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RESEARCH ARTICLE

Synthesis of silicon nanowires supported Ag nanoparticles and their catalytic activity in photo-degradation of Rhodamine B

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Abstract Silver modified silicon nanowires were obtained and employed as photo-catalysts in the degradation of Rhodamine B (RhB), which demonstrated the excellent catalytic activity. These catalysts may be recycled and reused.

Keywords silicon nanowires, Ag nanoparticles, Rhodamine B (RhB)

1 Introduction

Noble metal nanoparticles have attracted increasing interest due to their size and shape dependent optical and electronic properties, which are expected to have wide applications in optics, microelectronics, sensors, and catalysis [1,2]. In recent years, nanometer-scale silver particles have attracted the interest of researchers because of their unique properties: large surface-to-volume ratio, high surface reaction activity, high catalytic efficiency and strong adsorption ability. Therefore, they have potential applications in many areas, such as: nonlinear optical switching [3], immunoassay labeling [4], second harmonic generation [5] and a wealth of optical phenomena directly related to their geometry-dependent surface plasmon resonance.

Synthesis of noble metal nanoparticles has been the subject of many scientific reports in consideration for applications. Several preparation methods have been devised for silver nanoparticles, including surfactant-based seed mediated growth [6–8], thermal methods [9], and photoreduction processes [10]. The assembly of noble metal nanoparticles on planar surfaces was the key step in their application. And it still requires more sophisticated methods, such as lithography [11,12], electroless deposition [13], electroplating on insulators and the formation of colloids under constant reagent flow [14].

In spite of the above effects, yet, the agglomeration of nanoparticles during the preparation remains a formidable problem [15]. Over the past years, an alternative method for generating stabilized metal nanoparticles involves synthesis in nanoporous supports, which help define particle size and serve to immobilize the resulted particles.

Herein, we present a new strategy for synthesizing Ag nanoparticles with easy recycle by using silicon nanowires (SiNWs) as a carrier. As a kind of typical one-dimensional nanomaterials, SiNWs were produced via numerous methods [16–18], which provided a number of remarkable advantages, such as easy surface modification with various metal particles [19], a vast surface-volume ratio [20], and stability to atmosphere environment. In this work, SiNWs were successfully prepared and then modified with Ag nanoparticles. This new surface was a significant improvement over traditional unsupported Ag nanoparticles for applications. The experiments showed that this Ag/Si nanostructure exhibited highly active catalysis and excellent stability recycle in the degradation of Rhodamine B (RhB). This meant that the substrate has much effect on the behavior of Ag nanoparticles.

2 Experiment

2.1 Synthesis of Ag nanoparticles

0.005 g as-synthesized SiNWs, obtained via the high-temperature method, were etched with 10 mL 5% HF aqueous solution for 30 min, then rinsed with de-ionized

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water and immersed in 10 mL 10^{-3} mol/L $AgNO_3$ aqueous solution. When the yellow SiNWs gradually turned black, they were modified with Ag nanoparticles. Unsupported Ag nanoparticles were prepared by reducing silver nitrate 0.25 mL (1×10^{-3} mol/L) with sodium borohydride 0.15 mL (1×10^{-2} mol/L). The solutions were mixed with continuous stirring until the solution turned yellow at room temperature [21].

2.2 Degradation process

In a representative degradation experiment, 3.0 mL 10^{-6} mol/L RhB was added into a quartz cuvette with an optical path of 1 cm long, and then the as-prepared Ag/Si catalysts were added. The progress of the degradation was monitored using a fluorescence and UV-vis spectrophotometer.

