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# Optimization of the preparation methods
# Synthesis of mesostructured $TiO_2$ with high photocatalytic activities

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## Abstract

Using a triblock copolymer surfactant as a template, mesostructured $TiO_2$ was prepared under completely different conditions. Properties of the prepared samples were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption and desorption isotherms, and absorption spectra. The results showed that hydrothermal treatment was in favor of formation of channels with higher order and crystallinity. The removal of the template by refluxing the prepared samples in an EtOH/$H_2O$ solution was superior to that of calcination. The photocatalytic activity of the prepared samples was also investigated by using methylene blue (MB) solutions as modal pollutants. For comparison, Degussa P25 powder was made as a reference catalyst. It was found that the prepared samples had higher photocatalytic activity than Degussa P25.

*Keywords:* Mesostructured $TiO_2$; Photocatalytic activity; Absorption spectra

## 1. Introduction

Since researchers at Mobil discovered MCM-41 [1,2] in 1992, the first example of a well-ordered mesoporous material, there has been a great deal of interest in extending this class of materials to transition metal oxide analogues [3] due to the potential application of mesoporous transition metal oxides with ordered pore structures in catalysis [4–6], separation technology [7–9], polymerization [10] and nanoelectronics [11]. To date, various mesoporous transition metal oxides have been successfully synthesized using various strategies [12–16]. In most of the studies, ionic [17–19] and neutral [20–23] surfactants, e.g. phosphates, sulfates, carbonates and primary amines surfactants, have been employed as templates, which direct the mesophase formation on the basis of the electrostatic and hydrogen bonding interactions, respectively. However, after the calcinations to remove the template, these oxides lost their structural order or showed lower surface area than expected from that of corresponding mesoporous silica.

Recently, block copolymers have been increasingly used to organize mesostructured composite solids, because the architectures of the amphiphilic block copolymers can be rationally adjusted to control the interactions between the inorganic and organic species, self-assembly and especially processibility more than possible with low-molecular-weight surfactants.

Mesoporous $TiO_2$ was first prepared using a phosphate surfactant through a modified sol–gel process by Antonelli and Ying [13] in 1995. It is well known that the effectiveness of titania as a photocatalyst is very sensitive to its crystal phase, particle size, crystallinity, specific areas and pore structure and the mesoporous $TiO_2$ prepared using phosphate surfactants has low photocatalytic activity because phosphorous from the template was bound so strongly to the meso-

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porous $TiO_2$ that it could not be removed completely by either calcinations or solvent extraction. The synthesis of mesostructured $TiO_2$ materials with high photocatalytic activity is desirable.

Calcination of the as-synthesized mesoporous $TiO_2$ at high temperature is essential for the crystallization of titania in the channel wall. However, damage to the integrity of the mesoporous structure will take place upon calcinations at high temperature, thus the preparation of mesoporous $TiO_2$ with well-ordered channel walls and high photocatalytic activities still have challenges.

In this paper, we improved the traditional sol–gel method, and used multi-step crystallization and hydrothermal treatment to have successfully synthesized high-ordered mesoporous $TiO_2$ with crystalline channel walls respectively. The mesostructured $TiO_2$ prepared have showed higher photocatalytic activity than Degussa P25. It is expected that such kind of mesostructured $TiO_2$ may make a breakthrough in the application of photocatalysis.

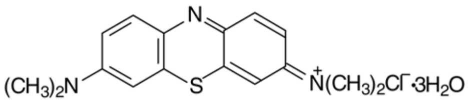
## 2. Experimental

### 2.1. Materials

Block copolymer $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ ($M_{av} = 5800$, designated $EO_{20}PO_{70}EO_{20}$, Pluronic P123) was received from Aldrich and used without further purification. Titanium butoxide ($M = 340.36$, $Ti(OC_4H_9)_4$, TBT), acetyl acetone ($M = 100.12$, $CH_3COCH_2COCH_3$, AcAc) were also commercially available. Degussa P25 (average particle size 30 nm and specific surface area of 50 $m^2\,g^{-1}$) was used as reference and used as received. A cationic dye, methylene blue (MB), was purchased from Beijing Chemical Factory and used as received. Its structure is given in Scheme 1. All the other chemicals used in the experiments were analytical grade reagents. Doubly distilled deionized water was used for solution preparation.

