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Elongated titania nanostructures as efficient photocatalysts for degradation of selected herbicides

Mila Vranješ[a], Zoran V. Šaponjić[a], Ljiljana S. Živković[a], Vesna N. Despotović[b], Daniela V. Šojić[b], Biljana F. Abramović[b,**], Mirjana I. Čomor[a,*]

[a] Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia
[b] Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, Serbia

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ABSTRACT

Titanium dioxide nanotubes (TNT) were synthesized via hydrothermal method and calcined at various temperatures. The obtained calcined TiO_2 nanomaterials with specific elongation orientation were characterized by transmission and scanning electron microscopy (TEM, SEM), X-ray diffraction (XRD), UV/Vis diffuse reflection spectroscopy (DRS), Laser Doppler electrophoresis (LDE) and their textural properties were evaluated. The photocatalytic activity of obtained nanopowders was evaluated considering photodegradation rate of herbicide clomazone, rarely studied herbicide. The influence of calcination temperature of catalysts with elongated morphology on their photocatalytic activity was evaluated. The best results were obtained with TNT annealed at 700 °C, which can be assigned to the best balance between crystal structure, morphology and surface properties of nanoparticles induced by annealing. Also, the photocatalytic degradation rates of another two herbicides (picloram, and mecoprop) were compared, due to possibility that the efficiency of photocatalytic degradation is greatly influenced by the molecular structure. The mineralization degree of selected herbicides in the presence of TiO_2 based photocatalysts was evaluated applying total organic carbon (TOC) measurements.

1. Introduction

Nanocrystalline TiO_2 has attracted great interest in last few decades due to their unique properties, crystal structures, morphologies and promising applications in various fields, such as dye sensitized solar cells, photocatalysis, sensing and optoelectronic devices [1]. The TiO_2 is mainly used as photocatalytic material in the processes of water and air purification due to excellent photo and chemical stability, nontoxicity, superior redox ability and low cost [2]. The performances of TiO_2 nanomaterial are highly dependent on its crystal structure, size and shape [3,4]. The ability to control the size and shape of TiO_2 nanoparticles is becoming an important scope in materials science because it opens up the possibility to combine high aspect ratio, high surface area and versatile chemistry for efficient photoinduced charge separation [5]. Since discovery of carbon nanotubes, much effort has been directed towards synthesis of one-dimensional (1D) nanostructures like rods, wires, tubes and belts due to their shape and size dependent optical and electrical properties [6]. Convenient hydrothermal synthetic route applied for synthesis of titania nanotubes (TNT), using highly basic dispersion of TiO_2 nanoparticles as a precursor, was the most commonly applied method in the last decade [7,8]. These nanotubes were further used as a precursor for synthesis of anisotropic (1D) TiO_2 nanocrystals of different crystals structures capable of vectorial electron transport necessary for creating efficient photoconversion systems [9].

Recently, 1D titania nanocrystals have been used as photocatalysts for degradation of different persistent organic pollutants as reviewed by Liu and coauthors [10]; usually dyes were used as test molecules for obtaining degradation capabilities of photocatlysts, herbicides not yet in a greater extent. Hazardous contaminants such as pesticides constitute a serious risk for human health due to their high toxicity. The widespread use of pesticides can result in contamination of surface and ground waters in the areas of their application [11]. Furthermore, bioaccumulation and biomagnification can lead to hazardous concentrations in humans. Among the chemicals that are likely to be found in groundwater, pesticides have a non-negligible presence and their elimination is

* Corresponding author. Tel.: +381 11 380 41 92; fax: +381 11 3408 607.
** Corresponding author. Tel.: +381 21 485 27 53; fax: +381 21 454 065.
E-mail addresses: biljana.abramovic@dh.uns.ac.rs (B.F. Abramović), mirjanac@vinca.rs (M.I. Čomor).

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necessary, especially if the water is intended for human consumption. Advanced oxidation processes have provided a promising alternative for the remediation of contaminated water when compared to other treatment methods [12,13], while heterogeneous photocatalysis by TiO_2 appeared as one of the most efficient methods for the elimination of a number of pesticides from water [14,15].

This paper is mainly devoted to characterization of elongated titania nanoparticles obtained by calcination of hydrothermally synthesized TNTs, in the range of temperatures from 400 to 800 °C. The obtained calcined TNTs with specific elongation orientation are characterized by transmission and scanning electron microscopy (TEM, SEM), X-ray diffraction (XRD), UV/Vis diffuse reflection spectroscopy (DRS), Laser Doppler electrophoresis (LDE) and their texture properties were attained. We have further studied the influence of heat transformation of TNTs on their photocatalytic activity following decomposition rates and mineralization of herbicide clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone, Table 1) highly water soluble herbicide which can cause ground water contamination [16]. Also, in order to obtain the link between photocatalysts activity and molecular structure of the substrates, the photocatalytic activity of picloram (4-amino-3,5,6-trichloro-2-pyridin carboxylic acid) and mecoprop (*RS*-2-(4-chloro-o-tolyloxy)propionic acid) (Table 1) were studied. They were choosen because of their wide use in selective control of many annual and some perennial weeds, and because of their occurrence in drinking water [17,18].

