Communication

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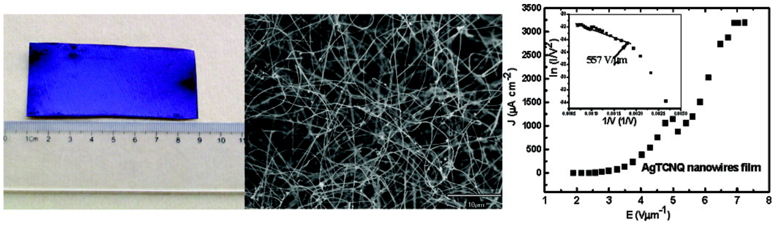

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Field Emission Properties of Large-Area Nanowires of Organic Charge-Transfer Complexes

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There is a great deal of interest in low-voltage electronic field emission driven by possible application in microwave power amplification,[1] space propulsion,[2] chemical analysis,[3] e-beam lithography,[4] display devices,[5] and high-efficiency lighting.[6] Several nanostructures, such as carbon nanotubes,[7] tungsten nanorods,[8] SiC nanoneedles,[9] $W_{18}O_{49}$ nanowires,[10] Mo/MoO$_x$ nanowires,[11] etc., are highly promising field emitters for large-area flat-panel displays. Some semiconductors nanostructures[12,13] have been demonstrated as field emitters, but often require high-temperature processing and expensive deposition equipment. Organic materials attract interests for potential application in functional nanoscale electronic and optoelectronic devices[14−16] owing to their many unique properties such as flexibility, high photoconductivity, and nonlinear optical effects.

Organic charge-transfer complexes of AgTCNQ and CuTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) have unique electrical properties and have been applied as optical and electrical recording media.[17] They show high densities of charge carriers and lead to high conductivity and optical field-induced phase transitions. The resistivity of these material switches from a high impedance state to a low impedance state within a few nanoseconds by applying an electric field, which suggests that they may become a novel class of excellent field emission materials. We report here the first preparation of large-area (8 × 3.6 cm^2, 14.3 × 3.4 cm^2) AgTCNQ and CuTCNQ nanowires on the surface of Ag and Cu foils by organic vapor−solid-phase reaction, which can be applied in an inexpensive process and patterned on various substrates. We also fabricate the field emission device based on AgTCNQ and CuTCNQ nanowires, and they show excellent field emission properties.

Large-area complex nanowires were prepared by organic solid-phase reactions that give good and simple control of the uniformity. In a typical procedure, the TCNQ powders were loaded in a ceramic boat and then placed at the center of a quartz tube that was inserted into a horizontal tube furnace. The copper or silver foil was placed on top of the ceramic boat. The furnace temperature was first increased to 120 °C for copper foil or 150 °C for silver foil and then kept at that temperature for 2 h. The TCNQs were deposited on the surface of the foil of the silver or copper for formation of AgTCNQ or CuTCNQ films. The full characterization data of the products indicate the typical characteristics of AgTCNQ and CuTCNQ (see Supporting Information). If the foil was replaced with silver or copper foil with glass and silicon coated with silver or copper, we also obtained AgTCNQ or CuTCNQ nanowires on those surfaces (Supporting Information). Figure 1 shows the AgTCNQ and CuTCNQ nanowires grown on the Ag and Cu foil through organic vapor−solid-phase reaction. Figure 1, parts A and B, displays the photographs of the large-area AgTCNQ and CuTCNQ nanowires, whose areas are up to 28 and 48 cm^2, respectively. The SEM image (Figure 1C) reveals that the blue film coated on the surface of the silver foil consists of large-scale AgTCNQ nanowires. The length of the nanowires is about several tens of micrometers, and the diameter of the nanowires is in the range of 40−150 nm. As seen in Figure 1D, the layer of blue-black film on the surface of the copper foil consists of a large quantity of oriented CuTCNQ nanowires. The diameter of oriented nanowires is smaller at the tip position than that at the bottom position, whose diameter of the nanowire tip is in the narrow range of 40−70 nm. Further characterization of the nanowires was performed by TEM. Figure 2A shows a typical TEM image of the single AgTCNQ nanowire with diameter of about 50 nm. The diameters of a typical individual CuTCNQ nanowire (Figure 2B) are about 70 and 110 nm at the tip and bottom positions, respectively.

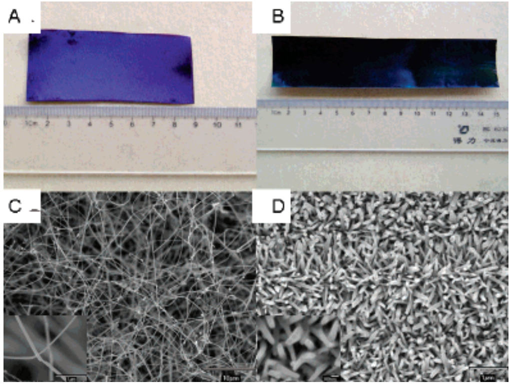

Figure 1. Photographs: (A) AgTCNQ nanowires grown on the silver foil with area of 8 × 3.6 cm^2. (B) CuTCNQ nanowires grown on the copper foil with area of 14.3 × 3.4 cm^2. SEM images: (C) AgTCNQ nanowires. The inset is higher magnification of AgTCNQ nanowires. (D) CuTCNQ nanowires. The inset is higher magnification of CuTCNQ nanowires.

