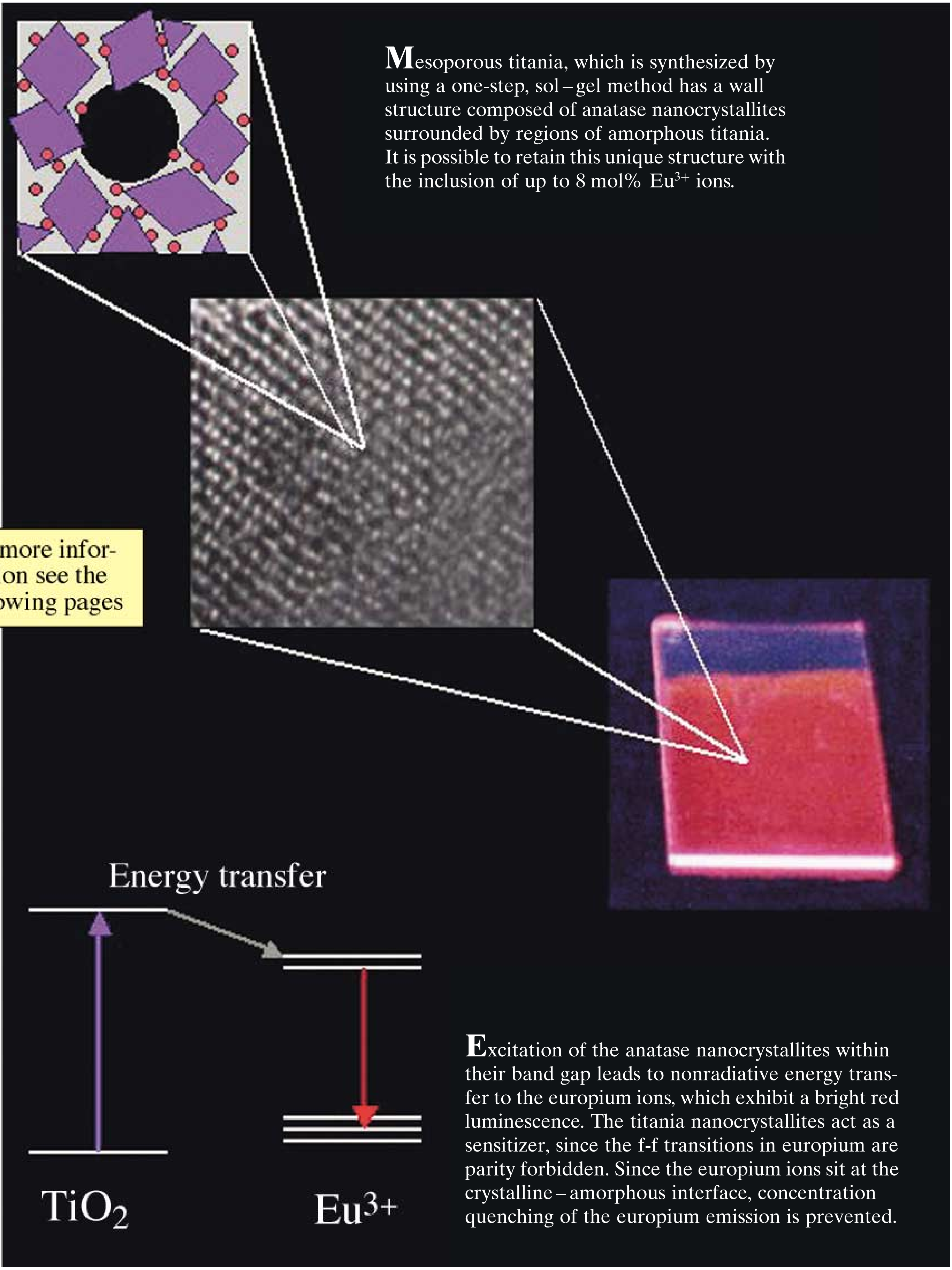

Mesoporous titania, which is synthesized by using a one-step, sol–gel method has a wall structure composed of anatase nanocrystallites surrounded by regions of amorphous titania. It is possible to retain this unique structure with the inclusion of up to 8 mol% Eu^{3+} ions.

