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Immobilization of self-assembled pre-dispersed nano-TiO₂ onto montmorillonite and its photocatalytic activity

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ABSTRACT

The immobilization of pre-dispersed TiO₂ colloids onto the external surface of the clay mineral montmorillonite (Mt) was accomplished and regulated via a self-assembly method employing the cationic surfactant cetyltrimethylammonium bromide (CTAB). The role of CTAB in the synthesis process was investigated by preparing a series of TiO₂-CTAB-Mt composites (TCM) with various CTAB doses. The results indicated that a uniform and continuous TiO₂ film was deposited on the external surface of montmorillonite in the composite synthesized with 0.1 wt.% of CTAB, and the TCM nano-composites showed much higher values for specific surface area, average pore size and pore volume than the raw montmorillonite clay. Then, the formed TCM materials were applied in photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution. The degradation efficiency reached as high as 94.7%. Based on the degradation intermediates benzoquinone, fumaric acid and oxalic acid identified by LC-MS analysis, a mechanism for the photocatalytic oxidation of 2,4-DCP on TiO₂/Mt nano-composites is proposed.

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Introduction

The photocatalytic oxidation process has been extensively utilized to directly mineralize hazardous pollutants to CO₂, H₂O and other inorganic ions. TiO₂ has been considered as a reference photocatalyst due to its low cost, stability and high photocatalytic activation (Henych and Stengl, 2013; Hoffmann et al., 1995; Li and Qu, 2009). Researchers have carried out a number of studies on the degradation of organic pollutants on semiconducting TiO₂ (Axelsson and Dunne, 2001; Chaliha and Bhattacharyya, 2009; Chu et al., 2005; Peller et al., 2001). To enhance the degradation efficiency, TiO₂ photocatalyst with a particle size in the range of 6–8 nm was prepared (Zhu et al., 2002). However, nano-scale TiO₂ particles easily agglomerated into larger ones, reducing the catalytic activity (Choi et al., 1994; Zhang et al., 2008).

Immobilization of nano TiO₂ particles on clay minerals was found to be an efficient way to solve the problem of aggregation (Liu and Zhang, 2014). Montmorillonite has been one of the most widely used clay materials to serve as a support for photocatalysts. Many prior works have proposed the preparation of TiO₂-pillared clay by intercalating positively charged titanium hydrate, [TiO(OH)_{x}]^{+}, into the interlayer space of montmorillonite via ion-exchange reactions (Awate and Sizuki, 2001; Mongyorósi et al., 2003). However, TiO₂ particles were poorly distributed on the internal surface with low crystallinity (Maes et al., 1997) and only limited amounts of organic pollutants could be adsorbed on the surface of the TiO₂ photocatalysts owing to the hydrophobicity of montmorillonite (Meng et al., 2008; Mongyorósi et al., 2002; Zhang et al., 2011).

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Hydrothermal treatment with organic surfactants has been shown to improve the distribution and crystallinity of nanoparticles (Kefi et al., 2011). Organic surfactants can increase the homogeneity of the pillar distribution, attributed to the interactions between functional groups of surfactants (Kun et al., 2006). Based on gallery-templated synthesis, the assembly of surfactants with the inorganic precursor occurred in the internal space of clay minerals, leading to a porous clay structure and plenty of pillars with enlarged size through the use of the proper quantity of surfactants (Liu et al., 2007; Ma et al., 2005). In addition, organic surfactants strengthened the affinity of TiO2/Mt composites for organic compounds by increasing their hydrophobicity (Fatimah et al., 2010; Ooka et al., 2003).

Our previous research developed a new method for the immobilization of pre-dispersed nano-scale TiO2 on the external surface of montmorillonite with the assistance of cetyltrimethylammonium bromide (CTAB) surfactant (Yuan et al., 2011). The synthesized photocatalysts were confirmed to have higher photocatalytic activity than Degussa P25 due to their optimal structural conformation via the interaction of the dispersant diethanolamine with CTAB. Herein, we further focused on the modulating effect of CTAB in the synthesis of TiO2-modified montmorillonite. The photocatalytic activity of the synthesized material was assessed by performing microwave electrodeless ultraviolet photodegradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution. A photocatalytic mechanism was proposed based on the degradation intermediates and the material structure.

