Transparent, conductive polystyrene in three dimensional configurations

Alexander Trachtenberg a, T.P. Vinod a, b, Raz Jelinek a, b, *

a Department of Chemistry, Ben Gurion University of The Negev, Beer Sheva 84105, Israel
b Ilse Katz Institute for Nanoscale Science and Technology, Ben Gurion University of The Negev, Beer Sheva 84105, Israel

A R T I C L E   I N F O
Article history:
Received 3 June 2014
Received in revised form 4 August 2014
Accepted 9 August 2014
Available online 20 August 2014

Keywords:
Flexible electronics
Polystyrene
Au nano-structures

A B S T R A C T
Development of technologies for constructing three-dimensional (i.e. non-planar) transparent conductive electrodes from polymeric materials is a major goal in diverse applications, including optoelectronic devices, flexible electronics, photovoltaics, and others. We present a facile new strategy for creating conductive, transparent gold layering on polystyrene, a widely-used polymer, in different shapes and surface morphologies. The approach is based upon amine functionalization of the polystyrene surface followed by incubation in an aqueous solution of Au(SCN)₄⁻ and brief plasma treatment. We show that this simple deposition process resulted in a homogeneous, transparent, and highly conductive crystalline Au coating. Importantly, electrical conductivity was attained for long distances, even in highly non-planar surfaces containing physical barriers. We further show that the approach can be employed for fabrication of conductive hollow tubes using electrospun polystyrene fibers as templates. The new synthesis scheme might make possible varied applications in polymer-based electronic and photonic devices.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer-based electronics exhibit broad potential for varied applications ranging from printed-polymer electrical circuits, flexible electronics, “intelligent labels”, large area displays, and solar panels [1]. A principal advantage of polymer electronics is that large, flexible and low cost substrates can be used. In addition, polymers exhibit great variety of physical properties such as molding capabilities, surface roughness and morphology, thermal expansion, and barrier properties, which can be readily modulated and exploited as substrates for electronic and photonic devices [1]. Indeed, the rapid development of this field in recent years could radically alter the electronics market by offering lighter, flexible, and more cost-effective alternatives to conventional materials and products [1].

A particular draw of polymers is the feasibility for constructing curved, flexible, or stretchable substrates for conductive surfaces [2–4]. Conventional “top-down” technologies, such as vapor deposition and lithography, are limited in their applicability to non-planar surfaces, as they exhibit less control of spatial dimensions and result in inadequate uniformity of deposited films [5]. “Bottom-up” strategies relying on molecular self-assembly have recently emerged as viable alternatives for the construction of conductive surfaces, providing simple, inexpensive, and environmentally benign solution-based synthetic routes [6–8].

We have recently developed a generic, single step solution-based “bottom-up” approach for assembling conductive, transparent nano-structured gold layers on varied surfaces [9–11]. The technology relies upon spontaneous crystallization/reduction of gold thiocyanate [Au(SCN)₄⁻] in aqueous solutions, without co-addition of reducing or stabilizing agents [9]. While previous studies have demonstrated conductive/transparent film formations upon glass [9], silicon [9], β-sheet peptide domains assembled at the air/water interface [10], and organo-silicon polymer substrates [11], implementation of the technology for coating organic polymers such as polystyrene (PS) would be significant, as this class of polymers has been widely used in diverse applications, and are considered promising electro-optic materials [12–14].

PS, in particular, is amenable for three dimensional applications. This polymer can be injection-molded and processed into thin films and fibers [15]. Thus, PS has been widely employed in the automotive, electrical and electronics, and consumer product areas [15]. PS is optically transparent, which has opened possibilities for opto-
electronic and photonic applications [12–14,16]. PS spheres, for example, have been particularly useful for the formation of photonic crystals [16]. Their high degree of shape and size uniformity aids their assembly into colloidal crystals, and the relatively high refractive index contrast between the spheres and air-filled voids within them allows for enhanced confinement of light [16,17].

