



Photocatalytic bleaching of aqueous malachite green solutions by UV-A and blue-light-illuminated TiO₂ spherical nanoparticles modified with tungstophosphoric acid

J.A. Rengifo-Herrera*, M.N. Blanco, L.R. Pizzio*

Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J.J. Ronco" (CINDECA), Calle 47 N 257, Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 47 No. 257, 1900 La Plata, Buenos Aires, Argentina

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ABSTRACT

Visible-light-responsive spherical TiO₂ particles were prepared by the sol–gel method by adding urea as pore-forming agent and tungstophosphoric acid (TPA) in different ratios (20% and 30% w/w) and by annealing at 500 °C for 2 h. Visible light absorption is probably due to WO_x formation (i.e. WO₃) resulting from the partial degradation of TPA and evidenced by XPS spectra. Besides, ³¹P NMR and XPS results showed evidence about the existence of mostly unaltered TPA within TiO₂ nanoparticles and on their surface, together with lacunar or dimeric species. TPA addition not only affected the optical properties of materials but also produced a strong decrease of their point of zero charge (pH_{pzc}). Results obtained under UV-A irradiation revealed that aqueous malachite green (MG) solutions were efficiently bleached through the oxidative process of *N*-demethylation being the TiO₂ powder containing 30% (w/w) of TPA (TiO₂–TPA–30%) (100% of bleaching in 60 min) the most active even than Degussa P-25 (80% of MG bleaching in 60 min). On the other hand, when blue-light irradiation was used, TiO₂–TPA–30% powder also revealed the highest photocatalytic bleaching of MG solutions which, as in the case of UV-A light irradiation experiments, was oxidized through *N*-demethylation processes. Finally, experiments carried out using blue-light irradiation under N₂ atmosphere showed that aqueous MG solutions were not bleached by TiO₂ powders containing TPA.

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1. Introduction

Since the early 1970s, when Fujishima and Honda [1] discovered that by using single crystals of rutile TiO₂ as photoelectrodes, it was possible to transform the light in chemical energy in order to generate H₂ and O₂ and Gravelle et al. found that reduced TiO₂ was able to oxidize isobutane at room temperature [2], the research about titanium dioxide (TiO₂) has increased drastically and has been extended to the area of environmental photocatalysis [3–5]. When this semiconductor is irradiated under UV light, it exhibits photocatalytic activity leading to the oxidative destruction of a wide range of organic compounds and inactivation of pathogen microorganisms on its surface. Although heterogeneous photocatalysis has shown to be a promising technology to eliminate pollutants and inactivate microorganisms in water, two important drawbacks must be overcome: (i) its

overall efficiency under natural sunlight is limited to the UV-driven activity ($\lambda < 400$ nm), accounting only for ~4% of the incoming solar energy on the Earth's surface, (ii) its highest electron-hole (e⁻/h⁺) recombination rate [6] (around 90% of e⁻/h⁺ pairs are recombined in the nanosecond range). Different strategies have been proposed to overcome these problems. For instance, the increase of TiO₂ absorption and photoactivity in the visible region has attracted a lot of attention [7]. Much progress has been achieved in the field of *visible-light-active* TiO₂ by incorporation of various metallic and nonmetallic dopants into its lattice [8–12]. Recently, several authors have demonstrated that the use of N- and S-doped TiO₂ seems to be not suitable to degrade organic pollutants under visible light or solar-simulated irradiation [13–15].

On the other hand, several strategies have also been used to decrease the recombination in TiO₂ nanoparticles by adding noble metals such as silver and platinum, which have shown good results, since metals behave as electron traps [16–18].

Heteropolyoxometallates (POMs) are widely used as oxidation as well as acid catalysts [19–21]. They are also employed as effective homogeneous photocatalysts in the oxidation of organic

* Corresponding authors. Tel.: +54 221 421 1353; fax: +54 221 421 1353x125.

E-mail addresses: julianregifo@quimica.unlp.edu.ar (J.A. Rengifo-Herrera), lrpizzio@quimica.unlp.edu.ar (L.R. Pizzio).

compounds [22] and in the degradation of organic pollutants in water [23].

The incorporation of POMs such as tungstophosphoric acid (TPA) has been explored to enhance the photocatalytic activity and the broadening of light absorption of TiO₂, obtaining good results in the destruction of organic pollutants [24,25]. In addition, it is well known that POMs could play the role of efficient photoinduced electron traps, enhancing the photocatalytic process and diminishing the e⁻/h⁺ recombination [26].

Herein, we report the preparation of spherical particles of TiO₂ by adding 20% and 30% (w/w) TPA via the sol–gel process and using urea as pore-forming agent. Morphological, bulk and surface features of these materials were characterized by X-ray diffraction (XRD), ³¹P magic angle spinning–nuclear magnetic resonance (³¹P MAS NMR), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), and the p*H*_{pzc} was also determined. Their photocatalytic activity was tested in the bleaching of aqueous solutions of malachite green oxalate (MG), a cationic triphenyl methane dye, under UV and blue light irradiation, and compared with the values obtained using Degussa–Evonik P-25 TiO₂.

