

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

Youyi Xia · Junmin Wan · Qianfeng Gu

Published online: 25 August 2011

© The Author(s) 2011. This article is published with open access at Springerlink.com

**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  $\text{HAuCl}_4$ , 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 over-

come 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.

Y. Xia · Q. Gu

Department of Polymer Science and Engineering,  
School of Chemistry and Chemical Engineering,  
Anhui University of Technology,  
Maanshan 243002, People's Republic of China

Y. Xia (✉) · J. Wan

Key Laboratory of Advanced Textile Materials and Manufacturing  
Technology, Ministry of Education, Zhejiang Sci-Tech University,  
Hangzhou, Zhejiang, People's Republic of China  
e-mail: xiayouyi@ahut.edu.cn

## Experimental

### Materials

Fresh *Bombyx mori* cocoons were purchased from Maanshan Textile Corporation, Anhui Province, China. Aniline,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{HSO}_3\text{Cl}$ , 1, 2-dichloroethane, and  $\text{HAuCl}_4$  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  $100^\circ\text{C}$  for 1 h, then were rinsed thoroughly in warm distilled water and dried in vacuum at  $40^\circ\text{C}$ .

### 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  $80^\circ\text{C}$ , the mixture was filtered and dried under vacuum at  $40^\circ\text{C}$ , 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.

$$(G - G_0) \times \frac{32}{75} \times 100\%, \quad (1)$$

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  $\text{HAuCl}_4$  aqueous solution ( $10 \text{ mmol L}^{-1}$ ) 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  $40^\circ\text{C}$ . Au/SPANI-modified SF composite fibers with different density of Au nanoparticles could be obtained by adjusting the concentration of  $\text{HAuCl}_4$  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  $\text{HAuCl}_4$  aqueous solution at different concentrations of

$\text{HAuCl}_4$  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  $40^\circ\text{C}$ . By contrast, to obtain the Au/SF composite fibers, pure SF fibers (0.01 g) were also dispersed in  $\text{HAuCl}_4$  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.

$$\Delta W = W - 0.1 \quad (2)$$

$$W\% = \frac{\Delta W}{0.1} \times 100\% \quad (3)$$

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,  $1.5 \times 10^{-3} \text{ mol L}^{-1}$ ), dried Au/SPANI-modified SF composite fiber (0.001 g) was put in a beaker and stirred. To this mixture,  $\text{NaBH}_4$  aqueous solution (2 mL,  $1.5 \text{ mol L}^{-1}$ ) 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

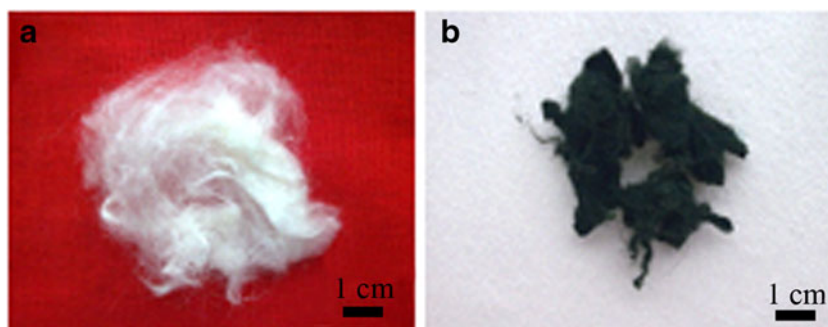
Scanning electron microscopy (SEM) and optical microscope experiments were performed with JSM-5610 and XPT-7 microscopes, respectively. Fourier transform infrared spectra (FTIR) were recorded on a Bruker VECTOR220 spectrometer. X-ray diffraction (XRD) data were acquired with a Rigaku D/MAX-RC diffractometer using  $\text{CuK}\alpha$  radiation in the  $2\theta$  range of  $35\text{--}80^\circ$  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

