

DOI <https://doi.org/10.1007/s11595-019-2051-9>

Carbonaceous Nanofibers-titanium Dioxide Nanocomposites: Synthesis and Use as a Platform for Removal of Dye Pollutants

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Abstract: A mild chemistry route was developed to prepare carbonaceous nanofibers-titanium dioxide (CNF-TiO₂) nanocomposites for removal of dye pollutants. In the process of the template-directed hydrothermal carbonization (HTC), ultrathin Te nanowires were adopted as templates and glucose as the carbon source, and TiO₂ was decorated on CNF via the hydrolysis of tetrabutyltitanate in the presence of CNF in ethanol. The as-prepared materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) and X-ray diffraction (XRD). SEM and TEM observations displayed that TiO₂ nanoparticles were anchored on the CNF. EDX and XRD data confirmed that the as-synthesized samples were CNF-TiO₂, and TiO₂ belonged to anatase titania. Taking advantage of combined benefits of carbonaceous nanofibers and titanium dioxide, these CNF-TiO₂ nanocomposites exhibited higher removal efficiency in a short time and showed good reusability. It was showed that over 97% of Rhodamine B could be removed in 15 min without generating the solid and liquid wastes. The removal efficiency of dyes was still over 80% after reuse in five cycles. All the results demonstrate that the as-prepared CNF-TiO₂ composites are effective materials for fast and effective removal of dye pollutants and thus can provide a new platform for dye decontamination.

Key words: carbon materials; nanocomposites; dye pollutants

1 Introduction

At present, many people suffer from malnutrition, sickness, and even die due to the lack of clean, fresh water^[1-3]. The main cause of water shortage is contamination. Among various pollutants, organic dyes has led to growing public and environmental concerns as the long lifetimes of dyes in water reservoirs causes food chain contamination^[4-7]. As a result, immense interest has been sparked in developing advanced

methods and materials to decontaminate water more efficiently.

Carbon materials (from the early activated carbon to mesoporous carbon, carbon nanotubes, and graphene, recently) and its composite materials have already been proved to be powerful adsorbents for treating dye pollutants as its remarkable properties, such as huge surface area, easy to perform and insensitive to toxic substances^[7-12,21-25]. For example, we have previously reported a novel magnetite/reduced graphene oxide nanocomposites as an adsorbent for dye pollutants^[7]. Although it was shown to be an efficient way to separate dye pollutants from the waste water, it would generate a large amount of hazardous solid and liquid wastes as it could not degrade the pollutants.

TiO₂ is one of the most studied materials owing to its chemical stability, cheapness, low-toxicity and high efficiency in the removal of pollutants in water and air^[13-27]. It is a robust way to treat the dye pollut-

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(Received: Feb. 10, 2018; Accepted: Apr. 21, 2018)

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Funded by the National Natural Science Foundation of China (No. 21501054), the Collaborative Grant-in-Aid of the HBUT National "111" Center for Cellular Regulation and Molecular Pharmaceutics (No. XBTK-2018003) and the Talents Program from Hubei University of Technology (No. BSQD14010)

ants via the TiO_2 /carbon materials. As a result, many nanocomposites, including TiO_2 /carbon nanotubes, TiO_2 /graphene and carbon@ TiO_2 , have been investigated recently^[21-25]. Although these new types of nanomaterials provide the possibility in treating waste water, some limitations still exist, such as complicated procedures and low performance. Hence, it is still a major challenge to develop a simple and efficient method to prepare TiO_2 /carbon materials.

