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Original Research Paper

Synthesis and catalytic performance of antimony trioxide nanoparticles by ultrasonic-assisted solid-liquid reaction ball milling

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ABSTRACT

In this study, the cubic antimony trioxide (Sb_2O_3) nanoparticles were successfully synthesized by ultrasonic-assisted solid-liquid reaction ball milling technique. And the synthetic process, using Sb powder as raw material, was conducted with an atmosphere of acetic acid aqueous solution at low temperature (⩽100 °C). Some controlled trials, including without the assistance of ultrasonic wave, different reaction solutions and diverse ultrasonic frequencies, were performed. The products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that the Sb_2O_3 nanoparticles with uniform and ultrafine particle size were obtained within short reaction time under the coaction of both ultrasonic wave and ball milling. Furthermore, the catalytic capacity of the Sb_2O_3 nanoparticles for decomposition of H_2O_2 was measured during the oxidative decomposition of methylene blue (MB). The test exhibited rapid and efficient color removal in the degradation of MB.

1. Introduction

Antimony trioxide (Sb_2O_3) is an important metal oxides with wide applications as flame retardant synergist [1], sensing materials [2], effective catalyst [3] and optical materials [4]. Because of its high surface-to-volume ratio, Sb_2O_3 nanoparticles possess more excellent properties than bulk materials [5,6]. Therefore, extensive efforts have been devoted to prepare the Sb_2O_3 nanoparticles with diverse morphology, structure and properties [7,8]. To date, they have been successfully synthesized by many various methods, including solution phase reduction [6], microemulsion [9], hydrothermal [10], biosynthesis [11], thermal oxidation [12], hybrid induction and laser heating [13], etc.

However, there are some unsatisfactory issues and limitations for these methods, such as high reaction temperature and pressure, long processing time, complex techniques, and expensive cost [14]. Ultrasonic-assisted solid-liquid reaction ball milling, which was developed by our group, have successfully prepared several kinds of ferrite [15,16] and metal oxide nanoparticals [17,18] without subsequent calcination. This approach possesses some merits on synthesis of inorganic materials, such as accelerating reaction rate, simple chemical reagent, easily controlled conditions and low manufacture cost. Herein, the Sb_2O_3 nanoparticles were synthesized using Sb powder as staring material by ultrasonic-assisted solid-liquid reaction ball milling at low temperature (⩽100 °C).

In addition, Sb_2O_3 possesses superior catalytic performance in poly(ethylene terephthalate) (PET) industry, because of its high catalytic activity for polycondensation [3]. Nevertheless, there have been few studies to investigate its catalytic performance for oxidative degradation of organic dye pollutants. In this investigation, the catalytic oxidation activity of Sb_2O_3 nanoparticles was tested during the degradation of methylene blue (MB) dye with H_2O_2.

2. Materials and methods

2.1. Synthesis of Sb_2O_3 nanoparticles

The chemicals used in this synthesis, including antimony (Sb) powder and acetic acid, were of analytical grade. The Sb_2O_3 nanoparticles were synthesized in an ultrasonic-assisted solid-liquid reaction ball milling device. The diagram of the device is described detailly in Ref. [18]. The procedures of the synthesis were as the following: The Sb powder was milled in this apparatus with an atmosphere of acetic acid aqueous solution (1500 mL). The mass ratio of 304 stainless steel milling balls (Φ = 2 mm) to Sb powder was 100:1, and the total weight of balls was 2 kg. The rotation speed of stirring rod was constant at 250 rpm. The ultrasonic frequency was 20 kHz, and the power of ultrasonic generator was

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66 W. The samples were collected at specific times by centrifugation, and washed with deionized water. Finally, the samples were dried at 60 °C for 24 h. Moreover, some controlled trials, whose experimental parameters were changed as shown in Table 1, were performed.

The phase constitutes of the as-prepared samples were examined by using a D-5000 Siemens X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.154056 nm). The morphology and size of the nanoparticles were analyzed by transmission electron microscopy (TEM, JEM-2100F).

2.2. Catalytic degradation

The catalytic performance of as-prepared Sb_2O_3 was tested in a round-bottom flask, which contained 20 mg of the prepared powders, 100 mL of 50 mg/L MB dye solution and 20 mL of 30 wt% H_2O_2 solution. And the flask was placed in a magnetic stirrer with a constant water-bath temperature (70 °C) and stirring speed (800 rpm). Subsequently, 5 mL of the liquid mixture was extracted at given time intervals, removed deposition by centrifugation and diluted with deionized water to 25 mL. Then the MB dye concentration of the solutions was determined by UV–vis spectrophotometer (UV-6000PC) at 664 nm.

During the test of catalytic degradation, the fluorescence intensities of the solutions was measured to determine the relative content of hydroxyl radical (·OH). The measurement was carried out under dark by adding buffer reagent (0.012 mol NaOH and 0.012 mol KH_2PO_4) and catcher reagent (0.01 mol terephthalic acid). The fluorescence intensities of the solutions were tested at given times by fluorescence spectrophotometer (Hitachi, Model F2500).

