Sonochemical fabrication of Ag\textsubscript{2}CO\textsubscript{3} nanomaterial and influencing factors on photocatalytic properties

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Abstract. Visible-light-active Ag\textsubscript{2}CO\textsubscript{3} nanoparticles were synthesized by a simple sonochemical method (ambient temperature for only 1 h). The effects of ultrasound pulse mode, ultrasound time and pH value on the photodegradation properties of Ag\textsubscript{2}CO\textsubscript{3} were investigated. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDS), UV-vis diffuse reflectance spectroscopy (DRS) and nitrogen adsorption–desorption techniques. The photocatalytic activity was evaluated by degrading methylene blue (MB) under visible light irradiation (λ=420nm). According to obtained results, it was found that MB degradation (about 99.4% after 20 min of irradiation) was higher compare to conventional stirring method, which might be due to the higher specific surface areas and active sites. The method described here can be used to improve the efficiency of visible-light sources and develop an ecologically friendly, practical wastewater treatment for pollutants.

1. Introduction

At present, the environmental pollution and energy shortage become more and more serious [1]. Semiconductor photocatalysts have attracted great attention worldwide by high photocatalytic activity and strong stability under visible light [2]. Semiconductor photocatalysts have been regarded as a promising candidate in solar energy conversion and water pollutant treatment [3-7]. As a typical photocatalyst, Ag-based semiconductor photocatalysts have narrow band gap, which can absorb visible light and usually show good catalytic activity [8-9]. In recent years, Ag-based photocatalysts such as AgX (X=Cl, Br, I) [10-11], Ag\textsubscript{3}PO\textsubscript{4} [12], Ag\textsubscript{2}W\textsubscript{4}O\textsubscript{16} [13], Ag\textsubscript{2}O [14], β-AgAl\textsubscript{1-x}Ga\textsubscript{x}O\textsubscript{2} [15], Ag@Ag\textsubscript{2}SO\textsubscript{4} [16] etc. have been demonstrated as an efficient photocatalytic materials under visible light irradiation for the photodegradation of organic pollutants. Dong [9] successfully prepared Ag\textsubscript{2}CO\textsubscript{3} semiconductor photocatalyst by a simple ion-exchange method based on a strategy incorporating of p-block C element into a narrow bandgap Ag\textsubscript{2}O. Liu [17] and co-workers reported the microwave hydrothermal synthesis of Ag\textsubscript{2}CrO\textsubscript{4} photocatalyst for fast degradation of PCP-Na under visible light irradiation. Lin [18] synthesized PVB/CdS composite materials via a microwave-assisted electrospinning process. However, in the process of photocatalysis, the above methods offered some defects such as low yield, undesired morphology and complex procedure.

In contrast, the sonochemical processing as a one-step process offers very important features such as low temperature processing and low cost [19]. Sonochemistry uses the ultrasonic irradiation to induce the formation of particles with smaller size and higher surface area in contrast to other
synthesis method. Sonochemistry has been employed extensively for the synthesis of nanostructured materials due to its rapid reaction rate, controllable reaction conditions, simplicity and safety. Moreover, powder particles synthesized through this method normally have uniform shape with narrow size distribution. Owing to its advantages, sonochemistry has experienced a large promotion in various fields concerning the production of novel nanostructured materials with improved properties in the recent years. The tailored preparation and improvement of chemical and physical properties of the synthesized materials are now the main objects of the recent researches [20].

However, to the best of our knowledge, reports on the preparation of visible light-driven Ag₂CO₃ photocatalysts by sonochemical route remain rare. Herein, Ag₂CO₃ was successfully synthesized via a simple ultrasonic method. In particular, we systematically investigated the influencing factors of Ag₂CO₃ and proved that ultrasonic method can offer higher surface areas and photocatalytic activity. This work may provide a more green and efficient strategy for exploring the excellent Ag-based composite photocatalysts.

2. Experimental

2.1. Materials
Sodium carbonate (Na₂CO₃), silver nitrate (AgNO₃), sodium hydroxide (NaOH), nitric acid (HNO₃), all the chemicals used in this study were analytical grade and purchased from Tianjin Yong Sheng Chemical Factory of China without further purification. Distilled water was used in all experiments.

2.2. Synthesis of Ag₂CO₃
The Ag₂CO₃ samples were prepared by a typically simple ion-exchange method under the effect of ultrasound at room temperature. In a typical procedure, 20 mL AgNO₃ solution (0.36 M) was added to a 100 mL beaker, 20 mL Na₂CO₃ solution (0.18 M) which pH was adjusted with HNO₃ and NaOH was added dropwise to the above suspension in sequence under ultrasonic irradiation for 60 min. The ultrasonic irradiation was performed with a high intensity ultrasonic probe (Xin zhi Co, China, JY92-2D, 10 mm diameter, Ti-horn, 20 kHz, 60 W cm⁻²) immersed in the reaction system. The obtained precipitate was collected by centrifugation, washed several times with distilled water and ethanol, and dried at 50°C for 12 h.

