Influence of neodymium ions on photocatalytic activity of TiO$_2$ synthesized by sol–gel and precipitation methods

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ABSTRACT

Titanium dioxide with and without the addition of neodymium ions was prepared using sol–gel and precipitation methods. The resulting catalysts were characterized by thermal analysis, X-ray diffraction and BET specific surface area. Neodymium addition exerted a remarkable influence on the phase transition temperature and the surface properties of the TiO$_2$ matrix. TiO$_2$ samples synthesized by precipitation exhibit an exothermic event related from the amorphous to anatase phase transition at 510 °C, whereas in Nd-doped TiO$_2$ this transition occurred at 527 °C. A similar effect was observed in samples obtained using sol–gel method. The photocatalytic reactivity of the catalysts was evaluated by photodegradation of Remazol Black B (RB) under ultraviolet irradiation. Nd-doped TiO$_2$ showed enhanced photodegradation ability compared to undoped TiO$_2$ samples, independent of the method of synthesis. In samples obtained by sol–gel, RB decoloration was enhanced by 16% for TiO$_2$ doped with 0.5% neodymium ions.

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1. Introduction

The advanced oxidation processes (AOP) are becoming more important in the area of wastewater treatment, since these processes result in efficient degradation and mineralization of toxic organic compounds that are resistant to traditional treatments such as biological processes [1]. They rely mainly on the formation of reactive and short-lived oxygen-containing intermediates such as hydroxyl radicals (•OH) [2]. The hydroxyl radical is a powerful oxidant and a short lived, highly reactive, non-selective reagent [2,3].

Heterogeneous photocatalysis is included in the class of processes which produce hydroxyl radicals. Semiconductors (e.g., TiO$_2$, Fe$_2$O$_3$, CdS and ZnO) can act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with energy $h\nu$ matches or exceeds the bandgap energy, E_g, of the semiconductor, an electron, e_{cb}^-, is promoted from the valence band, VB, into the conduction band, CB, leaving behind a hole, h_{vb}^+. Excited state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface [4]. The pair e_{cb}^-/h_{vb}^+ photogenerated in the semiconductor, in contact with O$_2$ or H$_2$O and OH$^-$ adsorbed in its surface, leads to the formation of radical species.

TiO$_2$ is by far the most useful material for photocatalytic purposes, due to its electronic properties, chemical stability, non-toxicity and low cost [3–7]. Titanium dioxide exists in three main crystallographic forms, anatase, rutile and brookite; in most cases, anatase has been found to be photocatalytically more active than the others [8]. In the literature, several preparation methods of TiO$_2$ in the form of powder, crystals or thin films have been proposed. The precipitation method involves precipitation of hydroxides by the addition of a basic solution (NH$_4$OH, NaOH and urea) to raw material, followed by calcinations to crystallize the oxide [9]. Sol–gel methods are normally used to form powder, thin films and membranes. There are many advantages of the sol–gel and precipitation methods such as homogeneity, flexibility in introducing dopants in large concentration, stoichiometry control and processing ease [10–12].

There are still basic problems to be solved to improve the photocatalytic activities of TiO$_2$. Because TiO$_2$ has a high band gap energy (E_g), it is excited mainly by UV light (for the anatase allotrope form E_g = 3.2 eV and $\lambda_g < 384$ nm). Thus, this practically precludes the use of sunlight or visible light as irradiation sources. Moreover, the high rate of electron–hole recombination on TiO$_2$ particles results in a low efficiency of photocatalysis [13].

Doping methods have been applied for modifying the electronic structure of TiO$_2$ nanoparticles, in order to improve catalytic activities. Dopants can be segregated on the TiO$_2$ nanostructure surface

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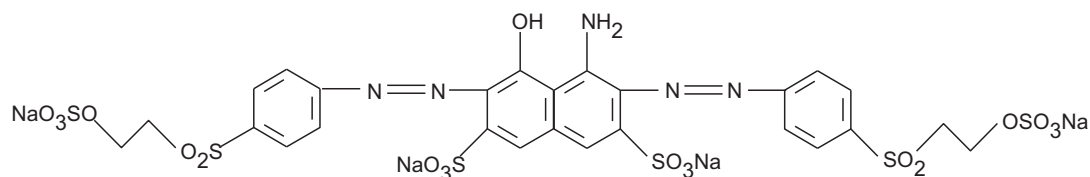
Scheme 1. Structure of the dye Remazol Black B.

or they can be incorporated into the lattice [14]. Different dopants do not have the same effect on the interaction with electrons and/or holes, due to the different position of the dopants in the host lattice. The coordination environments of the dopants are influenced not only by the nature of the dopants, such as ionic radii and concentration, but also by the synthesis method [15]. Lanthanide ions are known for their ability to form complexes with various Lewis bases (e.g., amines, aldehydes, thiols, etc.) via interactions of functional groups of the base with lanthanide f-orbitals. Thus, incorporation of lanthanide ions in a TiO_2 matrix could provide a means to concentrate the organic pollutant at the semiconductor surface, extend the photocatalytic response to visible region and improve the separation efficiency of photo-induced electron–hole pairs of titânia [16–19].