Fabrication of hybrid gold/PS materials has been reported, mostly based upon synthesis of Au nanoparticles (NPs) or Au colloids, which are subsequently adsorbed onto the PS surface [18]. Some studies have described simultaneous reduction and crystallization of gold salt precursors in the presence of the PS substrate targeted for deposition [19,20]. In general, almost all synthesis schemes developed thus far require addition of reducing agents as well as careful control of Au colloid structures and surface functionalization essential for directing Au NP adsorption. Moreover, the propensity of gold ions to assemble into colloids and nanoparticles in solution often impedes effective Au layering and coating of the PS surface [18]. We show that this process yielded uniform gold films upon the PS surface that were optically transparent in a broad spectral range, and exhibited excellent conductivity, even across significant physical barriers.

2. Materials and methods

2.1. Materials

96-well plate lids with condensation rings made of Polystyrene were purchased from Greiner Bio-One (Germany). HAuCl₄ · 3H₂O, KSCN, Polystyrene (PS) with average Mₙ ~280,000 by GPC, branched polyethyleneimine (b-PEI) with average Mₙ ~25,000 by LS and average Mₚ ~10,000 by GPC, 2-(N-morpholino)ethane sulfonic acid (MES), N-Hydroxysuccinimide (NHS), Na₂HPO₄, NaH₂PO₄ and Triton X-100 were purchased from Sigma–Aldrich (USA), KMnO₄ was purchased from SoluFix (Israel), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) 98% was purchased from Alfa Aesar (USA). Conductive silver paint was purchased from SPI Suppliers (USA). Dimethylformamide (DMF) 99.8% was purchased from Fisher Scientific (USA). H₂SO₄, HCl, NaOH and Toluene were purchased from Bio Lab (Israel). All above listed reagents were used as received. The water used in the experiments were doubly purified by a Barnstead D7382 water purification system (Barnstead Thermolyne, Dubuque, IA), at 18.3 MΩ cm resistivity.

2.2. Preparation of PS templates

1. Rectangular samples with dimensions of 1 cm × 1 cm (referred to in the article as “plate samples”) were cut out from the PS well plate lids, afterwards the surface of the side that contains the condensation rings was chemically modified (as specified below), 2. Preparation of PS micro-fibers through electrospinning was based upon a published protocol, using an electrospinning apparatus schematically shown in Fig. 1S [23]. Specifically, 30% (w/v) PS solution was prepared by dissolving PS in DMF at room temperature, after stirring for 5 h, a homogeneous and clear solution was obtained. The polymer solution was placed in a 5 ml syringe fitted with a metallic needle, of 0.483 mm of inner diameter, that was controlled by a syringe pump (PHD 22/2000 Infusion only, Harvard Apparatus). The electrode of the high voltage power supply (Gamma High Voltage Supply, PS/EL300P1.5–22) was clamped to the metal needle tip. The flow rate of polymer solution was 1 ml/h and the applied voltage was 15 kV. We collected randomly oriented nonwoven meshes of PS micro-fibers on a grounded stationary rectangular metal collector (15 cm × 15 cm) covered by a piece of aluminum foil, placed 10 cm below the tip of the needle (tip-to-collector distance). Then, a 0.5 cm long mesh of electrosprun PS fibers was transferred into water. Since PS is highly hydrophobic material, the mesh of fibers turned into a tightly entangled bundle. This bundle sample was chemically modified (as specified below).

2.3. Amine modification of the PS surfaces

In order to perform surface amine modification of the two different PS templates, we adapted and optimized a method described in a published protocol [24]. Specifically, the following steps were performed: carboxylation of PS surfaces was achieved by immersion of PS templates in a solution of K₂SO₄ in 1.2 N H₂SO₄ (5 g/100 ml) for 1 h at 60 °C under shaking. Afterwards the templates were washed with 6 N HCl (4 × 5 min, 23 °C, shaking) to remove the brown manganese oxide and rinsed with water (10 times). Carboxyl activation and amine grafting were therefore carried out at the same time (one-step procedure), under the following experimental procedure: the PS templates were immersed in a solution of 1.4 gr b-PEI in 20 ml of 0.1 M MES buffer, pH = 6, containing 105 mM EDC and 100 mg of NHS for 2 h at 23 °C under shaking. Afterwards the templates were washed with 0.1 M MES buffer pH = 6 (3 × 5 min, 23 °C, with continuous shaking), followed by a solution of Triton X-100 in 10 mM Phosphate buffer pH = 7.3 (100 µl/100 ml) (5 min, 23 °C, with continuous shaking). This was repeated 5 times), and finally distilled water (2 × 5 min, 23 °C, with shaking).

