



In situ anion-exchange synthesis and photocatalytic activity of $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell nanorods

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ABSTRACT

Usually, it is difficult to get small AgCl nanoparticles by a conventional aqueous solution route owing to their high nucleation and growth rate. In this study, AgCl nanoparticles with a diameter of less than 30 nm were uniformly coated on the surface of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods to form $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell heterostructures by a simple *in situ* anion-exchange route. It was found that the ion exchange reaction between Cl^- and WO_4^{2-} ions was preferable to occur on the surface of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods rather than in the bulk solution, resulting in the formation of core-shell nanorods. The AgCl shell layer could be easily controlled by adjusting the concentration of NaCl solution. With increasing NaCl concentration, more $\text{Ag}_8\text{W}_4\text{O}_{16}$ phase in the core transferred into AgCl-nanoparticle shell layer while the total size of the core-shell nanorods almost remained unchanged. The photocatalytic activity experiments of methyl orange aqueous solution under fluorescence light irradiation indicated that the AgCl nanoparticles coated on the surface of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods, which could be readily separated from a slurry system after photocatalytic reaction, exhibited a much higher photocatalytic activity than the bulk AgCl photocatalyst.

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1. Introduction

One-dimensional (1D) nanostructured materials, representing a group of ideal building blocks for the bottom-up assembly of integrated electronic and photoelectronic devices, have attracted considerable attention due to their unique physical and chemical properties [1–5]. Especially, the 1D core-shell heterostructured materials have recently become of particular interest as their functions can be easily tuned by adjusting their core and shell with different materials [6–12]. Usually, the template-directed route has been widely used to prepare various 1D core-shell nanostructures [6,7]. In this case, the shell component is directly coated on the surface of 1D core template to form a core-shell structure by various strategies. In order to prepare a uniform shell on the surface of the core template, the template-directed method requires the excellent compatibility between the different core and shell materials. In fact, the conventional template-directed method usually results in incomplete coverage, different thickness of shell and weak interac-

tions between the core and shell. Therefore, it still remains a major challenge to develop a facile and effective route for the preparation of 1D core-shell heterostructures.

In addition to conventional oxide semiconductor photocatalysts [13–19], recently, silver halides have been widely investigated and applied as a highly efficient visible-light photocatalysts [20–25]. Huang et al. reported that Ag@AgCl photocatalyst showed highly efficient and stable for the degradation of methyl orange under the visible-light irradiation [20]. Kakuta et al. found that the AgBr was not destroyed by successive UV irradiation after the formation of Ag^0 species in the early stage of the irradiation [22]. Hu et al. also reported the high efficiency and stability of Ag–AgI photocatalyst supported on mesoporous alumina for the photodegradation of toxic pollutants under visible-light irradiation [21]. All these results suggested that the silver halides could be a highly efficient and promising photocatalyst for the degradation of various organics. However, almost all of the present studies were focused on the silver halides with a size of larger than several hundreds nanometers and seldom works have been carried out on the preparation of nano-scale silver halides, especially the AgCl nanoparticles with a diameter of less than 30 nm [26–28]. One of the most possible reasons is the difficulty for its synthesis owing to its rapid nucleation and growth in aqueous solution. It is highly desirable to develop a new and facile strategy for the preparation of nano-scale silver halide photocatalysts.

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Usually, the photocatalytic activity of a sample is strongly depended on its size and specific surface area. It is expected that the photocatalytic performance of AgCl can be greatly improved by decreasing its particles size. However, conventional powdered photocatalysts have a serious limitation—the need for post-treatment separation in a slurry system after photocatalytic reaction. In addition, the nanosized powders have a strong tendency to agglomerate into larger particles, resulting in the decrease of their photocatalytic performance. Continuing efforts have been made to develop alternate methods to prepare the highly active photocatalysts, which can be readily separated after the photocatalytic reaction. In this work, the AgCl nanoparticles were uniformly coated on the surface of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods to form $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell 1D heterostructures. By combination of the nano-scale AgCl particles and the micro-scale $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods, it is expected that the obtained core-shell composite heterostructures not only exhibit high photocatalytic activity but also can be easily separated from a slurry system and re-used after photocatalytic reaction. The $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell nanorods were prepared by a two-step solution-phase route. The first step was to prepare 1D $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods, and the second was to coat AgCl nanoparticles on the surface of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods by an *in situ* ion-exchange reaction in a NaCl aqueous solution. The effects of the NaCl concentration on the morphology, composition and phase structure of the core-shell nanostructures were investigated and discussed. The photocatalytic activities of the $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell nanorods were evaluated by photocatalytic decolorization of methyl orange aqueous solution under fluorescence light irradiation.

2. Experimental

All reagents are analytical grade supplied by Shanghai Chemical Reagent Ltd. (PR China) and used as received without further purification.

