Catalysis Communications 11 (2009) 290–293

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Ag@C core/shell nanocomposite as a highly efficient plasmonic photocatalyst

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ARTICLE INFO

Article history:
Received 20 July 2009
Received in revised form 29 September 2009
Accepted 29 September 2009
Available online 7 November 2009

Keywords:
Photocatalysis
SPR
Silver
Nanocomposite

ABSTRACT

Ag@C core/shell nanocomposite was synthesized by a hydrothermal process and demonstrated as a new plasmonic photocatalyst. The as-prepared Ag@C exhibited high photocatalytic activity in the decomposition of aqueous tetraethylated rhodamine (RhB) and gaseous acetaldehyde (CH_3CHO) under visible-light irradiation. The origin of the high photocatalytic activity was discussed, which is mainly ascribed to the surface plasmon resonance (SPR) effect of silver nanoparticles in the Ag@C composite.

1. Introduction

Since the concept of plasmonic photocatalysis was proposed by Awazu et al. [1], the SPR effect of noble-metal nanoparticles on photocatalysis has attracted renewed attention recently. In their study, the photocatalytic behavior of TiO_2 was greatly boosted by the assistance of the SPR effect of the contacted silver nanoparticles. This type of noble-metal/semiconductor nanocomposite has been extensively studied before as highly active photocatalysts [2,3]. Besides this, another type of plasmonic photocatalyst, Ag/(AgCl or AgBr) with excellent photocatalytic activity, was also reported [4,5]. It was found a composite of silver nanoparticles formed on the photosensitive material of AgCl or AgBr particles is a stable photocatalyst under visible-light illumination. As is well known, both the semiconductor photocatalyst and the photosensitive material could respond to light and the light induced catalysis in these noble-metal incorporated nanocomposites is ascribed to a synergistic effect between the basis material and the SPR effect of noble metals. In order to further understand the SPR induced photocatalysis, the studies on the photocatalytic performance of pure noble metals or their composites with non-photoexcited materials are necessary. A recently study reported that gold nanoparticles on non-photoexcited oxide supports exhibited visible-light-driven oxidation on HCHO [6]. However, the photooxidation activity was suggested to ascribe to the thermal catalysis property of gold nanoparticles in this work, and more studies are needed for this new type of photocatalyst which is different from the extensively studied semiconductor based photocatalyst. Besides gold, silver nanoparticles also absorb visible light intensely because of the SPR effect [7]. By the SPR effect, the electromagnetic field of incident light couples with the oscillations of conduction electrons in silver particles, resulting in strong-field enhancement of the local electromagnetic fields near the rough surface of silver nanoparticles. The intensity of the enhanced local electromagnetic field is influenced by a number of factors, such as particle size, morphology, and the dielectric constant of the surrounding medium. Small particle size and dielectric constant of surrounding medium are advantageous for much enhancement of the local electromagnetic field [8,9].

Basis materials were usually used to support these noble-metal nanoparticles in order to disperse or stabilize these high active species. Besides the widely used oxide basis material [3,10–13], amorphous carbon is another type for better using the plasmonic performance of noble metals because it possesses smaller dielectric constant than that of oxides. Furthermore, previous studies have proved the feasibility of amorphous carbon as basis material for catalysis [14,15].

Therefore, we chose amorphous carbon as basis material to support and protect silver nanoparticles in the present study and an Ag@C core/shell spherical nanocomposite was synthesized for a photocatalytic study. The amorphous carbon can not be excited by light. If the Ag@C nanocomposite exhibits a photocatalytic activity, it will be mainly ascribed to the silver nanoparticles. Thus, a new type of thermal photocatalyst would be developed in the noble-metal/carbon system which has been proved as an excellent thermal catalysts before [10,16]. The present work is mainly focused on the photocatalytic behavior of the Ag@C core/shell

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doi:10.1016/j.catcom.2009.09.026

nanocomposite that was synthesized by a hydrothermal method modified from a previous report [17].

2. Experimental

In a typical synthesis, 4 g of glucose was dispersed in 35 mL of deionized water. Then 2 mL of $AgNO_3$ aqueous solution (0.03 M) was added into the above solution under vigorous stirring. After being stirred for more than 5 min, the solution was transferred into a 50 mL Teflon-lined autoclave. The autoclave was sealed in a stainless steel tank and heated at 180 °C for 3 h. Subsequently, the reactor was cooled to room temperature naturally. The resulting sample was collected, washed with deionized water and ethanol, and dried at 50 °C for 24 h in air. The nitrogen doped TiO_2 (N–TiO_2) photocatalyst was prepared by nitridation of commercially available TiO_2 powder (surface area $50\ m^2\ g^{-1}$) at 500 °C for 10 h under NH_3 flow [18].

The purity and the crystallinity of the as-prepared sample was characterized by powder X-ray diffraction (XRD) on a Japan Rigaku Rotaflex diffractometer using Cu Kα radiation while the voltage and electric current were held at 40 kV and 100 mA. The transmission electron microscope (TEM) analyses were performed by a JEOL JEM-2100F field emission electron microscope. Nitrogen adsorption–desorption measurements were conducted at 77.35 K on a Micromeritics Tristar 3000 analyzer. The Brunauer–Emmett–Teller (BET) surface area was estimated using the adsorption data. UV–vis adsorption spectrum of the ethanol-dispersed sample was measured by using a Hitachi U-3010 UV–vis spectrophotometer.

