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Influence of chelating agent and reaction time on the swelling process for preparation of porous TiO_2 particles

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Abstract

This study aimed to describe the preparation and characterization of porous titanium oxide particles of narrow particle size distribution by a single-step swelling process of polystyrene template microspheres. In this research, different specific surface areas, porous structures and densities of porous titanium oxide particles had been synthesized with various experimental parameters. Two main parameters were tested and discussed: (1) acetylacetone amount (from 0 to 1 ml) and (2) reaction time (from 2 to 32 h). Polystyrene template particles were polymerized by emulsifier free-emulsion polymerization (a kind of polymerization method). For the swelling process to be successful, a chelating agent (acetylacetone) was added to delay the aqueous hydrolysis of titanium (IV) isopropoxide in the water phase. The influences of various reaction parameters on size, morphology, composition, specific surface area, porous structure and density of particles were investigated. The properties of particles were analyzed by scanning electron microscope, Brunauer–Emmett–Teller, Fourier transform infrared analysis, thermogravimetric analysis, powder X-ray diffraction, and specific gravity meter.

Keywords: Swelling process; Porosity; TiO_2; Template; Chelating agent

1. Introduction

Titanium dioxide (TiO_2) has been widely used in many applications due to its particular properties, such as being non-toxic, low cost, chemical stability, and efficient photocatalyst without secondary pollution. TiO_2 is also a well-known bandgap material and has already been widely used as a photocatalyst in various applications, like degradation of wastewater and volatile organic compounds (VOCs) treatment.[1–3] However, its specific surface area must be increased to maximize the photocatalytic activity. One way to increase specific surface area is to prepare of porous TiO_2 particles. Porosity morphology with a large specific surface area has potential applications in chemical and physical processes.[4–7]

In recent years, a new method for synthesizing porous particles by the swelling process of polymer templates, such as polystyrene (PS), polypropylene and poly (dimethylsiloxane) was published.[8–13] The inorganic/organic materials have been swollen into polymer templates through the swelling process, and then a chemical or thermal method has been applied to remove the polymer templates for given molded inorganic/organic materials. This way, it would be like the so-called "template-free" approach proposed by Seshadri and his co-workers.[14–16]

Due to the strong reactivity of the alkoxide of titanium (IV) isopropoxide (TTIP) in the water, TTIP often results in an uncontrolled precipitation to form TiO_2 based materials. However, the major problem is to control hydrolysis rate that is generally too high, resulting in the formation of disordered precipitates[17] that make the swelling process difficult. The problem has been solved with the aid of a chelating agent that can delay the reactivity and prevent the precipitation of TTIP in the system, and then toward the formation of other final states. The added chelating agent reacts with TTIP and modifies the ligand structure, controlling and suppressing its hydrolysis reaction rate.[18–21] AcAc works as a chelating agent and are in two tautomeric forms: keto form and enol form, as shown in Fig. 1a.[22,23] AcAc plays an important role in the reaction, it can instantly chelate with Ti forming Ti/AcAc to prevent sol

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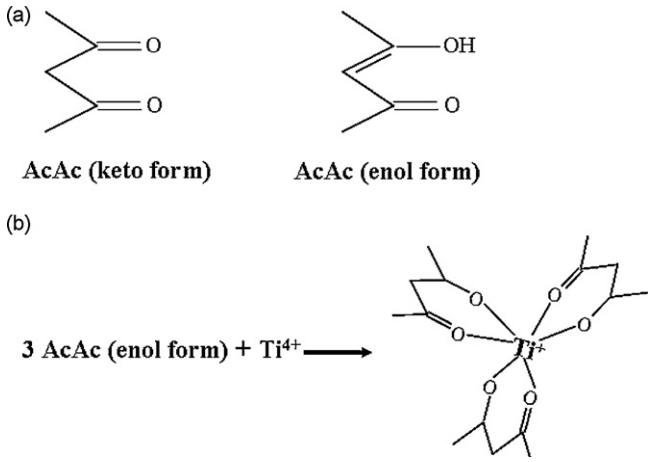

Fig. 1. (a) AcAc shows two tautomeric forms: keto form and enol form, and (b) AcAc chelates with Ti forming Ti/AcAc.

from agglomerating during the hydrolysis procedure, as shown in Fig. 1b.

Hence, the present paper characterizes the preparation of porous TiO_2 particles by a single-step swelling of PS template using AcAc modified TTIP as a precursor with various experimental parameters, such as AcAc amount and reaction time. When TTIP/AcAc had been impregnated into the PS template particles for a long time, the TiO_2/PS composite particles were prepared by hydrolysis/condensation reaction of the swollen template in the water. The TiO_2/PS composite particles were then used to form porous TiO_2 particles by the thermal decomposition of the swollen template particles.

2. Experiment

2.1. Materials

The following reagents were used as received from the manufacturer: styrene (99.5%, Showa) was used with further purification to remove inhibitor before use. Potassium persulfate (KPS) (99.4%, JT. Baker), sodium chloride (NaCl) (99.5%, Showa), p-styrenesulfonic acid sodium salt (NaSS) (Trade Mark), methanol (99.9%, Tedia), hydrochloric acid (HCl) (99%, Tedia), titanium (IV) isopropoxide (TTIP) (97%, Sigma Aldrich) and acetylacetone (AcAc) (99%, Sigma Aldrich).

