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Synthesis and photocatalytic property of a new silver thiocyanate semiconductor

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HIGHLIGHTS

- A new AgSCN photocatalytic material was synthesized successfully.
- The photodegradation efficiency over AgSCN was 2.74 times that of N-TiO_2.
- ·OH radicals were the main active species in the oxidation of RhB.

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ABSTRACT

A new AgSCN photocatalytic material with a novel nonmetal acid structure was synthesized by an ion-exchange method. Its structure and properties were characterized in detail. UV–vis absorption spectrum showed that AgSCN had the optical indirect band gap of 3.51 eV. The valence level of AgSCN was determined as 1.52 eV by X-ray photoelectron spectrometer. The photodegradation efficiency of rhodamine B over AgSCN was 2.74 times that of N-doped TiO_2 (N-TiO_2) under UV light radiation. The photodegradation rate constant was 4.8 times that of N-TiO_2. The high photocatalytic activity mainly resulted from SCN^- and the high position of valence band. ·OH radicals, as the dominant active species in photocatalysis, primarily originated from the multi-step reduction of O_2 by photogenerated electron.

1. Introduction

At present, environmental pollution is the major social issue awaiting solution, in which toxic substances can be effectively removed by photooxidation that completely mineralizes pollutants by sunlight without secondary pollution [1]. Therefore, photocatalysis is valuable in many areas of environmental pollution control [2]. Many semiconductor photocatalytic materials have been investigated hitherto, including oxides [3–7], sulfides [8], silver halide [9], composite oxides [10], organic polymers [11], and their modified products, etc. Oxides, which usually have wide band gap values, do not effectively utilize sunlight. Sulfides lead to photocorrosion under light irradiation by easily reacting with electrolytes. Besides, organic polymers generally have low efficiencies in charge separation. Thus, developing new highly efficient and stable photocatalytic materials remains overwhelmingly challenging.

Currently, most photocatalytic materials are based on composite metal oxides, while few nonmetallic acid salt photocatalysts have been reported [12,13]. Nonmetallic acid salts, such as PO_4^{3-}, are stably structured and readily crystallizable, thus restraining oxygen vacancy defects in their crystals. Therefore, photocatalytic activity is enhanced owing to reduced number of recombination centers [14]. Meanwhile, these acidic groups are barely chemically destroyed and corroded by light. In addition, the surface of nonmetallic acid salts strongly interacts with H_2O molecules, which facilitates the dissociation of H_2O to generate more ·OH radicals [15] and to further boost the photooxidation ability of the catalysts. Accordingly, nonmetallic acid salts are feasible photocatalytic materials.

We herein reported a novel nonmetallic acid salt of AgSCN with higher photocatalytic ability than that of N-doped TiO_2 (N-TiO_2) in the photodegradation of rhodamine B. TiO_2 is the main commercial photocatalyst at present, and N-TiO_2 shows a good photocatalytic activity under visible light radiation. The new AgSCN absorbed UV–visible lights at less than 550 nm, and exhibited good photocatalytic properties at the longer wavelengths. Silver salts

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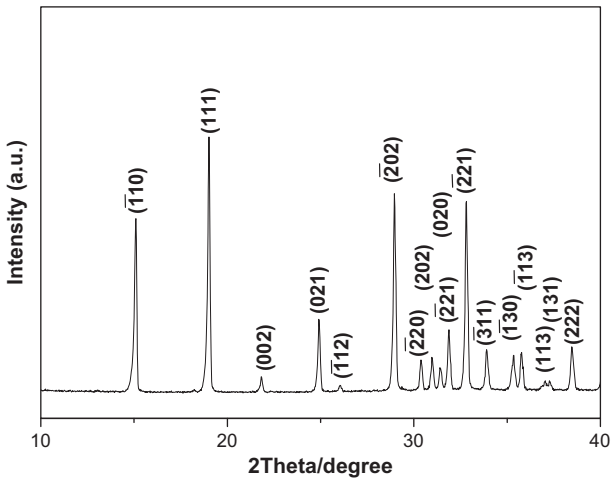

Fig. 1. X-ray diffraction patterns of AgSCN.

are commonly promising photocatalytic materials by having narrow band gaps and high light absorption capacities. To our knowledge, the photocatalytic activity of AgSCN has never been reported. In this study, AgSCN was synthesized by an ion-exchange route, the activity of which in photodegrading rhodamine B aqueous solution under UV light radiation was evaluated. The mechanism regarding the photodegradation of rhodamine B over AgSCN was also studied in detail.