2.3 Characterization

The phase and crystallography of the products were characterized by a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm). A scanning rate of $0.05°\cdot s^{-1}$ was applied to record the pattern in the 2θ range of 20°–100°. The morphologies of as-prepared products were analyzed with an S-4800 field emitting scanning electron microscopy (FESEM), equipped with an energy dispersive X-ray (EDX) spectroscope. Transmission electron microscopy (TEM), selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscope (HRTEM) image were captured with a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. Degradation process was tracked with a U-4100 spectrophotometer. The PL spectra of the sample were recorded using a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

3 Results and discussion

3.1 Synthesis of Ag nanoparticles

Figure 1(a) shows the X-ray diffraction (XRD) pattern of the as-prepared SiNWs, and all the diffraction peaks can be indexed as the cubic phase of Si. The cell parameter is calculated to be a = 0.5415±0.0009 nm, which is in agreement with the value of face-centered cubic silicon a = 0.5430 nm (JCPDS card No. 27-1402). Figure 1(b) shows the XRD pattern of the SiNW-supported Ag nanoparticles. No other characteristic peaks were observed except for Si and Ag, which indicates that the product has a high degree of crystallinity. The calculated lattice constant of Ag is a = 0.4080±0.0004 nm, which is consistent with the reported value, a = 0.4086 nm (JCPDS card No. 04-0783).

Figure 2 is the SEM image of silicon nanostructure, which exhibits their wire-like morphology. The average

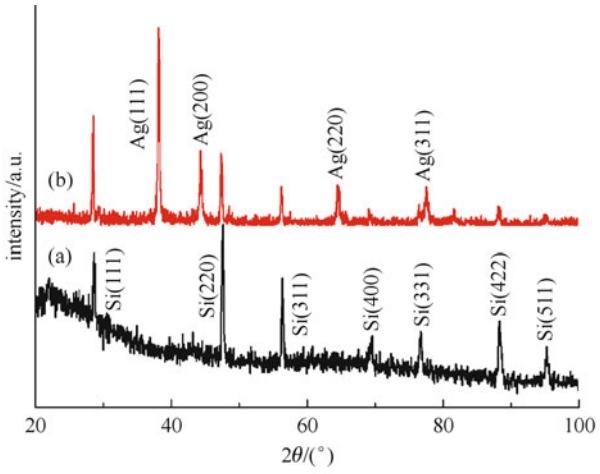

Fig. 1 XRD patterns of (a) SiNWs and (b) Ag/Si nanostructure

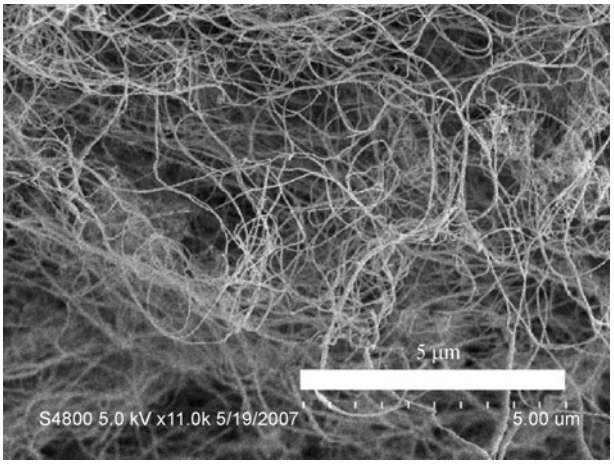

Fig. 2 SEM image of SiNWs

diameter of SiNWs is 50 nm.

Figure 3 presents a TEM image of one single wire with the average diameter of 86 nm modified with Ag nanoparticles, which are randomly attached to the surface of SiNW, taking an average diameter of 50 nm. Figure 3(a) shows the TEM image of single SiNW supported with Ag nanoparticles. The EDX (Fig. 3(b)) was further used to check the chemical composition of the products. The detected oxygen comes from the adsorption of the sample when exposed to the air. No peaks of other elements are detected except for Si and Ag. A close examination of the sample using HRTEM (Fig. 3(c)) reveals the lattice fringe of Si and Ag, both showing (111) crystal planes. The selected area electron diffraction (SAED) (Fig. 3(d)) taken from this area displays the crystalline structure of Si and Ag. The bright spots can be indexed as (1–11) and (111) of silicon respectively, taking the zone axis of (110), while the diffraction ring is consistent with the (200) plane of Ag nanoparticles.