2.2. Polymerization of PS template particles

PS particles were polymerized by emulsifier free-emulsion polymerization. A monomer solution, containing 0.08 g of NaCl, 0.103 g of NaSS, 130 ml of H_2O and 16.5 ml of styrene, was mixed into the reaction flask. Rapidly, pure N_2 bubbled through the monomer solution for 7 min to exclude O_2. An initiator solution containing 0.08 g of KPS and 20 ml of H_2O was then added to the reaction flask of monomer solution. The above solution with mixtures was shaken (120 rpm) with a machine to be polymerized at 70 °C for 24 h. After the polymerization reaction was finish, the final product was washed by extensive centrifugation cycles with methanol and HCl (0.1 M), and then dried in a vacuum oven. Finally, PS particles with an average diameter of 160 nm of narrow size distribution were obtained and used as templates to prepare porous TiO_2 particles, as shown in Fig. 2. The particles, which were spherical, with obviously smooth homogeneous surfaces. In the present research, only one diameter (160 nm) of PS particles was focused on for the swelling process. Those of other sizes (150, 180, and 200 nm) had also been polymerized in our laboratory. We are going to further study the influences of various PS templates on the swelling process in the future.

2.3. Preparation of porous TiO_2 particles by the swelling process and treatments of various experimental parameters

In the present experiment, 0.1 g of PS template particles and 30 ml of water were added in a reaction flask, being mixed by stirring at RT for 30 min. A TTIP/AcAc solution, containing a fixed amount of TTIP (0.4 ml) and various amounts of AcAc (0, 0.02, 0.05, 0.1, 0.2, 0.5, and 1 ml), was also well mixed by sonication for 30 min, and then was mixed into the above PS aqueous solution. The above mixture solution was then reacted based on a single-step swelling process by stirring at RT for different time (2, 4, 8, 16, and 32 h). When the reaction time was reached, the excess reagents were removed from the mixture solution with water, and then the solution was moved to a vacuum oven for dry up, to obtain the TiO_2/PS composite particles of various sizes and compositions. Finally, porous TiO_2 particles were then formed by calcining TiO_2/PS composite particles at 500 °C over 5 h. In this study, two experimental parameters of the swelling process were treated: (1) AcAc amount and (2) reaction time.

2.4. Analysis

Surface morphology of the product was appeared by a Hitachi scanning electron microscope (SEM) (Model S-4100). The specific surface area and porous structure of various porous TiO_2 particles were measured by the Brunauer–Emmett–Teller (BET) (ASAP 2020, Micromerities). Fourier transform infrared (FTIR)

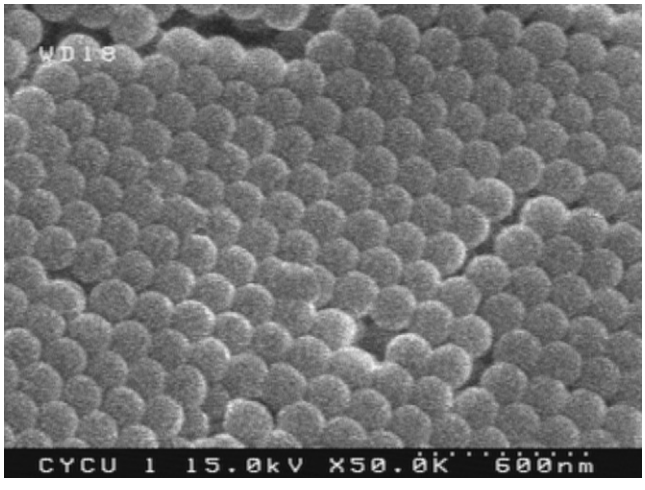

Fig. 2. SEM picture of PS template particles of narrow size distribution.

analysis (JASCO, FTIR-7000) was carried out with nearly 3 mg of the product and 50 mg of KBr pellets. The pellets were scanned for 8 times at 400–4000 cm^{-1} resolution. Thermogravimetric analysis (TGA) (TA, TGA-Q500) was used to measure the thermal behavior of the product. The analysis was carried out with dried samples of nearly 3 mg in a dynamic nitrogen atmosphere (60 ml/min) with a heating rate of 15 °C/min. Powder X-ray diffraction (XRD) patterns were recorded using a X-ray diffractometer (DIMAX-2500 V/PC) with Cu kα radiation for the range $2\theta = 10–60°$. The specific gravity/density of various porous TiO_2 particles was measured by specific gravity meter (micromertics 1330).

3. Results and discussions

3.1. The effect of AcAc amount

After being dried up, each product becomes powders, and it can be seen from the following SEM pictures that, obviously, the powders are in the form of discrete particles. The size of the TiO_2/PS composite particle before polymer was removed was larger than the size after calcination, and the particle surface was smooth, as shown in Fig. 3a and b. Fig. 4a–g are the SEM pictures illustrating porous TiO_2 particles after calcination prepared by a single-step swelling process of 0.1 g PS template particles with 0.4 ml of TTIP, and various amounts of AcAc. AcAc works as a chelating agent and it is a kind of good solvent for PS particles, so the PS template particles can be dissolved in pure AcAc. In this system, because the hydrolysis rate of TTIP was very high in the water phase in which TiO_2 solids can be formed by themselves, TTIP was not impregnated into the PS template particles at a small amount of AcAc (0 or 0.02 ml). Hence, Fig. 4a and b clearly show the aggregative TiO_2 particles, which were almost dots after calcinations. Fig. 4c shows uneven and bigger TiO_2 particles after calcination, so it is proved that the part of TTIP/AcAc was impregnated into PS particles at 0.05 ml of AcAc. When the amount of AcAc approached 0.1 ml, the spherical TiO_2 particles were approximately 450 nm, as shown in Fig. 4d. Fig. 4e–g indicate that TiO_2 particles with 480–600 nm prepared with large amounts of AcAc (0.2, 0.5, and 1 ml), and obviously show a rough and holey surface after calcination. Size measurements of the porous TiO_2 particles showed an apparently increasing trend in the diameter of particles as the amount of AcAc increased. The results of Fig. 4a–g demonstrate that TTIP/AcAc was successfully impregnated into PS particles as the amount of AcAc went over 0.1 ml, and then bigger TiO_2/PS composite particles were formed before calcination. Because the removal of the PS sections remained void to prepare porous TiO_2 particles after calcination, the surface of particles was rough and holey.

