Influences of photocatalytic activity by doping TiO_2 with different kinds of ions

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Abstract. Photocatalytic activity of doping TiO_2 with different kinds of ions were investigated. Through photocatalytic degradation of methylene blue solution, photocatalytic activities of the three materials after treatment and the influencing factors were compared. The result showed that the degradation rate of methylene blue by using La^{3+} doped TiO_2 or thiourea doped TiO_2 is higher than Fe^{3+} doped TiO_2. Compared with 45wt% thiourea in optimum condition, 0.5wt% La^{3+} addition have the same effect. After that, the study focus on La^{3+} doped TiO_2. The absorption intensity and particle size of undoped TiO_2 and La^{3+} doped TiO_2 were investigated, the result showed that absorption intensity of 0.5wt% La^{3+} doped TiO_2 have a high absorption in the visible region, UV region and have fine uniform particles with a narrow size distribution and less aggregate.

Introduction

Environmental photocatalytic have attracted more attentions in these years. Titanium oxide（TiO_2）is one of main photocatalysts in the field of environmental photocatalytic because of its low toxicity, easy reforming, long term stability and simple production[1-4]. Many efforts have been devoted to improve the photocatalytic performance of it in the past decade. A lot of methods were used to improve the photocatalytic performance[5-6]. Chemical methods, such as sol-gel process, allow various possibilities of synthesis of oxide materials with different structures, compositions and morphologies and proves especially a new route for TiO_2 materials recognized for their properties of photocatalytic [7-10].

In this study, Photocatalytic activity of doping TiO_2 with different kinds of ions were investigated. Through photocatalytic degradation of methylene blue solution, photocatalytic activities of the three materials after treatment and the influencing factors were compared. After that, the study focus on La^{3+} doped TiO_2. The absorption intensity and the particle size of undoped TiO_2 and La^{3+} doped TiO_2 were investigated.

Materials and method

Reagents and reactor used

The reagents used in this study are deionized water(resistivity>18MΩ.cm), Tetrabutyl Titanate(98%,Tianjin Guangfu Fine Chemical Research Institute), absolute ethanol(99.7% , Beijing Chemical Works), Nitric acid(65%-68%,Beijing Chemical Works),Acetic acid(99.5%,Tianjin Guangfu Fine Chemical Research Institute) Ferric nitrate(98%,Tianjin Guangfu Fine Chemical Research Institute), Lanthanum nitrate(98%,Tianjin Guangfu Fine Chemical Research Institute), Thiourea(99%,Tianjin Guangfu Fine Chemical Research Institute).

The photocatalytic reactor used in this study is a common reactor (PL-300D) with a lamp .The lamp used is of the range 200-500nm of 300W.The irradiation power was measured as 100mWcm^{-2}. The solution along with the catalyst in beaker with the volume capacity of 500mL was 30cm under the photocatalytic reactor. The sample is centrifuged before analysis of concentration.

Method

Titanium dioxide sol was prepared using tetrabutyl titanate as precursor. 30 mL of tetrabutyl titanate was mixed with 100 mL of ethanol and stirred well. After stirring 30 minutes, sol A was obtained.

To prepare sol B, 30 mL of deionized water and 10 mL of acetic acid were dissolved in100 mL, then adjusted the pH value equals to 2.0 by Nitric acid. At last added reagent such as Ferric nitrate, Thiourea, or Lanthanum nitrate to the, materials and stirred well.

The sol A was added to the sol B at the speed of 5ml/min. Dried under normal pressure, calcinated at 500˚C for 3h. The photocatalyst was obtained.

The photocatalyst was added to methylene blue solution to investigate the photocatalytic activity by using photocatalytic reactor.

Results and discussion

Fe^{3+} doped TiO2

The doping of TiO_2 with various metal or non-metal ions has been reported to be a good tool to improve its photocatalytic properties. Optical and structural properties of iron ion (Fe^{3+} doped TiO_2 prepared by sol–gel technique.

Add Fe^{3+} to the sol B. The addition amount of it is kept in the range of 0-4.0wt%. Reaction time is 60min. The degradation rate of the methylene blue under UV light have been studied. The result was shown in Fig. 1.

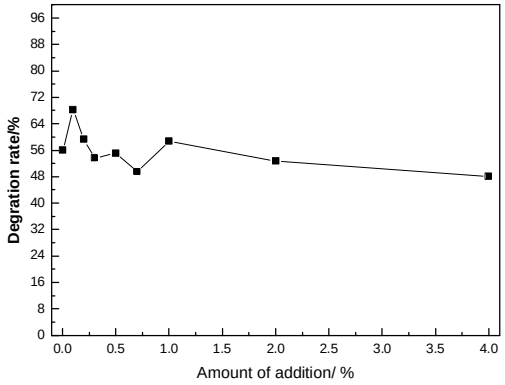

Fig. 1 Comparison of photocatalytic performance of different Fe^{3+} doping amounts