### 2.2. Experimental methods

In a typical preparation, 5 g of titanium butoxide was dissolved in 10 mL absolute ethanol and 1 mL acetyl acetone before 5 mL distilled water was added, followed by stirring for another 5–6 h. In a separate beaker, 3 g of Pluronic P123 was dissolved in 20 mL ethanol and 50 mL 2 mol $dm^{-3}$ HCl solution. After stirring for 3 h, this surfactant solution was slowly added to the titanium butoxide solution. Then the resulting solution was divided into two parts.



Scheme 1. Structure of dye MB.

The first approach to the synthesis of mesostructured $TiO_2$: one part solution was subsequently kept at room temperature with continuous stirring for several days. The obtained solid product was washed and centrifuged three times using distilled water and then crystallized step by step at 80 °C for 24 h, 120 °C for 24 h and 180 °C for 5 days. The dried powder was calcined at 500 °C for 6 h in air using an alumina boat to remove the surfactant (sample code TA).

The second approach to the synthesis of mesostructured $TiO_2$: the rest part of the solution was subsequently kept at room temperature with continuous stirring for 24 h, then transferred into a 100 mL Teflon-lined stainless steel autoclave. The hydrothermal treatments were conducted at 120 °C for 48 h. The product obtained was filtered, washed three times with deionized water and alcohol, and then dried at 80 °C. The surfactant was removed by refluxing in $EtOH/H_2O$ molar ratio of 1:1 for 3 days (sample code TH).

### 2.3. Characterization

Transmission electron microscopy (TEM) was performed with a Philips Tecnai 20 microscope operating at 120 kV. The TEM samples were prepared by dipping an alcohol suspen-

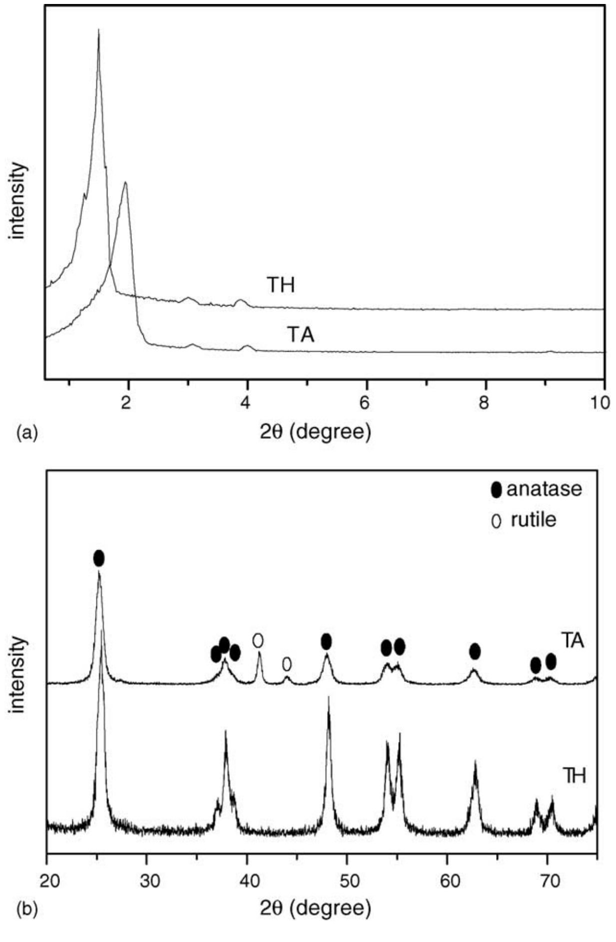


Fig. 1. XRD patterns of as-synthesized mesoporous $TiO_2$: (a) low-angle and (b) wide-angle.

