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RESEARCH ARTICLE

PREPARATION AND CHARACTERIZATION OF TB, N CO-DOPED TITANIA NANOCOMPOSITES

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ABSTRACT

In this paper, Tb-N-TiO_2 nanocomposites with different calcined temperature were synthesized through a facile step by sol-gel method. Besides, structural characteristics, morphology and photochemical properties of the nanocomposites were characterizedby X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), UV-vis diffuse reflectance spectroscopy (DRS) and Scanning electron microscope (SEM). The results showed that the Tb-N-TiO_2 composites were existed in the form of anatase. The absorption of Tb-N-TiO_2 in the ultraviolet and visible regions is stronger than that of TiO_2 and Tb-TiO_2.

INTRODUCTION

Photocatalysis is an emerging technology in the field of wastewater pollution treatment. It can not only eliminate a large number of pathogenic microorganisms , but also effectively degrade the pollutants.There are many common photocatalytic materials, including titanium dioxide (TiO_2), zinc oxide, tin oxide, zirconium dioxide, cadmium sulfide and other oxide sulfide semiconductors(1,3). Among many of the materials, TiO_2 has been the most commonly used in this field due to its chemical stability, high efficiency, non-toxicity, low cost, corrosion resistance and easy preparation(2-4).However, $TiO_2$was restricted in practical application by some limitations(5,6). First of all, TiO_2 can only absorb ultraviolet light, it does not respond to visible light. secondly, the intrinsic conductivity of TiO_2 is low, the photogenerated electron-hole pairs is easy to recombine on the catalyst surface, thereby reducing the carrier utilization rate. Therefore, modification of titanium dioxide is urgent and necessary. The modification of TiO_2mainly focus on ion doping, dye sensitization, semiconductor heterojunction recombination, structure and morphology control(7).It has been reported that different transition metal ions including Fe^{3+}, Cr^{3+}, Mg^{2+}, Zn^{2+}, are doped with TiO_2 can effectively reduce the band width of TiO_2 and generate more photogenerated electrons and holes(8). Thus, the redox ability of TiO_2 is improved.

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Compared with transition metal ions, rare earth metal ions have a special electronic layer structure. In addition to the above similar advantages of doping transition metal ions, they can also cause lattice distortion of TiO_2, forming traps for photogenerated electron holes, and increase the efficiency of photocatalytic materials. Villabonaleal found that the atomic number and concentration of lanthanides would affect the band gap energy and specific surface area of TiO_2(9).Asahi first published a report on N-doped TiO_2, and pointed out that nitrogen doping can make TiO_2 responsive in the visible light region(2).He synthesized C-doped TiO_2 nanocomposites, which not only changed the original morphology of the material, but also improved the capture efficiency of organic molecules(5).Metal and non-metal doping also shows remarkable synergisticadvantages. LeipreparedFe, N, C co-doped TiO_2 nanocomposites and used to the degradation of organic pollutants, and the degradation rate reached 100%(14). Chen prepared Ce and N co-doped TiO_2 nanocomposites and incorporated diatomite particles to degrade p-oxocycline under visible light irradiation for 240 min. The obtained composite exhibited better degradation rate than other catalysts(15). In this study, a series of novel photocatalytic nanocomposites were developed using butyl titanate as a precursor and a sol-gel method. Moreover, the structure, element composition and physicochemical properties of the obtained materials were characterized.

MATERIALS AND METHOD

Tetrabutyl titanate, terbium(III) nitrate hexahydrate, and urea were all purchased from Sigma-Aldrich Chemical Company.

All of the reagents were of analytical grade andused without any furtherpurification. Tb-N-TiO_2 was prepared by sol-gel method. Firstly,20 mL absolute ethanol (dispersant) and 20 mL of butyl titanate (precursor) were added to a three-necked flask at room temperature, keep stirring for 0.5 h, named as solution A. Urea and terbium nitrate were dissolved with 50 mL of absolute ethanol. 20 mL of distilled water and 10 mL ofglacial acetic acid were added and stirred for 0.5 h to obtain a transparent solution, named as solution B. Thereafter, solution B was transferred to a separatory funnel and slowly added to solution A. Keep reacting at 70 °C for 2 h.The obtained stable and uniform TiO_2 sol was aged at room temperature for 72 h. After drying, the samples werecalcined at different temperatures in a muffle furnace for 4 h. The preparation procedure of Tb-TiO_2, TiO_2 is similar to that ofTb-N-TiO_2 without the adding of urea and terbium nitrate.