1. Experimental

1.1. Synthesis procedure

Titanium tetrachloride (TiCl4), hydrochloric acid (HCl), ammonium sulfate ((NH4)2SO4), diethanolamine (DEA) and CTAB, of analytical grade, were purchased from Beijing Chemical Co. Ltd. TiO2 particles were prepared by a hydrothermal method. TiCl4 was added to a mixture of hydrochloric acid and ammonium sulfate in an ice bath under N2 atmosphere with vigorous stirring. Then, the temperature was elevated to 95°C and maintained for 1 hr. Subsequently, DEA was added into the mixture at a Ti/DEA molar ratio of 2 and allowed to react for 1 hr to form DEA-TiO2 particles. Then, CTAB of various amounts was added to the so-formed DEA-TiO2 sol at room temperature and stirred for 4 hr, forming DEA-TiO2-CTAB adducts through self-assembly reactions.

Na-montmorillonite (Na-Mt, D < 2 μm, purity 85%) was donated by the Zhejiang Fenghong Clay Company. Its cation exchange capacity (CEC) was 58.3 meq/g. Before use, the montmorillonite was washed with anhydrous ethanol and dried at room temperature. 1 g montmorillonite mixed with 100 mL deionized water was stirred vigorously for 5 hr and boiled overnight to produce montmorillonite dispersion. The immobilization of TiO2 was conducted by adding the so-formed DEA-TiO2-CTAB dropwise into the montmorillonite dispersion up to a Ti/CEC molar ratio of 15 at 70°C and stirring gently for 5 hr. The upper white foam layer was recovered by centrifugation and washed several times with deionized water and ethanol until no chloride could be detected. The products were dried in vacuum at room temperature or calcined at 500°C, designated respectively as as-synthesized TCM and calcined-TCM.

1.2. Characterization techniques

Fourier transform Raman spectra of clay samples were collected on a RFS 100 Bruker apparatus (Bruker, Rheinstetten, Germany). The operating power of for the exciting laser radiation was kept at 300 mW. 100 scans from 3500 to 50 cm\(^{-1}\) with a spectral resolution of 2 cm\(^{-1}\) were averaged to optimize the signal-to-noise ratio. The room temperature Fourier transform infrared spectra (FT-IR) were measured on a Bruker Tensor 27 FT-IR spectrometer having a frequency range of 400–4000 cm\(^{-1}\) and a 4 cm\(^{-1}\) resolution in 32 scans (Bruker, Rheinstetten, Germany). The crystalline phase composition and degree of crystallinity of the samples were estimated by a D/MAX-2500 VB2 X-ray Diffraction (Rigaku, Osaka, Japan) using Cu-Kα radiation (λ = 1.54056 Å), operated at 40 kV. The size of anatase TiO2 and the spacing of layers were calculated by using the Scherrer and Bragg equations, respectively. The morphology was observed with an H-800 Scanning Electron Microscope (Hitachi, Tokyo, Japan) at an accelerating voltage of 200 kV. Brunauer–Emmett–Teller (BET) surface areas and porosity were obtained from the adsorption/desorption isotherms of N2 at 77 K after the samples were degassed for 16 hr at 393 K using a Sorptomatic 1990 apparatus (ThermoFisher, Massachusetts, USA). The specific surface areas and pore volumes were calculated from the BET plot (P/P0 =0.96).

1.3. Photocatalytic test

The photocatalytic test was carried out in a microwave oven (660 W) containing a microwave electrodeless ultraviolet lamp fixed in a glass reactor. Detailed information about the lamp can be found elsewhere (Yu et al., 2013a, 2013b). A peristaltic pump was used for fluid circulation. A condenser tube was attached at the outlet of the microwave oven to cool the reactants once they flowed out of the reactor. The experimental setup can be found elsewhere (Yuan et al., 2011).

Certain amounts of TCM materials were added into 800 mL, 30 mg/L 2,4-DCP aqueous solution and stirred for 1 hr to reach the adsorption equilibrium in a wastewater vessel. Then, the circulation of the catalyst dispersion began. At the same time, the microwave oven was powered on, stimulating the lamp to emit ultraviolet radiation toward the mixture running in the reactor. After 90 min, small aliquots (5 mL) were sampled and filtered with a 0.22 μm membrane to remove the remaining powders. The concentration of 2,4-DCP was determined by using a TU-1901 UV spectroscopy (Pgeneral, Beijing, China) at 198 nm. All the photocatalytic experiments were performed in triplicate and the average concentration was adopted in the results. The photocatalytic decomposition products were detected by high performance liquid chromatography–mass spectrometry (LC-MS). A C18 column was used and the mobile phase was acetonitrile/water (30/70). Comparing the peak areas and retention times with those of standard samples, the intermediates could be identified.
2. Results and discussion

