Aerosol Spray Pyrolysis Synthesis of Porous Anatase TiO₂ Microspheres with Tailored Photocatalytic Activity

Wen-Ge Li¹ · Yan-Jie Hu¹ · Hao Jiang¹ · Chun-Zhong Li¹

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Abstract

Porous titanium dioxide (TiO₂) microspheres (MS) were prepared by a facile ultrasonic spray pyrolysis process with commercial colloidal silica as a sacrificial template. The morphology structure, Brunauer–Emmett–Teller surface areas and pore size distribution of TiO₂ microspheres were studied by changing the content and diameter of the silica template in detail. These porous micro-sized MS are composed of anatase TiO₂ nanocrystallites of 5–10 nm and have unique bimodal mesopores. The largest specific surface area of 112.3 m²/g has been achieved using 60 wt% 20 nm silica as a template. When used as photocatalysts, the best photocatalytic activity of the as-prepared porous MS is comparable to commercial P25 nanopowders. Moreover, the micro-size and tailored properties from the design that appear during the ultrasonic spray pyrolysis process give these porous MS a promising application in photocatalytic reaction.

Keywords Ultrasonic spray pyrolysis · TiO₂ microspheres · Porous structure · Photodegradation

1 Introduction

The removal of hazardous organic compounds in water has become an issue of serious concern for those involved in environmental harnessing [1]. As an attractive technique for wastewater treatment, photocatalysis is a green strategy because it is an ambient-temperature process that can effectively decompose organic pollutants to harmless chemicals and eliminate toxic and inorganic compounds from wastewater by utilizing inexhaustible and clean solar energy [2, 3]. Since the pioneering work of Fujishima and Honda [4], titanium dioxide (TiO₂), as a wide-bandgap semiconductor ($E_g = 3.2$ eV), has become the most extensively studied oxide semiconductor for many applications, especially for environmental cleaning due to its

affinity for UV light and the ability to degrade organic compounds [4, 5]. For example, the famous commercial P25 (TiO₂: average size 21 nm, 50 m²/g, from Evonik-Degussa Company) has been developed in large quantities using aerosol flame pyrolysis process for various applications [6]. Many studies on the photocatalytic activity of TiO₂ particles have shown that the optimum particles size is in the nanosize range [7, 8]. However, the nanosize TiO₂ photocatalysts are generally expensive to recycle as their nanoparticles can create an environmental problem. Although the high catalytic activity of TiO₂ nanoparticles is found to be useful, the health effect of nanoparticles in common conditions limits their practical applications [9, 10].

The design and preparation of hierarchical structures assembled by nanosize components is an effective way to increase the effective surface area of TiO₂ photocatalysts for enhanced photocatalytic activity [11, 12]. For instance, Lu et al. [13] synthesized mesoporous anatase TiO₂ sphere with high surface area via a template-free method and showed enhanced photocatalytic activity, and Liu et al. [14] fabricated hierarchically porous TiO₂ microspheres by a solvothermal method and displayed their improved photocatalytic degradation performance. In addition, Qian et al. [15] prepared nano-TiO₂-decorated radial-like mesoporous silica which exhibited excellent

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✉ Yan-Jie Hu
huyanjie@ecust.edu.cn

✉ Chun-Zhong Li
czli@ecust.edu.cn

¹ Key Laboratory for Ultrafine Materials of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

photodegradation behavior and good durability. Importantly, TiO₂ microspheres (MS) with porous structure have a larger size than nanocatalysts, which can easily be recycled after the catalytic process [16, 17]. Furthermore, the existence of pores could produce photocatalytic activity similar to nanoparticles. Many methods have been devoted to the preparation of macroporous or mesoporous TiO₂ spheres with large surface areas [18, 19]. However, many of them are based on wet chemistry processes, such as sol-gel, hydrothermal and solvothermal methods, which involve high costs, are time-consuming, have low throughput and are difficult to use in large-scale production [20, 21].

