



Nitrogen-doped, metal-modified rutile titanium dioxide as photocatalysts for water remediation



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ABSTRACT

A comparison study of metal (Fe, Co, or Ni) – modification, nitrogen – doping of rutile titanium dioxide via impregnation followed by calcination method is presented. The aim of this study was to obtain a highly photoactive rutile titanium dioxide and to establish the origin of its photoactivity with reference to the influence of the physicochemical properties of the modified materials and the type of the applied metal. Moreover, the properties of the co-modified photocatalysts were compared to those of the single (metal or nitrogen) modified materials. For this purpose highly advanced analytical methods such as SEM with EDS, XPS, EPR–AFMR, XRD, ICP–OES, UV–vis/DR, N₂ adsorption/desorption at 77 K and elemental analysis were employed. We have proved that a proper modification of rutile may lead to obtaining highly visible and/or UV light active materials. It has been revealed that the metal applied for rutile titanium dioxide modification plays a crucial role in its photocatalytic performance. In case of visible light the Fe > Ni > Co order and in case of UV light activity the Ni > Fe > Co order, for both single-modified and co-modified materials, is followed. Moreover, it was proven that the co-modified samples exhibited significantly higher activity than the single-modified rutile. An effort has been made in order to shed light on this new, unexplored area of titanium dioxide modification and application.

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1. Introduction

Titanium dioxide is undoubtedly the most studied semiconductor for photocatalytic water and air remediation due to its high stability, fine optical properties and availability [1,2]. Nevertheless, despite many advantages of this material, its commercial application is still limited. The main obstacles to be overcome before titanium dioxide can be successfully used for solar light applications are: (1) Wide band gap of 3.2 eV and 3.0 eV for anatase and rutile TiO₂, respectively, which implies application of, additionally to solar, UV light irradiation source [3,4]; (2) Rapid electron–hole pairs recombination [5,6] resulting in low electron concentration in conduction band of TiO₂, which diminishes the photocatalytic efficiency of the semiconductor [7].

In order to overcome these difficulties the researchers employed numerous modification methods among which the non-metal doping [8,9] as well as transition metal-doping [10] seem to be the

most promising for TiO₂ band-gap narrowing, whereas titanium dioxide modification with metals [11], graphene [12,13] or semiconductors coupling [14,15] are mainly used in order to inhibit electron/hole pairs recombination rate. Among non-metals, it is nitrogen, which attracts the most attention. Starting from the paper by Asahi et al. [16], every year numerous publications considering this subject are published [17]. The significantly higher interest in nitrogen in regard to other non-metals arises from the fact that nitrogen can be relatively easily incorporated in TiO₂ structure [18]. Moreover, the position of newly formed, after nitrogen-doping, energy state above the valence band of TiO₂ possesses sufficiently high oxidation potential for water contaminants photodegradation [19] which is not always the case for carbon, sulfur or fluorine-doped TiO₂ [17]. Theoretical studies discuss different influence of titanium dioxide N-doping on anatase and rutile form of TiO₂ [20]. Di Valentin et al. [21] claim that whereas the position of the valence band of N-doped anatase increases by 0.14 eV or 0.73 eV for substitutional and interstitial doping, respectively, the valence band position of N-doped rutile decreases by 0.03 eV and the position of the rutile conduction band increases by 0.05 eV, resulting in higher band gap energy than for pure rutile (3.08 eV for N-doped vs. 3.0 eV

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for pure rutile). Although, to the best of our knowledge, there is no experimental work available to confirm this statement, it cannot be neglected.

Surface metal modification of titanium dioxide may increase the photocatalytic efficiency of the material by working as the so called co-catalysts, which induce electron transport from TiO₂ conduction band to the metal/semiconductor inter-phase thus inhibiting electron/hole recombination rate [22–24]. Creutz et al. [22] studied photocatalytic activity of Ti³⁺ doped titanium dioxide. The photocatalyst was inactive even under UV light irradiation. Only after its surface modification with copper(II) or iron(III), which significantly increased charge separation, the photocatalytic activity of TiO₂ increased dramatically. Liu et al. [25] obtained visible light active materials by simultaneous doping and surface modification of TiO₂ using iron ions. Doped-iron allowed successful absorption of visible light fraction whereas iron grafted on the TiO₂ surface increased quantum efficiency by allowing effective separation of photo-generated electron–hole pairs.

In our previous work [26,27] we have discussed the possibility of obtaining visible light active rutile-TiO₂ photocatalysts by the nitrogen-doping and metal (Me = Fe or Ni) modification. The obtained results were very promising. In this study, we describe nitrogen-doped cobalt-modified rutile titanium dioxide and compare it to our earlier works, focusing on the cobalt modification and referring to the materials from the previous publications. Moreover, in this paper we provide some new information about the earlier described materials and focus on the origin of the visible and UV light activity of rutile-TiO₂ photocatalysts.

