

One-dimensional electron transport in Cu-tetracyanoquinodimethane organic nanowires

Zhixian Zhou^{a)}

Materials Science and Technological Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Kai Xiao

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

R. Jin, D. Mandrus, Jing Tao, D. B. Geohegan, and Stephen Pennycook

Materials Science and Technological Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 21 March 2007; accepted 18 April 2007; published online 9 May 2007)

The temperature and bias voltage dependent electrical transport properties of *in situ* fabricated Cu-tetracyanoquinodimethane organic nanowire devices are investigated. The low bias conductance and current exhibit a power-law dependence on temperature and bias voltage, respectively. The overall behavior of these nanowires can be well described by a theoretical model of nearly independent parallel chains of quantum dots created by randomly distributed defects. © 2007 American Institute of Physics. [DOI: 10.1063/1.2738380]

Chemically synthesized one-dimensional (1D) nanostructures serve as model systems for investigating transport mechanisms on the nanoscale, where the quantum confinement effect, Coulomb charging energy, electron-electron interactions, and disorder all play important roles. In particular, the effects of disorder in 1D systems are significantly more pronounced than in systems of higher dimensionality. Unlike in two-dimensional or three-dimensional systems, current is unable to bypass the impurity sites in 1D systems. In a disordered 1D system the underlying transport mechanism is usually variable range hopping (VRH) conductivity: a hopping electron will always try to find the lowest activation energy ΔE and the shortest hopping distance r to maximize the hopping probability as determined by $P \sim \exp(-2r/a - \Delta E/k_B T)$, where a is the localization length and k_B is Boltzmann's constant. The standard Mott VRH model predicts $G \sim \exp[-(T_0/T)^{1/2}]$ for disordered 1D systems without electron-electron interactions.¹ On the other hand, when Coulomb interactions are taken into account, a disordered 1D system can also be considered as a chain of weakly coupled 1D quantum dots in the Coulomb blockade regime.² According to a recent theory,² in such a system the 1D Mott law is restricted to low temperatures. When the temperature is not too low, function $I(T, V)$ is predicted to behave approximately as one of the two power laws: $I \propto VT^\alpha$ at low voltage and $I \propto V^{\beta+1}$ at high voltage. The exponents, α and β , depend on interaction and disorder.

The intriguing electrical properties of Cu-tetracyanoquinodimethane (TCNQ) such as switching and memory effects make them a promising candidate for organic memory devices.^{3,4} Nanowire devices of Cu-TCNQ and closely related compounds have been fabricated and electrically characterized at room temperature,^{5,6} and temperature dependent electrical transport properties were reported on bulk samples only.^{7,8} In this letter we present re-

sults of the electrical transport measurements on self-assembled Cu-TCNQ organic nanowire devices for $105 < T < 330$ K.

Cu-TCNQ is a quasi-one-dimensional organic charge-transfer complex with segregated columns of Cu cation and TCNQ anion. Cu-TCNQ has two phases: the high conductance phase (phase I) and the low conductance phase (phase II). In phase I the TCNQ⁻ units are involved in close π -stacking interactions at ~ 0.324 nm whereas in phase II the closest approach of the rings is ~ 0.68 nm, leading to dramatically different conductivities for the two phases (0.25 and 1.3×10^{-5} S cm⁻¹ for phases I and II, respectively). The latter is believed to be responsible for the electrical switching and memory effects.⁷

The Cu-TCNQ nanowire devices were fabricated on degenerately doped Si wafers with 500 nm of thermal SiO₂. The electrodes were defined using electron beam lithography followed by electron gun assisted deposition of a 10 nm Ti adhesion layer, 60 nm of Au, 50 nm of Cu, and 100 nm of Au. The Cu-TCNQ nanowires were grown by the reaction of TCNQ vapor with the Cu layer in the electrodes via vapor-solid reaction.^{5,9,10} In our devices, individual Cu-TCNQ nanowires with diameters between 20 and 100 nm were routinely found to bridge the opposing electrodes through the sidewalls of the Cu layer.

