Preparation of highly crystalline mesoporous TiO$_2$ by sol–gel method combined with two-step calcining process

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ABSTRACT
Mesoporous TiO$_2$ samples, with large specific surface area and high crystallinity, were prepared by a sol–gel method using polyethylene glycol and polyacrylamide (PAM) as composite templates and by two-step calcining process (at 500—700 °C in nitrogen and 500 °C in air). As a comparison, the sample was prepared using same composite templates by one-step calcining process (at 500 °C in air). The samples were characterised by X-ray diffraction, transmission electron microscopy, N$_2$ adsorption-desorption, and diffuse reflectance UV-visible absorption spectra. The results showed that when the samples were fabricated using two-step calcining process, they exhibited typical mesoporous structure, large specific surface area, and high crystallinity. The properties of samples were studied. The results showed that PAM accelerates gel rate. The crystallinity and specific surface areas of samples were increased by using two-step calcining process. Compared with the sample prepared using one-step calcining process, the visible light absorption of samples synthesised by the two-step calcining process was improved.

KEYWORDS
Mesoporous TiO$_2$; composite templates; two-step calcining; high crystallinity; visible light absorption

1. Introduction
Mesoporous TiO$_2$ materials have attracted much attention in recent years,[1–5] since Antonelli and Ying first reported the synthesis of mesoporous TiO$_2$ (named as Ti-TMS1) in 1995.[6] Mesoporous TiO$_2$ materials have been synthesised via several approaches for immense potential applications in photocatalysis, sensors, and electrode materials because of its catalytic, optical, and electronic properties, especially in photocatalytic application.[7–12] However, the practical application of mesoporous TiO$_2$ is still limited because it only absorbs UV light in solar spectrum. Many studies suggest that the photocatalytic activity depends on the amount of electrons and holes on the surface of the photocatalyst in the reaction.[13–15] In addition, the small grain size leads to a shorter distance for the electrons and holes to transfer to the photocatalytic reaction sites, and many other factors, so efforts should be made to increase the specific surface area and decrease the grain size, thus improving photocatalytic activity.
Mesoporous TiO$_2$ is synthesised by sol–gel method which is simple to handle,[16,17] but the traditional methods still have some disadvantages such as tedious preparation cycle, and mesoporous TiO$_2$ synthesised by this method has low crystallinity because of low calcining temperature. Nevertheless, many applications can only be maximised in the highly crystalline state. For example, when mesoporous TiO$_2$ is applied in photocatalysis, the amorphous regions are known to be trap sites for the recombination of photo-excited electrons and holes.[3,18–21] Despite many efforts, up until today it remains a large challenge. Recently, Lee et al. reported a new method in which an amphiphilic diblock copolymer, poly (isoprene-block-ethylene oxide), was used as the template to synthesise mesoporous TiO$_2$, which was calcined in Ar atmosphere first and subsequently recalcined in air atmosphere. The mesoporous TiO$_2$ prepared by this method has high crystallinity and large surface area.[22] However, the cost of the template and Ar is expensive in this method, and the experimental procedure is tedious, limiting the application of the method.

In our previous work, we used composite templates by sol–gel method combined with two-step calcining process to synthesis mesoporous TiO$_2$.[23–25] In this study, we have used polyacrylamide (PAM) and polyethylene glycol (PEG) as composite templates to fabricate mesoporous TiO$_2$ samples with large specific surface area and high crystallinity by sol–gel method combined with two-step calcining process (500–700 °C in nitrogen and 500 °C in air). The crystallinity, crystallite size, and other properties of the samples are studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), N$_2$ adsorption–desorption, and UV-visible (UV-Vis) diffuse reflectance spectra. The synthesis mechanism of high crystalline mesoporous TiO$_2$ by sol–gel method combined with two-step calcining process was also studied.