2. Experimental

Chemicals: TiO_2 powder (p.a., Fluka), clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone Table 1) (98.8%, Riedel-de Haën) and picloram (4-amino-3,5,6-trichloro-2-pyridincarboxylic acid, Table 1) (99.4%, pestanal quality, Riedel-de Haën), H_3PO_4 (85% Lachema), acetonitrile (ACN) (99.8%, J.T. Baker), H_2SO_4 (conc., Aldrich), NaOH (ZorkaPharm), HCl (conc. Aldrich) were used without further purification. The commercial herbicide mecoprop (*RS*-2-(4-chloro-o-tolyloxy)propionic acid, Table 1), 98% purity, obtained from the Chemical Factory "Župa" Kruševac, Serbia, was purified by conventional recrystallization from water–ethanol (1:1, v/v) solution. Milli-Q deionized water was used as a solvent. Air and argon gases were of high purity (99.5%). As reference material the TiO_2 Degussa P25 (75% anatase and 25% rutile form, 50 m^2/g, about 20 nm, non-porous, hereafter P25) was used. The pH of water suspension of P25, as prepared and annealed TNT-700 was ~5.6, 9 and 7.8, respectively.

Computer modeling procedures used in this study were performed using Hyperchem 8.0.6 (Hypercube Inc.). The compounds formulae were entered into the data set as two-dimensional sketches into Hyperchem. Full optimization geometry and calculation of the positive and negative molecular electrostatic potentials MEPs for the best conformer were performed using the semi-empirical method AM1 running on Hyperchem. Electronic properties were computed from single point calculations.

2.1. Synthesis of TiO_2 nanotubes

Titania nanotubes were synthesized by a hydrothermal treatment (48 h/120 °C) of TiO_2 powder (Fluka) used as a precursor in proton deficient aqueous solution (10 mol/dm^3 NaOH) without shaking [7,8,19]. After autoclaving in Teflon vessel, the ensuing powder was separated from the solution using centrifuge. The powder was washed once using 1 mol/dm^3 HCl aqueous solution for 2 h and then several times using pure water. This washing procedure with water was repeated until the water reached pH = 7. Finally, the powder was separated from the washing solution by centrifugation. Synthesized nanotubes were dried at 70 °C until attainment of constant weight. Portions of TNT powder were calcined in an oven, at 400, 500, 600, 700, and 800 °C.

2.2. Characterization of TNTs

XRD patterns of the TNT were obtained using standard powder diffraction methods with a Philips PW1830 X-ray powder diffractometer using Cu K_α line. Phase composition (anatase/rutile) was estimated using characteristic diffraction peaks: for anatase (101) and for rutile (110).

The sizes and shapes of the used titania nanoparticles were determined using TEM, Hitachi H-7000 FA TEM operated at 125 kV. TEM samples were prepared by ultrasound treatment of particles water dispersion for 10 min in an ultrasound bath before drop-wise placing volume of 6 μl onto a holey carbon film supported on a copper grid. The specimen was air-dried overnight. A scanning electron microscope JEOL JSM 6460 LV and field emission scanning electron microscopy (FESEM) TESCAN Mira3 XMU at 20 kV were used to characterize the morphology of the titania powders. Gold-coated particles were examined on a SEM, JSM-6460LV JOEL instrument, operated at an accelerating voltage of 25 keV.

UV/Vis spectroscopy was performed using Thermo Scientific Evolution 600 UV–Vis spectrophotometer.

Nitrogen adsorption–desorption isotherms, for obtaining texture properties of the samples, were collected on a Micromeritics ASAP 2020 surface area and pore size analyzer at 77 K. Prior to adsorption, the samples were degassed at 423 K for 10 h, under a reduced pressure. The specific surface area of the samples was calculated by applying the Brunauer–Emmet–Teller (BET) equation from the linear part of the adsorption isotherm. The total pore volumes of micro and meso pores were obtained from the N_2 adsorption at $p/p_0 = 0.998$.

Zeta potential (ζ) of TNT nanoparticles was measured by Zeta-Sizer Nano ZS with 633 nm He-Ne laser (Malvern, UK), utilizing electrophoretic light scattering method [20]. The ζ-potential was calculated by instrument software, applying the Henry equation and the Smoluchowski approximation, from the electrophoretic mobility of particles measured by laser Doppler velocimetry. Series of dispersion samples containing 1 mg TNT/1 cm^3 NaCl (1×10^{-3} mol/dm^3) as inert electrolyte [21], were shaken for 24 h at room temperature. The as-prepared and calcined TNT were used. The ζ-potential measurements were performed in duplicate in the pH range from ~9 to ~3, and the average data presented.

2.3. Photodegradation procedure

The photocatalytic degradation of substrates were carried out in a cell made of Pyrex glass (total volume of ca. 40 cm^3, liquid layer thickness 35 mm), with a plain window on which the light beam was focused. The cell was equipped with a magnetic stirring bar and a water circulating jacket. A 125 W high-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335, and 366 nm, with maximum emission at 366 nm), together with an appropriate concave mirror, was used as the radiation source. In a typical experiment, and unless otherwise stated, the initial herbicides concentration was 5.0×10^{-2} mmol/dm^3, and the TiO_2 loading was 1.0 mg/cm^3. The total suspension volume was 20 cm^3. The aqueous suspension of TiO_2 was sonicated (50 Hz) in the dark for 15 min before illumination, to uniformly disperse the photocatalyst particles and attain adsorption equilibrium. The suspension thus obtained was thermostated at 25 ± 0.5 °C and then irradiated at a constant stream of O_2 (3.0 cm^3/min). During the irradiation, the mixture was stirred at a constant speed. The initial pH of reaction mixture clomazone, picloram and mecoprop in the presence of TNT were ~7.8, 7.2, and 7.4, respectively, while in the presence of