



# Macroscopic TiO<sub>2</sub>–SiO<sub>2</sub> porous beads: Efficient photocatalysts with enhanced reusability for the degradation of pollutants



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## ABSTRACT

A series of TiO<sub>2</sub>–SiO<sub>2</sub> photocatalysts in the shape of macroscopic spherical beads (300–500 μm) with highly porous structure and different amount of TiO<sub>2</sub> as active phase was synthesized using a polymeric bead-shaped resin as template. The materials were characterized by a combination of techniques (SEM, TEM, XRD, N<sub>2</sub>-physisorption, UV–Vis and FTIR spectroscopy) to correlate their physicochemical properties with their photocatalytic activity in the degradation of phenol and methylene blue under UV irradiation. The innovative shape of these photocatalysts allows straightforward separation and recycling of the material without centrifugation or filtration steps, thus circumventing one of the major issues of TiO<sub>2</sub> in powder form. The optimum activity of the bead-shaped photocatalysts is determined by a balance between high specific surface area and TiO<sub>2</sub> content. The most active among the synthesized TiO<sub>2</sub>–SiO<sub>2</sub> porous bead materials showed higher photocatalytic turnover compared to P25 TiO<sub>2</sub>.

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## 1. Introduction

Photocatalysts are materials that enable the use of electromagnetic radiation as energy source for performing a chemical reaction. The growing interest for photocatalysis is related to the relevance of its applications, which range from the degradation of pollutants [1,2] and the water splitting reaction [3], to the reduction of CO<sub>2</sub> [4,5] and to selective oxidation reactions [6]. Photocatalytic systems are generally categorized into homogeneous and heterogeneous [7,8]: the former are typically based on metallic complexes [9,10], while the latter are based on semiconducting materials [11]. Among semiconductors, the use of metal oxides gained a lot of attention because of their favorable properties: high stability, negligible solubility in water, low toxicity and accessible synthesis methods. Since the discovery of its photocatalytic activity in 1972 [12], TiO<sub>2</sub> is the most studied metal oxide for photocatalytic applications [13]. Besides the above-mentioned advantages, TiO<sub>2</sub> shows a suitable band gap (3.0 eV for rutile and 3.2 eV for anatase [14,15]) and band position for promoting the water splitting reaction and the degradation of pollutants, though its applicability is limited to the use of UV radiation as excitation source. One of the main advantages in the use of heterogeneous photocatalysts is the possibility to recover and recycle the material [16]. However, the most widely used and highly active form of TiO<sub>2</sub>, *i.e.* Degussa P25 [17], consists of nanoparticles with an average size of 25 nm. The small size of these particles strongly hinders the separation and

recover of the photocatalyst for reactions carried out in liquid phase, such as the degradation of pollutants in wastewater. The preparation of TiO<sub>2</sub> particles with a magnetic core consisting of iron oxide or a ferrite has been proposed as an approach to improve the recovery of the photocatalyst through the simple application of a magnetic field [18–21]. However, the produced heterojunction between TiO<sub>2</sub> and the magnetic core led to an increased electron–hole recombination rate, thus lowering the photocatalytic activity of the material [22]. Another point of concern is the stability of the magnetic core during the photocatalytic tests. These issues can be mitigated by introducing a SiO<sub>2</sub> layer between the TiO<sub>2</sub> shell and the magnetic core, but this decreases the magnetic response of the material and increases the complexity of the synthesis [18]. In this work, we propose a novel and efficient approach to prepare TiO<sub>2</sub>-based photocatalysts with optimum features for separation and reuse. TiO<sub>2</sub>–SiO<sub>2</sub> composites in the shape of porous macroscopic beads (300–500 μm) were synthesized using a resin with a spherical bead shape (Amberlyte IRA-900) as template. The obtained composite materials were tested in the photocatalytic degradation of pollutants (phenol and methylene blue) under UV irradiation. The macroscopic TiO<sub>2</sub>–SiO<sub>2</sub> beads spontaneously and rapidly deposit upon stopping stirring of the reaction mixture, thus allowing an extremely efficient and straightforward recycling procedure compared to P25 TiO<sub>2</sub>. A second asset of the TiO<sub>2</sub>–SiO<sub>2</sub> beads originates from their porous structure and the dispersion of the active TiO<sub>2</sub> phase into the silica matrix. The porosity and the consequent high surface area of the photocatalyst will facilitate the interaction of the reagent with the TiO<sub>2</sub> domains, while the dispersion of the TiO<sub>2</sub> phase into a