2.4. Synthesis of the KAu(SCN)₄ complex

Synthesis was based upon a published protocol [9]. Briefly, 1 ml of an aqueous solution of HAuCl₄ · 3H₂O (24 mg/ml) was added to 1 ml of a solution of KSCN in water (60 mg/ml). The precipitate formed was separated by centrifugation at 4000 g for 20 min. The supernatant, containing KCl and excess of KSCN, was decanted, and the residue was dried at room temperature.

2.5. Growth of Au films on amine-modified PS surfaces

An aqueous solution of Au(SCN)₄²⁻ (0.7 mg/ml) was prepared in doubly distilled water. The amine-modified PS templates were vertically immersed in the solution and kept at 4 °C for 3 days. After the gold growth had reached completion, the templates were taken out of the growth solution and washed thoroughly with water to remove non-reacted materials and subsequently dried at room temperature.

2.6. Scanning electron microscopy (SEM)

SEM Images were recorded on a JEOL JSM-7400F (JEOL LTD, Tokyo, Japan) scanning electron microscope, at an acceleration voltage of 2 kV.
2.7. **Atomic force microscopy (AFM)**

Average cross-section measurements were conducted by generating two perpendicular scratches on gold film, grown on PS plate sample, using soft tweezers. An AFM height measurement near the edge of the scratch was then carried out. (The perpendicular scratch was aimed to ascertain that the basis from which height measurement was carried out is indeed the PS substrate.) AFM images were recorded at ambient conditions in tapping mode using a Dimension 3100 SPM instrument from Digital Instruments (Veeco, NY) mounted on a passive anti-vibration table.

2.8. **X-ray photoelectron spectroscopy (XPS)**

Analysis was conducted using a Thermo Fisher ESCALAB 250 instrument with a basic pressure of $2 \times 10^{-9}$ mbar. The plate samples were irradiated in two different areas using monochromatic Al Kα, 1486.6 eV X-rays, using a beam size of 500 μm.

2.9. **Powder X-ray diffraction (XRD)**

Measurements were taken using a Panalytical Empyrean powder diffractometer equipped with a parabolic mirror on the incident beam providing quasi-monochromatic Cu Kα radiation ($\lambda = 1.54059$ Å) and an X'Celerator linear detector.

2.10. **Transmittance measurements**

UV–Vis and IR transmittance measurements in the range of 300 nm–2000 nm were carried out in Caria 5000, Varian Analytical Instruments, Melbourne.

2.11. **Attenuated total reflectance – Fourier transform infrared (ATR-FTIR)**

FTIR measurements were carried out in a Nicolet 8700 FTIR spectrometer fitted with a MCTA detector. All single-beam spectra were measured against a background recorded from clean Diamond crystal. The spectra were recorded in the range from 4000 to 650 cm$^{-1}$, at 8 – resolution and 36 scans with optical velocity – 1.4 and aperture – 20. The FTIR data were collected and analyzed using the OMNIC software.

2.12. **Conductivity measurements**

Room temperature conductivity measurements were performed on a Keithley 2400 sourcemeter in a two-probe configuration. Two different methods were used to prepare the two different templates for conductivity measurements: 1. Gold coated PS plate samples were mounted in a thermal evaporator with a stainless steel shadow mask attached. Cr (10 nm) and Au (90 nm) were evaporated onto the substrates to obtain the electrode patches at a predefined spacing (50 μm, 100 μm, 500 μm and 1 mm). 2. Gold coated PS bundle sample was attached, using silver paint, between two vertically evaporated gold electrodes with a predefined spacing of 2 mm.