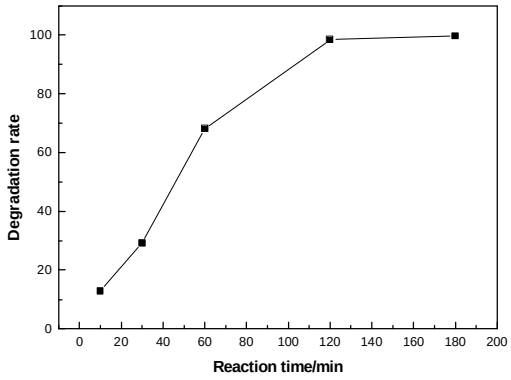

Fig. 2 Photocatalytic performance as time growing of Fe^{3+} doped TiO_2

As shown in Fig.1, photocatalytic performance of different Fe^{3+} doping amounts have little effect. Compare to pure TiO_2, 0.1wt%Fe^{3+} doped TiO_2 has a little higher degradation rate. But the degradation is still very low.

Action time is an important factor to investigate the photocatalytic properties. The photocatalytic performance as time growing was shown in Fig. 2.

As shown in Fig. 2, the degradation rate is growing as the reaction time growing. When the reaction time was 120min, the degration rate was above 90%. However, 120 min is a very long time to solve methylene blue solution.

Thiourea doped TiO2

Non-metal ions addition is a good tool to improve photocatalytic properties. Thiourea is doped in TiO_2. After did many experiments, the optimum addition amount 45wt% was chosen. The degradation rate of the methylene blue under UV light have been studied. The result was shown in Fig. 3

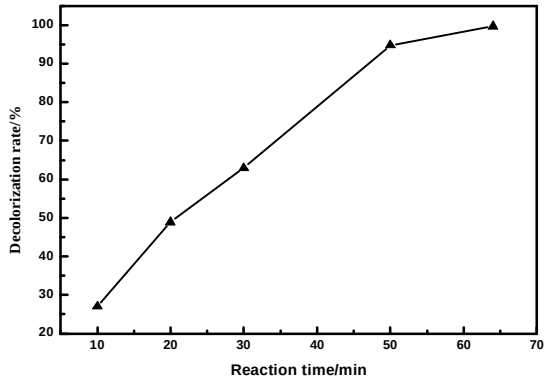

Fig. 3 Photocatalytic performance as time growing of thiourea doped TiO_2

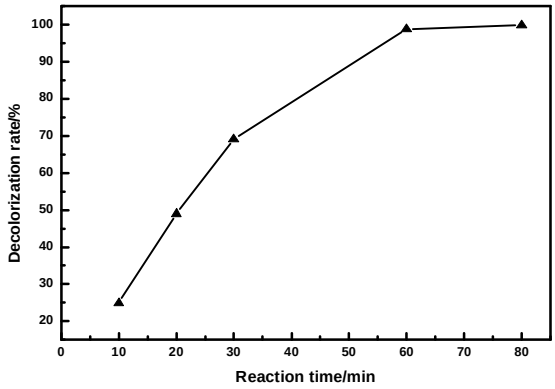

Fig. 4 Photocatalytic performance as time growing of 0.5wt%La^{3+} doped TiO_2

As shown in Fig. 3, the degradation rate is growing as the reaction time growing. When the reaction time was 50min, the degration rate was 94.74%. Although the degration rate can be higher than 99%, Addition amount is still very high.

La^{3+} doped TiO2

Rare earth metal is a very good additive to improve photocatalytic performance. Add La^{3+} to the sol B. After did many experiments, the optimum addition amount 0.5% was chosen. The degradation rate of the methylene blue under UV light have been studied. The result was shown in Fig. 4.

As shown in Fig. 4, the degradation rate is growing as the reaction time growing. When the reaction time was 60min, the degration rate was 98.78%. Compare to Fe^{3+} doping TiO_2, La^{3+} doping TiO_2 has a higher photocatalytic performance in a short time. Compare to Thiourea doping TiO_2, doping amount is so far below and photocatalytic performance is as high as it. As these reasons, La^{3+} doped TiO_2 is a better photocatalyst than Fe^{3+} doped TiO_2 or Thiourea doped TiO_2.

The absorption intensity of undoped TiO_2 and 0.5wt% La^{3+} doped TiO_2 were examined with ultraviolet–visible (UV–vis) in the wavelength range of 200–800nm. The representative results are shown in Fig. 5. It reveals that absorption intensity of 0.5wt% La^{3+} doped TiO_2 have a high absorption in UV region have a high absorption in the visible region.