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support (e.g. carbon, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>) has been reported to prevent the agglomeration phenomena suffered by unsupported TiO<sub>2</sub>, thus helping to preserve the photocatalytic activity of the material [23–27].

## 2. Experimental section

### 2.1. Synthesis of the TiO<sub>2</sub>–SiO<sub>2</sub> porous beads

**Reagents:** tetrapropylammonium hydroxide (TPAOH) 25% aqueous solution; distilled water; titanium tetrabutoxide (Ti(OBu)<sub>4</sub>); tetraethylorthosilicate (TEOS); Amberlyte IRA-900 resin (chloride form) in beads form. The synthesis method was inspired by a previously published procedure for the preparation of titanosilicate beads [28]. A series of seven photocatalysts with Ti:Si ratio ranging from 10% to 70% in molar composition was prepared. First, a 0.43 M aqueous solution of TPAOH was prepared by diluting 4.06 ml of TPAOH (25% in water) with 7.5 ml of distilled water. The solution was stirred for 5 min to homogenize the system and then Ti(OBu)<sub>4</sub> and TEOS were added in the amount necessary to obtain the desired Ti:Si molar ratio. The solution was stirred vigorously for 5 min and then transferred into a stainless steel autoclave with a Teflon insert. The autoclave was heated at 140 °C for 4 h in static condition and then cooled down naturally to room temperature. The turbid solution was transferred into a plastic bottle, into which Amberlyte IRA-900 resin beads (chloride form) were added with a solution to resin weight ratio of 15:1. The mixture was placed on an orbital shaker at room temperature for 24 h to achieve the adsorption of the solution on the resin and then it was transferred into a stainless steel autoclave with a Teflon insert and heated statically at 60 °C for 24 h. The autoclave was then allowed to cool down naturally to room temperature. Yellowish beads were obtained. The beads were recovered and washed with distilled water (20 ml, 5 times) and then dried overnight at 80 °C. Finally, the material was calcined in air at 550 °C for 8 h with a heating rate of 1 °C/min, yielding white macroscopic TiO<sub>2</sub>–SiO<sub>2</sub> porous beads.

The photocatalysts were denoted as X%TiO<sub>2</sub>–PB, where X represents the molar percentage of titanium dioxide in the material.

### 2.2. Characterization

The materials were characterized with a combination of techniques. Powder X-ray diffractograms (XRD) were measured on a high-throughput STOE Stadi P instrument with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The materials were ground before recording the diffractograms. Solid-state UV–Vis spectra of the materials in bead shape were measured in air on a Varian Cary 5000 UV–Vis spectrometer equipped with diffusive reflectance accessory. The band gap of the TiO<sub>2</sub>–SiO<sub>2</sub> beads was evaluated from the absorption spectra with the use of the Tauc plot for an indirect transition [29,30]. This method consists in plotting the function  $[F(R)h\nu]^{1/2}$  vs.  $h\nu$ , where  $F(R) = (1 - R)^2/2R$  is the Kubelka–Munk function calculated from the Reflectance (defined as  $R = [1 - \text{Absorbance}]$ ) and  $h\nu$  is the photon energy expressed in eV. The band gap value is evaluated by extrapolation of the linear part of the function: the intercept with the  $x$ -axis corresponds to the band gap energy. Inductive coupled plasma optical emission spectroscopy (ICP–OES) was performed on an Ultima Jobin Yvon Emission instrument. Nitrogen physisorption analyses were performed on a Micromeritics Tristar 3000 apparatus. Scanning electron microscopy (SEM) pictures were recorded on a JEOL JSM 6010LV equipment. Transmission electron microscopy (TEM) pictures were taken with a JEOL JEM 2010 instrument (at the University of Alicante, Spain). For the TEM analysis, the beads were first impregnated with Epofix

