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Preparation, characterization, and photocatalytic properties of silver carbonate

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ABSTRACT

Silver carbonate (Ag_2CO_3) short rods were prepared using a precipitation method. It was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflective spectra (DRS) and photocatalytic degradation of organic pollutants and destruction of *E. coli* measurements. The results of DRS suggested that the optical transition of Ag_2CO_3 was indirectly allowed, and its band gap was determined to be 2.08 eV. The prepared Ag_2CO_3 displayed a high activity towards degradation of phenol and MB under visible light. The total organic carbon (TOC) value decreased during the photocatalytic process, which suggests that phenol was truly photodegraded. The stability of Ag_2CO_3 was greatly improved when Na_2CO_3 was added into the photocatalytic system. In addition, Ag_2CO_3 displayed enhanced photocatalytic activities for the destruction of *E. coli* due to its photogenerated electron–hole pairs.

1. Introduction

Energy shortage and environmental pollution are two challenges to the sustainable development of modern human society. Since 1972, Fujishima and Honda reported TiO_2 as photocatalyst splitted water into oxygen and hydrogen [1], much admirable researches on the preparation of the environmentally friendly photocatalysts, especially visible light sensitive photocatalysts to efficiently utilize solar energy and indoor light, have been investigated [2–4]. Various new photocatalysts were developed, such as Ag@AgX (X = Cl, Br, or I) surface plasmon photocatalyst [5–7], $In_{(1-x)}Ni_xTaO_4$ [8], $Ga_xZn_{(1-x)}N_xO_{(1-x)}$ solid solutions [9,10], g–C_3N_4 [11] etc. The semiconductor with specific d10/d10s2 metal ions (Bi^{3+}, Ag^+, etc.) attracted special interest, as the valence bands of these photocatalysts consist of Bi 6s and Ag 4d orbitals hybridized with the O 2p orbitals, respectively, resulting in a higher valence band, and thus leading to a narrower band gap [12]. Bi_2WO_6 [13], $BiVO_4$ [14,15], $Bi_2O_2CO_3$ [16–18], $AgGaO_2$ [19], Ag_2ZnGeO_4 [20], and $AgSbO_3$ [21] etc. were reported to be good photocatalysts either in decomposing organic compounds or antibacterial activity under visible light. For silver-based photocatalysts, Ye and co-workers stated that the p-block elements are actually important ingredients for high photocatalytic activity. However, the previous works were focused on metallic elements in the p-block atoms [22]. Recently, they reported that Ag_3PO_4 nanoparticles displayed strong oxidation power, and the quantum yield of O_2 generation from water splitting marks nearly 90% under visible light [23]. This is the first example which incorporated nonmetallic p-block elements phosphorus into Ag_2O in the context of photocatalysis research.

C element also belongs to the p-block elements, and silver carbonate (Ag_2CO_3) is a common compound. Ag_2CO_3 can be formed when Ag_2O was exposed to CO_2 pressure [24]. Tseng et al. discovered the presence of Ag_2CO_3 during the electric spark discharge process through a reaction with atmospheric CO_2, and they found that Ag_2CO_3 is beneficial to the stability of colloidal silver [25]. Buckley et al. prepared silver carbonate nanoparticles stabilised over alumina nanoneedles, and found that they are promising antimicrobial agents against diverse bacterial strains [26]. Herein, Ag_2CO_3 short rods were prepared using a precipitation method. Its optical properties, photocatalytic degradation of organic pollutants and destruction of *E. coli* were also studied.

2. Experimental

2.1. Synthesis of Ag_2CO_3

All reagents used in our experiments are of analytical grade. In a typical procedure, 2.5 mmol Na_2CO_3 was first dissolved into 100 ml water, and then 5 mmol $AgNO_3$ was added into the above solution. After being magnetically stirred at room temperature for 1 h, the resulting product was washed with distilled water and

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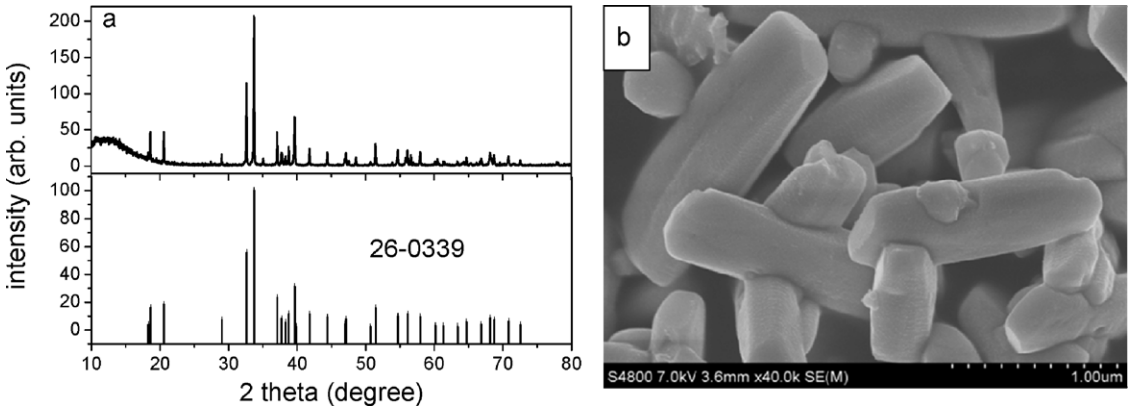

Fig. 1. XRD patterns (a) and SEM images (b) of the prepared Ag_2CO_3 powder.

ethanol. Then the powder was centrifuged and dried at ambient temperature under vacuum.

