

Preparation of nano-TiO₂ composite photocatalytic material and its degradation performance on aldehydes

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Abstract. Chitosan-TiO₂ photocatalytic composite was prepared using anatase nano-TiO₂ and edible chitosan. Fourier Transform Infrared Spectroscopy (FT-IR), ultraviolet visible (UV-vis) and scanning electron microscopy (SEM) was used to characterize the structure of the composites. The photocatalytic degradation performance of the composites was studied by constructing a simulation system. The stability of the combination between chitosan and TiO₂ in the composite can be confirmed by the results of FT-IR, UV-vis and SEM. The composite had a good photocatalytic degradation effect. When the addition amount of chitosan-TiO₂ was 0.4%, the degradation efficiency of heptanal, octanal, (E)-2-heptenal and (E)-2-octenal reached the highest values of 83.82%, 81.73%, 96.33% and 93.36%, respectively.

1. Introduction

Blue clam (*Aloididae aloidii*) is a low-value shellfish, which is rich in the coast of China. Blue clam is delicious, and its flavoursome amino acids account for about 50% of the total amino acids, which is an ideal raw material for producing flavor seasonings [1]. Enzymatic hydrolysis is an important method of producing seafood seasonings [2]. However, the aquatic enzymatic hydrolysate usually have unpleasant flavor such as fishiness and bitterness, which directly affect the sensory acceptability [3]. The substances that cause the fishy smell of aquatic products mainly include aldehydes, ketones, alcohols, nitrogen-containing, sulfur-containing, and hydrocarbon substances, which are mainly formed by lipid oxidation, microorganisms and enzymes. It has been reported that aldehydes, alkenals and alcohols produced by lipid oxidation and degradation are the main substances that cause fishy odor [4].

Recently, photocatalytic technology is one of the research hotspots in applied materials. It mainly uses the narrow energy gap of semiconductor materials to receive light energy and initiate electronic transitions [5]. Strong oxidizing hydroxyl radicals are generated in the surrounding environment by electron transfer, which can degrade and remove some gas or liquid pollutants. At present, photocatalytic technology has been widely used in many fields such as water purification, indoor harmful gas removal, and antibacterial material preparation [6]. However, the application of photocatalysis technology in the field of food processing, especially in the improvement of food flavor, is still rarely reported.

Therefore, photocatalytic composite material was prepared by nano-TiO₂ and edible chitosan, and its

structure was characterized by FT-IR, UV-vis and SEM. Four typical fishy substances (heptanal, octanal, (E)-2-heptenal and (E)-2-nonenal) in the blue clam hydrolysate were selected to construct the photocatalytic simulation system to evaluate the photocatalytic degradation performance of composite material.

2. Materials and methods

2.1. Materials

The heptanal, octanal, (E)-2-heptenal and (E)-2-octenal were purchased from Sigma-Aldrich (St Louis, MO, USA). Nano-sized TiO₂ with particle size of 20 nm was provided by Deke Daojin (Beijing, China). Chitosan of edible grade was produced by Sinopharm Reagent (Beijing, China). All chemical reagents used in this experiment were of analytical grade.

2.2. Synthesis of Chitosan-TiO₂ Composite Material

According to the method of Karthikeyan et al. [5], chitosan (1.4g), nano-TiO₂ (1.4g) and NaCl (0.5g) were accurately weighed, acetic acid (100 mL 0.1mol/L) and deionized water (40 mL) were added. After adequate mixing, the mixture was stirred continuously at 700 rpm for 24 h. Then the precipitate removed by centrifugation was rinsed with ionized water for 5-6 times and dried at 80 °C for 5 h to prepare chitosan-TiO₂ composite material.

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2.3. FT-IR spectroscopy

TiO₂, chitosan and chitosan-TiO₂ composite material were measured by KBr tablet method using Varian640-IR infrared spectrometer (Wallis, Germany), the spectral range was 4000-400 cm⁻¹.

2.4. UV-vis spectroscopy

The spectra of TiO₂ and chitosan -TiO₂ composite material were recorded by UV-2550 spectrophotometer (Shimadzu, Japan) using barium sulfate as the contrast.

2.5. SEM observation

The S-4800 field emission scanning electron microscope (Hitachi, Japan) was used to characterize the microscopic morphology of TiO₂ and chitosan-TiO₂ composite material at 3 kV after gold spraying.

2.6. Determination of photocatalytic degradation performance

Preparation of standard liquid for aldehydes: heptanal, octanal, (E)-2-heptenal and (E)-2-octenal were dissolved with a small amount of anhydrous ethanol, then diluted and mixed with deionized water, and prepared into standard liquid for odorous substances with a concentration of 1 mg/L, which was sealed and refrigerated standby at 4 °C .

