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Hydrothermal synthesis and photocatalytic activity of combination of flowerlike TiO_2 and activated carbon fibers

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ABSTRACT

The three-dimensional flowerlike TiO_2 microstructure was successfully deposited on the surface of activated carbon fibers (ACFs) pre-coated with TiO_2 seed layer via a hydrothermal process. The flowerlike structure was constructed by rutile-phased TiO_2 rods and the formation mechanism of anchoring TiO_2 onto ACF to form the TiO_2/ACF composite was also discussed. The TiO_2/ACF exhibited a relatively higher photocatalytic activity than the nanometer rutile TiO_2 in the degradation of methyl orange, presumably due to a red shift, restraint of the photogenerated hole and electron recombination and high light-harvesting efficiency. In addition, the TiO_2/ACF is favorable to reuse by emptying off the supernatant solution.

1. Introduction

As a photocatalyst, TiO_2 has many advantages such as non-toxicity and excellent photochemical stability [1]. However, there are two main drawbacks for the TiO_2 powder during its use in the practical photocatalytic process [2]: (1) separation and recovery of the powder from the reaction medium is difficult; and (2) the suspended powder tends to aggregate especially at high concentrations. In these regards, an alternative method is to immobilize TiO_2 powder on an inert and suitable supporting matrix [3]. Activated carbon (AC) is widely used as a support in water purification due to its excellent adsorption capacity, and exhibits a synergistic effect with supported TiO_2 to accelerate the decomposition of pollutants [4]. Nevertheless, AC is commonly used in the form of granule or powder, and there remain some difficulties in filtering and recovery of AC from wastewater. Compared to AC, active carbon fibers (ACFs) are fabricated in the form of felt and preferable in handling [5].

In order to improve the physical and chemical performance in the devices, designing the morphology of TiO_2 is a focus of current research. Nguyen and co-workers [6] reported that the three-dimensional (3D) hierarchical TiO_2 was more efficient than the analogs in low dimensional form. The aim of the present work is (a) to develop a feasible procedure of anchoring TiO_2 with 3D morphology onto ACF, (b) to characterize the structure and property of the obtained composite material and (c) to evaluate its related photocatalytic activity in the degradation of methyl orange (MO).

2. Experimental

Rutile TiO_2 (R-TiO_2) powders with an average particle size of 40 nm were purchased from Aladdin Chemical Reagent. First, PAN-based ACFs (0.1 g) were dispersed in anhydrous EtOH (20 mL) in a beaker with stirring to form a homogeneous suspension. 1 ml of $Ti(OBu)_4$ was injected into the homogeneous suspension, and the suspension was further stirred at room temperature for 60 min, followed by filtering and rinsing with anhydrous EtOH to remove excess $Ti(OBu)_4$. The obtained product was annealed at 400 °C for 2 h in nitrogen atmosphere to acquire TiO_2-seeded ACFs. Subsequently, the TiO_2-seeded ACFs were mixed with HCl (15 mL), deionized water (35 mL), and $Ti(OBu)_4$ (1 mL) in a Teflon container (100 mL). Afterwards, the container was subjected to hydrothermal treatment at 150 °C for 4 h. The as-prepared product, denoted as TiO_2/ACF, was washed with deionized water and anhydrous EtOH successively and finally dried in a vacuum oven at 60 °C for 4 h.

X-ray diffraction (XRD) patterns were recorded on a D8 Advance diffractometer using Cu Kα radiation. UV–vis absorption spectroscopy was conducted on a U-4100 spectrometer. Scanning electron microscopy (SEM) was performed by an S-4800 scanning

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electron analyzer with an accelerating voltage of 15 kV. Photoluminescence (PL) spectra were executed on an F-7000 fluorescence spectrometer.

The photocatalytic experiments were carried out in a XPA-1 photoreactor (Xujiang Electromechanical Plant, Nanjing, China) equipped with a 300 W high-pressure mercury lamp (λ=365 nm) as the UV light source. At first, 100 mg of sample was added to 50 mL of a solution of MO (10 mg/L) in a quartz tube. Then, the tube containing the suspension was mounted onto the carrousel inside the photoreactor and aerated with a constant air flow for 70 min in dark to reach surface adsorption equilibrium. Afterwards, the tube was exposed to a distance of 20 cm UV light irradiation with continuous purging of air to provide oxygen. At regular intervals, 4 mL of suspensions were extracted and centrifuged to separate the supernatant liquid. The supernatant liquid was collected and analyzed by recording the characteristic absorption of MO (464 nm) using a UV–vis spectrometer.