All of the above characterization results are consistent

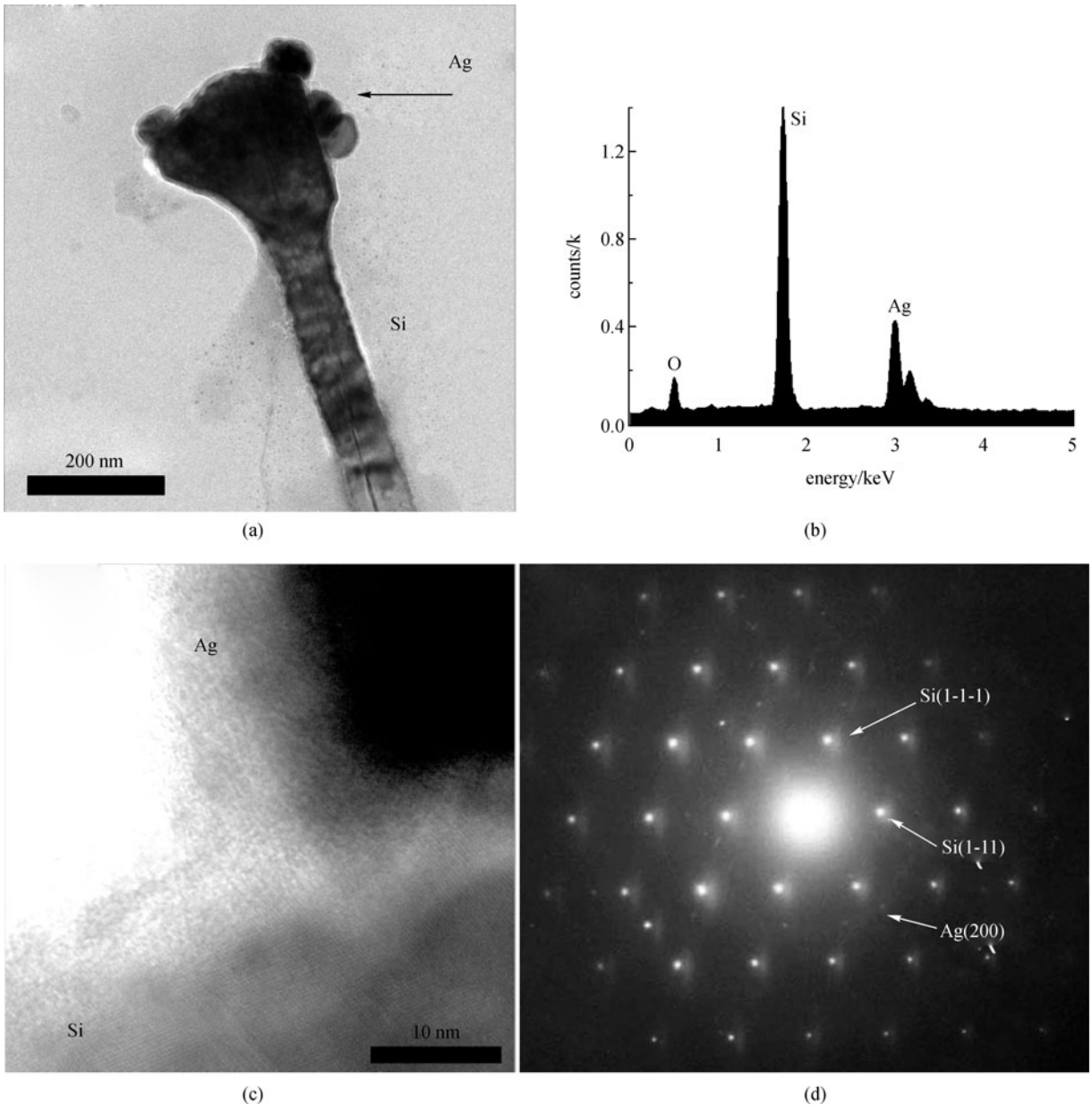

Fig. 3 (a) TEM image of single SiNW supported with Ag nanoparticles; (b) EDX of SiNW revealing its chemical composition of Si and Ag; (c) HRTEM image showing both (111) crystal planes of Si and Ag; (d) SAED pattern indicating bright diffraction spots of Si and weak diffraction ring of Ag nanoparticles

with each other and adequately prove the fact that the SiNWs have been modified with Ag nanoparticles.

