In-situ Reduced Silver Nanoparticles on Populus Fiber and the Catalytic Application

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Abstract: One kind of composites involved in silver nanoparticles (AgNPs) loading in-situ on natural populus fiber (PF) matrix was prepared by polyamidoamine (PAO) functionalized the cellulose fiber. In which PAO worked as trapping and stabilizing agents chelating silver ions and made it reduced in-situ to obtain AgNPs by borohydride at room temperature. The synthesized composites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Moreover, the composites showed significant catalytic activity $1.87 \text{ s}^{-1} \cdot \text{g}^{-1}$ and repeated usability more than 7 cycles in reducing 4-nitrophenol (4-NP) into 4-aminophenol (4-AP) detected by UV-vis spectrophotometer in aqueous solution due to the surface-enhanced immobility and large amount of AgNPs. The natural cellulose fiber provides a green platform to react and support other noble metals for wide catalytic reactions.

Keywords: populus fibers; polyamidoamine; silver nanoparticles; in-situ reduction

Introduction

Silver nanoparticles (AgNPs) have excited intensive research for their fascinating catalytic properties in diverse organic/inorganic reactions such as reduction of nitroarenes to aromatic amino compound, oxidation of CO to CO₂ and conversion of benzene to phenol owing to their significant catalytic activity, chemical stability and economic viability [1-3]. However, the applications of AgNPs to the above industrial processes are greatly restricted by two challenges. On one hand, AgNPs in small size as a catalyst exhibit excellent catalytic properties due to their high specific surface area and exposed active sites. But, the higher the surface energy is, the easier the nanoparticles reunite [4]. Therefore, a great deal of work has been made to reduce the size of the nanoparticles and simultaneously made efforts to avoid their agglomeration [5-9]. On the other hand, because large amount catalytic procedures are carried out in solution, the noble nanoparticles are difficult to recycle and reuse which result in metal contamination and waste of resources [4]. Hence, many matrixes such as polymer, hydrogels, porous monoliths, metal oxides, silicates, colloids and porous carbon have been selected for loading the AgNPs to the practical applications of catalysts in industries [10-17]. Among these materials, polymeric matrixes are attractive candidates due to a great number of active sites and easy designation in the structure and function [18].

As a natural and renewable polymeric material, cellulose has already been used for depositing AgNPs for its easy obtaining and environment-friendly. Several methods have been developed for the functionalization of natural cellulose with nanoparticles, such as padding, spraying, washing, sonochemical coating, sputtering and dip-coating method, etc [19-23]. Among these methods, chemical modification is the most direct approach to stably loading nanoparticles on the cellulose matrix without adding any stabilizers or dispersants. Cellulose can be easily modified for their chemical structure, microtube morphology and high specific surface area. Some researchers reported the deposition of AgNPs on the surface of modified cellulose through introducing functional groups such as –COOH or –CN, but the loaded AgNPs are few and unstable [24-26]. Moreover, some approaches reported in literatures involved in a complex preparing

process (nitrile-modified cellulose, dissolving, adsorbing silver ions and electrostatic spinning) with the wasteful of noble metals [27]. Thereby, considering the stability and amount of these nanoparticles on cellulose and the stability for reusing, it is necessary to improve the interactions between AgNPs and cellulose. The approach involved cellulose chemically bonded with polymers containing active groups for fixing AgNPs is challenging but practical. In our previous work, we have successfully grafted polyacrylonitrile followed by amidoxime from populus fiber and used to firmly adsorb chromium ions in aqueous solution [18].

Herein, a facile, large loading and rapid approach was developed to fabricate polyamidoxime grafted from populus fibers and in-situ deposited AgNPs without adding stabilizing reagents or dispersants. The microstructure characterization and formation mechanism of the composites were characterized. Meanwhile, the catalytic activity of Ag nanoparticles loaded populus fiber-*graft*-polyamidoxime (PF-*g*-PAO/AgNPs) composites was checked by catalyzing the reduction of 4-nitrophenol (4-NP) by using NaBH₄ as the model reaction. The reusability of PF-*g*-PAO/AgNPs was also detected in the catalytic applications. The composites were certified to be of excellent catalytic properties and can be repeatedly used in this system.

