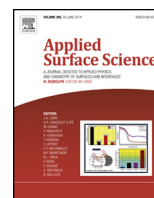




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Studies on the photocatalysis of core-shelled SiO₂–Ag nanospheres by controlled surface plasmon resonance under visible light

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ABSTRACT

Abundant core-shelled silica–silver nanospheres with uniform diameter and morphology were successfully synthesized by Stöber and seed-mediated method, in sequence. By the different additions of glucose, the silver nanoparticles were deposited on silica spheres by redox reaction, which well controlled in the range from 10 to 50 nm. The surface plasmon resonance absorption band shifted toward infra-red region and became broader gradually during the dimensions of silver nanoparticles were increased in the growth range. The amazing data imply that using core-shelled silica–silver nanospheres efficiently enhances the degradation of the organic pollutants under solar energy, which means the core-shelled silica–silver nanospheres is not only a cost-effective route but an energy-saving way to our planet.

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1. Introduction

During the last decades, the photocatalyst materials have attracted substantial scientific and technological interests in biomaterials due to its potential of changing solar energy into chemical energy [1,2]. In general, many metal oxides are used as semiconductor photocatalysts, e.g., TiO₂ [3], ZnO [4], SnO₂ [5], ZrO₂ [6] and so on. Thanks to its good chemical stability and effective photodegradation activity for organic pollutants in air and water, TiO₂ is the most popular in current semiconductor photocatalysts. However, the extra light must provide the energy above 3.26 eV, which be able to trigger the TiO₂ electrons to conduction band from valence band, and it also means the ultraviolet light (UV light) can be only useful in this condition [7,8]. It is a challenge to overcome this limitation in the TiO₂ photocatalyst materials because the dominant part of solar energy is visible light not UV light in our daily life.

Fortunately, several literatures exhibit core-shelled silica–metal nanostructures consisting of silica nanocore and metal nanoshells have drawn a lot of attentions due to their special properties and

applications, such as catalysts [9], SERS [10], bio-sensors [11], solar cells [12] and so on. Up to now, various routes have been explored to produce such a nanostructure, i.e., sono-chemical deposition [13], surface functionalization [14], photoreduction [15] and electroless plating [16,17]. Metal–silica core-shelled nanostructures are more stable than pure metal nanoparticles because the latter is always tending to aggregate in solution. On the other hand, the surface plasma resonance (SPR) frequency is under control easily by modifying geometries of core-shelled silica–metal nanostructures [18]. Throughout the previous papers, the resonance spectrum is related for the particle parameters as size, morphology and surrounding media, which explained via Mie scattering theory [18–21].

Base on this concept, core-shelled silica–silver nanospheres (SiO₂@Ag NSs) were synthesized by a step-by-step manufacture in this task. First, the silica nanospheres were prepared by Stöber method [22]. Second, silver shells were deposited on silica spheres by seed-mediated method, which means the growth of the silver seeds on silica spheres in a simple process by various additions of glucose as the reduction. In order to investigate the relations between the SPR absorbance region and photocatalyst efficiency, the authors tuned the SPR absorbance region of SiO₂@Ag NSs from 420 nm to 700 nm and used methylene blue (MB) as the probe to estimate the photocatalyst efficiency under visible light illuminations [23].

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2. Experimental

2.1. Reagent

Eight reagents are used in this study as follows: tetraethyl orthosilicate (TEOS, 98%, Alfa Aesar), absolute ethanol (99.99%, Sigma–Aldrich), silver nitrate (99.9%, Mallinckrodt), aqueous ammonia solution (30–33%, Sigma–Aldrich), (D-+) glucose monohydrate (99%, Alfa Aesar), tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%, Sigma–Aldrich), sodium hydroxide (NaOH, 99%, Sigma–Aldrich), and methylene blue (MB, 99.9%, Sigma–Aldrich). All reagents without additional purification and Milli-Q water ($\Omega > 10^{18}$) were used in the whole procedure.

2.2. Synthesis of SiO_2 nanospheres

Silica spheres with diameter around 150 nm were prepared by well-known Stöber method with a diverse dispersion of size less than 13%. First, 3 ml TEOS and 20 ml DI-water were mixed and then the mixed solution was kept heating on the hot plate. When the temperature of mixed solution had reached 75 °C, 10 ml aqueous ammonia drops were added into this mixed solution one by one in 2 min; meanwhile, the temperature of the mixed solution was maintained at 75 °C. After the additions of aqueous ammonia drops, the solution was maintained at 75 °C for 3 h. When the reaction was done, the SiO_2 nanospheres were obtained by centrifuge at 7200 r.p.m. for 10 min. Then the products were washed 3 times by ethanol and dried in an oven at 60 °C for 5 h.

2.3. Preparation of core-shelled SiO_2 –Ag nanospheres

2.3.1. Sn^{2+} -sensitized SiO_2 nanospheres

First, 0.597 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 ml HCl aqueous solution (0.01 M). The addition of HCl is to prevent the $\text{Sn}(\text{OH})\text{Cl}$ caused by the hydrolysis of SnCl_2 in the products. Second, 0.5 g as-prepared SiO_2 powders were dispersed in the above solution under ultrasonic for 30 min and then the Sn^{2+} -sensitized silica nanospheres were collected by the centrifugation and dried in the oven at 60 °C for the next step.

