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Ultraviolet and visible upconversion emissions in Er^{3+}-Yb^{3+} doped titanium dioxide nanopowder under the 980 nm laser diode excitation

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Abstract. Er^{3+}-Yb^{3+} co-doped titanium dioxide upconversion nanoparticles were synthesized by sol-gel method. White upconversion emissions were observed after excitation of nanoparticles with 980 nm Near-Infrared laser diode. Upconversion emissions consist of red (640-690 nm), green (520-570 nm), and blue (408 nm) emissions. Ultraviolet upconversion emissions were also detected with wavelength about 210 nm. Ultraviolet emissions are probably the results of relaxation from $^2I_{13/2}$ (220 nm) and $^2L_{15/2}$ (210 nm) states to $^4I_{15/2}$. Visible and ultraviolet emissions of these nanoparticles can be used in photodynamic therapy. High penetration of Near-Infrared light into the body tissue makes these nanoparticles appropriate for aiming tumors in deeper tissues in comparison with older methods of photodynamic therapy.

1. Introduction

Upconversion emissions can be seen in materials that are doped with lanthanides, actinides, and transition metals. Trivalent lanthanides have been used more than others because of metastable electronic states, excellent luminescence characteristics, long luminescence lifetime, and low absorption [1]. Upconversion phenomenon occurs by three major mechanisms: Energy Transfer Upconversion (ETU), Excited State Absorption (ESA), and Photon Avalanche (PA). Erbium (III) and Ytterbium (III) electronic states have equal gaps that are well matched for use in co-doped upconversion systems. Yb^{3+} can be excited by 980 nm photon. Sequential transfer of energy from Yb^{3+} to Er^{3+} can make an electron go higher in ladder-like states in Er^{3+}. Relaxation from higher states results in an upconversion emission with higher energy than the exciting emission. Host materials must have low phonon energy. High phonon energy of matrix causes a decrease in the number of energy transfers; as a result, upconversion yield decreases [2-4].

Unique optical properties, such as minimized auto-fluorescence background and the high depth of light penetration in body tissue, are of interest for bioimaging and biomedical detection [5,6]. Photodynamic therapy (PDT) is a non-invasive method for the treatment of numerous diseases that has attracted interests in last decades [7,8]. In cancer treatments, photosensitizers (PS) that are excited by visible or UV light remove tumor cells by photocatalysis process [9]. Because of low penetration of visible light in tissue, PDT has been limited to the treatment of the skin or shallow tumors [10]. Body tissue has a transparent window in Near-Infrared (NIR) region (700-1100 nm);

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therefore, photosensitizers can be loaded onto a carrier that converts NIR light to Visible or UV light in deeper tissues [11,12].

Among the well-known biocompatible materials that are appropriate for biomedical applications, TiO_2 has relatively low phonon energy (about 700 cm^{-1}) that makes it suitable for use as a host in upconversion transducers [13]. In this research, TiO_2 nanoparticles were doped by Er^{3+} and Yb^{3+} using sol-gel method. Then, nanocrystals were irradiated by 980 nm NIR laser diode. White upconversion emissions, consisting of red, green, blue, and also ultraviolet range of spectrum, were observed. To the best of our knowledge, there are very few reports on ultraviolet and blue upconversion emissions in TiO_2:Er^{3+}:Yb^{3+} system.

2. Materials and methods

Sol-gel method was used to synthesize co-doped TiO_2 nanoparticles. The procedure is one of common sol-gel methods for the synthesis of doped TiO_2 [14], mainly adopted from synthesis method of Wenlan Wang et al. [15]. Two separate solutions, A and B, were prepared simultaneously. In solution A, 7 mL absolute ethanol was mixed with 1 mL nitric acid and stirred for 10 minutes. Then, 3.7 mL Titanium tetra isopropoxide (TTIP) was added to the mixture and stirred for one hour. In solution B, 5 mL ethanol and 1.4 mL deionized distilled water were mixed and stirred for 10 minute. Rare earth salts $Er(NO_3)_3.5H_2O$ and $Yb(NO_3)_3.5H_2O$ were dissolved in the mixture in molar ratio Er^{3+}:Yb^{3+}:Ti^{4+} = 0.01:0.09:1 under vigorous stirring for one hour. Then, solution B was added to solution A dropwise. The final solution was stirred for one hour and aged 72 hours for gelation. The gel was dried for 24 hours at 80-100°C. The obtained powders were grounded and calcined at 880°C for 17 h.