2. Experimental

2.1. Synthesis of modified TPA–TiO₂ particles

Titanium isopropoxide (Aldrich, 26.7 g) was mixed with absolute ethanol (Merck, 186.6 g) and stirred for 10 min to obtain a homogeneous solution under N₂ at room temperature, then 0.33 cm³ of 0.28 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol–gel reaction and was left for 3 h. Then 120 g of urea–alcohol–water (1:5:1 weight ratio) solution was added to the hydrolyzed solution under vigorous stirring, to act as template, together with an ethanol solution of H₃PW₁₂O₄₀·23H₂O (Fluka p.a.). The amount of TPA solution was fixed in order to obtain a TPA concentration of 0%, 20% and 30% by weight in the final material.

The gels were kept in a beaker at room temperature till dryness. The solids were ground into powder and extracted with distilled water for three periods of 24 h to remove urea, in a system with continuous stirring. Finally, the solids were thermally treated at 500 °C for 2 h. The samples will be named TiO₂–TPA–0%, TiO₂–TPA–20%, and TiO₂–TPA–30%, respectively.

2.2. Sample characterization

2.2.1. Scanning electron microscopy (SEM)

The secondary electron micrographs of the samples were obtained by scanning electron microscopy (SEM), using Philips Model 505 equipment, at a working potential of 15 kV, and samples coated with graphite.

2.2.2. Point of zero charge measurements

The point of zero charge (p*H*_{pzc}) of each sample was estimated using the mass titration method proposed by Noh and Schwarz [27]. Suspensions of the solid in deionized water ranging from 0.01% to 20% (w/w) were prepared and the pH measured after 24 h of stirring.

2.2.3. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance spectra of the materials were recorded using a UV–visible Lambda 35, Perkin–Elmer spectrophotometer, to which a diffuse reflectance chamber Labsphere RSA-PE-20 with an integrating sphere of 50 mm diameter and internal Spectralon coating is attached, in the 250–600 nm wavelength range.

2.2.4. Nuclear magnetic resonance spectroscopy (NMR)

The ³¹P magic angle spinning–nuclear magnetic resonance (³¹P MAS–NMR) spectra were recorded with Bruker Avance II equipment, using the CP/MAS ¹H–³¹P technique. A sample holder of 4 mm diameter and 10 mm in height was employed, using 5 ms pulses, a repetition time of 4 s, and working at a frequency of 121.496 MHz for ³¹P at room temperature. The spin rate was 8 kHz and several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference.

2.2.5. X-ray photoelectron spectroscopy (XPS)

XPS analyses were carried out with XPS Analyzer Kratos model Axis Ultra with a monochromatic AlK α and charge neutralizer. The deconvolution software program was provided by Kratos, the manufacturer of the XPS instrument.

All the binding energies were referred to the C 1 s peak at 285 eV of adventitious carbon. Powder samples were prepared by deposition of the solid on carbon type stuck to the sample holder.

2.3. Photocatalytic activity under UV and blue-light irradiation

TiO₂ (1.0 g dm⁻³; this concentration showed the best photocatalytic activity towards MG discoloration under the experimental conditions used (data not shown)) was added to a 5.0 × 10⁻⁴ M aqueous malachite green oxalate solution contained in cylindrical Pyrex bottles of 50 cm³. Prior to UV or blue-light irradiation, the resulting suspension was kept under magnetic stirring in the dark for ca. 30 min to ensure that dye/TiO₂ surface adsorption/desorption processes were reached. The suspension was then irradiated by 5 UV black light lamps Philips TLD 18 W (emission spectra: 330–400 nm and UV intensity between 300 and 400 nm: 38 W m⁻²) or 5 fluorescent lamps Philips TLD-18 W blue (emission spectra: 400–500 nm with UV intensity: 0.1 W m⁻² and global intensity between 290 and 1100 nm: 60 W m⁻²). UV and global intensity were monitored with a Kipp and Zonen (CM3) power meter (Omni instruments Ltd, Dundee, UK). The atmosphere in the cylindrical Pyrex bottle was adjusted by continuously bubbling either air or nitrogen (99.999% Carbagas, Switzerland) ensuring saturated oxygen and nitrogen conditions. Samples taken at different illumination times were filtered through membranes of 0.22 μ m pore size, and the discoloration of the MG solution was followed by UV–vis spectrophotometry (Varian Cary 1-E) monitoring the absorbance at 618 nm. The initial pH of each solution was adjusted at 3.0 by adding HCl (Cl⁻ concentration in solution was approximately below 1 mM). The running temperature was never higher than 38 °C.

3. Results and discussion

3.1. Nanoparticle morphology, bulk and surface characterization

SEM images (Fig. 1a and b) reveal that these materials consist of spherical nanoparticles with an average diameter around 500 nm. However, when the image is magnified (insert, Fig. 1a and b), it is observed that the spherical particles are formed by the aggregation of smaller particles (see arrows). This effect is induced by urea presence. As has already been reported [28–30], urea decomposition in aqueous solution during sol–gel synthesis might produce a smooth pH increase, leading to the formation of TiO₂ nanoparticles with a controlled morphology, in this case, spherical.

In a previous work, it was found that the crystalline structure of TiO₂ nanoparticles containing TPA and annealed at 500 °C was mainly anatase. No XRD evidence of TPA, its decomposition products or WO₃ presence was found [31].

Moreover, DRS spectra (Fig. 2) showed that spherical titania nanoparticles containing TPA absorb visible light between 400 and

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