Photocatalytic degradation treatment: a 500ml standard solution of odorous substance was taken and added into the chitosan-TiO₂ photocatalytic composite material (0.2%, 0.4%, and 0.6%), mixed and exposed to ultraviolet light at 254 nm, and samples were taken every 30 min. The photocatalytic degradation rate was calculated as follows:

$$\text{Degradation rate}\% = \frac{C_0 - C_t}{C_0} \times 100\%$$

C₀: initial peak area of odorant; C_t: peak area of odorant at time t

3. Results and discussion

3.1. Analysis of FT-IR

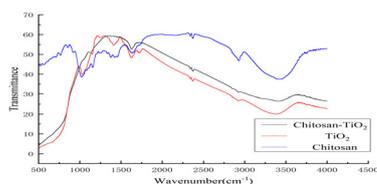


Fig. 1 FT-IR patterns of TiO₂, chitosan and chitosan-TiO₂ FT-IR is frequently used to characterize the structure of composite material [7]. The FT-IR spectrum of chitosan-TiO₂ composite material was shown in Fig. 1. The fluctuations of composite material were similar to those of TiO₂, which indicated the main structure of composite material was TiO₂. The peak at 3436 cm⁻¹

was attributed to the stretching vibration of hydroxyl and amino groups in the composite material, which was lower than that of chitosan. This was because some groups in chitosan molecules acted on the OH bond on the surface of TiO₂, which formed a strong hydrogen bond [8]. The band at 2924 cm⁻¹ was due to the tensile vibration of C-H. About 1400 cm⁻¹ was the bending vibration peak of CH₃. The absorption peak at 1080 cm⁻¹ was assigned by the tensile vibration of -C-O-C in the chitosan. The characteristic peaks of chitosan all appeared in the spectrogram of the composite material, indicating its existence in the composite material and its interaction with TiO₂.

3.2. Analysis of UV-vis

Fig. 2 showed the UV-vis absorption spectrogram of chitosan-TiO₂ photocatalytic composite material. The slight red shift of chitosan-TiO₂ absorption peak revealed that chitosan could expand the absorption wavelength of titanium dioxide to some extent. The possible reason was that the chitosan molecules in the vicinity of TiO₂ could adsorb and capture the electrons nearby, which not only reduced the energy required for TiO₂ electron transition, but also retarded the rate of electron-hole recombination. In addition, the increase in the absorbance of the composite material turned out chitosan could achieve improving the absorbance performance of TiO₂ to a certain extent. Z. X. Ji et al. [9] adopted a sol-gel approach to prepare chitosan-TiO₂ modified material and found that TiO₂ could decompose methyl orange under visible light.

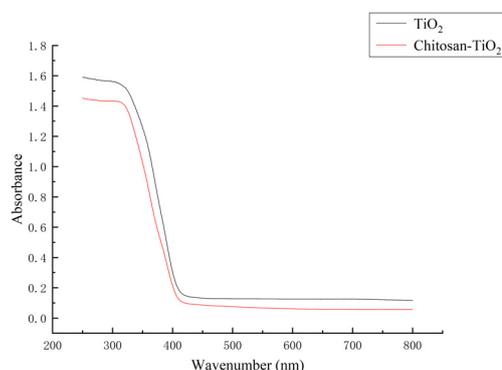


Fig. 2 UV-vis analysis of TiO₂ and chitosan-TiO₂

3.3. SEM characterization

The microscopic morphology of the photocatalytic composite was observed by electron microscope, and the results were represented in Fig. 3. Fig. 3 (A) and (C) respectively indicated the microstructure of TiO₂ and the chitosan-TiO₂ at 20K times, (B) and (D) represented at 30K times. Chitosan-TiO₂ had smaller voids and denser structure, as shown in Fig. 3 (B) and (D), because chitosan could be filled in the voids of TiO₂ and formed a stable complex. During the process of photocatalysis, electrons leaping from the surface of TiO₂ could be

captured by the surrounding chitosan, which prevented the electron-hole compound on the surface of TiO₂ to some extent, improving the photocatalytic efficiency of composite [10].

