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Hierarchical assembly of AgCl@Sn-TiO_2 microspheres with enhanced visible light photocatalytic performance

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ABSTRACT

The hierarchical silver chloride loaded tin-doped titania (AgCl@Sn-TiO_2) microspheres were first time prepared by a hydrothermal method and annealing at different temperatures. The catalyst showed the enhanced visible light photocatalytic activity as compared to the plasmonic photocatalysts of AgCl and Ag/AgCl, and commercial Degussa P25 (TiO_2). The improved efficiency is considered to local surface plasmonic resonance (AgCl could reduce to Ag^0 during photocatalytic reaction) in enhanced broad band visible light absorption in addition to the characteristics of heterojunction between Sn-TiO_2 and AgCl NPs. Moreover, the surface and bulk properties of as-synthesized samples were analyzed by ^{119}Sn Mössbauer spectroscopy. The magnetic property of the bulk was studied as a function of magnetic field with different temperatures. These results signify the clear details of the magnetic and visible light photocatalytic activities of hierarchical AgCl@Sn-TiO_2 microspheres.

1. Introduction

Energy conversion and waste water treatment on the basis of solar energy and highly efficient photocatalysts attract progressively attention [1–3]. The improvement of stabilizations of photoinduced charge carrier/separation is the key factor for light-harvesting systems in both photocatalytic and photovoltaic solar cells, which convert light energy into chemical reaction and electrical power generation. Titanium dioxide and TiO_2-based materials are widely used in environmental and energy-related applications like photocatalysis and photovoltaics, including but not limited to artificial photosynthesis and spintronics, have been often foreseen, where they are usually employed as nanocrystals or nanostructures [4–6]. However, the photocatalytic efficiency need to improve in visible-light or sunlight. Noble metal (Pt, Pd, Rh, and Au) modified TiO_2 photocatalysts has been taken attention [7–9]. In this context, investigation of Ag-loaded TiO_2, Ag cluster-incorporated AgBr nanoparticles (NPs) on TiO_2 [10], TiO_2 with Ag NPs and CuO nanoclusters [11] and Ag/AgCl/TiO_2 [12] photocatalysts are certainly interesting [13]. The heterojunction between TiO_2 and SnO_2 can have a synergetic effect on the photoactivity [14]. Furthermore given that Ag/AgCl is a plasmonic system, any agglomeration in the system due to the nature of materials process used can have an influence on the observed photoactivity.

However, the hierarchical assembly of nanoscale building photocatalyst blocks with a tunable dimension and structure complexity offers an essential strategy towards the realization of multifunctionality of nanomaterials in order to enhance the photocatalytic activity by extending the photoresponse range and to increase the electron-hole pair separation efficiency [15]. Generally, hierarchical heterostructures are assembled from two different materials with low-dimensional nanostructures, providing an ultrahigh specific surface area and a network system consisting of parallel connective paths and interconnections of dissimilar functional components [16].

Recently, we have reported some number of papers related to the magnetic properties and photocatalytic activity of titania based photocatalysts such as metal oxide coupled TiO_2 [17], Sn-TiO_2 nanocrystals [18], iron oxide coupled and doped TiO_2 [19], nickel-imidazole//TiO_2 [20] and hierarchical (Sn, N)TiO_2 microspheres [21]. In order to take high activity of the coupled, doped, surface modified or co-doped semiconductor nanocomposites, the concept of ferromagnetic photocatalysts shows better charge carrier separation function. Hence, furthermore development needs to improve the photocatalytic efficiency of titania based photocatalyst. Hence, AgCl NPs loaded on tin doped titania microsphere in tune with visible-light activity has become an important topic in the photocatalytic plus photovoltaic research today

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[22,23]. However, there are no reports on the applications of hierarchical AgCl@Sn-TiO_2 microspheres in photocatalyst and perovskite solar cells until now.

Herein, we report for the first time a simple hydrothermal method to successfully fabricate hierarchical AgCl@Sn-TiO_2 (hereafter it denotes as AST) microspheres using samples with different temperatures used in post-calcination. All as-prepared samples have been characterized in detail by the conventional analytical techniques and ^{119}Sn Mössbauer spectroscopy. The main aim of this work is to modify TiO_2 with Sn by loading AgCl NPs loaded in order to improve the photocatalytic performances. A significant absorption of visible light was observed for the AST microspheres as compared to Sn-TiO_2, AgCl, Ag/AgCl and commercial Degussa P25 photocatalysts. The rhodamine B (RhB) and 3-nitrophenol aqueous solutions were used as the model systems to estimate the photocatalytic performance of the as-obtained AST microspheres under visible light ($\lambda \geq 420$ nm). The results indicate that the hierarchical AST microsphere photocatalysts has a higher photodegradation rate as compared with Ag/AgCl, AgCl, Sn-TiO_2 and TiO_2 (P25). However, the study on various levels of AgCl contents in the AST microsphere is important in order to clarify their photocatalytic performance. To the best of our knowledge, this is the first report on the preparation, visible-light photocatalytic performance of hierarchical AST microspheres and in addition, the magnetic behavior of these catalysts characterized by ^{119}Sn Mössbauer technique. The noble metal halide and metal doped titania represents a new kind of semiconductor and provides new opportunities for TiO_2-based materials.