Crystal structure of powders was examined by X-Ray diffractometer (Stoe, Germany) with Cu-Kα tube (λ = 1.5460 Å). Raman spectra obtained by dispersive Raman microscope were equipped with 785 nm laser source (Senterra, Bruker, Germany). Scanning Electron Microscopy (SEM) image was provided by the Razi Metallurgical Research Center SEM lab. UV-vis absorption spectra were measured by spectrophotometer (Jenway, England). The 980 nm laser diode was used to excite the powders. Upconversion emissions were analyzed by spectrophotometer (USB4000, Ocean Optics, USA).

3. Results and discussion

3.1. Structural and morphological characterization

Figure 1 shows the XRD patterns of pure TiO_2 nanocrystals and TiO_2:Er^{3+}:Yb^{3+} calcined at 500°C and also the TiO_2:Er^{3+}:Yb^{3+} calcined at 880°C. The pattern shows that, in TiO_2:Er^{3+}:Yb^{3+} calcined at 500°C, only anatase phase is present (Figure 1(b)), while, in pure TiO_2, rutile and anatase phases coexist (Figure 1(a)). It shows that dopants postpone anatase to rutile transformation. It is because of the formation of Ti-O-Er and Ti-O-Yb bonds. Larger radius of Yb and Er makes them be located at the interface of crystals; therefore, they inhibit further crystal growth and phase transformation [13,15]. Figure 2 shows the Raman spectra of TiO_2:Er^{3+}:Yb^{3+} calcined at 500°C. The peaks at 637 and 513 cm^{-1} are characteristic bands of anatase phase. These peaks confirm that only anatase phase is present in the doped sample calcined at 500°C.

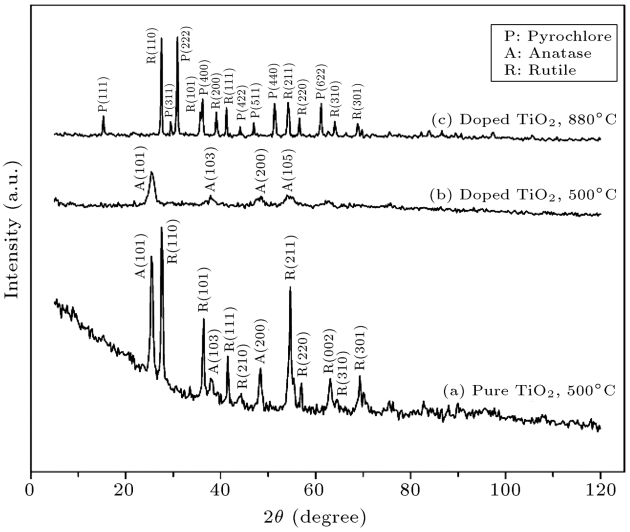


Figure 1. XRD patterns of pure TiO_2 (a) and doped TiO_2 (b) calcined at 500°C, and doped TiO_2 calcined at 880°C (c).

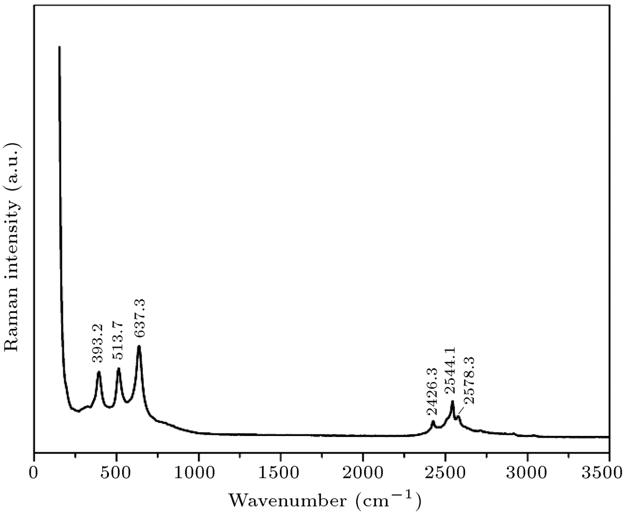


Figure 2. Raman spectra of TiO_2:Er^{3+}:Yb^{3+} calcined at 500°C.