Recently, Yu and co-workers reported a new type carbon materials named nanofibers (CNF), which were prepared by the template-directed hydrothermal carbonization (HTC) process^[28,29]. Benefiting from the unique advantages of the CNF scaffolds, the multi-functional composites of CNF- TiO_2 could be prepared in a simple way. Taking advantages of TiO_2 and CNF, we report here for the first time using CNF- TiO_2 nanocomposites for dye pollutants removal. Several advantages of these composites make it especially attractive. First, the as-prepared CNF- TiO_2 nanocomposites is environmental friendly and inexpensive. Second, the dye pollutants can be degraded by the CNF- TiO_2 nanocomposites in a short time without generating the solid and liquid wastes. The last but not the least, the as-prepared CNF- TiO_2 nanocomposites exhibited higher degradation of dyes than CNF and commercial P25 under UV-light irradiation.

2 Experimental

2.1 Synthesis of highly uniform CNF

The first step involved the synthesis of ultrathin Te nanowire templates via a simple hydrothermal method^[28]. Then the CNFs were prepared by a template-directed hydrothermal carbonization procedure

developed by Yu and coworkers^[29]. Briefly, 1 mL of Te nanowire suspension (0.05 mol/L) was dispersed into 20 mL of glucose solution (1.25 g of glucose). Then the mixture were transferred to a Teflon-lined stainless-steel autoclave at 160 °C for 12 h to obtain Te@C. Then Te templates were removed by chemical etching in 30 mL of acidic H_2O_2 solution ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=2:5:23$, v/v). Pure CNF was obtained by centrifugation (6000 rpm) and washing by ethanol solutions ($\text{EtOH}:\text{H}_2\text{O}=1:1$, v/v). The removal of Te nanowire was investigated by EDX patterns.

2.2 Preparation of CNF- TiO_2 composites and pure TiO_2

0.1 mL of tetrabutyltitanate was dissolved in 10 mL of absolute ethanol to form a mixture solution. Next, 25 mg of CNF was dispersed in this freshly prepared solution. Then 5 mL of water/ethanol mixture (water/ ethanol = 0.5:9.5, v/v) was added slowly to the above suspension over a period of 10 min. Finally, after hydrothermal treatment of the above products at 180 °C for 12 h, well-defined CNF- TiO_2 composites were yielded. Pure TiO_2 was obtained in the same condition as the preparation of CNF- TiO_2 while without adding CNF.

2.3 Photoreactivity measurement

20 mg photocatalyst (CNF- TiO_2 , P25, CNF or TiO_2) were suspended in 40 mL of Rhodamine B (10^{-4} mol/L or 10^{-5} mol/L) solution. The suspension was sonicated for 5 min and then was irradiated using a 250 W high-pressure mercury lamp (central wavelength of 365 nm). The solution was analyzed on a UV-vis spectrophotometer. After each cycle, the catalyst was collected and washed with ethanol several times. Then, the catalyst was fully dried at 40 °C in an oven.

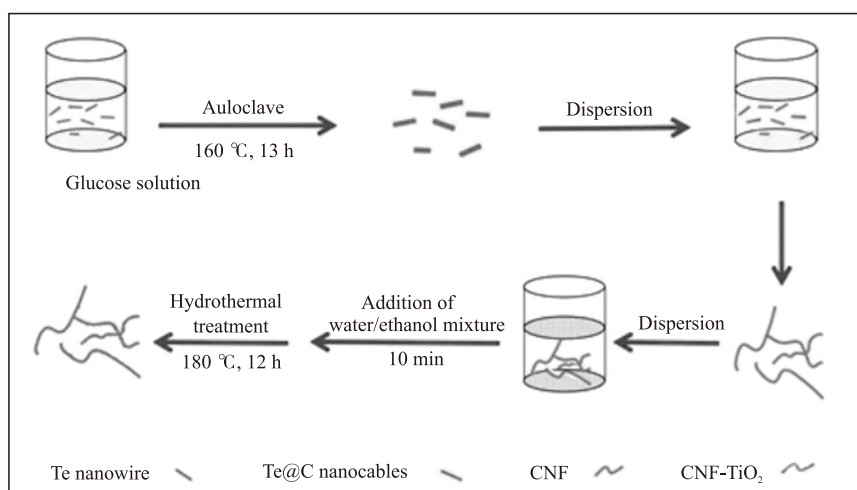


Fig.1 Schematic illustration for the synthesis of carbonaceous nanofibers-titanium dioxide (CNF- TiO_2) composites