Excitation of the anatase nanocrystallites within their band gap leads to nonradiative energy transfer to the europium ions, which exhibit a bright red luminescence. The titania nanocrystallites act as a sensitizer, since the f-f transitions in europium are parity forbidden. Since the europium ions sit at the crystalline–amorphous interface, concentration quenching of the europium emission is prevented.

For more information see the following pages

Sensitized Luminescence of Trivalent Europium by Three-Dimensionally Arranged Anatase Nanocrystals in Mesostructured Titania Thin Films**

Karen L. Frindell, Michael H. Bartl, Alois Popitsch, and Galen D. Stucky*

In the last several years various routes have been developed to synthesize mesostructured titania powders[1] and transparent titania thin films[1a, 2, 3] with three-dimensionally arranged, nanometer-sized pores. The thin films developed in our group have a well ordered cubic array of mesopores and a wall structure composed of 1–5 nm anatase nanocrystallites embedded in an amorphous titania matrix.[1a, 2] This interesting two-phase wall structure makes them a particularly attractive host matrix for optically active species such as trivalent rare earth metal (RE) ions. While the glasslike amorphous regions provide an ideal environment for the RE ions, the semiconducting nature of the anatase nanocrystallites can be used to sensitize the RE luminescence.[4] Sensitization is an important process for technological applications of RE ions in photonic devices and color displays, since direct excitation of the parity-forbidden intra-f-shell RE metal ion crystal-field transitions is inefficient.[5]

Here we report on a new luminescent material that combines a three-dimensional mesoscopically ordered array of nanocrystalline semiconductor particles with the nearly monochromatic emission of rare earth ions. We demonstrate that excitation of a cubic mesoporous titania thin film within its semiconductor band gap leads to bright narrow bandwidth emission from the europium activator ions by energy transfer from the semiconducting titania nanoparticle array, which acts as an effective antenna for the excitation light. Furthermore, we show that the unique two-phase composition of the mesopore walls allows high loading of Eu^{3+} ions without quenching their photoluminescence.

The europium-doped cubic mesoporous titania thin films were synthesized by a one-step sol–gel method, where trivalent europium ions were incorporated as the chloride salts into the mesopore walls (see Experimental Section). When the films are heat-treated, the chloride is removed and the europium ions remain in the two-phase titania walls surrounded by an oxide environment. Due to a large mismatch in ionic radius between Eu^{3+} and Ti^{4+} (0.98 and 0.68 Å, respectively)[6] the europium ions are not expected to occupy titanium sites within the anatase nanocrystallites, but rather to sit close to the grains in a glasslike environment.

Transmission electron micrographs (Figure 1) show that the titania films doped with up to 8 mol% Eu^{3+} have a cubic arrangement of pores, which are about 7–8 nm in size. This is in accordance with the undoped titania films and it is important to note that the incorporation of europium into the films does not destroy the mesostructure. Figure 1a and 1b show a view of the cubic structure of a Eu^{3+}-doped (8 mol%) titania film along the [100] zone axis, and Figure 1c shows a view along the [111] zone axis of the same sample. The high content of Eu^{3+} ions present in the walls of this sample is confirmed by energy dispersive X-ray spectroscopy (EDX) measurements (Figure 1d).

