Aggregating TiO_2 (B) Nanowires to Porous Basketry-like Microspheres and Their Photocatalytic Properties

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Porous basketry-like TiO_2 (B) microspheres consisting of nanowires were fabricated via hydrothermal and spray-drying process. The calcined microspheres exhibited effective photocatalytic performance on photodegradation of organic pollutant. In addition, it was very easy to recycle the TiO_2 (B) nanowire microspheres for reuse.

As a result of its unique physicochemical properties, e.g., high quantum efficiency, nontoxicity, low cost, chemical stability, etc., TiO_2 has demonstrated to be one of the most widely known photocatalysts for advanced environmental applications in water and air purification. Recently, various morphologies of one-dimensional (1D) nanosized TiO_2, e.g., wires, fibers, and tubes, have been widely prepared by various physical and chemical methods.[1–5] These 1D nanosized TiO_2 materials exhibit superior properties relative to conventional bulk materials as a result of large surface area and nanosize effect. Although these 1D nanosized TiO_2 materials are easier to reclaim than TiO_2 nanoparticles, from the engineering application point of view, the separation and recovery are still a major obstacle for these materials.

Spray-drying is a continuous and low-cost process that can readily be scaled up and has extensively used in industry. Recently, Sanchez et al. and Okuyama's group have prepared porous submicron-sized TiO_2 spheres by spray-drying a Ti-sol containing templates.[6,7] However, the crystal phase of the calcined porous TiO_2 was either semicrystalline or amorphous.[8]

In this communication, for the first time, we report the fabrication of completely new 3D porous basketry-like TiO_2 (B) nanowire microspheres via a hydrothermal reaction and spray-drying process prior to calcination without degradation of surface area and photocatalytic activity.

In a typical fabrication process, a mixed suspension of 1 g of Degussa P25 and 10 M NaOH were hydrothermally reacted at 180 °C for 48 h. After sufficient proton exchange with diluted HCl (0.1 M) under ultrasound assistance, the solution was neutralized by deionized water washing the as-prepared white powders were collected and added into 0.2 wt % aqueous polyethylene glycol (PEG, MW 5000) solutions to get 8 g/L TiO_2 spray-drying suspension. A spray dryer (EYELA SD-1000) was run at normal mode to produce the TiO_2 microspheres (Supporting Information). The microspheres were then calcined at 500 °C for 2 h to obtain the final products.

The field emission scanning electron microscope (FESEM) images of the as-prepared and calcined TiO_2 nanowire microspheres are shown in Figure 1, indicating that the TiO_2 nanowire microspheres can be readily produced in copious amount by this method. The resulting TiO_2 microspheres are of 3–8 µm in the diameter. The TiO_2 nanowire microspheres are assembled by aggregating the nanowires, creating a unique porous morphology. From TEM image (Figure S1),[11] these microspheres were made of high length to diameter aspect ratio TiO_2 nanowires which are 20–100 nm in diameter and up to several micrometers in length. The porous morphology resulted from the aggregation of flexible TiO_2 nanowires during spray drying. The feed suspension of TiO_2 nanowires is pumped into the nozzle of the spray dryer and forced out of the orifice as droplets of nanowires. As soon as the droplets come into contact with the drying air, evaporation takes place and a saturated vapor film is rapidly established on the droplet surface. Due to evaporation of water, the size of the droplet decreases significantly. PEG prevents the collapse of the droplets during evaporation by increasing the surface tension. The resulting TiO_2 nanowires aggregate tightly to form a microsphere. Subsequent calcination removed PEG from the microsphere. In addition the TiO_2 crystallization results in less elasticity of nanowires and hence retains the spherical shape.

The crystal phases of the as-prepared and calcined microspheres were confirmed by wide-angle XRD as shown in Figure 2. The diffraction pattern of the as-prepared nanowires is similar to that expected for protonated titanate ($H_2Ti_2O_5$) with lepidocrocite-related layered structure (JCPDS 47-0124). No additional peaks of other impurities including starting P25 TiO_2 and NaCl were detected. Upon calcination at 500 °C, the peak positions of sample match well with the diffraction of the monoclinic TiO_2 (B) (JCPDS 35-0088), indicating the protonated titanates were fully dehydrated and converted into TiO_2 (B) at elevated temperature. Our experiments demonstrate that the TiO_2 (B) originates after annealing titanate at 300 °C, and then

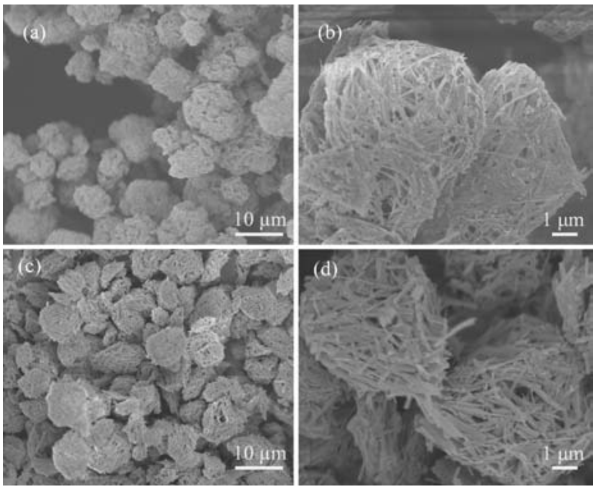

Figure 1. FESEM images of (a), (b) as-prepared and (c), (d) calcined porous basketry-like TiO_2 microspheres at different magnifications.