sion of sample powders on a Formvar coated copper grid and dried at room temperature. X-ray powder diffraction (XRD) patterns were measured using Rigaku DMAX-2000 X-ray diffractometer with the Cu Kα radiation ($\lambda = 1.54056$ Å) at a scan rate of 0.02°/s. The samples for XRD were supported on glass substrates. Nitrogen adsorption and desorption isotherms were obtained with a Micromeritics ASAP 2000 system after the samples were vacuum-dried at 473 K overnight.

### 2.4. Adsorption study

All experiments were conducted in the darkness. A detailed procedure is as follows: the fixed amount of $TiO_2$ sample powder was dispersed in the aqueous solution containing MB (with a concentration of $1.8 \times 10^{-5}$ mol dm$^{-3}$). After electromagnetic stirring for 3 h, dispersions were centrifuged and measured immediately. Here, the dye adsorption got to saturation. Absorption spectra were recorded on a Shimadzu UV-1601 UV–vis spectrometer. For comparison, Degussa P25 powder was made as a reference. The dye solution without $TiO_2$ sample powder was made as a blank.

### 2.5. Photocatalytic experiments

All the photoreactions were carried out in a home-built photochemical reactor described previously [24]. A total of 0.04 g sample powder was dispersed in 40 mL of solution containing the dye at a desired concentration, and the pH of the system was adjusted using 0.1 mol dm$^{-3}$ HCl. The mixture was stirred ultrasonically for about 30 min to obtain well-distributed $TiO_2$ powder, then electromagnetic stirring not less than 2 h to make absorption got to saturation. Above experimental procedures were conducted in the darkness. The dispersion was irradiated with a 300 W high-pressure mercury lamp ($\lambda > 330$ nm) with continuous stirring and $O_2$ bubbling (approximately 0.5 dm$^{-3}$ min$^{-1}$), cooling was provided by cold water. At the desired irradiation times, 4 mL dispersions were sampled and centrifuged immediately. The solutions were used for analysis. Absorption changes caused by irradiation were measured on a Shimadzu UV-1601 UV–vis