2.3. Characterization
The phase of the Ag₂CO₃ samples was characterized by power X-ray diffractometer (Shimadzu XRD-6000) equipped with a Cu-Kα radiation at a scanning rate of 5°/min in the 20 range of 10~80°. The morphological characteristics and microstructure of the nanoparticles were observed using scanning electron microscopy (SEM; Hitachi S-4100, Tokyo, Japan). The chemical composition of the samples was determined by EDS. The UV–vis diffuse reflectance spectra (DRS) were obtained on UV–vis spectrophotometer (U-3010, Hitachi, Japan) by using BaSO₄ as the matrix. Nitrogen adsorption–desorption isotherms were collected on an Autosorb-iQ sorption analyzer and analyzed using the Brunauer-Emmett-Teller (BET) equation and Barret-Joyner-Halenda (BJH) model.

2.4. Photocatalytic activity measurement
In a typical measurement, 0.1 g samples were added into 100 ml of MB (20 mg/L). Prior to irradiation, the suspensions were magnetically stirred for 0.5h in the dark. This was to ensure that the dye could reach the absorption–desorption equilibrium on the photocatalyst surface. Subsequently, the suspension was continuously magnetically stirred under visible light irradiation supplied by a 280 W Xe lamp (Color temperature 6000K, PHILIPS) with a 420 nm cut-off filter. The degradation of MB was monitored by UV-vis spectrophotometer (PG, TU-1901) every 10 min. Before measurement, the photocatalysts were removed from the photocatalytic reaction system by centrifugation.
3. Results and discussion

3.1. Effects of ultrasonic pulse mode and reaction time
The degradation efficiency of MB by photocatalysts prepared at different ultrasonic pulse mode was illustrated in Figure 1a. The photocatalytic activity of Ag$_2$CO$_3$ changed with different pulse mode [21]. The photocatalysts prepared at pulse mode of “1 s off / 9 s on” displayed the highest degradation efficiency. The results show that degradation efficiency increases with increasing ultrasound power. The pulse mode “1 s off / 9 s on” was selected as the optimal condition for the following section. Moreover, the degradation efficiency of MB by photocatalysts prepared at different ultrasonic time was illustrated in Figure 1b. The photocatalytic activity of Ag$_2$CO$_3$ increased with the increase of ultrasonic time. Therefore, the ultrasonic time for 60 min was also selected as the optimal condition for the following section. The increase of photocatalytic efficiency might be due to the advantages of sonochemical method for smaller size and higher surface areas.

Figure 1. (a) Effect of ultrasonic pulse mode (pH: 11, ultrasonic time: 60 min); (b) Effect of ultrasonic time (pH: 11, ultrasonic pulse mode: 1 s off / 9 s on) on the degradation efficiency of MB

3.2. The effect of pH

The degradation efficiency and XRD patterns of Ag$_2$CO$_3$ prepared at different pH were showed in Figure 2. Figure 2(b) presents XRD patterns of the as-prepared Ag$_2$CO$_3$ by ultrasonic method. All the diffraction peaks of Ag$_2$CO$_3$ could be well indexed with monoclinic Ag$_2$CO$_3$ (JCPDS No. 70-2184),

Figure 2 The photocatalytic degradation of MB (a) and XRD patterns (b) of Ag$_2$CO$_3$ prepared at different pH (ultrasonic pulse mode: 1 s off / 9 s on, ultrasonic time: 60 min)
and no other impurities were found, which indicates that pH does not influence the purity of samples. However, the photocatalysts prepared at pH 9.0 displayed the highest degradation efficiency (Figure 2(a)). This suggests that pH will influence the degradation efficiency of Ag₂CO₃. The pH of the raw material solution can neither be too high nor too low, because the acidic conditions lead to low yield of samples and alkaline conditions can lead to poor degradation ability. Thus, pH played an important role in the formation and photocatalytic degradation of pure Ag₂CO₃. And the Ag₂CO₃ prepared at pH 9.0 was selected as the optimum catalyst for the following sections. According to the above experimental results, the optimum conditions of preparation of Ag₂CO₃ samples are pulse mode for 1 s off / 9 s on, pH for 9.0 and ultrasonic time for 60 min.

3.3. The effect of methods

![SEM images of Ag₂CO₃ obtained using different methods](image)

