



Pressure dependent luminescence in titanium dioxide particles modified with europium ions



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ABSTRACT

Particles of titanium dioxide were prepared in the presence of europium ions ($\text{TiO}_2:\text{Eu}$) by a solvothermal method and thermal annealed in air at 500°C . The spectroscopic properties of $\text{TiO}_2:\text{Eu}$ particles were analyzed indicating that the Eu^{3+} ions are likely distributed at the surface or near the surface of the titanium dioxide particles. The photoluminescence analysis showed that the intraionic emission was strongly sensitive to reduced pressure conditions, as seen by its absence under vacuum conditions. The ion emission was re-established as soon as the atmosphere was restored. Additionally, the ion integrated emission intensity follows a linearly dependence with pressure in the range of 150–800 mbar revealing a high sensitivity to small variations in pressure, which is an unprecedented result. This innovation will allow the study of new technologies in the area of low vacuum sensors where $\text{TiO}_2:\text{Eu}$ may act as the active element of an optical sensor for a pressure device.

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1. Introduction

Titanium dioxide (TiO_2) is one of the most investigated semiconductors. It occurs in nature in three mineral forms, anatase, brookite and rutile, being a wide energy bandgap (E_g) oxide semiconductor (3.25 eV for anatase, 3.0 eV for rutile and 1.9 eV for brookite at room temperature) [1]. Such high energy bandgap for anatase and rutile results in valence to conduction band photon absorption by the ultraviolet (UV) light, which is only 3–5% of the solar light spectrum [2]. There are several ways of extending TiO_2 light absorption/emission into the visible light. The most commonly used processes are those involving a controlled intentional doping of the material with extrinsic impurities such as transition metal ions and lanthanides. In bulk materials, these dopants lead to the introduction of 3d and 4f energy levels inside the material bandgap, promoting the tuning of the absorption and luminescence in a wide spectral range from UV, visible to infrared (IR). Particularly, it was recently reviewed by Candal R. et al. [3], the role of lanthanides in TiO_2 doping, which is becoming increasingly interesting [4]. This is due to the intra-4fⁿ transitions of lanthanides, which intensify

the optical absorption of TiO_2 , thus moving it into the visible-light range, while also promoting photo-generated electron–hole pair separation [5]. Traditionally, this rare earth (RE) doped TiO_2 have been explored for photocatalytic degradation of organic pollutants, dye molecules, and for photo-splitting of water under both UV and visible light conditions [6,7]. Additionally, TiO_2 particles could become valuable light emitting materials when doped with highly efficient RE ions [8]. These systems may present unique optical properties with prospective applications in optoelectronic devices and biosensors [9,10]. Noteworthy, TiO_2 is a non-toxic material, therefore the synthesis of nanocrystalline RE-doped TiO_2 may find interesting applications in a number of luminescence-based optical and biotechnological areas, like multiplexed labelling, signaling, bioassays, or biomedical purposes [4,11].

Luminescent nanomaterials, on the other hand, have attracted increasing technological and industrial interest [12,13]. This interest has been centered mainly on spectroscopic properties including the spectral shape of emission spectra, the luminescence quantum efficiency, and the influence of dopant concentration on the luminescence quenching. TiO_2 is a promising host material for the incorporation and optically activation of Eu^{3+} due to its low cost and high transparency in the visible spectral region [14]. In the present work we investigate the optical properties of $\text{TiO}_2:\text{Eu}$ nanoparticles by spectroscopic techniques. At room temperature (RT), the

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modified material synthesized by a solvothermal method and thermal annealed in air at 500 °C exhibit the characteristic orange/red fingerprint lines of the Eu^{3+} when the samples are analyzed in air with UV excitation. The intraionic emission was found to be strongly sensitive to the reduced pressure conditions, as seen by its absence under vacuum conditions. The ion emission was re-established as soon as the atmosphere was restored. The novel results achieved will allow the study of new technologies in the area of low vacuum sensors where $\text{TiO}_2\text{:Eu}$ may act as the active element of an optical sensor for a pressure device.

2. Experimental

2.1. Materials

The starting materials for the preparation of titanium dioxide with and without europium were titanium(IV) butoxide (97%), europium(III) nitrate pentahydrate and hydrochloric acid acquired from Sigma-Aldrich and absolute ethanol acquired from Applied-Chem. All chemicals were analytical grade and were used as received without further purification.

2.2. Synthesis procedure

Europium modified TiO_2 ($\text{TiO}_2\text{:Eu}$) samples were synthesized by a sol-gel solvothermal methodology adapted from the literature [15,16]. First, 1.8 g of titanium(IV) butoxide was dissolved in 10 mL of absolute ethanol followed by the addition of 55.9 mg of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and stirred during 30 min. Then, 4 mL of deionized water acidified with HCl to pH 3.0 was added dropwise under vigorous stirring to avoid the formation of europium hydroxide. The resulting cloudy solution was transferred into 20 mL Teflon-lined autoclave and then subjected to solvothermal treatment at 180 °C for 6 h. The finally obtained precipitate was filtered, washed with ethanol for several times and lastly with deionized water, and dried by lyophilisation to avoid particle aggregation. Finally the samples were annealed in air for 1 h at 500 °C, with a heating/cooling rate of 5 °C/min to promote the crystallization of the TiO_2 . For comparison, a similar procedure was followed to prepare nominal unmodified TiO_2 particles.