The internal part of the TiO_2/PS composite particle before polymer removal prepared by the swelling process with 0.1 or 0.2 ml of AcAc was compact, so the specific surface area (25.89 or 39.03 m^2/g) and pore volume (0.0832 or 0.0991 cm^3/g) were lower than those after calcination. The specific surface area, pore volume, and pore size of porous TiO_2 particles after calcination prepared by the swelling process with various amounts of AcAc were investigated by the BET measurements, as shown in Fig. 5a–c. Because TTIP was not impregnated into PS particles at a small amount of AcAc (0 or 0.02 ml) to form aggregative TiO_2 solids by themselves, the specific surface area (17.49 or 34.06 m^2/g) and pore volume (0.0791 or 0.0920 cm^3/g) of TiO_2 solids without the swelling process after calcination were very small. The swelling effect increased to advantageously form porous TiO_2 particles after calcination as AcAc amount increased, and resulted in the significant increasement in the specific surface area and pore volume of porous TiO_2 particles. When the amount of AcAc approached 0.2 ml, the specific surface area was 103.21 m^2/g and the pore volume was 0.2393 cm^3/g. Because the amount of TTIP/AcAc within PS particles was nearly saturated with a large amount of AcAc (0.2, 0.5, or 1 ml), the specific surface area and pore volume of porous TiO_2 particles were almost constants after calcination. Fig. 5c indicates that the pore size of porous TiO_2 particles significantly decreased as AcAc amount increased until the pore size was about 9 nm. According to the date of BET measurements, the porous TiO_2 particles kept large specific surface area and pore volume as AcAc amount increased, resulting in the density of particles obviously lowering as AcAc amount increased, as

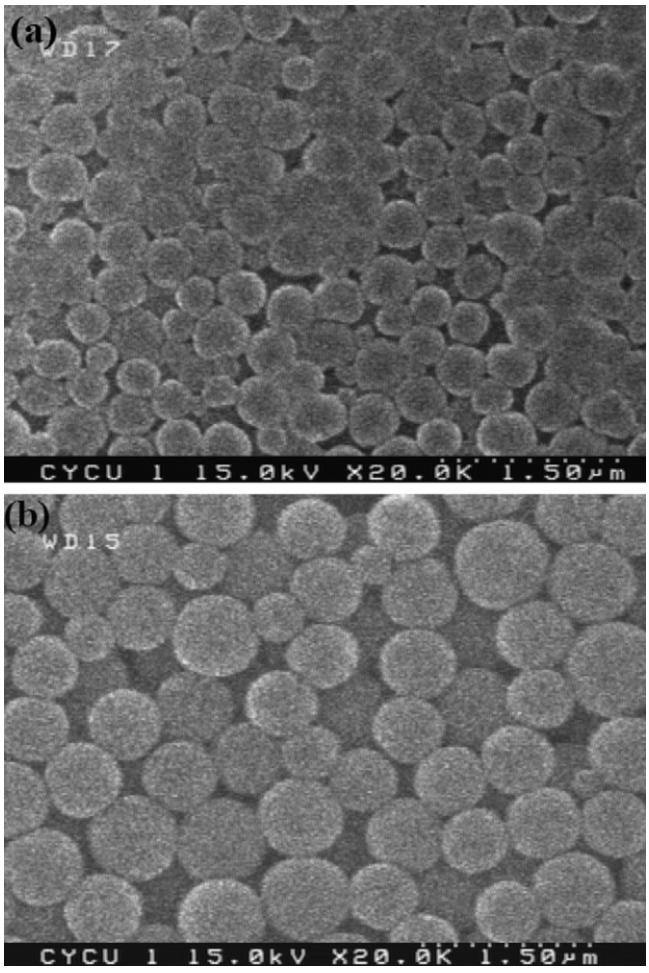

Fig. 3. SEM pictures of the TiO_2/PS composite particle prepared by a single-step swelling of 0.1 g PS template particles with (a) 0.4 ml of TTIP, 0.05 ml of AcAc and (b) 0.4 ml of TTIP, 0.1 ml of AcAc.

