



Preparation of photoactive nitrogen-doped rutile

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ABSTRACT

An easy way of preparing highly N-doped rutile photocatalysts (N-TiO₂/R) in tubular furnace in a constant ammonia (NH₃) flow at 800–1000 °C temperature range is presented. New materials were compared to TiO₂ samples prepared at the same temperatures in air atmosphere as well as to the starting material. Complete transformation of amorphous and anatase phases to rutile was confirmed by XRD method. Successful incorporation of relatively high amounts of nitrogen (up to 17% at.), in form of either TiO₂(N), TiO_xN_y or TiN, on photocatalysts' surface and in their lattice was confirmed using XPS and XRD analysis. Also presence of Ti³⁺ was revealed by EPR studies. In contrast to pristine TiO₂, the UV-vis/DR absorption spectra of N-modified photocatalysts extended significantly into the visible light region. Whereas nitrogen concentration as well as visible light absorption were found to increase with increasing modification temperature, photocatalytic activity was, on the contrary decreasing. This may be due to the very high nitrogen concentration, obtained at higher modification temperature, as well as the presence of small amount of conductive TiN phase on the N-TiO₂/1000 °C photocatalyst surface. The artificial solar light activity of new photocatalysts after thermal treatment in NH₃ increased in comparison to starting material, due to nitrogen modification and presence of Ti³⁺ ions. Activity under UV(-vis) light, though, decreased after modification procedure, probably due to smaller surface areas of new photocatalysts and complete anatase to rutile transformation.

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1. Introduction

One of the most challenging requirements for modern water purification systems is to degrade hazardous organic pollutants. One of the most effective and relatively cheap method seems to be advanced oxidation processes (AOPs) that generally involve generation of very powerful and non-selective oxidizing agent – hydroxyl radical (OH^{*}), which destroys organic waste [1–3] via its mineralization, which eventually leads to CO₂ and H₂O formation. For the purpose of AOPs different semiconductors as heterogeneous photocatalysts are used. Recently, the most commonly used semiconductor is TiO₂ as a non-toxic, cheap material of relatively high chemical stability [4]. In order to enhance the photocatalytic activity of TiO₂ under visible light irradiation, what is essential from the economical point of view, many different ways of modification have been widely studied. Thus researchers focused on TiO₂ metal doping using iron [5–7], nickel [8,9], vanadium [10,11], chromium [12,13], platinum or cobalt [14,15].

Nevertheless, titanium dioxide metal doping often leads to the recombination centers increase [16] and can be very expensive. For this reasons other ways of TiO₂ modification have been employed. The most promising seems to be non-metal modification, using carbon [17,18], sulfur [19], phosphorous [20], and nitrogen [21–23]. Doping with nitrogen is advantageous because nitrogen can be easily incorporated by annealing the sample in a nitrogen-containing gas flux, or by ion implanting nitrogen into the TiO₂ [24]. The behavior of N in TiO₂ has been widely discussed [21,25–28], but the fundamental mechanism underlying the visible-light absorption remains unclear [29]. It is generally accepted that the visible-light transitions involve electrons from N-related states migration to the conduction band. Nonetheless, whether the predominant active species are N atoms at interstitial sites or on substitutional O sites (N_O), and whether the behavior of N in rutile is different from that in anatase are still open issues. There are only relatively few papers describing rutile nitrogen-modification in comparison to the number of publications concerning N-doped/modified anatase materials. Most of the experimental works has been, so far, performed using either anatase or mixed anatase/rutile TiO₂ powder systems [24].

Irie et al. [25] prepared TiO_{2-x}N_x (x = 0, 0.0050, 0.011, 0.019) powders by titanium dioxide annealing under NH₃ flow at 550,

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575, and 600 °C and investigated the quantum efficiency of decomposing gaseous 2-propanol (IPA) under the same absorbed photon number of visible or UV light. They found out that nitrogen substituted some of the oxygen sites in TiO₂, forming a narrow N 2p band above the valence band. Wang et al. [30] prepared N-doped TiO₂ (anatase/rutile) by thermal treatment of commercial P25 TiO₂ in NH₃ flow at 400–700 °C for 4 h. Later also Wang et al. [31] obtained series of photocatalysts by annealing different precursors (nanotubular titanic acid, raw P25 TiO₂ and novel TiO₂) in flowing NH₃ at 600 °C for 4 h in order to study the origin of the visible light absorption and photoactivity. They proved that the visible light photocatalytic activity of N-doped anatase TiO₂ is co-determined by the formation of SETOV (single-electron-trapped oxygen vacancies) and the presence of 'doped-N'. The absorption edge observed in the visible spectral region was closely related with SETOV, while 'doped-N' played a role in preventing photogenerated electrons and holes from recombination, resulting in visible light photocatalytic activity.

