Metal Nanoparticles on Natural Cellulose Fibers: Electrostatic Assembly and In Situ Synthesis

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ABSTRACT The conformal deposition of metal nanoparticles (Au, Pd, and Pt) onto natural cellulose fibers using two chemical strategies is reported. The driven mechanism responsible for the high surface coverage of the substrates was identified as the electrostatic interactions between the positively charged cellulose and the either negatively charged nanoparticles or negative metal complex ions. The natural cellulose fibers were rendered cationic by grafting ammonium ions, using an epoxy substitution reaction, to the abundant hydroxyl groups present in cellulose molecules. The first method involved the electrostatic assembly of citrate-stabilized metal nanoparticles directly onto the cationic surfaces of cellulose. The second method involved the adsorption of negative metal complex ions onto the cationic cellulose followed by a reduction reaction. The attained metal nanoparticles bound with cellulose fibers were characterized by electron microscopy (TEM and SEM) and energy-dispersive X-ray spectroscopy (EDX). Both pathways generated metal nanoparticles with high packing densities on the cellulose substrates even when very dilute solutions of metal colloids or metal salts were used. Achieving high surface coverage with low-concentration precursor solutions may open an avenue for the production of flexible catalytic mantles or highly functionalized textile substrates.

KEYWORDS: natural−synthetic materials interface • cellulose fibers • cationic cellulose • cotton • metal nanoparticles • electrostatic assembly • in situ synthesis

INTRODUCTION

Metal nanoparticles have been supported on diverse substrates such as silica, metals or metal oxides, carbon, and polymers, tailored by their specific optical, electronic, catalytic, magnetic, or sensor applications (1−3). For example, carbon nanotubes and nanofibers have been among the different types of supports used for depositing catalytic metal nanoparticles (3). Natural cellulose fibers with nanoporous surface features have also been recently reported as substrates for the in situ synthesis of noble metal nanoparticles (4). The metal ions were impregnated into the cellulose fibers by taking advantage of their inherent porosity followed by reduction of these ions into metal nanoparticles. The nanoporous structure and the high oxygen density of cellulose fibers appear to form an effective nanoreactor suitable for the in situ synthesis and stabilization of metal nanoparticles (4). A limiting feature of that approach, as revealed by the authors, is that this method is applicable only to porous cellulose fibers (4).

Our group have recently demonstrated layer-by-layer deposition of polyelectrolytes on the surfaces of cationic natural cellulose substrates (5, 6). The cationically charged cellulose substrates were produced through chemical modification of cellulose molecules using (2,3-epoxypropyl)trimethylammonium chloride (EPTAC). The reaction efficiency of cellulose cationization has been studied previously (7). In this process, the positive ammonium ions are grafted to the

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Scheme 1. Molecular Structure of Cationic Cellulose
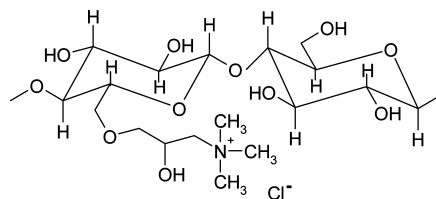
cellulose molecules through two reactions: the formation of the epoxide EPTAC by reacting (3-chloro-2-hydroxypropyl)-trimethylammonium chloride with sodium hydroxide in solution and the reaction of this epoxide (EPTAC) with the hydroxyl groups of cellulose (7). The structure of cationic cellulose is shown in Scheme 1. It is feasible that these surface cationic charges, induced by the ammonium ions onto the cellulose substrates, can be used not only to coat the substrate with layers of polyelectrolytes but also to conformally deposit moieties such as metal nanoparticles or carbon nanotubes, as was recently demonstrated by Kotov et al. (8)

In this paper, we describe two approaches toward the conformal deposition of metal nanoparticles on the surface of natural cellulose fibers. The approaches take advantage of the electrostatic interactions between cationically modified cellulose surfaces and negatively charged metal nanoparticles or negative metal complex ions and are applicable to both porous and nonporous cellulose fibers. In the first pathway, metal nanoparticles capped with negative citrate ions were synthesized and assembled onto cationic cellulose surfaces by electrostatic interactions. In the second pathway,

negative metal complex ions were adsorbed onto cationic cellulose substrates followed by subsequent reduction. Both approaches yielded high surface coverage of the cellulose substrates by the metal nanoparticles.