Figure 1(a) depicts a typical example of a few suspended Cu-TCNQ nanowires electrically contacting two electrodes separated by 500 nm. The self-assembled nanowires between electrodes were characterized by Raman spectroscopy and confirmed to be composed of Cu-TCNQ.⁵ Transmission electron microscopy (TEM) experiment performed on nanowires synthesized under identical conditions reveals that the nanowires are largely single crystalline phase I Cu-TCNQ growing along the a axis (or the π -stacking direction). Figure 1(b) schematically illustrates the crystal structure of phase I Cu TCNQ, where the Cu atoms are coordinated to four nitrogen atoms in a highly distorted tetrahedral environment and the quinoid rings of the TCNQ units are engaged in face-to-face stacking to form segregated columns along the a axis. The

^{a)} Author to whom correspondence should be addressed; electronic mail: zhouz@ornl.gov

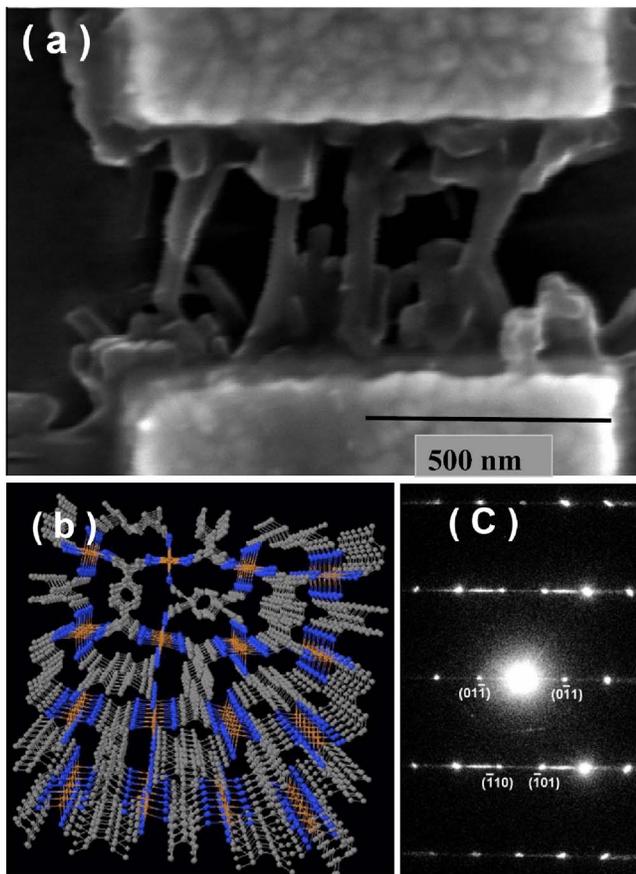


FIG. 1. (Color online) (a) Scanning electron microscopy image showing a Cu-TCNQ nanowire device, where the electrodes are separated by approximately 500 nm. (b) Crystal structure of phase I Cu-TCNQ (Cu: yellow, N: blue, and C: gray). (c) SAED pattern obtained from a representative single Cu-TCNQ nanowire at zone axis [111], where the long bright streaks along the $\langle 011 \rangle$ direction are attributed to the defects arranged parallel to the a axis (the nanowire growth direction).

strong π - π stacking of TCNQ⁻ radicals along the a axis favors the 1D growth of nanowires and may also enhance the carrier mobility along the a direction.^{10,11} Selected area electron diffraction (SAED) experiment performed on Cu-TCNQ nanowires synthesized under identical conditions reveals significant structural defects as indicated by the long bright streaks in Fig. 1(c). The electrical transport measurements were performed in the two-probe geometry inside a variable temperature cryostat, using a Keithley 6430 source-measure unit.

