Applied Catalysis B: Environmental 127 (2012) 175–181

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Mesoporous Fe-doped TiO_2 sub-microspheres with enhanced photocatalytic activity under visible light illumination

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ARTICLE INFO

Article history:
Received 9 April 2012
Received in revised form 31 July 2012
Accepted 14 August 2012
Available online 23 August 2012

Keywords:
Mesoporous
Titania
Photoactivity
Visible light

ABSTRACT

Mesoporous Fe-doped TiO_2 sub-microspheres (m-Fe-TMS) with high surface area, accessibility, and crystallinity were prepared using a rapid and continuous aerosol-assisted self-assembly (AASA) process for visible-light photocatalytic degradation of persistent pharmaceuticals. The results of X-ray absorption near-edge structure (XANEX) spectroscopy indicate that iron exists as octahedrally coordinated Fe^{3+} ions substituting Ti^{4+} in the TiO_2 lattice. The similarity of the Fe/Ti ratios in the bulk and on the surface, as determined by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), reveals that the substitution of Ti^{4+} by Fe^{3+} ions uniformly occurs within m-Fe-TMS. UV–vis diffuse reflectance spectroscopy shows that m-Fe-TMS exhibits a shift in the absorption threshold toward the visible spectrum. Under visible light irradiation, m-Fe-TMS exhibits a maximum rate of pharmaceutical photodegradation four times that of m-TMS. The photocatalytic degradation rates are reproducible with m-Fe-TMS, even after 10 repeated runs. The formation of chemical Fe—O—Ti bonds, and not of isolated Fe_2O_3 particles, leads to the inhibition of photocorrosion and leaching in the photocatalytic reactions. The ease and scalable production of m-Fe-TMS using the AASA process will facilitate the development of visible light-driven photocatalysts for decomposition of environmental contaminants.

1. Introduction

Considerable attention has been given to mesostructured metal oxides because of their potential use in energy- and environment-related fields [1–4]. Their effectiveness in practical applications varies with their mesoporosity, chemical composition, crystallinity, specific surface area, and most importantly, the morphology and texture of the material [5–7]. In this family of materials, mesoporous titania is of particular interest because it has a photoactive semiconductive framework with mesoporous channels that offer increased surface area and enhanced accessibility. However, limited by titania's low quantum efficiency and high band gap (3.0–3.2 eV) in the ultraviolet (UV) wavelength range, the use of mesoporous titania as highly active photocatalyst remains challenging to date.

Researchers have reported several approaches to resolve this intrinsic limitation, which include doping titania with either anions or metallic species or photosensitizing with organic dyes that are often efficient but unstable [8–12]. Doping with metallic species has been viewed as an effective way to lower the band gap of TiO_2 and to restrict the electron–hole recombination, thus enhancing the quantum efficiency [2,13–15]. A more intimate and conformal metallic dopant/TiO_2 junction is desired. That provides homogeneously doping within the titania framework while minimizing deposition at the channel entrances, thus allowing easy access of outer light and free diffusion of reactant molecules into the nanochannels.

The aerosol-assisted self-assembly (AASA) process obtains mesoporous sub-microspheres with high surface area and crystallinity through a continuous and large-scale production route. The first report on AASA was published in 1999 by Lu et al. [16], in which they prepared silica-based mesostructured spherical nanoparticles. Subsequently, non-silicate single-component materials, such as TiO_2, ZrO_2, and Al_2O_3 spheres, have become overwhelmingly dominant; they are produced using modified AASA [17–19]. However, the dissimilar hydrolysis and condensation behaviors of metal alkoxides make building mixed-metal oxide frameworks with AASA difficult. Stucky and co-workers [20] induced the growth of

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http://dx.doi.org/10.1016/j.apcatb.2012.08.011

metal oxoacetate ligands in the starting solution with the esterification of acetic acid to inhibit condensation of certain metal ions. A few multi-component spheres, such as $CuO—TiO_2$, Al—Si—O, and $BaTiO_2$, have been successfully fabricated.

In this work, we utilized AASA to substitutionally dope iron within the titania framework, wherein the surfactant, titania, and the iron building clusters were cooperatively assembled in a one-step process. The optical and electronic structural properties of the prepared samples were characterized by UV–vis diffuse reflectance spectroscopy (UV-Vis DRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption near-edge structure (XANES) spectroscopy. Their morphological structure was also examined by field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDX), and N_2 sorption isotherms at 77 K. Paracetamol, a widely occurring human-derived pharmaceutical in the environment [21], was chosen as the target organic compound for the photocatalytic oxidation reactions. The photocatalytic activity of the mesoporous titania sub-microspheres with different iron contents was determined under visible-light illumination. Repeated experiments on the photocatalytic degradation of paracetamol in an acidic solution were also carried out to evaluate the durability of the prepared photocatalytic samples.

2. Experimental methods

2.1. Preparation of photocatalysts

The mesoporous TiO_2 (m-TMS) and mesoporous Fe-doped TiO_2 (m-Fe-TMS) sub-microspheres were prepared by AASA. A precursor solution of ethanol contained 1 $Ti(OBu)_4$:4 acetic acid:1.2 HCl:20 EtOH:0.01 F127 in molar ratio and iron ions were added with in concentrations ranging from 0% to 5.0%, relative to the Ti weight. The temperature of the furnace was kept at 400 °C during the spray process. The dry powder was collected using a 0.45 μm filter. These as-synthesized mesostructured hybrid spheres were then calcinated at 350 °C (ramp rate 1 °C/min) in air for 5 h.

