Silk fibroin fibers supported with high density of gold nanoparticles: fabrication and application as catalyst

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Abstract Silk fibroin (SF) fibers were modified with sulfonated polyaniline and, via an in situ redox technique, a high density of gold (Au) nanoparticles were supported directly on the surface of the fiber. The morphology, formation, and application of the as-prepared product, Au/SPANI-modified SF composite fiber, were investigated. By controlling the concentration of HAuCl₄, the density of Au nanoparticles on the composite fiber could be effectively adjusted. It is suggested that sulfonated polyaniline contributes to the generation of a high density of Au nanoparticles supported on the SF fibers. The composite fiber exhibited good activity when taking the reduction of p-nitrophenol as a model reaction.

Keywords Fibers · Nanoparticles · Scanning electron microscopy (SEM)

Introduction

Nanostructured noble metals have been widely used as catalysts for a variety of organic reactions [1–3] due to their surface-to-volume ratio and high surface energy. To overcome the problem of particle aggregation and catalyst deactivation, the metal is generally immobilized on a solid support such as carbon, a metal oxide, or polymer microspheres [4]. However, in recent years researchers have shown an increasing interest in the preparation and use of polymer fiber-supported noble metal catalysts [5–7].

Silk fibroin (SF), which can be obtained by removing the outer sericin of silk fiber, has been extensively studied in biomedical and chemical fields [8]. Indeed, recent years theoretical and experimental studies have uncovered a number of novel phenomena [9, 10]. One of the most interesting finds is that a noble metal ion can be reduced by SF fiber to form zero-valent metal [11–13], which could lead to a new class of polymer fiber-supported catalysts. The tyrosine residue (Tyr) component in the SF has strong electron donating complex properties and can provide a redox-active site to construct nanostructured noble metal crystallites. However, even when the reaction is carried out at a high concentration of noble metal ions, only a low density of noble metal nanoparticles are generated on the surface of SF fiber due to the low content of tyrosine residue (5.17 mol%) [13] on the SF backbone. This restricts the catalytic activity of SF fiber-supported noble metal composites. Therefore, identifying a novel method to produce high density of noble metal nanoparticles on the SF fiber is of significant interest and importance to the field.

In our previous reports [14, 15], we showed that water-soluble sulfonated polyaniline (SPANI) could reduce noble metal ions at room temperature. Herein, we build on these data by demonstrating a convenient route to prepare a high density of Au nanoparticles on the SF fiber. This as-prepared composite fiber could have many other applications in a range of fields such as biosensors and textiles.
Experimental

Materials

Fresh *Bombyx mori* cocoons were purchased from Maanshan Textile Corporation, Anhui Province, China. Aniline, (NH₄)₂S₂O₈, H₂SO₃Cl, 1, 2-dichloroethane, and HAuCl₄ were purchased from Beijing Chemical Co. in their reagent grades. Those reagents were used without further purification.

Preparation of SF fiber

Fresh *B. mori* cocoons were degummed twice with a 5-g/L anhydrous sodium carbonate solution at 100°C for 1 h, then were rinsed thoroughly in warm distilled water and dried in vacuum at 40°C.

The modification of SF fibers with SPANI

SF fibers (0.001 g) were dispersed in 20 mL of SPANI aqueous solution (5 wt.%), which was synthesized using the method previously reported [14]. After being stirred for 1 h at 80°C, the mixture was filtered and dried under vacuum at 40°C, thus obtaining the SPANI-modified SF fibers. The SPANI content in the modified fibers could be estimated from the weight of S atoms according to expression 1.

\[
(G - G_0) \times \frac{32}{75} \times 100%,
\]

where \(G\) and \(G_0\) are the weights of S atom in the SPANI-modified and pure SF fibers, respectively.

Generating a high density of Au nanoparticles on the surface of SF fibers

Typically, SPANI-modified SF fibers (0.001 g) were dispersed in 20 mL of HAuCl₄ aqueous solution (10 mmol L⁻¹) without stirring for 24 h at room temperature. Then, the product, Au/SPANI-modified SF composite fiber, was obtained after being filtered with distilled water and dried in vacuo at 40°C. Au/SPANI-modified SF composite fibers with different density of Au nanoparticles could be obtained by adjusting the concentration of HAuCl₄ aqueous solution.

Analysis of the loading and content of Au nanoparticles on SF fibers

To measure the actual loading and content of Au nanoparticles on Au/SPANI-modified SF composite fibers, a sample of the fibers (0.01 g) were dispersed in 200 mL of HAuCl₄ aqueous solution at different concentrations of HAuCl₄ aqueous solution without stirring for 24 h at room temperature. Then, the product was collected and weighed after being filtered with distilled water and dried in vacuo at 40°C. By contrast, to obtain the Au/SF composite fibers, pure SF fibers (0.01 g) were also dispersed in HAuCl₄ aqueous solution according to the same procedure. The actual loading (\(\Delta W\)) and content of Au (\(W\%\)) were calculated using Eqs. 2 and 3, respectively.

\[
\Delta W = W - 0.1
\]

\[
W\% = \frac{\Delta W}{0.1} \times 100\%
\]

where \(W\) is the weight of Au/SPANI-modified SF composite fibers (or Au/SF composite fibers).