Recently, functional porous metal oxide microspheres (MS) have been rapidly realized using aerosol spray pyrolysis [22–25]. The formed droplets have different sacrificial templates that can serve as individual microreactors, thereby exhibiting great advantages for preparing porous sphere materials with large surface areas and high purity. Iskandar et al. [26] prepared macroporous (200 nm porous size) TiO₂ particles by spray drying method using pre-existing nanoparticles of silica or titania (brookite, anatase and Evonik-Degussa P25) with polystyrene latex particles (PSL) as a template. The particles' morphology and porosity could be controlled by the tailoring the weight fraction and diameter of PSL. However, the photocatalytic activity of porous particles is much smaller than that of nanoparticles because of their larger pore size. On the other hand, organic template agents such as P123 and F127 have also been employed to design and prepare TiO₂-based mesoporous spherical particles, such as TiO₂, V₂O₅/TiO₂, In₂O₃/TiO₂, Cu-doped TiO₂ and WO₃/TiO₂ for various catalytic applications [27, 31]. Further, porous TiO₂ MS have been reported by using a spray pyrolysis method with colloidal silica template [32]. These porous microspheres show superior specific photoactivity per surface area for decomposition of NO_x compared to commercial P25. The results suggest that template-assisted aerosol spray pyrolysis is an efficient way to produce porous TiO₂-based materials [33, 34]. Nevertheless, there are few reports about the detailed relationship between pores' structural parameters and the photocatalytic properties of TiO₂ porous spheres made by the aerosol process.

In the present work, porous TiO₂ MS was prepared by the facile ultrasonic spray pyrolysis (USP) technique with colloidal silica for the sacrificial template. The pore size distribution of TiO₂ MS was studied by changing the content and diameter of silica template in detail. When these prepared MS were applied to the photocatalytic degradation of methylene blue molecules in aqueous solutions, these porous TiO₂ MS exhibited a tailored photocatalytic performance.

2 Experimental

2.1 Chemicals

Silica colloid (20, 60 and 110 nm in diameter, 40 wt% suspension in water) was purchased from Xinanna Technology Co. Ltd (Shanghai, China). Titanium tetrachloride (TiCl₄, 99.5%) and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was prepared in the laboratory. All used chemicals had no further purification.

2.2 Preparation of Porous TiO₂ Microspheres

For the synthesis of porous TiO₂ MS, a 0.5 M precursor solution was obtained by dissolving TiCl₄ in 100 ml cold DI water. Designed amount of colloidal silica was then added into the solution, and the mass ratio of SiO₂ template to as-prepared TiO₂ was 20%, 60% and 100%, respectively. Then the solution containing TiCl₄ and silica template was delivered into an ultrasonic spray generator (1.7 MHz) to generate fine droplets. These microdroplets were subsequently carried into a high-temperature quartz-tube reactor (inner diameter 60 mm; length 600 mm) with a temperature of 400 °C by a carrier gas (air, 500 L/h). Ti-containing precursor spheres with a silica template were obtained after the evaporation and pyrolysis of droplets and collected by a glass fiber filter (GA-55, Japan) with the aid of a vacuum pump. Figure 1 shows the illustrated experimental setup in detail.

TiO₂/SiO₂ MS were obtained by the subsequent calcination of the as-prepared precursor particles at 450 °C for 1 h in air. Then, the silica template was etched and removed with HF 10 wt% in water at room temperature. After 2 h, the particles were centrifuged and washed three times with purified water and ethanol. Porous TiO₂ MS were obtained after drying in air at 80 °C for 12 h. When the precursor solution was set as 100 mL, TiO₂ MS powder around 2.9 g was finally obtained, and thus the yield of this preparation technique was determined as about 73%. For comparison, TiO₂ solid spheres were also synthesized using the same procedure, but without adding colloidal silica as a template.

