

Fabrication of Continuous Conducting Gold Wires by Electrospinning

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An innovative approach is developed to electrospin Au polymer wires, dissolving HAuCl₄ salt in ethanol followed by addition of poly(acrylic acid) with several modifications in the conventional electrospinning system. The as-prepared Au polymer wires are assembled on the rotating drum in between the spinneret (+ electrode) and the conducting substrate (− electrode). The as-prepared Au polymer wires via sintering transformed to the Au wires comprised of compact Au nanocrystals keeping their one-dimensional identity. By collecting a single Au polymer wire on a gold interdigitated electrode during electrospinning followed by its successive sintering, the conductivity of the single gold wire is measured. Reaction parameters such as the amount of the precursor/polymer, change in the solvent, and change in the wire collecting substrate are optimized. Interestingly, gold dendrites are formed when aluminum foil is used as an Au polymer wire collecting support, which retains its shape even after sintering.

Introduction

Recently, intensive efforts have been made to synthesize one-dimensional¹ (1D) metal nanostructures because of their unique optoelectronic and mechanical properties and potential applications in mesoscopic research and nanodevices.^{2–4} Among the synthetic approaches for the preparation of 1D gold metal nanostructures, the two most widely used are the template-directed⁵ method to control their shape and the anisotropic crystal growth of a certain plane induced by a capping reagent.⁶ The conventional electrospinning approach is known for the fabrication of 1D nanofibers of polymers, ceramics, carbons, and composites.⁷ Kim et al. fabricated 1D arrays of Au nanoparticles within nanofibers in which the intrinsic nature of the semicrystalline polymer poly(ethyleneoxide) was employed as a template⁸ for the controlled nanoscale organization of the nanoparticles. Very recently, they also reported on the preparation of poly(vinylalcohol) nanofibers containing⁹ gold nanoparticles by an electrospinning method, and they used NaBH₄ as a reducing agent for the Au precursor. Transient thermal characterizations of

micro-/sub-microscale polyacrylonitrile wires are studied by Guo et al.¹⁰

Electrospinning was proven in recent years as a simple method for the preparation of various polymers or oxide nanowires. The standard setup for electrospinning consists of a spinneret¹¹ with a metallic needle, a syringe pump, a high voltage power supply, and a grounded collector. A polymer, a sol–gel, or a composite volatile solution is loaded into a syringe. The viscous liquid is driven to the needle's tip by a syringe pump, forming a droplet. When the voltage is applied to the metallic needle, the droplet is first stretched into a structure called a Taylor cone and finally into an electrified jet. The jet is then elongated and whipped continuously by electrostatic repulsion until it is deposited on the grounded collector. The elongation by bending instability results in the formation of uniform fibers with nanometer scale diameters.¹² The as-spun fibers are usually collected on conducting substrates, which have already found application in the reinforcement of composite materials, ultrafiltration, tissue engineering, catalysis, as well as in solar cells, sensors, and batteries.^{13,14} However, the synthesis of continuous conducting metal wires via electrospinning remains a challenge, due to the following three limiting factors: (i) the risk in charging metals that may spark at very high voltage (10–40 kV), (ii) the conventional electrospinning technique which is not suitable for corrosive solutions due to the presence of a metallic needle, and (iii) the need to change the oxidation potential of the metal precursor after the electrospinning process, unlike other inorganic materials such as metal oxides. During the electrospinning of oxides

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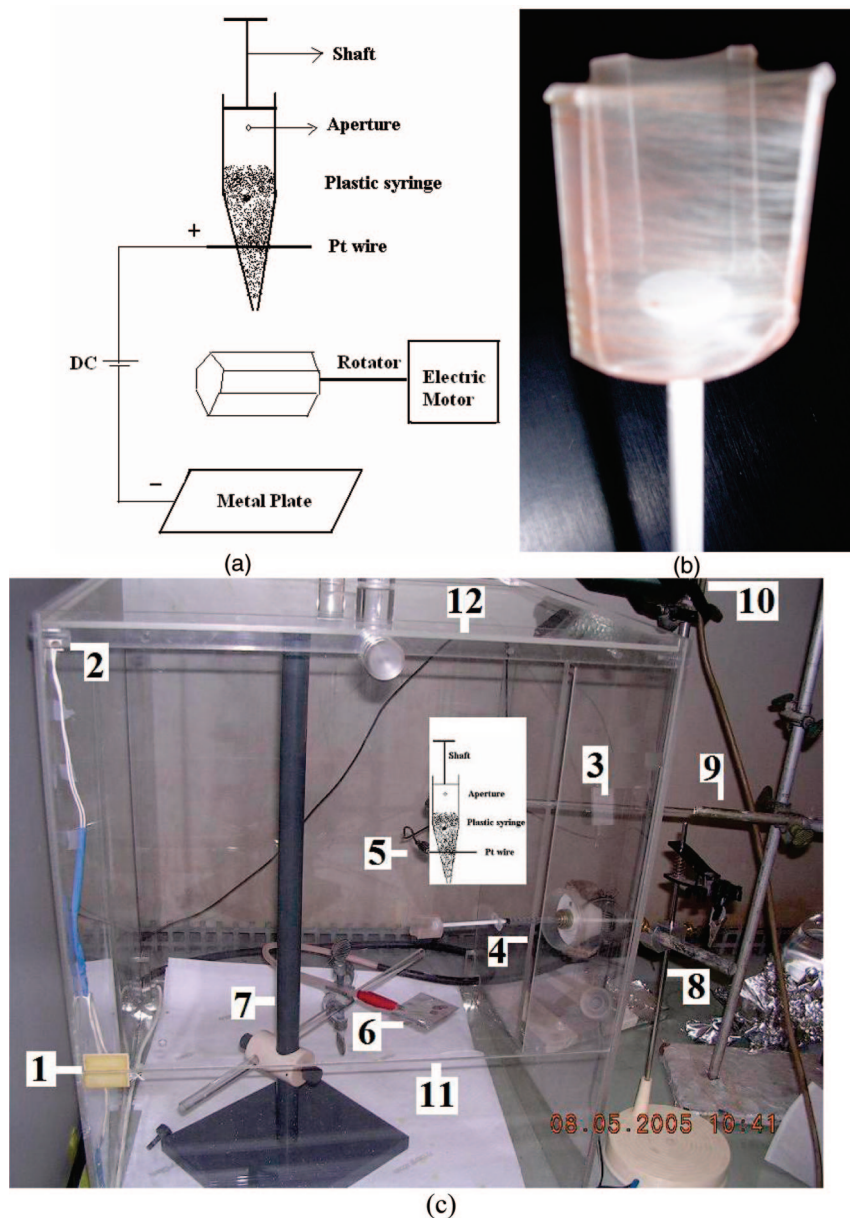