2. Experimental Section

2.1. Materials

Populus fibers (PF) were collected during the blooming period in June from plants in Shandong, China. N,N-dimethylformamide (DMF), ceric ammonium nitrate (CAN), and HNO₃ were purchased from Sigma-Aldrich. Acrylonitrile (AN) was purchased from Tianjin Fuchen Chemical Reagent Factory (China). NaOH and hydroxyl amine hydrochloride (NH₂OH·HCl) were purchased from Chengdu Kelong Chemical Reagent Co, Ltd. (China). NaBH₄ and 4-nitrophenol (4-NP) were purchased from Xi Ya Chemical Reagent. AgNO₃ was purchased from Tianjin Guangfu Chemical Reagent Factory (China). All the chemicals were analytical grade and used without further purification.

2.2. Preparation of PF-g-PAO/AgNPs and their catalytic activity

A two-step preparation process of PF-g-PAO/AgNPs and their application as catalysts to speed up the reduction from 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) are illustrated in Sch 1. The populus fiber-graft-poly(amidoxime) (PF-g-PAO) was synthesized followed by in-situ reducing Ag nanoparticles to result in PF-g-PAO/AgNPs. Then the PF-g-PAO/AgNPs composites were used as a catalyst in catalyzing the reduction reaction from 4-NP to 4-AP.

2.2.1. Synthesis of PF-g-PAO

The PF-g-PAO was synthesized according to our previous paper [18]. Here, the percent of the grafted polyacrylonitrile (PAN) was 125%, which was prepared as follows. 0.8 g purified PF was dispersed into 40 mL NaOH solution (5 wt%) and stored at 25 °C for 4 h for activation and washed thoroughly by water. Then, the activated PF was dispersed in 50 mL water under stirring at room temperature followed by adding initiator (0.0146 mol/L CAN and 0.15 mol/L HNO₃) under N₂ protection for 20 min. Next, 3.6 mL of acrylonitrile monomer was added into the above mixture dropwise to make it polymerized under N₂ for 60 min. The reaction mixture was separated by suction and the precipitate was washed in turn with DMF and water to remove homo-polyacrylonitrile, dried at 60 °C in vacuum for 24 h to result in PF-g-PAN. The percent of grafted PAN (W_{PAN}) from PF was calculated by using the equation $W_{\text{PAN}} (\%) = (W_2 - W_1)/W_1$, where W_1 was the dry weight of PF and W_2 was the dry weight of PF-g-PAN. Finally, this PF-g-PAN was transformed to PF-g-PAO through dispersing it into NaOH/NH₂OH·HCl (1:1 in mole ratio) aqueous solution (50 mL) and stirring for 12 h at 50 °C followed by separating and washing.

2.2.2. Preparation of PF-g-PAO/AgNPs composites

The PF-g-PAO/AgNPs were synthesized by a two-step approach. First, 25 mg PF-g-PAO was dispersed into 100 mL solution of AgNO₃ in water with concentration 3.4×10^{-3} mol/L under stirring for 150 min at 25 °C to reach adsorption equilibrium. Then the precipitate was washed with water to remove the

remaining silver nitrate to result in PF-g-PAO/AgNO₃.

Next, 0.1 g PF-g-PAO/AgNO₃ was dispersed into 20 mL solution of NaBH₄ in water with concentration 0.33 mol/L under stirring for 60 min at 25 °C [15]. Throughout this process, the mixture was separated by suction and the precipitate was washed with water to result in PF-g-PAO/AgNPs.

2.2.3. Catalytic activity of PF-g-PAO/AgNPs

To study the catalyst activity, 12.5 mg PF-g-PAO and PF-g-PAO/AgNPs were dispersed into 50 mL aqueous solution containing 4-NP (0.3 mmol/L) and NaBH₄ (264 mmol/L) at room temperature under stirring constantly. The reduction process was monitored by UV-vis absorption spectra of the reaction mixture at 250 ~ 500 nm wavelength range and every 5 min intervals during the reaction. The rate constants of the reduction reaction were calculated by measuring the absorbance intensity evolution every 5 min at wavelengths of 400 nm for 4-NP. The reaction kinetics equation can be written as equation (1) [9, 15, 17].

$$\frac{d(\ln(A_t/A_0))}{dt} = \frac{d(\ln(C_2/C_1))}{dt} = -k \quad (1)$$

Where A_0 and A_t denote the absorbance of initial 4-NP/NaBH₄ aqueous solution at 400 nm and that depending on time, respectively; C_1 and C_2 denote the initial 4-NP concentration and that depending on time, respectively; k denotes the reaction rate constant of 4-NP reduction.