3 Results and discussion

The CNF-TiO₂ composites were fabricated through two steps of hydrothermal processes. This approach started with the template-directed hydrothermal carbonization (HTC) using ultrathin Te nanowires as templates and glucose as the carbon source and further decorated TiO₂ on CNF via the hydrolysis of tetrabutyltitanate in the presence of CNF in ethanol. A schematic illustration of the preparation of CNF-TiO₂ composites is presented in Fig.1.

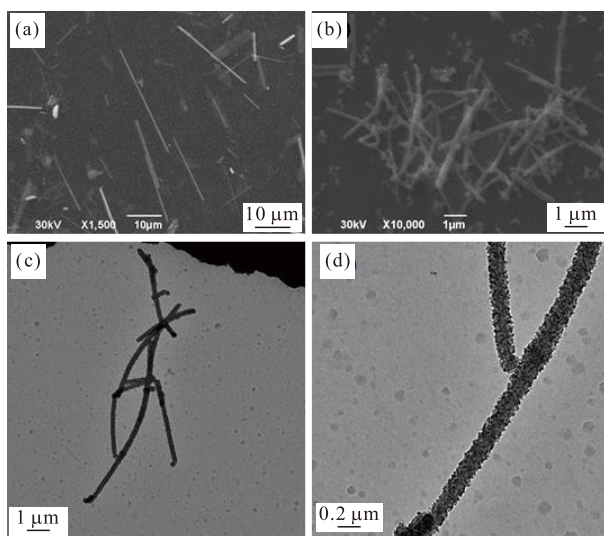


Fig.2 (a, b) SEM and (c, d) TEM images. (a) Te nanowires, (b) CNF, (c, d) CNF-TiO₂

Scanning electron microscopy (SEM) showed Te nanowires with the diameter of about 220 nm and length up to tens of micrometers had no evidence

of aggregation (Fig.2(a)). Benefited from these templates, the as-prepared CNF is composed of numerous interweaving nanowires with diameter of 280 nm and length up to several micrometers (Fig.2(b)). A typical transmission electron microscopy (TEM) image of CNF-TiO₂ appears in Fig.2(c) and 2(d). As noted, TiO₂ nanoparticles were homogeneously anchored onto the surface of the CNF.

The energy-dispersive X-ray (EDX) spectrum analysis showed strong Te peak from Te nanowires (Fig.3(a)). After hydrothermal carbonization, Te peak disappeared, and C increased dramatically. It confirmed the formation of CNF via template-directed hydrothermal carbonization process (Fig.3(b)). Spectrum of CNF-TiO₂ demonstrated the presence of Ti element, indicating the successful preparation of CNF-TiO₂ (Fig.3(c)). The crystallographic structures of the as-prepared CNF-TiO₂ were confirmed by X-ray diffraction (XRD). It showed that the diffraction peak assigned to the (101) corresponding to anatase titania (JCPDS card no. 86-1157), suggesting the good photocatalytic ability of the as-prepared materials (Fig.3(d)).

Next, the photocatalytic activity of CNF-TiO₂ was evaluated by monitoring the degradation of Rhodamine B (RB)-an azo dye-under ultraviolet (UV)-light irradiation. Firstly, we investigate the relation between the concentration of the RB and the removal efficiency using the same amount of CNF-TiO₂. As indicated in Fig.4, the characteristic UV-vis absorption of RB at 554 nm decreased on increasing the irradiation time. When the amount of RB was 10⁻⁴ mol/L and

