

Self-Assembly of Electrically Conducting Biopolymer Thin Films by Cellulose Regeneration in Gold Nanoparticle Aqueous Dispersions

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Electrically conducting cellulose films comprising interconnected networks of gold nanoparticles were prepared by a facile self-assembly procedure. The hybrid films were produced by immersing spin-coated viscous *N*-methyldimorpholine-*N*-oxide/dimethyl sulfoxide solutions of cellulose into aqueous dispersions of gold nanoparticles of variable concentration. Regeneration of an intact cellulose fiber matrix with integrated gold nanoparticles occurred spontaneously to produce self-supporting, defect-free metallized films, 2.5–12 μm in thickness and with nanoparticle loadings of up to 44 wt %. The hybrid films displayed surface plasmon resonance bands consistent with discrete or uniaxially coupled nanoparticles depending on the extent of gold loading. Stress/strain measurements indicated that the cellulose films were not mechanically compromised by the incorporation of the gold nanoparticles, which were stabilized within the biopolymer matrix by interactions with the ether oxygen and hydroxyl groups of D-glucopyranose (FTIR spectroscopy results). Room temperature Van der Pauw measurements indicated that the hybrid films were electrically conducting above a gold nanoparticle loading of 20 wt %. In addition, measurements of resistivity from 4.2 to 300 K showed a transformation from metallic band-like conduction (44 wt %) to Mott-type carrier hopping behavior at lower gold nanoparticle loadings (33 wt %) and low temperatures ($T < 100$ K). Given the widespread nature of the existing cellulose industry, self-supporting gold nanoparticle/cellulose hybrid films could have diverse applications in smart papers and textiles, as well as in numerous devices involving microelectronic components, catalysts and chemical sensors.

Introduction

Gold-nanoparticles (AuNPs) play a special role in nanoscience and nanotechnology due to their high stability, electrical conductivity, optical properties, and unique surface chemistry.^{1,2} In many cases, stable dispersions of AuNPs are prepared by wet chemistry methods in which the nanoparticle surfaces are protected by organic capping ligands, such as citrate anions in aqueous media,^{3,4} or alkanethiols in organic solvents.⁵ In recent years, AuNPs have been combined with various polymers not only to enhance colloidal stability, but also to produce

hybrid materials with potential applications in electronic devices,⁶ catalysts⁷ and chemical sensors.⁸ Most of those polymer–nanoparticle composites contain sulfur either as a protective ligand on the AuNP surface,⁷ or from sulfur-containing functional groups associated with the polymer chain,^{9,10} and are therefore less environmentally benign compared with hybrid materials prepared from sulfur-free AuNPs and natural biological polymers.^{11,12} Indeed, most reports of electrically conducting AuNP/polymer hybrid films involve the assembly of alkylthiol-terminated AuNPs deposited on an electrode surface,^{13,14} or if self-supporting, the films are either linked by sulfur-containing compounds,⁶ or composed mainly of organic conducting polymers.¹⁵ In contrast, there appears to be few reports on the preparation of electrically conducting

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AuNP/polymer hybrid films based on inexpensive, highly biocompatible polymers. Recently, nanoparticles of Ag, Au, Pt, or Pd have been synthesized in the presence of cellulose fibers,^{11,16} although the resulting hybrid materials were not electrically conducting. In this paper we show that electrically conducting cellulose films comprising dense networks of discrete gold nanoparticles can be prepared by spontaneous regeneration and assembly of biopolymer fibers in an aqueous dispersion of citrate-stabilized metallic nanoparticles. We use *N*-methylmorpholine-*N*-oxide (NMMO) as a highly effective solvent for cellulose dissolution,^{17–19} and as a means to spin-coat viscous wet films. These are then immersed in aqueous gold colloids of variable concentration to initiate self-assembly of the cellulose fibres and concomitant intercalation of the nanoparticles specifically within the biopolymeric matrix.

