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# ROOM-TEMPERATURE SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF TITANIA NANOPARTICLES DOPED WITH GADOLINIUM IONS

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$Gd^{3+}$-doped titania nanoparticles have been synthesized via acidic hydrolysis of $Gd^{3+}$ and $Ti^{4+}$ organic precursors. The resulting products were characterized by X-ray diffraction, transmition electron microscopy and diffuse reflection spectra. Experimental results indicated that $Gd^{3+}$-doping makes great impact on the optical properties and photocatalytic activity of the obtained $TiO_2$ nanoparticles. All applied doping concentrations induced enhancement of photoactivity regarding degradation of Rhodamine B, compared to pure $TiO_2$. The inter-band defect states formed as a result of incorporation of $Gd^{3+}$ ions in the $TiO_2$ matrix are most probably the cause of observed improved photoacatalytic activity and optical properties of the doped $TiO_2$ nanoparticles.

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## 1. Introduction

The photocatalytic degradation of pollutants in water and air has attracted much interest in the last several decades. A special attention is focused on the application of titania for photodegradation of various organic pollutants under ultraviolet (UV) or solar light [1-3]. Titanium dioxide can be obtained in three crystalline phases: anatase, rutile and brookite. The most stable phase is rutile and it is usually obtained after annealing at temperatures above $500^0$ C. $TiO_2$ is transparent normally in the visible light region; its band gap being 3.0 eV for rutile and 3.2 eV for anatase crystalline phase. The band gap of anatase (3.2 eV) is not ideal for solar light absorption (only 5 % of UV light), which limits its wide application in visible range. The development of titania based photocatalysts that can be excited by visible light has received lately great attention. Many methods are attempted, such as dye sensitization, surface modification and transition metals doping [4]. Lanthanide ions doping can also be beneficial. Lanthanide ions are known for their ability to form complexes with various Lewis bases (including organic acids, amines, aldehydes, alcohols, and thiols) in the interaction of these functional groups with the f-orbitals of the lanthanides. Xu et al. [5] reported that doping with $La^{3+}$, $Ce^{3+}$, $Er^{3+}$, $Pr^{3+}$, $Gd^{3+}$, $Nd^{3+}$, or $Sm^{3+}$ was beneficial to $NO_2^{\ -}$ adsorption. Ranjit et al. [6, 7] reported that doping with $Eu^{3+}$, $Pr^{3+}$, or $Yb^{3+}$ increased the adsorption capacity and also adsorption rate of $TiO_2$ catalysts simultaneously in aqueous salicylic acid, *t*-cinnamic acid, and *p*-chlorophenoxy-acetic acid solutions. Further, lanthanides have special electronic structure of $4f^x5d^y$, which would lead to different optical properties and dissimilar catalytic capacity, and a redox couple of $Ln^{n+}/Ln^{(n+1)+}$,which would be able to form the labile oxygen vacancies with the relatively high mobility of bulk oxygen species [8]. Incorporation of lanthanide ions in a $TiO_2$ matrix could provide a mean to concentrate the organic pollutant at the semiconductor surface on one side and to improve its optical response on the other side, therefore enhancing the overall photo-activity of titania.

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In the scope of this study, homogenous hydrolysis of titanium (IV) salts in acidic solution (pH about 1) was used as very simple preparation method, which can be easyly executable in production of titania nanostructures doped with various metal ions [9]. Modification of previously described method [9] was used in preparation of series of titania photocatalysts doped with gadolinium ions. Obtained materials were characterized using X-ray powder diffraction (XRD, transmission electron microscopy (TEM), UV/Vis reflectance, absorption and emission, and their photocatalytic activity was checked. Rhodamine B dye (RB) was selected as a model reactant for photodegradation.

## 2. Experimental

Chemicals including titanium(IV)isopropoxide ($Ti(O\text{-}i\text{-}C_3H_7)_4$, Sigma-Aldrich), isopropanol ($C_3H_7OH$, Baker, HPLC grade), $Gd^{3+}$ -acetylacetonate (Aldrich), etc. were commercial products and used as received without further purification. Water was purified by a Milli-Q system (Millipore) and had a resistivity ≥ 18 MV cm.