We have characterized dozens of Cu-TCNQ nanowire devices and observed both phases of Cu-TCNQ. In this study we focus on the devices chiefly consisting of the phase I Cu-TCNQ nanowires as indicated by the linear current-voltage (I - V) dependence at low V and the absence of memory effect. Figure 2 shows the temperature dependence of the conductance G as determined by measuring the dc I - V characteristic and taking the slope at zero bias for three representative devices. Nonmetallic behavior ($dG/dT > 0$) is observed over the entire temperature range measured, with the conductance decreasing by up to over three orders of magnitude upon cooling from 330 to 105 K (S3). The data for all the three samples approximately fit to the 1D VRH model. With further decrease of temperature, the conductance becomes immeasurably small possibly due to Coulomb blockade effects. While simple activation behavior was ob-

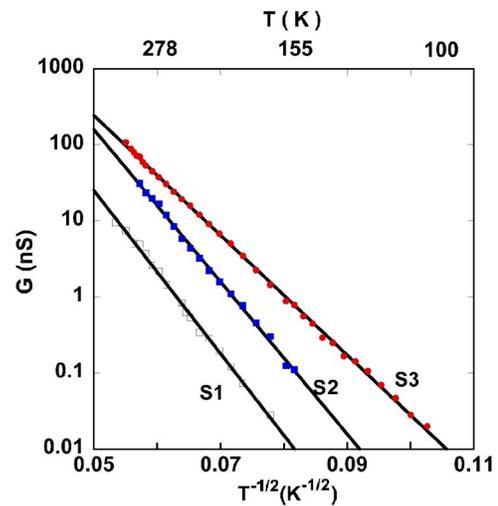


FIG. 2. (Color online) Low bias conductance of three Cu-TCNQ nanowire devices (symbols) and fits (solid lines) to the 1D variable range hopping model.

served in bulk Cu-TCNQ crystals,⁷ neither the three-dimensional VRH model nor the simple activation model fits our data (not shown). This finding is consistent with the 1D structure of the phase I Cu-TCNQ nanowires with defects.

Fogler *et al.* have demonstrated in their recent theoretical calculations that a 1D wire with a finite density of random impurities (or defects) can also be modeled as a chain of weakly coupled quantum dots when Coulomb interactions are taken into account.² They showed that for such a system there exists a broad parameter regime where the current can exhibit T and V dependences that can be approximated by power laws ($I \sim VT^\alpha$ at low V and $I \sim V^{\beta+1}$ at high V) usually with $\alpha \gg \beta$. Figure 3(a) shows the conductance ($G = I/V$ at low V) vs T in the double logarithmic plot for the same samples, as depicted in Fig. 2. A power-law dependence $G \sim T^\alpha$ is indeed observed for more than two decades of conductance in all the three samples with a single α in the range between 7.4 and 8.1.

Further support for the weakly coupled quantum dot chain model can be found in the I - V characteristic for $V \gg k_B T$. Figure 3(b) shows the log-log plot of I - V curves at different temperatures for one of the samples (S3). A transition between Ohmic ($I \sim V$) and power-law behavior ($I \sim V^{\beta+1}$) is observed as V increases. The exponent β obtained from the data in the voltage range between 3 and 8 V is slightly temperature dependent and increases from 2.5 to 3.4 as the temperature decreases from 215 to 145 K. Moreover, the I - V curves measured at different temperatures for the same sample collapse remarkably well on to a single curve as we plot $1/T^{\alpha+1}$ vs $eV/k_B T$, where $\alpha \sim 7.4$ is the exponent in $G(T) \sim T^\alpha$ [inset of Fig. 3(b)]. Table I lists α and β for all the three samples. In general, we find that α is significantly larger than β , consistent with the theoretical predictions.² The smaller power-law exponent at higher T can be attributed to reduced typical hopping distance.¹² Power-law behavior has been observed in various 1D systems, including molybdenum selenide nanowires, single and multiwalled carbon nanotubes, and conducting polymers.¹³⁻¹⁷ The power-law dependences in these systems were attributed to the tunneling of electrons into a Luttinger liquid (LL). However, the unusually large α and α/β ratio makes it unlikely for the power laws in our devices to origi-