2.3 Materials Characterization

The phase compositions of the as-synthesized TiO₂ MS were investigated by X-ray diffraction (XRD), which was performed on a Rigaku D/max 2550VB/PC diffractometer at room temperature. The corresponding patterns were recorded over the angular range 10°–80° (2θ) with a step size of 0.2°, using Cu Kα radiation (λ = 0.154056 nm) with a working voltage of 40 kV and a current of 100 mA,

Fig. 1 Ultrasonic spray aerosol process used to synthesize $\text{TiO}_2/\text{SiO}_2$ microspheres

respectively. The morphology microstructures were further characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100) and field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) with energy-dispersive X-ray spectroscopy (EDS). The specific surface area of particles was determined by nitrogen adsorption–desorption (ASAP 2010 N) according to the Brunauer–Emmett–Teller (BET) method. The chemical state analysis of the components was performed on an X-ray photoelectron spectroscopy (XPS) instrument (Thermal Scientific, ESCALAB Xi 250) using an Al $K\alpha$ radiation source of 1486.6 eV. The binding energy values were calibrated by correlating C 1s peak to 284.8 eV. The photoluminescence (PL) spectra were recorded on Perkin Elmer LS55 spectrophotometer using a 300-nm irradiation.

2.4 Photocatalytic Degradation of Dye Molecules

The photocatalytic activity of porous TiO_2 MS was evaluated by the degradation of the MB dye (10 mg/L) under ultraviolet light irradiation in a BL-GHX-V multifunctional photochemical reactor (Shanghai Bilon Experiment Equipment Co., Ltd., Shanghai, China). 80-mg samples were added into 80 mL MB aqueous solutions (10 mg/L). The mixed suspension was magnetically stirred in the dark for 30 min to reach an adsorption–desorption equilibrium. The suspension was then exposed to the UV light ($\lambda < 400$ nm) produced by a 400-W metal halogen lamp with a cutoff filter. At certain time intervals, the extracted 3-mL suspension was subsequently centrifuged to remove the catalyst particles. The residual concentration of MB was analyzed by measuring its absorbance at 664 nm using a UV–Vis spectrophotometer (UNICO UV-2102PC). The catalytic stability of the as-prepared catalyst was studied by the degradation behavior of MB under the same conditions

during a six-cycle experiment. After each cycle, the photocatalyst powder was centrifuged and recollected for the next cycle.

3 Results and Discussion

3.1 Composition and Morphology

Porous TiO_2 microspheres were obtained by a colloidal silica template-assisted USP technique. Figure 2 shows the XRD patterns of the as-prepared TiO_2 MS before and after HF etching with 20, 60 and 110 nm silica as a template. It is clearly seen that all the diffraction peaks are well

Fig. 2 XRD patterns of the obtained $\text{TiO}_2/\text{SiO}_2$ MS and porous TiO_2 MS after HF etching (the mass ratio of $\text{SiO}_2/\text{TiO}_2 = 0.6$, 20, 60 and 110 nm silica as the template)

matched with the anatase TiO₂ (JCPDS No. 21-1272). When silica was used as a template, the broad diffraction peaks at 20°–30° were observed. After the removal of the silica template, the amorphous patterns vanished. Clearly, all the patterns are broad, indicating the existence of TiO₂ particles of a smaller size. As determined from the anatase (101) peaks by the Scherrer formula, the crystalline size of TiO₂ is 7.5 nm, indicating that the synthesized porous TiO₂ MS are composed of small nanocrystallites.

To investigate the components and chemical states of the as-prepared TiO₂ MS, the XPS analysis of TiO₂ MS before and after HF etching using 20 nm silica as a template was performed as shown in Fig. 3. The peak around 103.5 eV in the general spectrum (Fig. 3a) demonstrates the existence of silica component in the TiO₂ MS before HF etching. On the contrary, the disappearance of this peak after etching suggests the complete removal of the silica

template. In the Ti 2p spectra (Fig. 3b), two typical sharp peaks at 458.8 and 464.5 eV along with a satellite around 472.3 eV indicate the TiO₂ MS consist of Ti⁴⁺ ion and have no Ti³⁺ ion. There are three distinct O species in Fig. 3c, and lattice O is found to be the main O species in TiO₂ MS before and after HF etching, in good agreement with the crystal structure of TiO₂. It should be noted that the O species from Si-O bonds contribute to a broad peak around 530.0 eV, which is attributed to the existence of silica template.