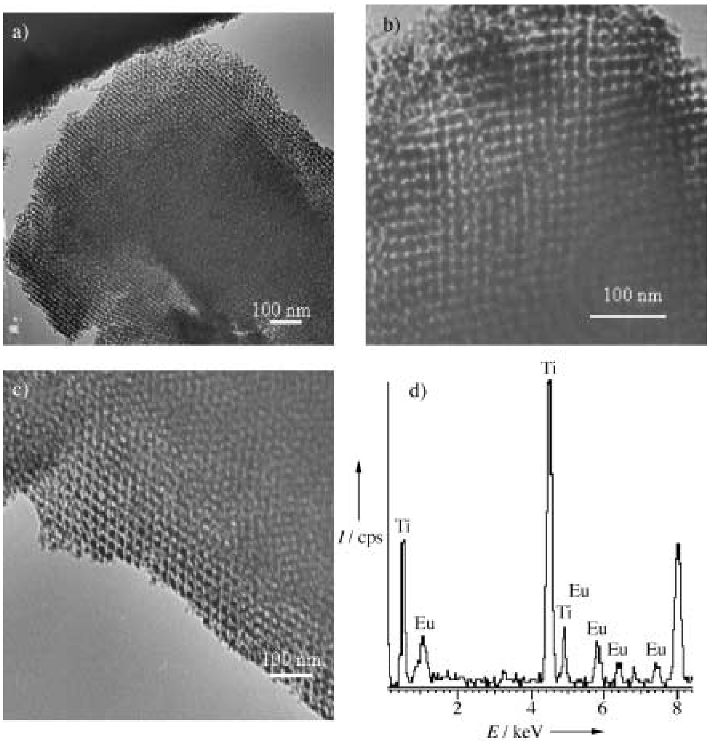

Figure 1. Transmission electron micrographs and EDX of Eu^{3+}-doped (8 mol%) cubic mesoporous titania thin films: a) View along the [100] zone axis, b) magnified view along the [100] zone axis, c) view down the [111] zone axis, d) EDX spectrum confirming the presence of europium in the mesopore walls. The measured europium content is 12 ± 4 mol%; this is an average value taken over several large areas.

Figure 2 shows the UV/Vis absorption spectra of mesoporous titania films both undoped (spectrum a) and doped with 1 and 8 mol% Eu^{3+} (spectra b and c, respectively). In all three spectra a strong sharp increase in absorption corresponding to the titania semiconductor band gap appears at about 360 nm to 365 nm (3.45 to 3.40 eV). The shift in the band edges compared to that of bulk crystalline anatase, which has a band

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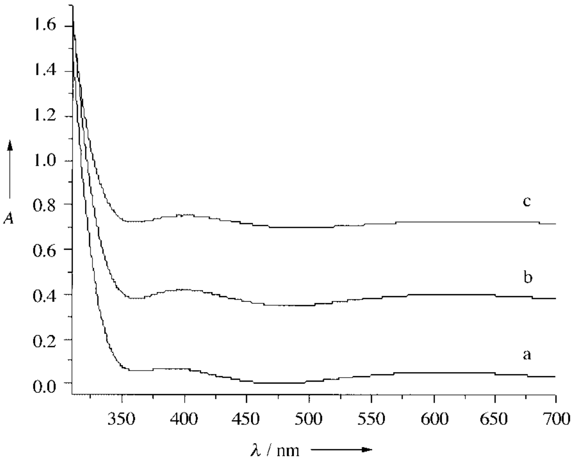

Figure 2. UV/Vis absorption spectra of undoped (spectrum a) and Eu^{3+}-doped (1 and 8 mol%; spectra b and c, respectively) cubic mesoporous titania thin films.

edge of about 380 nm (3.25 eV),[7] is attributed to the small size of the anatase nanocrystallites (with radii between 0.5 and 2.5 nm) located in the amorphous titania walls.[1a, 2] It is noteworthy that the position of the absorption band edge as well as the slope of the absorption band is the same for the undoped and doped films. Therefore it can be concluded that doping the films with europium ions does not significantly modify the nucleation and growth of the titania nanocrystallites. Importantly, no absorption peaks are observed arising from transitions within Eu^{3+} crystal-field states, which can be explained by the small thickness of the titania films in combination with the inherently low absorption cross sections of the parity-forbidden Eu^{3+} intra-f-shell crystal field transitions.[5a] The broad absorption bands observed in the visible region are caused by interference colors that arise as a result of the thickness of the films.

