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High performance photocatalysts: Montmorillonite supported-nano TiO_2 composites

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ABSTRACT

In this paper, montmorillonite supported-nano TiO_2 photocatalytic composites are synthesized by an easily-operated solid diffusion process, in which montmorillonite is used as a support matrix. And the microstructures, morphologies and photocatalytic properties of the montmorillonite supported-nano TiO_2 composites are characterized and analyzed by scanning and transmission electron microscopy, X-ray photoelectron spectroscopy, UV–vis spectroscopy, fluorescence spectroscopy and methylene blue degradation tests. The results show that montmorillonite matrix reduces agglomeration of nano-TiO_2 and enhances the absorption ability within the UV–vis range, consequently increases the photocatalytic activity of the composites. Meanwhile, the influence of TiO_2/montmorillonite proportion on photocatalytic performances is explored, which indicates that 90 wt% TiO_2/montmorillonite has optimal photocatalytic properties.

1. Introduction

Nano-TiO_2 is one of the most promising photocatalysts because of its strong catalytic activity, high chemical stability, anti photo-corrosion ability, and biocompatibility. [1–4] And it is widely used in the field of environmental protection of air pollution and water pollution treatment. [5–10] Due to separation and recycle problems of fine photocatalyst particles, practical applications of aqueous TiO_2 are limited by its particle suspensions. Compared with fine TiO_2 particles, supported and immobilized photocatalysts have better photocatalytic degradation performances and become recent research hotspots of photocatalysts. Moreover, cellular materials are popular as load carriers of nano-TiO_2 for supported and immobilized photocatalyst. And montmorillonite has an obvious layered structure, high specific surface area, strong adsorption capacity, low cost and targeted enrichment of water and air pollutants, therefore, montmorillonite supported nano TiO_2 photocatalytic composites have recently attracted much attention. [11,12].

Mineral supported-TiO_2 composite photocatalysis materials have been prepared by different compound methods, such as sol-gel method, settling method, cross- coupling method, power sintering method. [13–16] Among these methods, power sintering or solid diffusion method is a simple process to build strong binding force between each phase because of its

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thermal diffusion effect. However, there are few reports about the preparation of montmorillonite supported-nano TiO_2 composites with this method.

In this article, we report a new and easily-operated solid diffusion process of synthesizing montmorillonite supported-nano TiO_2 composites. The montmorillonite acting as the carrier can increase the photocatalytic activity of the composites by reducing agglomeration of nano-TiO_2 and enhancing the absorption ability within the UV–vis range. This method is simple and potential to meet the requirements of broader application. And meanwhile, our experiment includes the influence of different load ratios on the photocatalytic activity of montmorillonite supported-nano TiO_2 composites.

2. Experimental

2.1. Preparation of the montmorillonite supported-nano TiO_2 composites

The main raw materials of experiment were: pure TiO_2 (P25, Degussa, Germany, TiO_2 content >98 wt%); montmorillonite (Sihui City Klippe Non-metallic Mineral Material Co., Ltd.); ethanol (AR); NaOH (AR); terephthalic acid (AR); methylene blue (AR); distilled water. At first, different weight of montmorillonite powder and 1 g of pure TiO_2 were mixed, and secondly, a certain amount of ehanol was added. Then the mixture was milled for 30 min and dried at 300 °C for 6 h. After cooling down to room temperature slowly, the sample was grinded until its particle size was well-distributed. A series of montmorillonite supported-nano TiO_2 composite materials of different loads were obtained. According to TiO_2 weight percentage, these materials were respectively marked as 40%T/M (TiO_2/montmorillonite), 70%T/M, 80%T/M, 90%T/M, 95%T/M, 98%T/M. The percentages involved in this paper are all mass ones.

2.2. Characterizations

The morphology observations and chemical composition analysis were characterized by using a scanning electron microscope (SEM, FEI SIRION, the Netherlands) equipped with an EDAX energy dispersive X-ray spectrometer (EDS).The characterizations of microstructure and light absorption were performed on an X-ray diffraction (XRD, Bruker D8 Advanced, German) and a UV–vis spectrophotometer (UV–vis, Shimadzu UV-2550, Japan).

2.3. Photocatalytic activity test

The high oxidative hydroxyl radicals •OH generated on the surface of TiO_2 in photocatalysis process decomposes the oxidative degradation of organic pollutants to CO_2, H_2O and other unharmful substances. And thereby, the •OH concentration produced during photocatalytic reaction can be used to characterize the photocatalytic activity. Due to the capture effect of terephthalic acid on •OH, the as-produced hydroxylate 2-hydroxy terephthalic acid (TAOH) can transmit unique signals near the spectral peak of the fluorescence at 426 nm, and therefore indirectly indicated •OH concentration formed in the solution.

In this experiment, •OH relative concentration caused in the reaction time of 90 min was used to characterize photocatalytic activity of composites. A certain amount of composites containing 40 mg TiO_2 or 40 mg pure TiO_2 were added into terephthalic acid solution (80 mL, 0.498 g/L). After stirring 30 min, this moment of adsorption equilibrium was marked as the initial time of the fluorescence test. While keeping stirring and the high-pressure mercury lamp (250 W) was turned on. 2 mL solution was extracted and centrifuged every 10 min, and then the supernatant was tested for fluorescence until 90 min. Fluorescence test was examined by Shimadzu RF-5301PC Molecule fluorescence photometer.

2.4. Photo-decomposition test

The photocatalytic activity of the photocatalysts was measured by the cyclic decomposition of methylene blue. A certain amount of composite materials containing 80 mg TiO_2 or 80 mg pure TiO_2 was separately added into methylene blue solution (100 mL, 10 mg/L). The mixture was placed in a darkroom for 60 min, and then irradiated by a high-pressure mercury lamp for 180 min. And then 3 mL solution was taken out to test the residual concentration of methylene blue. The changes of maximum absorbance of methyl blue concentration were measured by the UV–vis spectrophotometer. UV irradiation in fresh methylene blue solution was repeated up to 5 times for the sample.

3. Results and discussion

3.1. Morphologies and microstructures of montmorillonite supported-nano TiO_2 composites

Fig. 1 shows typical microstructures of pure TiO_2 (P25). And the average grain diameter of the pure TiO_2 is about 20 nm.

In Fig. 2, through EDS analysis, the elementary compositions of montmorillonite material in the experiment include: Na 0.91 wt%, Al 7.05 wt%, Si 37.90 wt%, K 1.86 wt%, Mg 0.68 wt%, Ca 0.71 wt%. And as shown in Fig. 3h, diffraction peaks of the XRD patterns at $2\theta = 5.9^\circ$, $2\theta = 19.7^\circ$ and $2\theta = 35.1^\circ$ reveal the existence of montmorillonite, diffraction peaks at $2\theta = 21.9^\circ$