Figure 1. (a) Schematic illustration of the original setup used to electrospin an as-prepared Au polymer wires. (b) Photograph of the as-prepared Au polymer wires rolled on four fingered plastic support (photographed by a digital camera). (c) Safe, transparent, nonconducting, perspex box designed shown with an exact instrumental setup used for the electrospinning of Au polymer wires.

from their respective alkoxide (Ti, Si), the oxidation state of the reactant remains the same^{15,16} in the product. However, the synthesis of metal from its respective salt (HAuCl₄ in the present case) requires reduction after electrospinning, so that no precipitation occurs before the solution leaves the needle.

Experimental Details

A new approach to electrospinning is presented that facilitates synthesis of metal nanowires. A scheme of the new system used to electrospin as-prepared Au polymer wires is shown in Figure 1a, emphasizing the required modifications with respect to the conventional electrospinning system. The metallic needle was replaced by a plastic or Teflon needle (0.8 mm diameter) to spin the corrosive precursor solution that was charged using a Pt electrode. The as-

prepared Au polymer wires were assembled in between the spinneret and the conducting substrate, using a plastic drum connected via a Teflon shaft to a rotator. The as-spun continuous Au polymer organized wires (diameter 50 nm to a few micrometers) and lengths of kilometers were transformed via sintering to Au wires comprised of compact Au nanocrystals, maintaining their 1D identity. The conductivity of the gold wires was measured by collecting a single Au polymer wire on a gold interdigitated electrode during electrospinning and the successive sintering. Figure 1b demonstrates reddish as-prepared Au polymer wires rolled on four fingered plastic support with an unlimited length scale. From Figure 1b, it is evidenced that as-prepared Au polymer wires are free-standing. The as-prepared Au polymer wires we could not sinter on plastic support. However, when we wrap the glass support or gold interdigitated electrode on the top of the plastic collector and further sintered at 400 °C, remain continuous or wrecked depending upon the concentration of gold precursor as demonstrated in the results and discussion section.

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Table 1. Summary of Precursor's Amount, Solvents, and Their Obtained Morphology by Electrospinning

solution	gold precursor	ethanol/acetone	PAA	morphology after sintering
A	100 mg	3 mL ethanol	100 mg	wires
B	100 mg	3 mL ethanol	150 mg	wires
C	150 mg	3 mL ethanol	100 mg	wires
D	150 mg + NaCl	3 mL ethanol	100 mg	necklace
E	150 mg	3 mL acetone	100 mg	wires

Figure 1c demonstrates the assembly with an exact setup of the equipments used for the Au polymer wire electrospinning. At high voltages, considering the risk of sparking the metal wires while electrospinning, a methodical, safe, transparent movable box is fabricated from nonconducting perspex materials and located in a fume hood. The box is equipped with safety door locks [1,2], a spinneret holder [3], a notch for adjustable rotating shaft [4, the motor is located outside the box], and easy access to move the + [5] or - [6] electrode position while placing the high-voltage power supply outside. The possibility for placing supporting stands is either inside [7] or outside [8, 9], and also a bright light focus [10] is mounted on the top of the box for experimental observations. For setting the electrospinning experiment, the easy access is provided from the front half-door [11] and from the top door [12]. While opening any one of the doors, the safety locks were initiating the emergency power cut off that was connected to high-voltage power supply.

The electrospinning setup for our experiments is different from the one usually reported. In a typical procedure, 100 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in 3 mL of anhydrous ethanol while stirring for 5 min. A 100 mg portion of poly(acrylic acid) (PAA, $\text{C}_3\text{H}_4\text{O}_2$, Aldrich, Mw 450 000) was added to the solution to make a viscous liquid [solution A; see Table 1]. The viscous liquid was then loaded into a plastic syringe equipped with a plastic/Teflon needle wedged by a platinum wire that was connected to a high-voltage power supply (Glassman High Voltage, Inc.). In the initial step, a droplet of an Au polymer solution was formed at the tip of the plastic syringe by a manual push to the viscous liquid. The application of 25 kV between the platinum electrode and the collecting electrode stretched the droplet into an electrified elongated jet that was whipped continuously by electrostatic repulsion until deposition on the central collector. The as-prepared Au polymer wires are sintered at 400 °C to burn off carbonaceous materials and further called as gold wires. Here, we avoided connecting the wires in between two electrodes by rolling the as-prepared Au polymer wires on the rotating drum. An aperture made at the upper part of the syringe released a local vacuum, thus allowing a continuous flow of the viscous liquid. The organized as-prepared Au polymer wires were collected on a rotating drum located between the spinneret and the counter electrode that was placed 15 cm below the syringe. No additional reducing agent was required for the synthesis of Au wire.