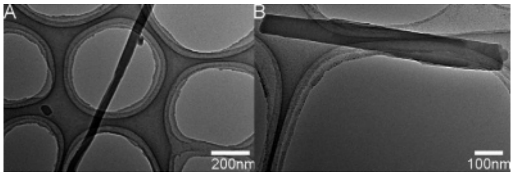

Figure 2. (A) TEM image of a typical AgTCNQ nanowire. (B) TEM image of an individual CuTCNQ nanowire.

As expected from the charge-transfer complex nanowires, excellent field emission properties have been observed in both the

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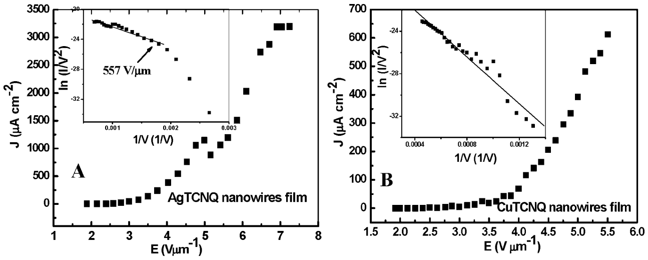

Figure 3. (A) Field emission *J*−*E* curve of the AgTCNQ nanowires and the corresponding FN plot (inset). (B) Field emission *J*−*E* curve of the CuTCNQ nanowires and the corresponding FN plot (inset).

AgTCNQ and CuTCNQ nanowire films. Figure 3 shows typical plots of the field emission current density versus the applied electric field of the AgTCNQ and CuTCNQ nanowires films. The AgTCNQ and CuTCNQ nanowire films exhibit a turn-on field of 2.58 and 3.13 V μm^{-1}, respectively, which are defined to be the macroscopic fields required to produce a current density of 10 μA cm^{-2}. Although these values are higher than the best data from carbon nanotubes[7b] and SiC nanowires,[9b] they are much lower than those of organic semiconductor nanowires[15] and many other inorganic nanomaterials.[12b,13b,c] The turn-on field of AgTCNQ is little higher than that of Mo nanowires and is almost the same as that of MoO_2 nanowires.[11] The fact that the field emission of the AgTCNQ nanowires is much better than that of CuTCNQ nanowires may arise from the difference in the electron affinity between the AgTCNQ and CuTCNQ. More importantly, as field emission materials, AgTCNQ and CuTCNQ nanowires have the advantage over other nanomaterials in that they were prepared at low temperature, benchtop experimental conditions, and on the surface of any substrates sprayed with a layer of silver and copper with appropriate thickness. Therefore, it is not necessary to worry about the possibility of degradation of these nanowire emitters during the process of fabrication of vacuum electronic and microelectronic devices caused by oxidation.

The emission characteristics were analyzed using the Fowler−Nordheim model described as follows:[18] $J = E_{\mathrm{loc}}^2 \exp(-6.8 \times 107\phi^{3/2}/E_{\mathrm{loc}})$ (1), where J is the current density from the emitting tip, E_{loc} is the local electric field, and ϕ is the work function of the sample. For an isolated hemisphere model: $E_{\mathrm{loc}} = V/(\alpha R_{\mathrm{tip}})$ (2), where V is the applied voltage, R_{tip} is the tip radius of curvature, and α is a modifying factor. From eqs 1 and 2, we get: $\ln(I/V^2) = 1/V(-6.8 \times \alpha R_{\mathrm{tip}}\phi^{3/2}) + \mathit{offset}$ (3). $\alpha R_{\mathrm{tip}}\phi^{3/2}$ can be estimated from the slope of the FN plot of $\ln(I/V^2)$ against $(1/V)$, as depicted in the inset in Figure 3. For the CuTCNQ sample, the variation of $\ln(I/V^2)$ with $(1/V)$ is a rough straight line, indicating that the field emission process from the nanowires film is a quantum tunneling process. Taking $\alpha = 10$ (as used in another report[19]) and $R_{\mathrm{tip}} = 35$ nm in our case, the evaluated work function of the CuTCNQ nanowires is around 2.77 eV, whereas in the AgTCNQ sample, it is noteworthy that the FN plot has a two-stage slope characteristic. The FN plot shows a linear relationship in a higher electric field region when the applied electric field is larger than 557 V/μm. Deviation from the linear in the FN plot occurs in a low electric field, which is usually observed in carbon nanotubes.[20] Using $\alpha = 10$ and $R_{\mathrm{tip}} = 25$ nm in this case, we estimated the work functions of the AgTCNQ nanowires to be 1.19 eV, corresponding to the high field region ≥557 V/μm, which is lower than that of CuTCNQ nanowires. Typically, the work function of graphite is about 4.34 eV.[21] The work functions obtained for both of our sample are much smaller than that of the graphite, which is typically around 4.34 eV,[21] demonstrating that the TCNQCu and TCNQAg nanowire films have great potential as very competitive candidates for field emitters.

In summary, large-area organic charge-transfer complex (AgTCNQ and CuTCNQ) nanowires were synthesized by organic vapor−solid-phase reaction. These nanowires can be facilitated on the surface of different kinds of substrates coated with a layer of silver and copper on a large scale under mild experimental conditions. The excellent field emission properties were observed in the as-grown AgTCNQ and CuTCNQ nanowires. They should have great potential in vacuum device applications.

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Supporting Information Available: Synthetic procedures and full characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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