The Microwave Synthesis and Photocatalytic Activity of Sb^{3+}-doped TiO_2 Nanocomposite

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Abstract. Stibium doped titanium dioxide nanocomposite was prepared with stibium(Ⅲ) chloride, titanium sulfate as raw materials and Sodium dodecyl sulfate as surfactant under microwave irradiation. Then the X-ray diffractometer (XRD) and the scanning electron microscopy (SEM) were used to observe the antimony-doped TiO_2 nanocrystalline composite. The results show that the as-prepared nanocomposite of inventory molar ratio of 2% calcined at 500 ℃ for 2 h is anatase, the morphology is irregular sheet structure composed of many particles. We studied the photocatalytic activity of the as-prepared samples by using degradation of methyl orange. The result indicates that the as-prepared Sb^{3+}-doped TiO_2 nanocomposite is a good photocatalyst. The effects of photocatalytic activity of the composite with different ratios of qualities of inventory molar ratio,calcined at different temperature, different amount of hydrogen peroxide, different amount of nanocomposite, and the acidity of the solution were investigated. Also, different concentration of methyl orange as model affects it. When the catalyst was 1.0 g/L, pH value was 2.5, C(H_2O_2) was 3 mL/L, the degradation rate of sample for methyl orange of 20 mg/L reached 99.27% in 40 min.

Introduction

Because of its good chemical stability, wear resistance, non-toxic, low cost, strong oxidizing power and direct usage of solar energy, etc, Titanium dioxide becomes the world's most popular photocatalysts material. It has wide application prospect in photochemical synthesis, photocatalysis oxidation environment pollutants and photoelectric conversion etc [1].

However, there still exist some issues as follows: low quantum efficiency, low solar energy utilization, short life, weak photo-electron reduction capability, small amount of wastewater processed per unit of time and so on[2].

To overcome these shortcomings, it uses a variety of means such as surface photosensitizing dyes, semiconductor and metal ion doping coupling of nano- titanium dioxide modified. The method of ion doping which is easier, better in improving its quality and more propitious to the enhance the rate of photocatalysis among such methods, is paid more attention[3].

Metal ion doping makes dopant ions into the titanium dioxide lattice structure internally in physical or chemical method to achieve the purpose of introducing a new charge, changing the type or the formation of lattice defects, affecting the hole and the movement of electrons photo generated conditions, distribution or change the band structure of titanium dioxide, and resulting titanium dioxide changed in the photo catalytic activity. Reasonable titanium dioxide doped metal ions can make absorption wavelength red shift light absorption capacity increase, titanium dioxide surface absorption of the target reactants increase, the electron and hole recombination rate reduce, thereby improving the photocatalytic properties of titanium dioxide[4-10].

This paper was prepared by the direct feeding microwave antimony-doped nano-titania composite synthesis and usage of methyl orange solution, using visible light to examine its catalytic degradation of its photocatalytic activity. The results show that under the constant temperature heat of 500 °C, the concentration of methyl orange is 20 mg/L, the molar ratio of doping Sb^{3+}/TiO_2

composites is 2 %, the amount of catalyst is 1.0 g/L, the pH of the solution is 2.5, the dosage of H_2O_2 is 3 mL/L, the photocatalytic performance is the best.

Experimental Sections

Instruments and Reagents

Microwave oven with 650W (Sanle general electric corp. Nanjing, China) with refluxing system was used. Powder X-ray diffraction (XRD) was used to characterize the sample. Data were collected on a Shimadzu XRD-6100 X-ray diffractometer (Cu Kα radiation, λ=0.15418 nm). The morphology and size were determined by TEM. The TEM images were recorded on a Quanta 200 FEG field emission scanning electron microscope. Lambda10 UV-vis spectrometer (Perkin-Elme Corp, USA) was used for monitoring the absorption spectra of photo-degradation of methyl orange. Ultraviolet-visible diffuse reflectance spectrum was carried out on a UV-2600 UV - visible spectrophotometer.

All the reagents used were of analytical purity. Doubly distilled water was used throughout the experiments.