Characterizations

The structure and phase purity of the as-prepared Au polymer wires and gold wires were examined by X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance Powder X-ray diffractometer (using $\text{Cu K}\alpha$, wavelength = 1.5418 Å radiation) operating at 40 kV/40 mA. To determine the percentage of elemental carbon in the as-prepared and gold wires, elemental analysis was carried out on EA 1110 C, H, N, S-O [carbon, hydrogen, nitrogen, sulfur, and oxygen], CE Instruments. Differential scanning calorimetry

(DSC) of the as-synthesized Au polymer wires was carried out on a Mettler Toledo TC 15 model, at a heating rate of 10 °C/min in a crimped aluminum crucible in the temperature range of 30–550 °C. The morphology of the as-prepared Au polymer wires and gold wires were studied with JEOL-JSM 840 scanning electron microscope and the elemental composition of the wires were analyzed by energy-dispersive X-ray (EDX) analysis attached to JEOL JSM 840 SEM. The high-resolution transmission electron microscopy (HR-TEM) images were taken using a JEOL-2010 with 200 kV accelerating voltage. The various digital camera photographs of the as-prepared Au polymer wires on different supports were taken using Nikon coolpix 3100, 3× optical zoom [3.2 effective megapixels] camera.

Results and Discussion

Figure 2a shows a scanning electron micrograph (SEM) of the as-prepared Au polymer wire using solution A. The diameter distribution of the as-prepared Au polymer wire ranges from 400 nm to 1 μm. The wires in Figure 1a are arranged in a zigzag fashion due to the slow rotation of the drum. To prepare uniform wires we increased the concentration of polymer [solution B, Figure 2b], keeping the same concentration of Au precursor. Retaining the drum rotation at ~100 rpm with the rate of Au polymer wire production (typically 2–5 m/s), the wires are uniform and better aligned. The high resolution SEM [inset of Figure 2b] shows one of the as-prepared Au polymer wire with the assembly of floppy Au polymer particles. The resulting wires (without beads) exhibit a 2.5 μm diameter. Sintering these wires at 400 °C in air transformed them into gold nanoparticle arrays or broken gold wires [Figure 2c]. This suggests that the concentration of Au precursor (eventually particles) is not sufficient to keep the wires intact after sintering. We noted that several parameters influence the exact morphology of the wires and the fabrication rate. Consequently, a change in one of the parameters requires the optimization of all the other parameters, with emphasis on the drum rotation rate. For example, with a 15 cm distance between the electrodes, a 25 kV bias, and a slow feeding rate (by keeping the syringe under partial vacuum) with ~100 rpm drum rotation is required.

To prepare continuous gold wires, we increased the concentration of Au precursor [solution C]. The gold wires are comprised of gold nanoparticles, which sinter during the sintering of Au polymer wires to form a continuous gold wire. Therefore, the concentration of the gold precursor into PAA plays an important role with respect to the final product properties. Specifically, we refer to wire stability during the sintering process. Low gold precursor concentrations [solution B, Figure 2b] lead to the formation of uniform Au polymer wires. However, these composites break during sintering at 400 °C, forming a nanoparticle array [Figure 2c]. In contrast, a higher gold precursor concentration [solution C] fabricates comparatively thicker Au polymer wires. Figure 2d shows a digital camera image of the free-standing Au polymer wires assembled on the four fingered plastic support. Figure 2e presents the SEM image of these Au polymer wires possessing diameters from 750 nm to 3 μm. The inset shows