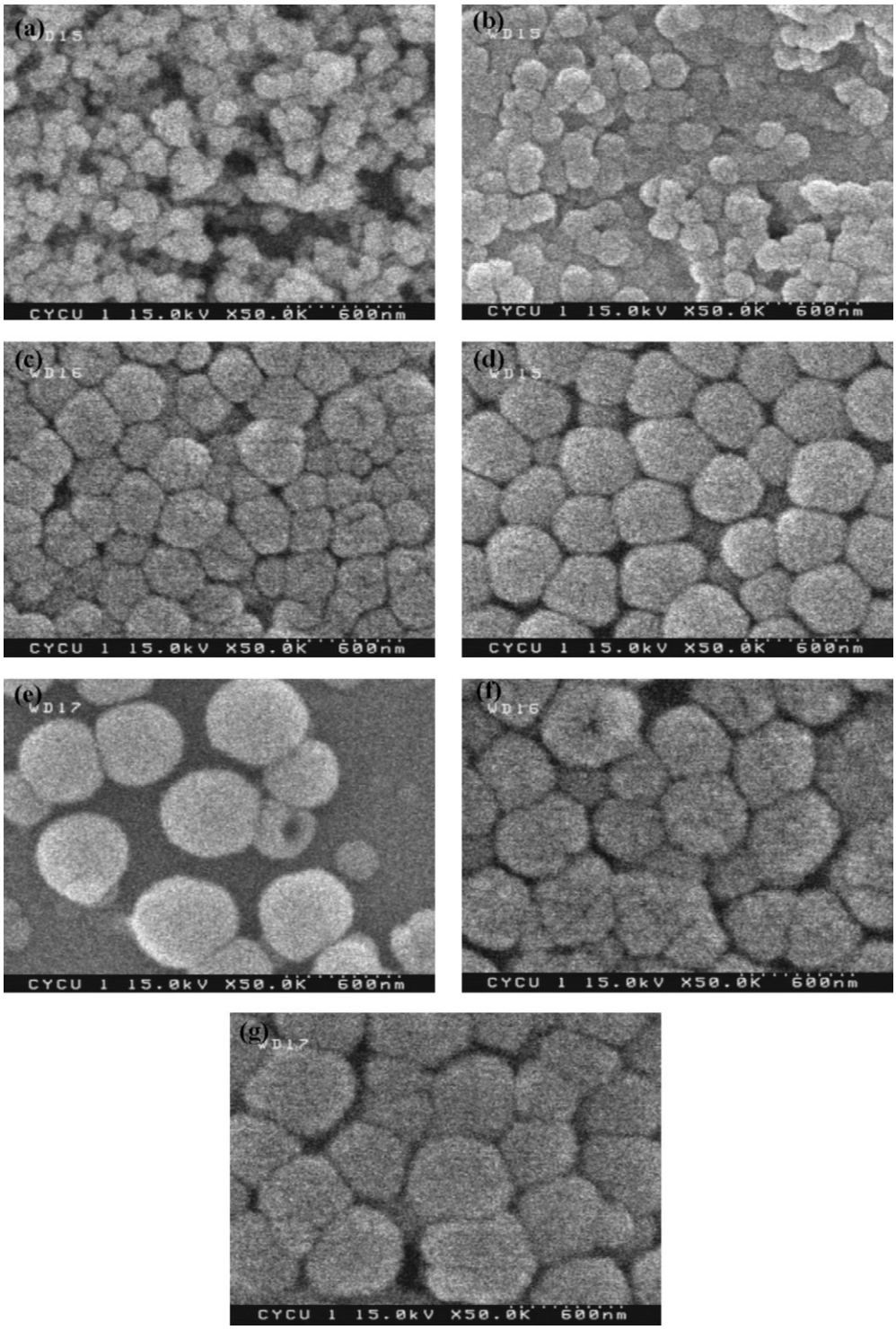

Fig. 4. SEM pictures of porous TiO_2 particles after calcination prepared by a single-step swelling of 0.1 g PS template particles with (a) 0.4 ml of TTIP, 0 ml of AcAc, (b) 0.4 ml of TTIP, 0.02 ml of AcAc, (c) 0.4 ml of TTIP, 0.05 ml of AcAc, (d) 0.4 ml of TTIP, 0.1 ml of AcAc, (e) 0.4 ml of TTIP, 0.2 ml of AcAc, (f) 0.4 ml of TTIP, 0.5 ml of AcAc, and (g) 0.4 ml of TTIP, 1 ml of AcAc.

shown in Table 1. Table 1 indicates that the density of TiO_2 solids without the swelling process (0 ml of AcAc) was 4.9781 g/cm^3 and the density of porous TiO_2 particles was 4.0093 g/cm^3 as AcAc amount reached to 1 ml.

Fig. 6 illustrates the FTIR spectrum of TiO_2/PS composite particles prepared with various amounts of AcAc (0.02, 0.1, 0.5, and 1 ml), of PS only, and of the final calcined TiO_2. The broad peaks around 800–500 cm^{-1}, which appeared to be at low spectrum energy, should be due to the envelope of the phonon bands of Ti–O–Ti bond of a TiO_2 network in Fig. 6a–d, and f.[24] Several characteristic peaks of PS template particles were found, and these peaks indicated the presence of PS in Fig. 6a–e.

