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Short Communication

Synthesis, characterization, and photocatalytic studies of copper-doped TiO_2 hollow spheres using rape pollen as a novel biotemplate

Dan Bu, Huisheng Zhuang *

School of Environment Science and Technology, Shanghai Jiao Tong University, No.800, Dongchuan Road, Minghang district, Shanghai 200240, P.R. China

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ABSTRACT

Copper/titanium dioxide (Cu/TiO_2) hollow microspheres were fabricated by direct coating of shells on the surface of rape pollen through an improved sol–gel process. Rape pollen grains were used as biotemplates, and they could be removed easily at high temperature. The average diameter of the as-synthesized hollow spheres was 15–20 μm, and the thickness of the hollow sphere shells was approximately 0.6 μm. These hollow microspheres had a higher specific surface area and exhibited stronger adsorptive capacity compared with the commercial p-25 system. The results indicate that Cu/TiO_2 hollow microspheres have promising photocatalytic applications.

1. Introduction

Semiconductor photocatalysts have been widely studied since 1972, with titania having received the greatest attention. Many efforts have been used to design and fabricate TiO_2 photocatalyst with highly photocatalytic efficiency. Among the various researches, there are two efforts which could widely develop the performance of photocatalysts. One approach is to fabricate special morphological TiO_2 photocatalyst, which is favorable to light harvesting and has large specific surface areas [1,2]. Many structures, like nanotube [3], nanosheets [4], nanobelts [5], and porous structure [6,7], had been reported. The other approach is noble or transition metals doping, which can inhibit charge carrier recombination and harvest the energy from the visible light. Integratively, metal doped TiO_2 with special morphology structure should be promising to improve the photoactivity.

To fabrication, biotemplate method has been demonstrated to be very effective in synthesizing special materials without complex preparation. Bacteria [8], butterfly wings [9], diatoms [10], and egg membranes [11] have been used to synthesize different morphological materials. However, the application of such biotemplates is often compromised by the significant shrinkage and deformation associated with their thermal removal [12]. In this respect, pollen grains are excellent candidates to be used as biotemplate — because their outer layer is relatively resistant to heat and oxidation [13]. Moreover, pollen has a uniform particle size as well as an elaborate and complex spherical morphology.

In this study, rape pollen was incorporated into an improved sol–gel procedure combined with immersion to prepare a Cu/TiO_2 hollow sphere. This method proved to be very simple and gentle. The as-prepared hollow spheres had a large specific surface area and strong absorbability. Previous studies have reported that TiO_2 with hollow spherical structure exhibits enhanced photocatalytic performance [12,14]. These findings suggest that photocatalysts with a large specific surface area will avail to transfer the carrier from photocatalysts to organics and organics and have higher catalytic activity.

2. Materials and methods

2.1. Synthesis and characterization

Titanium (IV) butoxide [$Ti(OC_4H_9)_4$] was used as the precursor in this study. Hydrolyzing water was released via the reaction of butanol and acetic acid to avoid rapid hydrolysis. Cu/TiO_2 hollow spheres were prepared as follows: First, titanium butoxide, n-butyl alcohol, and acetic acid (molar ratio = 0.5:4:4) were mixed with vigorous stirring. $CuCl_2$ (as copper precursor) and rape pollen (Fengpu Ltd. Shanghai) were added into the beaker after 3 h, and the mixture was stirred for 1 h to ensure that sol adhered to the surface of pollen. The resulting transparent brown sol was filtered, dried at 100 °C, and calcined in flowing air at 500 °C. The catalyst was then pulverized. The following optimal synthesis conditions were used: pH 3.0–4.0, mixing period of 3 h, and $CuCl_2$ at 2 wt.%. The hollow spherical photocatalysts were characterized by thermal analysis (WRT-3P, China), scanning electron microscopy

* Corresponding author. Tel.: +86 21 54748994; fax: +86 21 54740825/62419587.
E-mail addresses: budan198603@163.com (D. Bu), huishengzhuang@126.com, hszhuang@sjtu.edu.cn (H. Zhuang).