Prior to the thermal evaporation or bundle attachment, both kinds of samples were inserted to a plasma cleaner, PDC-32G, Harrick plasma, and were exposed twice to plasma for 0.5 min under vacuum of $2 \times 10^{-2}$ mbar at high RF (radio frequencies) and power of 18W.

3. **Results and discussion**

This study describes the construction of transparent, conductive film coatings upon polystyrene (PS) substrates exhibiting varied three-dimensional configurations. The thrust of the synthetic approach is a self-assembly process in which nano-structured Au films spontaneously form through anchoring of water-soluble Au(SCN)$_4$ onto amine moieties displayed upon the target surface [9]. Fig. 1 outlines the experimental scheme. We examined two PS configurations as substrates for gold coating: commercially-available “multi-well plates” (Fig. 1A), and long PS wires produced through electrospinning [23] (Fig. 1B). In both cases, the PS substrates were amine-functionalized through oxidation of the PS surface to produce carboxylic moieties followed by grafting of branched polyethylenimine (b-PEI). [24] The amine-displaying PS surfaces were then immersed in an aqueous Au(SCN)$_4$ solution resulting in deposition of a thin Au layer upon the PS substrates. After drying and brief plasma treatment [25] the Au films exhibited transparency and electrical conductivity.

![Fig. 1](image_url)  
*Fig. 1. Experimental schemes. A) Au coating of PS multi-well plate. The top photographs show the plates employed: images on the left – before Au deposition, right image: after Au deposition (note the red-brownish appearance indicating Au coating). Scale bar in top left image is 5 mm; scale bars in the two magnified images correspond to 1 mm. B) Au coating of electrospun PS fibers, followed by creating hollow Au tubes through dissolution of the PS fibers using toluene. Scale bar in left SEM corresponds to 10 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)*
Figs. 2 and 3 present microscopic and spectroscopic analyses of the Au films deposited upon the PS templates. Fig. 2 depicts a small region of the PS well-plate after gold deposition (Fig. 2A–B), and gold-coated PS fibers (Fig. 2C). As apparent in the scanning electron microscopy (SEM) image in Fig. 2A, the Au-coated PS plate displays a dense gold layer. Homogeneous Au coating was observed both upon the planar area of the plate (Fig. 2A, top magnified domain), as well as on the surface of the protruding well-barriers (the curved feature in Fig. 2A and magnified area in the bottom; note that the lack of focus in parts of the SEM image in the bottom magnification of Fig. 2A reflects the non-planar topography of the Au-coated PS surface). The atomic force microscopy (AFM) analysis in Fig. 2B, depicting the “edge” of a Au layer deposited upon PS, indicates that the Au film is fairly uniform, exhibiting an average thickness of around 65 nm.

Fig. 2C presents SEM images of PS fibers grown through electrospinning after amine functionalization and incubation with Au(SCN)₄ (The electrospinning apparatus is schematically depicted in Fig. 1,SI). Similar to the gold-treated PS plates (shown in Fig. 2A), the PS fibers appear encased by a dense and uniform Au layer. Importantly, the chemical reactions of the PS template fibers (amine functionalization and gold deposition) did not adversely affect the fibers’ morphology, lengths, and dispersion (Fig. 2C). Particularly remarkable are the results obtained after treating the Au-coated PS fibers with toluene, an organic solvent known to dissolve PS (Fig. 2C) [26]. Indeed, incubating the Au/PS fibers in toluene for 2 h generated hollow tubes, comprising only the gold coating after dissolution of the inner PS tubing. This was confirmed by Fourier transform infrared (FTIR) spectroscopy which demonstrated disappearance of FTIR peaks ascribed to PS following toluene treatment (Fig. 2,SI).

