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# Immobilization of self-assembled pre-dispersed nano-TiO<sub>2</sub> onto montmorillonite and its photocatalytic activity

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## ABSTRACT

The immobilization of pre-dispersed TiO<sub>2</sub> 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 TiO<sub>2</sub>-CTAB-Mt composites (TCM) with various CTAB doses. The results indicated that a uniform and continuous TiO<sub>2</sub> 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 TiO<sub>2</sub>/Mt nano-composites is proposed.

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## Introduction

The photocatalytic oxidation process has been extensively utilized to directly mineralize hazardous pollutants to CO<sub>2</sub>, H<sub>2</sub>O and other inorganic ions. TiO<sub>2</sub> 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 TiO<sub>2</sub> (Axelsson and Dunne, 2001; Chaliha and Bhattacharyya, 2009; Chu et al., 2005; Peller et al., 2001). To enhance the degradation efficiency, TiO<sub>2</sub> photocatalyst with a particle size in the range of 6–8 nm was prepared (Zhu et al., 2002). However, nano-scale TiO<sub>2</sub> particles easily agglomerated into larger ones, reducing the catalytic activity (Choi et al., 1994; Zhang et al., 2008).

Immobilization of nano TiO<sub>2</sub> 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 TiO<sub>2</sub>-pillared clay by intercalating positively charged titanium hydrate, [Ti(OH)<sub>x</sub>]<sub>m</sub><sup>n+</sup>, into the interlayer space of montmorillonite via ion-exchange reactions (Awate and Suzuki, 2001; Mongyórosi et al., 2003). However, TiO<sub>2</sub> 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 TiO<sub>2</sub> photocatalysts owing to the hydrophilicity of montmorillonite (Meng et al., 2008; Mongyórosi 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 TiO<sub>2</sub>/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 TiO<sub>2</sub> 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 TiO<sub>2</sub>-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 (TiCl<sub>4</sub>), hydrochloric acid (HCl), ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), diethanolamine (DEA) and CTAB, of analytical grade, were purchased from Beijing Chemical Co. Ltd.

TiO<sub>2</sub> particles were prepared by a hydrothermal method. TiCl<sub>4</sub> was added to a mixture of hydrochloric acid and ammonium sulfate in an ice bath under N<sub>2</sub> 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-TiO<sub>2</sub> particles. Then, CTAB of various amounts was added to the so-formed DEA-TiO<sub>2</sub> sol at room temperature and stirred for 4 hr, forming DEA-TiO<sub>2</sub>-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 TiO<sub>2</sub> was conducted by adding the so-formed DEA-TiO<sub>2</sub>-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<sup>-1</sup> with a spectral resolution of 2 cm<sup>-1</sup> 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<sup>-1</sup> and a 4 cm<sup>-1</sup> 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 TiO<sub>2</sub> and the spacing of layers were calculated by using the Scherrer and Bragg equations, respectively. The morphology was observed with a 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 N<sub>2</sub> 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/P*<sub>0</sub> = 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 C<sub>18</sub> 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.

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