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# Fabrication and photocatalytic activity of porous $TiO_2$ nanowire microspheres by surfactant-mediated spray drying process

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ABSTRACT

A novel, porous $TiO_2$ nanowire microsphere with a diameter of 3–8 μm was successfully fabricated via spray drying of $TiO_2$ nanowire suspension with the assistance of surfactant (F127). The products were characterized by FESEM, XRD and $N_2$ adsorption–desorption analysis and results revealed that the resulting $TiO_2$ nanowire microspheres possessed a hierarchically macro/mesoporous structure, as well as a high BET surface area of 38.2 $m^2/g$. Systematic studies showed that the presence of surfactant in the suspension feed for spray drying was critical in the formation of porous microspheres. The structure of the fabricated microspheres depends on the nanowire concentration in the feed. The $TiO_2$ nanowire microspheres exhibited significant photocatalytic degradation of Methylene blue (MB) as compared to commercial $TiO_2$ nanoparticles (P25). It was also revealed that the microspheres have excellent stability on photocatalytic activity and mechanical strength, which are both crucial factors when considering reuse of these photocatalysts.



## 1. Introduction

Due to its unique physicochemical properties, $TiO_2$ has received considerable attention in areas of environmental purification, solar cell and gas sensor, etc. [1,2]. Recently, one-dimensional (1D) nanostructured $TiO_2$ has gained greater popularity due to its superior performances relative to conventional bulk materials, as a result of its large surface area and nanosize effect. Recently 1D $TiO_2$ with various morphologies (wires, fibers and tubes) have been fabricated [3–5]. However, the practical environmental applications of these 1D $TiO_2$ materials is a huge problem. They are too small to be separated and reclaimed by conventional separation methods. From an engineering point of view, besides superior photocatalytic activity, proper photocatalysts should be easily reclaimed for repeated usages. Otherwise, it would be deemed impractical because too much $TiO_2$ catalysts would be expended. Additionally, the unreclaimed $TiO_2$ might result in secondary pollution [6].

Micron-sized solid spherical $TiO_2$ photocatalysts have been synthesized by some researchers [7–11] as an ideal candidate for easy separation and recovery, since they can settle down easily in aqueous suspensions by gravity. Unfortunately, a significant loss in contact area between the microspherical photocatalysts and UV light limits the photocatalytic efficiency. Grime and co-workers [12] and Wang et al. [13] proved that macroporous channels in $TiO_2$ could serve as light-transfer paths for the distribution of photon energy, which would improve the photoactivity. More recently, template-assisted methodology has been developed to fabricate $TiO_2$ microspheres with meso/macroporous framework. Sanchez's group has prepared multi-scale porous submicron-sized $TiO_2$ spheres by spray drying a Ti-sol containing supremolecular template (Pluronic F127) [14]. Okuyama's group has fabricated brookite $TiO_2$ multi-scale porous spheres by spray drying a suspension of brookite nanoparticles and polystyrene latex (PSL) particles [15].

In our previous work [16], we found that $TiO_2$ (B) nanowire basketry-like microspheres can be synthesized by spray drying a suspension of nanowire and polythethylene glycol (PEG). In this paper, the method was continually studied to fabricate $TiO_2$ nanowire microsphere with controllable structure with the assistance of surfactants. The formation mechanism of the $TiO_2$ nanowire microspheres was studied by investigating the effects of different operating parameters. Thereafter, its activity and stability were evaluated by the batch photocatalytic oxidation of a model pollutant.

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## 2. Experimental

### 2.1. Fabrication of the $TiO_2$ nanowire microspheres

The fabrication of nanowires was commonly referred in literatures [17–19]. In a typical synthesis, $TiO_2$ powder (Degussa, P25) was mixed with 10 M NaOH solution in a Teflon-lined autoclave container and placed in the oven at 180 °C for 2 days to undergo a hydrothermal reaction. The white pulp-like product in the autoclave was washed with 0.1 M HCl, with the assistance of ultrasound. Subsequently, pH was neutralized by repeated washing with deionized water.

The powdered nanowires were added into 0.1 wt% aqueous Pluronic F127 solution to obtain 8 g/L $TiO_2$ suspension feed for spray dryer (EYELA SD-1000). As-synthesized $TiO_2$ nanowire microspheres were constructed by spray drying the suspension feed. Finally, they were calcined at 300–600 °C for 2 h with a heating ramp of 2 °C/min to obtain the final nanowire microspheres.