3.2 Degradation of Rhodamine with Ag/Si nanostructure

To demonstrate the potential applicability of the present Ag/Si naonoparticles, we investigated the application of degrading RhB. The characteristic absorption of RhB at $\lambda = 551$ nm was chosen to monitor the degradation process. Figure 4(a) shows the successive UV-visible spectra of an aqueous solution of RhB. The absorption peak at $\lambda = 553$ nm diminishes gradually as the time gets prolonged, and completely disappears at about 20 min, which indicates the complete degradation of RhB during the reaction. Figure 4(b) shows that the relationship of $\ln(C_{\mathrm{RhB}})$ versus reaction time is nearly linear, and the slop is -0.23673 ± 0.01022; the intercept is -1.40436 ± 0.1209. So the reduction rate of RhB may be expressed as $r = 0.0581\exp(-0.23673\tau)$.

In order to have a comparison, a contrast experiment was performed. We kept other conditions constant and replaced Ag/Si nanoparticles with Ag-nanoparticles. Figure 5 shows that the reaction does not take place. The result adequately proves the activity of the as-prepared nanoparticles.

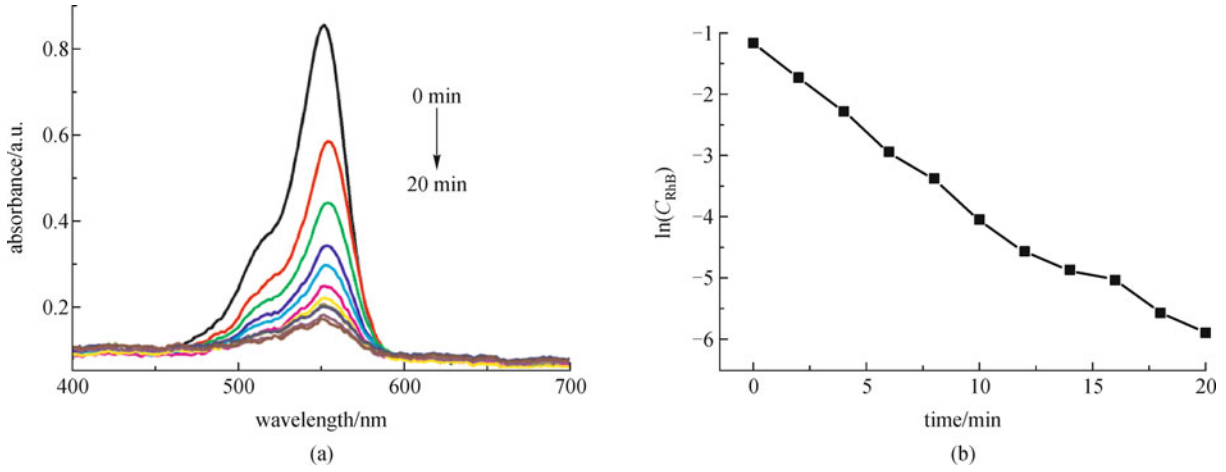

Fig. 4 (a) UV-vis spectra of degradation of RhB using Ag/Si catalysts at room temperature; (b) curve of ln(C_{RhB}) concentration versus time using Ag/Si catalysts

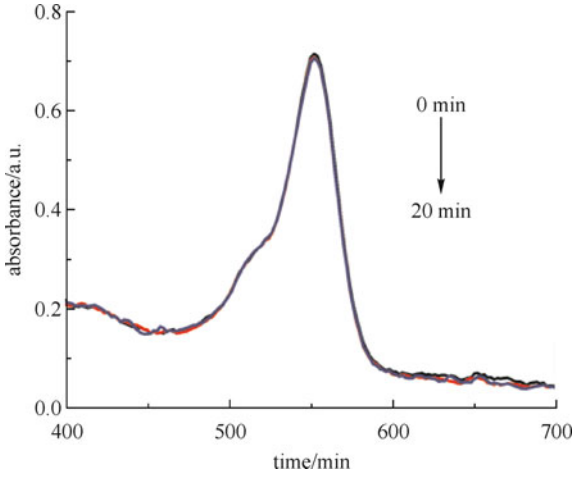

Fig. 5 UV-vis spectra of degradation of RhB using nano-Ag catalysts at room temperature