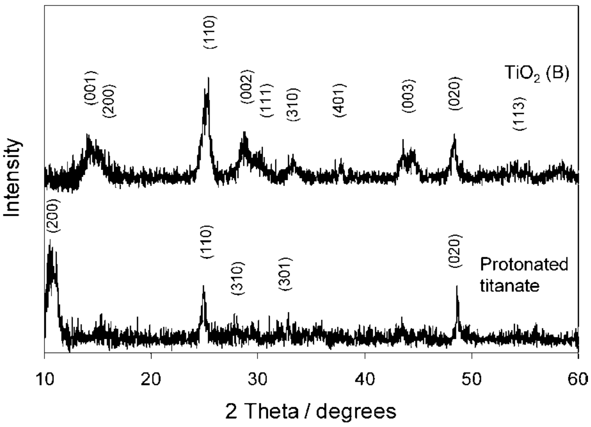

Figure 2. XRD patterns of as-prepared protonated titanate nanowires and the TiO_2 (B) microsphere calcined at 500 °C.

the phase transformation from TiO_2 (B) to anatase takes place at 550 °C. The Brunaur–Emmett–Teller (BET) surface area of the calcined TiO_2 (B) nanowire microsphere is $37.8\,m^2\,g^{-1}$, compared with $39.1\,m^2\,g^{-1}$ of the TiO_2 (B) nanowire powders prepared under other identical conditions without spay-drying. It indicates that the aggregating TiO_2 nanowires to microspheres using this method did not resulted in reduction of surface area.

To evaluate the photocatalytic activity of the TiO_2 (B) nanowires microspheres, they were used to photodegrade Methylene Blue (MB) in aqueous solution. An 11 W Upland 3SC9 Pen-ray lamp (254 nm) was immersed into solution to provide UV irradiation. The aqueous system containing MB (20 mg/L, 500 mL) and 0.25 g of TiO_2 (B) nanowire microspheres was magnetically stirred in the dark for 30 min to reach the adsorption equilibrium of MB with the photocatalyst before UV irradiation. Both commercial TiO_2 nanoparticles (Degussa P25) and TiO_2 (B) nanowire powder obtained by calcining protonated titanate at 500 °C directly without spray-drying process were adopted as the reference for comparison. The characteristic absorption at $\lambda = 670\,nm$ was chosen to monitor the concentration of MB during the photodegration processes.

The changes of MB concentration during photocatalytic degradation are shown in Figure 3. The photocatalytic degradation of MB in TiO_2 (B) nanowire microspheres, P25 and TiO_2 (B) nanowire powder suspensions were well described by pseudo-first-order model. The apparent rate constant (k) for the TiO_2 (B) nanowire microspheres ($0.0429\,min^{-1}$) was close to that of P25 ($0.0556\,min^{-1}$), indicating that the TiO_2 (B) nanowire microspheres has comparable photocatalytic activity with P25. The k for TiO_2 (B) nanowire powder was $0.0453\,min^{-1}$, similar to that of TiO_2 (B) nanowire microspheres, which indicates that the aggregating TiO_2 nanowires to microspheres prepared by using our spray-calcination method has little influence on their photocatalytic activity. Furthermore, the TiO_2 (B) nanowire microspheres were easily recovered by their gravity or filtration for reuse. After six cycles of photodegradations of MB, the catalyst did not exhibit any significant loss of photocatalytic activity and collapse of spherical structure, which indicates their excellent physical and chemical stability. Wang and Grimes et al.[9,10] proved that macroporous channels could serve as light-transfer paths for the distribution of photon energy, which means that this porous structure of these TiO_2 nanowire microspheres would allow UV light to cross their wall, so that the interior of these microspheres could be effectively utilized. This may explain the efficient photodegradation of MB by the TiO_2 (B) nanowire microspheres.

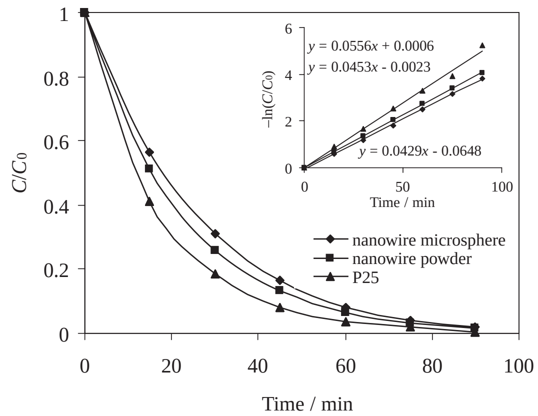

Figure 3. Photodegradation of Methylene Blue by TiO_2 (B) nanowire microspheres, TiO_2 (B) nanowire powder and P25. All solutions were stirred for 30 min in the dark prior to UV irradiation.

In conclusion, porous basketry-like TiO_2 (B) nanowire microspheres consisting of nanowires were fabricated via hydrothermal and spray-drying process. The calcined microspheres exhibited effective photocatalytic performance on photodegradation of organic pollutant and excellent stability on photocatalytic activity and structure. In addition, the TiO_2 (B) nanowire microspheres were easily recovered by their gravity or filtration for reuse.

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11 Supporting Information is available electronically on the CSJ Journal Website, http://www.csj.jp/journals/chem-lett/.

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