



Preparation of La-B-TiO₂ Photocatalyst by Sol-Gel and Solvothermal Methods

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La-TiO₂, B-TiO₂ and La-B-TiO₂ photocatalysts were prepared by sol-gel method. The La-TiO₂ containing 0.5 % La presented the maximum photocatalytic activity of 35.4 %. The sample doped with 3 % boron showed the optimum photocatalytic activity. When La content was below 3 %, degradation rate on La-3 % B-TiO₂ was nearly constant around 30 %. However, degradation rate dropped drastically on the sample containing 5 % La. La-B-TiO₂ photocatalysts were prepared by solvothermal method. The results indicated that the total volume of N₂ adsorbed on 1 % La-3 % B-TiO₂ increased with the increase of relative pressure P/P₀. The average pore size of the material was 16.29 nm and the total pore volume was 0.412 mL/g. Specific surface area of the material was 101.45 m²/g. When La content was 0.5 %, methyl orange adsorption rate on the material 0.5 % La-3 % B-TiO₂ was less than 5 % and photocatalytic degradation rate was 39.9 %.

Key Words: TiO₂, Photocatalysis, Doping, Sol-gel, Solvothermal.

INTRODUCTION

TiO₂ is considered to be the most widely studied and applied photocatalyst due to many of its properties. However, the activity of pure TiO₂ is not satisfactory and doping technology is applied as an effective method to improve photocatalytic activity. Metallic and nonmetal doping into the matrix of TiO₂ can greatly improve activity of this material. Several kinds of nonmetal ions such as N¹⁻³, C⁴ and B^{5,6} have been studied to promote photogenerated charges separation in TiO₂. Boron doped TiO₂ attracted much attention and there have been a great attention in doping rare earth metals into TiO₂ photocatalyst.

Boron-Doped TiO₂ showed higher photocatalytic activity than that of pure TiO₂ in photocatalytic NADH regeneration⁷. Yuan prepared B and N co-doped TiO₂ photocatalyst *via* sol-gel method and found that interstitial N and [NOB] species in the TiO₂ crystal lattice narrowed band gap and extended optical absorption of TiO₂⁸. Rare earth metal doped TiO₂ photocatalyst has shown enhanced activity in many reported literatures^{9,10}. Zaleska *et al.*¹¹ used a simple surface impregnation method to prepare boron modified TiO₂ and boron as a B-O-Ti species existed in the surface of TiO₂ grains. Xu *et al.*¹² indicated that low-temperature hydrothermal method could be used to prepared boron doped TiO₂.

In this paper, La-TiO₂, B-TiO₂ and La-B-TiO₂ photocatalysts were prepared by sol-gel and solvothermal method. The activities of the materials were evaluated by degradation of methyl orange solution under UV light irradiation.

EXPERIMENTAL

Photocatalysts were prepared by sol-gel method. Tetrabutyl titanate of chemical pure grade was chosen as the Ti precursor and tributyl borate (99.5 %) was used as the boron source. Lanthanum chloride was used to for lanthanum source. Hydrochloric acid and anhydrous ethanol were in the analytical reagent grade. 8 mL anhydrous ethanol and 0.1 mL hydrochloric acid were mixed in a beaker and then 2 mL tetrabutyl titanate and desired volume of tributyl borate were added dropwise to the former solution under constant magnetic stirring to prepare solution 1. Meanwhile, 1 mL of distilled water was mixed with 4 mL anhydrous ethanol to prepare solution 2. After solution 1 was stirred for 0.5 h, solution 2 was added dropwise into solution 1. The final mixed solution was continuously stirred until the formation of a gel. After aging for 24 h at room temperature, the gel was dried at 80 °C for 8 h. Subsequently, the obtained solid was grinded and calcinated at 400 °C for 3 h.

