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# In-Wire Conversion of a Metal Nanorod Segment into an Organic Semiconductor<sup>\*\*</sup>

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#### Keywords

chemical vapor deposition; multisegmented nanowires; nanojunctions; organic semiconductors

The development of chemical and physical methods for modifying the structure and composition of nanowires or nanorods<sup>[1-10]</sup> is necessary to expand the utility and function (e.g. electronic, optical, and magnetic properties) of one-dimensional nanomaterials. For instance, on-wire lithography (OWL) is based on a facile three-step process (1) electrochemical deposition of multisegmented nanowires,<sup>[11,12]</sup> 2) physical coating of one wire face with a material that can hold the rod segments together (post etching), and 3) selective chemical etching of sacrificial wire segments) and allows the rational preparation of a wide variety of structures with nanoscale control over compositional and architectural features along the longitudinal axis of the wires.<sup>[6]</sup> This includes nanogaps,<sup>[13,14]</sup> electrical nanotraps,<sup>[15]</sup> plasmonic disk arrays,<sup>[16]</sup> optimized Raman "hot spots",<sup>[17]</sup> and heterostructures that behave as catalytic nanorotors.<sup>[18]</sup> Organic semiconductor materials have recently attracted significant interest for their potential application in the context of functional nanoscale electronic devices<sup>[19-21]</sup> owing to their many unique properties such as their structural and compositional diversity and physical flexibility.<sup>[22,23]</sup> There are a variety of ways of making nanowire-based structures consisting of metal segments sandwiching an organic segment. For instance, methods to synthesize structures in which both the metal and conductive polymer segments are electrically deposited have been developed.<sup>[24,25]</sup> Also, a monolayer of organic molecules can be chemisorbed to the surface of electrochemically deposited rods followed by electroless deposition of a metal segment (which can be further lengthened by electrochemical methods).<sup>[26,27]</sup> Additionally, assembly of an organic layer within gaps formed by two metal nanowires has been reported.<sup>[6,13]</sup>

Herein, we present a new approach for creating nanowires with organic semiconductor nanojunctions. The basic concept involves the electrochemical deposition of multisegmented nanowires followed by selective conversion of a metal segment of these wires into an organic semiconductor material by a simple chemical vapor deposition (CVD) method (Figure 1a). Others have utilized a related approach for transforming certain segments into new inorganic compositions by ion exchange and electroless plating in solution.<sup>[28]</sup> In our

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work, the metal segment is predefined during the electrochemical deposition step and subsequently reacts with organic molecules delivered through the vapor phase to form a new material within the original nanowire structure. The unique features of this "in-wire conversion" method include direct positioning of the newly synthesized material, simple experimental steps, and compatibility with complementary metal-oxide-semiconductor (CMOS) fabrication processes. Also, because the reaction takes place on the nanoscale, the metallic segment is converted fully into semiconductor material owing to complete penetration of the reactant vapor, in contrast to surface-only conversion in the bulk scale. As a proof-of-concept, we selected 7,7,8,8-tetracyanoquinodimethane (TCNQ) as a model system, as organic charge-transfer complexes of MTCNQ (M = Ag, Cu, other metals) have been evaluated as new forms of electrical recording media.<sup>[29–32]</sup> They can be reversibly switched between two stable states, which differ substantially in conductivity.<sup>[33]</sup> We demonstrate that the resulting metal/AgTCNQ/metal nanojunctions show semiconducting behavior and can function potentially as memory devices.

In a typical experiment,  $\approx 9.2$ -µm-long, multisegmented Au-Ag-Au nanowires (diameter  $\approx$ 360 nm) were synthesized by sequential electrochemical deposition of gold (5  $\mu$ m), silver  $(0.2 \,\mu\text{m})$ , and gold  $(4 \,\mu\text{m})$  into AAO templates (Anodisc 47, Whatman). The length of each segment can be controlled by monitoring the charge passed during the electrochemical deposition process.<sup>[12]</sup> Scanning electron microscopy (SEM) revealed that a  $\approx$ 200-nm Ag segment is sandwiched between two Au segments. Chemical composition mapping experiments (energy-dispersive X-ray spectroscopy, EDS) confirmed the elemental identity of each segment (Figure 1b). Ag is an excellent candidate for the metal segment precursor since, under conventional CVD conditions, TCNQ vapor will react with it at a relatively low temperature (160 °C) to form AgTCNQ (Equations (1) and (2)).<sup>[34]</sup>