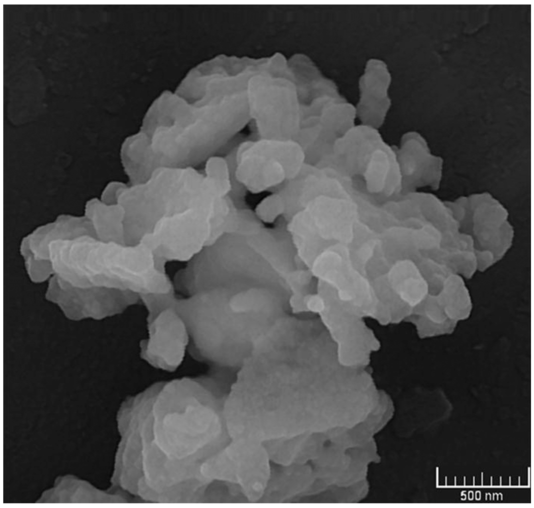


Figure 3. Scanning electron microscopy image of $TiO_2:Er^{3+}:Yb^{3+}$.

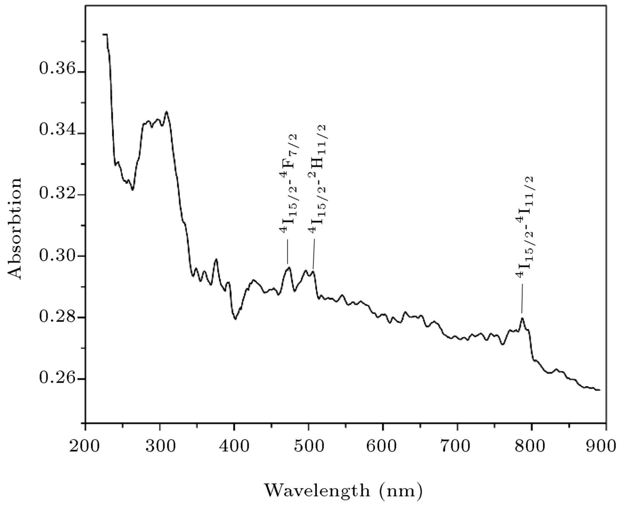


Figure 4. UV-vis absorption spectrum of $TiO_2:Er^{3+}:Yb^{3+}$ nanocrystals calcined at 880°C.

The increase in sharpness of the peaks in the XRD pattern of $TiO_2:Er^{3+}:Yb^{3+}$ calcined at 880°C (Figure 1(c)) shows that the crystalinity of nanocrystals obviously increases. Calculations done by Scherrer formula show that the average size of the crystals is about 80-90 nm, which is in close approximation to the size of the particles in SEM image (Figure 3). Particles are agglomerated because of extended annealing step, necessitating further sonication step for future functionalization works.

The peak at $2\theta = 15.32°$ corresponds to pyrochlore phase ($Er_2Ti_2O_7$ or $Yb_2Ti_2O_7$). The presence of pyrochlore phase confirms that Er^{3+} and Yb^{3+} are fully inputted into the basic structure of TiO_2 [15]. No characteristic peak for anatase is observed and rutile is the dominant phase. In comparison with the pure TiO_2 pattern, rutile peak at $2\theta = 27.7°$ shifted to $2\theta = 27.49°$ in the doped sample calcined at 880°C. This peak shift means that the plane space increased because of doping, and this confirms the entrance of dopants in crystal structure of matrix too.

