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Research article

Synthesis and photocatalytic activity of TiO_2 nanowires in the degradation of p-aminobenzoic acid: A comparative study with a commercial catalyst

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ABSTRACT

The photocatalytic degradation of p-aminobenzoic acid was studied using TiO_2 nanowires as the catalyst synthesized through a hydrothermal procedure. The as-synthesized TiO_2 nanowires were fully characterized by SEM, TEM, XRD and Raman with a very high surface area of 512 $m^2\ g^{-1}$. The photocatalytic degradation of p-aminobenzoic acid was carried out under 180 min of constant radiation and the results were compared with P25 as commercial catalyst. Optimal experimental conditions were determined for TiO_2 nanowires with a catalyst dosage of 1.0 g L^{-1} under acidic conditions with a 20 μM p-aminobenzoic acid solution obtaining 95% of degradation. Under similar experimental conditions comparative studies were performed obtaining 98% of degradation when P25 is employed. In both systems, a pseudo first order reaction was found to provide the best correlations, with constant rates of 2.0×10^{-2} min^{-1} and 2.4×10^{-2} min^{-1} for TiO_2 nanowires and P25, respectively.

1. Introduction

Water pollution has emerged as a primary concern in environmental issues due to the production and consumption of pharmaceuticals and personal care products (PPCP's). The PPCP's are chemical substances resilient to traditional remediation techniques and include among others, lotions, cosmetics and sunscreen products (Zhou et al., 2013). The sunscreen products or UV-filters are frequently used because of the concern of dangerous skill diseases caused by sun exposure like skin cancer (Ji et al., 2013a). Recent studies have identified these substances in the urine and blood from children and adults, and in indoor dust (Zhang et al., 2013; Wang et al., 2013). Also, Gago-Ferrero et al. (2013) studied the occurrence of octocrylene in marine mammals over a fifteen-years period. Their results showed this particular UV-filter was found in up to 70% of the individuals studied. Those results suggest that UV-filters residues are present in recreational waters then are absorbed through the skin and enter the bloodstream where prevail until the body secretes them.

P-aminobenzoic acid (PABA) is a UV-filter patented in 1943 but later, in the 80's, a study demonstrated that PABA caused a particular DNA damage in mammalian cells (Osgood et al., 1982). According to Wong and Orton (2011) PABA is included as one of the allergens most contained in sunscreen products. Due to the numerous recalcitrant compounds detected in recreational waters the advanced oxidation processes (AOP's) have been developed as promising decontamination methods able to generate radical species, being non-selective reactions with applications not only in liquid, but also in gaseous phase (De la Cruz et al., 2012; Ji et al., 2013a; Kontos et al., 2010). The photocatalytic process is a chemical reaction where a semiconductor acts as a catalyst when is activated with an incident radiation. This process promotes the migration of an electron from the valence band to the conduction band generating an electron–hole pair (An and Zhou, 2012). Photocatalytic reactions have demonstrated to degrade even persistent organic pollutants with high molecular weight such as dyes. Tang (2013) studied the photocatalytic degradation of methyl orange using synthesized ZnO nanostructured materials, reaching 99% of degradation modifying the catalyst shape. Other researches have employed TiO_2 to study the photocatalytic degradation of antibiotics, sunscreen products, polycyclic aromatic compounds and

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phenolic compounds (Zhu et al., 2013; Ji et al., 2013a; Zhang et al., 2011; Yang et al., 2010).

In this research we successfully studied the photocatalytic degradation of PABA with synthesized TiO_2 nanowires (TiO_2NWs). Additionally, and for comparative purposes, the same photodegradation study was performed with a commercial catalyst (P25) instead of TiO_2NWs.

2. Materials and methods

2.1. Reagents

All reagents used in the present study were used as received. Acetone, Isopropyl alcohol 99.9%, and HCl 37% ACS Reagent were provided by Acros Chemicals. Hydrogen Peroxide 50%, $TiCl_4$ 99.9% and NaOH $\geq$ 97% were obtained from Fisher Scientific. 4-Aminobenzoic acid $\geq$ 99% and HCl 1.0 M standard solution were provided by Sigma–Aldrich, and P25 from Degussa (nanopowder with 21 nm particle size and 35–65 $m^2\ g^{-1}$ surface area, $\geq$99.5%). All the experimental solutions were prepared using ultra pure water (Milli-Q water, 18.2 MΩ cm^{-1} at 25 °C). Si (100) substrates P-type boron doped, provided by El-CAT, were used for the hydrothermal growth of TiO_2NWs. For photocatalytic experiments 0.45 μm Whatman syringe filters and quartz cells were used. Additional physical and chemical data of PABA can be found in the Supplementary Information.

2.2. TiO_2NWs synthesis

The synthesis was performed according to Cotto et al. (2013). However, modifications were performed. In a typical synthesis, Si (100) substrates were rinsed sequentially with isopropyl alcohol, water, and acetone, then dried at 60 °C. A 1:1 (v:v) solution of HCl 35%:H_2O was prepared and magnetically stirred. After that, 3.5 mL of $TiCl_4$ were added dropwise and kept under vigorous stirring during 15 min. The solution was added to a Teflon liner contained on an autoclave with the Si substrates vertically placed in the bottom. The autoclave was exposed to 180 °C during 2 h and subsequently removed from the oven. After cooling to room temperature the autoclave was opened and the substrates with the TiO_2NWs grown on the surface were thoroughly rinsed with water, and then dried at 60 °C overnight. Then, TiO_2NWs were removed from the Si substrates and stored on seal cups until further use.

