Synthesis of submicron-sized carbon-doped TiO$_2$ for photodegradation of formaldehyde from wood-based panels

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Abstract. Carbon-doped TiO$_2$ particles were prepared by hydrothermal treatments and characterised via field emission scanning electron microscopy, powder X-ray diffraction and X-ray photoelectron spectroscopy. The results show that carbon was successfully doped into the TiO$_2$ structures. Photocatalytic reactions were further investigated in a simulated indoor environment, and the visible-light catalytic activity of the carbon-doped TiO$_2$ was evaluated by monitoring the photodegradation of the formaldehyde from wood-based panels. A degradation rate of 90% in 70 min was obtained, which demonstrated high photocatalytic performance.

1. Introduction

As listed in the category of carcinogens by the World Health Organization, formaldehyde has been reported to cause issues in the nervous and respiratory systems [1-3]. Nowadays, people are more concerned about the health implication of wood-based panels, especially the indoor-used panels, which usually emit excessive formaldehyde [4]. Adhesives play important roles in the production process of wood-based panels (widely used in the market), and they are mainly used to combine panels and other attachments [5]. Formaldehyde exists as a volatile compound in adhesives [6]. It is obtained from urea formaldehyde and phenol aldehyde resins. With strong adhesiveness, it increases the hardness of the board, and it also repels insects and prevents corrosion. Formaldehyde gradually diffuses to the surrounding as a source of pollution in indoor environments. Therefore, there is a need to investigate wood-based panels, including blockboard, particleboard, medium-density fibreboard, veneer and plywood, produced with adhesives to determine the formaldehyde emissions and minimise the possible harmful effect.

TiO$_2$ is known for its low cost, chemical and thermal stability, resistance to photo corrosion and nontoxicity [7,8]. Photocatalysts are developed for more effective utilisation of the natural light [9]. TiO$_2$ modified with non-metals has been extensively employed in formaldehyde degradation due to its outstanding performance [10-12]. Moreover, the photocatalytic activities of carbon-doped TiO$_2$ have attracted much interest owing to their potential in the removal of organic pollutants [13-15]. Thus, it is necessary to investigate visible-light active catalysts for formaldehyde degradation in a simulated indoor environment.

For this reason, submicron-sized carbon-doped TiO$_2$ particles were prepared via a hydrothermal method in this study, and their morphology and properties were characterised via field emission...
scanning electron microscopy (FE-SEM), powder X-ray diffraction (XRD), energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS). Simulated with 120-L environmental chambers, the formaldehyde emissions from wood-based panels were degraded in chambers under visible-light irradiation. The activity of carbon-doped TiO$_2$ was evaluated via photocatalytic tests, and the formaldehyde degradation was improved.

2. Materials and methods

2.1. Instruments and chemicals

The instruments used included a PANalytical X Pert Pro multifunction XRD (Netherlands), FEI Quanta FEG 650 field-emission scanning electron microscope (Netherlands), Thermo Scientific EscaLab 250Xi XPS (USA) and Agilent Cary 300 UV-Vis spectrophotometer (USA). An Eagle View Electronic Technology 80 W LED lamp (China), Markes International TC-20 multi-tube ageing set (UK), Talboys magnetic hotplate stirrer (USA) and 120-L Y40D3 environmental test chamber (China) were also used.

Titanium butoxide (99%), D-glucose (98%), ammonium hydroxide (25%), acetylacetone and ethanol of at least the analytical grade were purchased from Aladdin (China). Acetylacetone (0.25%) was obtained by treating with a certain proportion of ammonium acetate/water/glacial acetic acid/acetylacetone media. 1000 mg L$^{-1}$ standard solution of formaldehyde was purchased from TanMo (China).

2.2. Synthesis and characterisation of carbon-doped TiO$_2$

100 mL of anhydrous ethanol, 2.7 g of D-glucose and 16.4 mL of titanium butoxide were successively added to a beaker under stirring. The well-stirred mixture was added to a solution of ammonium hydroxide (0.5 mL) and ethanol (150 mL) using ultrasonic treatment for 10 min. Next, the resulting solution was transferred to a PTFE-lined hydrothermal reactor at 160 $^\circ$C and stirred for 6 h. The precipitate was washed with ethanol and water, and then dried in an oven at 70 $^\circ$C for 1 h. The precursors were calcined in a muffle furnace at 520 $^\circ$C for 3 h. Thus, the carbon-doped TiO$_2$ photocatalyst was obtained. For a systematic study, the pure anatase TiO$_2$ was synthesised via a hydrothermal treatment [7].