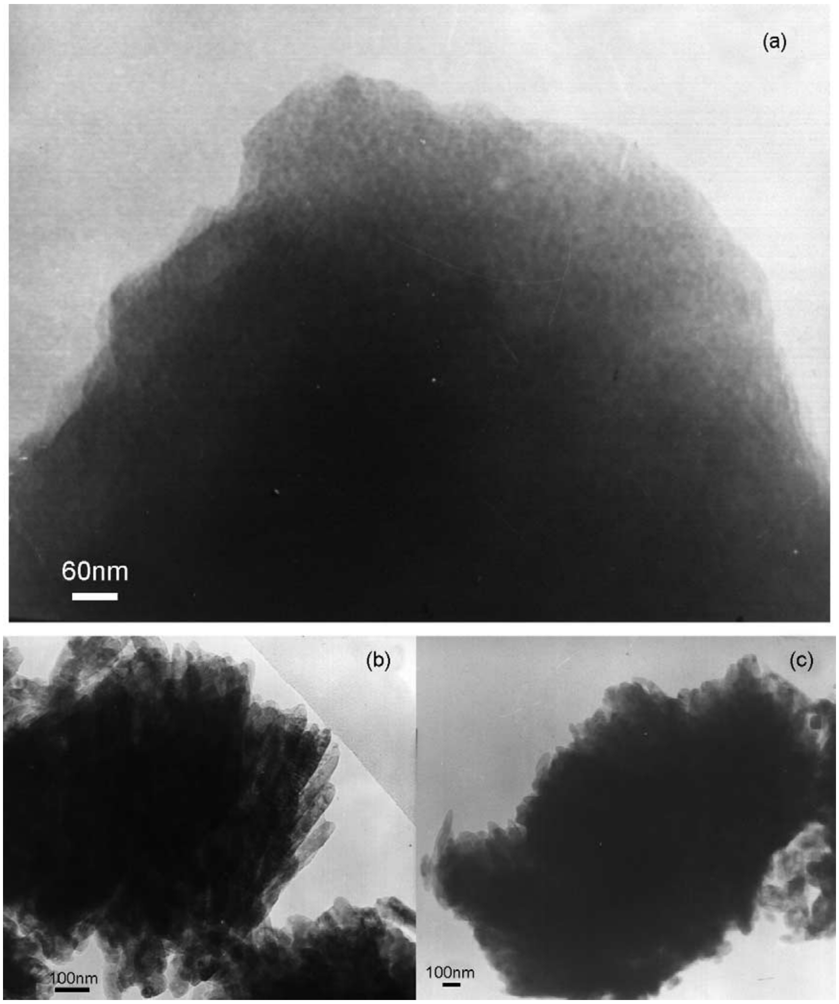


Fig. 2. TEM images of as-synthesized mesoporous $TiO_2$ (a) prepared from the first method and (b, c) prepared from the second method.

spectrometer. For comparison, the dye solution was also photolyzed in the presence of Degussa P25 powder under the same conditions.

## 3. Results and discussion

### 3.1. Characterization of mesostructured $TiO_2$

Fig. 1 showed X-ray diffraction (XRD) patterns of the prepared products. The products obtained from two methods both showed a sharp diffraction peak at low angle (Fig. 1a), which was the characteristic of a mesostructured material [25]. TEM images indicated that the products were indeed mesoporous (shown in Fig. 2). The presence of the diffraction peak was attributed to the order of the channels of mesostructured $TiO_2$. In addition to the major peak due to the (1 0 0) reflection, small peaks due to the (1 1 0) and (2 0 0) reflections were also observable. The average *d*-spacings of the products were 5.2 and 7.6 nm, respectively, as calculated from the positions of the XRD peaks, which were also consistent with the results determined from the TEM micrographs. Wide-angle XRD patterns (Fig. 1b) showed that the as-synthesized mesoporous $TiO_2$ was crystalline and had different phase composition. However, from XRD patterns and TEM images, it could be seen clearly differences between the samples obtained from two different methods. The samples prepared from the second approach (TH) showed stronger in the intensity and sharpness of the diffraction peaks than that of the first approach (TA), which corresponded to the higher-order and crystallinity of the channels. All the diffraction peaks of the sample TH can be readily indexed to anatase phase, which are in good agreement with the literature values (JCPDS No. 21-1272). But compared to the sample TH, the sample TA contained another two impurity diffraction peaks at around 41.2° and 44.0°. We consider that the rutile phase shows the peaks due to the (1 1 1) and (210) reflections at 41.2° and 44.0°, so we conclude the sample TA maybe contains a few rutile phase. And the samples prepared from two experimental methods displayed different morphology as shown in Fig. 2. This mainly attributed to the different synthesizing conditions. Above analysis results indicated that hydrothermal treatment is superior to general ageing approach. The channel walls of the mesoporous oxides can be successful crystallized at the relatively low hydrothermal treatment temperature and short treatment time. The method of removal of the template is also a significant factor. In our experiments, we found that there is a considerable increasing in the intensity and sharpness of the XRD patterns of the samples after the removed of template by reflux in EtOH/$H_2O$ mixture at suitable pH, as compared to the XRD patterns of the samples which the template was removed by calculation. This suggested that there is loss of structure and reduction in crystalline domain size on calcinations more than on reflux with solution. As well known, the major challenge to obtain mesoporous oxides is to well preserve the mesoporous structures during the templates being removed. So it is concluded that the solvent extraction method to remove templates was superior to the calcination method based on the results of XRD patterns in the present work. It could also be expected that adjustments of some of the synthesizing conditions may lead to a successful result for the aim.