2.3. TiO_2NWs characterization

The TiO_2NWs were fully characterized by Scanning Electron Microscopy (SEM), using a JEOL JSM6010LV operating at 20 kV. *Brunauer–Emmett–Teller* (BET) specific area was measured using a Micromeritics ASAP2020, according to N_2 adsorption isotherms at 77 K. The transmission electron microscopy (TEM) analyses were performed on a JEOL JEM2000FX with an accelerating voltage of 200 kV. The TiO_2NWs were ultrasound in ethanol and subsequently homogenized, and 5 μL were placed onto a copper grid coated with a lacy carbon film. Raman measurements were acquired with a DXR Thermo Raman Microscope employing a 532 nm laser source under 5 mW power and a 25 μM pinhole aperture with a 5 cm^{-1} nominal resolution. X-ray diffraction (XRD) patterns were obtained in Theta/2Theta configuration in the range of 20–80° at 2° min^{-1} using a Bruker D8-Advance X-ray Diffractometer at 40 kV and 40 mA.

2.4. Photocatalytic experiments

The reactor used for the photocatalytic experiments was a home-made type, consisting of seven spiral light bulbs and three mirrors surrounding the system. In the center of the system was placed the sample to be photodegraded (see Fig. 1). The irradiation was measured about 53,000 lux.

The system was filled with a PABA solution to which different amounts of catalyst were added. The pH was adjusted with 0.5 M HCl or NaOH solutions, and the system was left in darkness for 30 min in order to reach the adsorption–desorption equilibrium (Cotto et al., 2013). Then the oxygen sources which consist of a 0.05% solution of H_2O_2 and air bubbling were added at the time that the radiation was turned on. The photoreactor was covered with a black blanket in order to avoid any other incident radiation.

The photocatalytic reaction was maintained under constant stirring and monitored during 180 min by withdrawing aliquots at different time intervals. These aliquots were filtered with 0.45 μm membrane filters and analyzed with a Shimadzu UV-2401PC spectrophotometer. As a comparative study, the same procedure was developed using P25 as commercial catalyst.

3. Results and discussion

3.1. TiO_2NWs synthesis and characterization

TiO_2NWs were successfully synthesized, showing lengths of several microns. As shown in Fig. 2A and B, the synthesized nanowires consisted of very branched and homogenous structures in shape and size. The highly branched structures may explain the unexpected high surface area obtained of 512 $m^2\ g^{-1}$.

At higher magnification in Fig. 2B is observed that each nanowire is composed of thinner nanowires of several nanometers. This is confirmed with the TEM analysis shown in Fig. 3 where a single nanowire exhibits a diameter of ca. 50 nm. The electron diffraction pattern (SAED) of the inset of Fig. 3 shows the highly crystalline nature of this material, and the absence of amorphous phase.

The XRD of the TiO_2NWs (see Fig. 4) shows a typical diffraction pattern of TiO_2 in rutile phase, showing reflections at 27.4°, 36.0°, 39.1°, 41.2°, 44.0°, 54.2° and 56.3° that have been associated to (110), (101), (200), (111), (210), (211) and (220) planes, respectively. According to previous literature (Lin et al., 2011) anatase phase was not present.

The Raman spectrum of TiO_2NWs (see Fig. 5) shows two main peaks at 444 cm^{-1} and 608 cm^{-1}, that have been unambiguously associated to TiO_2 in rutile phase corresponding to Ti–O bond while the 236 cm^{-1} broad band is associated to the O–O bond (Lan et al., 2012; Hardcastle, 2011; Salari et al., 2011). The characteristic peaks related to anatase phase at 634 cm^{-1}, 514 cm^{-1} and 394 cm^{-1} were not presented confirming rutile as the unique crystal phase.

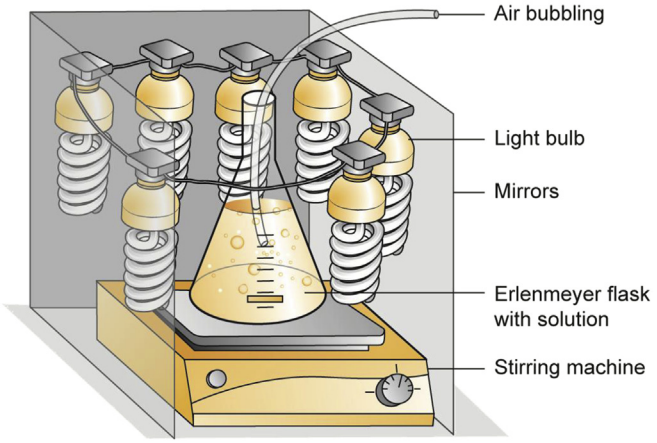

Fig. 1. Photoreactor used for the PABA degradation experiments.