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SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF ANATASE NANOPARTICLES DOPED WITH GADOLINIUM IONS

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Abstract
Gd^{3+}-doped anatase nanoparticles have been synthesized via acidic hydrolysis of Gd^{3+} and Ti^{4+} organic precursors. The resulting products were characterized by X-ray diffraction (XRD) and diffuse reflection spectra (DRS). Experimental results indicated that different Gd^{3+}-doping levels make 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 (RB), 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.

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 anatase titania for photodegradation of various organic pollutants under ultraviolet (UV) or solar light [1]. The band gap of anatase (3.2 eV) is not ideal for solar applications, 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 [2].

Homogenous hydrolysis of titanium (IV) salts in acidic solution (pH about 1) is very simple preparation method, which can be easy executable in production of titania nanostructures doped with various metal ions [3]. Modification of previously described method [3] was used in preparation of series of titania photocatalysts doped with gadolinium ions. Obtained materials were characterized using XRD, UV/Vis reflectance and absorption, and their photocatalytic activity was checked. Rhodamine B dye (RB) was selected as a model reactant for photodegradation.

Experimental

Chemicals including $Ti(O\text{-}i\text{-}C_3H_7)_4$ (Sigma-Aldrich), $i\text{-}C_3H_7OH$ (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.

Routinely, 2 mL of Ti(O-*i*-C_3H_7)$_4$, dissolved in 10 mL of *i*-C_3H_7OH, was added into 250 mL of a mixture of water and *i*-C_3H_7OH (1 : 1, pH~ 1 adjusted by HNO_3) when TiO_2 was synthesized, or solution of appropriate amount of Gd^{3+} - acetylacetonate dissolved into 250 mL of a mixture of water and *i*-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 RT 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.

Photocatalytic activity was obtained using whole spectrum of Xe-lamp, 150 W, as irradiation source used routinely when simulation of solar spectrum is neccesary. Experimental solutions were irradiated in cylindrical vessels (20 ml) in the stream of O_2. 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 observed as a fraction of RB (C/C_0) still present in the reactor after certain time of irradiation.

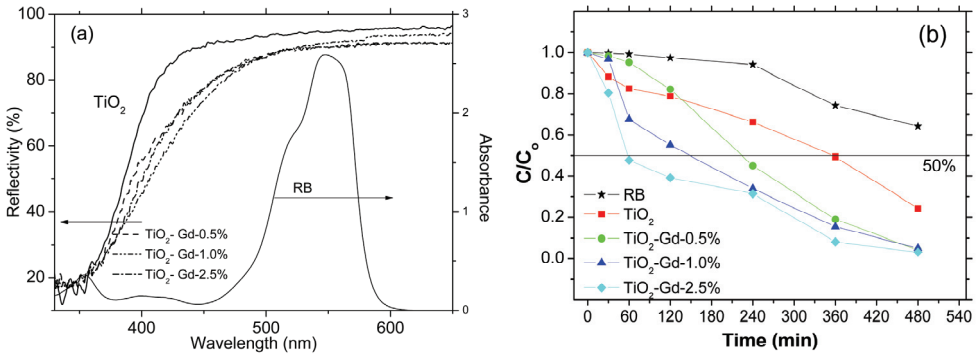

Figure 1 (a) DRS of the obtained powders and absorption spectrum of RB; (b) effect of different photocatalysts on the degradation of RB. Initial concentration of RB was 10^{-5} M; concentration of catalyst was 1 mg/ml. For comparison photolysis of RB is also presented.

Results and Discussion

The DRS spectra of synthesized samples are shown in Fig. 1 (a). 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 diffuse reflectance spectra of pure TiO_2 and Gd^{3+}-doped samples with Gd 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. Second, 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 photon 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.

In order to explore this possibility, we used photocatalytic degradation of RB dye. In Fig. 1 (b) comparison of photocatalytic activity of pure, 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. Furthermore, subsituting Ti^{4+} by Gd^{3+} creates a charge imbalance, which must be satiated [4]. Therefore more hydroxide ions would be adsorbed on the catalyst surface. The hydroxide ions act as hole traps that also inhibit electron/hole recombination and promotes degradation reactions.

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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