Short communication

Macroporous anatase titania particle: Aerosol self-assembly fabrication with photocatalytic performance

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ARTICLE INFO

ABSTRACT

An anatase titania particle with a honey-comb-like pore structure (200 nm-pore size) and a controllable outer diameter (0.2–1 μm) was successfully prepared using a spray-drying method. As a precursor, an anatase nanoparticle (5 nm) and a polystyrene particle (200 nm) were used as a titania source and a colloidal template, respectively. The outer diameter could be controlled by varying the precursor concentration. The photocatalytic performance of a porous particle was faster than that of a dense particle (with a similar outer diameter).

1. Introduction

Recently, titania has been widely studied due to its affinity for UV-light [1] and its ability to degrade organic compounds [2] and transfer energy (known as solar cell) [3]. For use in photocatalysis, titania in the nano-size range works best [4]. However, several problems persist: (i) the downstream processes for reuse or removal of the nanoparticle are typically expensive; (ii) when the nanoparticle is disposed of directly, there are environmental problems to overcome [5]; (iii) the application of nanoparticles is known to have greater adverse health effects than larger particles because of the possibility for them to be deposited into the alveoli [6]; and, they also can potentially be absorbed through the skin [7].

A material with a porous structure that is larger than nano-size could be the best alternative to nano-catalysts. The existence of pores would presumably produce photocatalytic activity similar to nanoparticles but without the high cost of maintenance associated with nanoparticles, and they can easily be re-collected or reused after catalytic treatment [8]. Furthermore, the design of particles in the submicron size reportedly makes them harmless, unlike nanoparticles [9].

The common process for developing a porous material uses a self-assembly template technique, which employs an organic material as the template (either surfactant or particle) [10]. The pore formation reflects the template shape [11], and easy removal of the template is one of the main advantages of using this process [12].

However, several disadvantages of the current materials remain. When producing mesoporous materials ($D_{pore} < 50$ nm), the surfactant typically used as template, unfortunately, could never be completely removed [13]. Although it could be synthesized via a template-free process [14], but, either heat treatment or UV-irradiation would induce the collapse of the porous structure [15]. Further, when a small pore size was used, difficulties associated with mass transfer, diffusivity, and penetration of molecules either into or out of the pore system became a limiting factor for several applications [10]. These were the concerns that prevented further application of mesoporous materials. Yamamoto and Imai [16] and Zhang et al. [1] reported the use of an organic material to produce an open cellular structure. However, an unordered porous structure was found. A promising method (using a polymer sphere as the template) was reported by Tang et al. [17], however, the material was in a film form and seemed difficult to manage, especially given the limited resources of most waste treatment plants. Klein et al. [18] have reported the synthesis of a titania porous particle, which has the best prospect for industrial application. However, the particle size is more than 10 μm with a large-size distribution and a material performance that is yet to be explained.

As a continuation of our work fabricating porous inorganic particles with a controllable morphology (i.e. shape, porosity, pore size, and particle size) [8,10,19–21], herein, we have introduced a method for the preparation of porous anatase particles. The purpose of this study was to demonstrate: (1) how to produce material with a highly ordered pore structure, and (2) how to fabricate material with catalytic performance that is better than that of the current material. In addition, the present novel technique could be broadly applied to the production of various types of functional inorganic

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porous particles with the possibility for large-scale production. For this reason, we believe this report contributes new information to the field of chemical engineering.

2. Experimental method

Submicrometer titania anatase particles with macropore structures were prepared using a mixture of titania anatase nanoparticles (TKS-203, Tayca Corp., Japan) and polystyrene (PSL, JSR Co. Ltd.; $D_{ave} = 200$ nm) as the template in aqueous solutions. Commercial colloidal titania nanoparticles were used in this study to simplify the process; thus, no predispersion method was required to disperse the titania into the aqueous solution. The mixed solution was sprayed using an ultrasonic nebulizer (Omron Corp., NE-U12, 1.7 MHz); then, it was introduced into a laminar-flow tubular furnace (a ceramic tube with two heating zones; $D = 13$ mm; $L = 1$ m), and collected by a filter similar to a previously described method [8]. The flow of N_2 gas (approximately 1 L/min), as the carrier gas, was used to propel the aerosol. The two heating zones played a role: (i) the first zone ($T = 200\,°C$) was used to evaporate the solvent in the droplets, resulting in large particles of a composite consisting of titania/PSL particles; (ii) the second zone ($T = 500\,°C$) was used to evaporate and release the PSL particles, which resulted in the formation of titania particles with a pore structure. In addition, a rapid synthesis (a residence time of less than 3 s) was obtained. The spray-dried particles were then characterized by scanning electron microscopy (SEM, Hitachi S-5000, 20 kV) for size, morphology, and pore structure determination; and X-ray diffraction (XRD; Rigaku Denki, RINT2000, Cu Kα, 20–80° (2θ) for crystallinity analysis. The photocatalytic performance of the prepared particles was investigated by measuring the photodegradation of 1.16 g/L of rhodamine-B (RhB, Wako Pure Chemicals, Japan) and 6.67 g/L of photocatalyst (titania) under UV illumination (Toshiba, 352 nm, each 20 W). As a comparison, the titania nanoparticles and titania dense particles (spray-dried titania nanoparticles with no addition of PSL) were also used as photocatalysts. The photodegradation was performed in the photoreactor system, which was similar to our previous work [8]. The suspension was left in the dark for 30 min to ensure the establishment of equilibrium (adsorption/de-sorption) between RhB/titania before beginning the photodegradation reaction. The first sample after dark conditioning was counted as the initial concentration (Co; $t = 0$). For measuring the degradation of the RhB in the solution, samples were taken from the reactor, counted as actual concentration at sampling time (C), and analyzed using a spectrophotometer (Shimadzu UV–vis-Spectrophotometer, UV-3150).