Worth to mention that the previous procedure was repeated several times to ensure its reproducibility which was confirmed by the characterization (§ 2.3) of the obtained particles.

2.3. Characterization

The structural properties of the samples were examined by powder X-Ray Diffraction (XRD) measurements performed at RT using PANalytical Empyrean diffractometer ($\text{CuK}\alpha$ radiation, with 45 kV and 40 mA). The diffraction patterns were obtained within the angular range of $20 \leq 2\theta \leq 80$ in continuous mode (linear detector with 0.013/step, 98 s/step and active length = 3.34°). The morphologies of the surfaces were characterized by Scanning Electron Microscopy (SEM). SEM images were acquired using high-resolution Hitachi SU-70 equipment working at 15 kV. Samples were prepared by deposition on aluminum sample holders followed by carbon coating using an Emitech K950X carbon evaporator. Microanalysis was performed by Energy Dispersive X-ray Spectroscopy (EDS) using the latter microscope working at 15 kV while employing either a Bruker Quantax 400 or a Sprit 1.9 EDS microanalysis system. The X-Ray Photoelectron Spectroscopy (XPS) spectra were collected with a Kratos Axis Ultra DLD electron spectrometer using monochromatic Al $\text{K}\alpha$ source operated at 150 W. Analyzer pass energy of 160 eV for acquiring wide spectra and a pass energy of 20 eV for individual photoelectron lines were used. The surface potential was stabilized by the spectrometer

charge neutralization system. The binding energy (BE) scale was referenced to the C 1 s line of aliphatic carbon, set at 285.0 eV. Processing of the spectra was accomplished with the Kratos software. Powder samples for the analysis were gently hand-pressed using clean Ni spatula into special powder sample holder. Micro-Raman spectroscopy measurements were performed in backscattering geometry, with the samples at RT, using a Jobin Yvon (Horiba) HR800 spectrometer. A microscope with a 50× objective focused the exciting light (532 nm laser line of a Ventus-LP-50085) onto the samples (spot diameter $\sim 1 \mu\text{m}$). Pump power and acquisition time were ~ 20 mW and 10 s respectively. The spectrometer was calibrated with a Si standard using the 520 cm^{-1} vibrational mode of crystalline Si. Photoluminescence studies were carried out at RT using the 325 nm (3.8 eV) cw He-Cd laser line as excitation source. The sample luminescence was dispersed by a Spex 1704 monochromator and detected by a cooled Hamamatsu R928 photomultiplier. Photoluminescence excitation (PLE) spectra were recorded at RT using a Fluorolog-3 Horiba Scientific modular apparatus with a double additive grating scanning monochromator in the excitation channel and a triple grating iHR550 spectrometer coupled to a R928 Hamamatsu photomultiplier for detection. A 450 W Xe lamp was used as excitation source. The measurements were carried out using front face acquisition geometry, and the obtained spectra were corrected for the spectral characteristics of the optical components and the Xe lamp.

3. Results and discussion

The XRD patterns of pure TiO_2 and $\text{TiO}_2\text{:Eu}$ particles are presented respectively in Fig. 1 a) and b). In both cases, the diffraction peaks correspond to pure anatase phase. The most pronounced diffraction maxima are indexed according to the JCPDS card No. 21-1272 [17,18]. No characteristic diffraction peaks associated with other crystalline forms, such as europium titanium oxides were detected in the XRD patterns. Comparing the intensity of the diffraction peaks of both spectra, there is a slightly decrease in the presence of europium indicating a loss of crystallinity. The crystallite size of the powders was determined by Rietveld analysis being the results of 12.2 nm for the TiO_2 and of 11.3 nm for the $\text{TiO}_2\text{:Eu}$. According to the literature [19], Eu doped TiO_2 samples display smaller crystal sizes when compared with undoped TiO_2 . Chen et al. [20] reported a difference in the crystallite sizes of 11.52 nm for undoped TiO_2 and of 6.49 nm with 2.0% Eu/Ti mole ratio (to refer that the synthesis method was different from our present study). Based on the marginally difference of 0.9 nm obtained in our study we cannot conclude about a possible doping of the TiO_2 structure with Eu ions.

From the Raman spectra (Fig. 2 a) and b)) it is also evident that both the nominal unmodified and Eu-modified TiO_2 particles are in the anatase phase. In both samples the identified resonances are in fair agreement with the expected vibrational modes for the anatase crystalline structure, corroborating the data obtained by XRD. The positions of the vibrational modes of anatase are marked in Fig. 2. The main characteristic peak appears at 145 cm^{-1} , which is attributed to the E_g anatase vibrational mode; the remaining vibrational peaks are around 197 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 513 cm^{-1} ($A_{1g} + B_{1g}$) and 639 cm^{-1} (E_g) [21]. The reduction in scattering intensity, particularly of the E_g mode, may be due to the breakdown of long-range translational crystal symmetry caused by incorporated defects in the presence of Eu ions.

Figs. 3 and 4 show the SEM images of unmodified and Eu-modified TiO_2 samples, respectively, revealing their general morphology. The formation of titanium dioxide aggregates is clear in both cases, likely promoted by the samples thermal annealing. At low magnification (Figs. 3 (a) and 4 (a)) the sample prepared

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