2. EXPERIMENTAL SECTION

Materials. Standardized TIC-400 woven cotton fabrics obtained from Textile Innovators, Inc. (Windsor, NC), were used as sources of cellulose substrates. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), sodium tetrachloroaurate dihydrate ($NaAuCl_4 \cdot 2H_2O$), sodium tetrachloropalladate (Na_2PdCl_4), sodium borohydride ($NaBH_4$), sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich and used as received. (3-Chloro-2-hydroxypropyl)trimethylammonium chloride was obtained from The Dow Chemical Company. All solutions were prepared using distilled/deionized water with a resistance of ~18.2 M$\Omega \cdot$ cm.

Preparation of Cationic Cellulose. Aqueous solutions of (2,3-epoxypropyl)trimethylammonium chloride (EPTAC) were prepared by reacting (3-chloro-2-hydroxypropyl)trimethylammonium chloride with NaOH. The cotton specimens were immersed into the EPTAC solutions, allowing the epoxide to react with the hydroxyl groups of cellulose, grafting ammonium ions to the cellulose molecules and hence rendering the fabrics cationic. The procedure for cationization of cellulose substrates has been described in detail in our previous reports (5, 6). The modified fabrics were cut into pieces of approximately 3 cm × 4 cm pieces with a weight of around 0.5 g.

Synthesis of Citrate-Stabilized Au or Pt Nanoparticles. Au nanoparticles were synthesized by employing the well-known Turkevich method (9). A 45 mL aqueous solution of $HAuCl_4 \cdot 3H_2O$ (19.7 mg) was heated to boiling. A total of 5 mL of 1 % or 2 % aqueous sodium citrate was introduced to the gold salt solution under vigorous stirring. Continuous boiling for 1 h completed the formation of the gold colloids, producing a stable solution with a wine-red color.

The solution of Pt nanoparticles was prepared following a previously reported protocol with minor modifications (10). A total of 45 mL of a H_2PtCl_6 solution prepared by dissolving 26.5 mg of $H_2PtCl_6 \cdot 6H_2O$ in water was mixed with a 5 mL solution of sodium citrate (73.5 g). This leads to a molar ratio of H_2PtCl_6 to sodium citrate of 1:5 in the solution. The mixture was heated to reflux, and it was kept refluxing for 1 h. A solution with a black color was yielded after reflux.

Assembly of Metal Nanoparticles on Cationic Cellulose Substrates. Pieces of the cationic cotton fabric and several cationic cotton yarns were immersed into a beaker containing 50 mL of either a solution of Au nanoparticles or a solution of Pt nanoparticles. After 24 h of soaking, the cotton specimens were removed from the container and rinsed thoroughly with water to remove loosely bound metal nanoparticles. The fabrics and yarns were dried in air before further analysis.

In Situ Synthesis of Metal Nanoparticles on Cationic Cellulose Substrates. Negative metal complex ions were adsorbed onto cationic cellulose substrates by immersing the cotton specimens in a 5 mM aqueous solution (50 mL) of $NaAuCl_4$ or Na_2PdCl_4 for 24 h. After removal of the samples from the metal salt solution, they were rinsed with water three times in order to remove the excess ions. The fabrics or yarns were then immersed in a 50 mM $NaBH_4$ solution (50 mL) for 10 min in order to reduce the metal ions to zero-valence metal. After reduction, the samples were rinsed copiously with water. The obtained specimens were dried in air prior to characterization.

Characterization. Transmission electron microscopy (TEM) imaging of cross sections of cotton fibers was achieved using a Hitachi H-7000 (100 kV) or a JEOL 1200EX (120 kV). Samples

FIGURE 1. Cotton fabrics decorated with (a) Au nanoparticles synthesized using 1 % citrate and (b) Pt nanoparticles. Both specimens were produced by electrostatic assembly.

for TEM imaging were prepared by embedding the cotton yarns coated with nanoparticles in a Spurr resin and hardening the resin at 60 °C for 16 h. The embedded specimens were cross-sectioned using an ultramicrotome equipped with a diamond knife. Cross sections of the embedding block with thicknesses of ~100−150 nm were collected on TEM copper grids and dried before imaging.

Field-emission scanning electron microscopy (FESEM) was performed on a LEO 1550 microscope, using an in-lens detector. The specimens were coated with a thin layer of carbon (~20−30 nm) prior to FESEM imaging. Elemental characterization was performed using an energy-dispersive X-ray spectroscope attached to the LEO microscope.