Spectroscopic characterization of the Au-coated PS samples in Fig. 3 illuminates the compositional and crystalline properties of

---

**Fig. 2.** Au-coated PS templates. A) SEM images of a small region containing part of the circular barrier within a multi-well plate after gold deposition, scale bar corresponds to 100 μm. Top magnification: flat region at the side of the well-barrier showing the dense Au film; bottom magnification: surface of the protruding barrier of the individual well showing complete Au coverage. Scale bars in the two magnified images correspond to 1 μm. B) AFM image (top) and an average cross-section (bottom) pointing to the thickness and uniform nature of the Au layer. Scale bar (blue color) corresponds to 1 μm. C) SEM images of Au-coated electrospun PS fibers (left), and the fibers after PS dissolution by toluene, resulting in formation of hollow Au tubes (right). Scale bars in top images correspond to 10 μm, magnified areas (bottom images) – 1 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
the Au films, and provides insight into the gold deposition process (the results presented in Fig. 3 were recorded for the Au-coated PS fibers; similar spectroscopic data were obtained in case of the Au-coated PS plates, shown in Fig. 3A). Consistent with the XPS data in Fig. 3A, plasma treatment of the Au-coated PS, including nanowires [29,30], and sheet-like structures [31,32]. Aurophilic interactions between closed-shell Au³⁺ atoms have been discerned in varied supramolecular systems comprising gold complexes, giving rise to diverse morphologies, including nanowires [29,30], and sheet-like structures [31,32].

Powder x-ray diffraction (XRD) data in Fig. 3B corroborate the XPS analysis and provide further information upon the crystalline properties of the Au films. Following incubation of the amine-functionalized PS fibers with Au(SCN)₄⁻, the XRD pattern in Fig. 3B, bottom, shows small peaks corresponding to crystalline gold, as well as three peaks corresponding to 5.12 Å, 3.0 Å and 2.6 Å, respectively, reflecting the prominence of the aurophilic organization of Au³⁺ [27,28]. Aurophilic interactions between closed-shell Au³⁺ atoms have been discerned in varied supramolecular systems comprising gold complexes, giving rise to diverse morphologies, including nanowires [29,30], and sheet-like structures [31,32].

Consistent with the XPS data in Fig. 3A, plasma treatment of the Au-coated PS transformed the gold layer into fully crystalline Au⁰, as indicated by the XPS peaks at 83.9 eV and 87.6 eV (Fig. 3A, top spectrum). Plasma treatment of Au films is known to induce efficient reduction of the metal [25].

Fig. 3. Spectroscopic characterization. A) XPS spectra of the Au-coated PS substrate before (bottom spectrum) and after (top spectrum) plasma treatment. B) Powder XRD spectra of the Au-coated PS substrate before (bottom spectrum) and after (top spectrum) plasma treatment.

One of the major goals of this work is to demonstrate possible practical applications of the Au-coating technology. Figs. 4 and 5 examine functionalities of the Au/PS assemblies, particularly optical transparency and electrical conductivity properties recorded for both the multi-well plate and the fiber constructs. Fig. 4 presents light transmittance and conductivity data acquired after gold deposition and plasma treatment of the multi-well PS plate. Fig. 4A underscores the transparency of the Au/PS material. Around 60% optical transmittance was retained both in the visible spectral region (above 450 nm) and well into the IR range (up to around 1650 nm) — indicating that the thin Au layer hasn’t strongly affected the intrinsic transparency of PS (depicted as the broken curve in Fig. 4A).

Fig. 4B demonstrates an excellent electric conductivity achieved in the Au-coated PS plate. The experimental setup is depicted in the image in Fig. 4B. Specifically, an array of gold electrodes at a
Fig. 5. Au-coated PS fibers. A) Photographs of the Au-coated PS fibers employed for electrical current measurements. Bottom picture: a bundle of fibers placed between two silver-paint electrodes, scale bar corresponds to 200 μm. Top picture: magnified area within the bundle showing the individual fibers. Scale bar corresponds to 20 μm. B) I/V curve recorded for the setup shown in A.

The current/voltage (I/V) curve in Fig. 4B was recorded at the distance indicated by the arrows (around 10 mm). Significantly, the linear appearance of the I/V curves and the high current values recorded (corresponding to sheet resistance of approximately 1.0 Ω/square) attest to excellent electron transport at the inter-electrode spacing examined. Particularly striking is the fact that the pronounced conductivity was measured even across the two protruding barriers enclosing the well depressions within the plate — confirming that effective Au film deposition was accomplished upon the entire three-dimensional PS substrate (the multi-well plate).