La-B-TiO₂ photocatalysts were prepared by solvothermal method. Tetrabutyl titanate of chemical pure grade was chosen as the Ti precursor and tributyl borate (99.5 %) was used as the boron source. Lanthanum chloride was used to for lanthanum source. Hydrochloric acid and anhydrous ethanol were in the analytical reagent grade. 8 mL of anhydrous ethanol and 0.1 mL of hydrochloric acid were mixed in a beaker and then 2 mL of tetrabutyl titanate and desired volume of tributyl borate and lanthanum chloride were added dropwise to the former solution under constant magnetic stirring to prepare

solution 1. Meanwhile, 1 mL of distilled water was mixed with 4 mL anhydrous ethanol to prepare solution 2. After solution 1 was stirred for 0.5 h, solution 2 was added dropwise into solution 1. The solution was moved to a 50 mL PTFE high pressure stainless reactor and was maintained at 120 °C for 24 h. After cooling, the solid was filtered and dried at 80 °C for 8 h. After that, the solid was grinded and calcinated at 400 °C for 3 h. The obtained materials were ascribed as La-3 % B-TiO₂ in the following experiments. Boron content in the materials was fixed at 3 wt % of the amount of TiO₂. La content was indicated in the following experiments.

Characterization: The N₂-adsorption and desorption of the sample was measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. Specific surface areas and pore size distribution were calculated from the N₂ desorption isotherms, according to Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively.

Photocatalytic activity: The activity of the material was evaluated by degradation of methyl orange solution under UV light irradiation. Before photocatalytic experiment, adsorption of methyl orange solution in the dark on the photocatalyst was measured in the suspension. 50 mL of 10 mg/L methyl orange aqueous solution was mixed with 30 mg photocatalyst in a 250 mL beaker. The suspension was stirred magnetically for 20 min to reach adsorption equilibrium. After that, 5 mL suspension was taken out of the reactor and filtrated through a millipore filter (pore size 0.45 μm) to remove the photocatalyst. Finally, absorbency of the solution was measured using a 721E spectrophotometer at the methyl orange maximum absorption wavelength of 468 nm.

Photocatalytic activities of the prepared catalysts were evaluated afterwards. A 20 W ultraviolet lamp was located over the 250 mL beaker with a distance of 11 cm from the lamp to the surface of the solution. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 1100 μW/cm². Irradiation time in the subsequent experiments was set for 0.5 h except for the prolonged time reaction. After photocatalytic reaction, 5 mL of the suspension was filtrated through millipore filter to measure the change of methyl orange concentration.

RESULTS AND DISCUSSION

La-TiO₂, B-TiO₂ and La-B-TiO₂ photocatalysts were prepared by sol-gel method. Fig. 1 shows photocatalytic activities of La-TiO₂ samples with different La contents. The adsorption of methyl orange on the materials changed with the increase of La content. When La content was less than 3 %, the adsorption of methyl orange on the materials was around 3 %. Whereas, adsorption rate on the sample containing 5 % La showed as high as 40 %. The sample containing 0.5 % La presented the maximum photocatalytic activity of 35.4 %. Photocatalytic activities of the sample containing higher content of La showed drastically decreasing activity.

Fig. 2 illustrates photocatalytic activities of B doped TiO₂ samples with different B contents. The addition of boron into the matrix of TiO₂ had a little effect on methyl orange adsorption on the boron doped TiO₂ materials. Meanwhile, photocatalytic