RESULTS AND DISCUSSION

Direct Assembly of Metal Nanoparticles. A commonly used method for the solution-phase synthesis of metal nanoparticles is chemical reduction of metal salts. The synthesis involves using a soluble metal salt as a precursor, a reducing reagent, and a stabilizer. In the synthesis of metal nanoparticles by citrate reduction, citrate groups serve in the dual roles of both reducing agent and stabilizer. The use of citrate groups imparts negative surface charges to the nanoparticles from weakly bound citrate ions, which prevent agglomeration of nanoparticles in solution (11, 12). The negative charges on the surfaces of metal nanoparticles have been employed to immobilize nanoparticles on various substrates (13) or to construct multiple layers of polyelectrolytes/nanoparticles via electrostatic self-assembly (14).

Cationic cellulose substrates, which are prepared through the grafting of positive ammonium ions, provide an opportunity for the electrostatic deposition of metal nanoparticles with negative charges onto cellulose substrates. Herein, Au nanoparticles synthesized via citrate reduction were used as the first example to demonstrate the electrostatic assembly of nanoparticles on natural cellulose fibers. Au nanoparticles were synthesized by the addition of 1 % or 2 % citrate to a $HAuCl_4$ solution under boiling, as described in the Experimental Section. After immersion of the cationic cotton fabric into a Au colloidal solution, the color of the fabric changed from white into purple, resulting from plasmon absorption of the assembled Au nanoparticles on the substrates, as shown in Figure 1a. The purple color of the Au-cellulose specimen prepared using 2 % citrate in the synthesis of Au nanoparticles was deeper than the one obtained using 1 % citrate. After the first cycle of deposition,
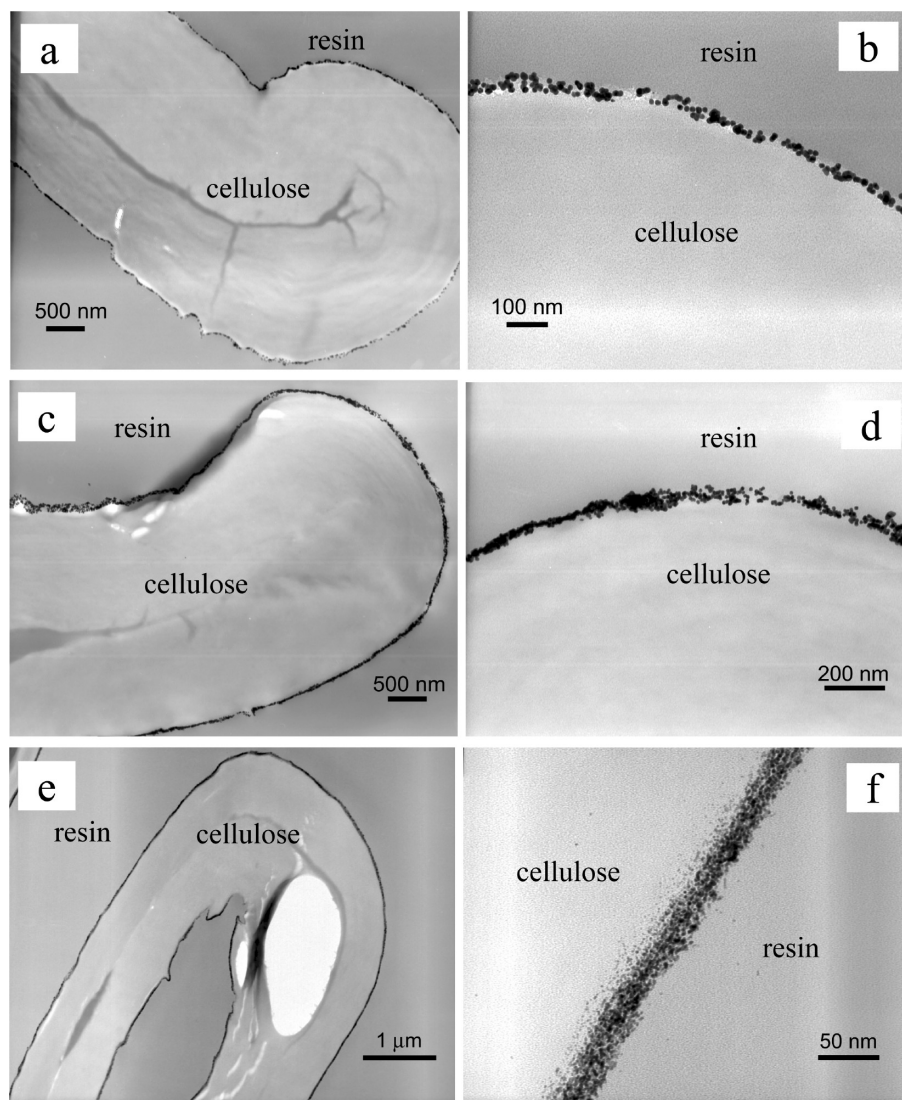
FIGURE 2. TEM images of the cross sections of cotton fibers coated with (a and b) Au nanoparticles synthesized using 1% citrate, (c and d) Au nanoparticles synthesized using 2% citrate, and (e and f) Pt nanoparticles.

the solution of Au nanoparticles synthesized using 1% citrate was stable and reusable for a second cycle of deposition, whereas the solution of Au nanoparticles synthesized using 2% citrate became unstable and aggregated nanoparticles formed along the wall of the vessel after the solution sat for a short period of time.

