Fabrication of nanocrystalline anatase TiO₂ in a graphene network as a bamboo coating material with enhanced photocatalytic activity and fire resistance

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A B S T R A C T

Many bamboo products are used in the textile industry and are exposed to dyeing wastewater. To improve its photocatalytic activity, nanocrystalline anatase TiO₂ in a graphene network on a bamboo substrate was synthesized by two hydrothermal processes. The crystal phase, morphology, microstructure and other physicochemical properties of the original bamboo timber (BT), BT coated with reduced graphene oxide (RGOBT), BT coated with TiO₂ (TiO₂BT) and RGOBT coated with TiO₂ (RGO@TiO₂BT) were characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray analysis. BT, RGOBT and RGO@TiO₂BT were analyzed by Fourier transform infrared spectroscopy. The RGO@TiO₂BT composite possesses excellent photocatalytic activity which are superior to those of BT, RGOBT and TiO₂BT. The photodegradation efficiency of methyl orange, methylene blue and rhodamine B are 87.2%, 85.1% and 73.9% after 60 min UV photodegradation respectively, which are superior to those of BT, RGOBT and TiO₂BT. Additionally, RGO@TiO₂BT exhibited improved thermal stability and fire-resistant properties with a limiting oxygen index of 33.2%.

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1. Introduction

Currently, one of the more pressing environmental problems that have been facing the textile industry is the removal of color from dye bath effluents prior to discharge to the local sewage [1]. Many synthetic dyes are resistant to microbial degradation under typically aerobic conditions. The photodegradation process of organic pollutants has attracted increasing attention during the past decades [2]. To improve photocatalytic efficiency, a variety of methods have been tested to inhibit the recombination of electrons and holes, such as metal particle loading [3], metallic doping [4], and non-metallic doping [5]. Among the various strategies, TiO₂-based materials have been the most promising candidates for photocatalytic decontamination [6]. Particularly, the composites of TiO₂ and carbon materials are currently being considered as potential photo catalysts in the purification of air and water [7]. Its interesting electrical and mechanical properties and high surface area make graphene a novel substrate for forming hybrid structures with a variety of nanostructure materials [8–10]. Graphene hybrids with metal oxides, metals and polymers have recently been developed for various applications [11–13]. TiO₂ nanocrystals directly grown on the underlying graphene oxide (GO) sheets appeared to exhibit strong interactions because sonication did not lead to their dissociation from the sheets. This strong coupling should lead to advanced hybrid materials for various applications, including photocatalysis [14].

More recently, it was shown in a preliminary study that porous supports, such as wood, can be impregnated with TiO₂ and used as immobilized photocatalysts [15]. In the textile industry, there are many bamboo products used that are exposed to dyeing wastewater [16,17]. Bamboo timber is a type of porous biomass material widely used in paper making, house decorating and building [18,19]. Research on making new bamboo products to aid in the photodegradation of dye pollution is important. The aim of the present work is to use a graphene network coating on bamboo timber further loaded with nanocrystalline TiO₂ on its surface. We herein fabricate new bamboo materials that exhibit enhanced photocatalytic activity and improved fire resistance.
2. Experimental

2.1. Materials

Graphite powder (<20 μm), concentrated sulfuric acid (95–98%), concentrated nitric acid (68%), hydrochloric acid (36–38%), potassium chlorate (99.5%), ammonium fluorotitanate and boric acid were supplied by Huipu Chemical Company (Hangzhou, Zhejiang, China) and used without further purification. The bamboo specimens were processed into blocks with

Fig. 1. Typical low- and high-magnification SEM images of BT (a, b), RGO@BT (c, d), TiO2BT (e, f) and RGO@TiO2BT (g, h).
dimensions of 20 mm × 20 mm × 5 mm (longitudinal × tangential × radial), which were then cleaned by washing sequentially with deionized water and then ethanol for 30 min, and finally dried under vacuum at 50 °C for 24 h. The original bamboo timber subjected to the above process was abbreviated as BT.

2.2. Preparation of RGOBT

GO was synthesized from graphite powder according to the modified Hummer’s method [20]. A 2 mg L⁻¹ GO solution was obtained by adding distilled water to the resulting GO powder, and then sonicated to achieve a uniform GO dispersion. The bamboo samples were subsequently placed into the GO dispersion and transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 140 °C for 3 h. After the hydrothermal reaction, the treated bamboo samples were removed, ultrasonically rinsed with deionized water for 3 min, and then dried at 50 °C for 24 h in vacuum. The GO dispersion treated bamboo timber with a reduced GO coating was abbreviated as RGOBT.