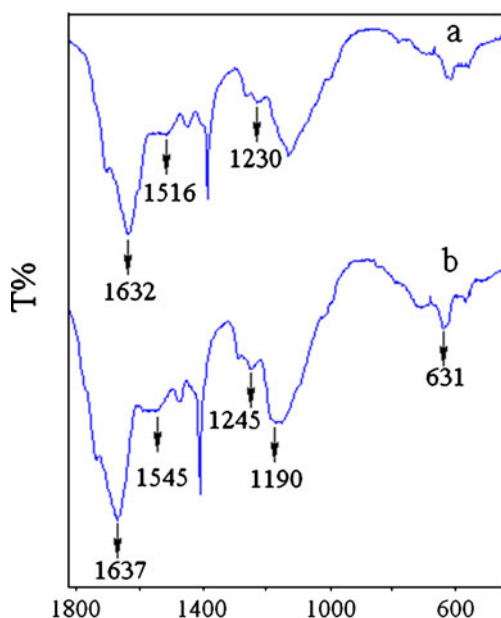
Using optical microscopy (Fig. 1), it can be seen that after the white SF fibers are modified by SPANI, the product becomes deep green, suggesting that the SPANI has been successfully absorbed on to the SF fibers. To confirm this, FTIR spectra of SF fibers before and after modification

**Fig. 1** The optical appearances of pure SF fibers (a) and SPANI-modified SF fibers (b)



were recorded. As shown in Fig. 2a, SF fibers have the characteristic peaks at  $1,632\text{ cm}^{-1}$  (amide I),  $1,516\text{ cm}^{-1}$  (amide II), and  $1,230\text{ cm}^{-1}$  (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  $1,190\text{ cm}^{-1}$  and  $631\text{ cm}^{-1}$ . 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  $1,545\text{ cm}^{-1}$ , 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



**Fig. 2** The spectra of pure SF fiber (a) and SPANI-modified SF fiber (b)

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  $\text{HAuCl}_4$  aqueous solution ( $10\text{ mmol L}^{-1}$ ) at room temperature. By contrast, pure SF fibers are also dispersed in  $\text{HAuCl}_4$  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  $77.2^\circ$ , 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  $\text{CuK}\alpha$  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

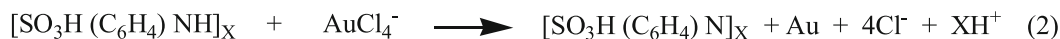
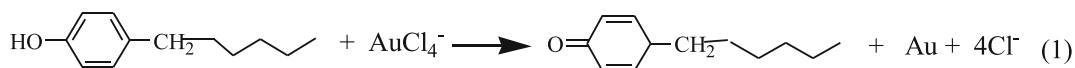
**Table 1** Quantitative analysis of main elements in SF fibers before and after being modified by SPANI

SF fibers	The weight of main elements (wt.%)			
	C	N	O	S
SF	66.10	13.20	20.13	0.57
SPANI-modified SF	66.04	13.16	20.11	0.69

C carbon, N nitrogen, O oxygen, S sulfur

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  $\text{AuCl}_4^-$  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.