Direct Feeding Microwave Synthesis of Antimony-doped Nanosized Titanium Dioxide

2.28 g of $SbCl_3$ was dissolved with 1 mol/L dilute hydrochloric acid, transferred to a 200 mL volumetric flask, then washed with dilute hydrochloric acid and dilutes to mark. At this point the concentration of the stock solution $SbCl_3$ is 0.05mol/L. 1.0 g of sodium dodecyl sulfate (SDS), 2.4 g Ti $(SO_4)_2$ and a certain amount of $SbCl_3$ were prepared by adding in 100 mL of Secondary distilled water, dissolving under ultrasonic dispersion. Then the solution was put into 250 mL round bottom flask with 5.0 g urea was added into it, refluxing for 20 min with 40 W of microwave irradiation, cooled to room temperature naturally. The precipitate was finally collected by centrifugation, washed 3 times with distilled water, dehydrated 1 times with acetone and then dried at 60 °C for 4 h. Grinding, heat treatment muffle furnace thermostat 2 h. To get a white powdery solid collected which was used for photo catalytic degradation experiment.

The Photocatalytic Experiments of Composite

A certain amount of antimony-doped TiO_2 was added to 100 mL 20 mg/L methyl orange solution and a certain amount of hydrogen peroxide, and with dilute hydrochloric certain pH, dissolved by ultrasonic dispersion, placed it under visible light photocatalytic degradation experiments.

Measurement of degradation rate: every 10 min sampling, centrifuged supernatant by UV - visible absorption spectra measured absorbance and observe the color of the solution changes. Until the color completely faded or the absorbance of the solution does not changes. Finally, according to the change in absorbance of the solution to calculate the degradation rate, calculated as follows: $Dt\%=(A_0-A_t)/A_0\times100\%$

Among: When Dt is methyl orange solution by visible light irradiation time t after the degradation rate, A_0 is the catalyst under visible light irradiation without catalyst methyl orange solution absorbance, through t for the catalyst after visible light irradiation, the absorbance of methyl orange solution.

Results and Discussion

Fig. 1 is the XRD patterns of as-prepared samples of 1%,2%, 3% Sb^{3+} doped TiO_2 sintered at 500℃ for 2 h,respectively. The XRD patterns showed demonstrate that's of anatase-type TiO_2. The Sb^{3+} doping amount almost has no effect on the TiO_2 crystal structure.

The SEM graph (Fig.2) shows the morphology of the as-prepared samples is irregular sheet structure composed of many fine particles. It seems obvious massing which is owning to tremendous surface energy of nanoparticles.