The microstructure of carbon-doped TiO$_2$ was determined using the FE-SEM at an accelerating voltage of 20.0 kV. Gold (Au) was used as a coating material in the analysis of the plane scan. The XRD analysis was conducted using Cu-Kα radiation with a Cu X-ray tube operated at 30 kV. The interval of data points was 0.01 $^\circ$, and the scanning speed was 3 $^\circ$ min$^{-1}$. The photocatalyst particles were scattered in ethanol by ultrasonic dispersion for 5 min, and then put on a copper mesh in a transmission electron microscope for EDX analysis. XPS spectra were obtained at a constant power of 150 W (binding energy: 100-700 eV) using monochromatic Al-Kα radiation.

2.3. Simulation conditions in environmental chambers

Prior to the operation of the chamber, its inner surface was scrubbed with alkaline detergent and rinsed with water. The simulation conditions of the chamber used for evaluation of formaldehyde levels from wood-based panels in indoor environments are listed in Table 1. A 5-level calibration curve was prepared in an aqueous solution with formaldehyde. The absorbance was in good agreement with the standard, and its correlation coefficient was 0.9993. The wood-based panels were cut to a size of 20 cm × 20 cm and sealed with aluminium foil tape at both the sides and the bottom surface (Figure 1A). Subsequently, the panels were placed in the chambers for testing (Figure 1B).

2.4. Photocatalytic activity measurement

A porous nickel foam net (20 cm × 20 cm × 1.6 mm) with 25 pores per linear inch was used as the catalyst carrier. 0.4 g carbon-doped TiO$_2$ photocatalysts was resuspended in 60 mL water and sonicated for 5 min. The suspension was sprayed to the net and placed under the LED lamp, thereafter,
it was illuminated to start the reaction. Furthermore, 100 mL formaldehyde solution (initial concentration of 20 mg L$^{-1}$) was added to quartz containers. Before degradation, formaldehyde emissions were contacted with catalysts for 30 min to attain adsorption equilibrium. The formaldehyde degradation was then carried out at room temperature with the light source located at a certain distance from the nets. After the photodegradation, 5 mL extract liquor of large bubbling absorber (centrifuged at 2000 rpm for 5 min and filtered through a hydrophilic membrane) was uniformly mixed with 0.25% acetylacetone, and then heated in boiling water. The absorbance of the resulting solution was determined via UV-Vis spectrophotometry at a wavelength of 415 nm. The degradation rate of the formaldehyde ($D_f$, %) was calculated by the following equation:

$$D_f = \frac{A_0 - A_t}{A_0} \times 100\%$$

(1)

where $A_0$ and $A_t$ are the absorbances of the solution before and after irradiation, respectively.

| Table 1. Simulation conditions in environmental chambers. |
|---------------------------------------------------------|
| **Parameters**                                   | **Conditions**             |
| Temperature                                     | 23 ± 1 °C                  |
| Relative humidity                               | 50 ± 2%                    |
| Surface air velocity                             | 0.1 m s$^{-1}$             |
| Sampler                                         | Large bubbling absorber    |
| Air flow rate                                   | 0.1 L min$^{-1}$           |
| Total sampling volume                           | 2 L                        |
| Sample loading factor                           | 0.33 m$^2$ m$^{-3}$        |
| Visible-light wavelength                        | 410 nm                     |
| Irradiation energy                              | 76.3 mW cm$^{-2}$          |
| Irradiation time                                | 70 min                     |

![Figure 1. Schematic of aluminum foil tape preparation for wood-based panels (A) and photodegradation of BTEX in environmental chambers (B).](image-url)
3. Results and discussion

3.1. Characterisations of carbon-doped TiO\textsubscript{2} photocatalysts

The carbon-doped TiO\textsubscript{2} particles appeared to be irregular shapes of submicron size (Figures 2A and 2B). The average grain size of the carbon-doped TiO\textsubscript{2} was measured to be 179 nm. The plane scans of micro-area for Ti and C are shown in Figures 2C and 2D. There was good compatibility between Ti and C during the calcination process, thus, a doped structure was obtained. Figure 2E indicates the XRD pattern of the carbon-doped TiO\textsubscript{2}, and the product is a mixture consisting of anatase phase with the remaining small part being in (110) crystal plane of the rutile phase. The peaks at 25.3°, 36.9°, 37.8°, 38.6°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3° and 75.1° were attributed to the diffraction of the (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) crystal planes of the anatase phase, respectively. The EDX spectrum (Figure 2F) shows the chemical compositions of products are C, Ti and O.