RESULTS AND DISCUSSION

In order to study the effect of calcined temperatures on crystal structure, crystallinity and crystallite sizeof Tb-N-TiO_2nanocomposites, XRD analysis was carried out. As shown in Fig. 1, obvious diffraction peaks appear in all of the samples when the calcined temperature is in the range of 300-600°C.The diffraction peaks at 2θ=25.38º, 37.88º, 48.10º, 54.10º, 55.28º and 62.75º is corresponded to (101), (004), (200), (105), (211), (204) crystal plane of anatase, respectively, indicating that there is no change in the crystal form of TiO_2 in the composite after doping. Generally, the sharpness and intensity of diffraction peaks are related to the crystallite size and crystallinity of the samples [10]. As shown in Table 1, the crystallinity of the samples increases with the increasing of calcination temperature. This suggests that calcination is beneficial to the crystallization of titanium dioxide.In addition, the crystallite size of the samples obtained at different calcined temperatures is between 10 nm and 14 nm. Combined with crystallinity and crystallite size of the samples, Tb-N-$TiO_{2\text{-}600}$ °C was selected for subsequent experiments.

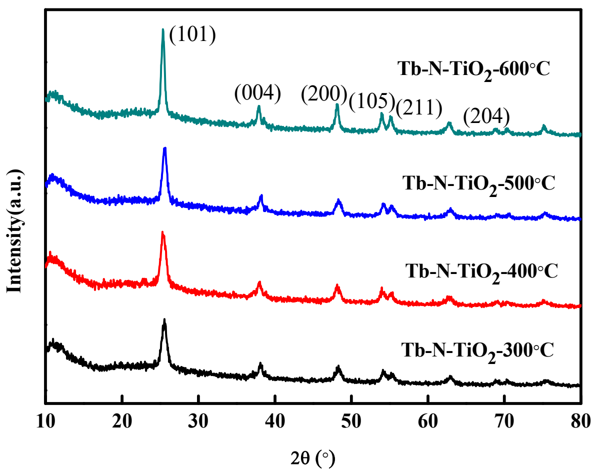

Fig. 1. XRD patterns of Tb-N-TiO_2 with different calcined temperatures

Table 1. Physical parameters of theTb-N-TiO_2 nanocomposites

Samples	Crystallinity (%)	Crystallite size (nm)
Tb-N-$TiO_{2\text{-}300}$ °C	94.97	11.40
Tb-N-$TiO_{2\text{-}400}$ °C	96.50	10.67
Tb-N-$TiO_{2\text{-}500}$ °C	97.90	10.49
Tb-N-$TiO_{2\text{-}600}$ °C	99.51	13.26

XPS was used to analyze the surface element morphology and chemical composition of the material. XPS Spectra of Tb-N-TiO2 samples are shown in Fig.2. It can be seen that Ti2s, O1s, Ti2p, N1s, C1s, Ti3s and Ti3p peaks appear between the binding energy of 0-1200 eV. As displayed in Fig.2(b), the binding energies of O1s appear at two peaks of 529.40 eV (Ti-O-Tb) and 527.62 eV (Tb-O), respectively, indicating that Ti-O-Tb is formed on the surface of Tb-N-TiO2 material(11). Fig.3(c) shows that in the narrow spectrum of Ti2p, peaks at 464.8 eV and 456.6 eV are assigned to Ti^{4+} $_{2p1/2}$ and Ti^{4+} $_{2p3/2}$, respectively, while 461.7 eV and 456.6 eV are corresponded to Ti^{3+} $_{2p1/2}$ and Ti^{3+} $_{2p3/2}$(12,13). It demonstrates that Tb-N-TiO2 contains two valence states including Ti^{4+} and Ti^{3+}. From the narrow spectrum of Tb3d in Fig. 2(d), the binding energy peaks of $Tb^{3+}3d_{3/2}$ and $Tb^{3+}3d_{5/2}$ appear at 1243.2 eV and 1224.7 eV, respectively. The presence of $Tb^{3+}$is beneficial for the formation of lattice defects. As shown in Fig. 2(e), the peak of 397.91 eV indicates that the exist of Ti-O-N bond.