The photocatalytic activity of the Ag@C sample was evaluated by the degradation of RhB and acetaldehyde under visible-light irradiation of a 500 W Xe lamp with a 420 nm cutoff filter. For the degradation of RhB, 0.05 g of photocatalyst was added into 100 mL of RhB solution (2×10^{-5} mol/L). Before illumination, the solution was stirred for 120 min in dark in order to reach the adsorption–desorption equilibrium between the photocatalyst and RhB. At every 10 min intervals, a 4 mL suspension was sampled and centrifuged to remove the photocatalyst particles. Then, the UV–vis absorption spectrum of the centrifuged solution was recorded using a Hitachi U-3010 UV–vis spectrophotometer. For the degradation of CH_3CHO, 0.1 g of the as-prepared photocatalyst was placed at the bottom of a gas-closed reactor at room temperature (capacity 600 mL). This reactor is made of glass and has a quartz window. The reaction gas mixture (1 atm) consisted of 100 ppm CH_3CHO and N_2 balance gas. Prior to irradiation, the reaction system was equilibrated for about 30 min until no changes in the concentrations of CO_2 were monitored. Gaseous samples (1 mL) were periodically extracted and analyzed by a gas chromatography (GC) equipped with a flame ionization detector (N_2 carrier) and the catalytic conversion furnace.

3. Results and discussion

The XRD pattern of the Ag@C nanocomposite clearly shows that the cubic phase of silver with lattice constant of $a = 4.086$ Å (JCPDS 87-0597) was obtained (Fig. 1). A low magnified TEM image of the Ag@C nanocomposite in Fig. 2a indicates a spherical core/shell structure and no other morphologies are observed. Higher magnified TEM image of the Ag@C core/shell nanocomposite (Fig. 2b) reveals that the silver cores with diameters in the range of 70–100 nm are covered with carbon shell with thickness of about 25 nm. As mentioned above, the silver nanoparticles could absorb visible light intensely because of the SPR effect. The UV–vis absorption spectrum (Fig. 3) of the ethanol-dispersed Ag@C nanocomposite displays a broad absorption band centered at 630 nm that may be attributed to the SPR effect of silver cores. The broad absorption is advantageous for the catalyst to utilize visible light better. The BET surface area of the Ag@C sample was $8.23\ m^2\ g^{-1}$.

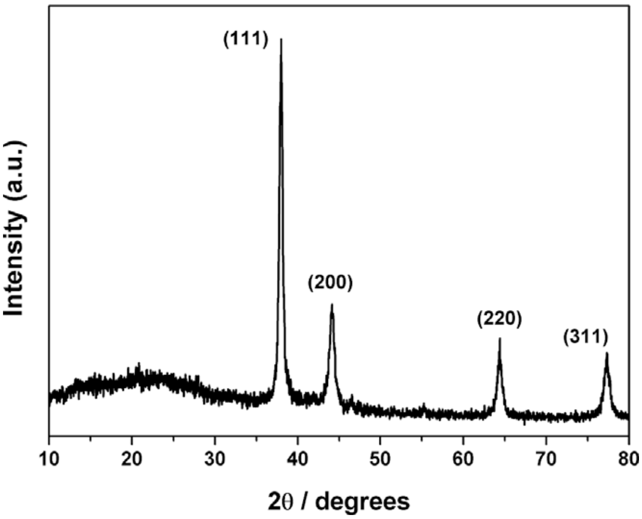

Fig. 1. XRD pattern of the as-prepared Ag@C sample.

To evaluate the photocatalytic activity of Ag@C nanocomposite, the photooxidation on a common air pollutant of gaseous CH_3CHO over the Ag@C sample was examined under visible-light irradiation. Fig. 4 represents the photocatalytic decomposition of CH_3CHO over Ag@C under visible-light irradiation. CO_2 is the final product in the photocatalytic oxidation of organic contaminants [19]. Although the CO_2 concentration was not increased obviously in the first 20 min by the Ag@C photocatalyst, it dramatically increased between the 30 and 50 min and about 75% of the CH_3CHO was degraded within the 20 min indicating an excellent photocatalytic activity of this Ag@C photocatalyst. After irradiation for 50 min, the conversion of CH_3CHO to CO_2 increased slowly. When the irradiation time was up to 65 min, the detected CO_2 concentration reached a stable value of 178 ppm, which indicates that 89% of CH_3CHO was degraded. By comparison, CH_3CHO decomposition over N–TiO_2 was also carried out under the same conditions, as shown in Fig. 4. The activity of N–TiO_2 on the photodegradation of CH_3CHO was much lower than that of Ag@C photocatalyst and only 31% of CH_3CHO was degraded when the irradiation time was up to 65 min.

To further investigate the photocatalytic performance of the Ag@C nanocomposite, the photodegradation of an aqueous contaminant, a widely used dye tetraethylated rhodamine (RhB), was tested. As shown in Fig. 5, the photolysis of RhB is not observed without a photocatalyst under visible-light illumination. However, with Ag@C nanocomposite as photocatalyst, 90% of RhB is decolorized after 60 min, showing the excellent photocatalytic activity of the as-prepared Ag@C nanocomposite. Under the same conditions, the degradation rate of RhB by N–TiO_2 was 15% only indicating the obvious advantage of the Ag@C nanocomposite as a visible-light-driven photocatalyst. To investigate the recyclability of the Ag@C photocatalyst for the degradation of RhB, the Ag@C sample after photocatalytic reactions was collected by centrifugation and dried for the subsequent photoreaction cycle. As shown in Fig. S1, Ag@C nanocomposite exhibited an excellent stability and maintained a broadly similar level of photocatalytic activity after four reaction cycles.

It is of interest to consider how Ag@C nanocomposite becomes an efficient photocatalyst under visible-light irradiation. This may be ascribed to the SPR effect of the silver nanoparticles. The irradiation of incident light with a wavelength in the range of the SPR band may result in two consequences. The first is that light absorp-