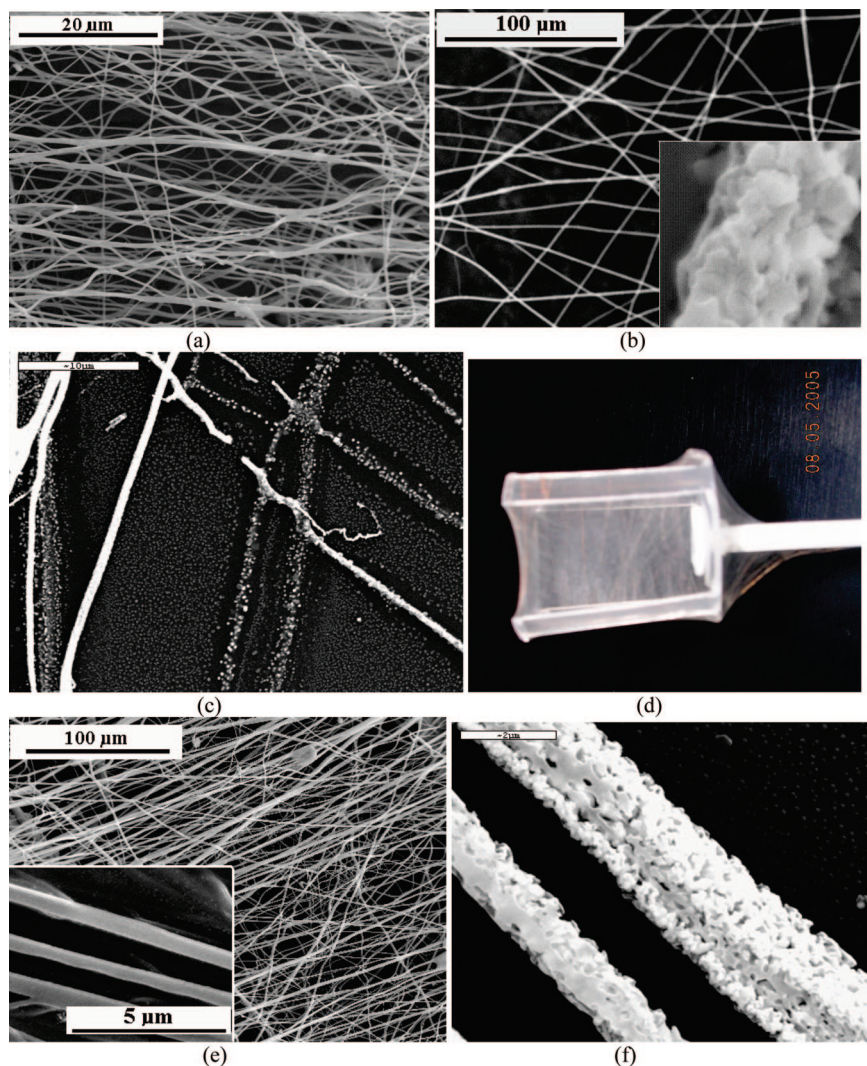


Figure 2. SEM of (a) the as-prepared Au polymer wires using solution A, (b) the as-prepared Au polymer wires prepared using solution B, and (c) the as-prepared Au polymer wires prepared using solution B and sintered at 400 °C in air. (d) Digital camera image of as-prepared Au polymer wires prepared using solution C. (e) SEM of part d. (f) As-prepared Au polymer wires prepared using solution C and further sintered at 400 °C in air.

the parallel arrangement of Au polymer wires. Moreover, these wires do not break during sintering due to the closely packed sintered nanoparticles that form the wire [Figure 2f]. Therefore, the detailed characterization is carried out for these continuous Au polymer wires before and after sintering and presented in the following section. Although continuous gold wires are obtained after sintering, the imperfection or defects [black holes] and rough surfaces are observed on the gold wires. The as-prepared Au polymer wires could form the gold wires since the gold nanoparticles can have significant decrease in the melting point¹⁷ by ~800 °C. The melting point of gold clusters¹⁸ supported on titania was reported at 400 °C by Akita et al. Meisel et al. reported the melting point of a silica-encapsulated gold¹⁹ core (1.5 nm) at 380 °C. Not only the experiments but also theory²⁰ support our claim that the melting point of nanogold can decrease

significantly. That facilitates the Ostwald ripening of the Au nanoparticles to form big islands, thus necking the gold nanoparticles to form continuous Au wires [Figure 2f]. Therefore, gold wires comprised of compact Au nanoparticles remain after the sintering process.

One of the control experiments is carried out in which 0.2 M NaCl salt [solution D] was added, to increase the charge density on the Au polymer wires [Figure 3a]. That resulted into the formation of chainlike “necklace” structure. In addition to the necklaces, few beads are also observed in the SEM image shown in Figure 3b. Similar increase in the net charge density carried by the moving jet forms the beads was reported in which 0.1 M NaCl was added to the PEO solution.²¹ The inset [Figure 3b] shows the closely packed arrangement of the gold nanoparticles after sintering the Au polymer wires at 400 °C. The 1–2 μm diameter gold wires are composed of sintered gold particles.

In another control experiments, the typical gold micro-dendrites are grown when the Au polymer wires were

