Synthesis and characterization of TiO₂ pillared montmorillonites: Application for methylene blue degradation

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ABSTRACT

TiO₂ pillared clay composites were prepared by modifying of montmorillonite (Mt) with cetyl-trimethylammoniumbromide (CTAB) and then using an acidic solution of hydrolyzed Ti alkoxide to intercalate into the interlayer space of the organic modified Mt. The as-prepared materials were characterized by XRD, FTIR, TEM, SEM TG–DTA, specific surface area and porosity measurements. The composites had a porous delaminated structure with pillared fragments and well dispersed TiO₂ nanoparticles. Introduction of CTAB into the synthetic system accelerated the hydrolysis and condensation of the Ti source, which promoted TiO₂ formation. In addition, the CTAB also significantly increased the porosity and surface area of the composites. A number of anatase particles, with crystal sizes of 5–10 nm, were homogeneously distributed on the surface of the Mt as the result of the templating role of CTAB. The resultant TiO₂ pillared Mt exhibited good thermal stability as indicated by its surface area after calcination at 800 °C. No phase transformations from anatase to rutile were observed even under calcination at 900 °C. The grain size of the anatase in prepared sample increased from 2.67 nm to 13.42 nm as the calcination temperature increased from 300 °C to 900 °C. The photocatalytic performance of these new porous materials was evaluated by using methylene blue degradation. The composite exhibited better photocatalytic property than P 25. The maximum removal efficiency of this composite was up to 99% within 60 min.

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1. Introduction

Dyes are widely used in textile, paper printing, and other industrial processes. These processes produce large volumes of dye-containing wastewater treatment which is a serious water pollution problem even at a low concentration [1,2]. Generally, dyes are generally non-biodegradable and cannot be removed effectively from water via the traditional biotechnology wastewater treatment process. However, adsorption and photocatalytic degradation have been reported to be effective for removing these dyes [3,4].

Up until now, titanium dioxide (TiO₂) has been the dominant photocatalyst for environmental applications due to its superior photocatalytic oxidation behavior, non-photocorrosive, non-toxic, and inexpensive characteristics [5–7]. However, the use of titania in the bulk form usually suffers from some practical problems, such as catalyst agglomeration, and it is difficult recovery, which limits its usefulness in practical applications. Consequently, it is important to improve the immobilization of nano-scaled TiO₂ in order to develop a catalyst with both good photocatalytic performance and recyclability.

The dispersion of TiO₂ particles into the layered clays (TiO₂ pillared clay) improves catalyst performance because these composite structures can stabilize the TiO₂ particles and permit access to the TiO₂ surfaces for various reactants [8,9]. The precursors of the TiO₂ particles are positively charged sol titanium hydrate particles, Ti(OH)ₓₙ⁺, which are 1–2 nm in size. These particles can intercalate into the clay interlayer spaces through an ion exchange reaction. Generally, the intercalation process can be realized by following two approaches. The first and the most common approach is the direct pillaring which involves the treatment of the Na form of the clay with a pillaring solution, followed by calcination of the resulting material [10,11]. However, the TiO₂ particles (the pillars) prepared by this method are too small to form a crystal phase, which is necessary for an efficient photocatalyst [12,13]. In addition, most of the TiO₂ pillared clays prepared by this method are microporous solids which limits the diffusion of organic substances into the interlayer of the clays. Therefore, these pillared clays exhibit poor photocatalytic activity. The other method employed to prepare TiO₂ pillared clays is the indirect method. This uses an intermediate step where the interlayer space is firstly expanded with a swelling agent. In our previous work, a polymeric surfactant poly(oxypropylene)-amines (POP) was used as an expanding agent of Mt. POP not only promoted the formation of a delaminated structure but significantly improved the porosity...
and surface area of the composites [14]. Some small molecule surfaces such as cetyl-trimethylammoniumbromide (CTAB) have also been used as expanding agents in the layered clay and these can control the size of the pillars [15–17]. However, only a few articles on the preparation of TiO_2 pillared clays by indirect method have been reported. The effect of a surfactant on the structure and photocatalytic properties of TiO_2 pillared clays need further study.