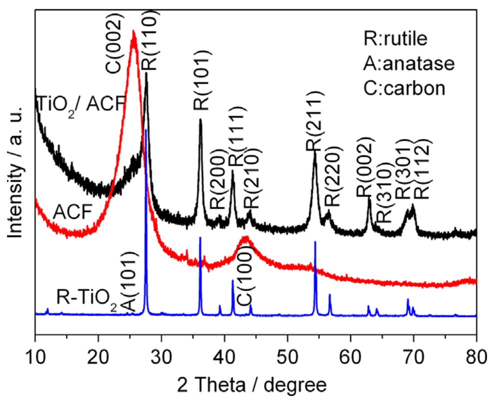

Fig. 1. XRD patterns of TiO_2/ACF, ACF and R-TiO_2.

3. Results and discussion

The two peaks centered at around 25° and 44° are attributed to the (002) and (100) planes of the carbon structure in ACF (Fig. 1a) [7]. Compared with TiO_2/ACF (Fig. 1b), it is observed that the carbon peaks still exist whereas their intensities decline due to TiO_2 loading. It is worthwhile to note that the structure of TiO_2 is well crystallized in the rutile phase (Fig. 1c).

A large quantity of 3D flowerlike TiO_2 microstructures almost overlaps the entire surface of ACF (Fig. 2a). Furthermore, observing the sample at different magnifications (Fig. 2b and c) shows more than one layer of such structure. The flowerlike TiO_2 microstructure is assembled of TiO_2 rods, approximately 1–1.5 μm in length (Fig. 2d), which are aggregated into clusters (Fig. 2b). It is appreciated that TiO_2/ACF exhibits the double-layer unit of the ACF surface, which constitutes TiO_2 rod array layer and TiO_2 seed layer, and the TiO_2 rods grow tightly on the TiO_2 seed layer (Fig. 2d). EDS analysis (Fig. 2e) indicates that only Ti, O and C are

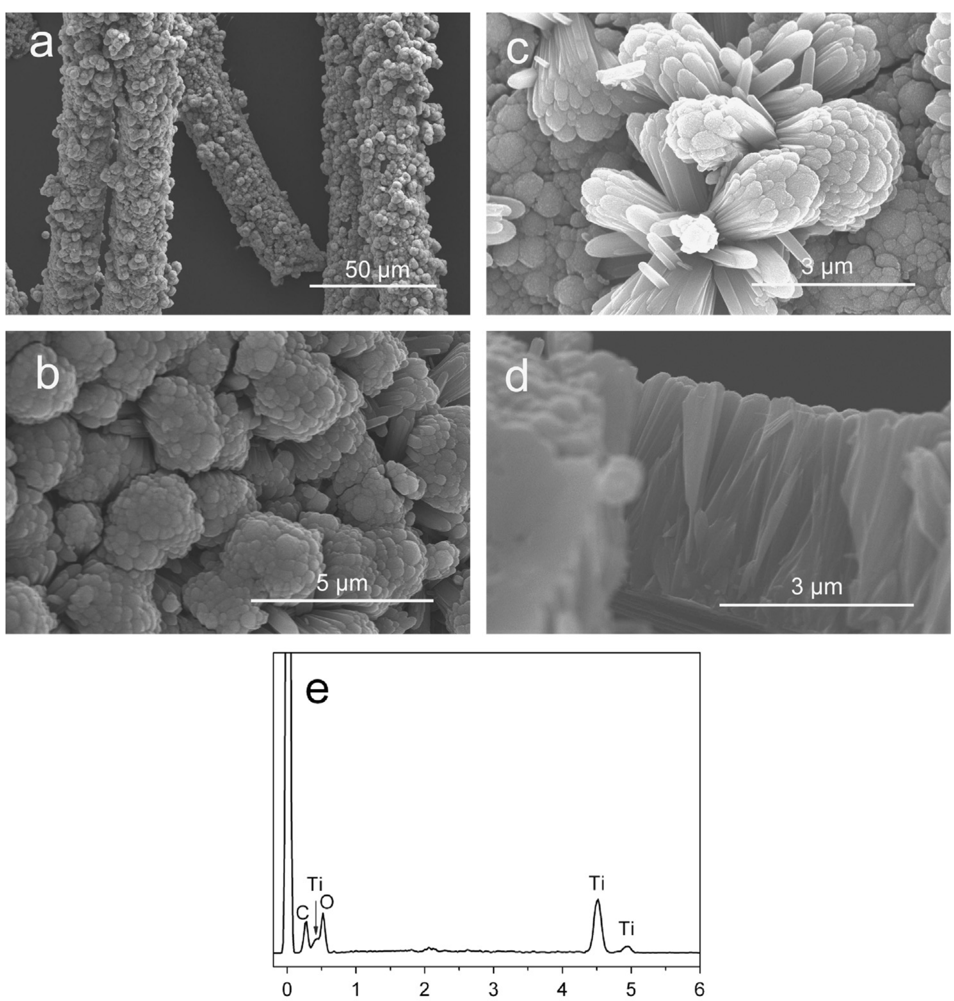

Fig. 2. Low- (a), and high-magnification (b)–(d) SEM images and EDS (e) of TiO_2/ACF.