The nitrogen adsorption–desorption isotherms of as-synthesized mesoporous $TiO_2$ and Barrett–Joyner–Halenda (BJH) pore size distribution analysis in the adsorption branch of the isotherm were shown in Fig. 3. The results indicated that the samples prepared from two experimental methods showed a large H1-type hysteresis loop at high relative pressure, which is related to the capillary condensation associated with large pore channels [26]. The narrow Gaussian pore size distribution curve implied that the samples had very regular pore channels in the mesoporous region. The textural properties of the samples prepared from two methods were listed in Table 1. The specific surface area, pore size and pore volume of TH are greater than those of TA, which further confirmed hydrothermal approach has the advantage of general ageing method.

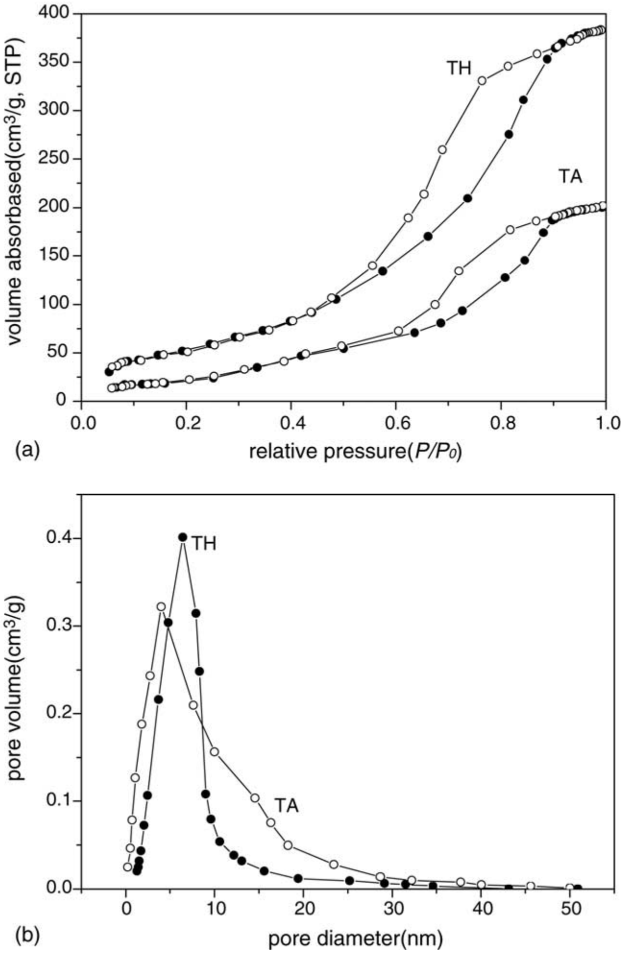


Fig. 3. Nitrogen adsorption–desorption isotherms (a) and BJH pore size distribution plots (b) of as-synthesized mesoporous $TiO_2$.

Table 1
Textural properties of as-synthesized mesoporous $TiO_2$ samples

| Sample | BET surface area ($m^2/g$) | Pore diameter (nm) | Pore volume ($cm^3/g$) |
|---|---|---|---|
| TA | 134 | 4.2 | 0.33 |
| TH | 201 | 6.4 | 0.46 |

### 3.2. Absorption spectra

Fig. 4 showed the absorption spectra of MB solutions with the addition of $TiO_2$ powder at the same time (for 3 h) and different pH values (3.0 and 7.0). MB exhibited a maximum absorption peak at 664 nm. It can be seen that the absorption spectra intensity decreased in the following order TH > TA > P25, and the sample TH showed the best adsorption efficiency. This was attributed to the surface state, surface area, preparation conditions, pore size distribution of $TiO_2$ samples.