2. Experimental

2.1. Materials

Commercial P25 TiO₂ (Evonik, Germany) with BET surface area of 55.5 m² g⁻¹ and commercial rutile (Catalysis Society, Japan) with BET surface area of 100 m² g⁻¹ were used as reference photocatalysts. Water suspension of crude, industrial grade titanium dioxide (TiO₂/A), consisting of water, TiO₂ (ca. 35 wt.%, including amorphous, anatase and rutile at the ratio of 61.5:35:3.5), and residual sulfuric acid (ca. 8 wt.% in regard to TiO₂ content, from sulfate technology) supplied by Chemical Factory “Police” S.A. (Poland) with BET surface area of 238 m² g⁻¹ was used as a pristine material for the synthesis of modified TiO₂. Metal nitrates (Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O) and ammonia were used as metal and nitrogen precursors, respectively. A model solution of acetic acid (5 vol.%) was applied in order to evaluate the photocatalysts’ activity. High purity water for the photocatalytic experiments and sample analysis was produced by a Millipore Elix Advantage water purification system that provides bacteria free water at 18 MΩ cm⁻¹, resistivity, and with less than 1 ppb total organic carbon.

2.2. Nitrogen doping, metal modification and metal, nitrogen co-modification procedure

The TiO₂ modification was conducted according to the procedure described in our previous publications [26,27]. Water suspension of an industrial grade amorphous titanium dioxide (TiO₂/A) from sulfate technology supplied by “Chemical Factory Police S.A.” (Poland) was used as a starting material. About 20 g of TiO₂/A was introduced into a beaker containing aqueous solution of Me(NO₃)₂·xH₂O (used as a source of iron, cobalt or nickel) and stirred for 48 h. The amount of metal nitrate introduced to the beaker was of 5 wt.% relatively to TiO₂ content. After water evaporation, the samples were dried at 80 °C for 24 h in an oven.

Subsequently, the materials were calcined for 4 h at 800 °C in either Ar flow (Me-modified samples denoted as Me-TiO₂/R, where Me = Fe, Co or Ni) or NH₃ (Messer, 99.85%) flow (co-modified samples denoted as Me,N-TiO₂/R). NH₃ was used as nitrogen and hydrogen source. Additionally, for comparison purpose, N-TiO₂/R was prepared without Me(NO₃)₂ impregnation step.

2.3. Photocatalysts’ characterization

The photocatalysts’ light absorption abilities were characterized by means of UV–vis/DR technique using Jasco V-650 spectrophotometer (Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra acquisition (Spectralon was used as a reference). The crystalline structure of the photocatalysts was characterized by X-ray powder diffraction (XRD) analysis (X’Pert PRO Philips diffractometer) using Cu Kα radiation. The specific surface area (S_{BET}) of the photocatalysts was determined on a basis of N₂ adsorption at 77 K using Quadrasorb SI (Quantachrome Instruments, U.S.A.) instrument. Prior to analyses, each sample was degassed at 105 °C for 24 h under high vacuum. The values of the S_{BET} were determined using multi-point analysis of adsorption isotherms applying Brunauer–Emmett–Teller (BET) equation. The X-ray photoelectron spectra (XPS) were obtained using Mg Kα (hν = 1253.6 eV) radiation for the samples containing iron and cobalt additives, while the sample with nickel addition was studied with use of Al Kα (hν = 1486.6 eV) radiation. Scienta SES 2002 spectrometer operating at constant transmission energy (E_p = 50 eV) was used to acquire the spectra. The samples were also analyzed with application of scanning electron microscopy with cold emission SEM SU8020 (Hitachi, Japan) coupled with energy-dispersive X-ray spectroscopy (SEM-EDS, EDS NSS 312, Thermo Scientific) allowing elemental microanalysis. Total nitrogen content in the samples was determined with application of Leco ONH836 elemental analyzer. The concentration of metals in the samples was determined by ICP–OES method using Perkin Elmer Optima 5300 DV spectrometer. Prior to these analyses the photocatalysts were diluted in a hot H₂SO₄ with addition of water and HCl.

2.4. Photoactivity evaluation method

The photocatalytic activity of all new materials as well as commercial photocatalysts for comparison purpose was determined on the basis of CO₂ evolution rate during oxidative decomposition of acetic acid. The evaluation of photoactivity of the different synthesized materials was conducted at a constant volumetric rate of photon absorption (VRPA) by providing photocatalyst concentration conditions which allowed all the light induced to be absorbed by the slurry. This method allows the evaluation of the intrinsic photoactivity of each material [28]. The procedure was conducted under irradiation using mercury lamp emitting wavelengths >290 nm. For visible light tests a cut-off optical filter providing irradiation wavelengths longer than 400 nm was applied.

3. Results and discussion

3.1. Crystal Structure

Fig. 1 presents XRD patterns of the cobalt-modified and cobalt, nitrogen co-modified rutile titanium dioxide materials together with the starting material (TiO₂/A). (The XRD patterns of all the other samples are available in our previous publications [26,27] as well as in Supplementary information—S1). According to XRD measurements all metal-modified photocatalysts (Me-TiO₂/R) consisted of two phases: rutile TiO₂ and ternary oxide, namely TiFe₂O₅, CoTiO₃ and NiTiO₃ for iron, cobalt and nickel modification, respectively. The mixed oxides are also semiconductors and

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