For the synthesis of pure $TiO_2$, 2 mL of $Ti(O\text{-}i\text{-}C_3H_7)_4$, dissolved in 10 mL of $i\text{-}C_3H_7OH$, was added into 250 mL of a mixture of water and $i\text{-}C_3H_7OH$ (1 : 1, pH~ 1 adjusted by $HNO_3$). Doped $TiO_2$ was obtained by adding 2 mL of $Ti(O\text{-}i\text{-}C_3H_7)_4$, dissolved in 10 mL of $i\text{-}C_3H_7OH$ into the solution of appropriate amount of $Gd^{3+}$ -acetylacetonate dissolved into 250 mL of a mixture of water and $i\text{-}C_3H_7OH$ (1 : 1, pH~1 adjusted by $HNO_3$) under vigorous stirring at 0º C. After being continuously stirred at room temperature (20ºC) for two days, the reaction solution was dialyzed for purification and adjustment of the pH of the colloidal solution as formed (pH~ 2.3). Finally, the solution was vacuum evaporated at room temperature to yield powder samples.

The UV/vis diffuse reflectance spectra (DRS) were recorded on an Evolution 600 UV/vis spectrophotometer (Thermo Scientific), equipped with DRA-EV-600 Diffuse Reflectance Accessory.

The XRD powder patterns were obtained by using a Philips PW 1050 powder diffractometer with Ni filtered Cu $K_\alpha$ radiation ($\lambda$ = 1.5418 Å). The diffraction intensity was measured by the scanning technique (step size of 0.05° and a counting time of 50 s per step).

A transmission electron microscope (TEM) images were obtained on a JEOL-JEM 2100 LaB6, operating at 200 kV. Samples were made by evaporation of one drop of dialyzed colloidal solution onto copper grids.

Photocatalytic activity was obtained using whole spectrum of Xe-lamp, 150 W, as irradiation source used routinely when simulation of solar spectrum is necessary. Experimental solutions were irradiated in cylindrical vessels (20 ml) made of quartz, in the stream of $O_2$ (1-2 $cm^3min^{-1}$). In certain time intervals, aliquots were taken from experimental solutions, centrifuged in order to separate powder catalyst and absorption at 552 nm (peak of RB) of the supernatant was measured. Photocatalytic activity was followed as a fraction of RB ($C_t/C_0$) still present in the reactor after certain time of irradiation (t). $C_0$ is initial concentration obtained measuring characteristic RB absorption after centrifugation of experimental dispersions (equilibrated in the dark for 2 h) before irradiation (t=0).

## 3. Results and discussion

The crystal structure of titanium dioxide greatly affects its photocatalytic activity. Amorphous titania seldom displays photoactivity due to some non-bridging oxygen in bulk titania. The Ti-O atomic arrangement defects can act as recombination centers of photo-generated electron–hole pairs. Additionally, different crystal phases will also affect photocatalysis. Generally, the anatase phase is reported to have high photocatalytic activity [1].

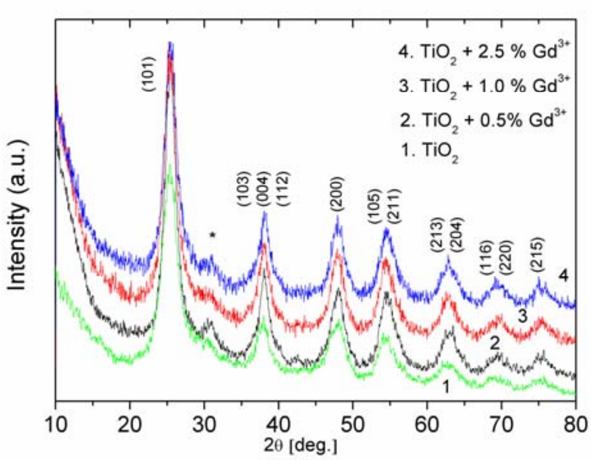

*Fig. 1. XRD patterns of pure and $Gd^{3+}$ doped $TiO_2$ nanoparticles.*

Therefore, the phase structure of obtained materials was investigated by XRD, and the results are shown in Fig. 1. It can be noted that samples have intensive diffraction peaks (25.5º, 37.9º, 47.6º, 54.7º, 63.0º, 69.7º) characteristic for anatase phase. Weak peak of brookite phase is detected at 31.0º (denoted with *) [10]. The doping with $Gd^{3+}$ ions does not cause any shift in anatase peak position of $TiO_2$. It may be due to the very small doping amount of $Gd^{3+}$ ions. Obviously doping induces some crystal lattice distortion due to large difference between ion radiuses of $Ti^{4+}$ (0.68 Å) and $Gd^{3+}$ (0.94 Å) [5]. The unit cell had to accept much larger volume of doping ion and it increases compactness of crystal lattice where doping took place so small amount of brookite is detected (density of anatase is 3.84 g $cm^{-3}$ and of brookite is 4.17 g $cm^{-3}$). The crystal sizes, determinated by Scherrer's equation from XRD, were almost the same for all samples, from 3-5 nm in diameter.