2.2. Structural characterization

X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (Bruker AXS D8). The morphology was determined by scanning electron microscopy (SEM, Hitachi S-4800 microscope), and the diffuse reflectance spectra (DRS) by UV/visible spectrophotometer (UV-2550, Shimadzu).

2.3. Photocatalytic properties

Photocatalytic decolorization of methylene blue (MB) or phenol was carried out with 0.1 g of the powdered photocatalyst suspended in 100 ml of MB or phenol solution (20 mg/l for MB and 30 mg/l for phenol). Prior to irradiation, the slurry was stirred in the dark for 1 h to obtain the equilibrium adsorption state. The optical source was a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd.), and the absorbance of MB or phenol was monitored using UV/visible spectrophotometer (UV-2550, Shimadzu). The repeated experiments were conducted as follows: at the end of each cycle, the suspension was centrifuged and the supernatant was discarded. The recovered catalyst was dried at ambient temperature under vacuum. Total Organic Carbon (TOC) and inorganic carbon (IC) were determined using TOC Analyzer (TOC-V CPH, Shimadzu).

The photocatalytic activities of Ag_2CO_3 for the destruction of *E. coli* ATCC25922 were measured by using 10^6 colony-forming-units/ml (cfu/ml) bacterial-cell concentrations. The photocatalytic reaction was started by irradiating the bacterial cell solution containing 0.1 g Ag_2CO_3 photocatalyst under visible light ($\lambda \geq 400$ nm). The reaction mixture was cooled by an ice/water mixture to prevent the influence of heat. During the reaction, the bacterial suspension was sampled at 10 min intervals. An aliquot of the reaction mixture was immediately diluted with phosphate buffer and spread uniformly onto a blood agar plate. After 24 h incubation at 37 °C, the number of viable cells was then determined by the plate count method.

3. Results and discussion

3.1. XRD patterns and SEM images

Ag_2CO_3 were obtained as yellow-green powders. Fig. 1a shows the XRD pattern of the as-prepared Ag_2CO_3. All diffraction peaks can be indexed to the phase of Ag_2CO_3 (PDF 26-0339). It displays a monoclinic phase, with lattice constant $a = 4.851$ Å, $b = 9.544$ Å, and $c = 3.253$ Å. No peaks from other impurities, such as metallic silver, can be detected. The high diffraction intensity suggests that the sample has good crystallinity. The SEM images of the prepared Ag_2CO_3 were displayed in Fig. 1b. Obviously, though some irregular particles exist, the major morphology is short rod, which is ca. 1 μm long and 300 nm in diameter.

3.2. DRS study

Fig. 2a shows the DRS spectra of Ag_2CO_3. As can be seen, the obtained Ag_2CO_3 absorb in the visible light range, and the wavelength for the absorption-edge lies at 480 nm. The optical band gap of a crystalline semiconductor was determined by the follow-

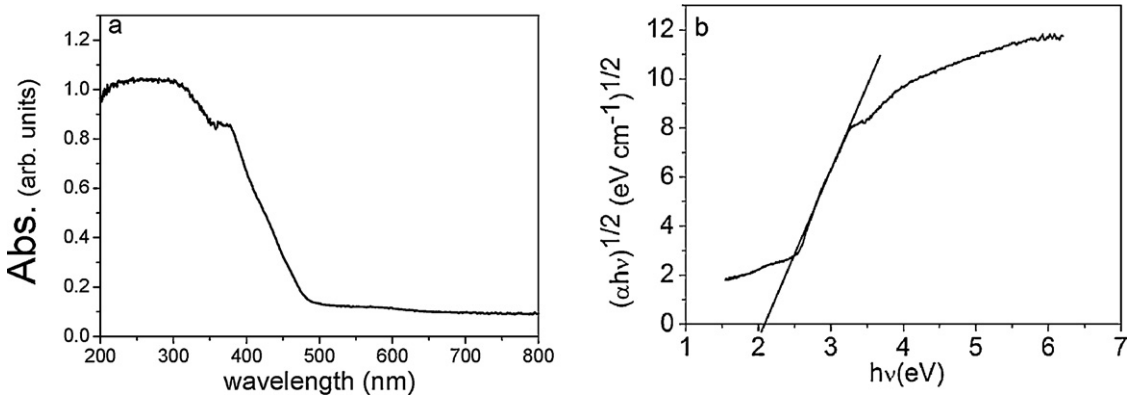

Fig. 2. (a) UV–vis DRS spectra; and (b) Plot of $(ah\nu)^{1/2}$ versus $h\nu$ of Ag_2CO_3.