

Structures and Electrical Properties of Ag–Tetracyanoquinodimethane Organometallic Nanowires

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Abstract—Ag–tetracyanoquinodimethane (Ag–TCNQ) nanostructures are synthesized using both solution reaction in acetonitrile and a novel vacuum-saturated vapor reaction method. Experiments show that the latter synthesis method produces Ag–TCNQ nanowires with better uniformity and higher aspect ratio. These nanowires, having diameters around 100 nm and lengths about 5 μm , could serve as potential building blocks of nanoscale electronics. Nanodevices based on these nanowires are fabricated using the electron-beam lithography technique. Electrical transport study shows reproducible I – V hysteresis with a change in resistance of four orders of magnitude, demonstrating electrical memory effect. This electrical bistability makes Ag–TCNQ nanowires a promising candidate for future applications in ultrahigh-density information storage.

Index Terms—Electrical switching, hysteresis.

I. INTRODUCTION

THE TREND of miniaturization of electronics is greatly accelerated by the discovery of new nanostructured materials. Instead of using lithographic methods, these nanomaterials, such as carbon nanotubes and nanowires, can be readily synthesized by the chemical vapor deposition method [1], [2]. Also, efforts of using them as the building blocks for nanoscale electronics and optoelectronics has achieved significant progress [2]–[5]. For example, programmable logic circuits [6], [7] and memory devices [8] based on carbon nanotube and semiconducting nanowires have been fabricated and tested. However, nanostructures of charge-transfer complex such as Cu–tetracyanoquinodimethane (TCNQ) and Ag–Tetracyanoquinodimethane (TCNQ) have rarely been reported. Because of their unique electrical properties, metal–TCNQ complexes have attracted extensive attention since the 1970s

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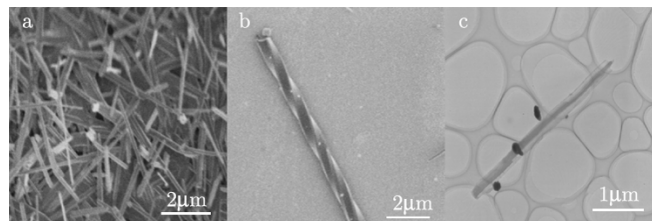


Fig. 1. Morphology of Ag–TCNQ nanostructures synthesized by solution reaction in acetonitrile. (a), (b) SEM images. (c) TEM image of a nano “twist.”

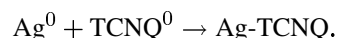
[9]. Electrical properties of their thin-film materials have been previously studied [9]–[12], and their prospective application as recording medium has been demonstrated [10].

In this paper, we report Ag–TCNQ nanostructures synthesized by two methods, i.e., solution reaction in acetonitrile and vacuum vapor reaction method. The Ag–TCNQ nanowire device is fabricated using nanolithography, and its electrical property is characterized.

II. EXPERIMENT

A. Synthesis and Characterization of Ag–TCNQ Nanowires

Metal–TCNQ thin film had been reported to be synthesized by dipping a metal plate into acetonitrile saturated with neutral TCNQ⁰ [9]. Micrometer-sized metal–TCNQ crystals had been achieved [11]. In our experiment, Ag–TCNQ nanostructures were synthesized using a similar method except that we used an Ag thin film instead of a metal plate. First, a 10-nm Ag film was deposited on a silicon (111) substrate by thermal evaporation at 2×10^{-3} Pa. Then the Ag thin film was put into degassed acetonitrile which had been saturated with neutral TCNQ⁰ (98%, Aldrich). In this procedure, the following chemical reaction took place [9]:



The sample was then taken out of the acetonitrile solution after 10 min and TCNQ⁰ residue was washed away with clean acetonitrile. A scanning electron microscopy (SEM) image [see Fig. 1(a)] of the sample shows Ag–TCNQ nanowires with diameters around 200 nm, which is much smaller than the size of Ag–TCNQ microcrystallites [13]. With this synthesis method, a unique twisted nanostructure of Ag–TCNQ is also obtained, as shown in Fig. 1(b).