(g)



the Ag segment was converted into needles of AgTCNQ, some of which bridged the two Au segments (Figure 1c). As expected, the volume of the resulting AgTCNQ product is substantially greater than that of the starting Ag segment; indeed each  $Ag^+$  ion is paired with a molecule of reduced TCNQ. The needles were characterized by Raman spectroscopy, which exhibit vibrational modes that are highly diagnostic of AgTCNQ (Figure 1d). For example, TCNQ exhibits four characteristic principal vibration modes (from 1000 to 2500  $cm^{-1}$ ) at 1208  $cm^{-1}$  (C=CH bending), 1455  $cm^{-1}$  (C–CN wing stretching), 1603  $cm^{-1}$  (C=C ring stretching), and 2227 cm<sup>-1</sup> (C $\equiv$ N stretching). The AgTCNQ salt complex also exhibits four modes in this region, but at different frequencies. For example the C-CN stretch (1383 cm<sup>-1</sup>) and the C $\equiv$ N stretch (2207 cm<sup>-1</sup>) undergo a red shift of 72 and 20 cm<sup>-1</sup>, respectively.<sup>[31]</sup> The Raman spectrum of the in-wire-synthesized AgTCNQ corresponds almost perfectly with that of bulk AgTCNQ.<sup>[35]</sup>

(1)

(2)

To confirm further the incorporation of TCNQ into the multisegmented nanowires and to characterize the electrical properties of Au/AgTCNQ/Au junctions, devices composed of Au-Ag-Au nanowires were fabricated for electrical measurement. First, the multisegmented nanowires were cast onto a substrate and connected to microelectrodes by electron-beam lithography. The entire substrate was then placed into a vessel (right of Figure 1a) for reaction with TCNQ by CVD for 2 h (Figure 2a). The current was measured and plotted as a function of voltage (I-V) before and after the reaction. In a typical experiment (Figure 2bd), prior to the in-wire growth of AgTCNO, the resistance of the device was  $\approx 10\Omega$  (black curve of Figure 2c), which reflects the metallic nature of the Ag segment. After the reaction of the Ag with TCNQ vapor, the Ag segment was converted into AgTCNQ, Figure 2b. Electrical measurements on devices constructed from a single Au/AgTCNQ/Au rod exhibit a nonlinear I-V curve at low applied bias (<5 V) (Figure 2c), which is typical for organic semiconductor materials. This result also provides a clear indication of the conversion of the Ag segment flanked by two gold segments into AgTCNQ, through which the current transport occurs. Moreover, the I-V curves for the forward bias and reverse bias are symmetrical at low bias. Of 41 devices tested, 19 show similar semiconductive I-Vresponses. When a higher bias voltage (10 V) with a full cyclic sweep ( $-10 \rightarrow 0 \rightarrow 10 \rightarrow 0$  $\rightarrow$  -10 V) is applied to prototype devices, reversible hysteretic switching behavior is observed (Figure 2d). As the voltage bias is swept from -10 to 10 V, the device exhibits low impedance, but when the voltage bias is swept from 10 to -10 V, it exhibits high impedance. Indeed, the resistance changes by more than two orders of magnitude during the voltage sweep. The threshold voltage of the device is approximately  $\pm 5$  V, at which point there is a sudden transition in current flow. One possible reason for the electrical switching is an electric-field-induced reversible redox reaction at the interface,<sup>[36,37]</sup> which generates neutral TCNQ and Ag species from the high-impedance AgTCNQ salt (Equation (3)). This cyclical response has been observed for macroscale AgTCNQ devices, which provides further evidence for the chemical transformation in the segmented wire structure.<sup>[33]</sup>

 $[Ag^{+}TCNQ^{-}]_{n} \underset{\text{High-impedence}}{\overset{\text{Voltage}}{\rightleftharpoons}} Ag_{x} + TCNQ_{x} + [Ag^{+}TCNQ^{-}]_{n-x}$ (3)

In summary, we have developed a new in-wire-conversion method for the fabrication of organic semiconductor nanojunctions sandwiched between gold segments. This method was developed as an integrated method for the synthesis of AgTCNQ and the fabrication of nanoscale devices in a single step. AgTCNQ was selectively synthesized between the gold gap electrodes and forms excellent electrical junctions. Furthermore, in contrast to conventional methods for the synthesis of sandwich geometries, our method produces a gap-junction arrangement that does not require further processing of the organic layer after vapor-phase deposition of the molecular material.