2.1. Characterization of the catalyst

2.1.1. Structure analysis by FT-Raman and FTIR

Fig. 1 depicts the FT-Raman spectra of as-synthesized TCMs. As mentioned by Yuan et al. (2011), the presence of the Ti–O stretching vibration at 156 cm$^{-1}$ indicates that the crystalline TiO$_2$ was successfully intercalated and grafted to the clay mineral. Peaks at 1444 cm$^{-1}$ are ascribed to the C–N stretching vibration while the bands in the range of 2924–2840 cm$^{-1}$ are attributed to the asymmetric and symmetric vibrations of CH$_2$ and CH$_3$ groups, verifying the interactions of CTAB molecules with montmorillonite via ion exchange reactions and electrostatic adsorption (Venkataraman and Vasudevan, 2001). However, for the TCMs with low CTAB contents (0.1 wt.%), such resonance was comparably weak or even invisible due to the poor amounts of CTAB assembled with the pre-synthesized DEA-TiO$_2$.

FTIR spectra for as-synthesized and calcined TCMs are shown in Fig. 2. The peaks near 1640 and 3430 cm$^{-1}$ are due to the bending vibration of crystalline water and the H–O–H stretching vibration of free water absorbed on the clay and titanium sol, in agreement with the study by Sadek and Mekhemer (2001). The peak at 1033 cm$^{-1}$ is assigned to Si–O–Si stretching vibration. Al–OH and Mg–Al–OH bending vibrations are respectively shown at 920 and 850 cm$^{-1}$. Low frequency bands in the region of 400–800 cm$^{-1}$ correspond to the characteristic IR adsorption bands of crystalline TiO$_2$ and montmorillonite itself. Few differences can be observed in as-synthesized TCM (Fig. 2a) and calcined TCM (500°C) (Fig. 2b), except for the peaks at 2800 to 3000 cm$^{-1}$ corresponding to –CH$_2$ and –CH$_3$ groups in the as-synthesized TCM. It can be deduced that the basic structure of montmorillonite can be well preserved even after calcination at the high temperature of 500°C, and CTAB molecules were successfully removed from as-synthesized TCM through heat treatment.

2.1.2. XRD analysis

XRD patterns for as-synthesized and calcined materials are displayed respectively in Fig. 3a and b to determine the influence of calcination treatment as well as CTAB contents on the properties of TiO$_2$ deposits and montmorillonite. After calcination at 500°C, a conspicuous shift of the d$_{001}$ peak, which was assigned to the characteristic layer structure of montmorillonite, can be observed, from 2$\theta$ of ~5° (Fig. 3a) to that of ~7° (Fig. 3b). The shift was the result of the decreasing interlayer distance due to the removal of organic templates.
and water by heat treatment. In addition, the d001 reflection was somewhat weakened after calcination, corresponding to structural disorder induced at the high temperature of 500°C. Furthermore, the calcined TCMs showed broader diffraction peaks of the anatase phase around $2\theta = 25.3^\circ$, ascribed to higher contents of anatase TiO$_2$ with smaller crystal size. The reflection peak of the rutile phase at $2\theta = 27.5^\circ$ can be observed in Fig. 3b, arising from the phase change from anatase to rutile during calcination. Similar results can be found in many previous works such as Mongyorósi et al. (2003) and Zhang et al. (2000).

The amount of CTAB addition also exerted a great impact on the material properties. A slight shift of the d001 peak in the direction of lower $2\theta$ can be identified after the addition of CTAB. This revealed an increase in the interlayer distance from 1.5 to 2.0 nm for as-synthesized samples, and from 1.01 to 1.03 nm for calcined samples. A similar result was reported by Sun et al. (2002) as well as many other researchers, who attributed this phenomenon to the intercalation of CTAB and TiO$_2$ into the clay materials. In addition, the characteristic reflection for the anatase phase at $2\theta = 25.3^\circ$ was slightly weakened by the addition of CTAB, from 0.1 to 0.5 wt.%. That is to say, higher CTAB contents lead to decreasing numbers and increasing particle size deposited TiO$_2$ particles. On one hand, excessive CTAB molecules may saturate the available sites for TiO$_2$ to incorporate into (and onto) the clay mineral platelets (Yuan et al., 2004, 2011). On the other hand, CTAB can also enhance the hydrophobicity of the clay materials, so that the few water molecules remaining in the interlayer were possibly strongly polarized (H$_2$O $\rightarrow$ H$_3$O$^+$) by Na$^+$ that remained non-exchanged (Liu et al., 2013). As a result, a great number of TiO$_2$ particles per unit mass failed to penetrate the clay layers by ion exchange but instead, to deposit on the external surface of the clay minerals where particle aggregation occurred, leading to the poor contents of TiO$_2$ deposits with large grain size in the products.