In the present study, a systematic investigation on the synthesis and characterization of the TiO_2 pillared montmorillonite (Mt) treated with the small molecule surfactant CTAB was conducted. The influence of the CTAB concentration and the calcination temperature on the structure of this sample was investigated. The photocatalytic activity of this composite was evaluated by methylene blue degradation. Finally, the effect of the surfactant on the structure and photocatalytic activity of the TiO_2 pillared Mt was elucidated in detail.

2. Experimental

2.1. Material

Sodium montmorillonite (Na-Mt, 90%) was supplied from Zhejiang Sanding Technology Co., Ltd., China. The cation exchange capacity (CEC) of the Na-Mt was 110 mmol/100 g, which was estimated using the ammonium acetate method [18]. All reagents used in the experiment were of chemical grade and purchased from Beijing Chemical Reagent Co., Ltd. without further purification.

2.2. Sample preparation

Mt (2.0 g) was dispersed into 200 mL of deionized water, and a given amount of CTAB was added into the clay suspension. The mixture reaction was stirred at 60 °C for 10 h, and stood for a night at room temperature. The resulting suspension was centrifuged to remove the excess CTAB and washed several times with deionized water. In order to obtain a 1% suspension of the surfactant-modified clay, the desired amount of the dried solid was dispersed in distilled water at 60 °C for 2 h. A sol solution of titanium hydrate was then added dropwise to the above mixture with continuous stirring. The ratio of titanium to clay in this study was 20 mmol Ti per gram of clay. The titanium hydrate sol was obtained by the hydrolysis of Ti(OH)_4 in 1 M HCl solution and aged for 4 h. The molar ratio of [Ti]/[H⁺] was 1:4. After stirring for a further 4 h, the resulting suspension was separated by centrifugation and washed with distilled water until free of chloride. The wet cake was dried at 80 °C for 6 h and calcined at 500 °C for 2 h at a rate of 2 °C/min. The final product was ground into a powder and labeled as Ti-CTABx-Mt, where x represents the mole ratio of the amount of CTAB to the CEC of the clay (0.3 CEC, 0.5 CEC, 0.7 CEC, 0.9 CEC, 1.1 CEC, 1.3 CEC, 1.5 CEC). A sample was also prepared using above procedures but without CTAB, and that sample was named Ti-Mt.

2.3. Characterization

X-ray diffraction (XRD) patterns of the resulting sample were obtained on Rigaku D/Max 2000 X-ray Diffractometer using Cu Kα radiation (λ = 0.15418) at 40 kV and 30 mA. Scanning electron microscope (SEM) (JSM7500F, Japan) and transmission electron microscopy (TEM) (JEOL LEM-100CXII) were used to observe the crystal microstructure of as-prepared pillared clays. The Fourier transform infrared (FT-IR) spectra were recorded on a Spectrum 100 spectrometer (PE, USA). N2 adsorption/desorption isotherms were measured at liquid nitrogen temperature using a gas sorption analyzer (Quantachrome Corporation, Autosorb-1). The samples were degassed at 573 K for 3 h prior to the adsorption measurement. BET (Brunauer, Emmett and Teller) surface area and total pore volume were calculated from the adsorption isotherm. The average pore diameter was calculated using the cylindrical pore model from the BET surface areas and the total pore volumes. Thermogravimetry–differential thermal analysis (TG–DTA) was performed on a Setaram TGA92 TG–DTA instrument. About 10 mg of uncalcinated solid before calcination was loaded onto a platinum pan and heated from room temperature to 1073 K at a heating rate of 5 K/min in an air flow of 80 mL/min. The TiO_2 content of the sample was calculated by diantipyrine methane spectrophotometry. The TiO_2 pillared Mt was melted by potassium pyrosulfate. The resulting fused mass was leached by dilute H_2SO_4 solution. In acid medium, Ti^4+ and diantipyrine methane will form yellow color dissoluble complex. Finally, the content of TiO_2 in the TiO_2 pillared Mt was determined with spectrophotometry at λ = 390 nm.