3. Results and discussion

In our previous work, a highly porous arrangement could be obtained when the optimal conditions were selected, which was dominantly affected by the mass ratio of the precursor to the templating agent [8]. In this study, after analyzing many different experimental conditions, it was determined that the mass ratio of titania nanoparticle/PSL was 1/2, which resulted in the best value for the obtainment of a good pore arrangement.

Fig. 1 shows SEM images of the particles prepared using the spray-drying method. When the PSL template was not added to the initial precursor, a dense particle was obtained (Fig. 1a). But, when the PSL was added, a porous particle was obtained (Fig. 1b). From analysis of the SEM image, we know that the pore diameter corresponded to the original size of the PSL, which suggests further
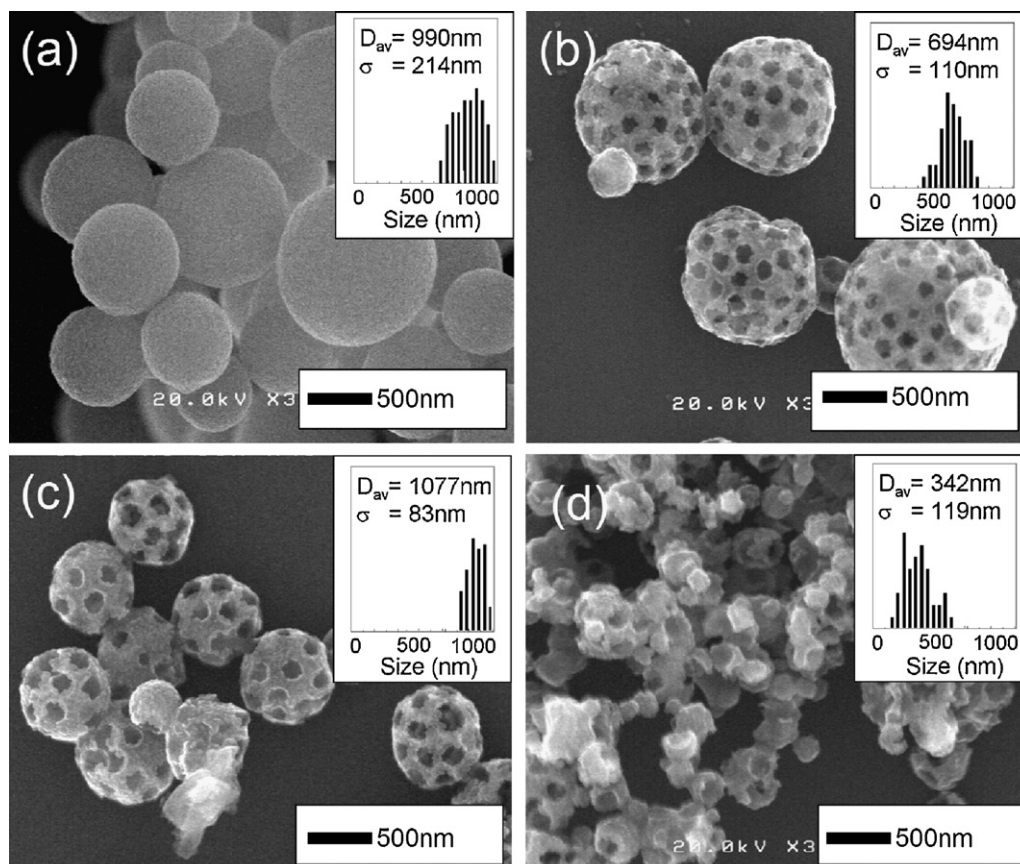