Generally speaking, since the anatase phase has much higher photocatalytic activity (Hoffmann et al., 1995), and smaller TiO$_2$ grains on the external surface of clay minerals can provide more easily accessible places for photocatalytic reactions (Zhu et al., 2007), the calcined TCM material synthesized with CTAB content of 0.1 wt.% was preferred.

2.1.3. Scanning electron microscopy

SEM studies were used to obtain information about the morphology of as-synthesized TCM. As shown in Fig. 4, the flaky structure of the montmorillonite can be observed in samples with CTAB contents of 0.1 and 0.5 wt.% due to the intercalation of cationic surfactant. In addition, certain amounts of TiO$_2$ grains were found uniformly dispersed on the flat plates. This was consistent

![Fig. 3 – XRD patterns of as-synthesized TCM (a) and calcined TCM (b) samples with CTAB contents of 0.1–0.5 wt.%](image)

![Fig. 4 – SEM images of as-synthesized TCM samples with CTAB contents of 0.1 wt.% (a) and 0.5 wt.% (b).](image)
Scheme 1 - Formation process of DEA-TiO$_2$-CTAB. DEA: diethanolamine; CTAB: cetyltrimethylammonium bromide.
with the observations in FT-Raman and FTIR spectra. Similar results were reported by Fatimah et al. (2010) and Yoda et al. (2004). In addition, the average particle size increased notably with the addition of CTAB, such that the majority of particles were about 100 nm for 0.1 wt.% CTAB while increasing to nearly 500 nm for 0.5 wt.% CTAB. Such effects of CTAB content on the particle size and loading amount of TiO$_2$ were in agreement with the XRD analysis.

2.1.4. BET analysis
All composites had higher values for BET surface area and pore volume than the raw Mt clay, which has a surface area of 28.09 m$^2$/g and pore volume of 0.09 cm$^3$/g (Yuan et al., 2011). But a decrease in specific surface area was detected at higher CTAB contents, from 76.38 to 39.52 m$^2$/g. This result can be related to the poor distribution as well as the large particle size of the titanium oxide deposits on the external surface of the clay minerals, as concluded from SEM and XRD analysis. On the other hand, larger CTAB loadings were found to bring about a decrease in pore volume from 0.56 to 0.25 cm$^3$/g, which was probably caused by the pore collapse taking place during calcination in the regions where there were no pillars. Thus, the decrease in pore volume caused by excessive CTAB addition possibly corresponded to the lower TiO$_2$ content. In order to maximize the surface area and the pore volume, which is useful in catalysis or adsorption of large organic species (Maes et al., 1997), a TCM catalyst prepared with CTAB content of 0.1 wt.% was favored.

2.2. Mechanism of nano-TiO$_2$ immobilization on Mt clay
The preparation process for the TCM materials in this study can be simply divided into two parts: the generation of self assembled DEA-TiO$_2$-CTAB and the formation of TCM materials.

Scheme 2 illustrates the formation of TCM with various contents of CTAB. The morphologies of prepared TCM composites were dependent on CTAB amounts. Once the

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Scheme 2 – Formation process of TiO$_2$-CTAB-Mt composite (TCM) materials according to different CTAB amounts. CTAB: cetyltrimethylammonium bromide; Mt: the clay mineral montmorillonite.

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**Fig. 5** – Photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) by P25 TiO$_2$ and TCM (pH = 5, catalyst loading: 0.1 g/L).
montmorillonite dispersion was added, the hydrogen bonds between two neighboring chains or segments were broken or weakened (Deng et al., 2006). Subsequent pathways contained three parts: (1) ion-exchange reactions and electrostatic attractions between negatively charged clay minerals and positively charged adducts; (2) hydrophobic attractions between carbon chains; and (3) protonation of the tertiary amide of CTAB (–N’ → =NH) and the secondary amide of DEA-TiO₂, DEA-TiO₂-CTAB (=NH → –NH₂) at the surface of clay layers (Stutzmann and Siffert, 1977).

For the TCM samples with low CTAB contents, more TiO₂ pillars can be immobilized in the interlayer space, where the assembly of ionic and neutral surfactants with the inorganic precursor occurred based on gallery-templated synthesis to form a porous structure (Liu et al., 2007; Ma et al., 2005). At the same time, a number of TiO₂ particles with smaller size were adsorbed on the external surface of montmorillonite, corresponding to an enlarged surface area. On the contrary, with regard to the TCM samples with high CTAB contents, many CTAB molecules acted as pore blocks, making it difficult for TiO₂ colloids to settle into the clay minerals. The decreasing number of TiO₂ pillars led to poor crystallization and limited pore volume after calcination. The extensive TiO₂ deposits on the external layer were responsible for the large surface area and grain size of these high CTAB samples.