To further examine potential applicability of the Au-coated/PS technology, we calculated the Figure of Merit (FoM) — a widely employed parameter for assessing the performance of transparent conductive electrodes (TCEs) or transparent conductive films (TCFs) [37], FoM is expressed as the ratio between DC conductivity and optical conductivity ($\sigma_{DC}/\sigma_{OP}$), and is commonly used for film thicknesses of less than the wavelength of light [38] (which is also the case here). A FoM greater than 35 is considered sufficient for industrial applications [39]. However, for many TCEs exhibiting sheet resistance that is smaller than 10 Ω/square coupled with a transmittance of 85% the FoM is greater than 220. We calculated the FoM for the Au/PS system depicted in the manuscript (sheet resistance of 1 Ω/square and transmittance of 60% in the visible region) using the equation [38]:

\[
T = \left(1 + \frac{Z_0}{2\pi R_s} \frac{\sigma_{OP}}{\sigma_{DC}}\right)^{-2}
\]

in which $Z_0$, $T$, and $R_s$ correspond to the impedance of free space (377 Ω), the transmittance, and sheet resistance, respectively. The calculated FoM value was around 650 confirming that the Au-coating technology might be successfully implemented for fabricating TCEs and electro-optical devices.

Electrical conductivity was also evaluated in case of the Au-coated PS fibers (Fig. 5). As depicted in Fig. 5A, a bundle of Au-coated fibers was placed between two electrodes using silver-paint contacts (black circularly-shaped areas on both sides of the bundle, Fig. 5A). The linear I/V curve recorded between the two electrodes and corresponding current values (Fig. 5B) confirm that excellent electron transport occurred through the Au-coated PS fibers. This result, similar to the conductivity measurements for the plate sample depicted in Fig. 4, is ascribed to the dense, continuous Au coating.

4. Conclusions

We present a new approach for creating transparent conductive polymers in different shapes and morphologies through surface coating with a nano-structured Au layer. The process was demonstrated for polystyrene (PS), a widely-used transparent polymer. The technique is based on amine functionalization of the PS surface and incubation of the amine-modified PS with Au(SCN)$_4$ in water. The strategy depicted here exhibits notable advantages in comparison with currently-applied metal deposition technologies. Specifically, the Au coating technique can be directly implemented on different polymer morphologies (i.e. surfaces with “steps” and three-dimensional protrusions, fiber-like structures), and does not require specific templates. Importantly, the gold coating demonstrated here involves single-step incubation of the target PS surface with the gold complex, without co-addition of reducing agents (or other reagents).

The Au-coated PS substrates were subjected to plasma treatment and displayed attractive properties, particularly optical transparency and excellent electrical conductivity. Importantly, the conductivity profiles attest to efficient electron transport even across surface “barriers” (e.g. the steep edges of the wells), indicating that continuous Au coating of the PS substrates was attained even in non-planar configurations. Good conductivity was also recorded for the Au-PS fibers. Furthermore, immersing the Au-coated fibers in toluene, which dissolves the PS fiber template, gave rise to remarkable hollow gold tubes. In conclusion, this work demonstrates a facile, versatile gold coating technology, employed for fabricating PS substrates encased with transparent and conductive gold layers. The technology can be easily expanded to include other types of polymers, since the only chemical requirement is amine surface display, which can be easily carried out through varied synthetic routes.

Acknowledgments

We are grateful to the Ministry of Trade, the Kamin Grant Program, for partial financial support. We thank Ms. Roxana Golan for AFM analysis, Mr. Jurgen Jopp for electrical current measurements of gold coated PS bundle sample, Dr. Dimitry Mogiliansky for XRD measurements, Dr. Natalya Froumin for XPS measurements, Dr. Sofiya Kolusheva for ATR-FTIR measurements, and Mr. Misha Volokh for transmittance measurements. We also thank Ms. Sharon Fleischer and Dr. Assaf Shapira from Dr. Tal Dvir lab (TAU, Israel) for introducing us to the electrospinning technique.

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.polymer.2014.08.026.