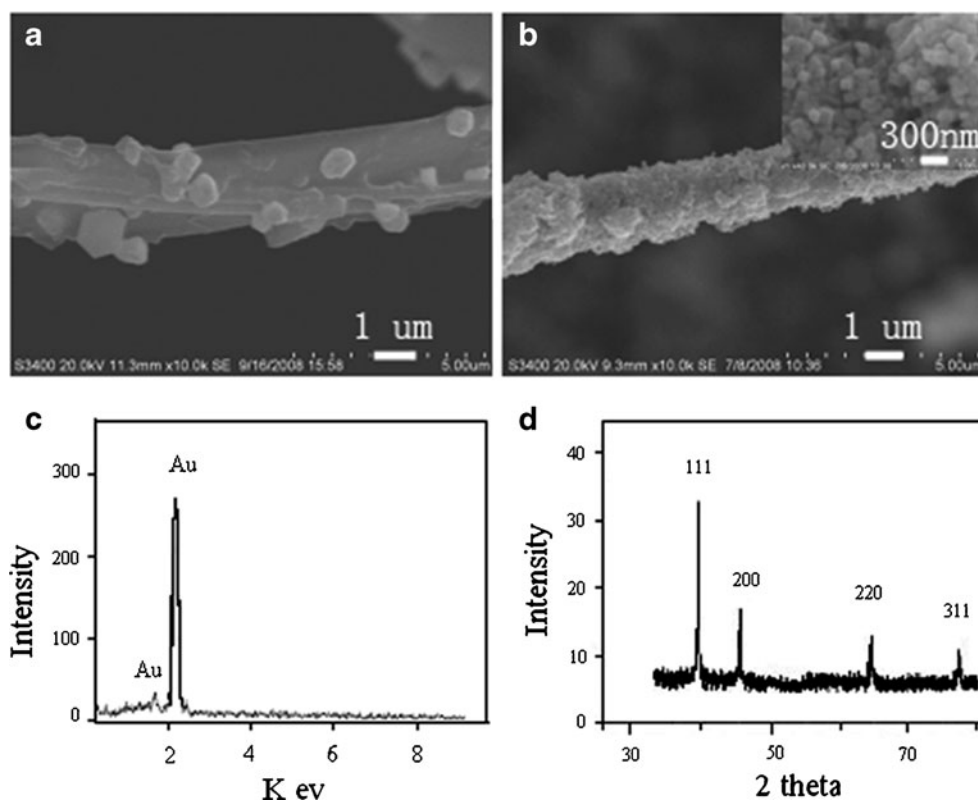


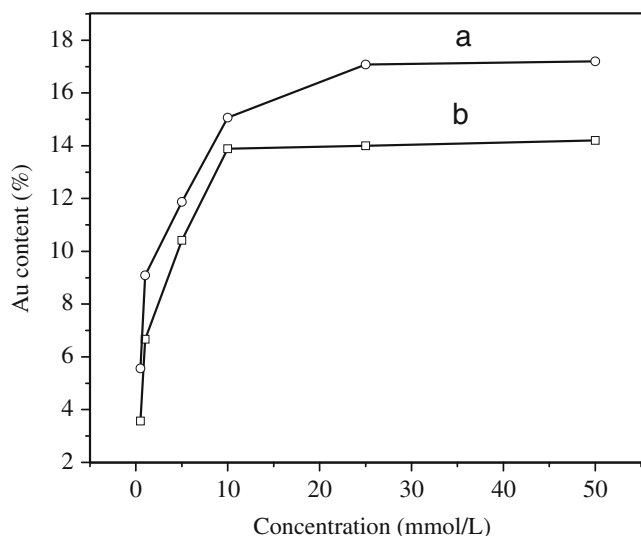
The effect of  $[\text{HAuCl}_4]$  on the density of Au nanoparticles on the au/SPANI-modified SF composite fibers

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

**Fig. 3** The SEM image of pure SF fiber after being immersed in  $\text{HAuCl}_4$  aqueous solution ( $10 \text{ mmol L}^{-1}$ ) for 24 h (a), SEM image (b), EDS spectrum (c), and the recorded XRD pattern (d) of the SPANI-modified SF fiber after being immersed in  $\text{HAuCl}_4$  aqueous solution ( $10 \text{ mmol L}^{-1}$ ) for 24 h. The inset of figure 3b is the magnified image of Au nanoparticles on the surface of Au/SPANI-modified SF composite fiber





**Fig. 4** The Au content on the surface of pure (a) and SPANI-modified SF fiber (b) after being immersed in different concentrations of  $\text{HAuCl}_4$

concentration of  $\text{HAuCl}_4$  and maximal content of Au nanoparticles are  $10 \text{ mmol L}^{-1}$  and 13.5 wt.%, respectively, while the optimal concentration of  $\text{HAuCl}_4$  for the modified SF fiber is about  $25 \text{ mmol L}^{-1}$  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

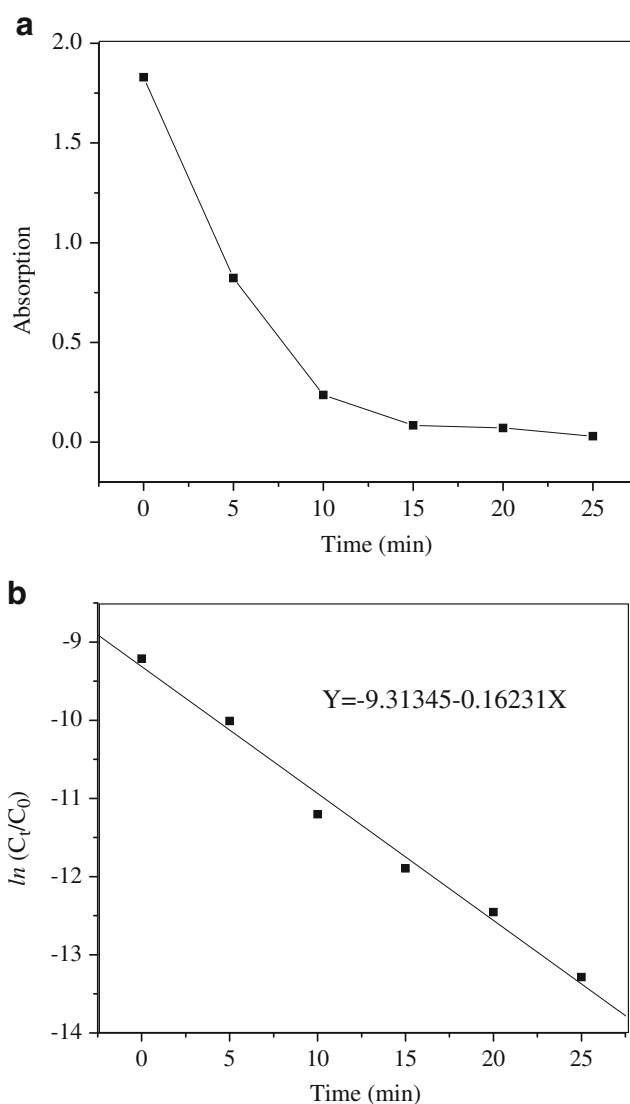
To investigate the catalytic activity of Au/SPANI-modified SF composite fibers, the model catalytic reduction reaction of p-nitrophenol by  $\text{NaBH}_4$  has been investigated. Pure SF does not catalyze this reaction alone. This reaction is easily monitored by following the absorption decrease of 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 ( $K=1.62 \times 10^{-1} \text{ min}^{-1}$ ) 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.