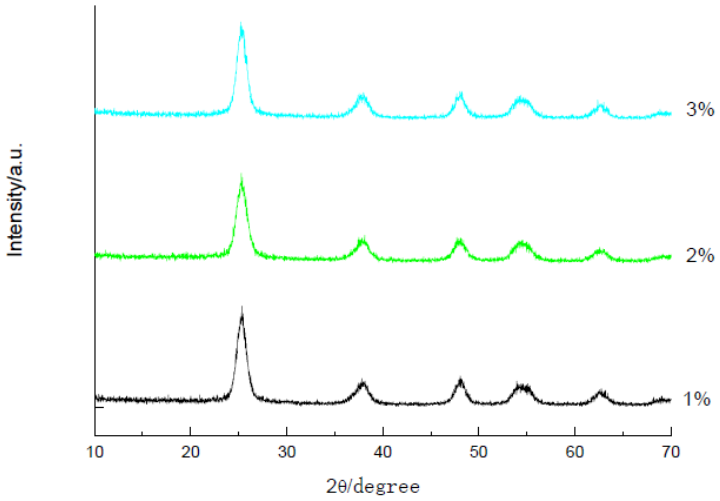

Fig.1 X-ray diffraction pattern of as-prepared sample

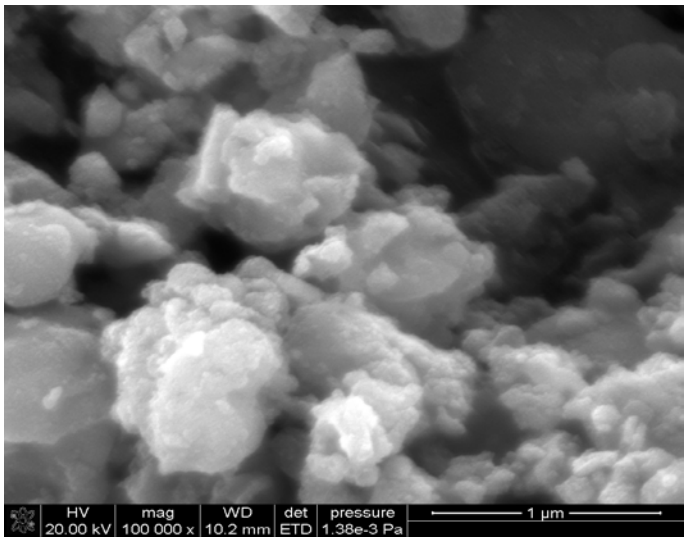

Fig.2 SEM image of as-prepared sample

Fig. 3 is the UV-visible diffuse reflectance spectrum of as-prepared sample. It can be seen that antimony-doped TiO_2 nanocomposites prepared at a wavelength of 200 ~ 330 nm UV region, the reflectance of light is only 4.5 % about complexes described in this region of strong absorption of light, 350 nm reflectance of light at 10 %, when the wavelength is 400 nm, the reflection rate is still 60 %, when 450 nm, the reflectance of 78 %, with growth wavelength light reflectance becomes large complex, 750 nm at 90 %, although weak absorption of light, but still absorb. Literature that, the diffuse reflectance of UV-TiO_2, only at wavelengths less than about 400 nm, was no absorption in the visible region. Comparison shows that antimony-doped TiO_2 nanocomposite optical absorption was significantly better than the TiO_2.

Fig. 4 shows that the degradation of methyl orange solution visible absorption spectrum of Sb^{3+}-doped TiO_2 nanocomposite photocatalyst. The fig. 4 shows that with the photocatalytic degradation proceeds, the absorbance of the solution decreases. After 30 min illumination, the absorption has been very weak in the visible range, after 40 min in light, the degradation of methyl orange has been relatively thorough. When the concentration of methyl orange is 20 mg/L, the solution is completely degraded by antimony-doped titanium dioxide in a short period of time, indicating that the photocatalytic property of the prepared catalysts is good.

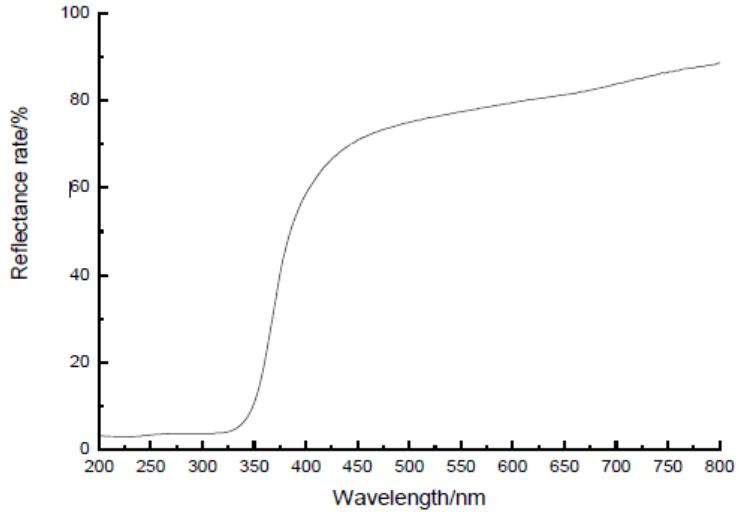

Fig.3 Ultraviolet-visible diffuse reflectance spectrum of as-prepared sample

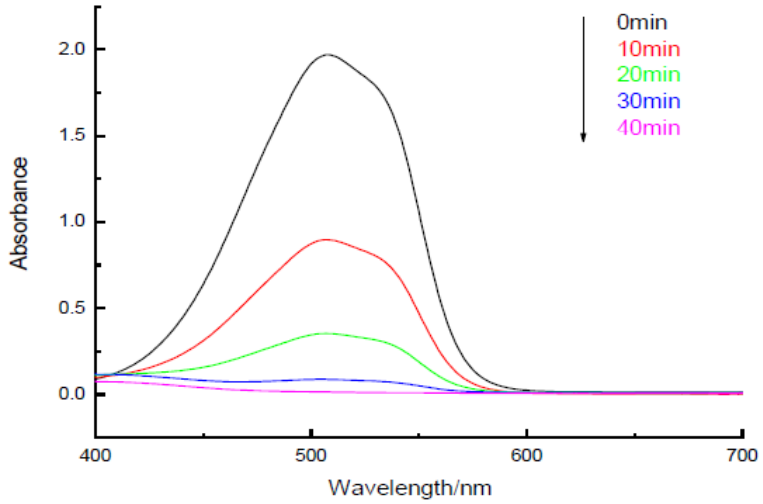

Fig.4 Visible absorption spectra of photo-degradation of methyl orange

Note: 1.0 g/L of 2% doped nanocomposite, C(H_2O_2) is 5 mL/L, while pH is 2.5 and 20 mg/L of methyl orange.