Since the Ag nanoparticles were supported on the SiNWs, the catalysts can be easily recycled and initiate the next degradation after being rinsed with distilled water. The reaction was studied using recycled catalysts. Along with the increment of the recycle times, the activity of the as-prepared samples diminishes slowly (Fig. 6(a)). The relationship of the reaction constant versus cycle times is shown in Fig. 6(b), which may be expressed as $k = 0.2578 - 0.0248N$, where k is the reaction rate constant and N is the cyclic time.

The above results obviously indicate that the catalytic activity and stability of Ag/Si catalysts are promising, which may find wider application in the catalytic field.

Although the precise mechanism for the degradation of RhB is still under discussion, the direct catalysis of Ag/Si is assuredly crucial. Ag nanoparticles in our experiment, with an average diameter of 50 nm, have a large surface-to-volume ratio compared to bulk metal. The SiNWs supported Ag nanoparticles are kept from congregating

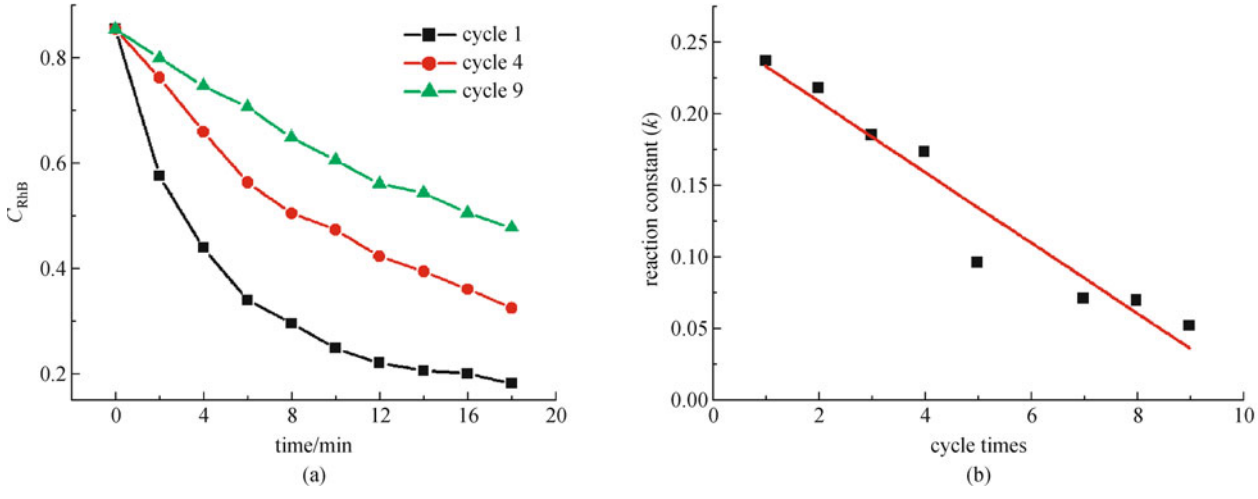

Fig. 6 (a) Recycling experiments of Ag/Si catalysts in degradation of RhB; (b) curve of reaction constant versus cycle times

and growing large because they are fixed on the SiNWs, which may facilitate Ag catalysts with a high efficiency during the reaction and in the use of recycling.

4 Conclusions

Ag/Si nanostructure was prepared using SiNWs as a carrier, which had reasonably high surface area and small crystal size. It made SiNWs an attractive host in support of nanoparticles. The results indicated that these SiNWs supported Ag catalysts provided strong activity in the process of degradation of RhB, which showed high mobility and excellent recycling stability. Moreover, the maneuverability and controllability of this fabrication enables Ag/Si catalysts to find applications in other fields.

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