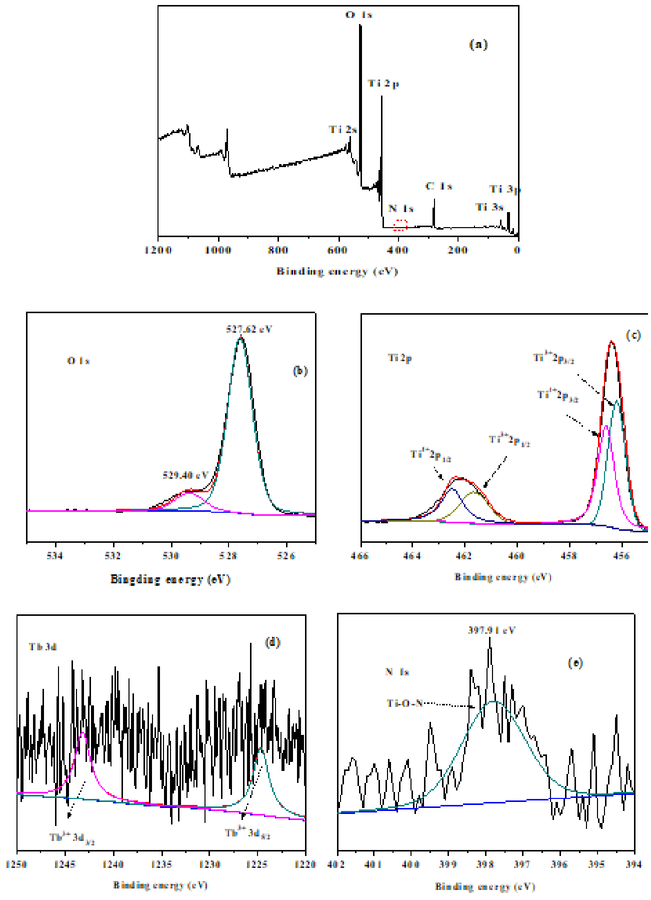

Fig. 2. XPS Spectra of Tb-N-TiO_2 samples

Fig.3 shows the UV-Vis diffuse reflectance spectra of pure TiO_2, Tb-$TiO_2$and Tb-N-TiO_2. Compared with pure TiO_2,a slight red shift in the absorption edge of the catalyst doped with other elements was observed. The absorption intensity in the ultraviolet region (less than 380 nm) is greatly improved, and the absorption intensity is in the following orderTb-N-TiO_2>Tb-TiO_2>TiO_2. It demonstrates that Tb and N do pants have an obvious synergistic effect on improving the optical properties of nanomaterials.

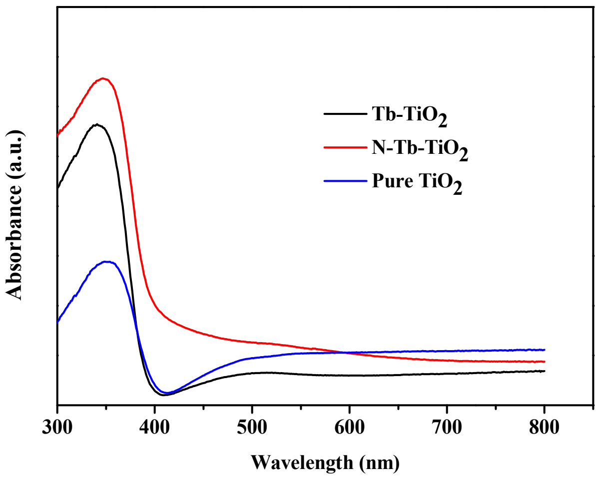

Fig.3. UV-Vis diffuse reflectance spectra of Pure TiO_2,Tb-TiO_2 and Tb-N-TiO_2

SEM image of Tb-N-TiO_2sample is displayed in Fig.4. It can be seen that the nanoparticles are agglomerated into irregular shapes and their surfaces are rough.

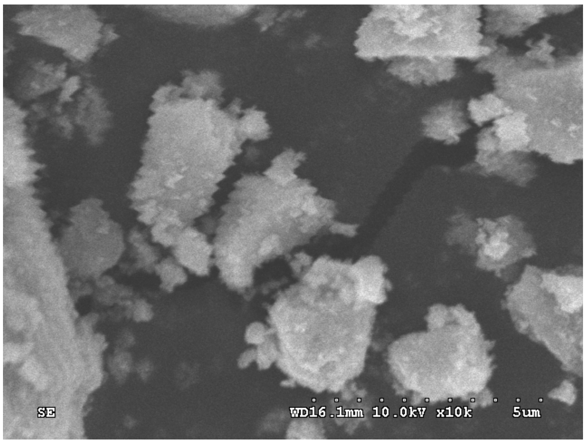

Fig. 4. SEM image of Tb-N-TiO_2sample

Conclusion

Tb-N-TiO_2 nanocomposites with different calcined temperatures were synthesized successfully through a facile step by sol-gel method. The composites crystallized well and the crystallinity was over 94%. The titanium dioxide in the composite existed in the form of anatase, and crastallite size was in the range of 10-14 nm. XPS spectra show that the exist of Ti-O-N bond in the Tb-N-TiO_2 nanocomposites. Tb and N dopants have an obvious synergistic effect on improving the optical properties of nanomaterials, suggesting that Tb-N-TiO_2 nanocomposite has broad development prospects in the field of photocatalysis.

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