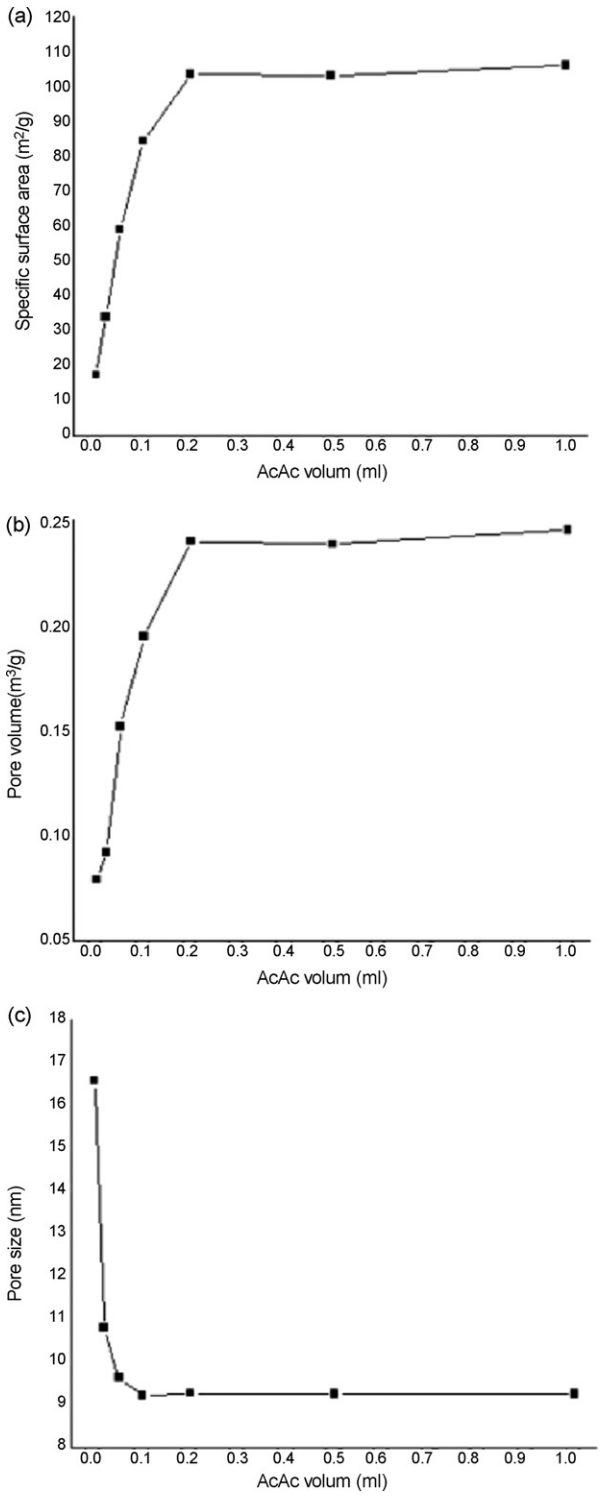

Fig. 5. BET measurements of porous TiO_2 particles after calcination prepared by a single-step swelling of 0.1 g PS template particles with 0.4 ml of TTIP, various amounts of AcAc (0, 0.02, 0.05, 0.1, 0.2, 0.5, and 1 ml). (a) specific surface area vs. AcAc amount, (b) pore volume vs. AcAc amount, and (c) pore size vs. AcAc amount.

Table 1
Influence of various amounts of AcAc (0, 0.02, 0.05, 0.1, 0.2, 0.5, and 1 ml) on the density of various porous TiO_2 particles.

AcAc amount (ml)	Density of porous TiO_2 particles (g/cm^3)
0	4.9781
0.02	4.8304
0.05	4.5765
0.1	4.3375
0.2	4.1279
0.5	4.0142
1	4.0093

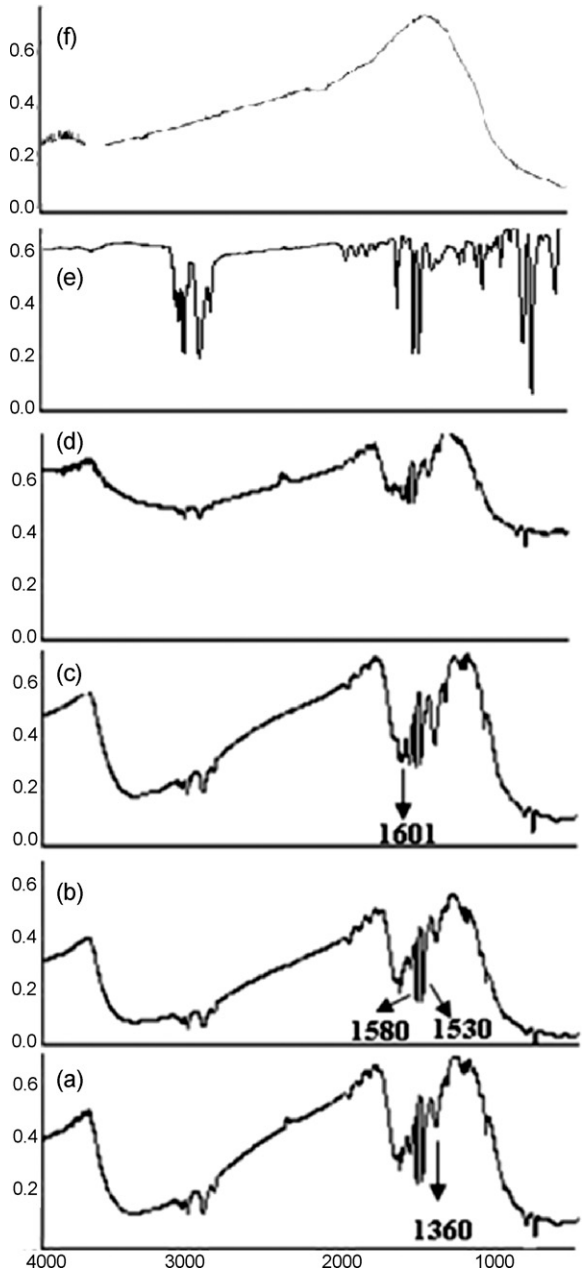

Fig. 6. FTIR spectrum of TiO_2/PS composite particles prepared with (a) 0.4 ml of TTIP, 1 ml of AcAc, (b) 0.4 ml of TTIP, 0.5 ml of AcAc, (c) 0.4 ml of TTIP, 0.1 ml of AcAc, (d) 0.4 ml of TTIP, 0.02 ml of AcAc, (e) PS only, and (f) the final calcined TiO_2.

In these cases of TiO_2/PS composite particles, the absorption peaks at 3400–3300 cm^{-1} because the stretching vibration of their hydroxyl groups and Ti–OH. A few characteristic peaks of chelating agent (AcAc) can be found in Fig. 6a–d and are described as below. A vibration band at 1601 cm^{-1} (C=O) corresponded to the enol form of AcAc bonded to Ti in Fig. 1b. When AcAc reacted with TTIP, the two sharp peaks at 1580 and 1530 cm^{-1} could correspond to AcAc chelating ligands.[25] A peak was observed at about 1360 cm^{-1} which was one of the characteristics of C–O deformation. The FTIR measurements revealed the presence of AcAc in Fig. 6a–d, and an increase in the characteristic peaks of AcAc as the amount of AcAc increased. This result also suggests that TTIP was chelated with AcAc, which slowed down the reaction of hydrolysis of TTIP to prevent all colloid solutions from precipitating fast.