2. Experimental

2.1. Chemicals

Titanium isopropoxide (97%), and $SnCl_4$ in methylene chloride (Sigma Aldrich), $AgNO_3$ (AR, 99.8%), ammonium hydroxides (99.9%), hydrogen peroxide (GR, 30 wt.% in H_2O), oxalic acid (98.0%), and nitric acid (98.0%) (Aladdin Chemicals, China) were used for the preparation of samples. Rhodamine B (AR, Sinopharm, China) and 3-aminophenol (98+%, Alfa Aesar) were used as a model organic pollutant to evaluate the activity of synthesized materials. TiO_2 (P25) was provided by Evonik Degussa and used directly without any further treatment. Deionized water was used for solution preparation. All chemicals were used as received without further purification.

2.2. Instrumentation

The instrumental details of X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution SEM, UV–vis diffuse reflectance spectrophotometer (UV–vis DRS), the X-ray photoelectron spectra (XPS) and ^{119}Sn Mössbauer spectroscopy were provided in our previous paper [21]. The surface states of Sn in AgCl@Sn-TiO_2 was measured by conversion electron ^{119}Sn Mössbauer spectroscopic (CEMS) study, using the same detailed instrumentation as reported work [24].

2.3. Preparation of hierarchical AgCl@Sn-TiO_2 microsphere

The AST microspheres were obtained by single step process. This preparation process was slightly modified from our previous reports [18,21]. Initially, 5 mol reddish brown titanium nitrate solutions were prepared [17] and then 0.50 mL $SnCl_4$ (1 M in methylene chloride) followed by 0.01, 0.05, 0.10 or 0.50 M $AgNO_3$ (50 mL) solutions were added into the titanium nitrate solutions under magnetic stirring. Then 100 mL oxalic acid solutions (0.6 M) was introduced drop wise within 4 h under magnetic stirring and the resulting solution was kept in dark place at room temperature for 48 hours. The resultant mixtures were transferred into 500 mL reagent bottle, sealed and heated at 121 °C for 3 h with the pressure maintained at 15 psi. Finally, the precipitates were filtered, washed with distilled water and ethanol, and dried in air at 90 °C for 12 h. The dried precipitates were calcined at two different temperatures such as 400 and 900 °C for 4 h in a muffle furnace to get AST microsphere. Hereafter, the AgCl@Sn-TiO_2 with different AgCl content level and samples post-annealed at various temperatures were denoted as AST-x-y (where “x” represents various concentrations such as 0.01, 0.05, 0.10 or 0.50 M of $AgNO_3$ solution used in preparation method and “y” represents the various calcination temperatures such as 400 and 900 °C, y = 0 is non-annealed sample).

For comparison, normal bulk AgCl powder was prepared by simple stirring method of $AgNO_3$ and HCl in aqueous solution at room temperature. The AgCl powder was put into an aqueous solution, which was then irradiated with a 360 nm UV lamp. Then the resulting precipitate, which consists of silver deposited on AgCl particles, was washed and dried in air. XRD was used to examine the phase structure of the obtained samples. As shown in Fig. S1, porous Ag/AgCl is mainly composed of AgCl, which can be characterized by the appearance of the Bragg diffraction peaks located at 2θ values of 28.0, 32.4, 46.4°, etc. Peaks centered at 38.2° and 44.4° (2θ) were attributed to the small quantity of residual Ag. In particular, no silver oxide phases were determined.

2.4. Photocatalysis procedure

The photocatalytic activities of the samples were evaluated by photodegradation of RhB (6.2×10^{-6} M) and 3-aminophenol (10^{-5} M) using PE.ILC CERMAX xenon illumination system model LX 175/ 300 attached with CX-04E power supply (10 A) and with a 420 nm long-pass filter was used as the light source and 10 mg of catalysts were used for photocatalysis process. The distance between the lamp and the solution was 8.0 cm. The photocatalysis procedure was reported in our previous paper [25]. The photocatalytic degradation of RhB with relatively low concentration is generally accepted to be a pseudo-first-order reaction [21].

3. Results and discussion

3.1. Materials characterization

Fig. 1 shows the XRD pattern of Sn-TiO_2 microspheres with different AgCl loading and calcination temperatures. As is evident from the diffractograms, the as-prepared samples exhibit good crystallinity at higher calcination temperatures. The XRD peak positions for all the samples matched well with rutile TiO_2 (values obtained from standard card JCPDS no. 01-076-1941; crystal sys tem = tetragonal, a = 4.623 Å and c = 2.986 Å). However, minute cassiterite SnO_2 phase was obtained for all as prepared samples. This can be attributed to the low loading amount, high dispersity or lack of crystallinity in the nanophase containing Sn. In addition, we find chlorargyrite AgCl peaks corresponding to a phase containing silver. The inability of Ag to enter the matrix can be understood by noting the significant difference in ionic radii of Ti^{4+} and Ag^{+}. For the coordination number 6, the ionic radius of Ti^{4+} is 0.75 Å [26] and that of Ag^{+} is 1.29 Å [27]. Hence it is reasonable to assume that Ag^{+} cannot substitute for Ti in the TiO_2 crystalline matrix and Ag^{+} is easily bound with Cl^{-} to form AgCl nanoparticles, hence Cl^{-} ions obtained from $SnCl_4$ in reaction solution. Some of the literature reports that the two steps process is involved for the preparation of AgCl/TiO_2 photocatalyst [28,29]. However, as our present report