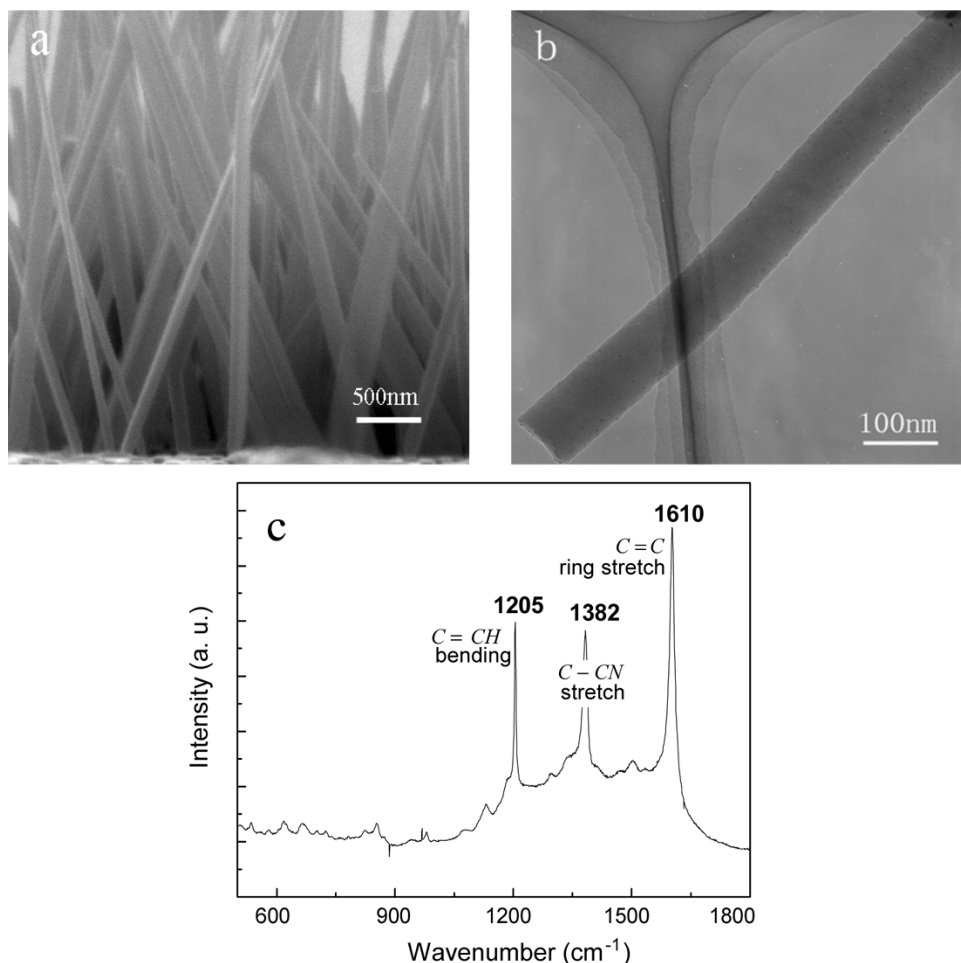


Fig. 2. (a) SEM image of Ag-TCNQ nanowires grow vertically on the substrate with lengths of around $5 \mu\text{m}$. (b) TEM image of a single Ag-TCNQ nanowire with 80-nm diameter. (c) Raman spectrum of nanowires shows C-CN stretching mode shift.

Compared with dipping a metal plate into TCNQ⁰ saturated acetonitrile solution, using Ag thin film resulted in a smaller metal-TCNQ crystal structure. This could be attributed to the fact that the thin film limits the amount of Ag needed in forming a large Ag-TCNQ crystal.