The influence of pH on absorption spectra of methylene blue in the $TiO_2$ suspension was very significant. It is well known that pH would influence both the surface state of titania and the ionization state of ionizable organic molecules. The point of zero charge (pzc) of $TiO_2$ is close to 6.2. For pH values higher than pzc of titania, the surface becomes negatively charged and it is the opposite for pH < pzc, according to the following equilibria:

$$\text{pH} < \text{pzc}: \quad \text{Ti–OH} + H^+ \rightarrow TiOH_2{}^+ \tag{1}$$

$$\text{pH} > \text{pzc}: \quad \text{Ti–OH} + OH^- \rightarrow TiO^- + H_2O \tag{2}$$

Since MB is a cationic dye (see Scheme 1), it is conceivable that at high pH, its adsorption on a negatively charged surface is favored. By contrast, at low pH, the adsorption is inhibited because of the opposite charged surface of $TiO_2$.

### 3.3. Photodegradation of the dye

The photocatalysis experiments were conducted to assess the photocatalytic ability of prepared mesostructured $TiO_2$ by the degradation of MB dye as a probe molecule. The results were given in Fig. 5. The corresponding performance

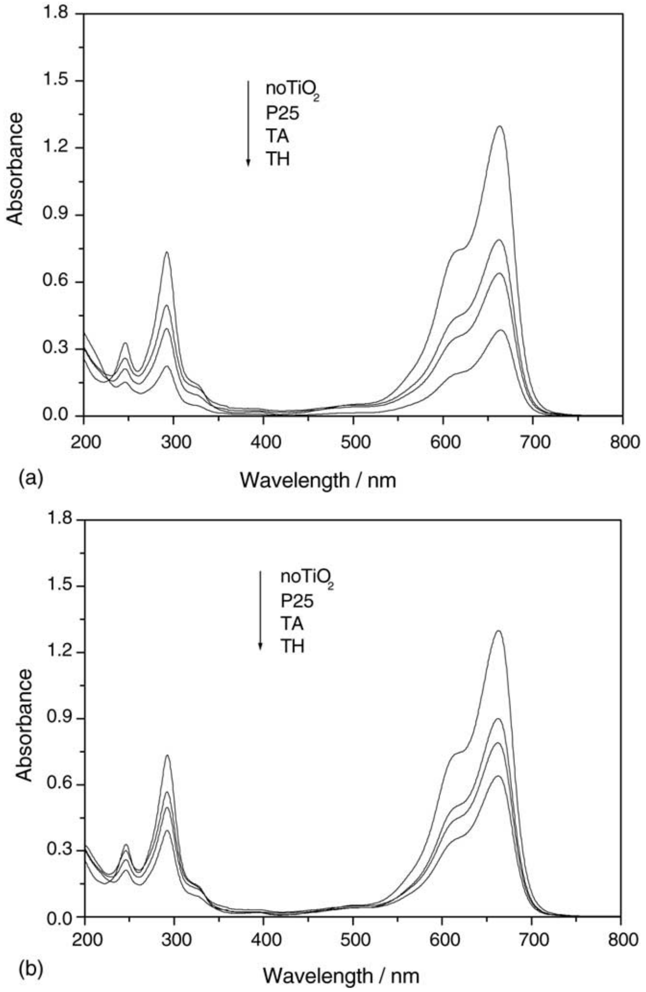


Fig. 4. Influence of pH on absorption spectra of methylene blue in the $TiO_2$ suspension (a) pH 7.0 and (b) pH 3.0.