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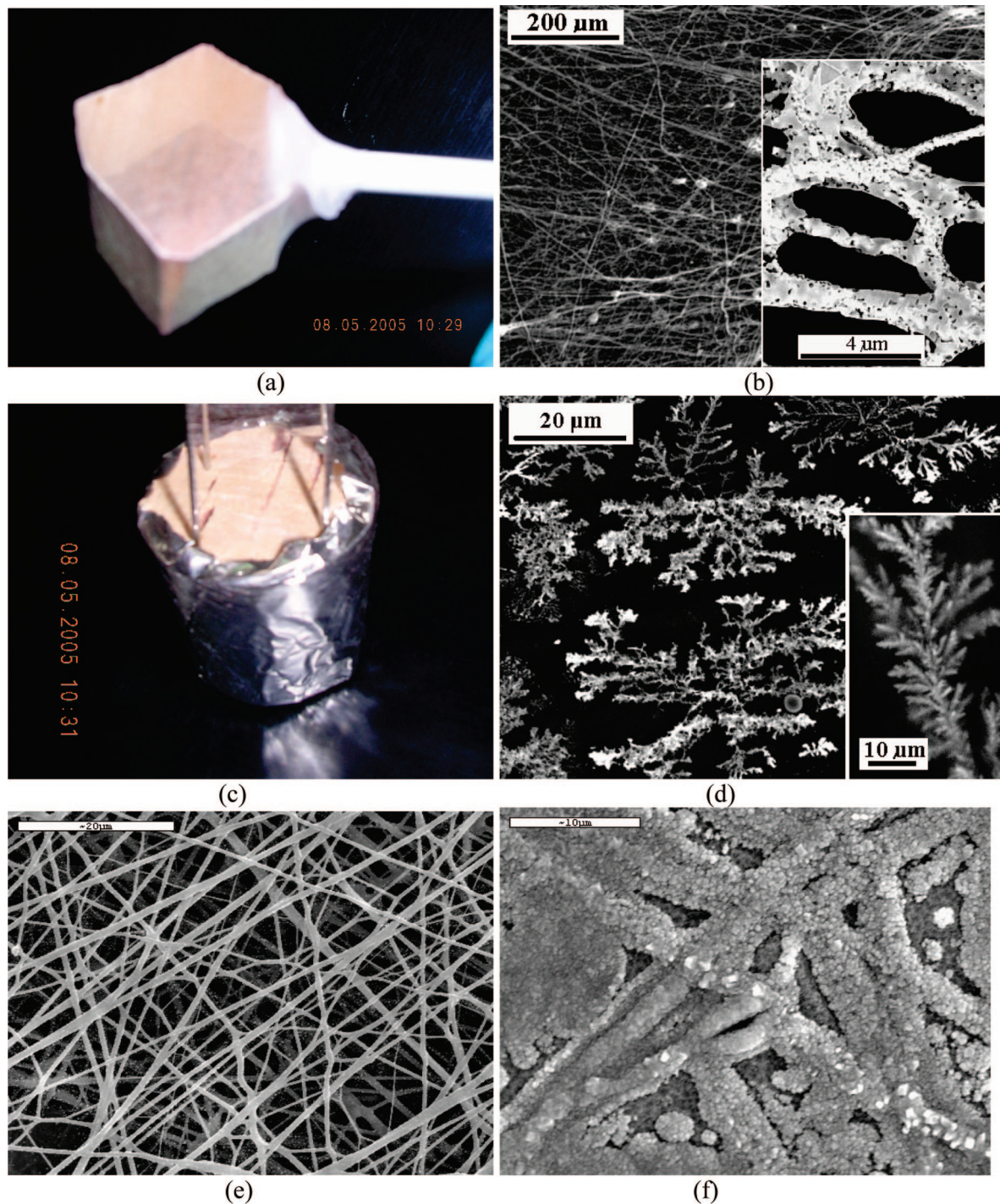


Figure 3. (a) Digital camera image of Au polymer wires collected on the hexagonal paper card support via electrospinning using 0.2 M NaCl salt in solution C. (b) SEM image of part a. (c) Digital picture of the as-prepared Au polymer wire [solution D] collected on the aluminum foil and aged for 2 days. (d) SEM image of part c. The inset shows the as-prepared Au polymer dendrites collected on the aluminum foil and sintered at 400 °C. (e) Acetone used as a solvent instead of ethanol for the preparation of Au polymer wires [solution E]. (f) Sintering of part e at 400 °C.

collected on the 2 mm aluminum foil [Figure 3c] and left as is for 2 days. Since the Au polymer wire contains the corrosive Cl from the HAuCl_4 precursor, that led to etching of the aluminum substrate, which finally carved into dendritelike structures [Figure 3d]. Sintering these dendrites until 400 °C, the microdendritic structure remains the same [inset of Figure 3d]. The dendrites of gold grow more than 50 μm long. This is one of the straightforward ways to fabricate

microstructures of gold nanocrystals. Such dendrites²² are produced, reducing HAuCl_4 in an aqueous surfactant solution of 3-heptafluorooctylsulfonylethyltrimethylammonium iodide ($\text{CF}_3(\text{CF}_2)_7-\text{SO}_2\text{NH}-(\text{CH}_2)_3\text{N} + (\text{CH}_3)_3\text{I}^-$) and the solution was allowed to stand for different time periods (incubation times), including very long periods of up to over 50 days at room temperature.

The implementation of different boiling point [BP] solvent is also considered. The solvent ethanol [BP 78 °C] is replaced