2.3. Preparation of RGO@TiO₂BT

Ammonium fluorotitanate (1.0 g) and boric acid (0.92 g) were dissolved in 50 ml of deionized water under vigorous magnetic stirring. When the mixture became clear, hydrochloric acid solution was added to adjust the pH until a value of 3.0 was reached. The RGOBT samples were transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 110 °C for 3 h. After the hydrothermal reaction, the treated bamboo samples were removed, ultrasonically rinsed with deionized water for 3 min, and then dried at 50 °C for 24 h in vacuum. The GO dispersion treated bamboo timber with a reduced GO coating was abbreviated as RGOBT. Using the BT sample to instead the RGOBT sample, simpler bamboo-TiO₂ system bamboo composite was made by the above method and was abbreviated as TiO₂BT.

2.4. Characterization

The surface morphologies of the samples were characterized by scanning electron microscopy (SEM, Quanta 200, FEI, USA). The surface chemical compositions of the samples were determined via energy dispersive spectroscopy (EDX, attached to the SEM). The transmission electron microscopy (TEM) experiments were performed on a Tecnai G20 electron microscope (FEI, USA) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. The crystalline structures of the samples were identified by X-ray diffraction (XRD, D/MAX 2200, Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å) at a 2θ scan rate of 4°·min⁻¹, 40 kV, 40 mA, ranging from 5° to 80°. The presence of functional groups in the samples was confirmed through Fourier transform infrared (FTIR) spectroscopy (Spectrum One, PerkinElmer, USA).

2.5. Photocatalytic activity test

The photocatalytic activity was confirmed by the degradation of common dyes, such as rhodamine B (RhB), methylene blue (MB) and methyl orange (MO), under irradiation of UV light. Each sample of BT, RGOBT, TiO₂BT and RGO@TiO₂BT with dimensions of 20 mm × 20 mm × 5 mm was dipped into 30 ml of dye solution with a concentration of 10 mg L⁻¹, and then the reaction suspension was kept in the dark for 60 min with stirring. Then the dispersion was centrifuged and the MB, MO and RhB solutions were taken to the UV–visible absorption measurement. We set the concentration of the dye solution after dark treatment as the initial concentration C₀. After that, under ambient conditions and stirring, the photo reaction vessel was exposed to the UV irradiation produced by a 1000 W high pressure Hg lamp with the main wave crest at 465 nm, which was positioned 30 cm away from the vessel. During the photodegradation, the temperature was kept at 20–23 °C recirculating cooling water system, and the working pH in the dispersion for the photodegradation was measured with a pH value of 6.35, 5.79 and 5.06, for MO, MB and RhB respectively. Under UV irradiation for 60min, the dye solution were analyzed every 10min using a visible spectrophotometer (TU-1901, Beijing Purkinje, China) at 554 nm for RhB, 668 nm for MB or 464 nm for MO. The efficiency was calculated by

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Y = 100 \times \frac{C - C_0}{C_0}
\]
where $C_0$ is the initial concentration after dark treatment and $C$ is the concentration at time $t$ under UV irradiation, respectively.

In order to evaluate the visible light active photocatalysis in RGO@TiO$_2$BT, firstly, MO, MB and RhB with RGO@TiO$_2$BT were treated under dark condition for 60 min. According to the same method in the UV irradiation experiment, the dye mixed with RGO@TiO$_2$BT under simulated visible light for 24 h were conducted. And the absorbance of MO, MB and RhB at time 0 h and 24 h were measured.