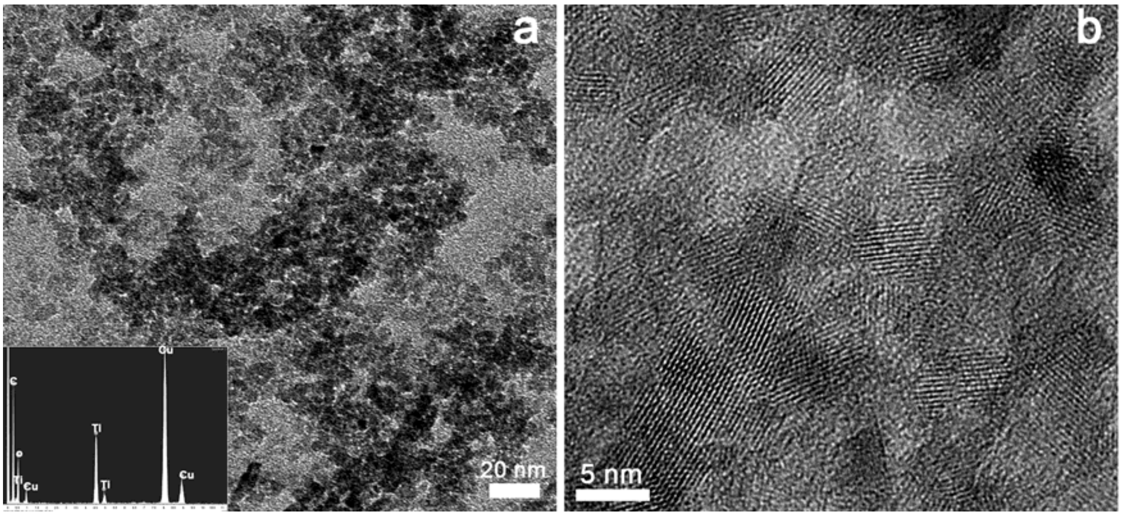

*Fig. 2. Typical TEM images, low (a) and high (b) magnification, of $TiO_2$ nanoparticles doped with 2.5at% $Gd^{3+}$ ions. Inset: EDS data.*

In Fig. 2 typical TEM images of $TiO_2$ nanoparticles are presented. Particles are well defined with clearly distinguishable crystal planes. The particle sizes are about 5 nm, the shape being elliptical/spherical. EDS measurements (Inset in Figue 2a) didn't prove presence of Gd in the samples, possibly because of its low concentration.

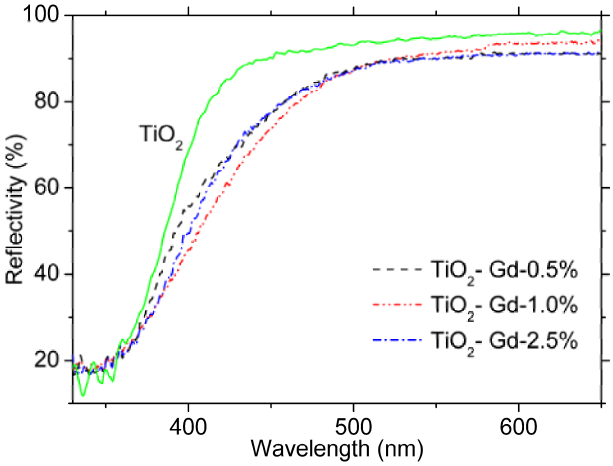

*Fig. 3. UV/vis reflectance spectra of pure* $TiO_2$ *and* $TiO_2$ *doped with different at.% of* $Gd^{3+}$ *ions.*