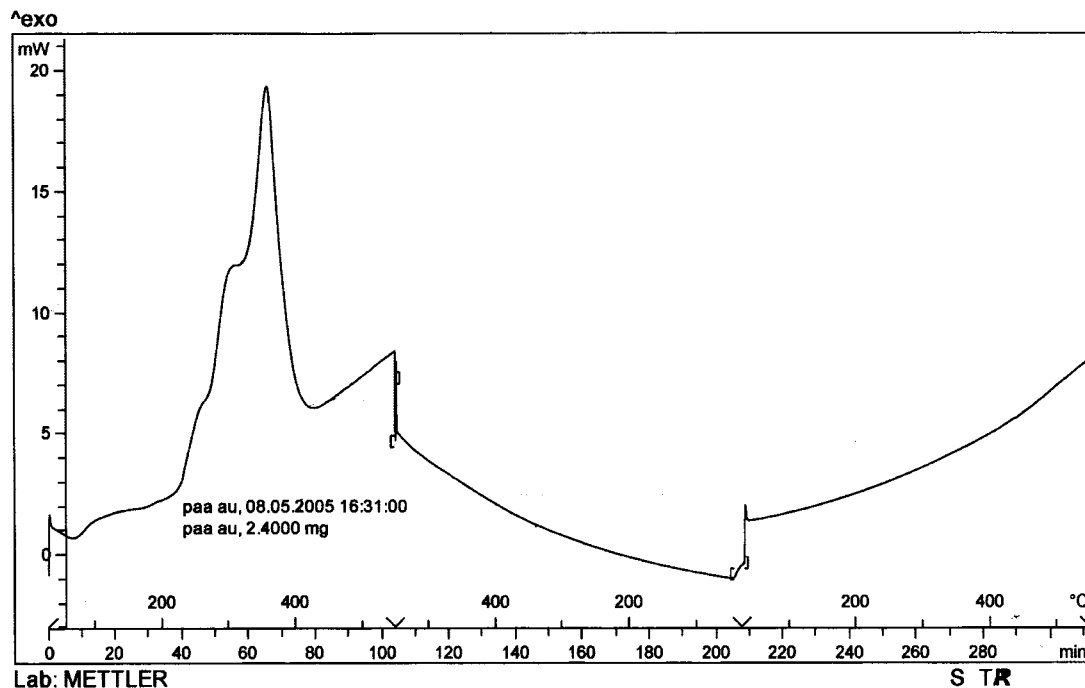


Figure 4. DSC pattern of an as-prepared Au polymer wires prepared using solution C, first heating [30–550 °C], cooling [550–50 °C], and second heating [50–500 °C] cycles.

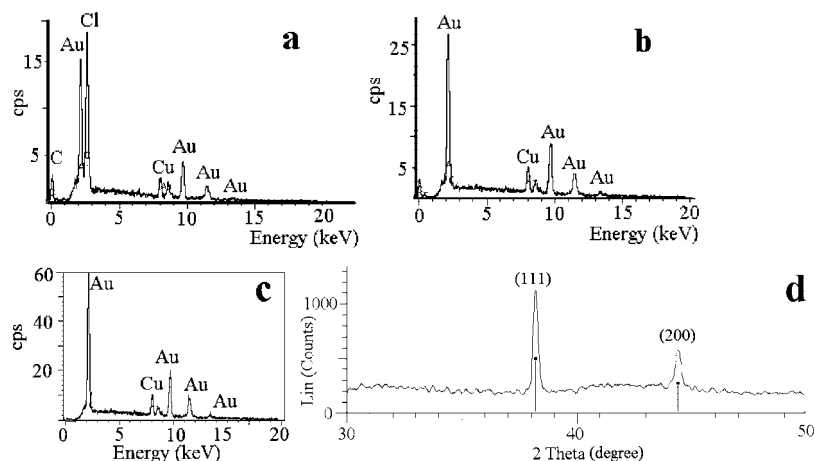


Figure 5. EDX of (a) as-prepared Au polymer wires prepared using solution C, (b) sintering the as-prepared Au polymer wires at 275 °C in air, (c) sintering the as-prepared Au polymer wires at 350 °C, and (d) XRD pattern of as-prepared Au polymer wires heated at 400 °C.

by acetone (BP 56 °C) for the preparation of Au polymer wires [solution E]. Around 2 μm Au polymer wires could be formed [Figure 3e]. The solvent evaporation was too fast. Before the second layer of the Au polymer wires arrived on the support, the first was getting dry [Figure 3e]. As a result, after sintering at 400 °C, very thick gold wires were produced [Figure 4f] and Au particles are not tightly packed.

Since the continuous Au wire could be prepared using solution C, further DSC, EDX and XRD measurements are carried out. The C, H, N, S–O analysis confirmed ~ 32 wt% of carbon in the as-prepared Au polymer wires. DSC measurements for Au polymer wires under air showed a very broad exotherm between 230 and 400 °C, consisting of three exotherms. These exotherms arise from the burning off of the carbon, as well as from the crystallization of the gold wires. To understand those individual exotherms, we annealed Au polymer wires separately at different temperatures

in a furnace under air. Heating the as-prepared Au polymer wires at 275 °C [where the first exotherm ends] results in a carbon residue of $\sim 10\%$ confirmed by C, H, N, S–O analysis. When Au polymer wires are sintered at 350 °C [where second exotherm ends], the C, H, N, S–O analysis detected the presence of carbon $\sim 1\%$ wt. The third strong exotherm is associated with the crystallization of the gold particles. In the DSC measurements, the first cooling and a second heating cycle of the Au polymer wire is featureless. Our EDX analysis also supports this claim. Namely, the as-prepared Au polymer wires [Figure 5a] are mainly composed of C, Au, and Cl (Cu is obtained from the sample support). Sintering the as-prepared Au polymer wires at 275 °C shows small amount of C, Au, and Cu [Figure 5b], and at 350 °C, only Au and Cu [Figure 5c] signals are observed. It means, the first two small exotherms in DSC measurements are—belong to—the burning—off—of the chlorine and the