Fig. 1. SEM images of a titania dense particle (a) and a porous particle (b–d). The effect of the precursor concentration (2.50% (b), 1.10% (c), and 0.22% (d)) on particle size.

investigation into the control of pore size by simply adjusting the PSL size [8]. Therefore, we concluded that the PSL particles were arranged inside the particle, and then were removed completely, leaving holes in the particles. The phenomenon of pore arrangement can be explained by considering three contacting PSL particles filling a space for a titania nanoparticle that develops a hexagonal structure [8]. The size of the titania nanoparticle (d) and diameter of the PSL sphere (D) are considered and denoted as $d = (2/3\sqrt{3} - 1)D$. With this equation, for 5 nm titania particles, the PSL spheres must be at least 32 nm to create a good titania/PSL arrangement in the particle. Therefore, a PSL of about 200 nm resulted in a good pore structure.

Consistent with our previous study, the outer diameter was defined by the precursor concentration [21]. Then, using an identical mass ratio for titania/PSL, we produced porous particles using different precursor concentrations (0.22–2.5 wt.%). Spherical particles with pore structures were obtained in all cases; the only differences appeared to be the outer diameters, which was a function of the initial concentration. In Fig. 1(c and d), when the initial concentration was decreased, smaller particles were produced. A broken particle is also represented in Fig. 1c to show that the pores existed both on the particle surface and inside the particles. After the Ferret diameter was measured, particles with mean diameters ranging from 342 to 1077 nm could be produced from a primary solution of 0.22–2.5 wt.%. These results suggest that changing the initial suspension easily controls the size of generated porous particles; but the pore structure was not good when the particles were too small (Fig. 1d). This is because when lower concentrations were used, only a small number of PSL particles could be carried within the droplet. Thus, after the PSL was removed, some particles were left with only one or two holes.

For an effective process, both the morphology and the crystallite phase of titania must remain unchanged both before and after spray drying. Hence, the effect of temperature on the titania crystallinity was also characterized by XRD analysis (Fig. 2). This is because the high temperatures and long heating times of the process could lead to the conversion of the anatase pattern. The analysis results confirmed that the phase and pattern of the nanoparticle and the spray-dried particle were the same. The Scherer's crystallinity sizes of the nanoparticle and the spray-dried porous particle were 4.9 and 6.8 nm, respectively, which were measured at the maximum peak of 25.1°. A small change in the crystalline size was observed due to a small amount of sintering, but there was no phase transformation. With these results, it can be stated with a degree of certainty that this preparation method is effective for the obtainment of a quality porous particle.
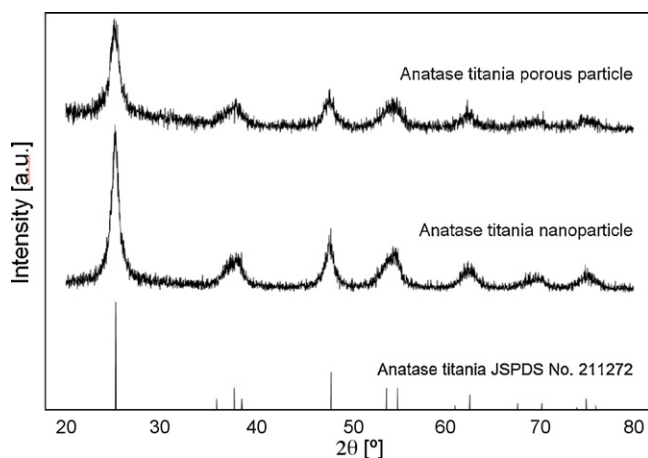
Fig. 2. XRD pattern of an anatase titania porous particle and a nanoparticle, along with the anatase reference (JSPDS No. 211272).
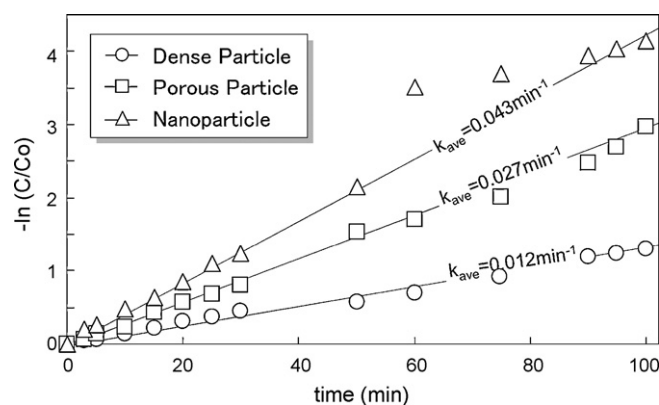
Fig. 3. Photocatalytic performance of different types of photocatalysts.