![Figure 2](image_url)

**Figure 2.** FE-SEM images (A,B), plane scans (C,D), XRD pattern (E) and EDX spectrum (F) of carbon-doped TiO\textsubscript{2}.
The XPS survey spectrum in Figure 3A shows the C 1s, Ti 2p, Ti 2s and O 1s core levels in the TiO₂. The high-resolution XPS spectra (Figures 3B-E) show two peaks at 284.1 and 288.1 eV, which indicate the presence of C element; they were assigned to the C-C and C-O bonds, respectively. Additionally, two typical peaks of the Ti-O bond at 458.0 and 463.9 eV were observed, which correspond well with the binding energy of Ti 2p₃/₂ and Ti 2p₁/₂. The Ti 2s-level had a binding energy of 564.6 eV, which superpose the loss structure of O 1s. The O 1s region was deconvoluted into two peaks located at 530.4 and 529.2 eV, which exhibited the characteristics of O-H and O-Ti bonds. These results proved the successful formation of carbon-doped TiO₂.

Figure 3. XPS survey spectrum (A), and high-resolution XPS spectra of C 1s (B), Ti 2p (C), Ti 2s (D) and O 1s (E) for carbon-doped TiO₂ as a function of binding energy.
3.2. Photocatalytic evaluation of carbon-doped TiO$_2$ for formaldehyde

The formaldehyde solution in quartz containers, described in Section 2.4, was placed in the chambers, and the activities of two catalysts were compared by monitoring the formaldehyde degradation as a function of irradiation time (Figure 4). The $D_f$ of the pure TiO$_2$ was less than 15% in 55 min (an indication of little growth), whereas that of the carbon-doped TiO$_2$ was 81% after 70 min of irradiation. Carbon-doped TiO$_2$ is considered to exhibit high catalytic activity due to the generation of hydroxyl radicals and trapped holes.

We hypothesize that the mechanism is as follows: C is incorporated to replace O or Ti in the TiO$_2$ lattice, which results in a reduction in the bandgap of the TiO$_2$; this allows photocatalytic reactions to proceed under visible-light irradiation. Herein, the carbon-doped TiO$_2$ was employed in the degradation of the formaldehyde from wood-based panels with excitation at 410 nm.

![Figure 4](image_url)

**Figure 4.** Effect of irradiation time on photocatalytic performance of catalysts under visible light; error bars represent standard deviations ($n = 3$).

The formaldehyde from the panels diffused into the chamber atmosphere. Without heating the chambers, the photodegradation was induced by illumination with the catalysts. The $D_f$ of the representative positive samples over the carbon-doped TiO$_2$ was determined. As listed in Table 2, the mean $D_f$ obtained are greater than 84%; a maximum of 90% is achieved, which demonstrate efficient removals. This implies that the catalytic application of carbon-doped TiO$_2$ was reliable, and the treatments with visible-light active catalysts enhanced the control of the formaldehyde at safe levels from the wood-based panels after 70 min of irradiation.

| No. | $A_0$ (before photodegradation) | $A_t$ (catalyzed by carbon-doped TiO$_2$) | Type of panel | $D_f$ (%) |
|-----|--------------------------------|----------------------------------------|---------------|----------|
| 1   | 0.421                          | 0.062                                  | Multilayer board | 85.3     |
| 2   | 0.318                          | 0.049                                  | Medium-density fiberboard | 84.6     |
| 3   | 0.325                          | 0.043                                  | Particleboard   | 86.8     |
| 4   | 0.592                          | 0.058                                  | Plywood         | 90.2     |
| 5   | 0.587                          | 0.060                                  | Veneer          | 89.8     |
| 6   | 0.380                          | 0.051                                  | Blockboard      | 86.6     |
| 7   | 0.602                          | 0.064                                  | Medium-density fiberboard | 89.4     |
| 8   | 0.285                          | 0.036                                  | Plywood         | 87.4     |
| 9   | 0.319                          | 0.050                                  | Blockboard      | 84.3     |
| 10  | 0.483                          | 0.047                                  | Particleboard   | 90.3     |
4. Conclusions
A new approach for hydrothermal synthesis of submicron-sized carbon-doped TiO$_2$ with enhanced catalytic performance is reported herein. The substitutional carbon was a functional composition in the photocatalytic reactions. The activities of the catalysts in environmental chambers were investigated, and it was revealed that the carbon-doped TiO$_2$ exhibited higher $D_f$ (81% within 70 min) than the undoped TiO$_2$ (15% within 55 min). The mean $D_f$ of the representative panels were obtained to be $>84\%$, and therefore the degradation of formaldehyde was promoted under visible light. Hence, carbon-doped TiO$_2$ is beneficial in the control of formaldehyde emissions from wood-based panels, and it could be utilised in corresponding photocatalytic applications.

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