

Aqueous-based synthesis of mesoporous TiO₂ and Ag–TiO₂ nanopowders for efficient photodegradation of methylene blue

Ipsita Hazra Chowdhury, Sourav Ghosh, Milan Kanti Naskar*

Sol–Gel Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700032, India

Received 14 August 2015; received in revised form 9 October 2015; accepted 9 October 2015

Available online 23 October 2015

Abstract

Mesoporous anatase TiO₂ was synthesized by a hydrothermal method at 180 °C/24 h using titanium (IV) oxysulfate (TIOS), urea and sodium dodecyl sulfate (SDS) under aqueous medium. The Ag nanoparticle doped anatase TiO₂ (Ag–TiO₂) was prepared by an impregnation method using water dispersible Ag obtained from green *carambola* extract at room temperature. The particles were characterized by X-ray diffraction (XRD), thermo gravimetric (TG) and differential thermal analysis (DTA), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), N₂ adsorption–desorption study, and transmission electron microscopy (TEM). The photocatalytic degradation of methylene blue (MB) was studied in the presence of TiO₂ and Ag–TiO₂ particles under UV and visible light. The initial enhancement of MB dye degradation in the presence of Ag–TiO₂ was due to its ability to trap electrons inhibiting electron–hole recombination. Pure anatase TiO₂ having higher surface area and pore volume also influenced predominantly in reducing the recombination of electrons–holes pair, reflecting higher efficiency for photodegradation of MB after a certain period of exposed time.

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Keywords: A. Powders; B. Microstructure; B. Porosity; D. TiO₂; E. Functional application

1. Introduction

Titania is becoming an important material with versatile applications as pigments, capacitors, solar cells, catalyst, photocatalysts etc [1]. It has been extensively studied as an effective photocatalyst for photocatalytic degradation of organic and inorganic pollutants in waste water [2]. Due to its unique properties like chemical inertness, non-toxicity and photostability, titania finds a wide range of applications [3]. However, the major constraints for TiO₂ photocatalyst are its low quantum efficiency, wide band gap (3.2 eV) energy, and relatively high electron–hole recombination rate [4]. Therefore, doping with metals in TiO₂ is becoming essential to increase the life time of the charge carrier as well as band gap tuning to a desired level [5]. Metal doping affects the physico-chemical properties like crystallinity, optical, textural and surface properties etc of TiO₂ toward its applications. The above

properties are influenced by different synthetic methods [6,7]. Silver doped TiO₂ is very much attractive for better photocatalytic activity in terms of enhancement of electron–hole separation by acting as electron traps, extending light absorption into the visible range and modifying surface properties of photocatalysts.

Different methods have been reported for the synthesis of TiO₂ nanoparticles, such as co-precipitation [8], mechanochemical [9], hydrothermal [10,11], solvothermal [12], sol–gel [13], microemulsion [14], microwave [15] etc. Mesoporous TiO₂ was synthesized by hydrothermal method using titanium butoxide in the presence of organic solvent to control rapid hydrolysis of titania precursor [16,17]. Kolen'ko et al. [18] hydrothermally synthesized nanocrystalline mesoporous TiO₂ from aqueous solution of titanyl oxalate acid via many processing steps. Mesoporous hierarchical TiO₂ nanostructures were prepared by the hydrothermal method using TiO₂ powder in the presence of H₂O₂ and NaOH [19] via controlled multistep process. To avoid the use of highly hydrolysable titanium butoxide as precursor, and to minimize processing

*Corresponding author. Tel.: +91 33 24733496x3516.

E-mail address: milan@cgcrici.res.in (M.K. Naskar).

step, in the present study, mesoporous TiO₂ nanoparticles with higher surface area were synthesized by a single step hydrothermal method at 180 °C/24 h in the presence of aqueous based precursors of titanium oxysulfate, urea, sodium dodecyl sulfate and water. For the preparation of Ag doped TiO₂ nanocomposites, photoreduction treatment [20,21] is applied for the reduction of Ag⁺ ions to metallic Ag using UV light. Zhang et al. [22] used L-Tyrosine as reducing agent for Ag doping in TiO₂ microspheres. In the present method, for doping Ag into TiO₂, an impregnation method was adopted using AgNO₃ and green *carambola* fruit extract at pH 10 under stirring for 12 h at room temperature in dark, in the absence of any photoreduction technique and high cost reducing agent. In this method, polyols and ascorbic acids present in the *carambola* extract was exploited for the reduction of Ag⁺ to Ag⁰ at room temperature. They also behaved as capping agents for well dispersion of Ag nanoparticles [23] during impregnation into TiO₂.