A TEM image of a cotton fiber coated with Au nanoparticles synthesized using 1% citrate (Figure 2a) shows a dark line of nanoparticles surrounding the fiber. A higher magnification image in Figure 2b reveals that the spherical nanoparticles with an average size of ~10−15 nm assemble along the outer edges of the cotton fiber. A cotton fiber coated with Au nanoparticles that were synthesized using 2% citrate is shown in Figure 2c,d. The packing density of Au nanoparticles on the surface of fibers appears to increase as the concentration of citrate in the precursor solutions increased from 1% to 2%. This behavior is likely caused by the enhanced negative surface potential of Au nanoparticles capped with more citrate groups (15). Although the electrostatic repulsion between assembled Au nanoparticles is increased by the presence of more citrate groups, this effect

appears to be counterbalanced by a greater attraction of the nanoparticles to the positively charged cellulose surfaces (15). The specimens were also imaged using FESEM, as illustrated in Figure 3, to assess the surface packing of the nanoparticles on the cotton fabrics. Well-dispersed nanoparticles were found to pack with high surface coverage on the fiber's surface. The nanoparticles in the FESEM images appear larger than those in TEM images because of the presence of a top layer of carbon coating required for SEM imaging purposes. Energy-dispersive X-ray spectroscopy (EDX) spectrum in Figure 4, which was collected from the sample imaged by FESEM, clearly shows the presence of a Au signal peak, indicating the effectiveness of the electrostatic assembly of the particles on the surface of the cotton fibers. The purple color of Au−cotton also suggests the presence of Au nanoparticles on the cotton surface.

The method followed to coat the cotton fibers with citrate-capped Au nanoparticles was also extended to the coating of Pt nanaparticles. The solution of Pt nanoparticles was synthesized by citrate reduction using a 1:5 molar ratio of precursor H_2PtCl_6 to sodium citrate as described in the
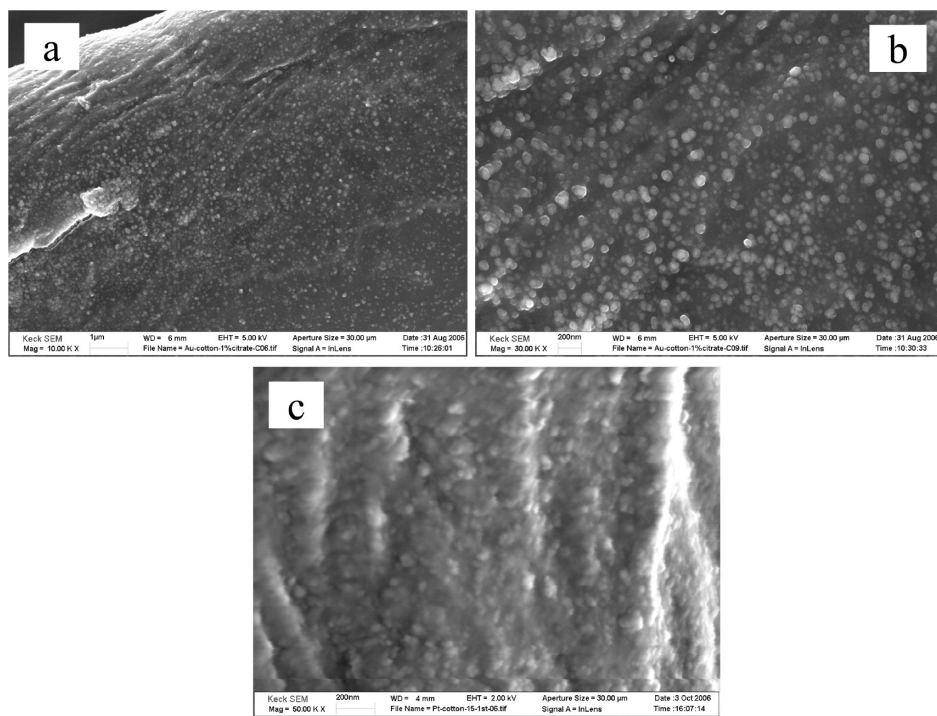
FIGURE 3. (a and b) FESEM images of the surface of a cotton fiber coated with Au nanoparticles. Au nanoparticles were synthesized using 1% sodium citrate. (c) FESEM image of the surface of a cotton fiber coated with Pt nanoparticles.
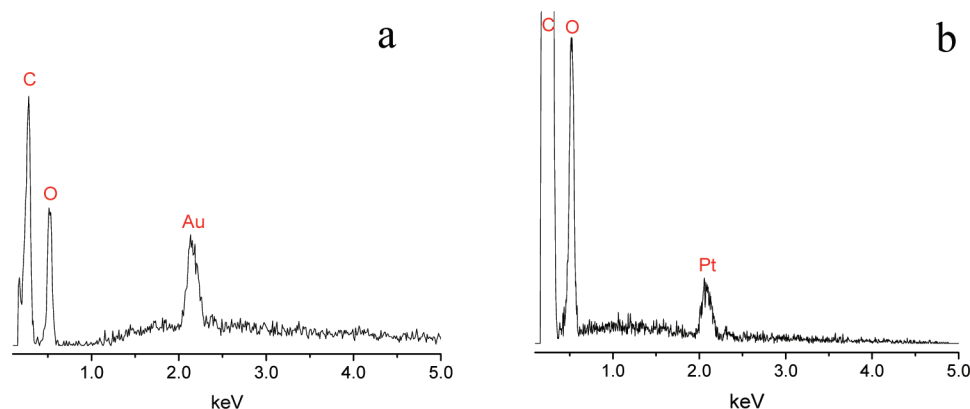