Experimental Section

Materials. α -Cellulose fibers, dimethyl sulfoxide (DMSO), propyl gallate, hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), and sodium citrate dihydrate were purchased from Sigma-Aldrich Inc. and used as received. *N*-methylmorpholine-*N*-oxide monohydrate ($\text{NMMO} \cdot \text{H}_2\text{O}$) was obtained by rotary evaporation of commercial available NMMO aqueous solution (50% w/w) in the presence of 0.05 wt % propyl gallate at 110 °C for 2 h. (Propyl gallate is an efficient antioxidant/free radical trapping agent and was added to minimize thermally induced side reactions and thereby increase the stability of the prepared NMMO/cellulose solutions.) Water with a resistivity of $18 \text{ M}\Omega \cdot \text{cm}^{-1}$ was used in all experiments. Colloidal AuNPs were prepared by the citrate reducing method^{3,4}. The average size and concentration of the AuNPs was $11.6 \pm 1.4 \text{ nm}$ and 1.089×10^{16} particles per liter, respectively. The concentration of gold in the stock solution of the colloid was 0.173 mg/mL. This was diluted with deionized water to produce sols with concentrations of 0.086, 0.058, 0.043, or 0.035 mg Au/mL.

Preparation of Cellulose Films and AuNP/Cellulose Hybrid Films. $X \text{ g}$ of α -cellulose was added into $(100-x-y) \text{ g}$ of $\text{NMMO} \cdot \text{H}_2\text{O}$ solvent at 90 °C with stirring for 24 h or until the cellulose was totally dissolved. $Y \text{ g}$ of DMSO was then added as a cosolvent to reduce the viscosity of the cellulose/ $\text{NMMO} \cdot \text{H}_2\text{O}$ solution. Values of x and y were varied, respectively, between 4 and 5 g and 18–50 g; typically, high quality films were prepared at $x = 4$ and $y = 50 \text{ g}$. (In general, the concentration of NMMO was reduced to a level that did not degrade the AuNPs after subsequent addition of the colloid). The hot cellulose solution was placed on a preweighed clean glass circular plate (5 cm in diameter, 2 mm in thickness, cleaned sequentially by aqua regia, deionized water, ethanol, deionized water, and acetone), and subjected to spin coating at 2000 rpm for 60 s to produce a viscous cellulose/NMMO/DMSO thin film. The weight of the wet films was measured immediately after spin coating. Intact films of regenerated cellulose were then produced by immersing the solvated cellulose/NMMO/DMSO-coated glass substrates

in water at room temperature for 30 min to extract NMMO and DMSO, and promote the in situ self-aggregation of cellulose fibres and bundles into an interlinked biopolymeric matrix. As a consequence, the regenerated material detached spontaneously from the glass substrate to give an intact self-supporting cellulose film that was washed thoroughly with deionized water. The films were kept suspended in deionized water or dried under vacuum at room temperature for 24 h.

Free-standing AuNP/cellulose hybrid films were produced using similar procedures except that the cellulose/NMMO/DMSO films were immersed in an aqueous colloid of AuNPs for periods from 30 min to 96 h prior to washing and storage. The initial colloid concentrations used were 0.035, 0.043, 0.058, 0.086, or 0.173 mg Au/mL.

Characterization. Cellulose-containing films were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray (EDX) analysis, UV-vis spectrometry, FTIR spectrometry, and powder X-ray diffraction (XRD), as well as by electrical resistivity and tensile strength measurements. Samples for SEM (JEOL JSM 5600LV and JEOL JSM 6330F) were prepared as small fragments of the dried cellulose or AuNP/cellulose films mounted on aluminum stubs either face-up or in cross sectional view. TEM (JEOL JEM 1200 EX, 120 keV) studies were undertaken on films prepared as thin sections. UV-vis spectroscopy (Perkin-Elmer Lambda II) was used to record absorbance spectra of the AuNP colloid solution before and after regeneration, as well as AuNP/cellulose films before and after drying. Freeze-dried samples were used for FTIR spectroscopy (Perkin-Elmer Spectrum 100, range $4000\text{--}650 \text{ cm}^{-1}$). Powder X-ray diffraction (XRD) profiles were recorded from dried films using a Bruker D8 diffractometer. Van der Pauw measurements on square-shaped films of length $L = 5 \text{ mm}$ and thickness $t = 5 \mu\text{m}$ were undertaken at 300 K to assess the electrical conductivity of the AuNP/cellulose hybrids prepared with different metal nanoparticle loadings. Electrical contacts using gold wires were fabricated at the corners of the film by depositing small drops of conductive silver varnish. The electrical in-plane resistivity ρ was estimated from the in-plane sheet resistance (R_s) and thickness (t) of the film using the relation $\rho = R_s t$. Temperature dependent measurements of the resistivity were also undertaken on hybrid films prepared with 33 or 44 wt % AuNP loadings. Mechanical tests were carried out on samples of the cellulose-containing films prepared as strips, $4.5 \times 15 \text{ mm}$ in size, and with a thickness of around $5 \mu\text{m}$. An INSTRON Force Transducer LCR-ULC-2519–101 with a tensile rate of 0.5 mm/minute at 18 °C and 50% relative humidity was used. The strips were stretched along their long axis.

