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PHOTOLUMINESCENCE PROPERTIES OF Eu^{3+} DOPED TiO_2 NANOPARTICLES

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Abstract

Eu^{3+} doped TiO_2 nanoparticles were synthesized during extended hydrothermal treatment of TiO_2 nanotubes dispersion in the presence of $\text{Eu}(\text{NO}_3)_3$. Eu^{3+} ions occupy two different sites of titania nanoparticles having different binding energies: core octahedral sites and undercoordinated surface sites. Photoluminescence spectra of Eu^{3+} doped TiO_2 nanoparticles independently of dopant concentration consist of three characteristic peaks located at $\lambda=543$, 596, and 617 nm attributed to the intra-4f transitions of Eu^{3+} ion. Removal of excess of Eu^{3+} ions from the surface and from the undercoordinated surface sites applying post synthetic dialysis of the sample affects its photoluminescence spectrum. The peak intensity at $\lambda=617$ nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition) decreases after dialysis. Such “self-purification” process of nanoparticles is a consequence of fact that dopant ions which substitute Ti atoms in the undercoordinated coordination environment of reconstructed surfaces are weakly bound to the anatase lattice.

Introduction

Rare earth ions doped semiconductors have attracted considerable attention in recent years due to their high potential of becoming a new class of luminescent materials with a wide range of applications in many different fields such as photoelectric devices, solid state laser materials, optical data storage, and medical diagnostics [1]. The TiO_2 is considered as promising host material for sensitizing luminescence of Eu^{3+} ions due to its wide band gap, low absorbance in the visible region and thermal properties. On the other hand, Eu^{3+} ions show stable and bright red luminescence due to intra-4f transitions at room temperature. The luminescence signal in doped materials coming from fixed lines of rare earth ions, and their positions are almost independent of the host matrix. However, the line width and its relative intensity are often affected by the nature of the matrix [2]. In this paper we report on the synthetic procedure of Eu^{3+} doped TiO_2 nanoparticles and their photoluminescence properties dependence of dopant position. Using titania nanotubes as a precursor we eliminated driving force problem that arises from the increase in the activation energy for nanocrystal nucleation in the presence of the dopant ions and consequent exclusion of the Eu^{3+} ions during nanoparticle growth.

Experimental

Titania nanotubes were synthesized according to procedure described elsewhere [3]. Eu^{3+} doped TiO_2 nanoparticles were synthesized using hydrothermal treatment

(90 min/250°C) of suspension of 3×10^{-2} M titania nanotubes (pH=3) in the presence of 6.4×10^{-4} M $\text{Eu}(\text{NO}_3)_3$. The excess of Eu^{3+} ions in dispersion of doped nanoparticles was removed by filtration or dialysis. The sample (25mg of $\text{Eu}^{3+}/\text{TiO}_2$ nanoparticles powder in 10ml H_2O) was dialyzed using Spectra/Por Dialysis Membrane, MWCO: 3,500 (Spectrum Laboratories) against 200ml of acidified water (pH=3) at 4°C for 3 days. Transmission electron microscopy (Hitachi H-700 FA TEM) at 125kV was used for determining the shape and size of the titania nanotubes and nanoparticles. The photoluminescence spectra of powdered samples were recorded on Perkin-Elmer LS-45 Fluorescence Spectrometer, in front-face mode ($\lambda_{\text{exc}}=396$ nm).

Results and discussion

We showed in our previous work that titania nanotubes contain large amounts of undercoordinated surface sites [3]. The TEM measurements revealed that the outer diameter of nanotubes is about 10 nm while the inner diameter is about 7 nm, Figure 1A. Hydrothermal treatment of nanotubes dispersion containing Eu^{3+} ions adsorbed on undercoordinated sites result in the formation of Eu^{3+} doped anatase TiO_2 nanoparticles. The majority of the nanoparticles have polygonal shapes with average dimension of ~15 nm, Figure 1B.