2.4. Photocatalytic activity test

The photocatalytic reaction was carried out in a 400 mL Pyrex reactor attached to an inner radiation type 250 W high-pressure mercury lamp. An aqueous suspension of methylene blue (250 mL, with an initial concentration of 30 mg/L) and the photocatalyst (50 mg) were placed in the Pyrex vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for 120 min to establish an adsorption/desorption equilibrium between the dye and the catalyst surface. At given intervals of illumination, an aliquot (3 mL) of the suspension was collected, centrifuged, and then filtered through a Millipore filter. The filtrates were analyzed by UV–Vis spectroscopy at 664 nm.

3. Results and discussion

3.1. X-ray diffraction and elemental analysis

Fig. 1 shows the small 2θ (1–10°) angle XRD patterns of the Na-Mt, CTAB-Mt, and Ti-CTAB1.1-Mt. A typical diffraction peak of Na-Mt at 6.85 °C corresponds to a basal spacing of 1.26 nm. After intercalation with the CTAB (CTAB-Mt), this peak moves to a low angle at 3.39°, which corresponds to a basal spacing of 2.20 nm. This result clearly indicates an enlargement of the clay’s interlayer space as a consequence of CTAB cations being introduced between their anionic sheets of the Mt. However, the XRD pattern of Ti-CTAB1.1-Mt does not contained a (001) diffraction, indicating a highly
Fig. 2. Wide-angle XRD patterns of Ti-CTAB-Mt-500 samples with different CTAB concentration (a) and Ti-CTAB0.7-Mt samples with different calcination temperatures, respectively. In Fig. 2a, the characteristic diffraction peak (101) at $2\theta = 25.3^\circ$ for anatase at 2 Theta (degree). In Fig. 2b, it can be observed that the intensity of the peaks for anatase increases with the increase of calcination temperature, reflecting that higher temperatures can promote the crystal growth. The mean size of the anatase particles in the calcined samples can be estimated by the broadening of the most intense X-ray diffraction peak (101) at $2\theta = 25.3^\circ$ using the Debye–Scherrer equation. These values are listed in Table 1. The crystal sizes of Ti-CTAB0.7-Mt increased from 2.67 nm to 13.42 nm as calcination temperature increasing from 300°C to 900°C. Generally, anatase-to-rutile phase transformations occur in the range of 500–900°C and vary with the preparation methods and conditions [24,25]. However, no phase transformation from anatase to rutile is observed in Fig. 2b even at a calcination temperature of 900°C. This suggests that the thermal stability of nanocrystalline anatase can patterns of Ti-Mt, Ti-CTAB0.3-Mt, Ti-CTAB0.5-Mt, and Ti-CTAB0.7-Mt samples. However, for Ti-CTAB0.9-Mt, Ti-CTAB1.1-Mt, and Ti-CTAB1.3-Mt, this peak is very faint or not present.

In order to confirm TiO2 formation, TiO2 content (wt%) in the composite was calculated by diantipyrine methane spectrophotometry, and the result are listed in Table 1. The amount of CTAB had a great influence on the formation of TiO2. As CTAB concentration increasing from 0 to 0.7 CEC, the TiO2 content increased from 18.55% to 25.90%. Further increasing the CTAB concentration from 0.7 CEC to 1.3 CEC caused a sharp decrease in the TiO2 content from 25.90% to 1.10%. It should be noted that the Ti-CTAB1.3-Mt sample has only 1.10% of TiO2 content, which is a little higher than the amount in Mt (0.52%). This fact suggests that a certain amount of surfactant can accelerate hydrolyze and condense of Ti source, thus promoting TiO2 formation. However, as CTAB concentration further increasing, more CTA+ species can intercalate into the interlayer space of Mt, resulting in an increase in the density of the CTA+ species. After the interlayer space is expanded by the CTA+ cations, the pillaring process involves the replacing of these cations by the titania species. Consequently, the accessibility of the interlayer space for the titania species decreases with the increase of CTAB concentration. Such behavior will lead to a decrease in the titania intercalation ability.