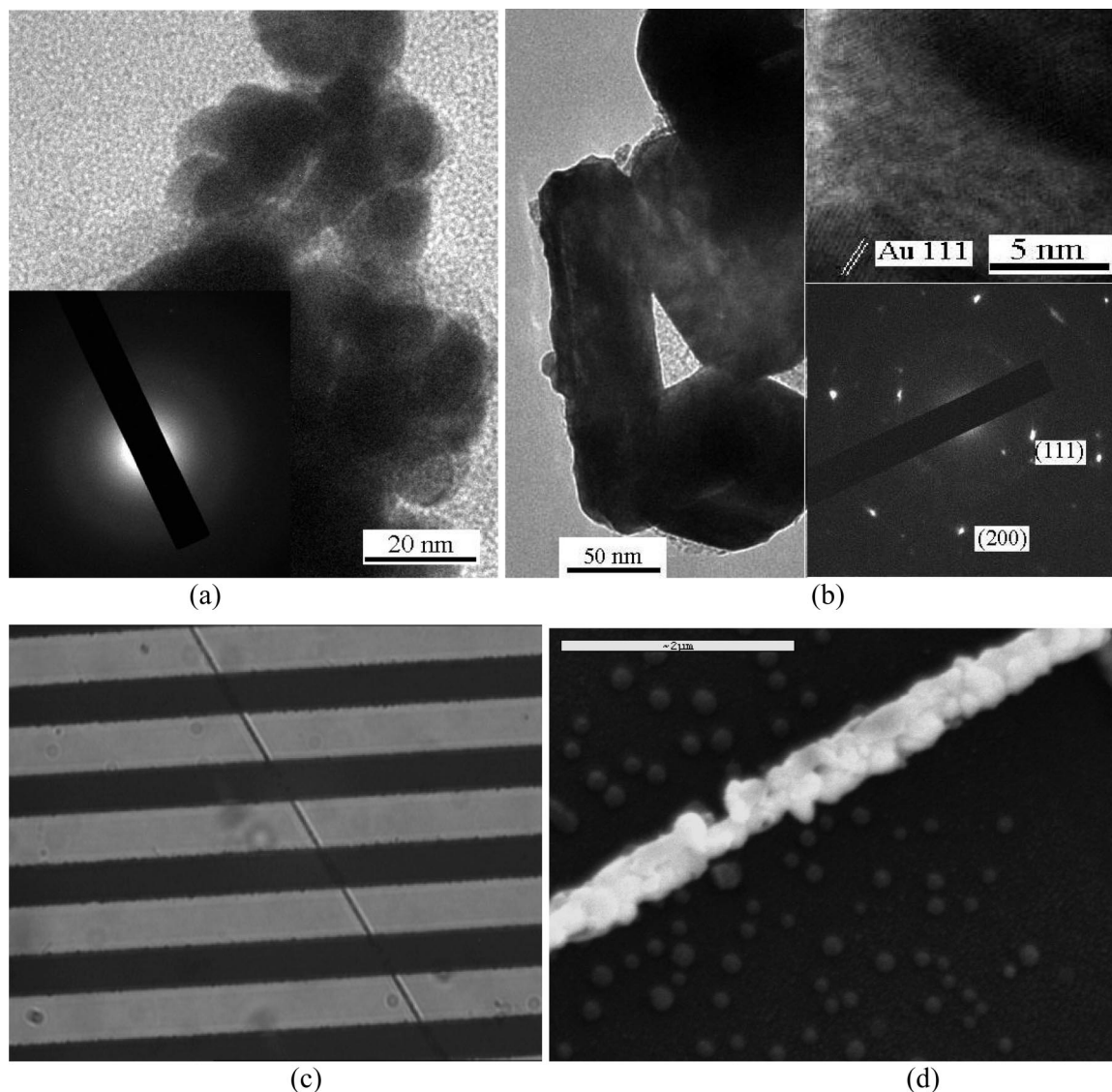


Figure 6. (a) HR-TEM of as-prepared Au polymer wire. The inset shows its electron diffraction (ED). (b) As-prepared Au polymer wire sintered at 400 °C. The top inset shows d spacing, and the bottom, ED. (c) Optical microscopy picture shows a single gold wire across the interdigitated electrodes with a gap distance of 10 μm . (d) HR-SEM image of the Au nanowire shown in part c.

carbon content. Although the C is not detected in Figure 5c, $\sim 1\%$ carbon impurities are still present when fibers sintered at 350 °C that remain attached to gold particles. The as-prepared Au polymer wires fabricated using solution C are XRD amorphous [data not shown] and sintered at 400 °C in air, is found to be crystalline FCC gold [Figure 5d]. From all of the above observations, it is clear that the as-prepared Au polymer wires are composed of gold precursor where the oxidation state of Au is III in an ethanolic solution with PAA polymer. The sintering process burns off the carbon, which might have initiated the reduction of gold (III) to Au(0). This is evidenced by the obtained XRD pattern for the pure FCC Au [Figure 5d] and the absence of Cl and C in the EDX [Figure 5c]. Using Scherrer's formula, the calculated particle size is 95 nm, which corresponds to the TEM picture shown in Figure 6.

The nature (amorphous/crystalline) of the as-prepared Au polymer wires fabricated using solution C and its transformation after sintering at 400 °C in air is checked by

transmission electron microscopy. The as-prepared Au polymer wires are comprised of 10 nm gold nanoparticles [Figure 6a]. These particles did not show any electron diffraction pattern [insert of Figure 6a] or the interlayer spacing, substantiated by the HR-TEM images confirming the amorphous nature of the as-prepared Au polymer wires. Figure 6b shows a HR-TEM micrograph of gold nanoparticle from the gold wire and its electron diffraction image (inset). Indeed, the obvious particle growth was observed after the sintering process. The average particle size increased to ~ 100 nm in diameter after the sintering process. On the surface of gold particles, a small amount of bounded amorphous carbon is also observed. That could be a trapped carbon in between the gold particles that formed the gold wire. This minor (1 wt % C) is also noticed in the C, H, N, S–O analysis. The HR-TEM image clearly shows crystal lattice fringes of 0.24 nm, corresponding to the (111). The bottom inset of Figure 6b shows the corresponding electron diffraction patterns featuring polycrystalline gold particles.