2. Experimental

2.1. Synthesis of the mesoporous TiO$_2$

A fast sol–gel preparation of the mesoporous TiO$_2$ was performed as follows. Fifteen millilitre deionised water and 8 mL nitric acid (5%) dissolved in 300 mL absolute ethanol were added in 10 mL tetrabutyl titanate. After the mixture was stirred at ambient temperature for about 1 h, the resultant solution was slowly added to the mixture of PAM (Mw = 3,000,000, a series of mass) and 3 g of PEG dissolved in 30 mL of deionised water under vigorously stirring. A white gel was formed and dried at 80 °C for 10 h. The obtained light yellow powder was calcined at 500–700 °C in nitrogen, and then recalcined at 500 °C in air. The gotten samples were defined as A-TiO$_2$. For comparison, the sample was prepared using same composite templates by one-step calcining process (at 500 °C in air), which was defined as B-TiO$_2$.

2.2. Methods of measurement and characterisation

The analyses of thermogravimetry – differential scanning calorimeter (TG–DSC) were performed using a SDT Q600 V 8.0 Build 95 instrument. The dry xerogel powders were heated from 25 to 800 °C in air at a scan rate of 5 °C/min, and observed mass loss was attributed to the quantitative pyrolysis of the polymer temple component. XRD patterns
of the photocatalysts were recorded at ambient temperature by a Bruker D8 Advance X-ray diffractometer (Cu Ka radiation, λ = 1.5406 Å) operated at 40 kV and 100 mA) and a 2θ scan rate of 2°/min. The crystalline size was estimated by applying the Scherrer equation. N2 adsorption–desorption isotherms were collected on an AUTOSORB-1 N2 adsorption apparatus at −196°C and all samples were degassed at 120°C for 2 h. TEM was recorded on a JEM-2100F made in Japan. Diffuse reflectance UV-vis absorption spectra of the powder samples were obtained using a Shimadzu-2501 spectrophotometer. BaSO4 was the reference sample, and the spectra were recorded in the range of 200–900 nm.

3. Result and discussion

3.1. The synthesis mechanism

Figure 1 shows the synthesis mechanism of mesoporous TiO2 using composite templates by sol–gel method combined with two-step calcining process. Sol–gel method is conducted by using tetrabutyl titanate as Ti source, and PAM and PEG as composite templates. The self-assemble reaction between the composite templates and tetrabutyl titanate is as follows.[26,27] Due to its strong hydrophilicity, PEG readily combines with the titania sol obtained from the hydrolyzation to form composite grains which are incorporated with PAM by hydrogen bonding. The above prepared precursor was calcined at 500–700°C in nitrogen first. Because of its low thermostability, PEG is readily decomposed and carbonised to form amorphous carbon which will be filled in the samples and support around pore to prevent the mesostructure from collapsing due to rising temperature, which is beneficial to enhancing crystallinity of the samples. Then the samples are recalcined at 500°C in air. The amorphous carbon and PAM are

Figure 1. The synthesis mechanism of mesoporous TiO2 by composite templates using two-step calcining process.
removed, leaving a large number of pores. As a result, mesoporous TiO₂ with high crystallinity and large specific surface area is successfully synthesised.

3.2. TG–DSC analysis

The TG–DSC curve of as-prepared xerogel is carried out to test if the volatiles and the composite templates have escaped after calcination. In Figure 2, the TG curve is shown as curve (a) and the DSC curve as curve (b). Curve (a) shows that there exists about 30% of weight loss below 220 °C, which is caused by the volatilisation of residual solvents covering on the xerogel. It is evaluated in curve (a) that 28% of weight loss happened in the range of 220–400 °C, being consistent with the strong peak at 338 °C in curve (b), which is due to the decomposition of the most of PEG and some of PAM in the composite of xerogel. It is notable that there is 2% of weight loss between 500–600 °C, which is correspondence with the peak at 575 °C in curve (b). This may be ascribed to the decomposing of the residual PAM which shows higher thermostability.