Electrical bistability and memory effect of metal-TCNQ [9]–[11] are the basis for implementing synthesized nanostructures into nanoscale electronics. However, solution reaction synthesized Ag-TCNQ nanostructures do not show high uniformity in the diameters, as illustrated in the transmission electron microscopy (TEM) image [see Fig. 1(c)]. Therefore, a novel vacuum vapor reaction synthesis method has been employed to grow high-quality Ag-TCNQ nanowires. Such a method can also be used to synthesize Cu-TCNQ nanowires.

Ag-TCNQ nanowires were synthesized following these procedures [12]. A 10-nm Ag thin film was deposited onto a silicon (111) substrate in a thermal evaporator under a base pressure of 2×10^{-3} Pa. The Ag thin film was placed together with 15 mg of 7,7,8,8-tetracyanoquinodimethane (98%, Aldrich) in a quartz tube (2.5-cm diameter, 15-cm length). The quartz tube was then molten and sealed to enclose the substrate and TCNQ after pumping down to 2.0×10^{-3} Pa. The sealed tube was then heated up to 368 K in 5 min in a furnace and kept for 2 h in a furnace. Finally, the substrate was taken out from the quartz tube

and baked at 373 K at 2.0×10^{-3} Pa pressure for 0.5 h to remove the TCNQ residue.

SEM and TEM were used to characterize the morphology of Ag-TCNQ nanowires. An SEM image [see Fig. 2(a)] shows that Ag-TCNQ nanowires have lengths of about $5 \mu\text{m}$ and they are grown more orderly on the substrate than those synthesized by solution reaction [see Fig. 1(a)]. The TEM image [see Fig. 2(b)] shows a uniform Ag-TCNQ nanowire with 80-nm diameter, indicating an improvement on nanowire quality using the vacuum vapor reaction synthesis method [see Fig. 1(c)]. Although Ag-TCNQ is reported to have an orthorhombic unit cell with $a = 6.975 \text{ \AA}$, $b = 16.686 \text{ \AA}$, and $c = 17.455 \text{ \AA}$ [13], a high-resolution TEM study on nanowires does not show lattice fringe. It is quite possible that a high-energy electron beam caused damage on the local crystal structure of the nanowires during imaging. In addition, experiments have shown that the thickness of the Ag film has a significant effect on the nanowire's morphology, i.e., thinner film results in a smaller diameter of nanowires. When the thickness of the Ag film is greater than ~ 200 nm, Ag-TCNQ nanowires can hardly be obtained. We believe that the nanowire synthesis is based on a vapor-liquid-solid mechanism, facilitated by the lower melting point of thinner films.

Raman spectrum of metal-TCNQ has often been utilized to identify the chemical bonding between the metal atoms and

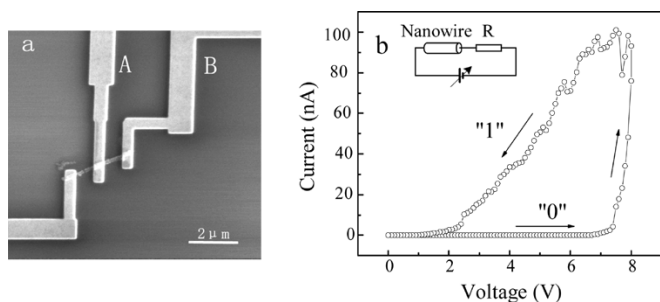


Fig. 3. (a) SEM image of an Ag-TCNQ nanodevice. Electrodes A and B are connected to the measurement circuit. (b) I - V hysteresis characteristics of the nanodevice shows electrical switching and memory effect. The inset plot shows a schematic of the measurement circuit.

TCNQ molecules [14], [15]. Fig. 2(c) shows a Raman spectrum of as-grown Ag-TCNQ nanowires. The Raman bands at 1205 and 1610 cm^{-1} are due to the C = CH bending mode and the C = C ring stretching mode of TCNQ molecules, respectively. Compared with the Raman spectrum of neutral TCNQ, C-CN stretching mode shifts from 1451 to 1382 cm^{-1} , showing evidence for a full charge transfer between Ag and TCNQ [15].