2.3. Characteristics

Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker-Equinox 55 FT-IR spectrometer by KBr-disk. X-ray photoelectron spectroscopy (XPS) was carried out on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al K α radiation. The morphology of the PF-g-PAO and Ag nanoparticles were characterized by JEOL, JSM-6460LV scanning electron microscopy (SEM). The X-ray diffraction pattern was obtained by using a Shimadzu XRD-7000 Maxima-D diffractometer with a rotating anode and Cu K α radiation ($\lambda = 0.154$ nm). The thermogravimetric analysis was performed on a TGA meter (TG Q-50, America) at heating rate 10 °C/min protected under N₂. UV-vis

spectra were recorded on Varian Cary 50 UV-vis spectrophotometer.

3. Results and Discussion

3.1. Synthetic route of PF-g-PAO/AgNPs

The natural PF is hollow hydrophobic microtube with an external diameter 3 ~ 12 μm and an average length of 4 ± 1 mm [28, 29]. Before using, the lignocellulosic material and wax in PF are removed by purification [18]. Then, polyacrylonitrile (PAN) is grafted from PF through radical polymerization as ceric ammonium nitrate is used as an initiator, followed by transforming the cyano groups in PAN into amidoxime groups to result in PF-g-PAO. Subsequently, when the PF-g-PAO is dispersed into AgNO_3 solution, the $-\text{C}=\text{N}-\text{OH}$ and $-\text{NH}_2$ groups on PF-g-PAO can anchor Ag^+ on the surface of PF denoted as PF-g-PAO/ AgNO_3 and no apparent color change under room temperature. The adsorption mechanism involves physical and chemical chelating procedures, and the adsorption kinetics conforms to pseudo-second kinetics [18, 30], as described in Fig S1 and Table S1. The Ag^+ is reduced into elementary silver (Ag^0) with weak yellow turning into dark brown once NaBH_4 solution is added. The chemical equation of the reaction can be written as equation (2) [11]. Eventually, the PF-g-PAO/AgNPs composites are obtained, as shown in Fig 1.

3.2. Microstructure characterization of PF-g-PAO/AgNPs composites

The XRD profiles of PF, PF-g-PAO and PF-g-PAO/AgNPs are shown in Fig 2. Comparing the profiles of PF and PF-g-PAO, there reveals two peaks at 47.9° and 56.3° respectively on the latter profile, which attribute to polyamidoxime (PAO) introduced through amidoximation of the grafted PAN from cellulose. From the profile of PF-g-PAO/AgNPs, besides of the diffraction peak of amorphous cellulose matrix at 22.7° , three typical diffraction peaks at 38.1° (111), 44.3° (200), and 64.4° (220) indexed to the Ag FCC phase appear [17]. Nevertheless, the diffraction peaks are broad, suggesting that AgNPs formed on

PF-g-PAO are small in size [31], corresponding to SEM images, shown in next part.

The morphologies of PF-g-PAO and PF-g-PAO/AgNPs composites are observed by SEM and the images are shown in Fig 3. The image shown in Fig 3a indicates that the PF-g-PAO has a smooth surface. However, as silver nanoparticles are attached via in-situ reduction, the morphology of the fiber surface observed by SEM as shown in Fig 3b exhibits that there exist small and large AgNPs with an average size ~ 200 nm, as shown in the inserted image in Fig 3b. It is consistent with the XRD profile of the broad three peaks detected at 38.1° , 44.3° , and 64.4° , as shown in Fig 2. The elemental analysis of the PF-g-PAO/AgNPs composites conducted by energy-dispersive X-ray spectroscopy (EDS) reveals the presence of Ag, C, N, and O elements in the composites, as shown in the image in Fig 3c.