The thermogravimetric analysis results of TiO_2/PS composite particles prepared with various amounts of AcAc (0.02, 0.1, and 0.5 ml), of PS only, and of the final calcined TiO_2 are shown in Fig. 7. The weight loss occurred at four temperature intervals: (1) when the temperature was below 150 °C, the weight loss was probably caused by adsorbed water and excess reagents on the grain surface and inside composite particles. (2) When the temperature was between 150 and 350 °C (about 2–5% of weight loss), the weight loss might be attributed to the decomposition of AcAc coordinated inside composite particles. (3) A steep weight loss when the temperature was between 350 and 420 °C was ascribed for the decomposition of PS polymer. (4) No weight loss was found when the temperature went over 420 °C, because of TiO_2 particles, high thermal stability. The above results of TGA obtained the weight ratios (Fig. 7) of the PS templates to the TiO_2 region of composite particles was about 1/2 and also proved the PS templates, AcAc, and excess reagents to be decomposed by heating from RT to 500 °C in the present experiment.

Fig. 8 displays the XRD experiment for two samples. Fig. 8a shows the composite particle obtained before calcination was an amorphous composite. With 500 °C calcinations, five obvious diffraction peaks, which were at $2\theta = 25.8°$, 38.2°, 47.7°, 53.3°, and 55.4°, corresponding to the TiO_2 anatase crystalline form were obtained, as shown in Fig. 8b.

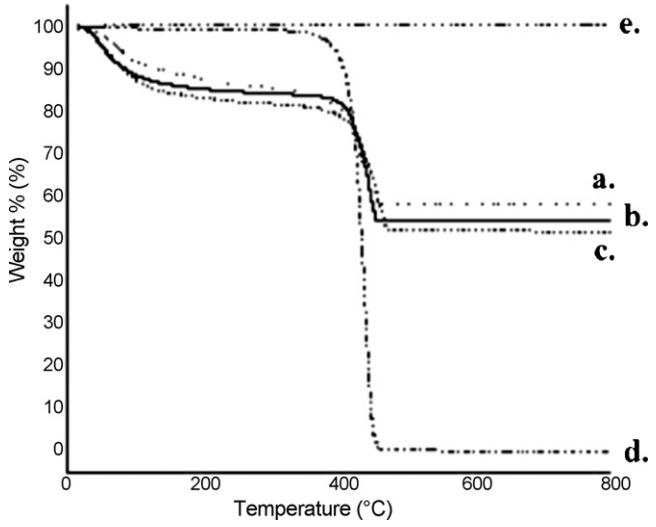

Fig. 7. TGA curves of TiO_2/PS composite particles prepared with (a) 0.4 ml of TTIP, 0.1 ml of AcAc, (b) 0.4 ml of TTIP, 0.02 ml of AcAc, (c) 0.4 ml of TTIP, 0.5 ml of AcAc, (d) PS only, and (e) the final calcined TiO_2.

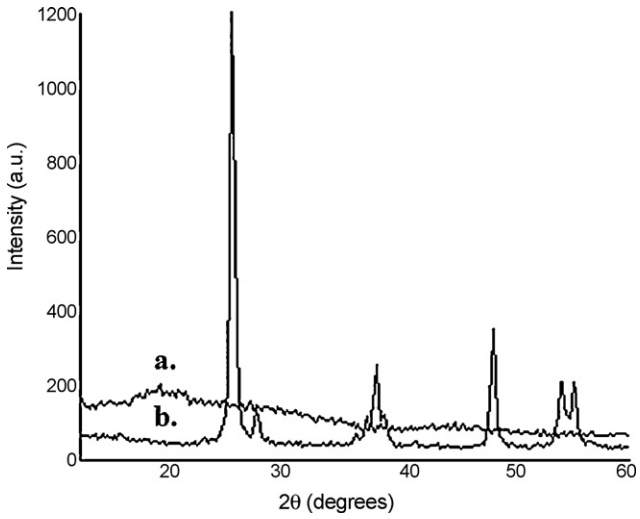

Fig. 8. XRD patterns of (a) TiO_2/PS composite particles prepared with 0.4 ml of TTIP, 0.1 ml of AcAc before calcinations, and (b) porous TiO_2 particles prepared with 0.4 ml of TTIP, 0.1 ml of AcAc after calcinations.

3.2. The effect of reaction time

Fig. 9 illustrates the SEM picture of the TiO_2/PS composite particle before polymer removal prepared with 0.4 ml of TTIP, 0.1 ml of AcAc, reacted by stirring for 8 h. The composite particle before polymer removal was bigger and smooth. Fig. 10a–e shows the influences of different reaction time on the diameter and morphology of porous TiO_2 particles. Because the reaction time (2 h) was brief, TTIP/AcAc was not complete impregnated into PS particles, resulting in the small and difform of TiO_2 particles after calcination, as shown in Fig. 10a. When the reaction time reached 4 h, the TiO_2 particles were big and spherical after calcination, as shown in Fig. 10b. Fig. 10c shows

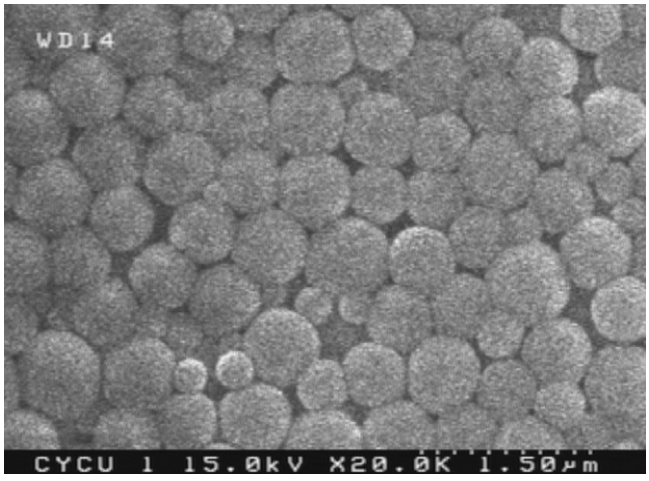

Fig. 9. SEM picture of the TiO_2/PS composite particle prepared by a single-step swelling of 0.1 g PS template particles with 0.4 ml of TTIP, 0.1 ml of AcAc, reacted by stirring for 8 h.