2.2. Characterization of photocatalysts

The prepared m-TMS and m-Fe-TMS were characterized by UV-Vis DRS, XRD using Cu-Kα ($\lambda = 1.54$ Å) radiation, FE-SEM (JEOL JSM-7000F), and HR-TEM (JEOL JEM-2100). The XPS measurements were performed using a Vacuum Generators ECSALAB MKII photoelectron spectrometer (VG Co., East Grinstead, UK) with an ALKαX-ray source (1486.6 eV) and a hemispherical 150 mm mean radius electron analyzer having a takeoff angle of 90°. The binding energies of the photoelectrons were determined by assuming that the energies of the carbon 1s electrons were 284.5 eV. During data acquisition, the pressure in the sample chamber did not exceed 5×10^{-10} Torr. The Brunauer–Emmett–Teller (BET) surface areas of the prepared samples were obtained from N_2 sorption isotherms at liquid N_2 temperature using the Micrometrics ASAP 2010 analyzer. XANES spectroscopy measurements were used to identify the electronic structure on the Fermi level (unoccupied state) of prepared samples. XANES spectroscopy measurements were performed at the National Synchrotron Radiation Research Center in Taiwan. The transition metal L-edge and the oxygen K-edge were recorded at the high-energy spherical grating monochromator BL20A1 beamline using the total electron yield mode, with a base pressure of 5×10^{-9} Torr and a resolving power of about $E/\Delta E = 8000$. Standard TiO_2 and Fe_2O_3 were used for energy calibration and for comparing the different electronic valence states and crystal symmetries.

2.3. Photocatalytic degradation of paracetamol

Paracetamol was used as a target compound to test the photocatalytic activity of the prepared photocatalysts. The photocatalytic degradation of paracetamol was evaluated using a Rayonet RPR-100 Photoreactor equipped with sixteen visible-light lamps. The spectral response was with a maximum at 420 nm, a FWHM of about 15 nm and <5% of the intensity in the UV region. The mixture containing the photocatalysts in an aqueous solution of 50 mg/L paracetamol (25 mL) was magnetically stirred for 30 min in the dark before switching on the light. The concentration of the photocatalysts was 4.0 g/L.

2.4. Sample analysis

One milliliter of the aqueous solution was filtered using a Millipore filter (25 mm diameter, 0.2 μm pore size) and analyzed immediately. The paracetamol concentrations were measured using HPLC (Agilent; column, ZORBAX Eclipse XDB-C18, 4.6 mm × 150 mm, 5 μm) with a flow rate of 1.0 mL/min and UV absorbance detection at 245 nm. The mobile phase was 25% methanol and 75% miniQ water. The injection volume was 10 μL. Each experiment was performed in triplicate, and all results were expressed as a mean value of the three experiments.

3. Results and discussion

3.1. Surface morphologies

Fig. 1a shows a typical SEM image of the m-0.5Fe-TMS prepared using the AASA process. The average size of the spheres is ~1 μm, and they are free of surface cracks and intersphere adherence. The as-prepared spheres have very smooth surfaces without obvious granular features (Fig. 1a). After calcinated at 350 °C for 5 h in air, spheres with comparatively rough surfaces were produced (Fig. 1b). As illustrated by the high-magnification SEM image (Fig. 1b), pores could be observed over the surface of the TiO_2 sphere. The uniform pore size distribution and close packing configuration of the TiO_2 spheres are clearly shown in the HR-TEM images (Fig. 1c). The high crystallinity is confirmed by the clear lattices, as shown in the inset of Fig. 1c. The EDX spectrum of the m-0.5Fe-TMS is shown in Fig. 1d, which was carried out under HR-TEM. The characteristic peaks in the spectrum are associated with Ti, O, and Fe. Quantitative analysis reveals that the weight ratio of Fe and Ti is close to 0.5, which is equal to what was distributed in the precursor solution. The nitrogen adsorption measurements demonstrate that all the materials exhibit the type IV isotherm behavior, with high BET surface areas ranging from 116 $m^2\,g^{-1}$ to 144 $m^2\,g^{-1}$ (Table 1; see also

Table 1
The BET surface area, pore size and pore volume of the prepared photocatalysts; and their observed pseudo-first-order reaction rate constants.

Photocatalyst	BET surface area ($m^2\,g^{-1}$)	Pore size (nm)	Pore volume ($cm^3\,g^{-1}$)	k_{obs} ($10^{-3}\,min^{-1}$)	r^2
m-TMS	144	7.3	0.25	6.7 ± 0.2	0.998
m-0.1Fe-TMS	120	5.7	0.17	9.2 ± 0.3	0.998
m-0.5Fe-TMS	116	6.2	0.18	25.5 ± 0.5	0.977
m-1.0Fe-TMS	117	5.7	0.16	9.6 ± 0.3	0.998
m-5.0Fe-TMS	117	5.9	0.17	3.8 ± 0.1	0.937