B. Ag-TCNQ Nanowire Device Fabrication

Successful synthesis of high-quality Ag-TCNQ nanowires could open up possibilities of utilizing them for nanoelectronics applications. Nanodevices based on Ag-TCNQ nanowires were fabricated in this study, and their electrical properties were characterized. To obtain nanowire devices, the as-synthesized nanowires with silicon substrate were first placed into isopropyl alcohol and sonicated for 6 min to form nanowire suspension. Then the suspension was deposited onto another silicon substrate which had predefined alignment marks. A high-magnification optical microscope was used to locate the positions of the nanowires, and their coordinates were calculated with respect to the alignment marks. The contact electrode patterns were then designed according to the coordinates. The resists for electron-beam (ebeam) lithography were spin coated to the substrate, followed by an exposure patterned by ebeam writer (Jeol JBX-5D11) with electron energy of 50 keV. Exposed resist was developed, and afterwards electrodes were metallized with Au (110 nm) on top of Ti (20 nm) using an ebeam evaporator. Finally, lift-off was done in acetone.

III. RESULTS AND DISCUSSION

An SEM image of a device is shown in Fig. 3(a). The current-voltage (I - V) characteristics of Ag-TCNQ nanowire were measured using a semiconductor parameter analyzer (Agilent 4156C) at room temperature. A 20-M Ω load resistor (R) was placed in series with the sample to protect it from current burst. A schematic of the measurement circuit is depicted in the inset of Fig. 3(b).

I - V curves were obtained by sweeping up and down a dc voltage, ranging from 0 to 8 V, applied between electrodes A and B as indicated in Fig. 3(a). Fig. 3(b) shows the reproducible I - V characteristics of the Ag-TCNQ nanowire. Similar electrical behavior was also observed under reversed polarity. An I - V hysteresis loop shows switching and memory effect.

Electrical switching indicates a transition from a high-resistance state to a low-resistance state. The threshold voltage for the resistance switching is 7.5 V, as shown in Fig. 3(b). Since the length of the Ag-TCNQ nanowire between electrodes A and B is 1 μm , the threshold electric field is close to 10^7 V/m. In the high-resistance state, the nanowire resistance is around 300 G Ω while it drops to 50 M Ω in the low-resistance state. After subtracting out the voltage drop on the 20-M Ω load resistor, the actual ON-OFF ratio for switching reaches 10^4 . Such electrical switching behavior of the metal-TCNQ complex is explained as an electric-field-induced reversible phase transition [9], [16]. This phase transition yields a partial neutral species of metal and TCNQ from metal-TCNQ and forms conduction channels in the material which substantially increases conductivity [16].

I - V characteristics also demonstrate electrical memory effect. As shown in Fig. 3(b), the resistance of the nanowire is kept in the low-resistance state when the voltage is being swept back to 0 V. If the high- and low-resistance states represent binary states "0" and "1," respectively, Ag-TCNQ nanowires hold promising application as an organic electrical memory material due to the large resistance change between the "0" and "1" states. If Ag-TCNQ nanowires are synthesized in precise orientation and fabricated into highly integrated devices, information storage density up to 10^{10} b/cm 2 can be potentially achieved.

IV. SUMMARY

Ag-TCNQ nanostructures have been successfully synthesized by two methods of solution reaction in acetonitrile and vacuum vapor reaction. Nanowires synthesized by vacuum vapor reaction show better quality. SEM images show that vacuum vapor reaction synthesized Ag-TCNQ nanowires have diameters of around 100 nm and lengths of approximately 5 μm . Nanodevices based on these nanowires are fabricated using ebeam lithography followed by ebeam evaporation. Electrical properties are characterized at room temperature. Reproducible I - V hysteresis is obtained, which shows large ON-OFF ratio electrical switching and electrical memory effect. These unique electrical properties of Ag-TCNQ nanowires demonstrate their promising applications in nanoelectronics, especially in ultrahigh-density information storage.

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