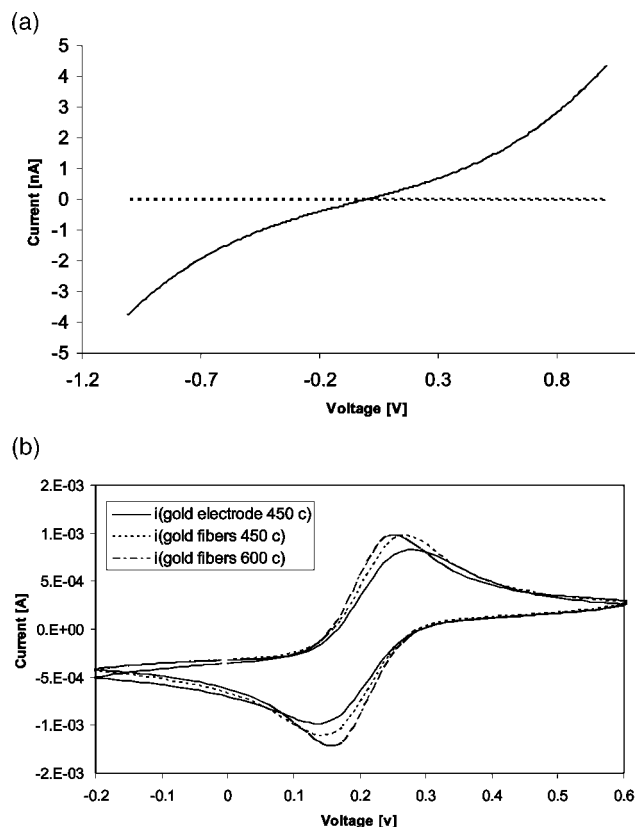


Figure 7. (a) Bias voltage I - V curve between ± 300 mV for the connected electrodes by a $0.3 \mu\text{m}$ gold wire revealing metallic behavior. For comparison, the data for the unconnected electrodes are given as a dashed line. At larger voltages, ± 300 mV, the Au wire shows nonlinear behavior. (b) Cyclic voltammogram for the reduction and oxidation of 0.010 M potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KNO_3 as a supporting electrolyte.

In order to determine the conductivity of the gold wires, we deposited one Au polymer wire on an interdigitated gold electrode as shown in Figure 6c and sintered at 450°C . The single as-prepared Au polymer wire deposition was achieved by fast movement of the gold electrode under the electrospinning syringe. The interdigitated electrode had 50 gold fingers which are separated by $10 \mu\text{m}$ distance. Here, the sintering temperature is increased to 450°C to improve the contact of Au wire with the gold electrode. The HR-SEM image of the Au nanowire used for conductivity measurement is shown in Figure 6d. The gold nanoparticles are well sintered to form continuous Au wire; however, several spherical particles are noticed beside the Au wire. Those unattached Au nanoparticles keep some imperfection in the Au wire.

The I - V curve for an applied bias voltage of $V_{\text{bias}} = \pm 300$ mV is linear, and thus, the electrical behavior of the Au wire is metallic. For a larger applied bias voltage $V_{\text{bias}} = \pm 1000$ mV seen in Figure 7a, the I - V curve shows a nonlinearity. A phenomenon of quantized conductance, observed in atomic-sized metallic contacts, gives rise to the nonlinearity²³ of I - V characteristics. If the nanowire has some strictures,

where only a few conductance channels exist [Figure 6d], then the observed nonlinear effects in the I - V characteristics are caused by the lack of sufficient conductance channels.²⁴ Additionally, the strictures are most likely located at the contacts between the gold wire and the gold electrodes. The 300 nm gold wire showed electrical conductivity of $\sim 1.2 \times 10^{-4}$ S/cm, which is lower than the bulk conductivity ($\sim 10^6$ S/cm). The obtained low conductivity can be results of the lack of interconnected domains or structures or surface defects in the Au wire or leftover amorphous carbon impurities [Figure 6b]. Previously, the conductive gold films have been successfully assembled on flexible electrospun PMMA ultrafine fibrous mat substrates containing gold nanoparticles reduced by a gold salt by filtering a $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution through the mats. In this procedure, the measured conductivity²⁵ of the bulk film of gold particles is reported as 9.3×10^3 S/cm.

The conductivity of the gold wires was further measured in an electrochemical setup. Here we compare the cyclic voltammograms²⁶ of a flat gold electrode with those of similar electrodes that were coated with gold wires. For compact electrodes, we used a conductive ITO glass coated with a thin layer (100 nm) of gold by evaporation. Some of the electrodes were used as the collecting electrodes in the electrospinning of the gold wires forming an array of Au polymer wires on the gold substrate. After calcination at 450 and 600°C for 30 min, the electrochemical behavior of all the gold electrodes in a Fe^{2+} - Fe^{3+} (0.01 M) solution was measured. As shown in Figure 7b, the peak current of the gold wire-coated electrodes (450 and 600°C) increased by $\sim 20\%$, compared with the reference bare gold electrode. This 20% increase in the current peak is proportional to the enhancement of the effective conductive surface area of the electrospun electrodes. This qualitative result confirms the conducting nature of the gold wires after sintering.

In conclusion, we report herein on an innovative electrospinning approach. We electrospun Au polymer wires, dissolving HAuCl_4 salt in ethanol, followed by the addition of poly(acrylic acid). The as-prepared Au polymer wires were assembled in between the spinneret (+ electrode) and the conducting substrate (- electrode), using a drum attached to the rotator via a Teflon shaft. The as-spun continuous Au polymer organized wires (diameters from 50 nm to a few micrometers and lengths of kilometers) can be transformed to the Au wires via sintering. The wires are comprised of compact Au nanocrystals, maintaining their 1D identity. The conducting nature of the single Au nanowires is confirmed by electrical conductivity and cyclic voltammetry measurement.

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