Results and Discussion

Typically, high quality free-standing films were prepared by spin coating hot viscous solutions comprising 4 wt % cellulose, 46 wt % $\text{NMMO} \cdot \text{H}_2\text{O}$ and 50 wt % of DMSO onto glass plates, followed by immersion of the coated substrates for 96 h in distilled water or an aqueous dispersion of AuNPs containing between 0.043 and 0.173 mg Au/mL. Immersion of the solvated yellow-brown precursor films in water resulted in decolorization due to extraction of NMMO (and DMSO) into the aqueous phase, and gave rise to detached self-supporting cellulose films exhibiting $\sim 20\%$ reduction in diameter. These observations were consistent with the formation of an

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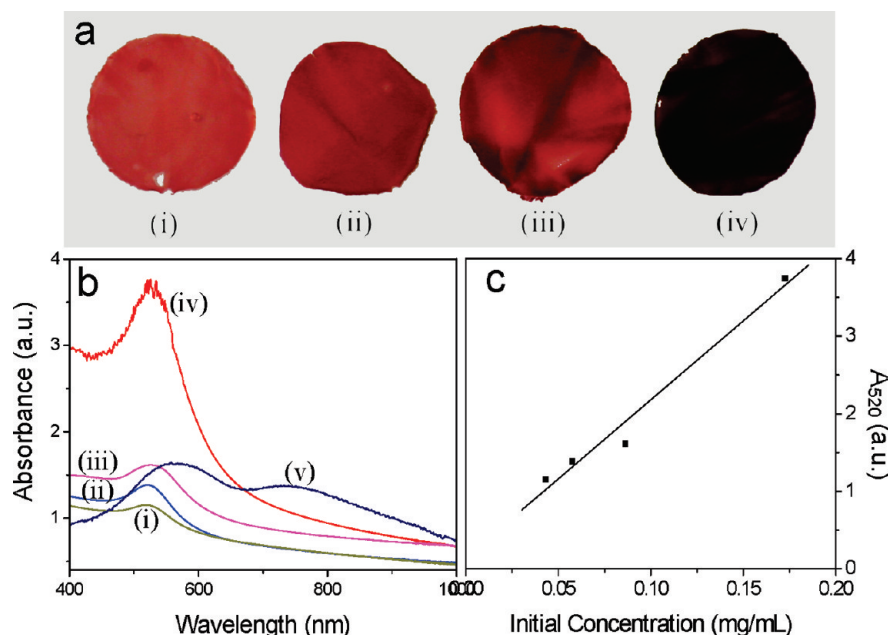


Figure 1. (a) Photograph of wet AuNP/cellulose hybrid films produced after 96 h by regeneration in aqueous colloids of variable AuNP concentration; (i) 0.043, (ii) 0.058, (iii) 0.086, and (iv) 0.173 mg/mL. (b) UV-vis spectra of samples highlighted in (a) showing concentration-dependent SPR bands at 520 nm (plots i–iv). Plot (v) corresponds to a cellulose film produced with a AuNP concentration of 0.086 mg/mL and subsequently dried under vacuum; the profile shows both transverse and longitudinal SPR bands at 560 and 740 nm, respectively. (c) Plot showing linear correlation between initial concentration of Au colloid (mg/mL) and corresponding peak intensities at 520 nm for regenerated cellulose films.