FIGURE 4. EDX spectra of (a) a cotton fiber coated with Au nanoparticles and (b) a cotton fiber coated with Pt nanoaprticles. The presence of the Au and Pt peaks indicate the effectiveness of electrostatic assembly of the particles on the surface of cotton fibers.

Experimental Section. Immersion of white cotton fabrics into the black Pt solution for 24 h produced a specimen with a gray color, indicating the successful deposition of Pt nanoparticles (Figure 1b). The anchoring of Pt nanoparticles on the cationic cellulose surface is evident in the TEM images of Figure 2e,f. In Figure 2e, a dark line of nanoparticles is observed around the edge of the fiber. A higher magnification image in Figure 2f presents closely packed Pt nanoparticles with an average size of ~2−5 nm. Perhaps the small size of the Pt nanoparticles, compared with that of the Au nanoparticles, allows a higher packing of nanoparticles on the surface of the cotton. It is interesting to notice that Au nanoparticles (Figure 2b,d) were not able to penetrate the lumen of the fibers, whereas Pt nanoparticles (Figure 2f) seemed to be effective in coating the lumen or interior of the fibers because of their smaller size. The examination using FESEM, shown in Figure 3c, cannot provide a clear assessment of the surface coverage of the Pt nanoparticles

because the small Pt particles were buried underneath the carbon coating. The EDX spectrum in Figure 4b, however, illustrates the presence of Pt on the surface of the cellulose fiber. The specimen also exhibited a grayish color brought about by the plasmon absorption of Pt nanoparticles. After the first deposition cycle, the solution of Pt nanoparticles remained stable, and it was used for coating of a second cationic cotton sample. The second specimen became a slightly lighter gray color than the first one, indicating a decrease in the packing density of the Pt nanoparticles. This behavior was expected as the concentration of the Pt nanoparticles in the solution decreased after the first deposition.

In addition to Au and Pt, several other metal nanoparticles have been synthesized either by using citrate as a reducing agent and a stabilizer or by employing other reducing agents and citrate or other negative ions as stabilizers. Examples include the synthesis of Ag nanoparticles from $AgNO_3$ (16) and of Pd nanoparticles from H_2PdCl_6 (17). The versatility
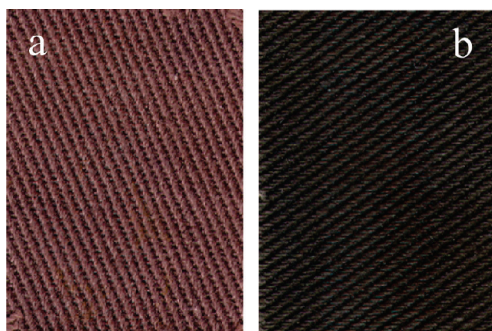
FIGURE 5. Cotton fabrics decorated with (a) Au nanoparticles and (b) Pd nanoparticles. Both specimens were prepared by the adsorption of metal ions followed by chemical reduction.

of using citrate or other negative ions as stabilizers in the synthesis of metal nanoparticles allows the electrostatic assembly of the nanoparticles onto the surfaces of cationic cellulose substrates by a simple procedure.