To study the thermal stability of AgNPs loading on the surface of PF-g-PAO, the three samples PF, PF-g-PAO and PF-g-PAO/AgNPs are determined by TGA under a nitrogen atmosphere up to 600°C . The TGA and the corresponding DTG curves are shown in Fig 4a and 4b respectively. From the curves of TGA, as shown in Fig 4a, the weight residue of PF is ~ 4.0 wt%, but the residue of PF-g-PAO is ~ 50.0 wt% and that of PF-g-PAO/AgNPs is ~ 53.3 wt%. From the curves of DTG as shown in Fig 4b, the weight loss peak attributed to removal of the physically adsorbed water occurs at 250°C for PF, but that for PF-g-PAO shifts to low temperature 200°C and that for PF-g-PAO/AgNPs disappears. It suggests that the water amount adsorbed by strong polar groups AO in PF-g-PAO is high but easy to remove. However, for PF-g-PAO/AgNPs, since the groups adsorbing water on PF-g-PAO is occupied by the deposited Ag nanoparticles, the amount of the adsorbed water reduces and the peak is too weak to be detected. Moreover, the other weight loss peak corresponding to the decomposition of carbon in cellulose occurs at 354°C for PF, but that for PF-g-PAO exhibits two peaks, one occurs at 252°C corresponding to the decomposition of PAO group and the other occurs at 330°C corresponding to the decomposition of carbon in cellulose. For PF-g-PAO/AgNPs, the decomposition of PAO shifts to temperature 234°C and the decomposition of carbon in cellulose shifts to temperature 320°C . It indicates that the deposition of AgNPs significantly

reduces the carbon decomposition temperature of PAO and PF due to their catalytic oxidation effect [17].

3.3. Adsorption and in-situ reduction mechanism

To reveal the adsorption and in-situ reduction mechanism of AgNPs deposited on PF-*g*-PAO, the FT-IR spectra of PF-*g*-PAO and the complexes before and after Ag⁺ reduced by NaBH₄ are shown in Fig 5. As is shown, comparing with the FT-IR spectrum of PF-*g*-PAO, no new peaks appear on PF-*g*-PAO/AgNO₃ and PF-*g*-PAO/AgNPs FT-IR spectra, there is only the transmission intensity difference. The transmission intensity of binds at 915, 1591 and 1649 cm⁻¹ corresponding to -N-OH stretching, C=N stretching and N-H bending may be influenced by the formation of metal-ligand complex ring, which is a strong evidence for adsorption and in-situ reduction mechanism of Ag⁺ on PF-*g*-PAO (as shown Sch 1) [32, 33]. On the other hand, the fact that no new peaks exhibit indicates that the preparation of PF-*g*-PAO/AgNPs involved in adsorption and reduction of Ag⁺ procedures have no obvious damage on the chemical structure of PF-*g*-PAO.

Furthermore, to make clear the surface component and reduction mechanism of Ag⁺ adsorbed on PF-*g*-PAO, XPS analysis is carried out. Fig 6a shows the XPS survey spectra of surface elements on PF-*g*-PAO and PF-*g*-PAO/AgNPs, mainly consisting of carbon, oxygen, nitrogen and silver, corresponding to EDS, shown in Fig 3c. The observed spectra of N 1s, O 1s, and Ag⁰(3d) are simulated using two-component Gaussian-Lorentzian sum functions, as shown in Fig 6b, 6c, and 6d, respectively. The N 1s XPS spectra as shown in Fig 6b show the difference between PF-*g*-PAO and PF-*g*-PAO/AgNPs. The N 1s spectrum of PF-*g*-PAO exhibits two peaks at the binding energies of 399.79 eV and 399.07 eV, which belong to nitrogen atoms in C=N-OH and C-NH₂ groups, respectively [18, 34]. However, in the case of PF-*g*-PAO/AgNPs, the relative intensity of C-NH₂ greatly decreased and the position of C=N-OH shifts to lower binding energy 399.50 eV, indicative of the increase in electron density for the nitrogen atoms. It demonstrates that the Ag⁺ interacts with not only C=N-OH but also C-NH₂ of the amidoxime group [34].

