

Temperature-dependent Structure and Photocatalytic Performance of TiO₂-based Cellulose Surface

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Keywords: Inorganic particles; temperature-dependent; surface; photocatalytic performances.

Abstract. Inorganic particles were successfully grown on cellulose surface using a mixture solution of boric acid and titanium ammonium fluoride by hydrothermal method. The synthesis was performed in a sealed atmosphere under optimized conditions, at temperatures between 50 °C and 130 °C. Scanning electron microscope (SEM), X-Ray Diffraction (XRD), and Fourier Transform Infrared spectroscopy (FTIR) analyses indicate a direct correlation between morphology and microstructure. The formation of TiO₂/cellulose composites, whose characteristics depend on the reaction temperature, is proposed to result from the synergistic combination of liquid/solid mechanism. The photocatalytic performances of various composites in the degradation of the methyl orange solution are investigated and compared to pure P25 powder without any treatment. The obtained results show a higher activity in the case of composites due to their peculiar morphology. Such the composite materials with the desirable degradation ability exhibit great potential, as they may be selectively used in the present widespread sewage treatment with different major sources of pollution.

Introduction

With the growing demand of more comfortable, healthier and environmentally friendly products, efforts in research and development activities in the industry have focused on the utilization of renewable and biodegradable resources. The requirements for materials' performance of people become increasingly multiple, a single material is often difficult to meet the different requirements.^[1-3] In such a situation, nanostructure materials have received steadily growing interest as a result of their peculiar and fascinating properties. Among them, nano-crystalline titania, which is one of the most basic inorganic functional materials in our daily life, has many important applications such as solar cells, photocatalysts for water photolysis, and degradation of environmental pollutants in air and wastewaters.^[4-6] In the primary stage of photocatalysis research, TiO₂ used as photocatalyst is always suspended phase which is more easily to reunite and recovery difficultly due to its too small particle size, also the absorption of light by suspended particle affects the radiation depth.^[7] In order to solve these difficulties, one frequently used method is to generate TiO₂ in situ in the presence of the cellulose fibers, a strategy that is investigated here. Recently, the organic-inorganic hybrid materials have been studied extensively.^[8] It was found that the morphology and properties of synthetic samples could be controlled by choosing the preparation conditions, such as solution pH and temperature.^[9] To create some desired celluloses of inorganic particles with the excellent photocatalytic performance becomes a challenging goal.

In this work, the aim was to achieve the desirable photocatalytic performance of cellulose surface that was used to regulate the reaction system temperature. Therefore, TiO₂ particles on the cellulose surface were prepared by a simple hydrothermal method with different reaction system temperatures.

Experimental Section

Material Bamboo cellulose fibers were supplied from Zhejiang. Boric acid being purchased from Taicang of Reagent Co. Ltd was analytically pure and titanium ammonium fluoride being obtained from Shanghai Three Ace Reagent Co. Ltd was chemically pure. All the chemicals were used as received. Deionized water was used for all experiments.

Preparation of TiO₂/Cellulose Composite Boric acid and titanium ammonium fluoride were used as the main starting material without further purification. 7.4g boric acid solid was added into 100ml deionized water under continuous stirring at room temperature. After fully dissolved, 8g titanium ammonium fluoride was added with further stirring at room temperature. And then the reactants were treated with hydrochloric acid solution HCl adjusting the value of pH is about 3 with further stirring at room temperature. Next, 0.5g bamboo cellulose fibers were added into the prepared solution. The products were put into vacuum drying oven at 50°C, 70°C, 90°C, 110°C and 130°C for five hours. Then samples were washed with absolute ethanol. The collected products were dried at 50°C for several days. The original cellulose that was not treated with solution was coded as RC. The TiO₂/cellulose composite, namely cellulose treated with the reaction temperature of 50°C, 70°C, 90°C, 110°C and 130°C, were coded as T5, T7, T9, T11, T13, respectively.

Characterizations The morphology of the samples was observed by scanning electron microscopy. The SEM images were obtained using an auto fine coater (S-3400N; Hitachi.) to coat the samples with gold to improve the conductivity. The accelerating voltage was 12.5kv.

The X-ray diffraction (XRD) patterns were measured for raw fibers and various treated composites with an XRD-6000 Shimadzu diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. Scattered radiation was detected in the range of $2\theta = 5\text{--}70^\circ$ at a scan rate of $4^\circ/\text{min}$.

The chemical compositions of the untreated and treated celluloses were measured by Fourier-transform infrared spectroscopy (FT-IR) (Nicolet Magna-IR 170, America) in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. Samples were ground into powders and the test specimens were blended with KBr before pressing the mixture into ultra-thin pellets.