In Situ Synthesis of Metal Nanoparticles. The second method described in this paper relates to the in situ synthesis of the nanoparticles onto the surface of the cellulose substrates. The in situ synthesis method was initiated by adsorption of negative metal complex ions onto the cationically modified cellulose surfaces. Chemical reduction of the metal ions led to the formation of metal nanoparticles on the substrates. Compared with the direct assembly of preformed metal colloids presented in the previous section, the in situ synthesis is absent of protective citrate ions on the surfaces of nanoparticles. This may be of technical importance because it was suggested that the surface coverage of organic species may decrease the reactivity of the nanoparticles in some applications such as catalysis (18).

Immersion of the cationic fabric into a yellow $NaAuCl_4$ (5 mM) solution for 24 h changed the color of the specimen from white to yellow, indicating the adsorption of $AuCl_4^-$ ions on the substrate. The sample was rinsed with water several times to remove loosely bound $AuCl_4^-$ ions. After reduction of the ions with $NaBH_4$ (50 mM), the yellow color of the fabric turned into brownish purple because of the formation of Au aggregates. The brownish-purple color can be attributed to the surface plasmon absorption of Au nanoparticles. The cellulose specimen decorated with the in situ synthesized Au nanoparticles is shown in Figure 5.

The formation of Au nanoparticles on the cellulose fibers was evident on TEM observations. A TEM image of the fiber's cross section (Figure 6a) shows that the Au nanoparticles contour the edge of the cotton fiber. The particles were found to be nonspherical with a large size distribution and have an average size of ~8−10 nm measured from a high-magnification TEM image (Figure 6b). The packing of the individual nanoparticles on the surface of a cellulose fiber was assessed by FESEM, as shown in Figure 7. EDX analysis confirms the presence of the Au peak and the absence of the Cl peak, indicating the complete reduction of the $AuCl_4^-$ ions.

A similar procedure was implemented to coat the cotton specimens with Pd nanoparticles. The formation of Pd nanoparticles is of particular interest because of various catalytic applications of the Pd metal. In this case, a 5 mM Na_2PdCl_4 solution was used as a Pd precursor. The $PdCl_4^{2-}$ ions were adsorbed onto the cationic surface of cellulose by immersion. After reduction with $NaBH_4$, the brownish color of $PdCl_4^{2-}$ on the cellulose substrate changed into black as a result of the formation of Pd nanoparticles. Similar to Au
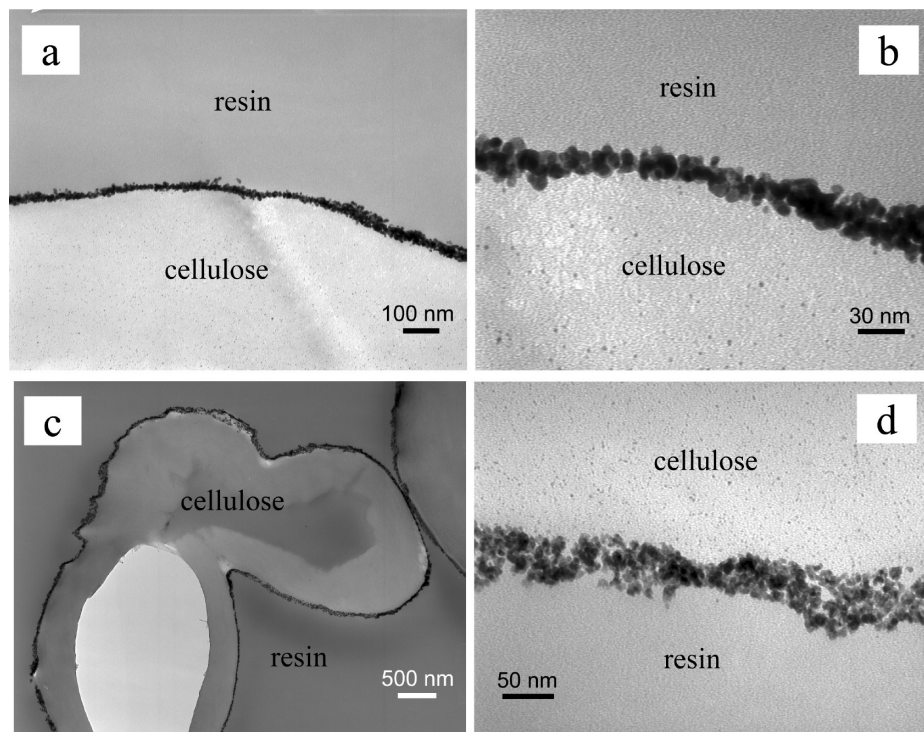