The O 1s XPS spectra of PF-*g*-PAO as shown in Fig 6c exhibits three peaks at the binding energy of 533.56 eV, 532.66 eV and 531.78 eV, corresponds to the oxygen atoms in adsorbed H₂O, terminal –OH, and bridging –OH [18, 34]. In the case of the spectra for PF-*g*-PAO/AgNPs, the relative intensity of adsorbed H₂O and terminal –OH decrease largely, while the relative intensity of bridging –OH increases and its position shifts to lower binding energy 531.60 eV. The results suggest that the formation of AgNPs mainly depends on the terminal –OH existed in –C=N–OH, which can bind Ag⁺ and transform into bridging –OH corresponding to the increasing of relative intensity of bridging –OH. In addition, the amount of adsorbed H₂O decreases due to the coordinative bond between hydroxyl and the reduction Ag⁺, which is consistent with the conclusion from TGA and DTG.

To better illustrate the species and valence of the bond Ag particles, the Ag3d XPS spectrum of PF-*g*-PAO/AgNPs is shown in Fig 6d. It shows two peaks at 374.10 eV and 368.10 eV, which belong to the main component of Ag⁰ corresponding to the AgNPs formed in the PF-*g*-PAO/AgNPs composites [17].

3.4. Catalytic application

4-nitrophenol (4-NP) as a serious toxic chemical can be reduced to form 4-aminophenol (4-AP) which is an important intermediate chemical in drugs and dye industry [11]. Therefore, choosing the reduction of 4-nitrophenol (4-NP) as a standard model reaction to evaluate the catalytic performance of PF-*g*-PAO/AgNPs is very significant. The aqueous solution of 4-NP in clear yellow color turns into yellow-green slowly and releases bubbles slowly when NaBH₄ is added. The catalytic procedure of PF-*g*-PAO/AgNPs is monitored by UV-vis spectroscopy, as shown in Fig 7a, the absorbance of 4-NP occurs at a wavelength 400 nm, and that of 4-AP occurs at 317 nm. With the addition of PF-*g*-PAO/AgNPs into the fresh 4-NP/NaBH₄ aqueous solution, the color of the solution fades rapidly from yellow-green to transparent depending on time due to the decreasing of 4-NP molecules, and bubbles release fast from the surface of PF-*g*-PAO/AgNPs. Meanwhile, a peak at 317 nm appears with the decreasing of the peak at 400 nm, indicative of the rapid occurrence of the reaction in the system. After 45 min, the peak at 400 nm disappears,

which indicates that the 4-NP is reduced into 4-AP completely (Fig 7a) [8, 17]. As a comparison, PF-g-PAO is also used as a catalyst in reduction of 4-NP in aqueous solution and the procedure is also monitored by UV-vis spectroscopy, as shown in Fig 7b. Obviously, with the addition of PF-g-PAO, the absorbance of 4-NP changes slowly and less 4-AP is detected, similar to no catalyst addition, indicative of no catalysis effect at all. The expected catalytic mechanism of the composite PF-g-PAO/AgNPs can be described as AgNPs adsorb BH_4^- ions and 4-NP molecules and then transport electrons from BH_4^- to 4-NP, 4-NP is transformed into 4-AP accompanying with releasing large amount of H_2 . Meanwhile, NaBH_4 in aqueous solution spontaneously reduces water to H_2 and further prevents the aerial oxidation of 4-AP [8, 11, 17]. The phenomenon can be supported by the chemical equation (3).

In order to demonstrate the catalytic activities of PF-g-PAO and PF-g-PAO/AgNPs more clearly, the reaction kinetics is depicted by the time-dependent absorption spectra. The results show that it is consistent with pseudo-first-order kinetics because of $\ln(A_t/A_0)$ decreasing linearly with reaction time. As shown in Fig 8a, the nearly flattened line indicates that pure PF-g-PAO is almost ineffective in 4-NP reduction reaction and can be ignored. To compare catalytic performance with previously reported catalysts employed for 4-NP reduction, k' ($k' = k/\text{g}$) is introduced which normalizes the rate constant k by mass (g) of the catalyst. Apparently, PF-g-PAO/AgNPs exhibit excellent catalytic property with a catalytic activity about $1.87 \text{ s}^{-1} \cdot \text{g}^{-1}$, which is relatively higher than the previous reports of AgNPs based catalysts such as $1.54 \text{ s}^{-1} \cdot \text{g}^{-1}$ (Ag/FeO_x, in ref 12), $0.25 \text{ s}^{-1} \cdot \text{g}^{-1}$ (micron-SiO₂@nano-Ag, in ref 14).