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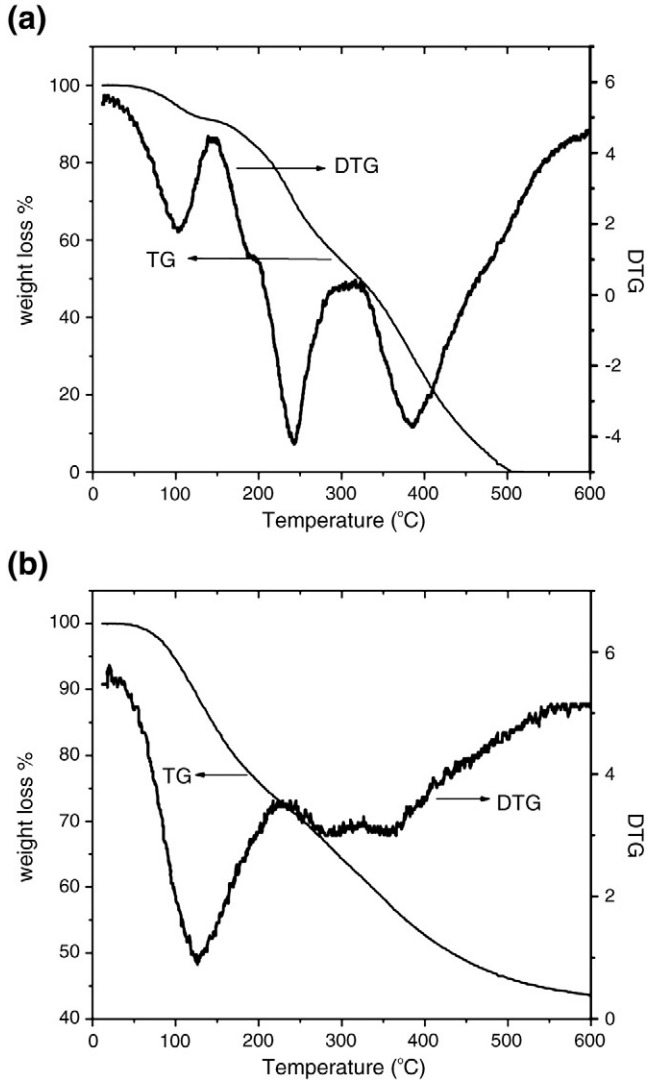

Fig. 1. Thermal analysis curves of (a) rape pollen grains and (b) photocatalyst precursor.

(JSM-6700 F, JEOL), X-ray diffraction (D/max-2550PC diffractometer, Rigaku), and UV-diffuse reflectance spectrometer (EV300, Thermo). Surface area was evaluated by N_2 adsorption in a constant volume adsorption apparatus (ASAP-2010, Micrometrics), using BET method.

2.2. Photocatalytic testing

The as-obtained hollow microspheres of photocatalysts and commercial p-25 (Degussa) were used to degrade chlortetracycline hydrochloride (CTC), which is an antibiotic compound, to estimate and compare their photocatalytic properties. Photolysis experiments were carried out in a photochemical reactor with UV or visible light illumination. The concentrations of the extracted and filtered clear CTC solution were measured with a UV/Vis spectrometer at 365 nm. The extent of the degradation of CTC was calculated as $De=(C_0-C_t)/C_0\times 100\%$, where C_0 is the initial concentration and C_t is the concentration after degradation time t.