In the present work, to the best of our knowledge, we first report Ag doped TiO₂ nanoparticles using *carambola* extract, and the influence of dual properties i.e., electron trapping efficiency of Ag in Ag–TiO₂, and higher surface area and pore size of undoped anatase TiO₂ toward photocatalytic efficiency of the synthesized powders for the degradation of methylene blue (MB) dye. The photocatalytic performance of Ag–TiO₂ obtained from pure ascorbic acid, and also P25 (**Evonik**) was also studied for comparison.

2. Experiment

2.1. Materials

Titanium (IV) oxysulfate (TIOS) (15 wt% solution in dilute sulfuric acid), P25 (**Evonik**), ascorbic acid were purchased from Sigma-Aldrich. Sodium dodecyl sulfate (SDS), silver nitrate (AgNO₃), urea and sodium hydroxide were purchased from Merck, India. Deionized (DI) and Millipore water was used throughout the experiment. Green *carambola* was purchased from local market.

2.2. Preparation of TiO₂ nanoparticles

In a typical experiment, 10 mmol urea and 2 mmol SDS were dissolved in 25 mL DI water followed by addition of 5 mmol TIOS (0.78 ml) into the former solution under stirring condition. After stirring for 30 min, the above solution was transferred into a 50 mL Teflon-lined autoclave, followed by hydrothermal treatment at 180 °C for 24 h. After the reaction, the particles were collected by centrifugation, and washed with DI water and acetone, followed by drying at 70 °C for 4 h. The dried as-prepared particles were calcined at 500 °C with a heating rate of 2 °C min⁻¹ and dwell time of 2 h.

2.3. Preparation of Ag doped TiO₂ nanoparticles

In a typical experiment, 0.2 mmol TiO₂ powder was dispersed in 50 mL DI water under sonication followed by

adding 0.1 mmol AgNO₃ into the dispersed solution. 10 mL of *carambola* extract was added into the above mix solution followed by dropwise addition of 1 M NaOH solution up to pH 10 under stirring condition. The whole reaction mixture was kept in dark under constant stirring for 12 h. The Ag impregnated TiO₂ nanoparticles were then separated by centrifugation, washed with Millipore water for several times to remove the biomolecules, followed by drying in air.

2.4. Characterization

Powder X-ray diffraction (XRD) studies of the samples were performed by a Philips X'Pert Pro PW 3050/60 powder diffractometer using Ni-filtered Cu-K α radiation ($\lambda=0.15418$ nm) operated at 40 kV and 30 mA. The thermal behaviors of the uncalcined (as-prepared) particles were studied by thermogravimetry (TG) and differential thermal analysis (DTA) with (Netzsch STA 449C, Germany) from room temperature to 1000 °C in air atmosphere at the heating rate of 10 °C/min. Raman measurements were performed by a STR500 Raman Spectrometer (Cornes Technology Make) using an excitation wavelength of 514 nm with a power of 50 mW. Scattered light was analyzed using a spectrometer grating with a spectral resolution of < 1 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI 5000 Versaprobe II Scanning XPS microprobe (ULVAC-PHI, USA). The spectra were recorded with monochromatic AlK α ($h\nu=1486.6$ eV) radiation with an overall energy resolution of ~ 0.7 eV. Nitrogen adsorption–desorption measurements were conducted at 77 K with a Quantachrome (ASIQ MP) instrument. The powders were outgassed in vacuum at 250 °C for 4 h prior to the measurement. The surface area was obtained using the Brunauer–Emmett–Teller (BET) method within the relative pressure (P/P_0) range of 0.05–0.20 and the pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.99 was used to determine the pore volume. The morphology of the particles was examined by the transmission electron microscopy (TEM), using a Tecnai G2 30ST (FEI) instrument operating at 300 kV. Elemental composition of the sample was analyzed with energy dispersive analysis of X-ray spectroscopy (EDS) coupled to TEM. The Na and Ag content in the samples was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Model: Spectro Ciros Vision, Germany). UV–visible spectra were recorded using a UV–vis–NIR spectrophotometer (UV-3101PC, Shimadzu) in the wavelength range of 200–800 nm.

2.5. Photocatalytic study

For a comparative study, the photocatalytic activity of synthesized TiO₂, Ag–TiO₂ (obtained from *carambola*), Ag–TiO₂ (obtained from ascorbic acid) and reference powder (P25, **Evonik**) was studied for the degradation of MB solution under UV ($\lambda=365$ nm) and visible ($\lambda=465$ nm) light irradiation each at room temperature in the photoreactor. In a typical photocatalytic test, 2 mg of the sample was mixed with 12 mL

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