interlinked matrix of regenerated cellulose fibres accompanying solvent removal from the precursor films. Significantly, immersion of the cellulose/NMMO/DMSO-coated substrates in aqueous suspensions of AuNPs produced free-standing cellulose films that were red in color (Figure 1a), and showed a surface plasmonic resonance band (SPR) at around 520 nm (Figure 1b(i–iv)) that increased linearly in intensity as the initial concentration of Au in the colloid was increased (Figure 1c). Thus, provided that the initial concentration of the colloid was greater than 0.03 mg Au/mL, metallized films with AuNP contents ranging from 4 wt % up to 35 wt % could be readily prepared within a regeneration period of 96 h.

The presence of a distinct SPR band specifically at 520 nm confirmed that the AuNPs were integrated into the wet cellulose films during regeneration as discrete nanoparticles and that significant aggregation did not occur within the polysaccharide matrix. Time-dependent changes in the intensity of the 520 nm band associated with the hybrid film during the regeneration process indicated that the kinetics of AuNP incorporation showed an exponential decay dependence (Supporting Information Figure S1), consistent with a diffusion based model of random sequential adsorption.²⁰ In contrast, UV-vis spectra of the vacuum-dried hybrid films prepared with a Au content of at least ~13 wt % showed two absorbance bands at around 560 and 740 nm (Figure 1b(v)). These peaks were attributed respectively to nonaxial (isotropic) and uniaxial (anisotropic) SPR

coupling between adjacent AuNPs,^{21,22} and suggested that quasi-linear networks of Au nanoparticles were formed in the cellulose film upon dehydration.

In general, drying of the regenerated cellulose films under vacuum in the absence or presence of AuNPs produced flexible self-supporting cellulose thin films that were, respectively, transparent or red/gold in color (depending on the AuNP loading). SEM images indicated that the dried hybrid films had relatively smooth surfaces (Figure 2a) with no macropores or significant surface defects (Figure 2b). The thickness of the dried hybrid films was in the range 2.5–12 μm . Significantly, EDX mapping of the gold distribution indicated that the AuNPs were uniformly distributed in the surface and near-surface regions of the hybrid film but were depleted within the middle section of the interior (Figure 2c). High resolution SEM images indicated that the surface particles were discrete and organized into interconnected networks (Figure 2d). These observations were confirmed by TEM studies of thin sections of the dry metallized films, which showed a distinct concentration gradient in the arrangement of the AuNPs in films viewed in cross-section, with the majority of particles being located within 200–500 nm of the surface depending on the concentration of the gold colloid used (Figure 3).

FTIR spectra of the dried pure cellulose films showed bands at 3356 (O–H str), 2896 (C–H str), 1641 (adsorbed H_2O), 1157 (C–O–C asym. str), 1020 (skeletal C–O str) and 896 cm^{-1} (ring C–O sym. str) (Supporting Information Figure S2).^{23,24} A similar set of absorption

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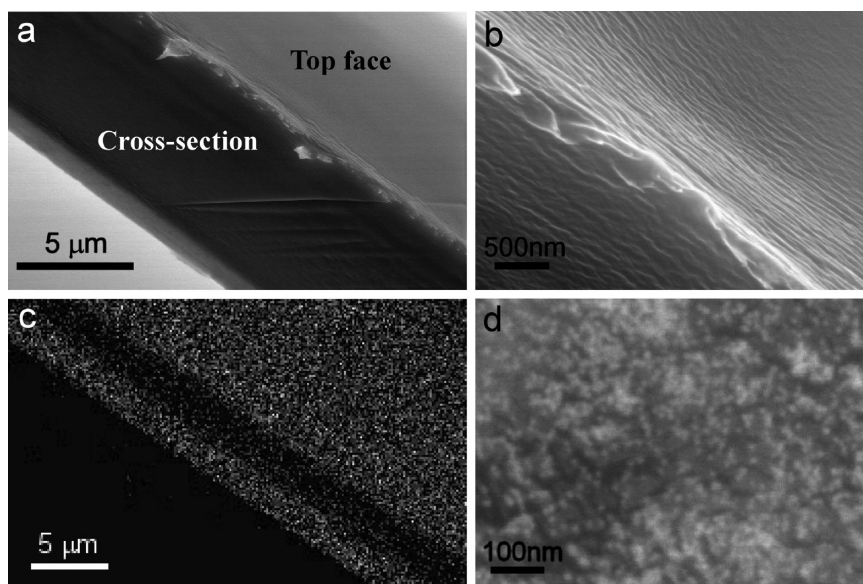