Figure 4a shows the TEM image of an as-synthesized porous TiO₂ MS made by an ultrasonic spray aerosol process followed by calcination and HF etching. The porous TiO₂ MS possesses a spherical morphology, while the particle size ranges from several hundred nanometers to several microns. Figure 4b, c shows the representative TEM image of single porous TiO₂ MS. It is clearly seen

Fig. 3 a XPS general spectrum, b Ti 2p spectrum, c O 1s spectrum of TiO₂ MS before and after HF etching (the mass ratio of SiO₂/TiO₂ = 0.6, 20 nm silica as template)

Fig. 4 TEM and HRTEM images of the as-prepared porous TiO_2 MS

that the existence of the foam-like and highly porous structure with meso- and micropores is interconnected. These pores have an average mesopore size of about 20 nm, which matches well with the size of the colloidal silica template. An HRTEM image in Fig. 4d demonstrates that porous MS are composed of TiO_2 nanocrystallites of 5–10 nm in diameter. It is clear that the obtained TiO_2 nanoparticles have good crystallization and the lattice spacing of 0.35 nm further depicts the (101) plane of anatase TiO_2 . Additionally, some small mesopores were also observed as evidenced by the accumulated TiO_2 nanocrystallites. Furthermore, as shown in Fig. 5, the EDS and elements mapping of TiO_2 MS before and after HF etching demonstrate that the colloidal silica template can be removed completely, indicating that silica particles are an excellent template for the construction of porous structures.

The addition of a silica template plays a key role in the formation of pore structures. Figure 6 shows SEM images of the as-prepared TiO_2 MS before and after the removal of the silica template with different mass ratios of $\text{SiO}_2/\text{TiO}_2$ (SiO_2 size 20 nm). Before the HF etching, the obtained $\text{SiO}_2/\text{TiO}_2$ MS possessed a perfect spherical shape with a smooth surface, as shown in Fig. 6a, c, e. However, after the removal of silica template, the porous structures were

clearly observed and extremely rough characteristics appeared replacing the original relatively smooth surface. With an increase in colloidal silica, the obtained precursor spheres had more silica content and the final TiO_2 MS exhibited higher porosity. As shown in Fig. 6f, when the mass ratio of $\text{SiO}_2/\text{TiO}_2$ increased to 100%, porous structures were very abundant and these TiO_2 MS maintained the perfect spherical morphology. However, the continued increase in the silica template can destroy the spheres into species after the HF etching, which is extremely unfavorable for the recycle and separation of catalyst particles.

To further investigate the influences of the silica template on the morphology of TiO_2 MS, three types of colloidal silica with different diameters (20, 60 and 110 nm) were used to design the porous structures. Figure 7 shows the corresponding SEM images of TiO_2 MS. The content of the silica template is identical to 60 wt% (the $\text{SiO}_2/\text{TiO}_2$ mass ratio). Obviously, pure TiO_2 MS with a relatively smooth surface was obtained without any template. And with the increase in silica diameter, the size of pores in the TiO_2 MS became larger. However, the size of the final TiO_2 MS shows no significant change, indicating that an ultrasonic spray aerosol technique is effective for the design and preparation of microsphere-related materials.

Fig. 5 EDS and element mapping of TiO₂ MS **a** before and **b** after the removal of the colloidal silica template

The design and construction of pore structure can facilitate the increase in specific surface area and improve the scattering ability of light and adsorption capacity of dye molecules, which is beneficial to the catalytic reaction [27, 29, 30]. Figure 8a depicts the corresponding N₂ adsorption and desorption isotherms curves in detail. Pure TiO₂ MS have a specific surface area of 46.1 m²/g, which is lower than that of commercial P25 (49.6 m²/g). After increasing the usage of the silica template, the specific surface area (SSA) increased to 87.2 m²/g for 20 wt% and 112.3 m²/g for 60 wt%. When 100 wt% silica was employed as a template, the decreased SSA value of 95.7 m²/g was obtained. The decreased SSA value is mainly attributed to the formation of macropores due to the accumulation of more silica template. As shown in Fig. 8b, the influence of different silica templates is also investigated with 60 wt% usage of silica templates. The specific surface area decreases to 97.3 and 86.4 m²/g when the diameter of silica increases to 60 and 110 nm, respectively. Figure 8c shows the pore distribution of the as-prepared TiO₂ MS with different silica templates. The formation of

