



# Controlled fabrication of ordered mesoporous titania/carbon fiber composites with high photoactivity: Synergistic relationship between surface adsorption and photocatalysis



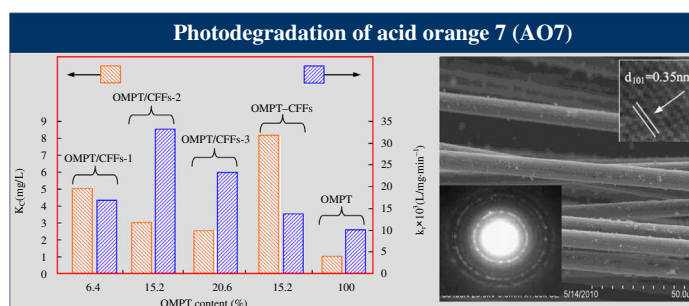
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## HIGHLIGHTS

- Carbon fibers (CFs) supported titania with the ordered mesopores.
- Photocatalytic degradation behavior of acid orange 7 is described by L–H kinetics.
- The dependence of the reaction rate on ordered mesoporous titania (OMPT) content.
- $K_{ads}$  and  $k_r$  in L–H depended on OMPT content, combination from of OMPT and CFs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ordered mesoporous  $\text{TiO}_2$  (OMPT) supported on carbon fibers (OMPT/CFs) were fabricated by supercritical deposition using liquid crystal as soft template. The OMPT/CFs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and nitrogen sorptometry, and their photocatalytic activity was studied through the degradation of acid orange 7 (AO7) aqueous solution. The results indicate that OMPT is dispersed on the CFs with crystalline size of 10–20 nm and pore size of 2–5 nm. Although with increasing amount of  $\text{TiO}_2$  coatings the surface area of OMPT/CFs decreased relative to that of CFs, OMPT/CFs- $n$  ( $n = 3$ ) ( $n$  is the number of precipitation/drying cycles used to prepare the composite), which had the maximum  $\text{TiO}_2$  content, still possessed a surface areas of  $538.6 \text{ m}^2/\text{g}$  because of the mesostructure characteristics of titania. The OMPT/CFs showed high activity in the photodegradation of AO7 in aqueous solution in comparison with P25, pure OMPT and OMPT–CF mixture. Such activity was facilitated by the synergistic relationship between surface adsorption characteristics and photocatalytic potential. Because of the mutual constraint between loading and surface area on the photocatalytic efficiency, the optimal loading of OMPT in OMPT/CFs-2 for AO7 degradation is 15.2 wt%. The photocatalytic behavior could be described in terms of a modified Langmuir–Hinshelwood model.

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## 1. Introduction

In recent years, application of photocatalysis in water treatment has attracted much attention because of its ability to

completely remove pollutants and applicability to a broad variety of compounds [1,2]. Nanosized  $\text{TiO}_2$  is one of the most efficient semiconductors currently available for the photocatalytic degradation of environmental pollutants [3,4]. However, the high

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fineness, poor adsorption of pollutants and difficulty of recovery from water have hindered the application of TiO<sub>2</sub> in photocatalysis [5,6]. An effective strategy has been applied to overcome the mentioned shortcomings. Porous materials are ideal catalyst supports because their large surface area and uniform pore size distribution, both of which facilitate diffusion of large organic molecules into internal active sites [4,6,7]. Some researchers have developed porous materials supported of TiO<sub>2</sub> as composite photocatalysts including ceramic, glass and metal using various techniques. These photocatalysts are efficient photocatalysts and exhibit increased absorption [7–11]. Porous carbon (PC) is widely used as a support in gas and water remediation because of its good adsorption properties. TiO<sub>2</sub> supported on PC exhibits a synergism that has marked that markedly enhances the photodegradation of pollutants [2,12–14]. However, PC is commonly used in the form of granules and powder, which are difficult to recycle from aqueous solution after photocatalytic reactions and cause secondary pollution. Carbon fibers (CFs), a new formulation of PC that is used as an adsorbent, have received increasing attention in recent years because of its high surface area, high adsorption capacity, and suitable pore structure [15]. CFs are produced in the form of felt or cloth [16] and are therefore amenable to their use as a catalyst support for various purposes [17–19].

Efficient oxidation of organics requires their adsorption onto the surface of TiO<sub>2</sub> because the photocatalytic process is surface-orientated [20–22]. It is well known that the photocatalytic effectiveness of titania is very sensitive to its crystal phase, particle size, crystallinity, specific area, and pore structure. Since mesoporous TiO<sub>2</sub> was first prepared by David and Jackie through a modified sol–gel process using a phosphate surfactant [23] in 1995, it has received increasing attention because of its high surface area. This property facilitates photocatalytic degradation of contaminants such as humic acid, phenolic compounds, pesticides, chlorinated compounds, and dyes [24–29]. Therefore, synthesis of mesostructured TiO<sub>2</sub> photocatalysts immobilized on highly porous materials and application of the photocatalytic process is desirable. A thorough understanding of the synergistic effects of adsorption and photocatalytic activity is also very important in the design and application of efficient OMPT/CF systems. Nevertheless, there are few reports on the preparation and photocatalytic efficiency of ordered mesoporous TiO<sub>2</sub> (OMPT) coated CFs (OMPT/CFs), and little experimental information concerning the synergistic effects is available.