2.3.2. Core-shelled SiO_2 –Ag nanospheres

In order to deposit silver layer on Sn^{2+} -sensitized silica nanospheres, the ammoniacal silver nitrate solution was first prepared as following: 0.5 g silver nitrate was added into 50 ml DI-water and then 0.2 ml NaOH (0.1 M). The color of this mixture gradually changed to yellowish-brown due to the formation of Ag_2O . Then 2 ml aqueous ammonia drops (6.6 wt%) were added into the above mixture one by one. Until the color of above solution became clear again, the $\text{Ag}(\text{NH}_3)_2^+$ solution was obtained. Next, 0.5 g Sn^{2+} -sensitized silica nanospheres were dispersed in the above ammoniacal silver nitrate solution under vigorous stirs. Then, after the reaction for 35 min, 1 ml glucose (10 mM) and 1 ml $\text{Ag}(\text{NH}_3)_2^+$ aqueous solution (10 mM) were added into the above solution once per 1.5 h for 4 times (1 cycle) and 8 times (2 cycles), separately. The pH of Ag deposited SiO_2 nanospheres processes was about 2–3. While the reaction was finished, the products were collected by the centrifugation and dried in the oven at 60 °C. Therefore, different morphologies and features of core-shelled SiO_2 –Ag nanospheres were discovered by the three conditions (0 cycle, 1 cycle and 2 cycles). To read simply, SA0, SA1 and SA2 will be the code to represent the three conditions (0 cycle, 1 cycle and 2 cycles), respectively.

2.4. Characterizations of core-shelled SiO_2 –Ag nanospheres

2.4.1. Physical analysis

The morphologies of SiO_2 @Ag NSs were characterized by high resolution transmission electron microscope (HRTEM, JEM2010) and scanning electron microscope (SEM, JSM-6500F). X-ray diffraction patterns of the SiO_2 @Ag NSs powder were examined by using the Shimadzu XRD6000 with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) scanning range (2θ) from 30° to 80°. X-ray photoelectron spectroscopy were measured at an angle of 0° using Perkin Elmer model PHI 1600 system with $\text{MgK}\alpha$ line as an X-ray source and the energy resolution was 1.6 eV. All the deconvolution of XPS curves were performed with the XPS Peak Fitting Program (XPSPEAK41, Chemistry, CUHK). UV–visible absorption spectra were recorded by a Hitachi U-3010 spectrophotometer.

2.4.2. Catalytic property of core-shelled SiO_2 –Ag nanospheres

Each three samples of 0.5 mg SiO_2 @Ag NSs were dispersed in 10 ml MB ($2 \times 10^{-5} \text{ M}$). In order to attach MB on three samples' surfaces, the previous solutions were under a 20-min stir, and then the solutions were exposed to a visible light source (wave length: 400–700 nm, 55 W/cm^2) for 1 h. The catalytic performances of SA0, SA1 and SA2 were recorded by monitoring the photodegradations in optical density at the fixed wavelength of the absorbance ($\lambda = 665 \text{ nm}$) of the typical dye, MB, in aqueous heterogeneous solution suspensions.

3. Result and discussion

3.1. Morphologies of core-shelled SiO_2 –Ag nanospheres

Fig. 1(a) shows the SEM image of silica nanoparticles with diameter about 130 nm prepared by Stöber method [22]. The silver nuclei decorated silica microspheres were manufactured by a seed-mediated method similar with electroless plating [16,17] developed by Zhu and co-workers [24]. First, a layer of Sn^{2+} was absorbed on negatively charged silica surface by electrostatic attraction, and then the $\text{Ag}(\text{NH}_3)_2^+$ were reduced immediately by Sn^{2+} through an ox-red process. From the TEM image of Fig. 1(b), after deposition of silver (SA0), the morphology was half sphere-shaped, which was getting tough and the silver nuclei on the surface of silica nanoparticles were well dispersed with the size range of 7–10 nm. Next, in order to control the morphology of silver shell, the Ag NPs were further grown with a seed-mediated method by using glucose as a mild reducing agent for 1 and 2 cycles. In the previous papers [24,25], the mixture of formaldehyde and ammonia is widely used as a reduction in a seed-mediated method, even though this combination is toxic and harmful to researchers at laboratories. Herein, a very great ideal was presented in this seed-mediated method, which was used glucose, an un toxic chemical, as a reduction. Fig. 1(c) displays the TEM image of SiO_2 @Ag NSs under a 1 cycled redox reaction with glucose (SA1); the Ag NPs became larger and the diameters were about 25 nm. Fig. 1(d) demonstrated the TEM image of SiO_2 @Ag NSs under a 2 cycled redox reaction with glucose (SA2); the Ag NPs are larger than previous one and the diameters were about 50 nm. All in all, judging from Fig. 1(b) to (d), the surface-modified core particles, SiO_2 nanoparticles, embedded with shell particles, Ag nanoparticles were demonstrated. Therefore, authors named these samples as core-shelled SiO_2 –Ag nanospheres [26]. It was notable that the Ag NPs get larger during this growing process, they turned to be elliptic or irregular spheres and these shape conditions strongly affect the optical properties [23].

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