resin and then cut in 100 nm thick sections with an Ultramicrotome RMC MT-XL; the sections were then deposited on copper grids (300 mesh). To perform the Fourier transform infrared spectroscopy (FTIR) analysis, the samples were ground and mixed with anhydrous KBr (the loading of the sample in the pellet was 3 wt.%). The FTIR analysis was performed on a Nicolet 6700 spectrometer.

### 2.3. Photocatalytic tests

The photocatalytic activity of the materials was tested by mean of the degradation reactions of two model compounds: methylene blue and phenol (Fig. 1). In a typical test, 15 mg of photocatalyst (corresponding to 60–70 TiO<sub>2</sub>–SiO<sub>2</sub> beads) was weighed in a Pyrex test tube with 5 ml of an aqueous solution of phenol or methylene blue (200 ppm, i.e. 20 mg/100 ml). First, the samples were stirred for 1 h in the dark to achieve equilibrium between adsorption and desorption. After that, the tubes were irradiated with UV radiation for 3 h. In the case of the kinetic experiments, the above procedure was followed and a separate test was performed for determining the conversion at each irradiation time. Selected tests for the degradation of phenol were conducted in an air-saturated solution. In these tests, air was bubbled in the solution during the whole photocatalytic experiment. The tests were conducted in a high-throughput photoreactor: a rotating carousel in the reactor allowed the simultaneous testing of up to 16 samples. The temperature in the reactor was set to 35 °C and controlled with a thermostat. The photoreactor was equipped with 12 Hitachi FL8BL-B lamps with  $\lambda$  maximum emission centered at 350 nm [31]. The aqueous solution was analyzed after 1 h in the dark to evaluate the adsorption capacity of the materials and after irradiation for further 3 h to evaluate the photocatalytic activity. The degradation of phenol was evaluated by gas chromatography with external standard method. The analyses were conducted with a Trace GC Ultra equipped with a Por. Q column (10 m, 0.25 mm, Interscience) and an Ultra Fast Module (UFM) for rapid heating and cooling of the column, which enables a short analysis time (5 min) for each sample. The external standard used was *n*-butanol, which was added to the aqueous solution at the end of the test, after separation of the photocatalyst. The degradation of methylene blue was evaluated by UV–Vis spectroscopy with a Perkin Elmer Lambda 12 UV–Vis spectrophotometer. Before the analysis, the sample was diluted 20 times to reach a methylene blue concentration in a range where the Lambert–Beer law is valid. The absorption spectrum was recorded in the range 400–800 nm and the absorption maximum at 665 nm was used to evaluate the residual concentration of methylene blue. P25 TiO<sub>2</sub> (Degussa) was used as reference in the evaluation of the photocatalytic activity of the materials. The recycling tests were conducted on our materials and on P25 TiO<sub>2</sub>. First, the bead-shaped materials were allowed to settle down naturally in the reactor tube (which takes less than 5 s), and then were washed with distilled water (2 times, 5 ml) and ethanol (2 times, 5 ml). To separate P25 TiO<sub>2</sub> from the reaction system, a centrifugation step (4000 rpm, 10 min) was necessary. The TiO<sub>2</sub> powder was washed in the same way as the bead-shaped materials and a cycle of centrifugation (4000 rpm,

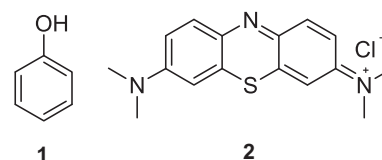


Fig. 1. Molecular structures of the probe compounds: phenol (1) and methylene blue (2).

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