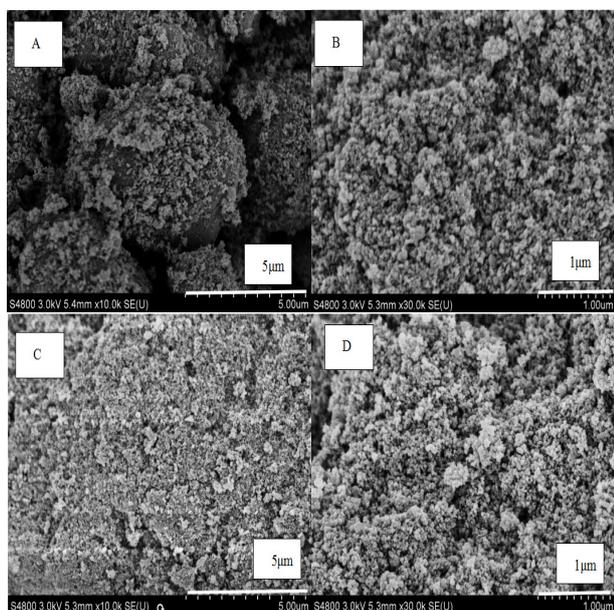


Fig. 3 SEM images of TiO₂ and chitosan-TiO₂

3.4. Determination of photocatalytic degradation performance

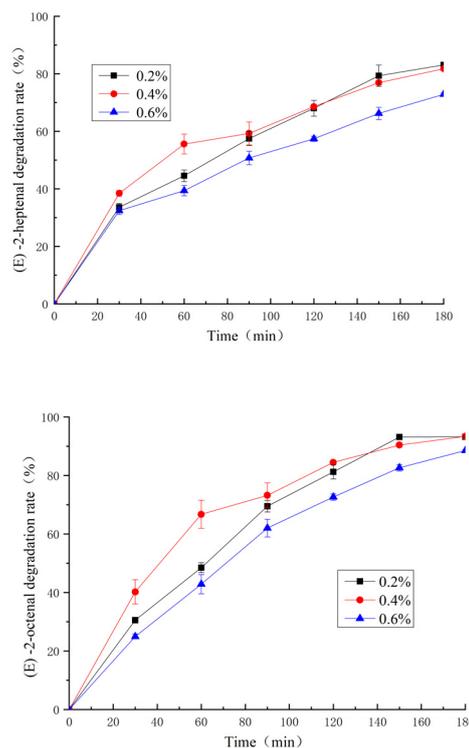
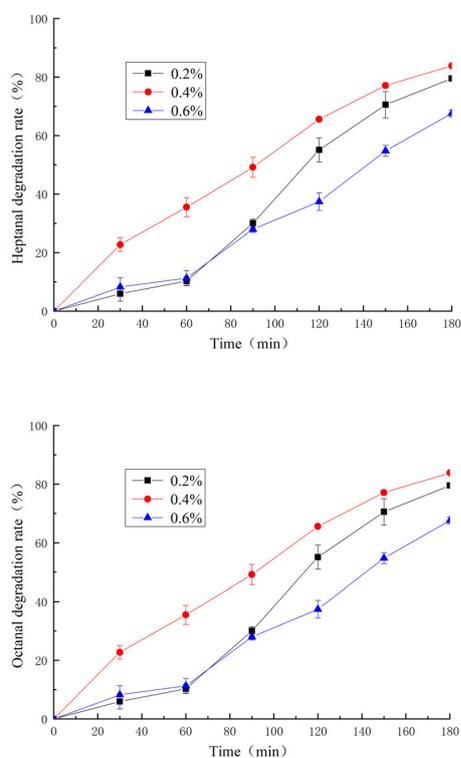


Fig. 4 Degradation curves of photocatalytic simulation system
 In order to study the photocatalytic degradation effect of chitosan-TiO₂ composite, four kinds of aldehydes with obvious odor activity in the enzymatic hydrolysate of blue clam were selected to construct a simulation system. The photocatalytic degradation curves of aldehydes in the system were shown in Fig. 4. There was a rising tendency in degradation rate of four aldehydes with the extension of photocatalytic treatment time. In addition, the photocatalytic degradation efficiency was higher when the addition of composite material reached 0.4%, but decreased at 0.6%. This might be because the transmittance of the solution in the simulated system decreased with the increase of the amount of photocatalytic materials, leading to the decline in receiving efficiency of the photocatalytic material. After three hours of photocatalytic treatment, the degradation efficiency of heptanal, octanal, (E)-2-heptenal and (E)-2-octenal reached the highest values of 83.82%, 81.73%, 96.33% and 93.36%, respectively.

4. Conclusions

Chitosan-TiO₂ photocatalytic composite material was prepared by combining anatase nano-TiO₂ with edible chitosan, and its structure was characterized by FT-IR, UV-vis and SEM. The results showed that TiO₂ and chitosan could combine stably in the composite material. Good photocatalytic degradation of composite material can be obtained from the results of photocatalytic simulation system. With the addition of 0.4% chitosan-TiO₂, the degradation efficiencies of heptanal, octanal, (E)-2-heptenal and (E)-2-octenal reached the highest values of 83.82%, 81.73%, 96.33% and 93.36%, respectively.

Acknowledgements

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