3.2. *UV-vis absorption property*

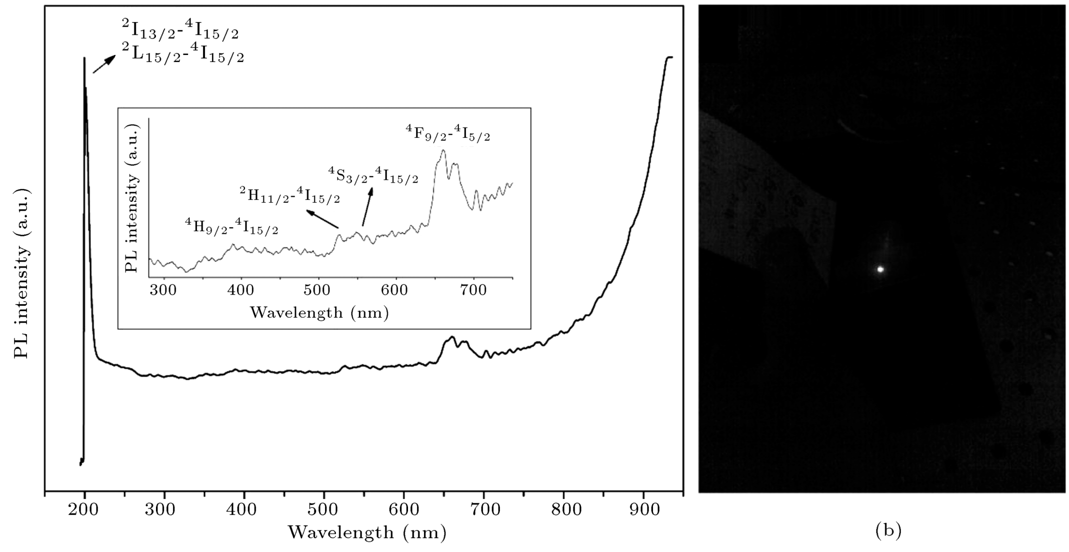
UV-vis absorption spectrum of $TiO_2:Er^{3+}:Yb^{3+}$ calcined at 880°C is shown in Figure 4. The bandgap of the nanocrystals can be roughly calculated by $E_g = 1240/\lambda_g$ formula [16]. λ_g can be found by drawing a tangent on absorption edge. The UV-vis spectrum shows that the bandgap for $TiO_2:Er^{3+}:Yb^{3+}$ is about 3 eV that matches the standard bandgap of rutile (3.02 eV) [15]. It shows that doping of TiO_2 with Er and Yb does not affect the bandgap as Sergio Obregon et al. [17] reported. The peaks at 476, 507, and 788 nm are respectively for electronic transitions in Er^{3+} ions from $^4I_{15/2}$ to $^4F_{7/2}$, $^4H_{11/2}$, and $^4I_{9/2}$.

3.3. *Upconversion luminescence property*

Upconversion emissions of $TiO_2:Er^{3+}:Yb^{3+}$ calcined at 880°C are shown in photoluminescence spectrum (Figure 5(a)). The peaks at 640-690 nm correspond to $^4F_{9/2}$-$^4I_{15/2}$ transition that makes the red emissions. Under excitation by 980 nm laser diode, the white bright upconversion emissions could be seen easily by naked eyes (Figure 5(b)). It means that the blue and green emissions also exist in the UC emissions. The peaks at 520 nm and 570 nm are green emissions attributed to $^2H_{11/2}$-$^4I_{15/2}$ and $^4S_{3/2}$-$^4I_{15/2}$, respectively, and the peak at 408 nm can be assigned to blue emissions as a result of $^4H_{9/2}$-$^4I_{15/2}$ transition [18].

The sharp peak at about 210 nm corresponds to the UV upconversion emissions that are the result of a multi-photon process [19]. The UV emissions are probably the result of relaxation from $^2I_{13/2}$ (220 nm) and $^2L_{15/2}$ (210 nm) to $^4I_{15/2}$ level. The possible mechanisms are shown in energy level diagram of Er^{3+} and Yb^{3+} in Figure 6.

The upconversion can be explained by most dominant mechanisms that are Excited State Absorption (ESA) and Energy Transfer (ET). Yb^{3+} as a sensitizer absorbs 980 nm exciting photon. Sensitizer transfers the energy to Er^{3+} ion by energy transfer mechanism. The ET also exists between the same neighboring ions of Er^{3+}, but, because of much higher concentration of Yb^{3+} and longer excited-state lifetime, ET mostly occurs between Er^{3+} and Yb^{3+} ions (dashed lines in Figure 6) that has a key role in co-doped upconversion systems [19]. Electron in ground state of Er^{3+} absorbs the energy from Yb^{3+} and then excites to higher level by Ground State Absorption (GSA) mechanism ($^4I_{15/2}$-$^4I_{11/2}$). Excited electron can absorb more energy packs by ET and excite to higher levels by ESA mechanism ($^4S_{3/2}$-$^2G_{9/2}$ for example). Radiative relaxations from higher states to ground ones generates upconversion emissions with higher energy than the exciting light.