Stability and recyclability of the catalyst have great importance for the practical applications of catalysts in industry. Hence the regeneration of the catalyst is also significance to study in this work. After each cycle of the reaction, the catalyst is separated from the solution and washed with water, and then used at intervals of two hours for the next cycle. The catalyst can be reused seven cycles without decreasing in catalytic activity as shown in Fig 8b.

4. Conclusions

In summary, the composites of AgNPs deposited on the surface of natural cellulose fiber are prepared by employing amidoxime functionalized cellulose fiber and AgNPs in-situ reduced by sodium borohydride at room temperature. SEM, EDS, XRD and TGA results suggest that the obtained AgNPs ~ 200 nm in size with a moderate thermal stability. The AgNPs provide sufficient active sites for reaction and ensure the effective diffusion and transport of reactants such as BH_4^- and 4-NP and thereby accelerate the reaction rate. The novel catalyst has been demonstrated with excellent catalytic activity and stability in 4-nitrophenol reduction reaction at room temperature. It is one of the most efficient and economical approach that converts harmful organic waste into valuable intermediate chemicals. We rationally deem that any kind of natural cellulose can replace the populus fibers used here and the composites based on cellulose may be promising candidates as selective catalysts.

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Figure Captions

Sch 1. Schematic illustration of the synthesis procedure of the PF-g-PAO/AgNPs composites and their catalytic function in the reduction reaction of 4-nitrophenol.

Fig 1. The color comparison of the synthesized PF-g-PAO, PF-g-PAO/AgNO₃, and PF-g-PAO/AgNPs.

Fig 2. XRD profiles of PF, PF-g-PAO and PF-g-PAO/AgNPs composites.

Fig 3. SEM images of PF-g-PAO (a), PF-g-PAO/AgNPs composites (b), and (c) the corresponding EDS image of that in (b).

Fig 4. TGA (a) and the corresponding DTG curves (b) of PF, PF-g-PAO, and PF-g-PAO/AgNPs.

Fig 5. Typical FT-IR spectra of PF-g-PAO, PF-g-PAO/AgNO₃ and PF-g-PAO/AgNPs.

Fig 6. (a) Typical XPS survey spectra for PF-g-PAO and PF-g-PAO/AgNPs. High resolution XPS spectra of (b) N1s and (c) O1s and (d) Ag3d for PF-g-PAO/AgNPs and PF-g-PAO/AgNPs, respectively.

Fig 7. UV-vis spectra of the reduction of 4-NP in aqueous solution recorded every 5 min using PF-g-PAO/AgNPs (a) and PF-g-PAO (b) as the catalysts, [NP]: 0.3 mmol/L, [NaBH₄]: 264 mmol/L, catalysts amount: 0.25 mg/mL.

Fig 8. Plots of $\ln[A_t/A_0]$ versus reaction time for the reduction of 4-NP with NaBH₄ over PF-g-PAO and PF-g-PAO/AgNPs (a) and catalyst reusability of PF-g-PAO/AgNPs (b). [NP]: 0.3 mmol/L, [NaBH₄]: 264 mmol/L, catalysts amount: 0.25 mg/mL.

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In-situ Reduced Silver Nanoparticles on Populus Fiber and the Catalytic Application

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One kind of composites involved in silver nanoparticles (AgNPs) loading in-situ on natural populus fiber (PF) matrix was prepared by polyamidoamine (PAO) functionalized the cellulose fiber. In which PAO worked as trapping and stabilizing agents chelating silver ions and made it reduced in-situ to obtain AgNPs by borohydride at room temperature. The synthesized composites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Moreover, the composites showed significant catalytic activity $1.87 \text{ s}^{-1} \cdot \text{g}^{-1}$ and repeated usability more than 7 cycles in reducing 4-nitrophenol (4-NP) into 4-aminophenol (4-AP) detected by UV-vis spectrophotometer in aqueous solution due to the surface-enhanced immobility and large amount of AgNPs. The natural cellulose fiber provides a green platform to react and support other noble metals for wide catalytic reactions.