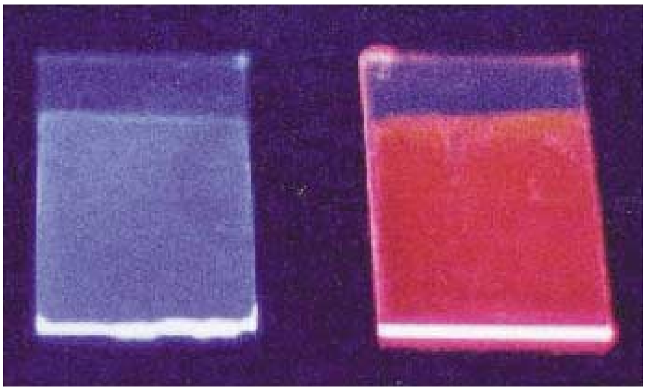

Figure 3. Color photograph of mesoporous silica (left) and titania (right) films, both doped with 8 mol% Eu^{3+}. The films are excited with a UV lamp at 300 nm.

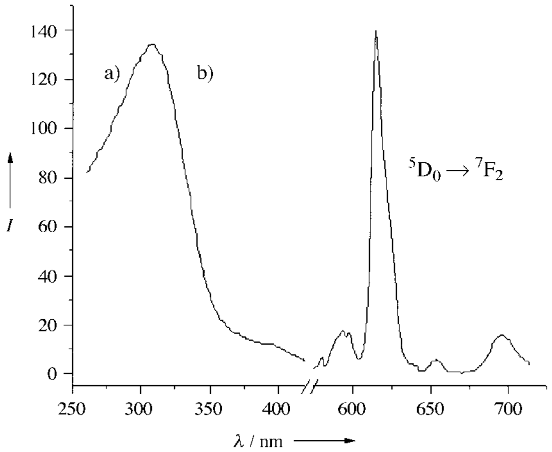

Figure 4. Photoluminescence excitation (spectrum a) and emission (spectrum b) spectra of a cubic mesoporous titania thin film doped with 8 mol% Eu^{3+}.

Excitation of these films above the measured titania nanocrystallites band gap (360–365 nm) results in strong red light emission (Figure 3 and Figure 4). Although Eu^{3+} has no crystal field absorption transition at 330 nm,[5a] emission bands between 550 and 720 nm, characteristic for Eu^{3+}, are present in the photoluminescence (PL) emission spectrum (Figure 4b). All of the five Eu^{3+} Russell–Saunders multiplets $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) show strong inhomogeneous broadening indicative of an amorphous oxide environment. A more detailed analysis of the most intense emission band, which is centered at 614 nm and corresponds to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition, shows that this band is completely unresolved with a FWHM (full width at half maximum height) value of about 300 cm^{-1}—a value typically found for europium ions in an oxide glass environment.[8] The PL excitation spectrum of the $^5D_0 \rightarrow {}^7F_2$ emission band at 614 nm (Figure 4a) exhibits an intense broad peak starting at 360 nm and centered at around 310 nm. This peak coincides very well with the titania nanocrystallites absorption band edge (see Figure 2) indicating that the Eu^{3+} emission is associated with a nonradiative energy transfer process from the titania to the Eu^{3+} crystal field states.[4] Moreover, we noticed that when the Eu^{3+}-doped films are excited below the titania band gap at 420 nm, no emission from europium ions is present. Instead, only a broad band between 600 and 750 nm is observed, which can be assigned to emission from titania defect centers.[4, 9] To further prove that the Eu^{3+} emission is highly sensitized by titania, we prepared mesoporous silica thin films doped with the same Eu^{3+} concentration as in the titania films. Figure 3 shows a photograph of a silica film (left) and a titania film (right) both doped with 8 mol% Eu^{3+} ions and excited with a UV lamp at 300 nm. While strong red emission from the europium ions can be observed from the titania film, the silica film, which is unable to absorb at this wavelength shows no red Eu^{3+} emission. This was also confirmed by PL spectroscopy measurements.