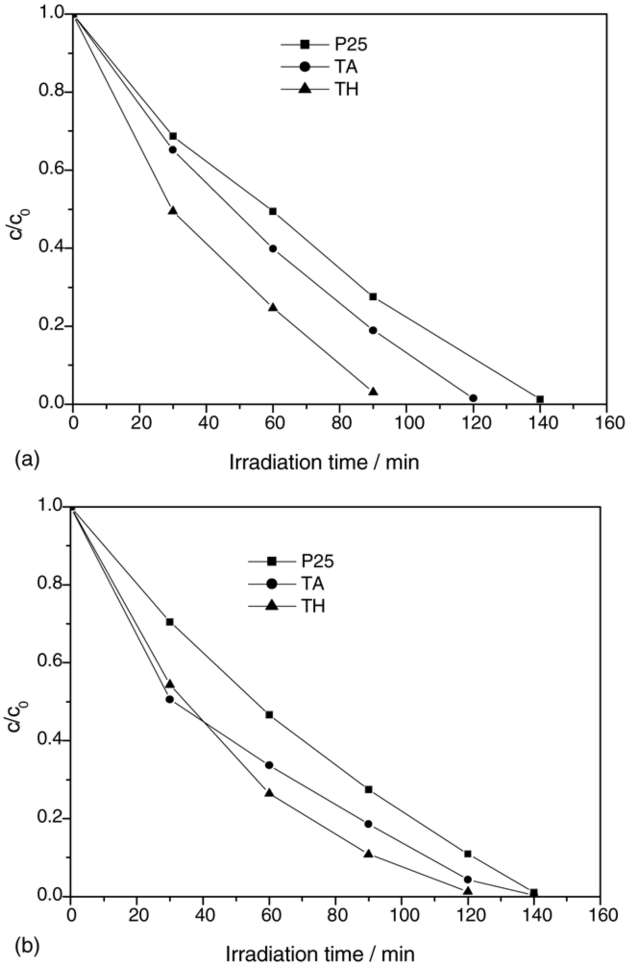


Fig. 5. Influence of pH on the photocatalytic degradation of methylene blue with various $TiO_2$ samples (a) pH 7.0 and (b) pH 3.0.

of the Dugessa P25 was also given for comparison. It was found that the photocatalytic performance of various $TiO_2$ samples decreased in the following order TH > TA > P25. The photocatalytic results can be explained in terms of the preparation steps involved in the synthesis of these samples.

Photocatalytic activity of mesoporous $TiO_2$ is strongly dependent on its phase structure, crystallite size, surface areas and pore structure [27–29]. It can be known that hydrothermal treatment generated the higher hexagonal order and crystallinity of the channels as indicated by the intensity and sharp diffraction peaks observed in the XRD pattern of the sample TH to compare with the TA samples. As well known, in general, anatase-type $TiO_2$ has higher photocatalytic activity than rutile type $TiO_2$, which also is consistent with the experimental results. Additionally, it has been reported that calcinations also reduces the number of hydroxyl groups (one of the highly reactive species responsible for mineralization of organic contaminants) on the surface of the catalyst, leading to an overall reduction in the photoactivity of catalysts [30], and the surface area of the titania, in which the surfactants was removed with solvent extraction, is much larger than that with calcinations [31]. The combination of these factors is envisaged to result in lower activity of the sample TA than TH.

Adsorption could play a prominent role in catalytic photodegradation of organic molecules [32–34]. The pH change in the medium can affect the amount of dye adsorbed on the surface of titania, and affect the photocatalytic ability of samples. Increasing the amount of dye adsorbed on the surface of titania can promote photocatalytic reaction. In the present work, adsorption ability of $TiO_2$ samples (as shown in Fig. 4) accorded with photocatalytic analysis results.

## 4. Conclusions

Mesostructured $TiO_2$ materials with a higher photocatalytic activity were successfully synthesized by two different kinds of methods using triblock copolymer as a template. The properties of mesostructured $TiO_2$ was found to greatly depend on the synthesis condition. It is likely that the adsorption of the dye on the surface of mesostructured $TiO_2$ play a prominent role in photocatalytic degradation of MB. Moreover, pH value is an important parameter in the adsorption and photocatalytic process of the dye.

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