A Simple Hydrothermal Synthesis of Flower-like Titanium Dioxide Microparticles and Their Application in Organic Waste Removal

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Abstract. In this paper, the flower-like titanium dioxide microparticles (F-Ti MPs) were synthesized by a simple treatment of titanium dioxide nanoparticles (Ti NPs) in the NaOH solution via a hydrothermal method. Size and morphology of the resultant samples were characterized with a scanning electron microscopy (SEM) and a transmission electron microscopy (TEM). The results showed that F-Ti MPs had a hierarchical and flower-like morphology with the diameter around 3-5 μm and constructed by numerous nanowires. When incubated with the solution of methylene blue (MB, model organic pollutant), F-Ti MPs showed much stronger adsorption capacity to remove MB from water than Ti NPs.

1. Introduction
In recent years, with the rapid development of economy, environmental pollution becomes a serious problem. Organic pollutants have been extensively found in the wastewater and strongly threaten the health of the human beings. Several classical methods have been available for removal of the organic pollutants, including adsorption [1], catalytic reduction [2], and photocatalytic decomposition [3]. Among them, adsorption method is the simplest method with low-cost price.

Titanium dioxide is one of the representative inorganic materials and takes advantages of low-cost price, easy synthesis, controllable morphology, and strong photocatalytic activity [4-5]. Titanium dioxide nanoparticles (Ti NPs) have been synthesized as catalysts for removal of organic pollutants. However, the surface area of Ti NPs is still very low. Recent research has indicated that flower-like materials are of special interest in the development of adsorbent for removal of organic pollutants because of their highly organized structure and ultrahigh surface area [6]. To improve the adsorption capacity for removal of organic pollutants, it is interesting in the development of flower-like titanium dioxide materials.

In this study, a very simple method was proposed to synthesize the flower-like titanium dioxide microparticles (F-Ti MPs) through hydrothermal treatment of Ti NPs in the NaOH solution via the hydrothermal route. Their microstructure and adsorption capacity for removal of methylene blue (MB) were investigated.
2. Materials and methods

2.1. Synthesis of Ti NPs
Tetraisopropyl titanate and water at a volume ratio of 1:10 were added together to a 50 mL-flask and then mixed on a stirring machine at room temperature for 30 min to produce Ti NPs. The resultant Ti NPs were collected by centrifugation at 5000 rpm for 3 min, washed with water three times, and finally freeze-dried.

2.2. Synthesis of F-Ti MPs
F-Ti MPs were synthesized through hydrothermal treatment of Ti NPs in the concentrated NaOH solution. Briefly, 2 g of Ti NPs was added to 30 mL of 10 mol/L NaOH solution which was held in 100-mL Teflon-lined autoclaved device and the mixture was hydrothermally treated at 150 °C for 12 h to produce F-Ti MPs. The resultant F-Ti MPs were removed from the NaOH solution and washed with HNO₃ (1 mol/L) and water, and dried at 70 °C overnight.

2.3. Removal of organic pollutants
To examine the adsorption capacity for removal of organic pollutants in the aqueous solution, MB was used as model organic pollutants. For adsorption experiment, 10 mg of Ti NPs and F-Ti MPs were separately soaked in 10 mL of MB solution (2 mg/L) and incubated at room temperature. The adsorption behavior of the samples for removal of MB was monitored with an ultraviolet-visible spectrophotometer (UV-8000S, Shanghai Metash, China). At pre-determined intervals, the UV spectra of the MB solution were collected.

3. Results and discussion
Figure 1 shows SEM photos of (a) Ti NPs and (b) F-Ti MPs. Ti NPs (a) possessed spherical morphology and had the diameter of 100-200 nm. After hydrothermal treatment in the NaOH solution, the F-Ti MPs had significantly different morphology. Each F-Ti MP had the diameter around 3-5 μm and showed the flower-like morphology. In contrast, the hydrothermal treatment caused a significant difference in size and morphology between Ti NPs and F-Ti MPs.

Figure 1. SEM photos of (a) Ti NPs and (b) F-Ti MPs.

Figure 2 shows TEM images of (a) Ti NPs and (b) F-Ti MPs and further revealed the structural difference between them. As shown in Figure 2a, Ti NPs had a dense structure with a sphere-like morphology and had the diameter around 155 nm. As shown in Figure 2b, F-Ti MPs also showed the dense structure after hydrothermal treatment. However, a significant difference in morphology between Ti NPs and F-Ti MPs were clearly observed. F-Ti MPs showed the hierarchical and flower-like morphology with the diameter around 3-5 μm. Each F-Ti MP was constructed by numerous nanowires and showed the hierarchical structure.
Figure 2. TEM photos of (a) Ti NPs and (b) F-Ti MPs.

MB is one type of the representative organic pollutants and widely exists in the industrial water [7]. To evaluate the adsorption capacity, MB was used as model organic pollutant and separately incubated with Ti NPs and F-Ti MPs. As shown in Figure 3, MB has the adsorption band at 664 nm. In the case of Ti NPs, the intensity of the peak at 664 nm was gradually decreased. After 80 min of incubation, around 54% of MB was removed from the MB aqueous solution. In the case of F-Ti MPs, the intensity of the peak at 664 nm was significantly decreased after 10 min. Around 88% of MB was successfully removed from the MB solution. This indicates that F-Ti MPs significantly enhanced the adsorption capacity due to the presence of the hierarchical and flower-like structure.

Figure 3. UV spectra of MB solution after incubation with (a) Ti NPs and (b) F-Ti MPs.

4. Conclusions
F-Ti MPs with hierarchical and flower-like structure were successfully synthesized using Ti NPs as the starting materials via a hydrothermal route. They showed the enhanced adsorption capacity for removal of MB from the aqueous solution.

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