Catalytic activity of Au/SPANI-modified SF composite fibers

A reaction mixture of water (6 mL), p-nitrophenol aqueous solution (5 mL, \(1.5 \times 10^{-3}\) mol L⁻¹), dried Au/SPANI-modified SF composite fiber (0.001 g) was put in a beaker and stirred. To this mixture, NaBH₄ aqueous solution (2 mL, \(1.5\) mol L⁻¹) was then added. The progress of the conversion of p-nitrophenol to p-aminophenol was monitored via UV–Vis spectroscopy by recording the time-dependent absorption spectra of the reaction at a regular time interval of 5 min at room temperature.

The catalytic activity of Au/SF composite fibers was also investigated according to the same procedure.

Instruments and measurements

Scanning electron microscopy (SEM) and optical microscope experiments were performed with JSM-5610 and XPT-7 microscopes, respectively. Fourier transform infrared spectra (FTIR) were recorded on a BrukerVECTOR220 spectrometer. X-ray diffraction (XRD) data were acquired with a Rigaku D/MAX-RC diffractometer using CuKα radiation in the 2θ range of 35–80° at 45 kV. UV–Vis spectra were recorded on a UV-240 spectrometer (Shimadzu, Japan).

Results and discussion

The modification of SF fibers with SPANI

Using optical microscopy (Fig. 1), it can be seen that after the white SF fibers are modified by SPANI, the product becomes deep green, suggesting that the SPANI has been successfully absorbed on to the SF fibers. To confirm this, FTIR spectra of SF fibers before and after modification...
were recorded. As shown in Fig. 2a, SF fibers have the characteristic peaks at 1,632 cm\(^{-1}\) (amide I), 1,516 cm\(^{-1}\) (amide II), and 1,230 cm\(^{-1}\) (amide III) [16]. In the spectra of SPANI-modified SF fibers (Fig. 2b), although the bands of SPANI are partly overlapping, there are still some distinct bands of \(-\text{SO}_3\text{H}\), for example, the peaks at 1,190 cm\(^{-1}\) and 631 cm\(^{-1}\). In addition, it is clear that both the peaks for amide I and amide III of SF move to higher wave numbers (1,637 and 1,545 cm\(^{-1}\), respectively) after modification. This indicates that SPANI has interacted with the peptide linkages bearing on SF macromolecular chains. These spectral results confirm that SPANI has been absorbed on the SF fibers.

Table 1 presents the elemental composition of SF fiber before and after modification. Because pure SF is mainly composed of amino acids (containing up to 85 wt.% of glycine, alanine, and serine), carbon, nitrogen, oxygen, and sulfur, all exist beside hydrogen in the SF fiber. After the modification procedure, there is a clear increase in the weight of sulfur, and from this measurement, it can be estimated that SPANI content in the SPANI-modified SF fibers is about 2.2 wt.% according to expression 1.

The characterization of Au/SPANI-modified SF composite fibers

In order to support a high density of Au nanoparticles on SF fibers, SPANI-modified SF fibers are immersed in HAuCl\(_4\) aqueous solution (10 mmol L\(^{-1}\)) at room temperature. By contrast, pure SF fibers are also dispersed in HAuCl\(_4\) aqueous solution according to the same procedure. After 24 h, it was found that there were only a few Au nanoparticles with the size of about 500 nm scattered on the surface of pure SF fibers (Fig. 3a). In contrast, the surfaces of SPANI-modified SF fibers (Fig. 3b and inset of Fig. 3b) are clearly adorned with many nanoparticles within a size range of 50–100 nm. In addition to the size of the nanoparticles, the density of coverage of the Au nanoparticles is obviously far higher on the SPANI-modified SF fibers. The EDS pattern (Fig. 3c) confirms that the nanoparticles on the SPANI-modified SF fibers are comprised only of pure Au. In the XRD diffraction pattern of the Au/SPANI-modified SF composite fibers (Fig. 3d), several sharp diffraction peaks are observed at 38.2\(^\circ\), 44.8\(^\circ\), 64.1\(^\circ\), and 77.2, which can be assigned to diffraction from the 111, 200, 220, and 311 planes [17] of Au crystal, respectively, indicating face-centered cubic structures (JCPDS, 04–0784) [17]. The size of Au nanoparticles on the Au/SPANI-modified SF composite fibers is estimated from the Au (111) diffraction line using Scherrer’s equation, \(L = k\lambda / \beta\cos\theta\), where \(L\) is the mean dimension of crystallites, \(\beta\) is the full width at half maximum of the diffraction peak, \(\theta\) is the diffraction peak angle, \(\lambda\) is the wavelength of the CuK\(\alpha\) radiation (0.154 nm), and \(k\) is equal to 0.89 [18]. The calculated average size of the Au nanoparticles on the Au/SPANI-modified SF composite fibers is approximately 86 nm, which is consistent with the SEM data.