### 2.2. Characterization of the $TiO_2$ nanowire microspheres

A JEOL 6340 field emission scanning electron microscopy (FESEM) and a JEOL 2010 transmission electron microscopy (TEM) were used to observe the morphologies of the $TiO_2$ nanowire microspheres. The crystal structures and the phase compositions of the samples were identified using a Bruker AXS D8 Advance X-ray diffractometer with monochromated high-intensity Cu K$\alpha$ irradiation ($\lambda$ = 1.5406 Å) at a scanning rate of 2°/min. The $N_2$ adsorption–desorption isotherms were obtained at liquid nitrogen temperature (77 K) using a Quantachrome Autosorb1 instrument. Before the measurement, the samples were outgassed under vacuum for 5 h at 150 °C. Specific surface area was calculated by the Brunaur–Emmett–Teller (BET) method using the adsorption data at the range from $P/P_0$ = 0.05 to 0.35 just below the capillary condensation, and the pore diameter distribution curve was derived from the adsorption branch by the BJH method. A thermalgravimeter analyzer (TGA) was used to monitor the degradation of surfactant in the sample. Measurements were taken with a heating rate of 5 °C/min from 30 to 700 °C.

### 2.3. Evaluation of the photocatalytic activities of $TiO_2$ nanowire microspheres

Methylene blue (MB) was used as the model chemical to investigate the photocalytic activity of the $TiO_2$ nanowire microspheres. An Upland 3SC9 Pen-ray lamp (254 nm) was immersed into the solution as the UV source. Air was pumped into the solution to mix for the catalysts and solution, as well as to induce oxygen into the system for oxidation. The aqueous system containing MB (20 mg/L, 500 mL) and $TiO_2$ nanowire microspheres (0.5 g/L) was mixed in the dark for 30 min to attain the adsorption equilibrium of MB with the photocatalyst, before the UV lamp was switched on. Commercial $TiO_2$ (Degussa P25) was adopted as the reference for comparison. The characteristic absorption at $\lambda$ = 670 nm was chosen to monitor the concentration of MB during the photodegration process. TOC (total organic carbon) was measured using a Shimadzu TOC-5000 analyzer.

## 3. Results and discussion

FESEM images of the as-synthesized and calcined $TiO_2$ samples at different magnifications are shown in Fig. 1. From the low magnification image (Fig. 1a) of the as-synthesized sample, it was found that microspheres, having 3–10 μm in diameter, were produced in vast amounts. The spherical structure of the $TiO_2$

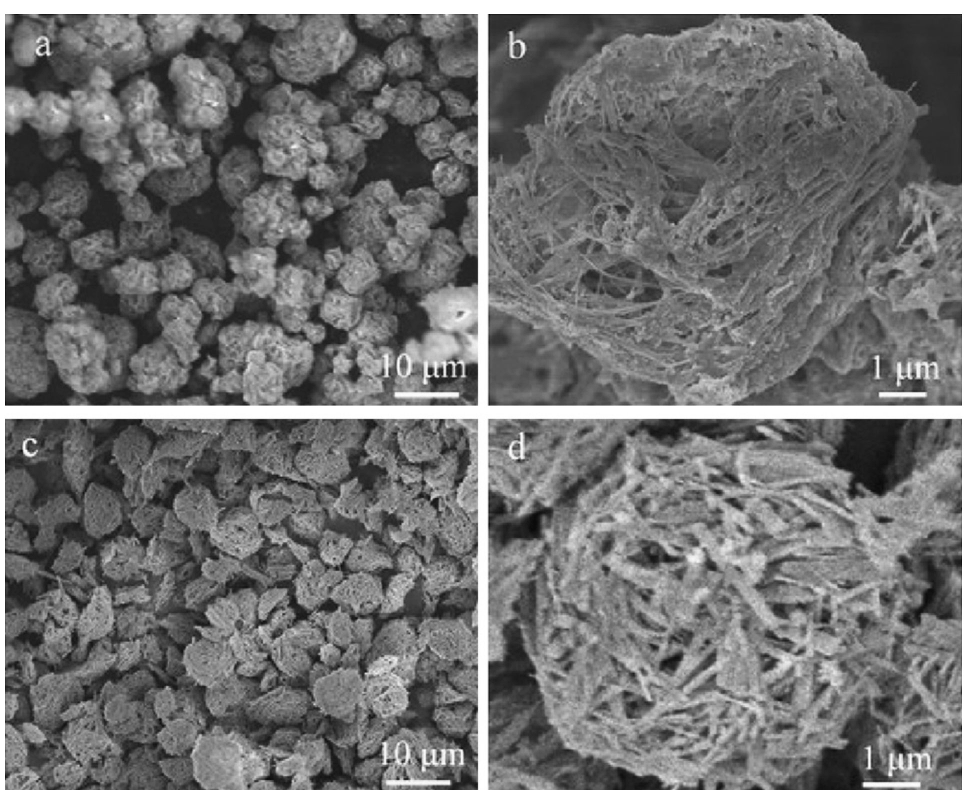


**Fig. 1.** FESEM images of (a and b) as-synthesized and (c and d) calcined nanowire microspheres at 600 °C. Nanowire and F127 concentration in suspension feed: 8 g/L and 0.1 wt%.