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LUMINESCENT PROPERTIES OF TiO_2: Gd^{3+}, Y^{3+} OBTAIN THROUGH SOL-GEL AND HYDROTHERMAL METHODS

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Abstract
The aim of this paper is to present the results of the synthesized TiO_2: Gd^{3+}, Y^{3+} nanoparticles by sol-gel and hydrothermal process. Phase-pure anatase TiO_2 nanocrystallites were synthesized directly from a $TiCl_4$ aqueous solution using $C_2H_2O_4$ as an additive [1, 2]. A sol-gel was formed when a mixture of $TiCl_4$ and $C_2H_2O_4$ was heated on a water bath. Ultrafine powders of TiO_2 were formed in the anatase phase, when the gel was decomposed at room temperature [3]. These powders were analyzed by X-ray diffraction (XRD) and characterized by scanning electron microscopy (SEM). Photoluminescence (PL) and photoluminescence excitation (PLE) measurements were obtained with a conventional lamp as an excitation source [4]. The obtained results are discussed.
Keywords: anatase TiO_2, sol-gel method, hydrothermal method

1. Introduction

The catalytic properties of a multicomponent system may be strongly influenced by the composition and the preparation procedure. Heterogeneous photocatalysis is a rapidly growing research area for the mineralization of toxic organic pollutants in the environment. In this context, due of its high catalytic activity extensive research [5], [6], [7] and [8] has been carried out with TiO_2 as a photocatalyst. In order to improve the catalytic activity, some papers have dedicated on the material aspects of the photocatalysts. Despite of that TiO_2 has a great potential, the fast recombination rate of photogenerated electron–hole pairs on the surface or in the lattice hinders the commercialization of this technology. Doping of TiO_2 with transition metal ions was reported [9] [10] as a good tool to improve the photocatalytic properties and for the enhancement of visible light response.

In this paper, the sol-gel and hydrothermal methods are used for obtain the nanocrystallines TiO_2 doped with Gd^{3+} and Y^{3+} and its optical properties are investigated. $TiCl_4$, $C_2H_2O_4$, Gd_2O_3, and $YCl_3 \bullet 6H_20$ were used as the starting materials.

2. Experimental

Titanium dioxide (TiO_2) is an important material as a main component of paint, pigment, cosmetics and as a support for vanadium DeNOx catalyst. The frequently used oxide material for thin film application (because of its high refractive index and low absorption) makes it a highly interesting transparent oxide. The sol-gel and hydrothermal process are an important technique for the synthesis of optical coatings [10]. It has also been used for optical coatings, beam splitters and anti reflection coatings because of its high dielectric constant and refractive index. There are reports on its use as a humidity sensor and high temperature oxygen sensor. The three crystalline polymorphs of TiO_2 are anatase, rutile and brookite. Rutile is a thermodynamically stable phase possessing a smaller band gap energy (3.0 eV) than the anatase phase (3.2 eV). Nanocrystalline anatase is generally synthesized as hydrothermal methods and sol–gel methods using titanium alkoxides. A mixture of anatase and rutile were produced by evaporation of Ti metal in a helium atmosphere, followed by the collection and subsequent oxidation of the Ti clusters thus formed.

Since $TiCl_4$ is commercially available and low cost, synthesis of TiO_2 using $TiCl_4$ is well known as exemplified by hydrothermal and sol-gel methods. As for hydrothermal and sol-gel synthesis using $TiCl_4$, the experimental conditions are very harsh: there are also drawbacks, for example, high $TiCl_4$ concentration leads to the formation of hair-like and aggregated rutile TiO_2 while low $TiCl_4$ concentration results in the concurrent formation of anatase and rutile phase TiO_2. During the investigation, we have found that $C_2H_2O_4$ (aq. 5%)suppresses the hydrolysis of $TiCl_4$ aqueous solution at room temperature, and, on the other hand, room temperature peptization of a highly concentrated TiCl4 aqueous solution gives rutile nanoparticles as embryos. These findings prompted us to synthesize phase-pure anatase or rutile nanocrystallites by hydrothermal and sol-gel methods using $TiCl_4$ aqueous solution or rutile TiO_2 embryos as starting materials. These mixed solutions in the Teflon vessel were then placed in a stainless-steel autoclave. The sealed autoclave was placed in a thermostatic oven and heated at a temperature of 200°C for 5h.

3. Results and discussion

3.1 X-ray diffraction

Powder X-ray diffraction (XDR) was carried out using Cu Kα radiation (BRUKERaxs-D8 advance diffractometer). XDR patterns of nanocrystalline $TiO_2:Gd^{3+}$, Y^{3+} obtained from sol-gel and hydrotermal methods. Observed as in the case when $TiO_2:Gd^{3+}$, Y^{3+} through sol-gel method appears just TiO_2 anatase, using the hydrothermal method appears TiO_2 anatase and rutile.