To study the effects of concentration quenching of the Eu^{3+} luminescence, we determined the PL lifetime of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ emission band at 614 nm (see Experimental Section). A reasonable fit of the decay curves is achieved by using a biexponential function. The long-lived component obtained for each of our cubic mesoporous titania films with Eu^{3+} concentrations of 1, 3, 5, and 8 mol% has a PL lifetime of 550, 520, 470, and 500 μs, respectively. Additionally, in all the films a very short component with lifetimes of between 40 and 90 ns was detected. While the long component is typical for the

Eu^{3+} parity-forbidden intra-f-shell crystal-field transition $^5D_0 \rightarrow {}^7F_2$, the short component is not attributed to Eu^{3+}, but to the very weak intrinsic background luminescence from the TiO_2 defect centers. Here it should be emphasized that no significant decrease in the PL lifetimes is observed when the Eu^{3+} content is increased. This indicates that even at europium concentrations as high as 8 mol% no quenching of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ luminescence is present.

In summary, for the first time, a cubic mesostructured matrix of titania with a three-dimensional array of embedded anatase nanocrystals has been doped with high concentrations of europium ions. The semiconducting anatase nanocrystallites sensitize the europium activator, which leads to an energy transfer system that produces a bright red, near-monochromatic luminescence. This work represents an interesting optical application of an all-inorganic mesoporous material. These have, because of their robust self-assembled framework, high surface area, simple processability, and air and moisture stability, potential to be incorporated into optical devices. The ability of the cubic mesostructured titania films to retain their structure and properties after the addition of a large amount of dopants opens the field to three-dimensionally ordered multicomposite materials for new electrical, magnetic, and optical applications.

Experimental Section

A typical trivalent europium ion doped, red photoluminescent film was prepared by dissolving $EuCl_3 \cdot 6H_2O$ (0.51 g) and Pluronic P123 (1 g) in absolute ethanol (12 g). This solution was added to a solution containing concentrated hydrochloric acid (2.7 mL) and titanium(IV) ethoxide (3.88 mL). After the solution had been aged, films were deposited on glass or quartz substrates by dip-coating at a rate of 1 mm s^{-1}. The films were heat-treated for 4 h at 400 °C.

UV/Vis absorption spectra of these films were measured by using a Shimadzu UV-1610 recording spectrometer. The PL emission and excitation spectra were recorded with a Cary Eclipse PL spectrometer. For the PL lifetime measurements the films were excited with the 337 nm line of a pulsed (1 ns pulse width) nitrogen laser. The emission was dispersed by a monochromator and analyzed by using a digital oscilloscope.

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Multiple Emissions from 1,3-Diphenyl-5-pyrenyl-2-pyrazoline Nanoparticles: Evolution from Molecular to Nanoscale to Bulk Materials[**]

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The size dependence of organic crystals has not been as well investigated as that of inorganic crystals. The strong effects of confinement on electron–hole pairs in all three dimensions result in the size-tunable optoelectronic properties of semiconductor quantum dots,[1, 2] but are not expected in organic molecular crystals (OMCs), because of the small radius of the Frenkel exciton.[3] The primary difference between inorganic and organic semiconductors is the bandwidth, or the degree of orbital overlap. In the case of OMCs, the electronic and optical properties are fundamentally different from those of inorganic semiconductors, because of weak van der Waals intermolecular forces.[3, 4] To date, the search for ways of controlling size, shape, and hence the properties of OMCs is still a challenge[5–9], and an important aspect in the development of nanoscience.

Size effects may also be significant in OMCs.[5, 6] In our previous work, the size dependence of the optical properties of nanoparticles consisting of 1-phenyl-3-((*p*-dimethylamino)-styryl)-5-((*p*-dimethylamino)phenyl)-2-pyrazoline (PDDP) was shown to originate from charge-transfer (CT) exciton formation, with increasing nanoparticle size.[10] Herein, the newly synthesized 1,3-diphenyl-5-pyrenyl-2-pyrazoline (DPP) is used as a model compound, in the light-emitting layer of an electroluminescent device, because of its strong, blue

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