### 2.6. Thermal stability and fire resistance test

Thermo gravimetric was performed using a STA409PC thermo gravimetric analyzer (Netzch Company, German). 5 mg samples were obtained and measured in the temperature range of 30 °C–900 °C at a rate of 10 °C·min$^{-1}$ under a nitrogen atmosphere. The limiting oxygen index was measured using a JF-5 oxygen index tester (Nanjing Jiangning Company, China).
3. Results and discussion

3.1. SEM analysis

As shown in Fig. 1(a and b), a typical cell wall structure with a clean and smooth surface can be easily observed on the surface of the BT sample. In the first hydrothermal process, the bamboo samples were immersed in a GO dispersion and coated with GO sheets. Then, at 140 °C, the GO sheets were reduced to reduced graphene oxide (RGO) sheets. After incubation for 3 h, the RGO sheets were observed on the bamboo surface aggregated together as a coating material, as shown in Fig. 1(c and d). When the BT sample was hydrothermally treated in the (NH4)2TiF6 and H3BO3 solution, TiO2 particles loaded on the clean bamboo surface as shown in Fig. 1(e and f). In the second hydrothermal process to make RGO@TiO2BT, more TiO2 particles assembled on the RGO sheet as shown in Fig. 1(g and h). The TiO2 particles with sizes of approximately 0.5–2 μm were clearly visible in the higher magnification image. Compare with the TiO2BT samples, from the SEM observation, the RGO@TiO2BT samples are loaded with a greater density of TiO2 particles.

3.2. EDS analysis

Fig. 2(a, b, c, d) shows the chemical elements and element content of the four samples including BT, RGOBT, TiO2BT and RGO@TiO2BT. Au in the four samples originates from the conductive coating material, as shown in Fig. 2(a and b). When the BT sample was hydrothermally treated in the (NH4)2TiF6 and H3BO3 solution, TiO2 particles loaded on the clean bamboo surface as shown in Fig. 2(c). The thickness of the graphene oxide sheets can provide a larger graphene network and guarantee easy loading of TiO2 particles, similar to the proven results [22,23].

3.3. TEM analysis

Fig. 3(a and b) shows the TEM results of graphene oxide dispersion and the diameter of the graphene oxide sheets is among 1–5 μm. The thickness of graphene oxide sheets is thin and large majorities were single-layer or few-layer. There are many wrinkles on the edge of graphene oxide sheets. Fig. 3(c and d) presents the typical structure of TiO2 particles formed from the hydrothermal solution composed of (NH4)2TiF6 & H3BO3 solution. The diameter of TiO2 particles is among 0.5–1 μm in Fig. 3(c). The thickness of the graphene oxide layer underneath is 3–11 nm in Fig. 3(d). The single-layer or few-layer graphene oxide sheets could form a cross network. The cross network formed many layers and continuously gathered together. The graphene oxide sheets can provide a lager graphene network and guarantee easy loading of TiO2 particles, similar to the proven results [22,23].

3.4. XRD analysis

The crystalline status of the materials over the bamboo surface were studied by XRD. In Fig. 4, the typical diffraction peaks of cellulose from BT and RGOBT at 2θ = 15.7°, 22.3° and 34.8° were clearly observed. Additionally, the typical diffraction peaks of 25.4°, 37.9°, 48.1°, 54.2°, 62.5°, 69.2°, and 75.3° corresponding to anatase TiO2 crystal (JCPDS cards: 21-1272), respectively, revealed that the obtained TiO2 on TiO2BT and RGO@TiO2BT possessed a typical anatase phase [24]. A diffraction peak at a 20 value at approximately 11.9° corresponds to a basal spacing of d001 = 0.961 nm, which agrees with the interlayer spacing of graphene oxide [25,26]. Additionally, no obvious diffraction peaks of GO can be observed in the RGOBT and RGO@TiO2BT; indicating the absence of layer-stacking regularity and that graphene oxide was reduced to an RGO structure on the bamboo surface.

3.5. FTIR analysis

Evidently, the peaks in the two spectra of BT and RGOBT in Fig. 5 were similar; the broad adsorption band of BT at approximately 3335 cm−1 was shifted to a lower wave number of 3332 cm−1 in the spectrum of RGOBT, the peak of the hydroxyl group of RGO@TiO2BT was the weakest. In the hydrothermal process, the −OH from RGO and bamboo surface would form hydrogen bond or happen dehydration reaction, so that a certain proportion of −OH were removed and the amount of −OH decreased [27,28]. The above results indicate the strong interaction formed between the RGO coating and the bamboo surface. An absorption band also exists at...
1641 cm\(^{-1}\) for RGOBT, confirmed by a strong C=C band, which showed that RGO was incorporated into the surface of BT [29,30]. The absorption band appearing at 1600 cm\(^{-1}\) of RGO@TiO\(_2\)BT clearly showed the skeletal vibration of the graphene sheets, indicating the formation of graphene during the hydrothermal reaction. RGO@TiO\(_2\)BT showed a low frequency band at approximately 690 cm\(^{-1}\), which corresponds to the vibration of Ti—O—Ti bonds [31]. With carboxylic acid groups distributed on the network, GO could be reduced to graphene via a hydrothermal reaction with a small amount of residual groups. Under the hydrothermal conditions, TiO\(_2\) particles were dispersed on the graphene network support and accumulated along the wrinkles and edge [14].