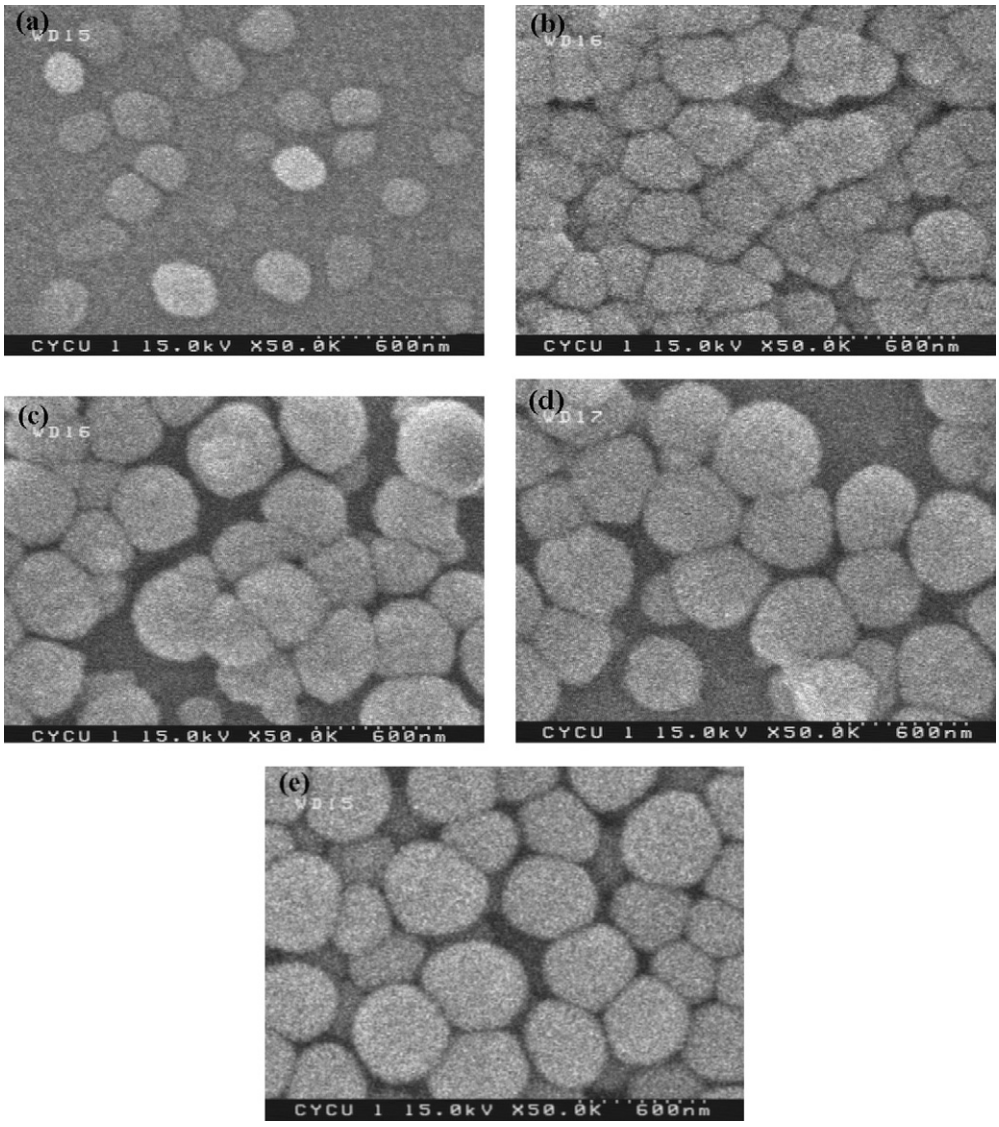

Fig. 10. SEM pictures of porous TiO_2 particles after calcination prepared by a single-step swelling of 0.1 g PS template particles with 0.4 ml of TTIP, 0.1 ml of AcAc, reacted by stirring for (a) 2 h, (b) 4 h, (c) 8 h, (d) 16 h, and (e) 32 h.

the uniform and rough TiO_2 particles after calcination, so most TTIP/AcAc was successfully impregnated into the PS particles after 8 h. Compared with Fig. 10c, the diameters and morphology of TiO_2 particles after calcination were almost invariable as the reaction time (16, and 32 h) increased, as clearly shown in Fig. 10d and e. After increasing the reaction time, the amount of TTIP/AcAc diffused into PS particles also increased, resulting in the larger size of porous TiO_2 particles. The above results indicated that: (1) TTIP/AcAc was impregnated into PS particles gradually as the reaction time went from 2 to 8 h. (2) The amount of TTIP/AcAc within PS particles was nearly saturated as the reaction time went from 8 to 32 h, and the morphology became invariable.