The DR spectra of synthesized samples are shown in Fig. 3. The onset of the absorption spectrum of pure $TiO_2$ appearing at about 400 nm matches well with the intrinsic band-gap of anatase (3.2 eV). Comparing DRS of pure $TiO_2$ and $Gd^{3+}$-doped samples (with $Gd^{3+}$ nominal amount of 0.5, 1.0 and 2.5 at%) it can be seen that there is a significant shift in the onset absorption towards the higher wavelengths for all the $Gd^{3+}$-doped samples. Firstly, it may be due to appearance of a new electronic state in the $TiO_2$ band gap. Therefore, the distance of charge transfer between *f* electrons of the rare earth ions and the conduction or valence band of $TiO_2$ is narrowed. Accordingly, it leads to visible light absorption response of obtained samples. Secondly, $Gd^{3+}$ ions enter into the anatase structure as substitutional defects on the Ti position and act as photo-electron traps, playing an important role in the separation of electron–hole pairs, which could increase the photoconversion efficiency. Consequently, doping with $Gd^{3+}$ might be favorable for the separation of photo-induced electron–hole pairs, which leads to the enhancement of the photo-catalytic activity.

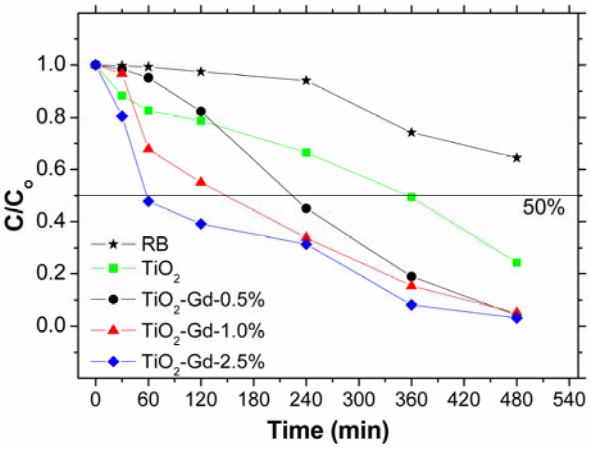

*Fig. 4. Effect of different photocatalysts on the degradation of RB. Initial concentration of RB was* $10^{-5}$ *M; concentration of catalyst was 1 mg/ml. For comparison photolysis of RB is also presented.*

In order to explore this possibility, we used photocatalytic degradation of RB dye. In Fig. 4 comparison of photocatalytic activity of pure and $Gd^{3+}$-doped $TiO_2$ and photolysis of RB using Xe-lamp is presented. As shown, there are great differences between photolysis and photocatalytic degradation of RB. After one hour of irradiation, 50% of RB is degraded using $TiO_2$ doped with 2.5 at.% of $Gd^{3+}$ ions, while photolysis yield almost no degradation and pure $TiO_2$ degraded ~ 20

% of RB in applied experimental conditions. With longer irradiation times, differences between doped samples decrease, but they are all more active than pure $TiO_2$ obtained using the same synthetic procedure. So, as already stated the presence of $Gd^{3+}$ ions is beneficial for photocatalytic activity because of separation of photoexcited charges and extended absorption threshold into visible spectral range. The $Gd^{3+}$ has 7 $f$-electrons with orbitals half filled. It is well known that half-filled electronic configuration is of more stability. When $Gd^{3+}$ ions trap electrons, the half-filled electronic configuration is destroyed and their stability decreases, the trapped electrons can easily be transferred to the oxygen molecules adsorbed on the surface of the catalysts, and the $Gd^{3+}$ ions return to the original stable half-filled electronic structure. This might promote charge transfer and efficiently separate the electrons and holes by shallowly trapping electrons [5]. Furthermore, substituting $Ti^{4+}$ by $Gd^{3+}$ creates a charge imbalance, which must be satiated. Therefore more hydroxide ions would be adsorbed on the catalyst surface [10]. The hydroxide ions act as hole traps that also inhibit electron/hole recombination and promotes degradation reactions.

## 4. Conclusions

$Gd^{3+}$-doped anatase nanoparticles were synthesized using room-temperature sol-gel process from organic precursors. Obtained powders had absorption thresholds moved to visible spectral range compared to pure $TiO_2$. Optical properties were correlated with photocatalytic activity of obtained powders. The best photocatalytic activity regarding degradation of Rhodamine B showed doped $TiO_2$ nanopowder with 2.5 at% nominal concentration of $Gd^{3+}$ ions. It is shown that doping of $TiO_2$ with $Gd^{3+}$ is beneficial for improvement of its photocatalytic activity regarding degradation of RB.

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