3. Experimental results

Fig. 1 depicts the XRD patterns of the products synthetized by acetic acid aqueous ball milling with ultrasonic-assisted technique for different durations, using Sb powder as raw material, as well as includes the patterns of the samples from controlled trials (see Table 1). In the case of 20 kHz ultrasonic assistance, the diffraction peak intensities of Sb reduce gradually till these peaks eventually disappear after 9 h, as shown in Fig. 1a. And the diffraction peaks of final products correspond to (222), (400), (331), (511), (440), (622), (444), (551), (731), (800), (733), (662), (840) planes, which match well with the crystal structure of cubic Sb_2O_3 [9]. What's more, there are no other phases found in the patterns of final products.

Moreover, the conditions with 40 kHz ultrasonic assistance are shown in Fig. 1b. Similar to the case of Fig. 1a, the diffraction intensities of raw materials decrease and that of cubic Sb_2O_3 increase with the ball milling time increasing. But completely pure products are obtained, even after 20 h ball milling. From this comparison, the ultrasonic frequency plays a significant role in accelerating reaction rate.

Table 1
Parameters of controlled trials.

Experiment number	Ultrasonic wave	Ultrasonic frequency (kHz)	Reaction solution
1	Yes	20	5 mol/L acetic acid solution
2	No	20	5 mol/L acetic acid solution
3	Yes	40	5 mol/L acetic acid solution
4	Yes	20	Deionized water
5	Yes	20	1 mol/L diluted hydrochloric acid solution

Fig. 1c shows the XRD patterns of the samples prepared without ultrasonic wave or by deionized water as reaction liquid after a long time milling. Though the content of Sb_2O_3 increases with the extension of ball-milling time, pure products couldn't be obtained after 40 h in the case without ultrasonic wave. In spite of 40 h milling, only a small fraction of Sb powder was transformed into cubic Sb_2O_3 in deionized water. By comparing the patterns of Fig. 1c and a, it is clear that ultrasonic wave and acetic acid play important roles in the synthesis process of Sb_2O_3 nanoparticles.

Fig. 1b shows the XRD pattern of the product using diluted hydrochloric acid solution (1 mol/L) as reaction medium after 10 h ball milling. From the pattern, what is certain is that there is no Sb_2O_3 found in the product.

TEM image and selected area electrons diffraction (SAED) pattern of the Sb_2O_3 nanoparticles prepared by ultrasound-assisted 5 mol/L acetic acid aqueous ball milling, using Sb powder as raw material, are shown in Fig. 2. From the TEM image (Fig. 2a and c), the average size of Sb_2O_3 nanoparticles prepared at 20 kHz is about 20 nm with a narrow distribution of size, but the Sb_2O_3 nanoparticles prepared at 40 kHz is much larger than at 20 kHz. The SAED pattern exhibited that the as-prepared Sb_2O_3 nanoparticles have the same cubic crystal structure as the XRD results.

The catalytic properties of Sb_2O_3 nanoparticles prepared in experiment 1 were measured by oxidative decomposition of MB with the assistance of H_2O_2. As shown in Fig. 3a, the UV–vis spectra of the MB dye solution were measured at specified time intervals. The intensity of absorption peaks of spectra decreases with the reaction time increases, and the characteristic peaks of MB at 614 and 664 nm faded away within 60 min. Fig. 3b reveals the curves of MB decoloration degree versus reaction for different experimental conditions. The results show that the degree of MB decoloration have almost no change under the condition of bare Sb_2O_3 nanoparticles and MB, which indicate that Sb_2O_3 nanoparticles can hardly absorb MB. In the existence of only H_2O_2 and MB, the degree of MB decoloration is approximately 27%. And in the coexistence of Sb_2O_3, H_2O_2 and MB, the decoloration degree attains 97%, showing an efficient effect of the combined action of Sb_2O_3 and H_2O_2 on the oxidative decomposition of MB.

4. Analysis and discussion

During the process of Sb_2O_3 nanoparticles preparation, the coaction of both ball milling and ultrasonic wave is the foundation of rapid and successful synthesis. The mechanical force of ball milling could generate a large number of defects and new active surfaces in the Sb particles. As a consequence, the chemical activity of the raw material is improved, and it could greatly promote the chemical reaction [19]. In addition, the ultrasonic wave has chemical and physical effects in a liquid medium to further accelerate the reaction rate as can be seen in Fig. 1, mainly due to the generation of strong physical forces and highly reactive radicals by acoustic cavitation [20]. In addition, the ultrasonic wave could prevent the growth and aggregation of fine particles by influencing crystal nucleus formation and growth [21,22]. As shown in Fig. 1b, the cavitation effect of the ultrasonic wave has a intimate relativity with its frequency. The lower ultrasonic frequency is, the greater mean cavitation bubble size and the stronger cavitation effect [23,24]. Under the action of the stronger cavitation, the Sb powder fining and the chemical bonds rupturing are easier. Therefore, the reaction speed is faster and the mean size of particles is much smaller in the 20 kHz condition.

The reaction solution is also an important parameter for reaction process of Sb_2O_3 nanoparticles preparation. The boiling point of acetic acid (117.9 °C) is higher than water (100 °C), as a result

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