Figure 2. (a,b) SEM images of a AuNP/cellulose films prepared with a AuNP loading of 11.6 wt %; (a) low magnification image showing the smooth texture of the hybrid film, (b) higher magnification image showing absence of macropores or surface defects. The surface rippling arises from dehydration. (c) EDX map of Au concentration associated with the SEM image shown in (a). The intensity of the spots relates directly to the local Au concentration, and indicates the presence of a depletion zone of AuNPs in the central interior of the film when viewed in cross-section. (d) High resolution SEM image of the surface of a metallized cellulose film showing an interconnected network of AuNPs.

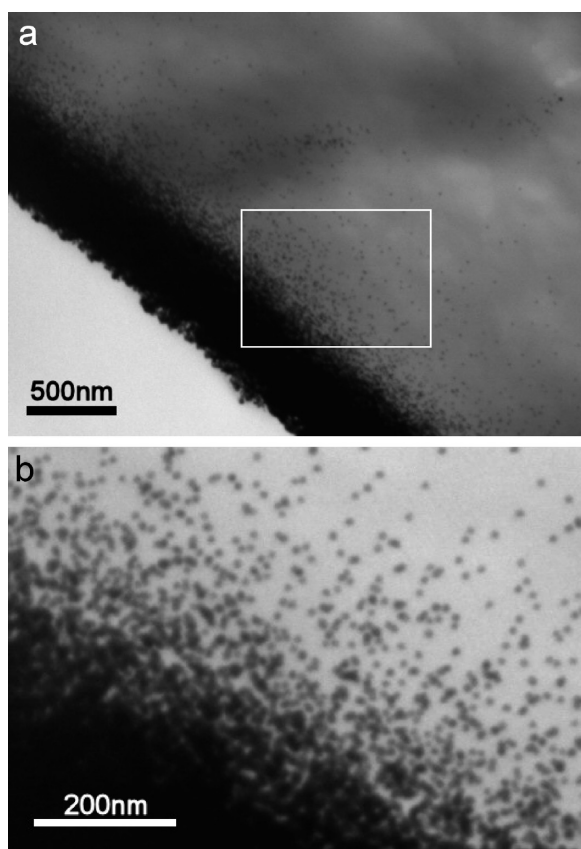


Figure 3. TEM images of thin slices of AuNP/cellulose hybrid films viewed in cross-section. (a) Low magnification image showing concentration of AuNPs in the near-surface regions. (b) Enlarged view of area framed by white square in (a) showing discrete AuNPs.

bands was observed in FTIR spectra of the dry AuNPs/cellulose films prepared with various metal colloid loadings (Supporting Information Figure S2). Significantly, whereas FTIR spectra of the AuNPs alone showed peaks

at 3413, 1586, and 1391 cm^{-1} corresponding to the O—H stretching mode, COO^- asymmetric stretch and COO^- symmetric stretch of surface-adsorbed citrate anions, respectively (Supporting Information Figure S2),²⁵ none of these bands were present in the metallized cellulose films. Moreover, a marked reduction in the normalized intensities of bands corresponding to the oxygen-containing groups of cellulose—in particular the C—O stretching mode of cellulose at 1020 cm^{-1} —was observed as the Au content in the films increased (Figure 4a). The results were consistent with stabilization of the AuNPs within the cellulose films via ligand exchange involving replacement of surface-adsorbed citrate by hydrogen bonding interactions with the ether oxygen and hydroxyl groups of the $\beta(1 \rightarrow 4)$ linked D-glucopyranose units of the biopolymer.¹¹