The formation of Au/SPANI-modified SF composite fibers

As to the formation of Au nanoparticles on pure SF fibers, it is generally believed that the reductive amino acid
tyrosine of SF provides both the necessary location and reductive environment. Because of the relatively low tyrosine residue content in the SF (only 5.17 mol%), only a few Au nanoparticles are produced and scattered on the SF fiber. Previous reports, including ours [19–21], suggest that conducting polymers such as polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene) could be used to reduce noble metal ions. As a soluble conducting polymer, sulfonated polyaniline can be also used as a dual reducing and structure-directing reagent in controlling the formation and shape of Au nanoparticles at room temperature, which was confirmed in our recent studies [14, 15]. Based on these experimental results, it is proposed that both tyrosine residues and sulfonated polyanilines on the surface of SPANI-modified SF fibers, play important roles in reducing the AuCl₄⁻ ions (Eqs. 1 and 2). It is intuitive that SPANI may determine the overall reduction process due to its higher content. Hence, more Au nanoparticles are produced and deposited on the surfaces of SPANI-modified SF fibers.

\[
\begin{align*}
\text{HO-CH}_2\text{-} + \text{AuCl}_4^- & \rightarrow \text{O-CH}_2\text{-} + \text{Au} + 4\text{Cl}^- \quad (1) \\
[\text{SO}_3\text{H (C}_6\text{H}_4\text{) NH}]_x + \text{AuCl}_4^- & \rightarrow [\text{SO}_3\text{H (C}_6\text{H}_4\text{) N}]_x + \text{Au} + 4\text{Cl}^- + \text{XH}^+ \quad (2)
\end{align*}
\]

The effect of \([\text{HAuCl}_4]\) on the density of Au nanoparticles on the au/SPANI-modified SF composite fibers

To further understand the formation process of Au nanoparticles on the SPANI-modified SF fibers, the influence of \([\text{HAuCl}_4]\) on the density of Au nanoparticles has been investigated. As shown in Fig. 4, it can be seen that with the increase of \(\text{HAuCl}_4\) concentration, the Au content increases gradually for both pure and SPANI-modified SF fibers. For the pure SF fibers (Fig. 4a), the optimal

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Table 1 Quantitative analysis of main elements in SF fibers before and after being modified by SPANI

|         | The weight of main elements (wt.%) |
|---------|-----------------------------------|
| SF      | Carbon 66.10, Nitrogen 13.20, Oxygen 20.13, Sulfur 0.57 |
| SPANI-modified SF | Carbon 66.04, Nitrogen 13.16, Oxygen 20.11, Sulfur 0.69 |

C carbon, N nitrogen, O oxygen, S sulfur

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The concentration of HAuCl₄ and maximal content of Au nanoparticles are 10 mmol L⁻¹ and 13.5 wt.%, respectively, while the optimal concentration of HAuCl₄ for the modified SF fiber is about 25 mmol L⁻¹ and the maximal content is about 17.1 wt.%. This result is in line with the SEM data.

The catalytic activity of Au/SPANI-modified SF composite fibers

To investigate the catalytic activity of Au/SPANI-modified SF composite fibers, the model catalytic reduction reaction of p-nitrophenol by NaBH₄ has been investigated. Pure SF does not catalyze this reaction alone. This reaction is easily monitored by following the absorption decrease of p-nitrophenol at 400 nm [21, 22]. Figure 5a shows a typical UV–Vis absorption change at 400 nm of the reaction mixture by the addition of Au/SPANI-modified SF composite fibers. In Fig. 5b, the ratio of \( C_t \) to \( C_0 \), where \( C_t \) and \( C_0 \) are p-nitrophenol concentrations at time \( t \) and 0, respectively, is measured from the relative intensity of respective absorbance, \( A_t/A_0 \). The linear relation of \( \ln(C_t/C_0) \) versus time is observed for the applied catalyst, indicating that the reaction follows first-order kinetics under this condition. The rate constant (\( K=1.62\times10^{-1} \text{ min}^{-1} \)) has been estimated from first-order reaction kinetics using the slope of straight line, indicating good catalytic activity.

For Au/SPANI-modified SF composite fiber, the Au nanoparticles are firmly integrated with the SF fiber even after repeated washing in water. This fact implies that the composite fibers could be used repeatedly. To support this point, we have not found obvious change of the rate constant, even after using the same sample on 16 occasions. Indeed, when compared with many other Au-based catalysts, the Au/SPANI-modified SF composite fiber catalyst described here has an obvious advantage of easy and convenient operation in the reaction system. Moreover, the tedious and time-consuming regeneration process which often includes precipitating, filtering, and redispersing can be simplified by washing only with excess water. These facts combine to make such composite fibers excellent materials for practical catalyst applications.

Fig. 5 Catalytic activity of the Au/SPANI-modified SF composite fiber. a The absorption of the mixed solution at 400 nm at different times. b Plot of \( \ln(C_t/C_0) \) versus time
residues on the SF backbone, SPANI also played an important role in controlling the formation and shape of Au nanoparticles on the surface of SF fibers. The as-prepared composite fibers exhibited good catalytic activity and may have other potential applications in a range of fields such as biosensors and textiles.

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