From the BET measurements of Fig. 11a–c, the influences of different reaction time on the specific surface area, pore volume, and pore size of porous TiO_2 particles were explored. Because TTIP/AcAc was not completely impregnated into PS particles when the reaction time (2 h) was brief, the specific surface area (34.43 m^2/g) and pore volume (0.0890 cm^3/g) of porous TiO_2 particles after calcination were very low. TTIP/AcAc within PS particles was blended well as reaction time increased and caused the increases of the specific surface area and pore volume of porous TiO_2 particles. When the reaction time reached 8 h, the specific surface area was 84.13 m^2/g and the pore volume was 0.1940 cm^3/g. The specific surface area and pore volume of

Table 2
Influence of different reaction time (2, 4, 8, 16, and 32 h) on the density of various porous TiO_2 particles.

Reaction time (h)	Density of porous TiO_2 particles (g/cm^3)
2	4.9638
4	4.5152
8	4.3375
16	4.2782
32	4.1944

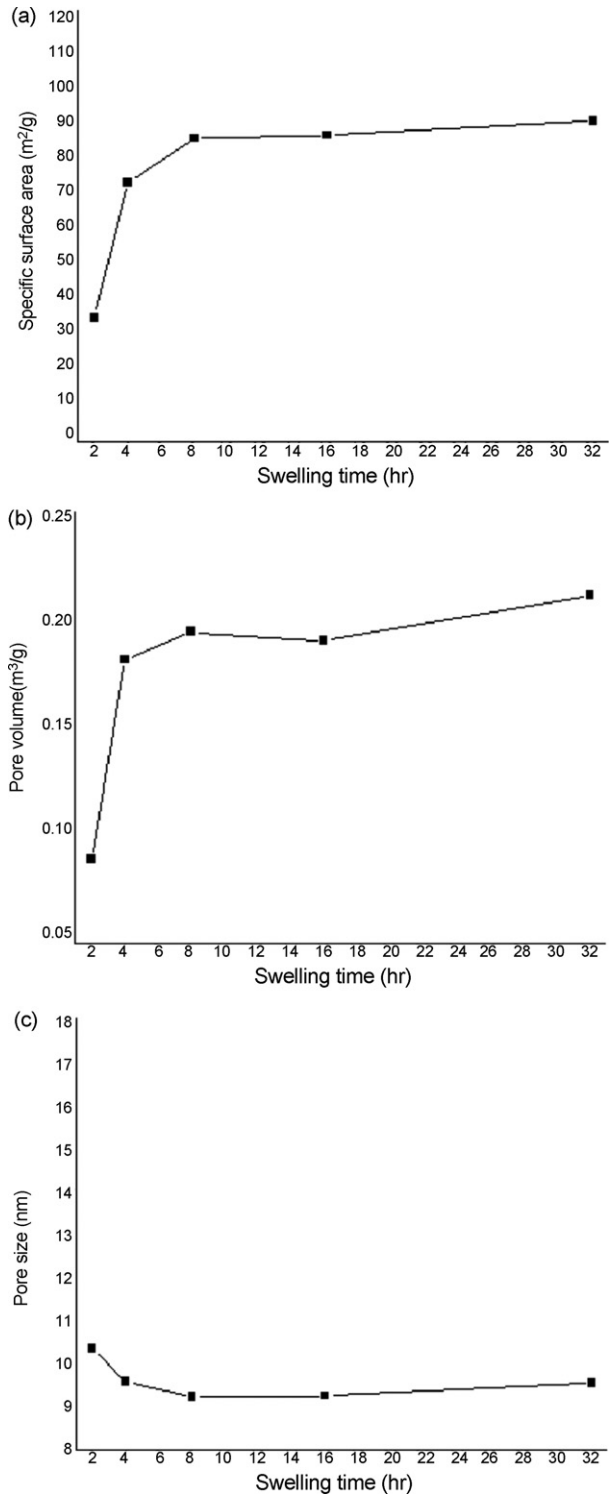

Fig. 11. BET measurements of porous TiO_2 particles after calcination prepared by a single-step swelling of 0.1 g PS template particles with 0.4 ml of TTIP, 0.1 ml of AcAc, reacted by stirring for different reactions.

porous TiO_2 particles were almost constants when the reaction time (8, 16, and 32 h) was long. The above results indicated that TTIP/AcAc within PS particles was nearly saturated and blended well as the reaction time went over 8 h. Fig. 11c shows that the pore size of porous TiO_2 particles was about 9–10 nm. The BET results demonstrate that TiO_2 particles with large specific surface area and pore volume were obtained as reaction time increased, and Table 2 shows the density of porous TiO_2 particles lowered obviously as reaction time increased. The density went from 4.9638 to 4.1944 g/cm^3 as the reaction time went from 2 to 32 h.

4. Conclusion

The present study was to prepare controlled porous TiO_2 particles of narrow particle size distribution by the swelling process, using AcAc modified TTIP as a precursor, and AcAc amount and reaction time of the swelling process were examined and discussed. SEM pictures show that TTIP/AcAc was successfully impregnated into the PS template particles when AcAc amount was over 0.1 ml and reaction time reached 8 h. And then after calcination rough and porous TiO_2 particles were formed. With the size measurements of the porous TiO_2 particles, it is indicated that there was an obviously increase in the diameter of particles as AcAc amount and reaction time increased. The porous TiO_2 particles, specific surface area and pore volume remained large and density remained low as AcAc amount and reaction time increased. Subsequently, the FTIR measurements show that TTIP was instantly chelated with AcAc forming Ti–AcAc to control hydrolysis rate and an increase in the characteristic peaks of AcAc as the amount of AcAc increased. From the result of TGA, it was obtained that the weight ratios of the PS templates to the TiO_2 region of composite particles was about 1/2, and also proved that the PS templates, AcAc, and excess reagents would be decomposed at 500 °C.

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