2.3. Photocatalytic activity

2.3.1. Degradation performance of TCM photocatalyst

The photocatalytic activity of TCM synthesized under optimal conditions was evaluated in comparison with P25 TiO₂. The results shown in Fig. 5 reveal that TCM had a slightly better photocatalytic activity than P25. Compared with P25, TCM consisting of TiO₂ particles and montmorillonite could be advantageous in certain applications utilizing catalysts in dispersion because it is easier to recover. Thus it can be concluded that TCM synthesized in the current work has the obvious advantage of easy separation due to its strong hydrophobicity, even though it performs only a slightly higher photocatalytic capacity than P25.

2.3.2. Degradation intermediates and mechanism

For most current studies on TiO₂/Mt composite materials, TiO₂ particles have been largely immobilized into the clay interlayers, so that the photochemical degradation must be facilitated by adsorption and transfer of organic pollutants from clay layers to the TiO₂ surface to be photo-catalytically oxidized. The decomposition of 2,4-DCP by TCM materials, which had large amounts of TiO₂ particles on the external surface of montmorillonite, may simply include two steps, the adsorption of 2,4-DCP on the TCM composites and then, its degradation on the surface of semiconducting TiO₂.

We proposed the degradation pathway in Fig. 6 based on the intermediates of 2,4-DCP degradation detected by LC–MS (Fig. 7) and some related works published previously. The formation of 4-chlorophenol was shown to be the first step in the photocatalytic degradation of 2,4-DCP (Gaya et al., 2009), related to the direct oxidation by positive holes. Subsequent-ly, hydroxyl radicals may most probably attack the chloride-carbon bond at the para position on the aromatic ring (D’Oliveira et al., 1990), giving rise to hydroquinone. At the same time, the chorine radical dissociated from the aromatic ring gained an electron on the TiO₂ surface to form chloride ion (Li et al., 1999). Benzoquinone, due to the oxidation of hydroquinone, was identified from LC-MS analysis, consistent with prior research by Gaya et al. (2009). Benzoquinone was not an important component, and benzenetriol was proposed to be produced by hydroxylation, following reaction with O₂ and elimination of HOO· (Hoffmann et al., 1995). Fumaric acid, subsequently identified by LC-MS, was probably formed by the isomerization of maleic acid, which was the most prominent four-carbon compound during the degradation of benzenetriol (Sun and Pignatello, 1995). Then, the aromatic rings of hydroquinone and benzoquinone were opened by hydroxyl radicals, transforming into simple acids such as oxalic acid (Chaliha and Bhattacharyya, 2005; Chu et al., 2005). Oxalic acid was found to be the final product in our experiments, due to the slow decomposition rate of oxalic acid (Axelsson and Dunne, 2001) related to the low concentration at 60 min (Waldner et al., 2003) or the lack of reactivity towards OH radicals (Peller et al., 2004).

![Fig. 6 – Reaction scheme proposed to account for the formation of degradation intermediates of 2,4-dichlorophenol (2,4-DCP) on TCM photocatalyst.](image-url)
Fig. 7 – LC-MS spectrum of the peaks at different retention time.
3. Conclusions

(1) The synthesis of TCM was based on the formation of self-assembled TiO$_2$ colloids via several steps: hydrolysis of TiCl$_4$, modification of TiO$_2$ by DEA; assembly of TiO$_2$-DEA with the cationic surfactant CTAB; linkage of self-assembled TiO$_2$-DEA-CTAB to montmorillonite through electrostatic force, hydrophobic attraction and reactions such as ion exchange and polarization.

(2) The amount of the organic surfactant CTAB had a conspicuous influence on the properties of the synthesized TCM materials. The proper loading of CTAB, here confirmed as 0.1 wt.%, resulted in even distribution of TiO$_2$ deposits with small grain size (5.9 nm) on the external surface of montmorillonite. The specific surface area was 76.38 cm$^2$/g and the pore volume was 0.56 cm$^3$/g.

(3) The synthesized TCM under optimal conditions had slightly stronger photocatalytic activity than P25. But when applied in wastewater treatment, TCM would be easier to recover. The degradation of 2,4-DCP on TiO$_2$/Mt nano-composites can be summarized into three steps: the oxidation of 2,4-DCP to benzoquinone, the opening of the aromatic ring to form fumaric acid and finally, the decomposition of the four-carbon acid to the simple acid, oxalic acid.

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References


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<td>Massey University, New Zealand</td>
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