The elemental analysis (Table 1) shows the TiO2 contents in Ti-Mt, Ti-CTAB0.3-Mt, Ti-CTAB0.5-Mt, and Ti-CTAB0.7-Mt are much higher than that in Na-Mt. However, if all of Na+ ions in Mt interlayer were exchanged completely by the hydrolyzed Ti species (e.g. TiO2+), a maximum of TiO2 content would only be about 7% as calculated from the CEC value. This is much lower than the determined Ti content. This divergence suggests that most of the hydrolyzed titanium species exist outside rather than inside the clay interlayers. So the Ti polyoxycations coaggregates with the clay particles to form a three-dimensional disordered structure [22], which is referred to as “delaminated clay.”

In Fig. 2b, it can be observed that the intensity of the peaks for anatase increases with the increase of calcination temperature, reflecting that higher temperatures can promote the crystal growth. The mean size of the anatase particles in the calcined samples can be estimated by the broadening of the most intense X-ray diffraction peak (101) at $2\theta = 25.3^\circ$ using the Debye–Scherrer equation. These values are listed in Table 1. The crystal sizes of Ti-CTAB0.7-Mt increased from 2.67 nm to 13.42 nm as calcination temperature increasing from 300°C to 900°C. Generally, anatase-to-rutile phase transformations occur in the range of 500–900°C and vary with the preparation methods and conditions [24,25]. However, no phase transformation from anatase to rutile is observed in Fig. 2b even at a calcination temperature of 900°C. This suggests that the thermal stability of nanocrystalline anatase can

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_i$ (cm$^3$/g)</th>
<th>$d$ (nm)</th>
<th>$D$ (nm)</th>
<th>TiO2 content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>10.21</td>
<td>0.04</td>
<td>14.67</td>
<td>–</td>
<td>0.52</td>
</tr>
<tr>
<td>Ti-Mt-500</td>
<td>136.33</td>
<td>0.164</td>
<td>6.67</td>
<td>–</td>
<td>18.55</td>
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<td>Ti-CTAB0.3-Mt</td>
<td>167.03</td>
<td>0.165</td>
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<td>–</td>
<td>20.49</td>
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<tr>
<td>Ti-CTAB0.5-Mt</td>
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<td>0.166</td>
<td>4.58</td>
<td>–</td>
<td>25.90</td>
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<tr>
<td>Ti-CTAB0.7-Mt</td>
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<td>0.165</td>
<td>4.35</td>
<td>4.87</td>
<td>21.11</td>
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<td>0.177</td>
<td>4.89</td>
<td>–</td>
<td>7.68</td>
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<tr>
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<td>0.175</td>
<td>5.96</td>
<td>–</td>
<td>7.24</td>
</tr>
<tr>
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<td>95.37</td>
<td>0.094</td>
<td>6.58</td>
<td>–</td>
<td>1.15</td>
</tr>
<tr>
<td>Ti-CTAB1.5-Mt</td>
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<td>0.085</td>
<td>7.32</td>
<td>–</td>
<td>1.10</td>
</tr>
<tr>
<td>Ti-CTAB0.7-Mt-300</td>
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<td>0.192</td>
<td>4.92</td>
<td>2.67</td>
<td>–</td>
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<tr>
<td>Ti-CTAB0.7-Mt-400</td>
<td>189.01</td>
<td>0.164</td>
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<td>Ti-CTAB0.7-Mt-600</td>
<td>162.92</td>
<td>0.178</td>
<td>5.13</td>
<td>5.37</td>
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<tr>
<td>Ti-CTAB0.7-Mt-700</td>
<td>128.97</td>
<td>0.188</td>
<td>6.27</td>
<td>7.65</td>
<td>–</td>
</tr>
<tr>
<td>Ti-CTAB0.7-Mt-800</td>
<td>71.66</td>
<td>0.174</td>
<td>7.54</td>
<td>8.93</td>
<td>–</td>
</tr>
<tr>
<td>Ti-CTAB0.7-Mt-900</td>
<td>18.77</td>
<td>0.079</td>
<td>9.76</td>
<td>13.42</td>
<td>–</td>
</tr>
</tbody>
</table>
be improved by immobilizing the TiO₂ onto the clays. This is because the clay particles separate the nanocrystalline anatase particles, which prevents the nanocrystalline anatase particles from aggregating and transforming to rutile [26,27].

