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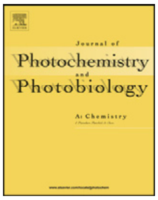

Radially organized pillars in TiO_2 and in TiO_2/C microspheres: Synthesis, characterization and photocatalytic tests

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ABSTRACT

Porous TiO_2 microspheres with robust texture and high photoactivity were prepared by inflowing a TiO_2 precursor in the confined space of polystyrene-co-divinyl benzene (PS-co-DVB) polymer, working as sacrificial scaffold. The impregnated polymer spheres, upon thermal treatments under N_2, N_2/air or pure air flow at temperatures in the 400–500 °C interval, are transformed into porous microspheres. Depending on the gas flow composition, the obtained microspheres are constituted by porous carbon, hybrid core–shell C/TiO_2 or of cemented TiO_2 nanoparticles assembled in elongated pillars. The composition of pure TiO_2 microspheres ranges from pure anatase (400 °C) to the prevailing rutile phase (>475–500 °C). All samples have been extensively characterized by means of SEM/AFM microscopes, N_2-volumetric porosimetry, XRD and UV–vis analyses. The photodegradation of NO has been used to check the photocatalytic activity of the TiO_2 materials. It is concluded that they exhibit higher photoactivity than the classical benchmark material (Degussa P25). This property together with porous character of the microspheres, the tunable anatase–rutile ratio and the high crystallinity makes these microspheres very interesting materials for applications in photocatalysis. From a physical point of view, the large axial pores and the columnar nature of the spheres can produce the entrapment of the light into the material.

1. Introduction

TiO_2 based materials with tailored shape, porosity, crystal sizes and composition are attracting great attention because of their use in application fields, such as photocatalysis and energy conversion [1–6]. As far as photocatalysis is concerned, many factors are known to play a key role, such as crystallinity, phase composition and surface area [1–3,7–11]. In particular it has been reported that mixed anatase/rutile TiO_2 materials may exhibit higher photocatalytic efficiency because their light harvesting efficiency may be favored by the presence of the rutile phase, characterized by a lower energy-gap and a more pronounced absorption in the visible. Moreover, anatase/rutile junctions might promote the charge separation in the surface region and the reduction of the combination of photogenerated electrons and holes [11–15]. This can be the explanation of the high activity of Degussa P25, a mixture of 85–80 wt% anatase and 15–20 wt% rutile nanoparticles, widely recognized as a benchmark material. As photocatalysis is involving the formation and the adsorption/desorption of reactants and products, surface area, nanocrystals morphology, the structure, and the exposed habit (in particular the dominant presence of anatase {0 0 1} facets) [3,10,16–19] are also playing a primary role [7,12]. Besides the presence of rutile, peculiar defects of TiO_2 materials acting as trap sites for photoexcited charge carriers [20], particle structuring at different length scales and spatial organization of the TiO_2 nanoparticles [21], doping with light and heavy elements (B, C, N, S, F, Br, and Cl) or metals, can increase the visible light absorption and the photon efficiency [3,22–28].

The presence of single nanoparticles characterized by high photocatalytic activity is not, however, the sole requisite for practical applications. In fact in industrial applications, the separation of TiO_2 material from the solution after irradiation is necessary and constitutes an important requirement for an efficient use of the material [29] as well as the presence of a hierarchical porosity, which provides, on one hand a fast accessibility and a facile fluid transport of matter (larger pores), and on the other hand the increased surface contact (smaller pores) [15]. As this efficient separation is not obtainable when the material is highly dispersed, TiO_2 samples containing robust microaggregates of cemented nanoparticles, characterized by intrinsic mesoporosity and high surface area, may facilitate the separation of the photocatalyst from the reaction medium [7]. Although the formation of nanoparticles agglomerates is accompanied by some surface area decrements, the resulting activity is not necessarily decreased because the interparticle charge transfer can advantageously act as compensating factor [7].

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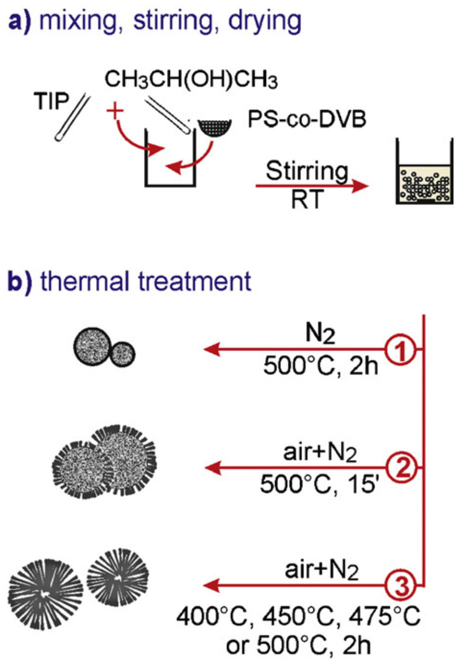

Scheme 1. Preparation steps of microspheres: (a) impregnation/stirring and drying of the PS-co-DVB polymer spheres in an alcohol solution of TIP; (b1) under pure N_2 at 500 °C; (b2) under air/N_2 mixtures at 500 °C for 15′; (b3) under air/N_2 mixtures at: 400 °C; 450 °C; 475 °C and 500 °C for 2 h, respectively.