FIGURE 6. TEM images of cross-sectional cellulose fibers with (a and b) Au nanoparticles and (c and d) Pd nanoparticles obtained by in situ synthesis.
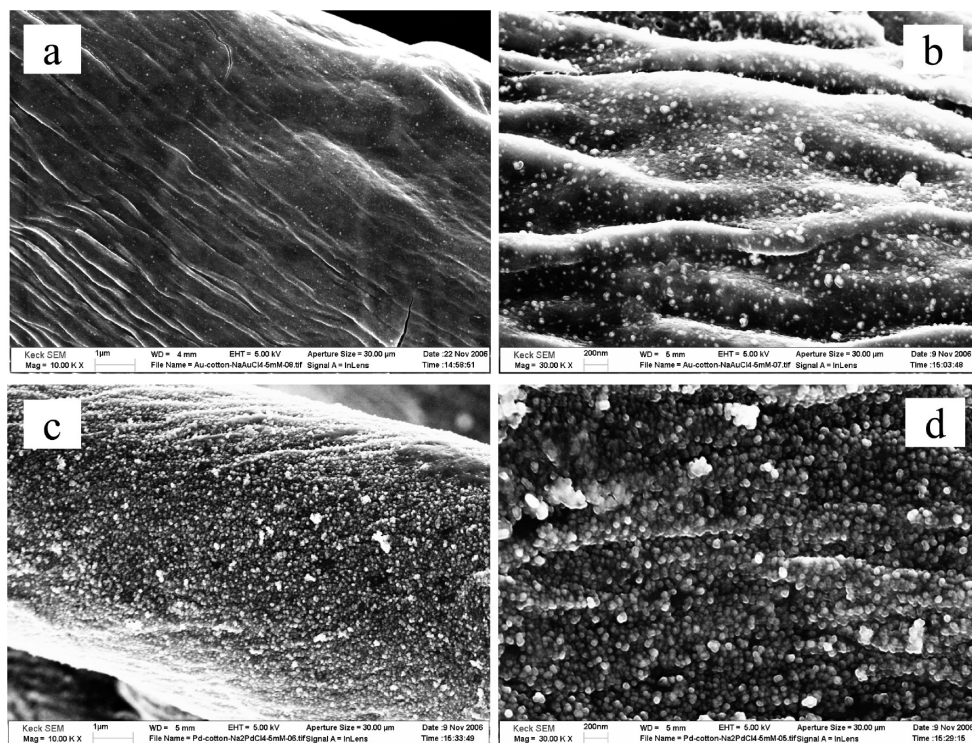
FIGURE 7. FESEM images of a cotton fiber coated with (a and b) Au nanoparticles and (c and d) Pd nanoparticles using in situ synthesis.
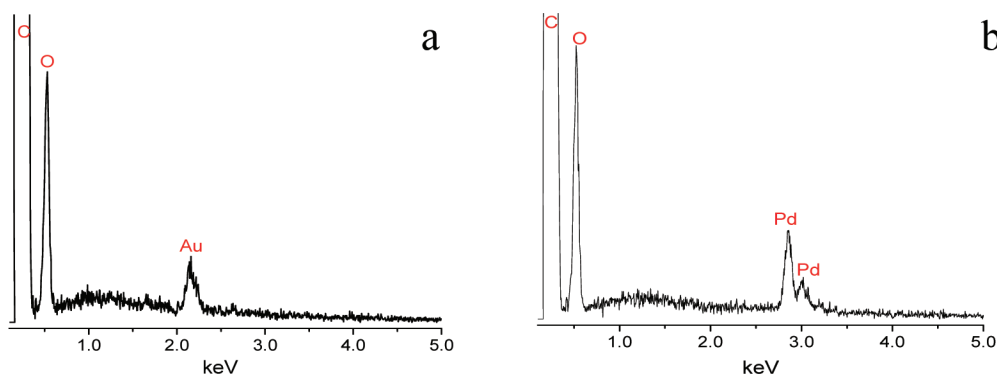

FIGURE 8. EDX spectra of (a) Au nanoparticles and (b) Pd nanoparticles synthesized on cationic cotton fibers. The spectra show the presence of metal peaks and the absence of Cl peaks, indicating complete reduction of the precursor metal ions.