3.3. The gel rate

Figure 3 shows gel rate varied with different mass of PAM. It can be seen that the gel time decreases sharply with the increase of mass of PAM, indicating the high gel rate. It is mainly based on following reasons. First, when PH is 3–4, amide of PAM will transform into quaternary ammonium groups, which combine with the large number of hydroxyl groups with strong electronegativity on the surface of TiO₂ colloid particles by intermolecular forces. Second, for PAM, oxygen atom forms p-π-conjugated structure with nitrogen atom of the amide group, reducing attraction of nitrogen atom to the two hydrogen atoms near it, which lead to the formation of hydrogen bonds of hydrogen atoms with the hydroxyl groups on the surface of TiO₂ colloid particles. Thereby PAM plays a similar role like colloidal nucleus to make TiO₂ colloid particles aggregated so that it accelerates gel rate. Therefore, we can adjust the gel rate by controlling the mass of PAM. However, the TiO₂ sol particles will be conglutate seriously with much of PAM adding, leading to the poor mesoporous structure. We adopted the eclectic mass with 0.05 g.

![Figure 2. TG–DSC curve of the xerogel of TiO₂ sample.](image-url)
3.4. Crystallinity

Figure 4 shows the XRD patterns of samples. The narrow and pointed diffraction peaks in the figure show that the crystallinity of all the samples is relatively high.\textsuperscript{[23,24]} It is obvious that the crystallinity of three A-TiO\textsubscript{2} samples is higher than that of the B-TiO\textsubscript{2} sample. The A-TiO\textsubscript{2} sample calcined at 700/500 °C in nitrogen/air has the most narrow and pointed diffraction peaks, meaning its highest crystallinity. The crystallinity of sample calcined at 600/500 °C takes second place and that of sample calcined at 500/500 °C is lowest, which verifies that crystallinity of the samples increases with temperature increasing. The crystallinity of B-TiO\textsubscript{2} sample is lower than that of A-TiO\textsubscript{2} sample calcined at 500/500 °C, which is because the heating time of latter is longer. From the above, the crystallinity of samples is enhanced by two-step calcining process.

Figure 3. Gel time at different mass of PAM.

Figure 4. The XRD patterns of three A-TiO\textsubscript{2} samples calcined at the temperatures of (a) 700/500 °C; (b) 600/500 °C; (c) 500/500 °C; and (d) B-TiO\textsubscript{2} sample.
3.5. Crystallite size

As shown in Table 1, the average crystallite sizes of samples is about 7–12 nm, based on the XRD results calculated by Scherrer equation. For A-TiO₂ samples, the crystallite size of the sample using PEG (Mw = 20,000) is the largest, and that of the sample using PEG (Mw = 6000) is smallest. The reason is that with PEG adding, critical micelle concentration (CMC) of composite grains in solution formed by PEG combining with TiO₂ sol particles by self-assembly methods will be lower,[28,29] which is more obvious for larger molecular weight of PEG due to its longer molecular chain. When PEG (Mw = 20,000) is added, the concentration of composite grains is above CMC, PEG molecular will combine with sol particles easily to increase the chance of collisions between sol particles, so the crystallite size of the sample increases. However, when PEG (Mw = 1000) is added, the concentration of composite grains is lower than CMC, the effect of which connecting with colloidal particles is not obvious, so the crystallite size of the sample is smaller.

3.6. Pore size and specific surface area

Figure 5 shows N₂ adsorption–desorption hysteresis loops of samples. Adsorption isotherms of all A-TiO₂ samples are type IV. Hysteresis loops appearing in medium pressure

| Samples | Molecular weight of PEG | Crystallite size (nm) |
|---------|-------------------------|-----------------------|
| B-TiO₂  | 1000                    | 9.52                  |
| A-TiO₂  | 20,000                  | 11.21                 |
| A-TiO₂  | 6000                    | 9.75                  |
| A-TiO₂  | 1000                    | 7.64                  |

Figure 5. N₂ adsorption–desorption hysteresis loops of three A-TiO₂ samples using PEG of different molecular weights: (a) Mw (PEG) = 1000; (b) Mw (PEG) = 6000; (c) Mw (PEG) = 20,000; and (d) B-TiO₂ sample.
zone (0.4 < P/P0 < 0.8) indicate that there exists either microporous structure or large particles aggregating in the sample, meaning that samples keep very good in mesoporous structure. While hysteresis loop of B-TiO2 sample is different from the others and it extends from medium to high pressure zone (0.6 < P/P0 < 0.9), meaning that the sample does not show homogeneous mesoporous and even exhibits macropore structure which is not benefit to its properties. Figure 6 shows Barret—Joyner—Halenda (BJH) pore size distribution plots calculated from the adsorption isotherms. Table 2 shows the data of Brunauer—Emment—Teller specific surface areas as well as BJH pore sizes of samples. It can be seen from Figure 6 and Table 2 that the average pore size of A-TiO2 samples remains at 16.9 nm.

