Enhanced Emission in Composite Multilayers of Amorphous TiO_2-Gel and Eu^{3+} Ions

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Ultrathin films of $(TiO_2/Eu^{3+})_n$ and $(TiO_2/PAA/Eu^{3+})_n$ composites were prepared by the surface sol-gel process and the subsequent chemisorption/coordination of Eu^{3+} ions. Amorphous TiO_2-gel layers were found to act as sensitizer for efficient emission of Eu^{3+}.

Lanthanide ions such as Eu^{3+} and Tb^{3+} are known for their unique luminescent properties such as long-lived, millisecond-order lifetime, narrow-width emission bands and hypersensitivity to coordinative environment. These properties make lanthanide ions useful materials in optoelectronic devices and displays, etc.[1,2] Direct excitation of lanthanide ions is not efficient because of their inherently small absorption cross-sections. To overcome this problem, an antenna function, which can harvest light effectively at a suitable wavelength and then transfer the energy to the lanthanide, is highly desired.[3] Up to now, most of the antennas used to facilitate luminescence of lanthanides are organic species. The amorphous TiO_2 has been examined simply as matrices of Eu^{3+} luminescence.[4,5] Interestingly, we have invariably observed UV absorption near 260 nm for ultrathin amorphous TiO_2 films that were prepared by the surface sol-gel process. In order to assess possible antenna effects of amorphous TiO_2 for Eu^{3+}, we examined herein two ways to fabricate composite films containing Eu^{3+} and TiO_2 in a layer-by-layer fashion and measured luminescence of Eu^{3+} in the presence of TiO_2 layers.

The preparation of TiO_2 and TiO_2/poly(acrylic acid) (PAA) ultrathin films by the surface sol-gel process has been described in our previous publications.[6,7] By combining this assembly process with adsorption or coordination of Eu^{3+} ions, we prepared binary $(TiO_2/Eu^{3+})_n$ and ternary $(TiO_2/PAA/Eu^{3+})_n$ films.[8] QCM measurement and UV-Vis spectroscopy were employed to monitor the film growth. For $(TiO_2/Eu^{3+})_n$ films, the frequency decreases in one adsorption cycle were 17 ± 20 Hz for TiO_2 and 148 ± 24 Hz for Eu^{3+}. The frequency decreased almost linearly with the increase in the number of adsorption cycle, showing satisfactory reproducibility of the assembly process. UV-Vis absorption spectra of TiO_2/Eu^{3+} films with different adsorption cycles have an absorption peak near 260 nm with a threshold at 318 nm, in agreement with spectral characteristics of nanosized TiO_2 materials.[9] With increasing numbers of the adsorption cycle, the absorbance at 260 nm was enhanced accordingly. Because of probable desorption of Eu^{3+} in the subsequent immersion in $Ti(O\text{-}n\text{-}Bu)_4$ solution, it is difficult to estimate the contents of TiO_2 and Eu^{3+} in the film by using QCM data alone. Therefore, XPS measurement was conducted for direct determination of the film composition. XPS spectra of a TiO_2/Eu^{3+} multilayer film indicated the presence of titanium at 458.9 eV (Ti $2p_{3/2}$) and europium at 1124.7 eV (Eu $3d_{5/2}$). The Eu/Ti atomic ratio was 0.24, as calculated from the relative peak area after correction of sensitivity factors. Adsorption of Eu^{3+} on a TiO_2-gel layer is probably caused by their strong electrostatic interaction. Eu^{3+} ions appear to be dispersed in TiO_2 layers without aggregation, as illustrated in Figure 1a. On the other hand, chemisorption of PAA on a TiO_2 layer and subsequent coordination of Eu^{3+} ions can produce $(TiO_2/PAA/Eu^{3+})_n$ films (Figure 1b). When PAA is used as a binding layer of Eu^{3+}, the amount of Eu^{3+} incorporated in multilayers could be widely altered with the pH of aqueous $Eu(NO_3)_3$. The Eu/Ti ratios in $(TiO_2/PAA/Eu^{3+})_4$ films were 0.65, 1.83 and 3.53 with the pH adjusted to 3.0, 5.0 and 7.0, respectively. Dissociation of acrylic acid groups of PAA is enhanced in high pH conditions, so that coordination of PAA with Eu^{3+} is promoted.

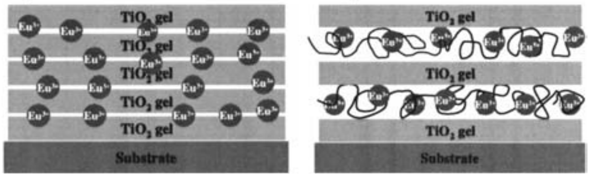

Figure 1. Schematic illustration of composite films of (a) $(TiO_2/Eu^{3+})_n$ and (b) $(TiO_2/PAA/Eu^{3+})_n$.