3.2. Nitrogen adsorption–desorption isotherms

Fig. 3 shows the nitrogen adsorption–desorption isotherms of the initial Na⁺-Mt and the Ti-CTAB-Mt samples with different CTAB concentrations. The adsorption isotherm of Na⁺-Mt is a type III (BDDT classification [28]), which is characteristic of nitrogen adsorption on macroporous adsorbents. The adsorption isotherms of the Ti-CTAB-Mt samples are type IV, corresponding to mesoporous adsorbents. This suggests that the mesoporosity constitutes most of the total porosity. The hysteresis loops of these isotherms seem to be of type H3 (IUPAC classification [29]), corresponding to slit-shaped pores in layered materials.

The structural parameters of the pore structure, including the specific surface area (S₅₇₅), the total porous volume (Vₕ), the average pore diameter (d), and the crystal size (D), are summarized in Table 1. Except Ti-CTAB-Mt calcinated at 900 °C, the BET surfaces area and pore volumes of all pillared Mt samples are much larger than those of the purified Mt (10.21 m²/g). This suggests that the pillaring process leads to a dramatic increase in the porosity in the layered clays. The BET surface areas of Ti-CTAB0.3-Mt, Ti-CTAB0.5-Mt, and Ti-CTAB0.7-Mt samples are larger than that of Ti-Mt-500, indicating that the introduction of CTAB greatly increased the porosity of the composite samples. However, when the CTAB concentration was higher than 0.7 CEC, the BET surface areas of the Ti-CTAB-Mt sample sharply decreased and was much smaller than that of Ti-Mt-500. The structural parameters of the Ti-CTAB-Mt samples calcinated at different temperature are also shown in Table 1. An increase in calcination temperature from 300 to 900 °C leads to an obvious decrease in the specific surface areas and pore volumes of the Ti-CTAB-Mt samples. When the calcination temperature was up to 500 °C, Ti-CTAB0.7-Mt had the maximum of BET surface area (194.30 m²/g). After calcination at 800 °C, the Ti-CTAB0.7-Mt sample maintained a high surface area (71.66 m²/g), indicating that the Ti pillared Mt has a good thermal stability. However, calcination at 900 °C resulted in a dramatic decrease in the surface areas, reflecting the collapse of the porous pillared structure.

Fig. 4 gives that the pore size distributions (PSDs) of the Ti-CTAB0.7-Mt samples calcinated at different temperatures. All the Ti-CTAB0.7-Mt samples except for the samples calcinated at 300 °C and 900 °C have peaks around 3.78 nm, which may result of the spaces or pores generated by the 3D co-aggregation of the clay particles and the Ti polyoxycations [20,23]. The interlayer pores of TiO₂ pillared Mt were formed by the intercalation of small-sized hydrolyzed titanium cations cannot be observed in Fig. 4 because Barrett–Joyner–Halenda (BJH) method for deriving PSD of mesopores solids is not appropriate for calculating the size and volume of micropores. When the temperature was up to 600 °C, another peak at about 4.89 nm occurred. As the calcination temperature increased from 600 °C to 800 °C, the pores become larger and the distribution became wider with the peak centered around 7.5 nm at 800 °C. This is because of the crystal growth of the anatase TiO₂ at high temperature. Since the crystal sizes of the TiO₂ particles become bigger, the pores between the TiO₂ particles and clays become larger. These results can further confirm the delaminated structure of Ti-CTAB-Mt. At 900 °C, no peak can be observed, due to the collapse of the porous pillared structure. These results are in good agreement with the BET surface area of the samples.