these pores is mainly attributed to the accumulated TiO₂ nanocrystallites, as shown in the HRTEM image in Fig. 4d. It is found that pure TiO₂ MS have small size pores ranging from 3 to 4 nm (the inset in Fig. 8d). Further, it is clearly noted that the usage of 60 wt% silica has the biggest pore volume and relatively narrow distribution of pore diameter. More silica particles than 60 wt% result in wide pore distribution ranging from 4 to 80 nm and smaller pore volume. However, higher usage of silica could still maintain perfect spherical morphology, demonstrated by the SEM images in Fig. 6e, f. With further increase in the content of silica template (> 100 wt%), TiO₂ sample is difficult to retain perfect spherical shape and crushes into pieces. Figure 8d displays the corresponding pore distribution profiles of pure TiO₂ MS and porous TiO₂ MS made from different sizes of silica template. With colloidal silica serving as the template, larger pores of size from 10 to 60 nm formed after the removal of silica, and the pore size was related to the diameter of the employed silica particles template [26, 32]. The results indicate that the usage of the colloidal silica template in spray pyrolysis synthesis of

Fig. 6 SEM images of the as-prepared TiO_2 MS before and after HF etching with different mass ratios of $\text{SiO}_2/\text{TiO}_2$: **a, b** 20%; **c, d** 60%; **e, f** 100% (**a, c, e**: before etching)

TiO_2 MS is an effective route for the construction and design of pore structures, which may play a key role in tailoring the photocatalytic performance of the obtained TiO_2 materials.

3.2 Photocatalytic Properties

It is well known that the unique porous structure can scatter more incident light for photocatalytic reactions and enhance the activity of photocatalysts [19, 32]. Herein, the photocatalytic activity of the as-prepared samples was evaluated by the degradation of methylene blue (MB) under irradiation of UV light (Fig. 9a). It is clear that only 2.2% of the MB was degraded after 1-h irradiation without

any catalyst. About 24.2% degradation was obtained for pure TiO_2 MS used as a photocatalyst under identical conditions. Meanwhile, the effect of the SiO_2 (20 nm) content on the photocatalytic activity of TiO_2 MS was also investigated. When the mass ratio of $\text{SiO}_2/\text{TiO}_2$ increased from 0, 20%, 60% to 100%, the degradation of MB also increased from 24.2%, 68.3% and 93.9% to 99% after 1-h UV light irradiation. This is mainly because of the light scattering ability of porous structures and high specific surface areas. However, when the silica template content was further increased, the crushed nanoparticles were obtained instead of the perfect microspheres, which do not facilitate the separation of catalysts owing to their smaller size. Compared to commercial P25 nanopowder, the

Fig. 7 SEM images of **a** pure TiO₂ MS and **b–d** porous TiO₂ MS made from different colloidal silica template diameters: **b** 20 nm; **c** 60 nm; **d** 110 nm

considerable photocatalytic activity of porous TiO₂ MS was achieved with a 100% mass ratio between SiO₂ and TiO₂. Moreover, the best photocatalysis performance in these samples is also comparable to that of TiO₂-based photocatalysts in Refs. [15, 35].

Furthermore, the effect of the silica template's size on the catalytic performance of porous TiO₂ MS was also investigated. As shown in Fig. 9b, with the same mass ratio of SiO₂ to TiO₂, the photocatalytic activity gradually decreased as the size of colloidal silica particles increased. These results indicate that the pores from large-sized silica have a diverse effect on the photocatalytic ability although the decrease is minor. This can be attributed to the decreased specific surface area of TiO₂ MS. The above results demonstrate that the design of pore structures can provide an effective enhancement for TiO₂ MS with controllable photocatalytic activity; furthermore, the silica template-assisted ultrasonic spray pyrolysis technique is a promising route for the synthesis of porous materials. Figure 9c displays the catalytic performance of the TiO₂ MS using 60 wt% silica (20 nm) as the template in six consecutive cycles. The photodegradation of MB in 1 h under the same condition only drops from 93.2% to 92.0% after 6 cycles. This slight decrease demonstrates that the

as-prepared porous TiO₂ MS photocatalyst has a remarkable recyclability and an excellent catalytic stability.