nanoparticles, a dark line composed of individual nanoparticles can be observed in the TEM images in Figure 6c,d. The particles were found to be of irregular shape and have a large size distribution. The packing density of Pd nanoparticles on the cellulose fibers appears to be higher than that of the Au nanoparticles, as observed from the FESEM images in Figure 7c,d. This is likely caused by the stronger interaction between the cationic cellulose and the −2-charged $PdCl_4^{2-}$ ions than that between cationic cellulose and −1-charged $AuCl_4^{-}$ ions. The EDX spectrum collected on the FESEM image (Figure 8b) confirms the presence of Pd peaks and the absence of Cl peaks, indicating the complete reduction of $PdCl_4^{2-}$ ions. The Pd nanoparticles synthesized on cellulose substrates were found to be catalytically active. Using the coated Pd nanoparticles as seeds, we have achieved electroless plating of copper particles and layers on the surface of cotton fibers, hence improving their electrical conductivity.

CONCLUSIONS

The deposition of metal (Au, Pt, and Pd) nanoparticles on the surface of natural cellulose fibers was demonstrated. It was achieved using two pathways: electrostatic assembly of preformed negatively charged metal nanoparticles and in situ synthesis of metal nanoparticles on the cationic cotton fabrics. Both methods yielded high surface coverage of the fibers. The grafting of ammonium ions onto cellulose molecules rendered cationic charges on the surface of cellulose substrates, allowing deposition of metal species with opposite charges. The two procedures are simple and compatible with existing wet-processing equipment available in textile processing. The procedures and the general preparation methods described here promise extended use of the approaches for the deposition of various metal nanoparticles or other types of negatively charged particles onto cationically modified cellulose substrates. These findings have important technological implications because they can open

a new avenue to produce flexible catalytic mantles as well as multifunctional fabrics.

REFERENCES AND NOTES

(1) Rotello, V. M. *Nanoparticles: Building Blocks for Nanotechnology*; Kluwer Academic Publishers: New York 2004.
(2) Shipway, A. N.; Katz, E.; Willner, I. *ChemPhysChem* **2000**, *1*, 18–52.
(3) Serp, P.; Corrias, M.; Kalck, P. *Appl. Catal. A* **2003**, *253*, 337–358.
(4) He, J.; Kunitake, T.; Nakao, A. *Chem. Mater.* **2003**, *15*, 4401–4406.
(5) Hyde, K.; Rusa, M.; Hinestroza, J. *Nanotechnology* **2005**, *16*, S422–S428.
(6) Hyde, K.; Dong, H.; Hinestroza, J. P. *Cellulose* **2007**, *14*, 615–623.
(7) Hashem, M.; Hauser, P.; Smith, B. *Textile Res. J.* **2003**, *73*, 1017–1023.
(8) Shim, B. S.; Chen, W.; Doty, C.; Xu, C.; Kotov, N. A. *Nano Lett.* **2008**, *8*, 4151–4157.
(9) Turkevich, J.; Stevenson, P. C.; Hiller, J. *Discuss. Faraday Soc.* **1951**, *11*, 55–75.
(10) Huang, M.; Shao, Y.; Sun, X.; Chen, H.; Liu, B.; Dong, S. *Langmuir* **2005**, *21*, 323–329.
(11) Henglein, A. *J. Phys. Chem. B* **1999**, *103*, 9533–9539.
(12) Pillai, Z. S.; Kamat, P. V. *J. Phys. Chem. B* **2004**, *108*, 945–951.
(13) Kakkassery, J. J.; Abid, J.-P.; Carrara, M.; Fermín, D. J. *Faraday Discuss.* **2004**, *125*, 157–169.
(14) Bai, Y.; Zhao, S.; Zhang, K.; Sun, C. *Colloids Surf., A* **2006**, *281*, 105–112.
(15) Sadtler, B.; Wei, A. *Chem. Commun.* **2002**, *15*, 1604–1605.
(16) Lok, C.-N.; Ho, C.-M.; Chen, R.; He, Q.-Y.; Yu, W.-Y.; Sun, H.; Tam, P. K.-H.; Chiu, J.-F.; Che, C.-M. *J. Proteome Res.* **2006**, *5*, 916–924.
(17) Turkevich, J.; Kim, G. *Science* **1970**, *169*, 873–879.
(18) Dokoutchaev, A.; James, J. T.; Koene, S. C.; Pathak, S.; Prakash, G. K. S.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 2389–2399.

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