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Grafting TiO_2 nanoparticles onto carbon fiber via "thiol-ene" click chemistry and its photodegradation performance for methyl orange

Lei Xiong *, Daosong Lan, Hongbo Liang, Liang Chen, Qiuping Wang

School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330063, China

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ABSTRACT

In this article, we presented a novel and facile method for obtaining a photocatalyst of carbon fiber grafted with TiO_2 (CF-TiO_2) via "thiol-ene" click chemistry. The as-prepared CF-TiO_2 was characterized by FT-IR, TGA, SEM, TEM and XRD. The results demonstrate the successful grafting of TiO_2 onto the CF surface and the grafting content of TiO_2 is about 9%. The photocatalytic activity of CF-TiO_2 was evaluated by measuring the photodegradation of methyl orange (MO) under UV irradiation. The photodegradation rate of CF-TiO_2 (89%) is significantly higher than that of pure CF (5.4%) and pure TiO_2 (56%). In addition, the photostability test of CF-TiO_2 demonstrates that it is reusable and stable due to strong covalent bonds between CF and TiO_2.

1. Introduction

Titanium dioxide (TiO_2) is considered as an effective and environmentally friendly photocatalyst, which has been widely used in the treatment of environmental pollution [1,2]. However, the powdered TiO_2 is easy to aggregate and difficult to recover from the reaction medium, which limits its practical application. In order to overcome these shortcomings, a feasible way is to immobilize TiO_2 onto certain substrates, including silica, carbon nanotubes, active carbon and carbon fiber [3–6].

Here, we used carbon fiber (CF) as substrate for grafting TiO_2 nanoparticles. In comparison with other substrates, CF shows some unique performances, such as good flexibility, excellent mechanical properties, good adsorptivity and large surface area. Much research has been carried out to introduce TiO_2 onto CF by using different techniques, including sol-gel method, surface coating and vapor deposition [7–10]. However, these methods are somehow complex and demand specialized equipments.

Recently, "thiol-ene" click chemistry has received much attention for its application in surface grafting of inorganic substrates. Compared to the traditional surface grafting techniques, this technique has many advantages, such as high selectivity and conversion, simple experimental condition and rapid reaction speed [11–13]. Through thiol-ene click chemistry, TiO_2 can be grafted onto CF substrate by UV irradiation in a short time (<1 h), and strong covalent bonds can be formed between TiO_2 and substrate. The immobilization of TiO_2 onto CF by using covalent bonds is much tighter than that by physical adsorption, which may enhance the photostability and recycling ability of photocatalyst. Thus, thiol-ene click chemistry is a very promising method to graft TiO_2 onto CF surface in a rapid and energy saving fashion.

Here, we have designed a facile and rapid technique for grafting TiO_2 onto CF via "thiol-ene" click chemistry, producing a highly efficient and UV-responsive composite photocatalyst. The photocatalytic activity of composite photocatalyst was evaluated based on the photodegradation of MO under UV irradiation.

2. Materials and methods

2.1. Grafting of KH590 onto CF surface

The PAN-based CF (Toray Co., Ltd) was first immersed in 65% nitric acid under stirring at 80 °C for 2 h, followed by rinsing and drying, obtaining oxidized CF. The oxidized CF was then added into a (3-mercaptopropyl)trimethoxysilane (KH590) solution ($V_{ethanol}$: $V_{KH590} = 95:5$) and stirred at 70 °C for 6 h. After that, the CF grafted with KH590 (CF-KH590) was washed with ethanol for several times, and dried in vacuum at 60 °C for 24 h.

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* Corresponding author.
E-mail address: x_lei81@163.com (L. Xiong).

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2.2. Synthesis of vinyl TiO_2

The 3-aminopropyltriethoxysilane (KH550) was immobilized onto TiO_2 surface to prepare amino-functionalized TiO_2 (TiO_2-KH550), and the procedure was presented in our previous work [14]. Then, the TiO_2-KH550 was dispersed into ethanol, and reacted with allyl glycidyl ether for 48 h at 30 °C. At the end of reaction, the crude products were washed completely by ethanol and dried under vacuum to give vinyl TiO_2.

2.3. Synthesis of CF-TiO_2 via click chemistry

The CF-KH590, vinyl TiO_2 and dimethylformamide (DMF) were charged into a reactor and sonicated for 30 min at room temperature. Then, the UV photoinitiator 2, 2-dimethoxy-2-phenylacetophenone (DMPA) was added into the reactor. The click reaction between CF-KH590 and vinyl TiO_2 was performed at room temperature for 20 min by irradiation with a 365 nm UV light. After reaction, the mixture was washed with DMF for several times. The obtained CF-TiO_2 was dried under vacuum at 90 °C for 48 h. The whole synthetic route of CF-TiO_2 is shown in Fig. 1a.

2.4. Characterization

TGA was performed with a TGAQ50 TA instrument in the range from room temperature to 1000 °C, with a heating rate of 10 °C/min under air atmosphere. FT-IR spectra of samples were recorded on a Shimadzu IR Prestige-21 spectrometer. The morphology of samples was analyzed using a FEI Nova Nano SEM450 scanning electron microscope (SEM) and a JEM-2010 transmission electron microscope (TEM). X-ray diffraction (XRD) patterns of samples were detected by a Bruker D8 X-ray diffractometer. The photocatalytic activity of CF-TiO_2 was studied by degradation experiments under UV irradiation from a mercury lamp (300 W, 365 nm), using MO aqueous solution (100 mg/L).