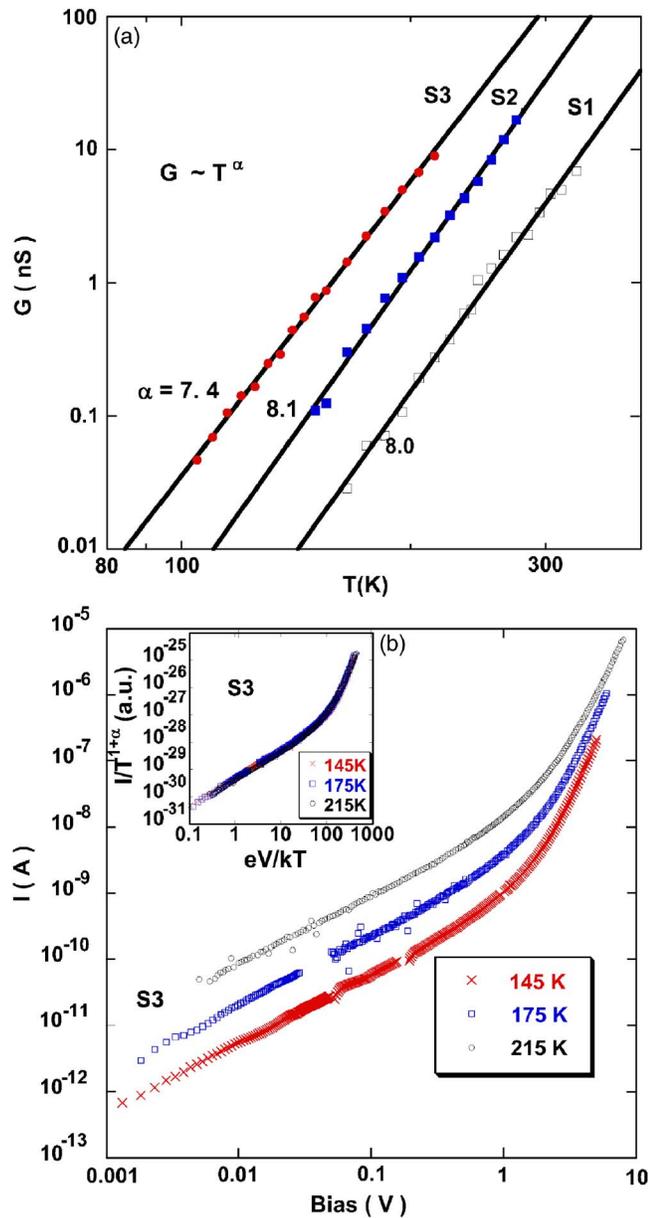


FIG. 3. (Color online) (a) Low bias conductance vs T for the same Cu-TCNQ nanowire devices, as shown in Fig. 2; solid lines are fits to the power law, $G \sim T^\alpha$. (b) I - V data taken at different temperatures. All curves show a change from linear response ($\beta \sim 0$) to power-law dependence at a temperature dependent high bias voltage. Inset: $1/I^{\alpha+1}$ determined from the I - V data plotted against $eV/k_B T$.

nate from the LL effects. On the other hand, the 1D quantum dot chain model can explain not only the power laws but also the large α/β .

The coincidence of power-law temperature dependence and 1D VRH behavior in our Cu-TCNQ nanowires may be

TABLE I. Exponents α and β determined from the temperature dependent conductance and I - V characteristic of three representative Cu-TCNQ nanowire devices. Values of the slightly temperature dependent β are listed for three different temperatures (in parentheses): β_1 , β_2 , and β_3 .