**Figure 3.** SEM images of Ag₂CO₃ obtained using different methods: ultrasonic method (a), stirring method (b); Size distribution histogram of Ag₂CO₃ nanoparticles over ultrasonic (c) and stirring (d) methods calculated from the corresponding SEM image; N₂ adsorption and desorption isotherms of the as-prepared Ag₂CO₃ (e); EDS spectrum of Ag₂CO₃ obtained with ultrasonic method (f)
Figure 3(a) and 3(b) show the SEM images of Ag$_2$CO$_3$ synthesized through ultrasonic and stirring method. The uniform and small size of Ag$_2$CO$_3$ nanomaterials can be clearly observed (Figure 3(a) and 3(c)). Figure 3(f) shows the EDS spectrum of the Ag$_2$CO$_3$ sample that contains C, O and Ag element, which indicates that the preparation process does not bring any impurities. To consider the effect of ultrasound, comparative experiments such as conventional stirring instead of the ultrasonic treatment were performed, as shown in Figure 3(b). Compared with Ag$_2$CO$_3$ formed by ultrasonic treatment (Figure 3(a)), the Ag$_2$CO$_3$ formed by conventional stirring did not show uniform structure, the main form of Ag$_2$CO$_3$ consist of irregular nanorods 1 2.5 μm (Figure 3(b) and (d)). N$_2$ adsorption and desorption isotherms and the Brunauer-Emmett-Teller (BET) specific surface area of the samples was measured (Figure 3(e)). Specific surface area 5.265 m$^2$ g$^{-1}$ of Ag$_2$CO$_3$ was bigger than 2.166 m$^2$ g$^{-1}$ of stirring method. And the porous structure of Ag$_2$CO$_3$ prepared via ultrasonic method is illustrated. The above results indicate that a more uniform small size of Ag$_2$CO$_3$ nanostructures have been formed by the sonochemical route without the use of any surfactants or templates, which means that high-intensity ultrasonic irradiation is necessary for the shape-controlled synthesis [22].

Figure 4(a) and 4(b) show the absorption spectral changes of MB by different samples. After stirring for 30 min in dark, the adsorption capacities of ultrasonic method (19.5%) is higher than stirring method (10.4%), which might be due to the bigger specific surface areas. The large specific surface areas are useful for the better adsorption of organic compounds and also provide a greater number of reactive sites for the photocatalytic process, thereby enhancing the photocatalytic activity [23]. In addition, the samples formed by stirring method exhibits obvious photocatalytic activity with degradation rate of 59.4% after visible-light irradiation of 20 min (Figure 4(c)). Dong [9] reported that all of MB (100 mL 10 mg/L) was degraded after 30 min by 0.05 g samples prepared with stirring method. Figure 4(d) indicated that MB solution was degraded within 30 min under the same amount samples and solution, which means pH will strongly influence the photocatalytic performance. Song [24] reported that about 65% of MB (100 mL 20mg/L) was degraded in 60 min by 0.075 g samples prepared with stirring method. After changed the method to ultrasonic, the photocatalytic activity has been further improved. Specifically, the degradation efficiency is 99.4% (0.1g samples) after visible-light irradiation of 20 min (Figure 4(c)). These results confirmed the excellent photocatalytic activity of Ag$_2$CO$_3$ prepared through an ultrasonic-assisted route. The DRS of the samples prepared using different method are examined and the results are showed in Figure 4(e). The two samples showed its fundamental absorption edge around 470 nm [25]. However, the transition band-gaps of two samples estimated from inset of the curve edges are about 1.58 and 1.98 eV. The absorption range of the samples using ultrasonic method apparently increased in the visible light and did have obvious red shifts to the long wavelength, which may be due to the narrow band-gap (1.58 eV) that caused by preparation condition and method. The absorption intensity of the samples in the visible light region became more prominent, which was in accordance with the color change. All above results suggested that ultrasonic cavitation played a vital factor in formation of Ag$_2$CO$_3$. Ultrasonic cavitation could provide high temperature, pressure and cooling rate, which lead to the smaller size, larger specific surface area, more active sites exposing and porous structure formation [26]. The smaller size and larger specific surface area can offer better adsorption capacities that make pollutants degrade in time. More active sites provide high activity of photocatalysts and porous structure makes catalysts good stability. Figure 4(f) shows the XRD patterns of Ag$_2$CO$_3$ after reactions. The new peak with 20 values of 38.1 corresponding to (111) crystal plane of Ag (JCPDS 65-2871) is observed, which confirmed that Ag$_2$CO$_3$ prepared by stirring method is partially decomposed to Ag. However, the peak does not appear in samples that synthesized by ultrasonic method. The results indicate the better photocatalytic stability of Ag$_2$CO$_3$, which might be due to porous structure and reaction times of ultrasonic method for only 20 min and stirring method for 50 min.
Figure 4. The absorption spectral changes of MB by the samples using ultrasonic method (a) and conventional stirring method (b); The degradation of MB (c) by the samples; The degradation of MB (100 mL 10 mg/L) by the 0.05 g samples (d); The UV-vis DRS and the bandgap (inset) by the samples (e); The XRD patterns of Ag$_2$CO$_3$ after reactions (f).

4. Conclusion
In summary, Ag$_2$CO$_3$ was successfully prepared via an easy and convenient sonochemical method. The effects of influencing factors on photodegradation ability were investigated at the first time. The optimum conditions are 9.0 value of pH, 60min of total sonication time and “1 s off / 9 s on” of sonication pulse mode. When Ag$_2$CO$_3$ nanoparticles were used as photocatalyst, the MB degradation percentage was 99.4% after 20 min irradiation of visible light. The DRS results and XRD patterns of
Ag$_2$CO$_3$ after reactions indicated that the Ag$_2$CO$_3$ nanoparticles synthesized by these conditions have high activity and good stability.

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