Since the synthesis technique described in this paper is effective and can be broadly applied in the production of particles with porous structures, the possible range of practical applications for such material becomes important. The photo-oxidation process was investigated via the degradation of an organic compound after the addition of a prepared particle under UV illumination [22].

When the concentration of oxygen is enough for the above reaction, observation could be focused on the concentration of the organic compound (e.g. RhB) during UV illumination catalyzed by titania. Thus, the simple absorption spectra could be measured and normalized using Beer's law, which is equal to the normalized concentration of the solution.

The Langmuir–Hinshelwood kinetics equation was typically used as a qualitative model to describe solid–liquid photochemical reactions [23], which can be written as $-dC/dt = k_t \cdot K_c \cdot C/1 + K_c \cdot C$, where C is the concentration of the chemical, k_t is the apparent reaction rate constant, and K_C is the apparent equilibrium constant for adsorption of the chemical on the catalyst surface. The use of a very low concentration of RhB is the best choice for a reaction rate calculation because the equation can be reduced to become a first-order reaction. When $C \ll 1$, we can approximate $1 + K_c \cdot C \approx 1$. Using $k_t \cdot K_c = k$, the equation can be re-written as $-dC/dt = k \cdot C$. Thus, the degradation kinetics rate among titania (nanoparticle, porous, and dense particle) can be compared easily by calculating the kinetics constant of each component using the simplified function of $k = -\ln(C/C_o)/t$.

Fig. 3 shows the photocatalytic performance rate using different photocatalysts. The reaction was performed in 100 min, which is an ample time for comparing different catalytic rates. The removed RhB measured 45, 80, and 96%, which corresponded to dense particles, porous particles, and nanoparticles, respectively. The rate of photocatalysis for a porous particle (mean size of 1077 nm), shown by the k value in Fig. 3, was faster than for the dense particle (with the same outer diameter) and approached the rate of photocatalysis for nanoparticles. The difference in reaction rates could have been caused by the dissimilar effective surface area on the catalyst. An increase in surface area increases the possibility of RhB molecule to be contacted a surface-active catalyst and degraded into smaller molecules. Because of this possibility, the mechanism of the catalytic process and the kinetic rate were increased. This explanation is similar to theories explained elsewhere [24].

Based on a similar geometrical model described in our previous work [8], the rate ratio of porous/dense particles (in a similar diameter) was 2.71. Using this model approximation, the theoretical k model was 0.032 min^{-1}, which approached to nanoparticle performance. A considerable deterrence of the k-value (Table 1), as compared with the theoretical results, was caused by difficulties with the penetration of UV-light into the pores. Thus, only several

Table 1
The theoretical effective surface area with its ratio of photocatalytic reaction rates (calculated and experimented value).

Type of titania particle	$[A_{max}/A_{max}^{dense}]_{theoretical}$	$[k/k_{dense}]_{experimental}$
Nanoparticle	–	3.58
200 nm pores	2.71	2.25
Dense particle	1.00	1.00

parts of the catalyst surface could be activated to degrade RhB. Besides, the release of an absorbed RhB molecule, with no degradation, into the porous catalyst was possibly due to the size of the RhB molecules, which were very small compared with the size of pores [10].

The preparation of a porous structure particle is the main focus of this work. The photodegradation analysis was only used to compare porous, non-porous, and nanoparticle photoactivity (using similar material). Thus, it is reasonable to say that if Degussa P25 is used as the titania source [25], the photodegradation ability of a macroporous particle should increase. Macroporous particles, however, retain their structure in the liquid phase, and, unlike nanoparticles, they can be easily collected and reused [8]. For this reason, further detailed characterization of the prepared particle performance (i.e. surface area, porous volume), the reaction kinetics (i.e. the effect of ratio titania/RhB and concentration of RhB), and the application of this method using other material (e.g., Degussa P25) is necessary and will be provided in our future work.

4. Conclusions

In summary, we developed an efficient method for the preparation of a macroporous anatase particle, as an alternative to nanoparticles, from an anatase nanoparticle and an organic particle (as a template). The spray-drying method with a vertical tubular furnace (two-fixed temperature zones) was used as a model of template-derived self-assembly process. Using present method, particle outer diameter could be achieved easily by only adjusting the concentration of initial precursor. The photocatalytic performance of prepared porous particles was found to be superior to that of dense particles and approaching that of nanoparticles. We believe these results are due to the relationship between the effective surface area of the catalyst and its catalytic properties.

Acknowledgement

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