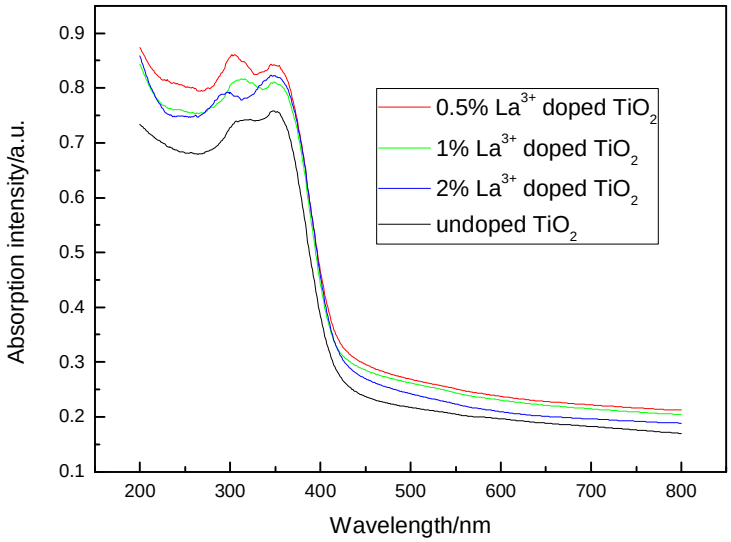

Fig. 5 Absorption intensity of undoped and La^{3+} doped TiO2

The TEM images of undoped TiO_2 and 0.5wt% La^{3+} doped TiO_2 are presented in Fig 6. As shown in Fig. 6, the particle size of undoped TiO_2 ranging between 15-25nm while the particle size of 0.5wt% La^{3+} doped TiO_2 ranging 8-12nm.Compare to undoped TiO_2, 0.5wt% La^{3+} doped TiO_2 has

fine uniform particles with a narrow size distribution and less aggregate. All these phenomenons indicated that 0.5wt% La^{3+} doped TiO_2 may have a better photocatalytic performance.

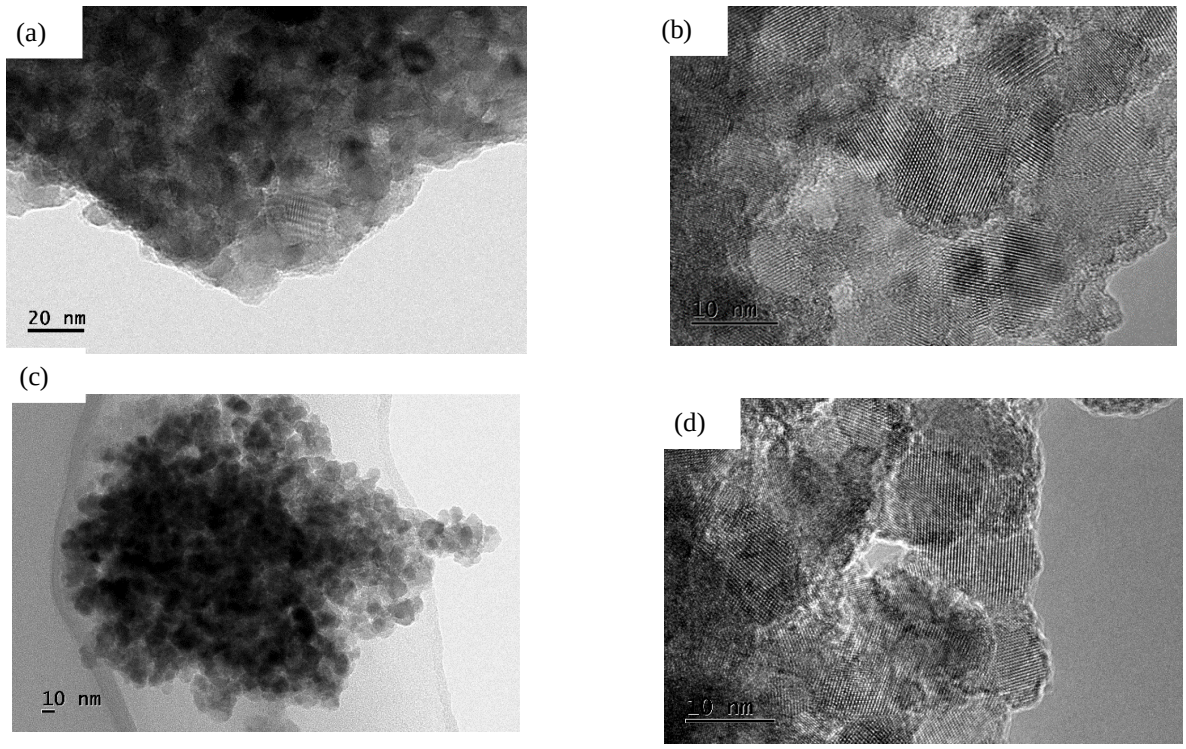

Fig.6 TEM images of undoped TiO_2 and 0.5wt% La^{3+} doped TiO_2
(a), (b) undoped TiO_2, (c), (d) 0.5wt% La^{3+} doped TiO_2

Conclusions

Through photocatalytic degradation of methylene blue solution, photocatalytic activities of the three materials after treatment and the influencing factors were compared. The degradation rate of methylene blue by using La^{3+} doped TiO_2 or thiourea doped TiO_2 is higher than Fe^{3+} doped TiO_2. Compared with the 45% thiourea in optimum condition, 0.5% La^{3+} addition have the same effect. The absorption intensity and particle size of undoped TiO_2 and 0.5% La^{3+} doped TiO_2 were investigated. The 0.5% La^{3+} doped TiO_2 have a high absorption in the visible region, UV region and have fine uniform particles with a narrow size distribution and less aggregate.

Acknowledgements

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