2. Experimental

2.1. Synthesis of samples

All the chemicals were bought from Tianjin Reagent Company. All the chemicals and solvents were used without further purification. In a typical synthesis of AgSCN, 0.5 g of $AgNO_3$ and 0.23 g of NH_4SCN were simultaneously dissolved in 10 mL of distilled water. The above mixture was stirred for 30 min. And then the above precipitation was centrifuged at 4000 rpm, washed, and dried for 6 h at 80 °C in a vacuum oven. N-TiO_2 was synthesized by a sol–gel method. Tetrabutyl titanate (7.5 mL) was added to ethanol (20 mL). Acetic acid (5 mL) and deionized water (2.5 mL) were added to ethanol (20 mL). The latter solution was dropwise added to the former one under stirring. $NH_3{\cdot}H_2O$ (5 mL) was added to the above mixture and a sol–gel formed. The sol–gel was dried at 65 °C for 12 h to remove the remaining water and alcohol. Finally, a white xerogel formed. The xerogel was calcined at 500 °C for 3 h in air to obtain N-TiO_2.

2.2. Characterization of samples

The X-ray diffraction (XRD) measurements of samples were performed with powder diffractometer (Rigaku D/max 2500, Cu

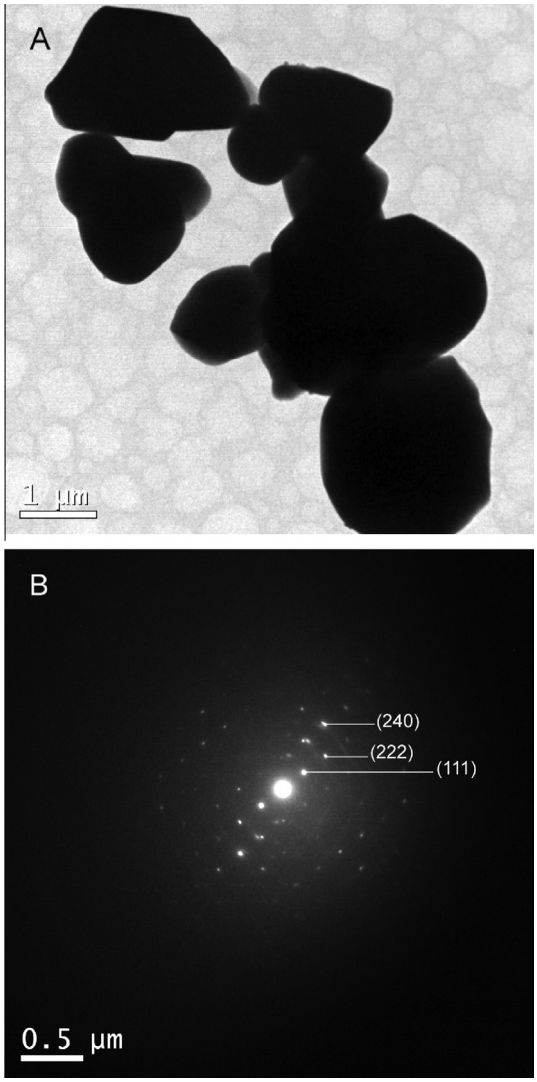

Fig. 2. (A) TEM image and (B) SAED pattern of AgSCN.

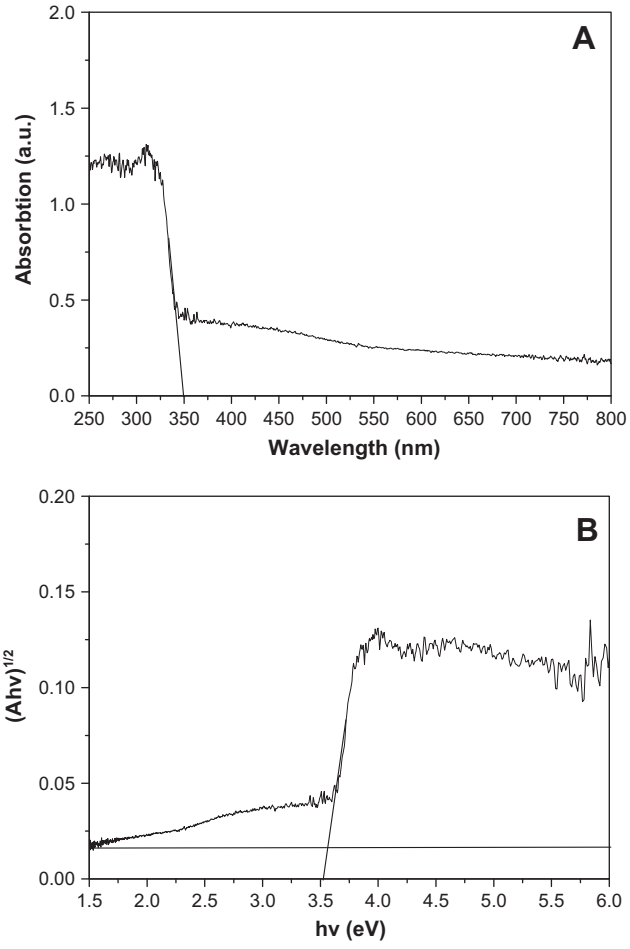

Fig. 3. UV–vis absorption spectra of the as-synthesized AgSCN.