3. Results and discussion

Thermal analysis was carried out in N_2 current, from 10 to 600 °C, at the rate of 20 °C·min^{-1}. Fig. 1 shows the thermal analysis results for the pollen and as-prepared samples. The exothermic peaks of the pollen and photocatalyst precursor at 100 °C were mainly caused by loss of water or solvent. The DTG curve of the rape pollen revealed two exothermic peaks at different temperature ranges (200–350 and 350–400 °C), reflecting the oxidation or decomposition of a vulnerable inner layer and a resistant outer layer [15], respectively. At 500 °C, the quality loss of rape pollen reached 100%. Fig. 1b shows the DTG curve of the photocatalyst precursor, from which two exothermic peaks were also detected at 250 and 400 °C. These peaks were smaller than those observed in pollen because the precursor adhered to the surface of the pollen, thereby resulting in lower quality loss. The rate of weight loss was stable until 500 °C, and 40% quality was retained at 600 °C.

The morphology and structure of the photocatalysts and rape pollen were further investigated using scanning electron microscopy. The pollen grains were spherical, measured 21–35 μm, and possessed a porous surface (Fig. 2a). Fig. 2b–f shows the hollow structure of the photocatalysts after calcination. It was confirmed that the uncoated template particles and freely precipitated titania particles were present (Fig. 2b). The hollow spheres basically maintained the morphology of the pollen. The thickness of the hollow sphere shells was estimated to be 0.6 μm. The diameter of the hollow spheres was smaller than that of the pollen, ranging from 15 to 20 μm. After calcination, some microspheres broke down (Fig. 2e), but some biotemplate remained in the hollow shell (Fig. 2f). These results indicate that the hollow microspheres were fabricated by direct coating of shells onto the surface of the biotemplates, which were removed at high temperature.

Fig. 3a shows the XRD patterns of pure TiO_2 calcined at different temperatures. At 400 °C, the anatase and amorphous phases were dominant and did not exhibit any other crystalline peak. The diffraction peak intensity and amount of anatase phase increased as temperature increased. When the calcination temperature was increased to 600 °C, a trace amount of rutile phase was observed. Fig. 3b shows the XRD patterns of the TiO_2 hollow spheres doped with 2 wt.% Cu. Rutile phases were observed at 400 °C and dominated at 600 °C. These results indicate that metallic ion could reduce the phase-transition temperature and accelerate phase transition. Effect of metal ion on TiO_2 crystal phase transformation depends on many factors, like ionic radius, concentration, and valence state. Although the ionic radius of Cu^{2+} (0.072 nm) is similar to that of Ti^{4+} (0.068 nm), copper ion did not enter into the lattice, because of the large difference in valence states. Meanwhile, CuO (*tenorite*) diffraction peaks appeared at $2\theta=35.7°$ and 38.78°for all the samples [16,17]. It is also proved that the copper is ionic formation rather than element formation in the Cu/TiO_2. However, the peak of crystalline CuO was less noticeable. This may be due to the CuO species dispersed on the surface of the TiO_2. The dispersed CuO will form Ti–O–Cu chemical bond [18,19], change the lattice-periodicity, and further affect the transformation of crystalline phase.

Table 1 lists the specific surface areas of the as-prepared photocatalysts. The specific surface area of the hollow spheres decreased as temperature increased, which may be attributed to the crystalline phase. The specific surface area of the Cu/TiO_2 hollow spheres increased but subsequently decreased with the amount of copper. Compared with solid spheres, the hollow ones increased their specific surface area and developed their adsorption capacity.

Different metal doping qualities and calcination temperatures affected the photocatalytic activity. The performance of hollow spherical photocatalysts initially improved and then declined as copper doping increased from 1 to 4 wt.% (Fig. 4a). The copper ions on the TiO_2 substrate could act as electron traps facilitating the photo-generated electron–hole separation [20]. However, a higher content of copper not only enables it to act as a recombination center but also triggers the screening effect [20]. Therefore, in this study, copper doping at 2 wt.% was selected as the optimum value for obtaining the maximum degradation rate of CTC. Fig. 4b illustrates the photocatalytic performance of Cu/TiO_2 hollow spheres calcined at various temperatures,