Stress/strain measurements, recorded on strips of the cellulose or AuNP/cellulose films stretched under tension, indicated that the films were not mechanically compromised by nanoparticle incorporation. The stress/strain profiles showed an initial elastic region followed by nonlinear viscoelastic behavior (Figure 4b). The elastic region was extended in the hybrid films from a strain value of 3% for pure cellulose to approximately 5% in the AuNP/cellulose materials. Corresponding elastic moduli of films containing 0, 0.04, or 6.34 wt % AuNPs were 730, 900, and 840 MPa, respectively, indicating a slight increase in the stiffness of the films in the presence of the metallic nanoparticles. In addition, the hybrid materials exhibited modified viscoelastic behavior compared with the pure cellulose films. Overall, the data were consistent with integration of the AuNPs into the cellulose films without significant disruption of the extended hydrogen bonding network of the polysaccharide matrix. Indeed,

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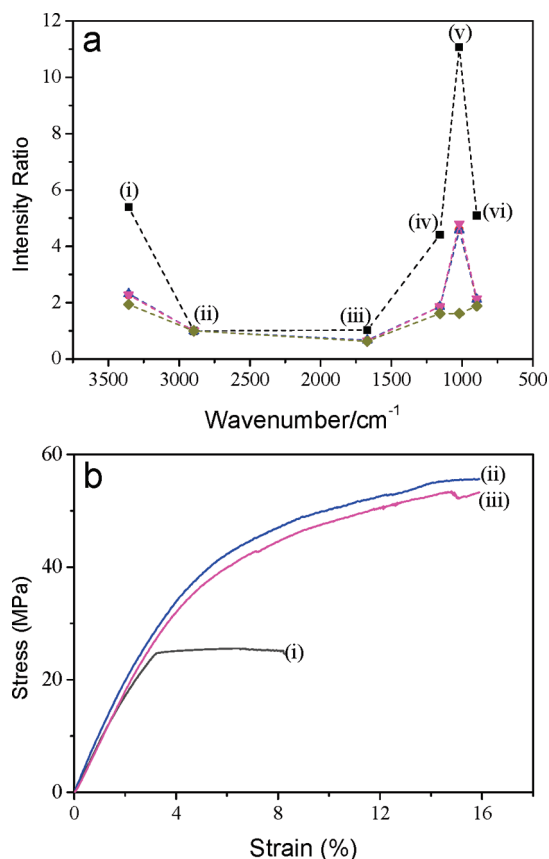


Figure 4. (a) Normalized peak intensities obtained from FTIR spectra of dried films of pure cellulose (■) and AuNP/cellulose hybrids with metal loadings of 0.11 wt % (●), 1.78 wt % (▲), 2.88 wt % (▼), and 3.58 wt % (◆). Plots for 1.78 and 2.88 wt % are superimposed. Peak intensities in each spectrum corresponding to O—H str (i), C—H str (ii), adsorbed H₂O (iii), C—O—C asym str (iv), skeletal C—O str (v) and ring C—O str (vi) were normalized to the intensity of the associated C—H stretching band. (b) stress/strain profiles for cellulose film (i), and AuNP/cellulose films (ii,iii) with Au loadings of (ii) 0.04 and (iii) 6.34 wt %.

some reinforcement of the matrix occurred possibly due to additional attractive interactions between the cellulose molecules and the AuNP surfaces.

The electrical in-plane resistivities (ρ) of metallized films containing different AuNP loadings were measured using Van der Pauw measurements on square-shaped samples of known size and thickness. At room temperature ($T = 300$ K), values of ρ decreased by more than a factor 10^6 when the AuNP loading in the cellulose film was increased from ~ 10 to ~ 40 wt %. (Figure 5a). The change in resistivity was nonlinear and appeared to approach the value measured for a pure Au film ($2.2 \times 10^{-8} \Omega\text{m}$) at 300 K.²⁶ A threshold value of ~ 20 wt % Au was required to establish stable and reproducible values of the resistivity. To probe the nature of the electronic conduction, for example whether it was mediated by free carriers (band-like conduction) and/or by carrier hopping between localized states, we investigated the temperature dependence of ρ from 4.2 to 300 K. As shown in Figure 5b, for a high concentration of Au (44 wt %), ρ exhibited a monotonic increase with rising temperature,