## Conclusions

SF fibers supported with high density of Au nanoparticles have been easily obtained by modifying SF with sulfonated polyaniline (SPANI) and subsequently in situ reduction of  $\text{AuCl}_4^-$  on the fiber surface. In addition to the tyrosine



**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.

**Acknowledgments** We thank Dr. Trevor Keel (World Gold Council) for help with formatting the manuscript, and are grateful for Anhui Provincial Natural Science Foundation (10040606Q08), China Postdoctoral Science Foundation (20110491393), SRTP Fund of Anhui University of Technology (2011013), and the financial support (2010004) from the Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution and reproduction in any medium, provided the original author(s) and source are credited.

## References

1. Stephen A, Hashmi K, Salathé R, Frost TM, Lothar S, Choi JH (2005) Homogeneous catalysis by gold: the current status of C, H activation. *Appl Catal A: General* 291:238
2. Quintanilla A, Butselaar-Orthlieb VCL, Kwakernaak C, Sloof WG, Kreutzer MT, Kapteijn F (2010) *J Catal* 271:104
3. Stephen A, Hashmi K, Frost TM, Bats JW (2002) *Catal Today* 72:19
4. Astruc D, Lu F, Aranzaes JR (2005) *Angew Chem Int* 44:7852
5. Macanás J, Ouyang L, Bruening ML, Muñoz M, Remigy JC, Lahitte JF (2010) *Catal Today* 156:181
6. Ishida T, Watanabe H, Bebeko T, Akita T, Haruta M (2010) *Appl Catal A: General* 377:42
7. Wu H, Zhuo LM, He Q, Liao XP, Shi B (2009) *Appl Catal A: General* 366:44
8. Xia YY, Gao GA, Li YW (2009) *J Biomed Mater Res Part B: Applied Biomaterials* 8:654
9. Xia YY, Lu Y (2008) *Comp Sci Tech* 68:1471
10. Zhang YG, Liu Y (2000) *J Membrane Sci* 177:153
11. Singh A, Shantesh N, Sastry M (2007) *Small* 3:466
12. Dong Q, Su HL, Zhang D (2005) *J Phys Chem B* 109:17429
13. Zhou Y, Chen WX, Itoh H, Naka K, Ni QQ, Yamane H, Chujo Y (2001) *Chem Commun* 44:2518
14. Xia YY, Xiao HP (2010) *Mater Chem Phys* 122:333
15. Xia YY (2010) *J Nanoparticle Res*. doi:10.1007/s11051-010-9926-1
16. Teramoto H, Miyazawa M (2009) *Biomacromolecules* 2005:6
17. Lu LH, Randjelovic I, Capek R, Gaponik N, Yang JH, Zhang HJ et al (2005) *Chem Mater* 17:5731
18. Sarma TK, Chowdhury D, Paul AJ (2002) *Chem Commun* 10:1048
19. Xia YY, Shi ZQ, Lu Y (2010) *Polymer* 51:1328
20. Xia YY, Su Q, Lu Y (2009) *Polymer* 50:5065
21. Xia YY, Xiao HP (2010) *J Mol Catal A: Chemical* 331:35
22. Lee J, Park JC, Song H (2008) *Adv Mater* 20:1523