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Preparation and characterization of boron-doped titania nano-materials with antibacterial activity☆

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ABSTRACT

Boron-doped TiO_2 (B/TiO_2) nano-materials were synthesized by a sol–gel method and characterized by X-ray diffraction pattern (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectrum (FT-IR) and UV–vis diffuse reflectance spectra (DRS). With the test of bacterial inhibition zone, the antibacterial properties of B/TiO_2 nano-materials on *Escherichia coli* were investigated. The results show that the structure of TiO_2 could be transformed from amorphous to anatase and then to rutile by increasing calcination temperature; part of the boron atoms probably have been weaved into the interstitial TiO_2 structure or incorporated into the TiO_2 lattice through occupying O sites, whereas others exist as B_2O_3. The results of antibacterial experiment under visible light irradiation show that the B/TiO_2 nano-materials exhibit enhanced antibacterial efficiency compared with non-doped TiO_2. Ultimately, the action mechanism of B/TiO_2 doping is discussed.

1. Introduction

As an important photocatalyst, TiO_2 has a large application potential. But TiO_2 wide band gap greatly limits its application range. As an effective modification means, ion doping can reduce TiO_2 band gap width and expand its light response range, which can make use of abundant solar energy resources to replace the expensive artificial UV sources. So in recent years, nano TiO_2 has been paid more attention by many researchers [1–4]. Ion doping can be divided into metal ion doping and non-metal ion doping. The non-metal ions (such as C [1], N [2], S [3], and F [4]) doped TiO_2 with a strong visible light response and a good catalytic activity, become research hotspot. Boron and its compounds doped TiO_2 also get more attention [5–8]. In 2004, Zhao et al. [9] had improved appreciably the photocatalytic efficiency by doping TiO_2 with both boron ions and nickel ions. It was concluded that by incorporating boron atoms in the TiO_2 bulk, the absorption spectrum can be extended to the visible region. Chen et al. [10] prepared photocatalyst materials with different doping ratio by sol–gel method, and studied that the effect of doping boron ion on the microstructure and photocatalytic activity of TiO_2. Xu et al. [11] reported the boron atoms were often replaced by oxygen atoms or incorporated into the lattice. Therefore, boron-doped TiO_2 can make the absorption edge red-shifted, and then improve the photocatalytic efficiency.

As well known, boric acid is typical microbicides. It has inhibition for various bacteria and fungi. However, the melting point of boric acid is only 185 °C, and boiling point is 300 °C, so it cannot be applied in high temperature products. This greatly limits the application of boron-doped in antibacterial material. So in this study, boron-doped TiO_2 nano-materials were prepared by a sol–gel method, and firstly applied to the fields of antibacterial materials. B/TiO_2 nano-materials crystal structure, energy band structures, and antibacterial mechanism were studied in detail. This study will contribute researches greatly in pursuit of better technology in antibacterial materials.

2. Experimental

2.1. Preparation of B-doped TiO_2 nano-materials

The sol–gel synthesized TiO_2 was obtained from tetrabutyl titanate by injecting acid solution which consisted of distilled water, ethyl alcohol and acetic acid, under constant magnetic stirring for 3 h. In order to obtain nanoparticles, the soliquid was dried for 48 h. Sintering processes were subsequently carried out to

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Table 1
Effect of calcination temperature on phase structure of B/TiO_2.

Catalysts	Phase composition and mass percentage		
TiO_2-550 °C	Anatase: 100%		
B/TiO_2-500 °C	Anatase: 100%		
B/TiO_2-600 °C	Anatase: 100%		
B/TiO_2-700 °C	Anatase: 99%	Rutile: 1%	
B/TiO_2-800 °C	Anatase: 33%	Rutile: 48%	Rutile$TiB_{0.024}O_2$: 19%
B/TiO_2-900 °C	Anatase $Ti_{0.784}O_2$: 2%	Rutile $Ti_{0.924}O_2$: 84%	Rutile$TiB_{0.024}O_2$: 14%

obtain desired TiO_2 crystalline. The ion doped nanoparticles were synthesized with the same method mentioned above, except for the addition of the corresponding boron doping solution into the acid solution. The doping solution was prepared by dissolving boron compound (H_3BO_3) in acid water.

B/TiO_2 materials were prepared by impregnating pure TiO_2 nano-materials with boric acid under constant magnetic stirring for 24 h. Suspension was dried for 48 h and then calcinated at 500 °C.

2.2. Characterization

X-ray diffractometry (XRD; Shimadzu) equipped with a copper target ($\lambda_{K\alpha1}$ = 0.1541874 nm) was used to identify the formation phase of the obtained powder samples. The morphology and crystallite size of the powder were taken with TECNAI G2 F20 transmission electron microscope (TEM). The binding energy was identified by X-ray photoelectron spectroscopy (XPS) with Mg Kα radiation (ESCALAB250). Fourier transform infrared (FT-IR) spectrum was recorded on a Nicolet 380 instrument. The UV–vis absorption spectra were recorded on a Shimazu UV-2500 spectrophotometer.