(a)

(b)

Figure 5. (a) Photoluminescence spectra of TiO_2:Er^{3+}:Yb^{3+} nanocrystals calcined at 880°C under the excitation of 980 nm laser diode (125 mW). (b) Emission of bright white light by sample under 980 nm laser diode excitation.

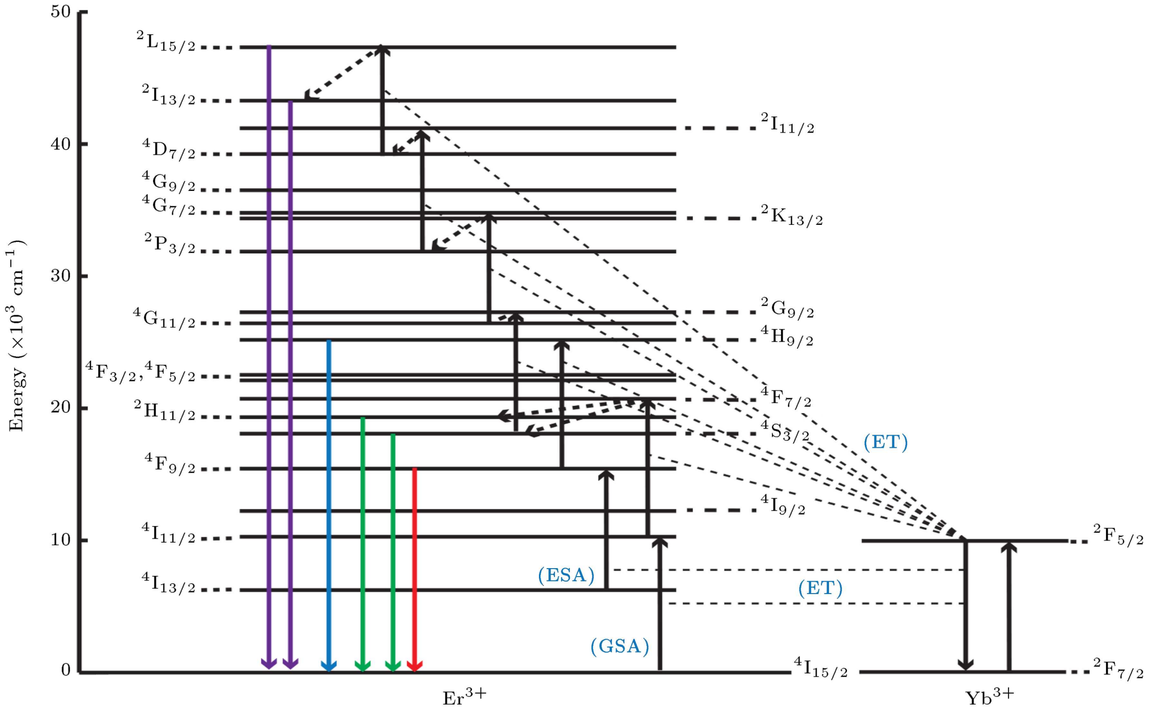


Figure 6. Schematic energy-level diagram of Er^{3+} and Yb^{3+} ions doped in TiO_2 and probable upconversion mechanisms.

4. Conclusion

TiO_2:1%Er^{3+}:9%Yb^{3+}nanoparticles were synthesized via sol-gel method. The formation of pyrochlore phase confirmed that dopants successfully entered the basic structure of the matrix. Photoluminescence spectroscopy showed that the bright white upconversion emissions were made of red, green, blue, and UV upconversion emissions with the wavelengths of about 640-690 nm, 520-570 nm, 408 nm, and 210 nm, respectively. The upconversion properties and biocompatibility of TiO_2:1%Er^{3+}:9%Yb^{3+} make it potentially appropriate for use in photodynamic therapy as a drug carrier.

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