3.6. Synthetic mechanism analysis

According to the above analysis, a schematic illustration of the coating process and a possible synthetic mechanism for the RGO@TiO\(_2\)BT composite are showed in Fig. 6. The GO solution was first absorbed by the original bamboo timber and reduced to an RGO coating on the bamboo surface with a graphene network by a hydrothermal process [32]. Afterward, multiple layers of the RGO sheet were assembled onto the bamboo surface via hydrogen bonding and physical adsorption. In the second hydrothermal step, TiO\(_2\) nanocrystals were formed from a (NH\(_4\))\(_2\)TiF\(_6\) & H\(_3\)BO\(_3\) solution and dispersed on the graphene network via adsorption and crystallization. Additional reaction sites and loading positions provided by the graphene coating allow for more opportunities for TiO\(_2\) nanocrystal growth [33]. After the two steps, the RGO@TiO\(_2\)BT samples were prepared with TiO\(_2\) nanocrystals in a graphene network coating on the outermost layer of the bamboo substrate.

3.7. Evaluation of photocatalytic activity

TiO\(_2\)-based materials are the most promising candidates for photocatalytic decontamination. Porous materials with large specific surface areas, such as bamboo and graphene, were loaded with TiO\(_2\) nanocrystals, which greatly improved their catalytic performance. Because of the adsorption effect of BT and RGOBT samples, which were porous and had high specific surface area, when BT and RGOBT were treated with the three types of dyes, each exhibited a decrease in final concentration after photocatalytic degradation. When coated with graphene materials on the BT surface, the graphene network on RGOBT can provide more active sites to adsorb dye molecule. As more TiO\(_2\) particles are decorated on the RGO sheet, RGO@TiO\(_2\)BT can not only absorb the dye molecules but can also degrade the dye molecules via catalytic reaction. By setting the dye concentration after dark treatment as C\(_0\), then the photocatalytic performance were analysis according to the C/C\(_0\) value of dyes.

As shown in Fig. 7 and Table 1, the photodegradation of dye materials were tested with BT, RGOBT, TiO\(_2\)BT and RGO@TiO\(_2\)BT under visible light, including RhB, MB and MO. The results show that all the dye concentrations in the solution dropped when the above four samples were immersed in the dye solutions. After 24 h photodegradation under visible light over RGO@TiO\(_2\)BT sample, the decline rates of MO, MB and RhB are 4.8%, 2.2% and 0.6%.
respectively. The data showed that the concentration reduction of all the 3 kinds of dyes under visible light for 24 h was less than 5%. As shown in Fig. 8 and Table 1, after 60 min UV irradiation, the C/C₀ value of dyes was lowest for RGO@TiO₂BT and highest for BT. The photodegradation efficiency of TiO₂BT and RGO@TiO₂BT mixed with all the three dyes under UV irradiation were significantly increased than BT and RGOBT. TiO₂BT and RGO@TiO₂BT have a coating material that contains TiO₂ particles, which leaded to the as-prepared bamboo materials with excellent UV photocatalytic performance. The RGO@TiO₂BT sample has enhanced photocatalytic properties than the TiO₂BT sample. We further inferred that by coating with an RGO sheet and then loading with TiO₂ particles, the photocatalytic activity of RGO@TiO₂BT could be enhanced significantly. When the photodegradation reaction under visible light compared with UV light, the visible photocatalytic properties is not very obvious. Therefore at present our hybrid in RGO@TiO₂BT can only be mainly used for photocatalytic degradation under UV light.