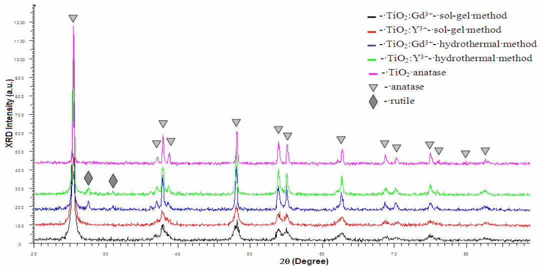


Fig 1. XRD pattern of Gd^{3+}, Y^{3+} doped TiO_2 nanoparticles by sol-gel and hydrothermal process

3.2 Photoluminescence

Photoluminescence (PL) measurement with Xenon flash lamp, pulsed at line frequency (50 and 60 Hz). Figures 2, 3 display the emission spectra of Y^{3+}, Gd^{3+} doped TiO_2 under 432 nm for Y^{3+} and 430 nm for Gd^{3+} irradiation. The spectra consist of sharp lines ranging from 540 to 750 nm. The largest peak of the emission line for Y^{3+} by sol-gel method is to 611.51 nm, with hydrothermal method is to 611.91 nm; for Gd^{3+} by sol-gel method is to 608.04 nm, with hydrothermal method is to 607.86 nm.

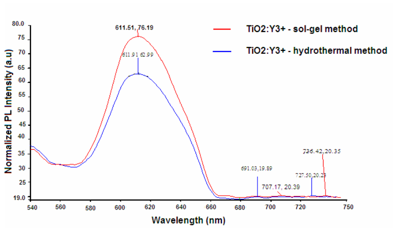


Fig. 2. 432 nm- excited PL spectra of nanocrystalline TiO_2:Y^{3+}

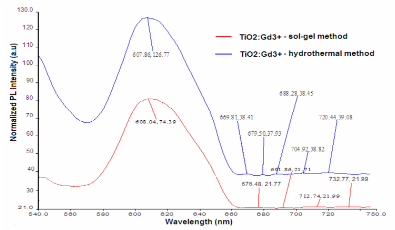
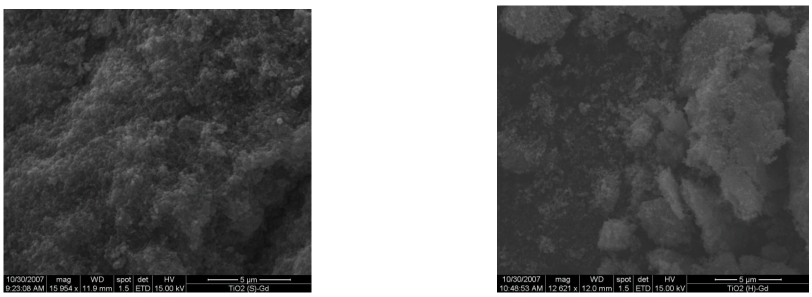


Fig. 3. 430 nm- excited PL spectra of nanocrystalline TiO_2:Gd^{3+}

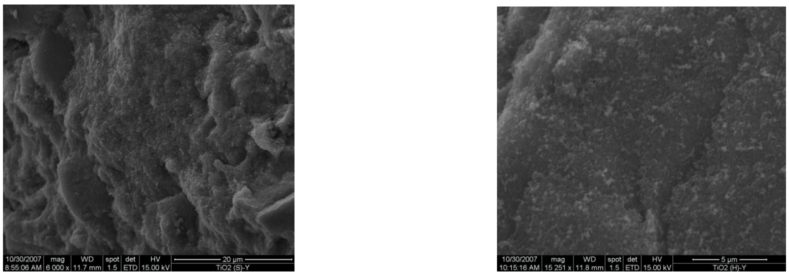
3.3 SEM- analysis

The morphology of obtained sample were observed with field emission-scanning electron microscopy (SEM). SEM images of nanocrystalline TiO_2:Gd^{3+} are shown in Fig 4 (a-sol-gel method, and b-hydrothermal method), respectively in Fig. 5 is images of nanocrystalline TiO_2:Y^{3+} (a-sol-gel method, and b-hydrothermal method).



a) b)

Fig. 4. SEM image of nanocrystalline TiO_2:Gd^{3+} a) sol-gel method, b) hydrothermal method



a) b)

Fig. 5. SEM image of nanocrystalline $TiO_2:Y^{3+}$ a) sol-gel method, b) hydrothermal method

4. Conclusions

Synthesis and characterization nanocrystalline TiO2:Y^{3+}, Gd^{3+} by sol-gel and hydrothermal methods has done and their luminescent properties have investigated. The largest peak of the emission line for $Y^{3+}:TiO_2$ obtained by sol-gel method is situated at 611.51nm whiles the same peak in the case of $Y^{3+}:TiO_2$ obtained by hydrothermal method were placed at 611.91nm; for $Gd^{3+}:TiO_2$ obtained by sol-gel method the peak is placed at 608.04nm whiles for the same nanocrystal obtained by hydrothermal method it is at 607.86nm.

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