# **Experimental Section**

#### Materials

Multisegmented nanowires were prepared according to literature methods.<sup>[6,11]</sup> Ag metal (200 nm) was evaporated on the back of anodic aluminum oxide (AAO) membranes (Whatman, Anodisc 0.02-µm pores, 47-mm outer diameter). These membranes were then placed in an electrochemical cell, which contained a Pt counterelectrode and an Ag/AgCl reference electrode. In all experiments, commercially available 1025 Silver (Ag) and Orotemp 24RTU (Au) electroplating solutions (Technic Inc.) were used for electrochemical deposition. The total charge passed during deposition determined the desired nanowire structure. Ag was deposited as an initial electrical contact layer under DC current at -800

mV (vs. Ag/AgCl), whereas gold was plated at -950 mV. TCNQ was obtained from Sigma and used without further purification (>98%).

#### Characterization

Scanning electron microscopy (Hitachi S4800 and S5500) was used for morphology and elemental-analysis measurements. Raman spectra were recorded with a confocal Raman microscope (CRM300 WiTec) equipped with a piezo scanner and ×100 microscope objectives (N.A. = 0.90; Nikon, Tokyo, Japan). Samples were excited with a 632.8-nm He– Ne laser (Coherent, Inc., Santa Clara, CA) with a spot size of  $\approx 1 \,\mu\text{m}$  and a power density of  $\approx 10^4 \,\text{W cm}^{-2}$ .

#### Photolithography and E-beam Lithography

Si wafers with 600-nm oxide layers were cleaned by sonicating in acetone and ethanol for 30 min. They were subsequently rinsed with ethanol and dried with N2. A photoresist (AZ 1518 Photoresist, Shipley, USA) was applied to the wafer, which was subsequently spun at 3000 rpm for 30 s. After the spin coating, the wafers were put in an oven (90  $^{\circ}$ C) for 30min. The resist was patterned by using a mask aligner (Q-2000 Quintel Mask Aligner, San Jose, CA, USA) and developed with AZ 300 MIF. Cr (5nm) and Au (50 nm) were then thermally evaporated onto the patterned wafer. Finally, the microscopic electrodes were formed after the patterned wafer was immersed in acetone for liftoff. One drop of an aqueous solution of multisegmented nanowires with an Ag segment was deposited on a chip containing prefabricated Au electrodes, and the chip was dried in vacuum. E-beam lithography was utilized to define an inner electrode pattern that connected the nanowires with the microelectrodes. A resist layer of poly(methyl methacrylate) (PMMA) was prepared by the following procedure: 950 PMMA C7 was spincoated at 500 rpm (10 s) and 3000 rpm (45 s) followed by baking at 180 °C for 2 min. EBL was carried out with a FEI Quanta FESEM equipped with the Nabity Pattern Generation System (NPGS, JC Nabity Lithography System, Bozeman, MT, USA) at 30-kV acceleration voltage and 30-pA beam current. Cr (20 nm) and Au (500 nm) were then thermally evaporated onto the PMMA-coated substrate after it was developed with an IPA/MIBK solution (3:1 v/v) for 1 min, and then rinsed with IPA and water.

#### **Electrical Measurements**

The electrodes were wire-bonded to a chip carrier by using a wedge wire-bonder (K&S 4526 wire-bonder, Kulicke & Soffa, Willow Grove, PA, USA). The current–voltage characteristics of the devices were measured with a two-probe configuration, in which a 16-bit digital acquisition board (DAQ, National Instruments, Austin, TX) and preamplifier (Model 1211, DL Instrument, Ithaca, NY, USA) were used for the voltage source and current measurements.

## Supplementary Material

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### Figure 1.

a) Left: Scheme showing selective chemical conversion of a metal segment into a metalorganic semiconductor charge-transfer complex through in-wire conversion. Right: Homebuilt simple CVD setup (for detailed information see Supporting Information, Figure S1). b) SEM image (top) of an Au–Ag–Au multisegmented nanowire and EDS mapping images (bottom) of Au and Ag segments. c) SEM image of AgTCNQ needles synthesized by inwire conversion. d) Raman spectra of both TCNQ and as-grown AgTCNQ.



#### Figure 2.

a) Scheme of the in-wire-conversion device-fabrication method. b) SEM of Au–Ag–Au nanowire device after in-wire conversion. c) *I–V* response of a nanowire device before (black line) and after (grey curve) the TCNQ reaction. d). *I–V* characteristics of Au/AgTCNQ/Au devices showing reversible bistable switching behavior. The arrows indicate the voltage sweep directions.