On the basis of these results, we have attempted to prepare novel photocatalytic materials in the present work. This has entailed loading OMPT onto the surface of CFs by supercritical deposition using liquid crystal as a soft template, which is very different from simple mixing among OMPT, CFs, and the similar composites. To explore the synergistic relationship between surface adsorption characteristics and photocatalytic potential, the as-prepared photocatalysts have been examined by the modern analytical techniques. The performances of these new materials have been tested in the photocatalytic degradation of acid orange 7 (AO7; C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>Na) solution [30].

The dye under consideration is AO7, which is a highly water-soluble, acid red dye of the azo class. It is widely used as a colorant in textiles. Hence, the photodegradation of AO7 is important with regard to the purification of dye effluents [4,30]. Thus, AO7 was selected as the probe molecule in this study, and its decolorization was monitored upon varying the operational parameters, including TiO<sub>2</sub> content and initial concentration of AO7. Besides, the photocatalytic behavior could be described in terms of a modified Langmuir–Hinshelwood model.

## 2. Experimental

### 2.1. Reagents

Raw carbon fibers were used as supports, prepared by spinning of polyacrylonitrile and obtained from Hunan East Grand Reagent Company. Tetra-*n*-butyl titanate, hydrochloric acid, absolute ethanol and cetyltrimethylammonium bromide were all analytical grade and were purchased from Beijing Zhonglian Chemical Reagent company. The chemical structure of AO7 (Biochemical Reagent, Shanghai Jufeng Chemicals) and its absorption spectrum are given in Supporting information Fig. S1. Deionized water, purified with an Elga-Pure water purification system, was used to prepare all solutions for the experiments.

### 2.2. Preparation of OMPT/CFs

OMPT/CFs were fabricated by deposition in supercritical CO<sub>2</sub>, using tetra-*n*-butyl titanate and liquid crystals as the precursor and soft templates, respectively. First, 5 g of cetyltrimethylammonium bromide was accurately weighed, and then completely dissolved in 30 mL of distilled water to form the liquid crystal template by stirring for a specified period. Next, 25 mL of tetra-*n*-butyl titanate was dissolved in 50 mL ethanol and 3.3 mL of HCl, and the mixture stirred for 2 h (100 rpm) with a magnetic stirrer. While still stirring at an ambient laboratory temperature, the obtained liquid crystal was added dropwise over 1 h. After the sol was aged for 12 h at room temperature, it was deposited on CFs in moderately supercritical CO<sub>2</sub>. Subsequently, organics in the resulting composite was extracted in a Soxhlet apparatus for 48 h. The composites were dried for 30 min at 100 °C in an oven and then calcined at 500 °C for 1 h in a nitrogen atmosphere to synthesize OMPT/CFs. The precipitation and drying procedure was repeated three times before the last cycle of drying to calcination. Accordingly, the product was named OMPT/CFs-*n*, where *n* is the number of times precipitation/drying cycles used to prepare the composite. For comparison, the aged sol was also calcined at 500 °C for 1 h to synthesize pure OMPT powder.

### 2.3. Characterization of the composite photocatalyst

The profiles of the OMPT/CF photocatalysts were observed by scanning electron microscopy (Hitachi S3400N, Japan) at an accelerating voltage of 20 kV. High-resolution transmission electron microscopy/selected area electron diffraction, (HRTEM/SAED) was performed on a JEOL microscope (JEM 2100F) at an accelerating voltage of 200 kV. Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U SAXS system (Bruker, Germany) using Cu K $\alpha$  radiation (40 kV, 35 mA). Wide-angle X-ray diffraction (WAXRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation (40 kV, 40 mA).

Nitrogen adsorption–desorption isotherms were used to determine the Brunauer–Emmett–Teller (BET) surface area and pore size distribution (ASAP2010, Micromeritics Company, USA) at 77 K. UV/Vis absorbance spectra of the catalysts were recorded with a JASCO V-560 UV–vis spectrophotometer. The chemical states of samples were determined using X-ray photoelectron spectroscopy (XPS) (VG Scientific ESCALAB Mark spectrometer, England, Mg K $\alpha$  radiation, 1253.6 eV). TiO<sub>2</sub> loading was determined by thermogravimetric analysis (WCT-2C, Optical

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