When comparing the three types of common organic pollutants under degradation by RGO@TiO₂BT treatment, the photodegradation efficiency of MO, MB and RhB are 87.2%, 85.1% and 73.9%. The photodegradation efficiency of MO was the highest, this indicated that TiO₂ particles decorated the RGO sheet and were
most effective in the catalytic degradation of MO. The highest photocatalytic activity of RGO@TiO$_2$BT and MO might be attributed to the good dispersion, potentially higher surface area, and smaller crystallite size of the formed anatase TiO$_2$ [34,35]. When the surface of RGO@TiO$_2$BT was illuminated by UV light, the high photocatalytic activity of RGO@TiO$_2$BT could be attributed to the strong coupling between TiO$_2$ and GO, which facilitates interfacial charge transfer and inhibits electron-hole recombination [36]. In addition, the conjugated dye molecules could bind to the large aromatic domains on GO sheets via π-π stacking, which could favor increased reactivity [37].

3.8. Thermal stability analysis

The results of the TG analysis were shown in Fig. 9. Three stages of the thermal degradation of the BT, RGOBT, TiO$_2$BT and RGO@TiO$_2$BT were clearly visible in Fig. 9. The three stages can be classified as: (1) loss of physically adsorbed water and partial degradation of hemicelluloses; (2) cellulose degradation; (3) aromatization and carbonization of lignin [38,39]. Lignin was the most difficult chemical composition to decompose, which occurred slowly and was maintained during the entire calcining process [40,41]. As shown in the TG curve, after the thermal degradation from 30 °C to 900 °C, the weight percentages of mass residues remaining for BT, RGOBT, TiO$_2$BT and RGO@TiO$_2$BT were 18.8%, 23.5%, 25.1% and 32.6%, respectively. The RGOBT samples had higher content of mass residues than the BT samples. The reason may be that the coating surface of RGO sheet lead to higher content of carbon residues remaining, which is consistent with the EDS analysis. The RGO@TiO$_2$BT and TiO$_2$BT samples had higher content of mass residues than the BT and RGOBT samples. This observation is attributed to the higher weight percentage of TiO$_2$ particles coated on the bamboo surface, which were non-thermal decomposition components. The RGO@TiO$_2$BT samples coated with more TiO$_2$ particles and had a higher content of Ti elements. As a result, the RGO@TiO$_2$BT sample has a minimum value of mass loss, which indicates that RGO@TiO$_2$BT has improved thermal stability.

3.9. Flammability analysis

The limiting oxygen index (LOI) is one of the most common parameters for evaluating the flammability of materials, which is defined as the minimum concentration of oxygen in an oxygen-nitrogen mixture [42]. Materials that have a higher LOI value will have better flame resistance. Bamboo timber is a type of easily flammable material, which has a low LOI value (26–28%). As shown in Fig. 10, in this experiment, the LOI value of BT was 27.8% and TiO$_2$BT increased to 33.2%. Bamboo coated with TiO$_2$ particles have better flame resistance. The LOI value of RGOBT was only 23.2%, but increased to 33.2% after the hydrothermal reaction with the TiO$_2$ particles coating. When bamboo is coated with RGO sheet, as graphene materials make the bamboo-based composite more flammable [43]. With more TiO$_2$ particles are coated on the bamboo surface, TiO$_2$-graphene composites make RGO@TiO$_2$BT harder to burn,
which displayed significant improvement in flame resistance. Fig. 11 shows the combustion processes of BT, RGOBT, and RGO@TiO2BT. In the earlier stage, BT and RGOBT samples can be easily ignited from alcohol fire. However, TiO2BT and RGO@TiO2BT can only be heated to burn red in an air atmosphere, and it can be extinguished by itself when the flame is left unattended. In the middle stage, RGOBT shows strong burning and a higher flame height than BT. In the last stage, BT burns out with an ash coating on the surface and the RGOBT sample burns out with a black carbon materials coating. Both TiO2BT and RGO@TiO2BT samples are not easy to burn and at last are carbonized. Meanwhile, the results about the last time of combustion show that RGO@TiO2BT has improved flame retardant property while compared with the other three kind of samples.

4. Conclusions

In summary, we have demonstrated a two-step protocol method of fabricating nanocrystalline anatase TiO2 in a graphene network on bamboo substrates. A possible synthetic mechanism is that the original bamboo timber first absorbs graphene oxide, forming a graphene structure on its surface, followed by dispersion of TiO2 nanocrystals on the graphene network via adsorption and crystallization. RGO@TiO2BT possessed excellent photocatalytic activity, and the photodegradation efficiency of MO, MB and RhB are 87.2%, 85.1% and 73.9%. Additionally, RGO@TiO2BT exhibited improved thermal stability and fire-resistant properties with a limiting oxygen index of 33.2%.

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