Neodymium is one of the lanthanide ions that can be employed to improve the photoactivity of TiO_2. Xu et al. [20] prepared a series of Nd–TiO_2 nanotubes by sol–gel method and hydrothermal treatment. The photocatalytic activity of TiO_2 nanotubes pure and doped was evaluated in the degradation of methyl orange dye. The nanotubes containing 0.3% of Nd had a better photocatalytic response compared to pure TiO_2. Shahamoradi et al. [21] prepared TiO_2 nanoparticles doped with Nd by hydrothermal method. The effect of neodymium on the photocatalytic activity of TiO_2 was evaluated in the degradation of municipal wastewater. All materials containing Nd showed better photocatalytic response compared to pure TiO_2. The photocatalyst containing 5% neodymium degraded up to 95% of the wastewater. Wang et al. [22] evaluated the effects of Nd content on the physical structure and photocatalytic activities of doped titania hollow sphere samples, it is found that the optimal Nd-doped concentration was 3.9%.

This work reports the degradation of the azo dye Remazol Black B (RB) by Nd-doped TiO_2. Non-doped and doped TiO_2 were prepared using the sol–gel and precipitation methods, thus allowing for evaluation of the effects of neodymium ions on the surface characteristics and on the photocatalytic properties of TiO_2.

2. Experimental

2.1. Preparation of pure and Nd doped TiO_2 nanoparticles

Nominally pure TiO_2 and neodymium-doped TiO_2 were prepared by sol–gel and precipitation routes. The procedure for the preparation of these catalysts had been reported previously [23,24]. The concentration of neodymium ions in the titania matrix was 0.5 wt%. The sol–gel route started from titanium isopropoxide (Gelest) and hydrated neodymium chloride (99.9% Aldrich). The appropriate amount of $NdCl_3 \cdot 7H_2O$ was dissolved in propanol and mixed with 13 mL titanium isopropoxide. The titanium–neodymium solution was then added dropwise under vigorous stirring to 200 mL of an aqueous nitric acid solution. Stirring was maintained until a transparent solution was obtained. The transparent sols were dried at 70 °C and calcinated under air at 580 °C for 1 h. Undoped TiO_2 was synthesized using an identical method. The titanium precursor in the precipitation route was titanium chloride ($TiCl_4$, Aldrich). An appropriate amount of neodymium chloride dissolved in distilled water was added to a

$TiCl_4$ solution. The Nd/Ti^{4+} mixture was slowly added to 100 mL of a solution of NH_4Cl at pH 10. The resulting $Nd(OH)_3/Ti(OH)_4$ precipitate was washed twice with water and subsequently washed with n-propanol and n-butanol, dried at 70 °C and calcined in air at 580 °C for 1 h. All products were kept in desiccators under $CaCl_2$ prior to use.

2.2. Characterization

X-ray diffractograms of the calcinated samples were recorded using a Philips powder diffractometer. The diffraction patterns were recorded at room temperature using Ni-filtered CuK_α radiation (λ = 1.5418 Å). The percentage of anatase can be estimated from the respective integrated XRD peak intensities using the following equation [25]: $X(\%) = 100/(1 + 1.265 I_R/I_A)$, where I_A represents the intensity of the anatase peak at 2θ = 25.3° and I_R is that of the rutile peak at 2θ = 27.9°. X is the weight percent of anatase phase in the sample.

Nitrogen adsorption measurements were carried out at −196 °C using a Micromeritics Model ASAP 2010 Volumetric Adsorption Analyzer. The surface area was determined according to the standard Brunauer, Emmet and Teller (BET) method. The particle size was calculated using the following equation: $D_{BET} = 6000/\rho S$; where D_{BET} is the average nanoparticles size (nm), ρ is the powder density (g cm^{-3}) and S is the specific surface area (m^2 g^{-1}) measured via the BET method.

Thermogravimetric/derivative thermogravimetric (TG/DTG) curves were obtained with a Shimadzu TGA-50 thermobalance in a temperature range 25–800 °C, using a platinum crucible, approximately 1.5 mg of the sample, dynamic air atmosphere (50 mL min^{-1}) and a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) curves were obtained on a Shimadzu DSC-50 cell using partially closed aluminum crucibles with ca. 1.5 mg samples, under dynamic nitrogen atmosphere (100 mL min^{-1}) in a temperature range 25–600 °C and with the same heating rates used for TG. The DSC cell was calibrated with indium (mp 156.6 °C and ΔH_{fusion} = 28.54 J g^{-1}) and zinc (mp 419.6 °C).

2.3. Evaluation of the photocatalytic activity

Black Remazol B (DyStar Company), Scheme 1, was chosen as model dye to perform the catalysis tests. This commercial dye was used as received without any further purification step.

Experiments were performed in an open batch system. The system consisted of a 400 cm^{-3} glass cylindrical reactor that housed the dye solutions, a water cooling jacket to keep the reactor content at constant temperature (20 °C), a mechanical stirrer to keep the photocatalyst powder suspended (stirring rate: 500 rpm) and a gas disperser to bubble the solution with a stream (15 L h^{-1}) of oxygen. The photocatalytic investigation was performed using 300 mL of 250 mg L^{-1} RB aqueous solutions and 150 mg of the respective photocatalyst. The suspension was kept in the dark for 40 min. After this adsorption step the suspension was irradiated with a 125 W high pressure mercury lamp (Philips), which provided UV-A light intensity of 2.2 mW cm^{-2}. At convenient intervals, samples were