Photocatalytic Degradation of Methyl Orange The photocatalytic activities of the TiO₂/cellulose composites were assessed by monitoring the degradation of methyl orange solution. 0.05g TiO₂/cellulose composites were immersed into 50mL 12 mg/L aqueous methyl orange solution. Subsequently, the solution with the TiO₂/cellulose composite was magnetically stirred in the dark for 1h to reach the absorption equilibrium and then was irradiated under 1000 W mercury lamp at wavelength of 365 nm in photochemical reaction instrument (hanuo, Shanghai) with continuous stirring for 1h. After that, 5 ml the solution under ultraviolet irradiation was collected and measured by UV-Vis spectrophotometer (TU-1901, Beijing Purkinje, China) at every 10 min.

Results and Discussion

Fig. 1 shows the SEM images of the RC and the TiO₂-based cellulose obtained in the different reaction temperature varied from 50 °C to 130 °C, respectively. In Fig. 1f, the RC surface is smooth and straight, no defect is observed under a microscope. However, after treated by hydrothermal method in different reaction temperatures, there are a lot of small inorganic particles growing on the cellulose surface, and each case is unusual. It can be clearly seen from the Fig. 1a that the distribution of the inorganic particles growing on the cellulose surface is very non-uniform and there is almost no growth of particles on the surface of the part cellulose. Moreover, the raised particles are running from small to large. As temperature increases, the particles are grown to various shape and the size becomes smaller, but the number of each place is unbalanced (Fig. 1b). With the continuous increasing of the temperature, does the change. Fig. 1c displays that the surface is evenly covered in uniform size particles. When the temperature is 110 °C, the condition of the cellulose surface is similar to Fig. 1b, but the surface distribution is more brutal. Keeping on heating up to 130 °C, the

particles turn less and less, and the particle is too tiny to observe. Apparently, it can identify a distinct distribution changes of the cellulose surface at reaction temperature.

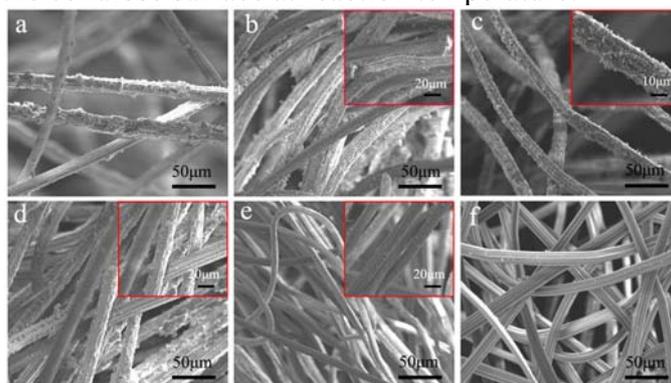


Fig.1. SEM images of (a-e) the TiO_2 /cellulose composites obtained successively under various reaction temperatures for T5, T7, T9, T11, T13, respectively, and (f) the RC.

FT-IR spectra of the TiO_2 /cellulose composites samples obtained at various temperatures are shown in Fig. 2. The composite samples show the main bands at $400\text{-}600\text{ cm}^{-1}$, which are attributed to Ti-O stretching and Ti-O-Ti bridging stretching modes.^[10] The C-H stretching absorption peak around 2900 cm^{-1} disappears and the peak at 3440 cm^{-1} corresponding to stretching vibration of hydroxyl groups of cellulose shifts to lower wavenumbers in the composite samples. This bond shift is attributed to the surface absorbed water induced by TiO_2 nanoparticles, indicating a strong interaction between the hydroxyl groups of cellulose and TiO_2 nanoparticles through hydrogen bond.^[11-13]

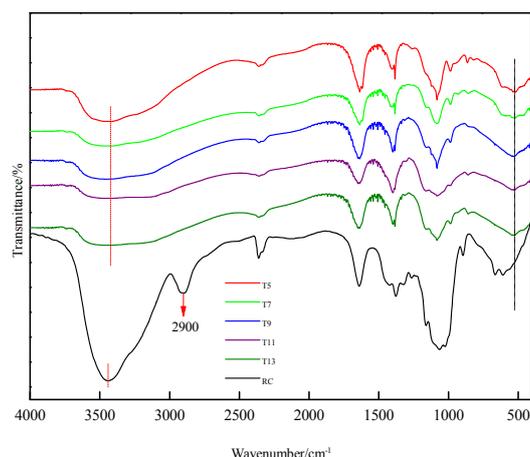


Fig.2. FT-IR spectra of the TiO_2 /cellulose composites obtained successively under various reaction temperatures respectively, and the RC.