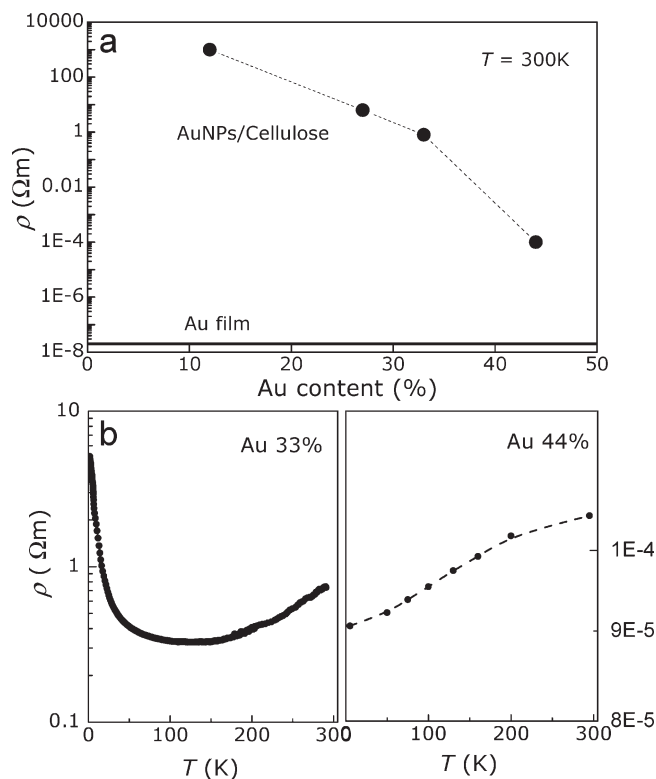


Figure 5. (a) Dependence of the in plane resistivity, ρ (Ωm) on the Au content (wt%) in AuNP/cellulose hybrid films at 300 K. The continuous line shows the resistivity of a pure Au film. (b) Temperature dependence of ρ for AuNP/cellulose films with Au content of 33 and 44 wt % showing changes in the nature of electronic conduction.

suggestive of metallic-like conduction mediated by band-like extended states, as observed in metallic Au,²⁶ in which the electron mobility and conductivity are limited by phonon-mediated inelastic collisions of the conduction electrons. In contrast, for cellulose films prepared with lower contents of Au (~ 33 wt %), an increase of temperature above 2 K and up to ~ 150 K resulted in a decrease of ρ , followed by a monotonic increase at higher temperature ($T > 150$ K) (Figure 5b). The sharp decrease of ρ at low temperatures ($T < 100$ K) is consistent with the relation $\rho = \rho_0 \exp\{(T_0/T)^v\}$, where $v = 1/4$ and $T_0 \sim 3 \times 10^3$ K. This corresponds to a Mott-type law for variable-range hopping conduction in three-dimensions.²⁷ Such behavior has been observed in a variety of conducting materials, including nanocrystals,²⁸ polymer nanocomposites,²⁹ and doped semiconductors,³⁰ and involves hopping of electrons between both neighboring and remote localized states whose energy levels are close to the Fermi energy. In the AuNP/cellulose hybrid films, these states may arise from the discrete energy levels generated by the randomly distributed metallic nanoparticles in the biopolymeric matrix. This behavior was limited to temperatures below ~ 100 K, after which values

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of ρ increased monotonically, suggesting the onset of a crossover to a regime of metallic conduction.

Conclusions

In summary, our studies indicate that electrically conducting, self-supporting cellulose films comprising interconnected networks of gold nanoparticles can be readily prepared by spin-coating of viscous *N*-methylmorpholine-*N*-oxide/dimethyl sulfoxide solutions of cellulose onto glass substrates followed by immersion into AuNP aqueous sols of variable concentration. The regeneration process results in a metallized, defect-free cellulose matrix with tunable optical and electrical properties. Moreover,

the hybrid films retain their mechanical integrity and exhibit either band-like or variable-range hopping conductivity depending on the AuNP loading. Given the widespread activity of the current cellulose industry, these observations open up realistic prospects for new cellulose-based materials not only in conventional areas such as paper and textiles but also in technologically advanced applications involving microelectronic components, sensors and catalysts.

Supporting Information Available: Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.