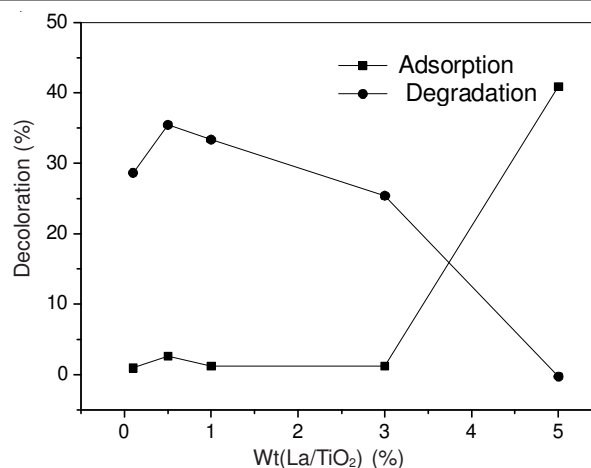


Fig. 1. Photocatalytic activities of La-TiO₂ samples with different La contents

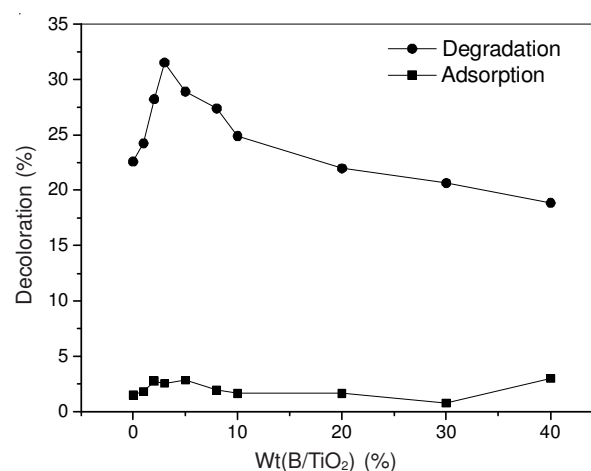


Fig. 2. Photocatalytic activities of B-TiO₂ samples with different B contents

degradation of methyl orange efficiencies on the materials varied with different boron contents. The sample doped with 3 % boron showed the optimum photocatalytic activity. The doping of boron into TiO₂ matrix inhibited the growing up of TiO₂ crystallites. Anatase TiO₂ crystallites could not form with the concurrence of too much boron ions. Due to the deficiency of electron density on boron ions, a suitable amount of doping of boron could be beneficial to more adsorption of OH⁻ on the material. Since OH⁻ can capture photogenerated holes on TiO₂ and convert the holes into ·OH, photocatalytic activity can be improved. However, excessive doping of boron ions can provide more electron traps for the photogenerated electrons. More holes and electrons recombined before migrating to the adsorbed reactants. Therefore, too much doping of boron in matrix TiO₂ could lead to obviously decrease of degradation activity.

Fig. 3 shows photocatalytic activities of La-B-TiO₂ samples with different La contents. In these materials, boron content was fixed at 3 % and lanthanum content changed as indicated in the Fig. 3. The adsorption of methyl orange on the materials changed with variation of La content. The adsorption rate was not more than 5 % when La content was less than 3 %. Whereas, adsorption rate rose to nearly 40 % when 5 % La was added into B-TiO₂. Photocatalytic activity followed a reverse trend. When La content was below 3 %, degradation rate was nearly

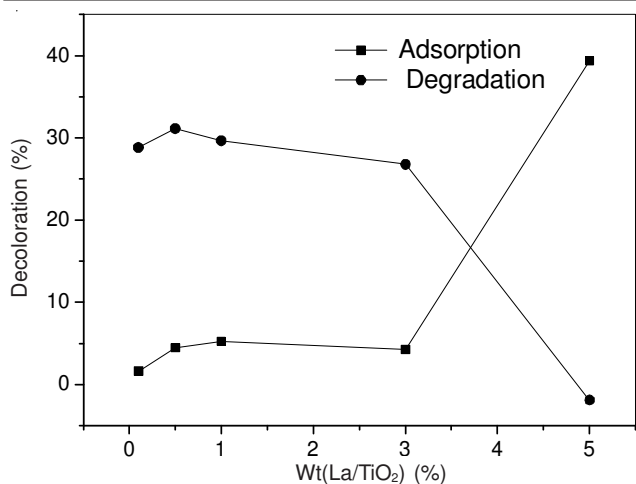


Fig. 3. Photocatalytic activities of La-3 % B-TiO₂ samples with different La contents