Several approaches to control the size, shape and agglomeration state of TiO_2 nanoparticles have been attempted [4]. Nanotubes [30], nanorods [31,32], monolithic porous structures [15,33,34], inverse opals [35] and microspheres [19,36–41] have been studied.

Among all investigated approaches, the template-based procedures look ideal to control the TiO_2 structure because the pore size distribution of the templating scaffold, where the desired material is formed, can be properly tailored [21,29,42]. In this paper, we describe a new method for the synthesis of spherical TiO_2-based porous aggregates, starting from porous polymer microspheres impregnated with a Ti molecular precursor. Depending on the synthesis conditions, from inert to oxidizing atmosphere, the resulting products can range from amorphous composite systems, to pure TiO_2 microspheres with selected anatase/rutile compositions.

The TiO_2 microspheres appear to be very robust because they are constituted by highly crystalline cemented nanoparticles and have surface area comparable with that of P25. The catalyst texture and structure were determined by XRD, SEM, AFM, N_2-adsorption isotherms and UV–vis spectroscopy. NO photodegradation tests demonstrate that TiO_2 microspheres are highly active and that their activity is influenced by the crystallinity, morphology, and by the anatase–rutile ratio.

This work provides new insights on the morphology, structure, phase composition and crystallinity with regard to the photocatalytic activity of TiO_2. This matter is of a broad and significant interest in photocatalysis and in the energy conversion fields.

2. Material and methods

2.1. Sample preparation

Poly[styrene-co-(divinyl benzene)] (PS-co-DVB) polymer microspheres as scaffold and Ti isopropoxide (TIP) from Aldrich as titania precursor, were used.

The preparation of materials is shown in Scheme 1. The polymer microspheres were first impregnated under stirring for 24 h in a solution 1:1 v/v of TIP in isopropyl alcohol. The solution was then filtered and dried (Scheme 1, step a).

The dried polymer was then treated under gas flow following different paths: (1) N_2 gas flow at 500 °C for 2 h (scaffold pyrolysis) (Scheme 1: step b, path 1); (2) N_2-air flow for 15′ at 500 °C (Scheme 1: step b, path 2) (partial combustion of the polymer scaffold); and (3) N_2-air flow for 2 h at temperatures comprised in the 400–500 °C range (complete combustion of the scaffold) (Scheme 1: step b, path 3). Time and temperature parameters of oxidation path 3 were selected step by step in order to obtain materials with specific phase compositions, ranging from anatase to rutile.

2.2. Characterization techniques

The morphology of samples has been investigated by means of scanning electron microscopy (1: Zeiss Evo50 SEM) equipped with an Oxford energy dispersive X-ray detector, and Field Emission SEM (2: ZEISS SUPRA 40 FESEM) equipped with a field emission tungsten cathode, and atomic force microscopy (3: Park Systems XE-100 AFM). The crystallinity and the phase composition of samples have been estimated by XRD analysis (PANalytical X'Pert PRO diffractometer equipped with a Ni filtered Cu radiation in a standard Bragg–Brentano geometry). Diffuse reflectance UV–vis spectra have been recorded directly on the materials at room temperature by means of a UV–vis spectrometer (Varian Cary UV 5000) equipped with a diffuse reflectance attachment. Materials used for the UV–vis analysis (nanoanatase, anatase and rutile from Aldrich) were diluted in $BaSO_4$ to obtain a correct intensity.

N_2 adsorption–desorption experiments have been carried out at 77 K (Micromeritics ASAP 2020 instrument) to determine the Brunauer–Emmett–Teller (BET) surface area and micropore volume (*t*-plot method). Before the surface area determination, the samples were degassed at 150 °C for 5–6 h. The pore size distributions (PSDs) were obtained by means of a non-negative least squares fitting on the absorption isotherm data by applying Density Functional Theory (DFT) method (N_2-DFT model, slit geometry) of ASAP 2020 4.0 software (Micromeritics). Microporous (S_{micro}) and mesoporous (S_{meso}) surfaces were obtained from *t*-plot and from $S_{meso} = S_{tot} - S_{micro}$, respectively.

2.3. Photocatalytic tests

In a typical photocatalytic test, the sample (~0.05 g) is placed in a glass flow reactor exposed to a continuous gas flow of He (60 ml/min) containing 4.5 ppm of NO. The reaction is kept in the dark for 1 h, in order to reach the adsorption equilibrium.

Then, the reactor chamber is irradiated by a solar-like light for 1 h. The test continues for at least four alternating light cycles on/off (see Supplementary material).

3. Results and discussion

The commercial microporous PS-co-DVB polymer (surface area $\approx 1000\ m^2/g$) is SEM and AFM imaged in Fig. 1a–b. The sample is constituted by apparently rounded polymer microspheres with diameters comprised in the 400–600 μm range (Fig. 1a and inset therein).

Rare cracks and surface defects are identified at higher magnification by image contrast (arrows in Fig. 1a). The microspheres are constituted by nanodomains 20–80 nm in size, as obtained by AFM height profile (inset of Fig. 1b). The pore size distribution, as obtained by DFT (density functional theory) model applied on the adsorption isotherm of N_2 at 77 K, shows that the pore diameter is ranging in the 8–20 nm interval (Fig. 1c). These domains are large enough to allow the easy accessibility to incoming molecules.