2.1. Preparation of precursor $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods

The starting aqueous solutions of AgNO_3 (0.01 mol L^{-1}) and Na_2WO_4 (0.005 mol L^{-1}) were first prepared. The synthesis of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods were achieved by a simple precipitation reaction between Ag^+ and WO_4^{2-} ions in distilled water. In a typical synthesis, 50 ml of AgNO_3 aqueous solution was poured into 50 ml of Na_2WO_4 aqueous without stirring. After the reaction solution was incubated at room temperature for 12 h, the light yellow precipitate was collected, rinsed with distilled water, and dried at room temperature to obtain $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods.

2.2. Preparation of $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell nanorods

The synthesis of $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell nanorods were achieved by an *in situ* anion-exchange reaction of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods in NaCl aqueous solution in a dark condition. Initially, 0.1 g of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods were added into a 200 ml NaCl solution without stirring. The NaCl concentration was controlled to be 0, 0.1, 0.5, 1 and 500 mM, respectively. After the reaction solution was incubated at room temperature for 6 h, the precipitate was collected, rinsed with distilled water, and dried at 60°C to obtain $\text{Ag}_8\text{W}_4\text{O}_{16}/\text{AgCl}$ -nanoparticle core-shell nanorods.

2.3. Preparation of N-doped TiO_2

N-doped TiO_2 (N- TiO_2) was prepared as follows: 17 mL of tetrabutylorthotitanate was added into an $\text{NH}_3\cdot\text{H}_2\text{O}$ solution ($\text{NH}_3 = 0\text{--}10 \text{ wt}\%$) under stirring. After stirring for another 1 h, the

suspension solution was aged at room temperature (25°C) for 24 h. The resulted suspension was filtrated, washed with distilled water for 4 times and dried at 60°C for 6 h, and then was calcined at 500°C for 2 h to obtain N- TiO_2 . It was found that when the concentration of NH_3 was controlled to be 1 wt%, the obtained N- TiO_2 showed the highest photocatalytic activity under the fluorescence light irradiation. Thus, in this study, the N- TiO_2 prepared from the 1 wt% of NH_3 solution was used as the reference in this study.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku Ultima III X-ray diffractometer (Japan) using $\text{Cu K}\alpha$ radiation. Morphological analysis was performed by an S-4800 field-emission scanning electron microscope (FE-SEM, Hitachi, Japan) with an acceleration voltage of 10 kV. UV-vis absorption spectra were obtained using a UV-visible spectrophotometer (UV-2550, SHIMADZU, Japan). X-ray photoelectron spectroscopy (XPS) measurements were done on a KRATOA XSAM800 XPS system with $\text{Mg K}\alpha$ source. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. Nitrogen adsorption-desorption isotherms were obtained on an ASAP 2020 (Micromeritics Instruments, USA) nitrogen adsorption apparatus. The sample was degassed at 60°C prior to BET measurements. The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.25.

2.5. Photocatalytic activity

The evaluation of photocatalytic activity of the prepared samples for the photocatalytic decolorization of methyl orange (MO) aqueous solution was performed at ambient temperature. 0.05 g of the prepared sample was dispersed into 10 ml of MO solution (15 mg/L) in a culture dish with a diameter of ca. 5 cm. A 55 W fluorescence lamp was used as a light source. The average light intensity striking the surface of the reaction solution was about 14,700 lx, as measured by a luxmeter (ZDS-10, Shanghai). The concentration of MO was determined by an UV-visible spectrophotometer (UV-2550, SHIMADZU, Japan). After visible-light irradiation for some time, the reaction solution was centrifuged to measure the concentration of MO. As for the methyl orange aqueous solution with low concentration, its photocatalytic decolorization is a pseudo-first-order reaction and its kinetics may be expressed as $\ln(c_0/c) = kt$, where k is the apparent rate constant, and c_0 and c are the methyl orange concentrations at initial state and after irradiation for t min, respectively [29,30].

3. Result and discussion

3.1. Morphology and phase structures of the precursor $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods

The precursor of $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods can be easily synthesized by simply mixing AgNO_3 and Na_2WO_4 aqueous solutions without stirring at ambient temperature (ca. 25°C) [31]. When AgNO_3 aqueous solutions were poured into Na_2WO_4 solutions, a white suspension was formed immediately and the precipitate showed a cotton-like product. After aging for 12 h, the product was changed from white color to light yellow. SEM image (Fig. 1a) clearly shows that the light yellow precipitate is composed of many nanorods with a diameter of 30–100 nm and a length of ca. 1 μm . According to XRD result (Fig. 2a), these nanorods can be attributed to $\text{Ag}_8\text{W}_4\text{O}_{16}$ (JCPDS no. 70-1719) with an orthorhombic structure. To further observe the surface morphology of the $\text{Ag}_8\text{W}_4\text{O}_{16}$ nanorods, a higher magnification SEM image is shown in Fig. 1b. It is clear that

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