2.3. Measurement of antimicrobial property

Escherichia coli (ATCC 25922) as model organisms, antibacterial properties of B/TiO_2 nano-materials were tested using inhibition ring method under visible light irradiation conditions. Observe the materials surrounding bacterial growth, measure transparent antibacterial circle diameter, and then determine antibacterial properties.

3. Results and discussion

3.1. XRD analysis

XRD was carried out to investigate the changes patterns TiO_2 phase structure after boron-doping and calcination treatment. Fig. 1 shows the effect of calcination temperatures on the phase structure of B/TiO_2 nano-materials. It is found that materials TiO_2-500 °C, B/TiO_2-500 °C, and B/TiO_2-600 °C, exhibit an anatase phase (2θ = 25.3°) as the predominant homogeneous crystalline phase but the FWHM decrease with the increase of temperature. It indicates the crystal becomes larger with increase of calcination temperature. B/TiO_2-700 °C begin to appear a small amount of rutile (2θ = 27.4°). It demonstrates the phase transformation of anatase to rutile occurs at 700 °C, which is consistent with that reported in the literature [10]. And the proportion of rutile phase becomes obviously great as the calcination temperature increases. When calcination temperature reaches 800 °C, rutile phases are increased significantly and a small amount of rutile $TiB_{0.024}O_2$ is also detected. Calcinated at 900 °C, anatase phases are nearly disappeared, rutile $Ti_{0.924}O_2$ phases are predominant phase. The ratio between anatase and rutile extracted from XRD spectra, which is often used to quantify the anatase-to-rutile transformation, is calculated with the semi-quantitative calculation of XRD analysis. Table 1 shows the percentage content of rutile and anatase. It is well known

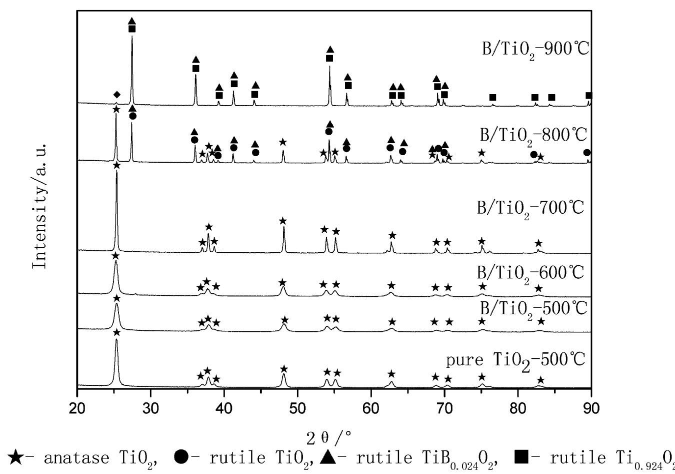

Fig. 1. XRD patterns of pure TiO_2-500 °C and B/TiO_2 calcined at different temperatures.

that the crystalline and the crystal phase are crucial factors in the antibacterial activity of TiO_2, where the crystalline anatase phase is considered as the most active form of TiO_2, while rutile and amorphous TiO_2 are believed to be relatively inactive.

To investigate the effect of boron-doping on the crystal structure of TiO_2, we calculated the lattice parameters of TiO_2 nano-materials listed in Table 2. Table 2 shows that the lattice parameters of all boron-doped nano-materials remain almost unchanged along the *a*-axis. Compare to pure TiO_2-500, the *c*-axis parameter of B/TiO_2-500 decreases, which means boron doped TiO_2 inhibiting grain growth. Subsequently, the increase of calcination temperature, the c-axis parameter increases. This is because those boron ions may enter the interstitial site of TiO_2 anatase crystal structure and lead to the swell of unit cell volume [10].

3.2. TEM analysis

The TEM micrographs of TiO_2-600 °C and B/TiO_2-600 °C are shown in Fig. 2. The morphology, grain sizes of the particles and crystallographic planes have also been verified using the TEM study. The TEM analysis has revealed that the grains are round-shaped. And after doping boron, the particles sizes become smaller and better dispersion. This shows that doping boron ions prevents the agglomeration of the particles in the process of heat treatment,

Table 2
Effect of calcination temperature on lattice parameters of B/TiO_2.

Catalysts	Crystallite diameter (nm)	Unit-cell parameter (1 0 1)		
		a (*b*) (nm)	*c* (nm)	*V* (nm^3)
TiO_2-500 °C	70	3.7820	9.5076	135.992
B/TiO_2-500 °C	40	3.7801	9.2531	132.219
B/TiO_2-600 °C	18	3.7821	9.3874	134.280
B/TiO_2-700 °C	48	3.7803	9.7237	138.958
B/TiO_2-800 °C	73	3.7897	9.5298	136.865
B/TiO_2-900 °C	–	–	–	