While the average pore size of B-TiO2 sample is about 44.3 nm, it is caused by some macropore structure existing in the sample, which is consistent with the analysis of hysteresis loop in Figure 5. The specific surface areas of A-TiO2 samples shown in Table 2 are large and increase slightly with the different molecular weights. As contrast, the specific surface area of B-TiO2 sample is only 78.51 m²/g, which is far smaller than the former. For B-TiO2 sample, when it is calcined directly in air, composite template will decompose easily without leaving amorphous carbon to prevent the pores as a result of disappearing of composite template, [30–32] then some pores collapse, causing inhomogeneity structure and small specific surface area.

Figure 6. Pore distribution of mesoporous TiO2 using PEG of three A-TiO2 samples using PEG of different molecular weights: (a) Mw (PEG) = 1000; (b) Mw (PEG) = 6000; (c) Mw (PEG) = 20,000; and (d) B-TiO2 sample.

Table 2. Pore structure parameters of A-TiO2 samples using PEG of different molecular weights and B-TiO2 sample.

| Sample   | Molecular weight of PEG | Specific surface area (m²/g) | Pore size (nm) |
|----------|-------------------------|------------------------------|---------------|
| B-TiO2   | 1000                    | 78.51                        | 44.32         |
| A-TiO2   | 20,000                  | 102.72                       | 16.93         |
| A-TiO2   | 6000                    | 104.25                       | 16.92         |
| A-TiO2   | 1000                    | 110.73                       | 16.80         |
3.7. TEM analysis

Figure 7 shows the TEM micrographs of A-TiO\textsubscript{2} samples. Figure 7(a,b) shows that samples have typical mesoporous structure like wormhole, being random and disorder in pores’ arrangement, and TiO\textsubscript{2} nanocrystals are embedded into the mesoporous frameworks. The average pore sizes are about 17.0 nm, which verifies the consequence of N\textsubscript{2} adsorption—desorption H\textsubscript{2} hysteresis loops. As is seen HRTEM micrograph in Figure 7(c), the average interplanar space of the sample is 0.35 nm by measuring lattice fringes. The grain size is about 9.5 nm, which are agreement with the results of Table 1. Selected area electron diffraction (SAED) pattern in the TEM image shows a series of diffraction rings, being consistent with the crystal structure of mesoporous material.[3] (Figure 7(d)).

3.8. UV-Vis diffuse reflectance spectra

The UV-Vis diffuse reflectance spectra of samples are shown in Figure 8. Compared with B-TiO\textsubscript{2} sample, the absorption intensity of A-TiO\textsubscript{2} samples is higher in the visible region, exhibiting a little red-shift. It may be because that little carbon leaving by composite templates during calcination procedure is doped into TiO\textsubscript{2} lattice. In consequence, 2p orbital of carbon atom overlaps with 2p orbitals of oxygen atom, forming new valence band
which migrates towards conduction band to narrow forbidden band.[33,34] The absorption intensity in visible region of A-TiO₂ samples improves with increasing of molecular weight of PEG. The reason is that it is more difficult to remove carbon absolutely for PEG with longer molecular chains.

4. Conclusions

The mesoporous TiO₂, with high crystalline and large surface area, was fabricated by using a fast sol–gel method combined with two-step calcining process, in which PAM and PEG were used as composite templates. PAM accelerated gel rate. When calcined in nitrogen, PEG converts to amorphous carbon, which prevents mesostructure from collapsing when it is heated to the temperature required to get high crystallinity, and specific surface area of A-TiO₂ samples increased using two-step calcining process. Besides, compared with the sample synthesised using one-step calcining process, the absorption intensity of the samples prepared by the two-step calcining process is higher in the visible region.

Disclosure statement

No potential conflict of interest was reported by the authors.

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