Subsequently, the photoluminescence (PL) property of Eu^{3+} embedded in $TiO_2$was examined. Figure 2a shows emission spectra of the $(TiO_2/PAA/Eu^{3+})_n$ films with different numbers of the adsorption cycle, as excited at 260 nm. In all emission spectra, there exist a main emission peak of Eu^{3+} at 615 nm ($^5D_0 \rightarrow {}^7F_2$) and four satellite peaks at 581, 593, 653 and 701 nm, which correspond to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 3, 4) transitions. Upon increasing the number of adsorption cycle, both the main peak and the satellite peaks become stronger. A linear relationship between the emission intensity at 615 nm and the number of deposition cycles is shown in the inset of Figure 2a, indicating satisfactory reproducibility of the film deposition process. Excitation spectra of the $(TiO_2/PAA/Eu^{3+})_n$ film monitored at 615 nm are shown in Figure 2b. The intensity of excitation spectra increased with the increase in the number of adsorption cycle, in accordance with the results of emission spectra. Most importantly, the close resemblance of the excitation spectra to the absorption spectra of $(TiO_2/PAA/Eu^{3+})_n$ films clearly endorses that emission of Eu^{3+} is sensitized by TiO_2 matrix. Direct excitation of Eu^{3+} ions at 411 nm ($^7F_0 \rightarrow {}^5D_3$) is relatively inefficient for the emission of Eu^{3+}. The schematic description of the energy transfer process from amorphous TiO_2 gel to Eu^{3+} ion is presented in Figure 3.

It is noteworthy that the luminescence intensity does not increase linearly with the Eu^{3+} content in the film. The luminescence of the film, in which Eu^{3+} was adsorbed at pH 5.0, is about 3.5 folds stronger than that at pH 3.0, but the luminescence of the film at pH 7.0 is only 10 percent stronger than

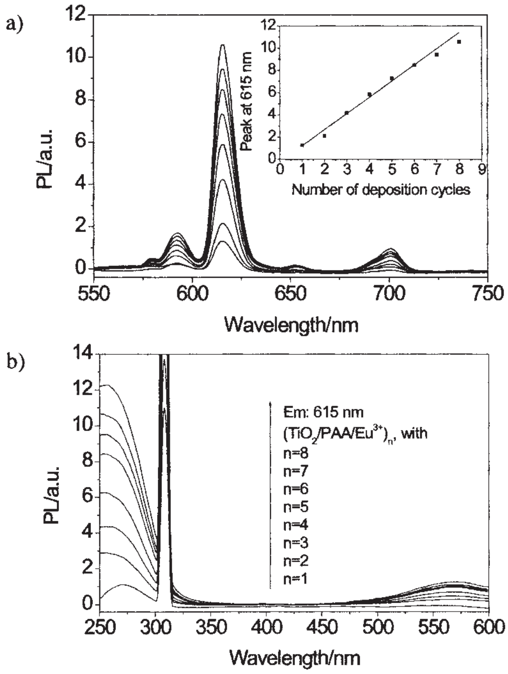

Figure 2. (a) Emission (Ex = 260 nm) and (b) excitation (Em = 615 nm) spectra of $(TiO_2/PAA/Eu^{3+})_n$ films with $n = 1, 2, 3, 4, 5, 6, 7$ and 8 from the bottom to the top). Inset in (a) shows the emission at 615 nm with increases in the number of deposition cycles.

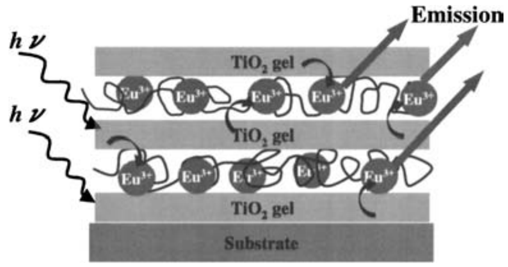

Figure 3. Schematic illustration of the energy transfer process from amorphous TiO_2 gels to Eu^{3+} ions in a composite film of $TiO_2/PAA/Eu^{3+}$.

that of the pH 5.0 film. This indicates the energy transfer from TiO_2 to Eu^{3+} at the pH 5.0 film is close to saturation in our system.

In the multilayer film of $(TiO_2/Eu^{3+})_n$, emission from Eu^{3+} is similarly sensitized by TiO_2-gel layers, although its intensity is only one quarter of that in $(TiO_2/PAA/Eu^{3+})_n$ film with the same number of adsorption cycles. Stronger emission of the $(TiO_2/PAA/Eu^{3+})_n$ film than that of $(TiO_2/Eu^{3+})_n$ film comes from larger amounts of Eu^{3+} ions loaded by PAA layers in the former case.

In conclusion, we demonstrated for the first time that amorphous TiO_2 gels can efficiently sensitize the emission of Eu^{3+} ions. In general, photocatalytic and photoelectronic properties of TiO_2 have been explained only in the crystalline states, including a recent report by Stucky et al. which described that nanocrystalline TiO_2 sensitized the emission of Eu^{3+} ions.[10] This was not the case in the present study, since the film prepared by the surface sol-gel process is amorphous. In comparison with crystalline TiO_2, amorphous TiO_2 is much easier to incorporate guest species to produce composite TiO_2 materials. The combination and composition of metal oxides with lanthanides are widely variable in our system. Efficient emissions of other lanthanides will be achieved by tuning antenna effect of metal oxide matrices. Such lanthanide-based luminescent thin films will have applications in many areas such as optoelectronic devices and displays.

References and Notes

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