To further clarify the relationship between pore structures and photocatalytic performance, Fig. 9d shows the UV–visible diffuse reflectance spectra of three as-made porous TiO₂ MS and a reference TiO₂ MS. Clearly, all the four samples have a significant increase in the absorption with the reduce of the wavelength below 400 nm, which can be attributed to the intrinsic band energy gap of TiO₂. However, compared with reference TiO₂ MS, the absorption edge of the obtained three porous TiO₂ MS is shifted to a shorter wavelength. The value of ΔW increases with the increase in the size of the employed silica template (20, 60 and 100 nm). However, the absorption in the UV region increases and subsequently decreases (ΔA is shown in Fig. 9d). The photocatalytic results demonstrate that the porous structure was derived from 20 nm silica, which has an optimal balance for the absorption of more UV light, thereby facilitating the production of more e^- and h^+ induced by UV light [26, 27, 32]. Figure 9e illustrates the photocatalytic process. Under the irradiation of UV light, the photo-induced electrons can transfer into the conductive band of TiO₂ and promote the formation of active oxygen species ($\cdot O_2^-$). And the separated hole reacts with H₂O molecules to form $\cdot OH$. Finally, these active free

Fig. 8 a, b Nitrogen adsorption–desorption isotherm profiles; c, d pore distribution curves of pure TiO_2 MS and porous TiO_2 MS made from silica template according to colloidal silicate template diameters

radicals could degrade the targeted MB molecules into CO_2 and H_2O . Since the production of e^- and h^+ plays a crucial role in the photocatalytic process, the lifetime of these carriers is correlated with the catalytic behavior. As shown in Fig. 9f, the PL intensity of the as-prepared porous TiO_2 MS is far less than that of solid TiO_2 MS, indicating the e^- and h^+ in porous TiO_2 MS are more easily separated and live longer. Therefore, the abundant pore structures facilitate the light harvesting because of the enhanced multi-angle scattering and the separation of e^- and h^+ , eventually leading to an improved photocatalytic performance of TiO_2 MS [28, 32].

4 Conclusion

In summary, porous TiO_2 microspheres have been prepared by combining the ultrasonic spray pyrolysis technique with the colloidal silica template method. Tailoring the diameter and content of the silica template, the pore structures and the specific surface area could be effectively controlled. The porous MS with micro-size are composed of anatase TiO_2 nanocrystallites with a diameter of 5–10 nm. These microspheres also have bimodal size mesopores that can range in size from the smaller diameters of 3–4 nm to larger diameters between 10 and 60 nm. The largest specific surface area of $112.3 \text{ m}^2/\text{g}$ can be achieved using 60 wt% 20 nm silica as a template. When used as

Fig. 9 **a** UV light-induced photodegradation of MB in aqueous solutions using P25 and TiO₂ MS made by 20 nm silica template with different contents; **b** the influence of silica template's size on the photocatalytic performance of porous TiO₂ MS for the degradation of MB (the mass ratio of SiO₂/TiO₂ is 60%); **c** the catalytic stability of TiO₂ MS in 6 cycles; **d** UV-Vis absorption curves of porous TiO₂ MS made from different sizes of silica template; **e** illustrated photocatalytic process under UV light irradiation; **f** the PL spectrum of solid TiO₂ MS and porous TiO₂ MS (20, 60 and 110 nm silica as the template)

photocatalysts, the as-prepared TiO₂ MS exhibit controllable photocatalytic activity for the degradation of MB dye molecules under UV light irradiation. The best photocatalytic performance of the prepared porous MS is comparable to commercial P25. Moreover, the micro-size and tailored properties from the design of the ultrasonic spray pyrolysis process give these porous MS a promising application in photocatalytic reaction. In addition, these results also demonstrate the ultrasonic spray pyrolysis technique as a potential route for the fabrication of porous oxide microspheres.

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