We also studied the influence factors of the photocatalytic performance, such as heat treatment temperature of the catalyst, the dosage of the catalyst, the pH value of the solution, the dosage of the H_2O_2. The results showed the best photocatalytic effect, when the heat treatment temperature is 500 °C, the dosage of the H_2O_2 is 3 mL/L, the pH value of the solution is 2.5, the dosage of the catalyst is 1.0 g/L.

Sb belongs to p-block elements. Sb^{3+} radius is 76 pm. Ti^{4+} radius is 68 pm. After the mixing of Sb^{3+} and Ti^{4+}, the direct hydrolysis products may cause antimony oxide more evenly distributed in the titanium dioxide crystals, then Sb^{3+} will destroy TiO_2 of the original lattice, and it will distort the lattice, then the distortion will cause strain. The strain energy will be compensated, the surface lattice oxygen atoms TiO_2 lattice easily escapes capture and plays a role in the hole, thereby reducing electron a whole pair recombination probability, and enhancing the catalytic efficiency of TiO_2 photocatalyst[12].

The heat treatment may stabilize synthetic crystalline product. The heat treatment temperature too high or too low is not good for photocatalytic performance. This may due to the heat treatment temperature of the crystalline product, the product temperature is too low, not regular polygonal block, which causes the temperature of the nanoparticles further sintering or crystal growth, the

particle size increases, leading to a serious decline in the specific surface area Photocatalyst, resulting in the efficiency of the photocatalytic decreases[13].

The amount of catalyst has different impact on the photocatalytic degradation of organic pollutants. When the amount of the catalyst solution is too little, the photon energy of the light source cannot be fully utilized, the reaction rate is slower, when the amount of the catalyst is excessive, the scattering catalyst light affects the transmittance of the solution, so that the reaction rate is reduced.

H_2O_2 plays a role in initiating the reaction of the photocatalytic degradation process. As the electron acceptor molecule has two hydrogen atoms linked to the oxygen atom, O_2 is greater than the positive charge, the excitation light is easier to cauterize the light generated electrons, electrons and holes but also inhibit the simple compound prolong the life of the hole. H_2O_2 can be generated in the solution after the seizure of electronic active species • OH, • OH with strong oxidizing ability, its offensive dye carbocation form hydroxylated products, after a series of redox generate H_2O and other inorganic small molecules, so as to achieve the purpose of degradation.

TiO_2 surface charge is strongly influenced by pH. It is amphoteric compounds, dicarboxylic acid in aqueous solution to form hydrated and isoelectric point of pH is typically 3.5-6.4. At lower pH values, TiO_2 surface mainly exited as $TiOH^{2+}$, so that the TiO_2 surface potential is positive, it is a good photo-generated electrons migrate to the surface of TiO_2, thereby inhibiting the photo-generated carriers compound. Addition of methyl orange that is Dimethylaminochlorophosphonazo benzene sulfonate in acidic medium sodium ions dissociate itself with a negative charge, while the TiO_2 surface under acidic conditions with a positive charge, easily visible at this time of methyl orange adsorbed on the surface, there must be conducive to the degradation of methyl orange . When the pH value is lowered, a study found that TiO_2 heavier agglomeration, thereby reducing the adsorption of dyes and photons, while low pH can cause excess H^+, it will attack such azo bond (-N = N-) so that the electron density around the azo bond reduced, thereby reducing the • OH on the-N = N-electrophilic attack capability, causing the degradation rate.

Conclusion

The method of direct feeding microwave synthesis Sb^{3+} doped nano-TiO_2 composite is simple.

The amount of Sb^{3+} doping, heat treatment temperature, the amount of catalyst, the dosage of H_2O_2, the acidity and other factors affecting the photocatalytic properties still exist.

The results shows that the concentration of methyl orange is 20 mg/L, the heat treatment is 500 °C, the nanocomposite doping amount is 2 % , hydrogen peroxide solution is in an amount of 3 mL/L, pH is 2.5, the amount of catalyst is 1.0 g/L when visible photocatalytic performs best.

Acknowledgments

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