3. Results and discussions

To confirm the successful synthesis of CF-TiO_2, FT-IR and TGA measurements were performed to characterize the CF-TiO_2, and the results are shown in Fig. 1b and c. As shown in Fig. 1b, the peaks related to C—H (2924 cm^{-1}), C=C (810 cm^{-1}) and Si—O (1090 cm^{-1}) appear in spectrum of vinyl TiO_2, confirming that the vinyl groups were introduced onto TiO_2 via the grafting KH550. Meanwhile, a weak peak assigned to —SH groups (2550 cm^{-1}) appears at the spectrum of CF-KH590, indicating the presence of KH590 on fiber surface. After click reaction, the —SH absorption peak completely disappears in the spectrum of CF-TiO_2. Furthermore, two new peaks ascribed to C—S—C (694 cm^{-1}) and Ti-O (610 cm^{-1}) can also be found in this spectrum. FT-IR analysis demonstrates that TiO_2 was successfully grafted onto CF surface via the click reaction between —SH groups in CF-KH590 and vinyl groups in vinyl TiO_2.

TGA was used to investigate the effect of the grafted TiO_2 on the thermal behavior of CF. T_5 (temperature of 5% weight loss) and T_{max} (temperature of the maximum degradation rate from DTG) of pure CF are 530 °C and 703 °C, respectively. However, T_5 and T_{max} of CF-TiO_2 increase to 644 °C and 835 °C, indicating that the

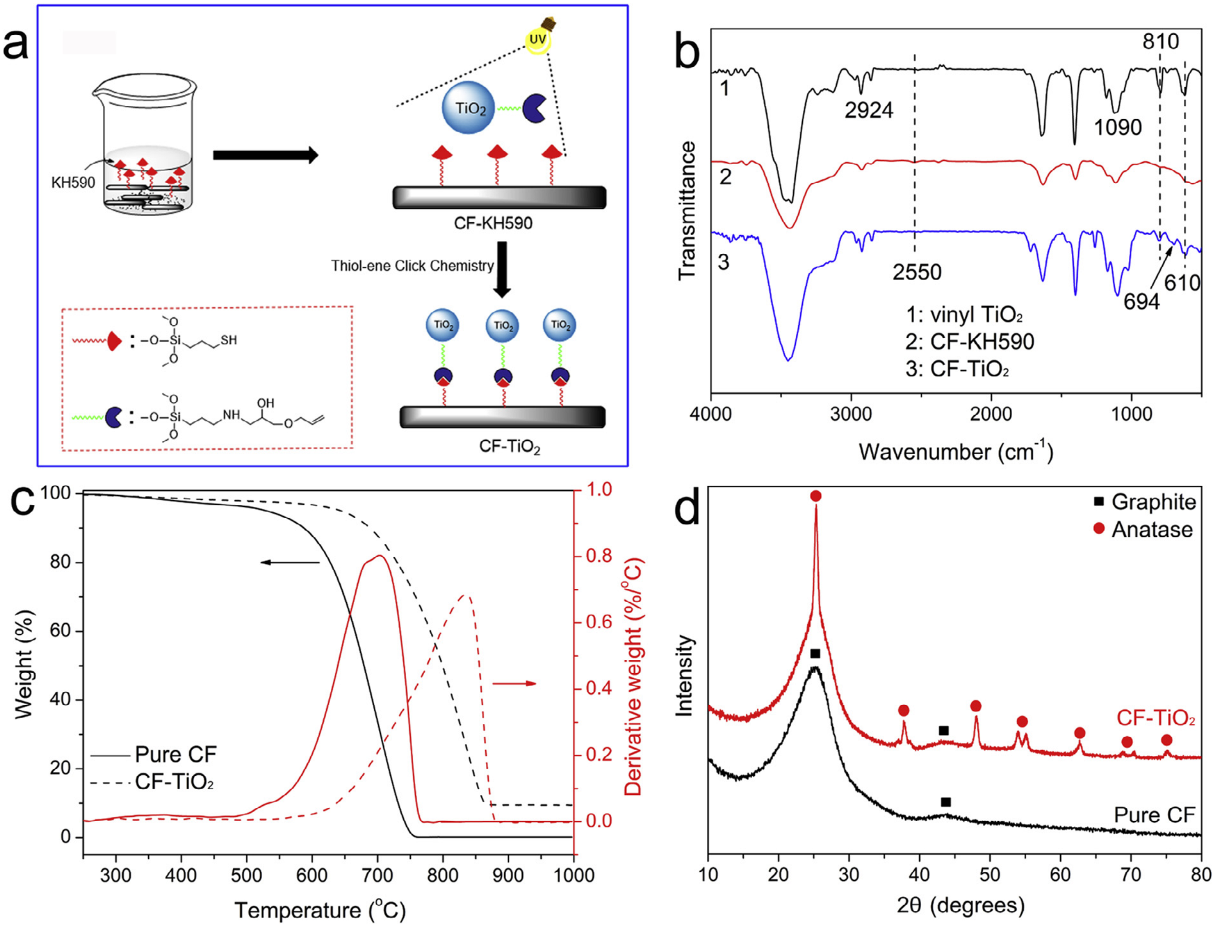

Fig. 1. (a) Schematic of the CF-TiO_2; (b) FT-IR spectra of vinyl TiO_2, CF-KH590 and CF-TiO_2; (c) TGA curves of pure CF and CF-TiO_2; (d) XRD patterns of pure CF and CF-TiO_2.