3.3. Thermogravimetric analysis

The TG curves of Na-Mt, Ti-CTAB0.7-Mt, Ti-CTAB1.1-Mt, and DTA curves of Ti-CTAB1.1-Mt are shown in Fig. 5. For Na-Mt, the major weight loss, about 9%, occurred below 200 °C, corresponding to physically adsorbed water. For Ti-CTAB0.7-Mt and Ti-CTAB1.1-Mt, the weight losses in this temperature region were relatively small, much less than 1%. This suggests that the modification of

![Fig. 3. Nitrogen adsorption–desorption isotherms on Ti-CTAB-Mt-500 samples with different CTAB concentration.](image)

![Fig. 4. Pore size distribution curves of Ti-CTAB0.7-Mt samples with different calcination temperature.](image)

![Fig. 5. TG curves of Na-Mt, Ti-CTAB0.7-Mt, and Ti-CTAB1.1-Mt.](image)
the Na-Mt by CTAB changed natural clay from the hydrophilicity to hydrophobicity, which is also testified by FT-IR spectras (Fig. S1). Larger weight loss of 17% and 20% occurred between 200 and 500 °C for Ti-CTAB0.7-Mt and Ti-CTAB1.1-Mt, respectively, whereas a loss of only 6% occurred in Na-Mt in the same temperature range. The weight losses between 200 and 500 °C, marked by the exothermic (217 and 334 °C) and endothermic peak (455 °C), are attributed to the evaporation and decomposition of CTAB. Above 500 °C, the weight loss is attributed to the dehydroxylation of the clay and pillars. The removal of the hydroxide groups associated with the interlayer pillars began to occur at 150 °C and caused a continuous weight loss up to 700 °C.

3.4. SEM and TEM

Fig. 6 shows the SEM images of Na-Mt (a), Ti-Mt (b) and Ti-CTAB0.7-Mt (c). These images reveal the variations in morphologies which are a result of the delaminated structures. The Na-Mt micrograph shows larger particle aggregates with smooth surfaces, whereas that of the TiO₂ pillared clay shows the disordered structures which are the result of the delamination process. In the image of Ti-Mt, the larger platelets and layer structure of the clay are not really seen. There are a lots of small aggregates, which are probably broken platelets and agglomerates of TiO₂ crystallites caused by the hydrolysis of the Ti(OCC₃H₇)₄ on the surface. For Ti-CTAB0.7-Mt, the titania particle agglomerates are uniformly dispersed on the surface of the clay. This suggests that the CTAB servers as a template to regulate the process of TiO₂ formation and it also makes the titania particles homogeneously distribute on the Mt clay layer.