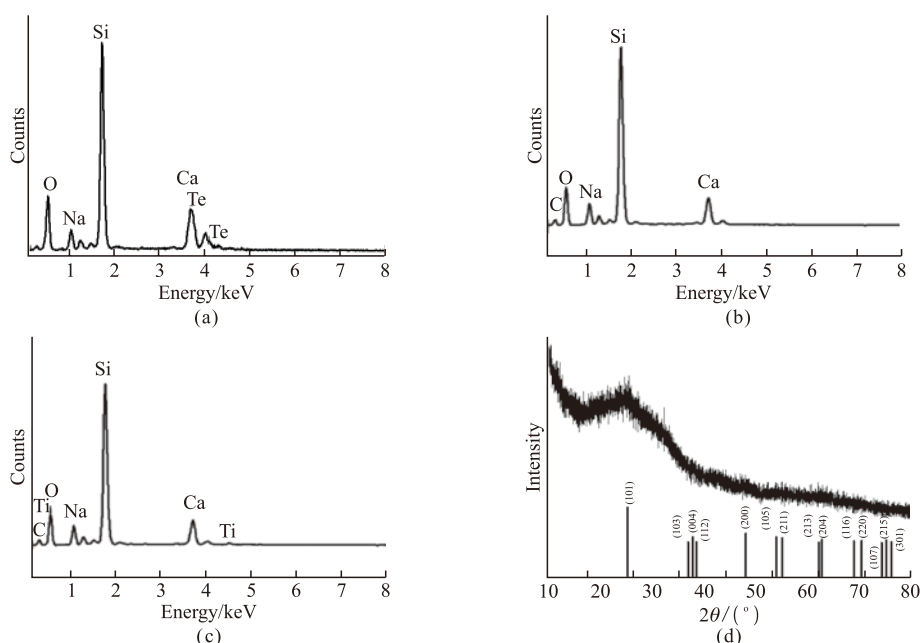


Fig.3 (a, b, c) EDX and (d) XRD patterns. (a) Te nanowires, (b) CNF, (c, d) CNF-TiO₂

10^{-5} mol/L, it showed that over 97% and 82% of RB could be removed within 15 min under the irradiation of UV lights respectively. Therefore, we chose the concentration of 10^{-4} mol/L in the next experiments.

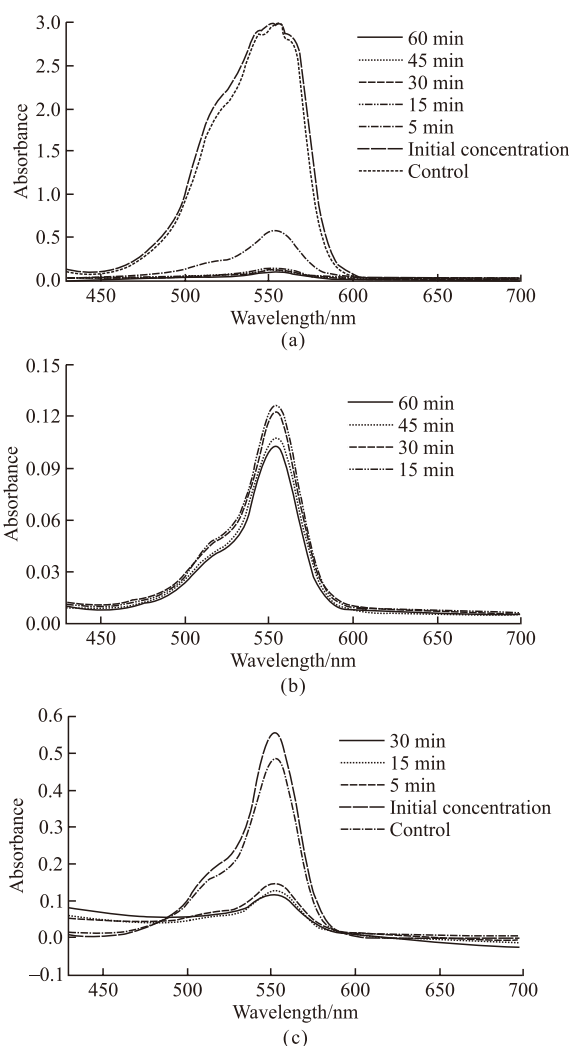


Fig.4 Removal of RB with CNF-TiO₂ at different time under the UV light. The initial concentration of RB was (a) 10^{-4} mol/L and (c) 10^{-5} mol/L. (b) was the magnification of (a). Control was the removal of RB for (a) 60 min and (c) 30 min without CNF-TiO₂ under the UV light