constant around 30 %. However, degradation rate dropped drastically on the sample containing 5 % La. It is interesting that the point of 5 % doping of La became a turning point. Although it is not possible to clarify the reasons, it can be deduced that doping of La at high content might cause great change in structure of the materials. Since adsorption capacity is in close relationship to porous structure of the materials, high content doping of La might lead to formation of porous structured materials. Excessive doping of La ions could provide more electron traps for the photogenerated electrons. More holes and electrons recombined before migrating to the adsorbed reactants.

La-B-TiO₂ photocatalysts were also prepared by solvothermal method. Fig. 4 shows the N₂ desorption isotherm of 1 % La-3 % B-TiO₂ sample measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. It indicates that the total volume of N₂ adsorbed on the material increased with the increase of relative pressure P/P₀. When P/P₀ value was low, monolayer of N₂ molecules were adsorbed on the surface. When the relative pressure P/P₀ was between 0.8-0.9, capillary condensation of N₂ molecules occurred inside the pores of the material and caused the drastic increase of total adsorbed N₂ volume.

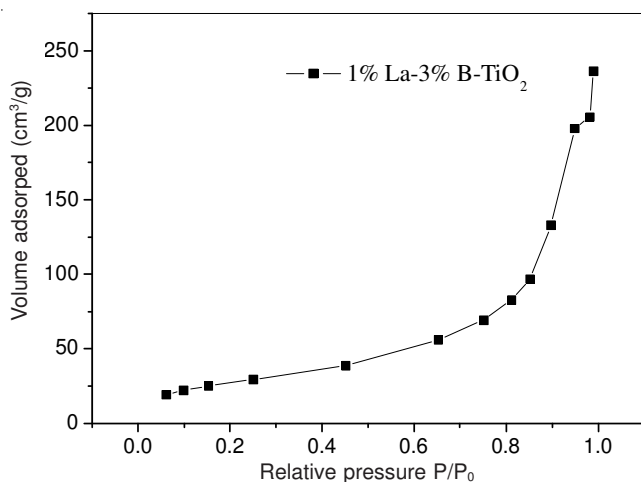


Fig. 4. N₂ desorption isotherms of 1 % La-3 % B-TiO₂ sample

BJH pore size distribution of 1 % La-3 % B-TiO₂ sample is illustrated in Fig. 5. Pore size distribution was calculated from the N₂ desorption isotherm, according to Barrett-Joyner-Halenda (BJH) method. The result revealed that pore size of the 1 % La-3 % B-TiO₂ sample mainly distributed in the range between 5-35 nm. That means mesoporous structure is the characteristic of the prepared composite material. As calculated from the N₂ desorption isotherm, the average pore size of the material was 16.29 nm and the total pore volume was 0.412 mL/g. Specific surface area of the material was 101.45 m²/g, which was calculated from the N₂ desorption isotherm using Brunauer-Emmett-Teller (BET) equation.