More structural information is obtained from the TEM micrographs for the prepared samples. As shown in Fig. 7a, the Na-Mt has a layered sheet structure with a smooth surface. For the Ti-Mt (Fig. 7b), a number of the TiO₂ crystallites and the clay’s platelets are aggregated together. Compared with Ti-Mt, the TiO₂ crystallites in Ti-CTAB-Mt are more homogenously and uniformly distributed on the surface (Fig. 7c). The crystal sizes are in the range of 5–10 nm. This fact shows that CTAB cannot only be regarded as a template to control TiO₂ formation, but is also a dispersant to keep the TiO₂ crystallites and the clay’s platelets from aggregating. Fig. 7d gives the HTEM image of Ti-CTAB0.7-Mt. The wires of uniform thickness of about one nanometer are believed to be the edges of the clay layers. The interlayer space is about 2 nm. It can be clearly observed that lots of small TiO₂ particles have intercalated into the Mt interlayer. This verifies that the surfactant intercalation method produced a good intercalation of titania clusters between the clay sheets when the CTA⁺ ions was replaced. During this intercalative process, the layered structure of the clay was preserved. In addition, the intercalation of titania species between the clay’s layers was accompanied by the formation of TiO₂ particles onto the clay surface, and the delaminated TiO₂ pillared Mts was formed. The preparation process of this delaminated TiO₂ pillared Mt is showed in Scheme 1. In fact, the delaminated TiO₂ pillared Mt is a kind of disordered three-dimensional coaggregation of clay particles and Ti polyoxycations. Both delamination and intercalation contribute to the formation of the disordered structure of the TiO₂ pillared Mt.

3.5. Photocatalytic performances

The catalytic performance of the TiO₂-Mt composite samples for the photodegradation of methylene blue under UV light is shown in Fig. 8a and b. The photolysis of methylene blue in the absence of the photocatalyst was only 8%, which can be neglected. Fig. 8a shows the photocatalytic activity of the TiPx-Mt-500 samples with different CTAB concentration. For comparison, the photocatalytic activity of TiO₂ P-25 Degussa was tested under the same conditions. The photocatalytic activity of TiO₂ P-25 Degussa is higher than those of Ti-CTAB0.9-Mt, Ti-CTAB1.1-Mt, Ti-CTAB1.3-Mt, and Ti-CTAB1.5-Mt, but lower than those of Ti-Mt, Ti-CTAB0.3-Mt, Ti-CTAB0.5-Mt, and Ti-CTAB0.7-Mt. The maximum methylene blue removal efficiency was for Ti-CTAB0.7-Mt, which is up to 99% in 60 min. These results indicate that both the amount of Ti loading in the samples and the contact between the catalyst and the dye are important factors in the photocatalytic activity of the catalyst. Fig. 8b shows the photodegradation of methylene blue by the
Scheme 1. Schematic for preparation of the porous Ti pillared montmorillonites with a delaminated structure.

Fig. 7. TEM images of Na-Mt (a), Ti-Mt (b), and Ti-CTAB0.7-M (c and d).
Ti-CTAB0.7-Mt samples that had been calcinated at with the different calcination temperature. From 300 to 500 °C, the photocatalytic activity increased with the calcination temperature. The sample calcinated at 500 °C had the highest photocatalytic activity due to the largest specific surface area and the better crystallinity. Further increasing the calcination temperature caused a decrease in the photocatalytic activity. The reason might be that increasing the calcination temperature led to the collapse of some pores in the photocatalytic samples. The reason might be that increasing the calcination temperature led to the collapse of some pores in the photocatalytic activity.

4. Conclusion

In this work, TiO₂ pillared Mt was prepared by intercalating colloidal titania particles into Mt in the presence of the surfactant CTAB as an expanding agent. The structure of the resultant sample is primarily a mesoporous delaminated structure, which is the result of the coaggregation of the clay particles and the Ti polyoxocations. The introduction of a certain amount of CTAB into the synthesis system not only accelerated the hydrolysis and condensation of the Ti source, thus promoting TiO₂ formation, but also significantly increased the porosity and surface area of the composites. At the same time, CTAB can be regarded as a template which controls the TiO₂ formation and makes the TiO₂ particles homogenously distribute on the surface of the Mt. The resulting TiO₂ pillared Mt exhibits good thermal stability as indicated by its surface area after calcination at 800 °C. Ti-CTAB0.7-Mt-500 had the best photocatalytic activity for methylene blue degradation (99% within 60 min) due to the largest specific surface area and the most crystallinity. These results suggest that the specific surface area is an important factor which influences the photocatalytic activity of a catalyst. This effect is due to the increase of the contact area between the catalyst and the dye.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2013.07.049.

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