The XRD patterns of RC, T5, T7, T9, T11 and T13 are shown in Fig. 3. There are three main peaks of RC at $2\theta=12.1^\circ$, 20.3° , and 21.8° , corresponding to the (101), (101), and (002) planes of cellulose II crystalline, respectively.^[14] Apparently, the diffraction peaks belonging to the cellulose disappeared in treated materials. New strong peaks were observed for the composites, which revealed the formation of the new crystal structures of the samples under various reaction temperatures. Can be clearly seen from the curve, TiO_2 was not formed when the temperatures lower than 90°C even keeping all the other conditions the same. But, at temperatures of 90°C , 110°C and 130°C , five obvious diffraction peaks at 25.7° , 38.6° , 48° , 54° , and 63° which are corresponding to the (101), (004), (200), (105), and (204) respectively, are believed to represent the crystalline region of the anatase TiO_2 .^[15]

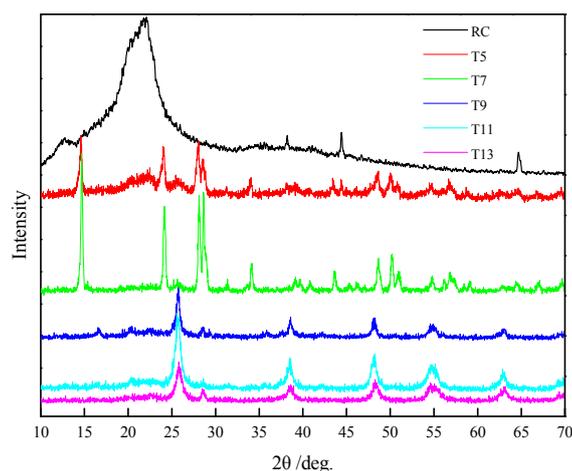


Fig.3. XRD patterns of the TiO₂/cellulose composites obtained successively under various reaction temperatures respectively, and the RC.

The photodegradation curves of methyl orange solution are shown in Fig. 4. As can be seen, the raw material can photodegrade the methyl orange under UV light irradiation to some extent, after 50 min, the degradation rate is basically unchanged, about 49.4% (Fig. 4a). Because the raw materials have large specific surface area and a large number of hydroxyl groups, they have a certain adsorption of methyl orange.^[16] When the raw materials combine with TiO₂ under various reaction temperatures, the obtained composites display superior photocatalytic activities. After 50 min, the catalytic effect of all the samples is better than P25 except T7. Especially when treated at 90 °C, the degradation rate is about 98.3%. Can be seen from the above FTIR and XRD analysis, under the condition of 90 °C, the size of the inorganic particles on the cellulose surface is uniform and balanced. Naturally, the larger specific surface area leads to optimal photocatalytic performance.

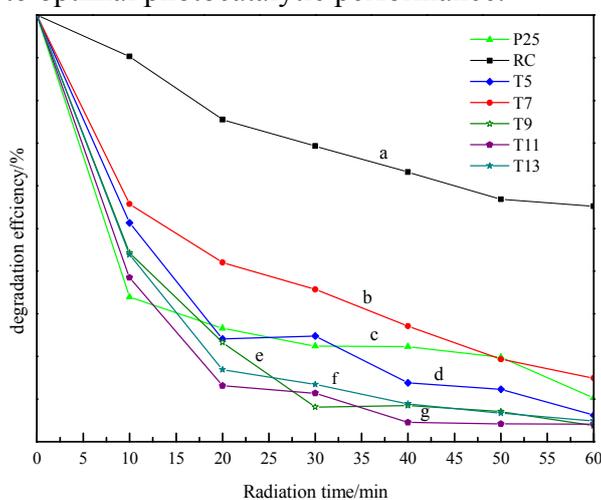


Fig.4. Photocatalytic activity of (a) the raw materials (b) T7 (c) P25 (d) T5 (e) T9 (f) T13 (g) T11

Conclusions

In the present paper, the TiO₂/cellulose composites were fabricated successfully by in situ synthesis of TiO₂ nanoparticles in the regenerated cellulose matrix with micronanoporous structure via a hydrothermal method. The current approach is facile, and appears to have various benefits and advantages for providing a cheap and effective waste water treatment and remediation option.

Acknowledgements

This work was financially supported by The National Natural Science Foundation of China.

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