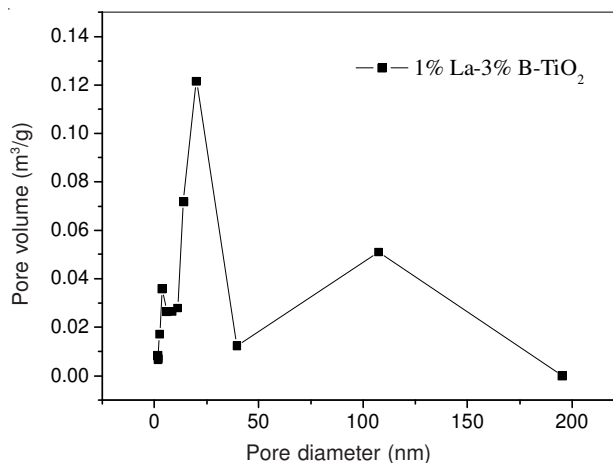


Fig. 5. BJH pore size distribution of 1 % La-3 % B-TiO₂ sample

Surface area and pore size distribution are the two major characters of porous photocatalytic material. In the development of photocatalytic technology, many researchers have devoted to prepare porous materials with suitable pore size and surface area. It is believed that large surface area and pore volume are benefit to adsorption and photocatalytic degradation activity of the materials. Surface area comes mainly from the porous structure inside the materials and rough external surface morphology can also add on some surface area at the same time. Porous materials are regarded as having high photocatalytic activity due to many of the reasons. The increasing adsorption capacity is the first reason. Meanwhile, the porous structure can also help on improving photocatalytic degradation process.

Photocatalytic activities of La-3 % B-TiO₂ samples with different La contents are shown in Fig. 6. The materials were prepared by solvothermal method, where the content of boron was kept at 3 % and a series of lanthanum content was chosen. The results indicated that photocatalytic activities of the materials were low when lanthanum content was below 0.5 %. Whereas, the sample containing 0.5 % La presented the maximum photocatalytic activity. Photocatalytic activities of the samples containing even higher contents of La showed decreasing trend.

The adsorption of methyl orange on the materials increased constantly with the increase of La contents. The maximum adsorption rate was nearly 10 % at La content of 5 %. Adsorption of the dye can reach its equilibrium after a certain time, while photocatalytic degradation is the major pathway for

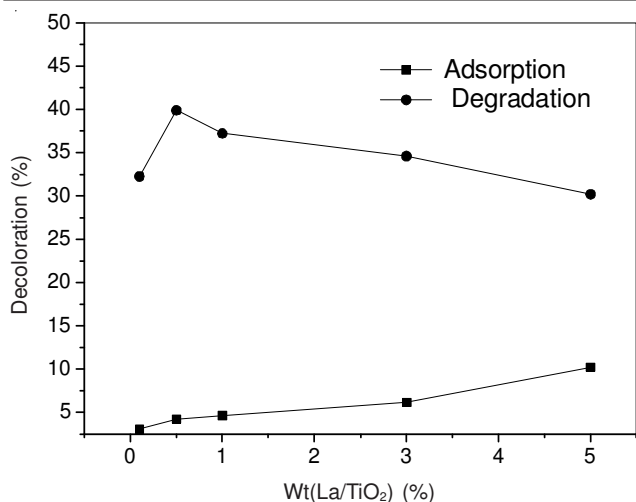


Fig. 6. Photocatalytic activities of La-3 % B-TiO₂ samples with different La contents

decolouration of the dye. When La content was 0.5 %, methyl orange adsorption rate on the material was less than 5 % and photocatalytic degradation rate was 39.9 %.

Conclusion

Firstly, La-TiO₂, B-TiO₂ and La-B-TiO₂ photocatalysts were prepared by sol-gel method. Photocatalytic activities of the sample containing higher content of La showed drastically decreasing activity. The sample containing 0.5 % La presented the maximum photocatalytic activity of 35.4 %. Photocatalytic degradation of methyl orange efficiencies on the materials varied with different boron contents. The adsorption rate on La-3 % B-TiO₂ was not more than 5 % when La content was less than 3 %. When La content was below 3 %, degradation rate was nearly constant around 30 %. However, degradation rate dropped drastically on the sample containing 5 % La. Secondly,

La-B-TiO₂ photocatalysts were prepared by solvothermal method. The result revealed that pore size of the 1 % La-3 % B-TiO₂ sample mainly distributed in the range between 5-35 nm. The average pore size of the material was 16.29 nm and the total pore volume was 0.412 mL/g. Specific surface area of the material was 101.45 m²/g. When La content was 0.5 %, methyl orange adsorption rate on 0.5 % La-3 % B-TiO₂ was less than 5 % and photocatalytic degradation rate was 39.9 %.

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