Theoretical investigation [32] demonstrated quite different effects of nitrogen doping on electronic structure of anatase and rutile, i.e., downward shifting of valence band maximum indicating increased oxidation power of holes in nitrogen-doped rutile TiO₂. Meanwhile, surface reconstruction of rutile by nitrogen doping was also observed experimentally [33]. These unique properties associated with nitrogen-doped rutile TiO₂ may greatly alter its photocatalytic activity. Di Valentin et al. [32] have confirmed very different photoactivity results for N-doped anatase and rutile. According to their theoretical studies, for anatase samples, the presence of substitutionally bound nitrogen causes a decrease in the absorption band edge, while in rutile, the opposite-increase in absorption band edge. However, on the contrary to their predictions, Liu et al. [34] have prepared two series of nitrogen-doped TiO₂ samples with different ratios of anatase to rutile phases by milling the mixture of P25 TiO₂ and C₆H₁₂N₄ in air and gaseous NH₃ atmosphere, respectively. It was found that nitrogen-doped TiO₂ with higher content of rutile phase demonstrated higher photocatalytic activity in photodegrading pollutant rhodamine B under both UV light and visible light irradiation ($\lambda > 420$ nm).

The aim of this work was to obtain photoactive rutile-TiO₂ by nitrogen doping. We wanted to determine whether efficient N-doping is possible in case of rutile titanium dioxide and how this modification can influence its photocatalytic activity under different types of irradiation. The relation between nitrogen content and the new materials' photocatalytic activity as well as the N-modification origin has been studied. For this purpose two series of rutile-TiO₂ materials obtained by thermal treatment of pristine amorphous titanium dioxide at 800, 900 and 1000 °C in tubular furnace were prepared. First group was annealed for 4 h in ammonia (NH₃) flow, the second one also for 4 h in the air flow. The photocatalytic activity was studied under UV(-vis) (of strong UV light intensity) and artificial solar light irradiation. The photocatalysts' crystallite and surface structure, light absorption abilities as well as magnetic response of N-TiO₂/rutile have been studied. Finally, the difference between anatase and rutile response to N-modification and its influence on these phases photocatalytic behavior is here discussed.

2. Materials and methods

2.1. Materials

Water suspension of commercial, amorphous titanium dioxide (TiO₂/A) from sulfate technology, containing ca. 8% of residual sulfuric acid relatively to TiO₂ content, supplied by Chemical Factory "Police" S.A. (Poland) with BET surface area of 238 m²/g was used

as a pristine material for the synthesis of N-modified rutile TiO₂ photocatalysts. Ammonia (NH₃) was used in photocatalysts preparation process was supplied by Messer (99.85%). Phenol was used as the model organic pollutant for the evaluation of the photocatalysts' activity. High purity water for the photocatalytic experiments and sample analysis was produced by a Millipore Felix Advantage water purification system. *Modification procedure:* Modification of TiO₂ was conducted with gaseous ammonia at the temperatures which guaranteed complete anatase and amorphous phase transformation to rutile (800–1000 °C). The crude TiO₂ from sulfate technology was modified with gaseous ammonia (NH₃) as follows. A defined amount – about 20 g, of water suspension of TiO₂, containing ca. 35% of titanium dioxide, was placed in the melting pot and introduced into the tubular furnace. Then samples were calcined at 800–900–1000 °C in NH₃ or synthetic air atmosphere for 4 h (samples prepared in air atmosphere were marked as TiO₂/800, TiO₂/900, TiO₂/1000 while those obtained in ammonia flow as: N-TiO₂/800, N-TiO₂/900, N-TiO₂/1000). After heating the furnace was cooled down for about 4 h to the room temperature, then at room temperature flushed with argon for 15 min. Subsequently, dried for 24 h at 105 °C in a muffle furnace.

3. Experimental

3.1. Photocatalysts characterization

The crystalline structure of the photocatalysts was characterized by means of X-ray powder diffraction (XRD) analysis (X'Pert PRO Philips diffractometer) using Cu K α radiation. The X-ray photoelectron spectra were obtained using Mg K α ($h\nu = 1253.6$ eV) radiation with a Scienta SES 2002 spectrometer operating at constant transmission energy ($E_p = 50$ eV). The spectrometer was calibrated by using the photoemission line Ag 3d_{5/2} $E_B = 368.3$ eV. Data processing involved background subtraction by means of Shirley profile and a curve-fitting procedure (a mixed Gaussian–Lorentzian function was employed) based on a least-squares method (software CasaXPS). The quantitative composition of the surface was calculated assuming homogeneous distribution of elements. The powder samples were loosely placed into the sample holder. The analysis chamber during experiments was evacuated to better than 1×10^{-9} mbar. Charging effects were corrected by using the O 1s peak with E_B fixed at 530.0 eV. The measurements of magnetic resonance spectra were performed on a conventional X-band ($\nu = 9.4$ GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation. Sample containing around 20 mg of powder was placed in 4 mm diameter quartz tube. The FMR thermal studies were performed in the temperature range 4–300 K using an Oxford helium-flow cryostat. The photocatalysts were also characterized by UV-vis/DR technique using a Jasco V-650 spectrophotometer (Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra acquisition (BaSO₄ was used as a reference). The N₂-BET specific surface area of the materials was measured at 77 K using an Quadrasorb SI (Quantachrome Instruments, USA) instrument. Prior to analyses, each sample was degassed at 105 °C for 24 h under high vacuum. The values of the specific surface areas (S_{BET}) were determined using multi-point analysis of adsorption isotherms applying Brunauer–Emmet–Teller (BET) equation. The total organic carbon (TOC) measurements were conducted in Analytic Jena Multi N/C 3100 (Germany).

3.2. Experimental procedure

The photocatalytic activity of new materials was studied under UV(-vis) and artificial solar light irradiation. Photocatalytic activities of the samples under both types of irradiation were evaluated

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