As seen from the Fig.5, all of the materials showed the decontamination activity of dyes. However, the removal efficiency of CNF was lowest, more than 70% RB remained after 60 min irradiation. It could be ascribed to the low photocatalytic activity of CNF and the removal of dyes was mainly due to the adsorption activity of CNF. In the presence of P25 and pure TiO₂, the degradation was remarkably improved, with 90% and 93% of RB decomposed respectively within 60 min irradiation due to its high photocatalytic activity compared with CNF. Apart from this, it was exciting to find that CNF-TiO₂ nanocomposites could remove 97% of RB within 15 min irradiation. The removing

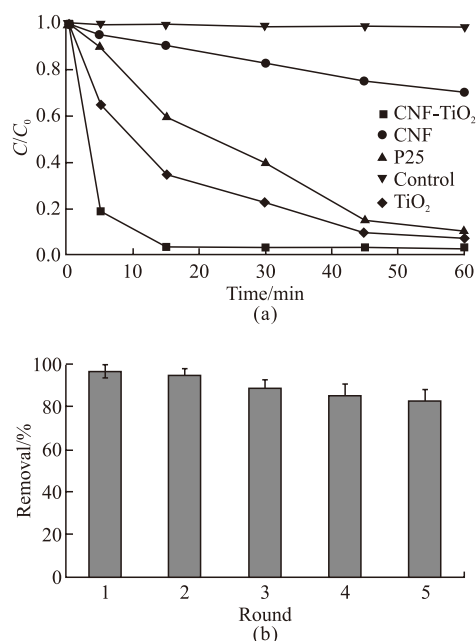


Fig.5 (a) Liquid-phase photocatalytic degradation of RB with (CNF-TiO₂, CNF, P25, TiO₂) and without (control) the photocatalyst under the irradiation of UV light. (b) Recycling of CNF-TiO₂ in the removal of dyes. The amount of photocatalyst (CNF-TiO₂, P25, CNF or TiO₂) was 20 mg

efficiency was better than many reported materials and commercial materials^[6,7, 23]. The mechanism of high removal efficiency of CNF-TiO₂ could be rationalized as follows. Firstly, RB molecules could be easily attached to the surface of CNF-TiO₂ nanocomposites by electrostatic attraction. Such adsorption enhancement increased the effective concentration of RB molecules near the CNF-TiO₂ composites, resulting in high catalytic degradation rate. Moreover, excellent contact between TiO₂ nanoparticles and CNF also prevented TiO₂ from leaching out in the catalytic reactions. Finally, an efficient charge separation and transfer of CNF-TiO₂ composites led to the enhancing photocatalytic activity^[23,24]. Moreover, the reuse of adsorbents is quite crucial in practical applications because of stringent ecological and economic demands for sustainability. Fig.5(b) shows that the removal efficiency of dyes was still over 80% after reuse in five cycles, indicating that the as-prepared CNF-TiO₂ had good reusability.

4 Conclusions

An efficient method has been developed for producing CNF-TiO₂ nanocomposites by using cost-effective precursors. Benefiting from the combined advantages of CNF and TiO₂, these CNF-TiO₂ nanocomposites were shown to be an efficient way to treat dye pollutants in a short time without generating

the solid and liquid wastes. The experimental results showed that the as-prepared CNF-TiO₂ had good reusability. All the results suggested that the CNF-TiO₂ composites are effective for removal of dye pollutants, and thus can be used as a new platform for dye decontamination.

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