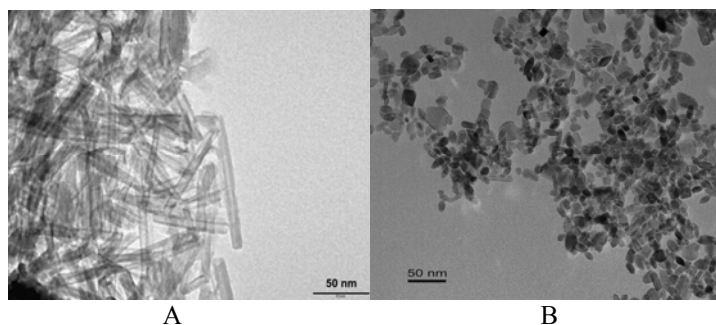


Fig.1. TEM images of scrolled titania nanotubes (A) and Eu^{3+} doped TiO_2 nanoparticles (B).

We used fluorescence spectroscopy to investigate the coordination environment of Eu^{3+} dopant ions within anatase TiO_2 matrix. Photoluminescence spectra of filtrated and dialyzed samples of TiO_2 nanoparticles doped with 6.4×10^{-4} M Eu^{3+} ions are shown in Figure 2. Three peaks in fluorescence spectra, Figure 2, located at $\lambda=543$, 596, and 617 nm are ascribed to the ${}^5\text{D}_1 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions of Eu^{3+} ion, respectively [2, 4]. As can be seen, there is a noticeable difference in photoluminescence spectra of filtrated and dialyzed samples.

Namely the intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition decreases in dialyzed sample. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is a hypersensitive forced electric-dipole transition being allowed only at low symmetries with no inversion center, whereas the magnetically allowed ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is almost independent of the surroundings of the Eu^{3+} ion [2]. In our samples the Eu^{3+} ion can be located at two

different sites: on the surface of the nanoparticles (low, unordered symmetry), and within crystal lattice replacing the Ti^{4+} ion with octahedral symmetry. After filtration of the sample the large amount of the Eu^{3+} ions located on the surface of the TiO_2 nanoparticles is left behind, and due to low site symmetry the probability of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is significant, that is manifested with strong intensity of the peak at $\lambda=617$ nm. Post-synthetic dialysis process represents a more efficient method for removing excess of dopant ions, leaving only Eu^{3+} ions that substitute Ti^{4+} ions located in the octahedral lattice sites. Due to the high symmetry of octahedral site the probability of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is low and the intensity of peak at $\lambda=617$ nm decreases, Figure 2.

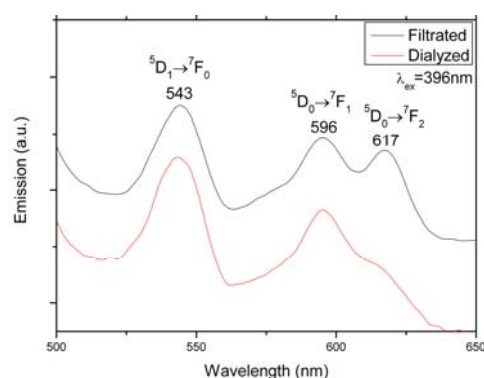


Fig.2. Photoluminescence spectra of filtrated and dialyzed Eu^{3+} doped TiO_2 NP.

Conclusion

TEM analysis revealed that nanoparticles mainly have polygonal shape with average dimension of 15 nm. Post-synthetic dialysis of doped titania nanoparticles affects its photoluminescence spectra. Intensity of the hypersensitive forced electric-dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition decreases in dialyzed samples, indicating the removal of the excess of Eu^{3+} ions and Eu^{3+} ions from the low symmetry surface sites, leaving only dopant ions that substitute Ti^{4+} ions located in the lattice site with octahedral symmetry. Post-synthetic treatment of Eu^{3+} doped TiO_2 nanoparticles open up possibility to manipulate the dopant position.

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