| Sample | S1 | S2 | S3 |
|-----------|-------------|-------------|------------|
| α | 8.0 | 8.1 | 7.4 |
| β_1 | 0.95(305 K) | 0.57(245 K) | 2.5(215 K) |
| β_2 | 1.15(245 K) | 0.71(225 K) | 3.2(175 K) |
| β_3 | 1.25(205 K) | 0.95(185 K) | 3.4(145 K) |

attributed to the rather limited temperature range. A second possibility is that our nanowires are close to the transitional parameter range between VRH and weakly coupled quantum dots. While the power-law behavior in the I - V characteristic cannot be explained in the context of the standard VRH model, our data agree with the 1D quantum dot chain model indicating that the Coulomb interactions in our Cu-TCNQ nanowires cannot be neglected. It is also worth pointing out that the Cu-TCNQ nanowires in our devices are quasi-1D systems with a large number of nearly independent 1D conducting channels in parallel. Therefore, mesoscopic fluctuations that would normally obscure the power-law behavior in strictly 1D wires are averaged out in our systems.²

In summary, the electrical transport properties of our Cu-TCNQ nanowires are consistent with their disordered 1D structure as determined by TEM. The power-law dependences indicate the existence of Coulomb interactions in our nanowires. Further experimental studies for a larger temperature range will be needed to fully understand the intriguing 1D transport phenomena in Cu-TCNQ organic nanowires by eliminating any potential ambiguity.

The authors would like to thank Pam Fleming for technical assistance and Michael M. Fogler, Jian-Min Zuo, and Pedro Schlottmann for helpful discussions. Research sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. Part of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

¹A. N. Bloch, R. B. Weisman, and C. M. Varma, Phys. Rev. Lett. **28**, 753 (1972).

²M. M. Fogler, S. V. Malinin, and T. Nattermann, Phys. Rev. Lett. **97**, 096601 (2006).

³R. S. Potember, T. O. Poehler, and D. O. Cowan, Appl. Phys. Lett. **34**, 405 (1979).

⁴C. Sato, S. Wakamatsu, K. Tadokoro, and K. Ishii, J. Appl. Phys. **68**, 6535 (1990).

⁵K. Xiao, I. N. Ivanov, A. A. Puretzy, Z. Liu, and D. B. Geohegan, Adv. Mater. (Weinheim, Ger.) **18**, 2184 (2006).

⁶Z. Fan, X. Mo, C. Lou, Y. Yao, D. Wang, G. Chen, and J. G. Lu, IEEE Trans. Nanotechnol. **4**, 238 (2005).

⁷R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, and K. R. Dunbar, Inorg. Chem. **38**, 144 (1999).

⁸S. Hüning and P. Erk, Adv. Mater. (Weinheim, Ger.) **3**, 225 (1991).

⁹Z. Zhou, R. Jin, G. Eres, A. Subedi, and D. Mandrus, Appl. Phys. Lett. **89**, 133124 (2006).

¹⁰K. Xiao, J. Tao, Z. W. Pan, A. A. Puretzy, I. N. Ivanov, S. J. Pennycook, and D. B. Geohegan, Angew. Chem., Int. Ed. **46**, 2650 (2007).

¹¹A. Datar, K. Balakrishnan, X. Yang, Z. Xiaobing, J. Huang, R. Oitker, M. Yen, J. Zhao, D. M. Tiede, and L. Zang, J. Phys. Chem. B **110**, 12327 (2006).

¹²T. B. Tran, I. S. Beloborodov, X. M. Lin, T. P. Bigioni, V. M. Vinokur, and H. M. Jaeger, Phys. Rev. Lett. **95**, 076806 (2005).

¹³L. Venkataraman, Y. S. Hong, and P. Kim, Phys. Rev. Lett. **96**, 076601 (2006).

¹⁴M. Bockrath, D. H. Cobden, J. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen, Nature (London) **397**, 598 (1999).

¹⁵Z. Yao, H. W. C. Postma, L. Balents, and C. Dekker, Nature (London) **402**, 273 (1999).

¹⁶A. Bachtold, M. de Jonge, K. Grove-Rasmussen, P. L. McEuen, M. Buitelaar, and C. Schönenberger, Phys. Rev. Lett. **87**, 166801 (2001).

¹⁷A. N. Aleshin, H. J. Lee, Y. W. Park, and K. Akagi, Phys. Rev. Lett. **93**, 196601 (2004).