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A Possibility of Cross-Bar Wiring in Three-Dimensional Crystallographic Space

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Abstract

Sheathed nanowires based on well-defined molecular structures can sometimes be crystallized. A possibility of using the three-dimensional translational symmetry of such nanowire crystals in a cross-bar wiring for molecular devices will be discussed.

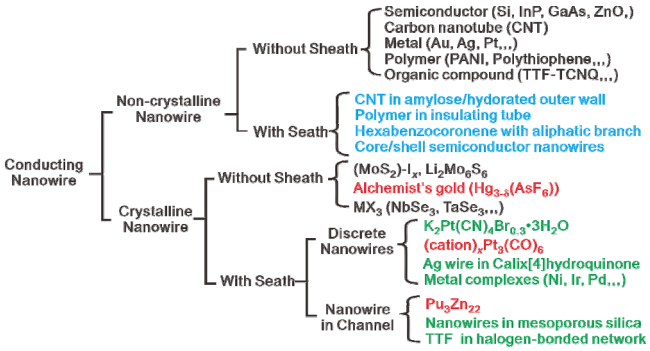
1. Introduction

Because of the translational symmetry of the crystal structure, crystallized nanowires might be used for wiring a three-dimensional (3D) and large-scale molecular memory array. In this paper, crystal structures involving ordered nanowire arrays that might be used for such a purpose will be discussed. In the first part, some crystallographic symmetries and conduction/insulation properties required for wiring application will be described. In the second part, the structural and conducting properties of known sheathed nanowires with crystalline periodicity will be introduced. These examples include both metal-complex nanowires and organic π-π stack nanowires, the latter of which are results from the author's group. Although most of the nanowire crystals show parallel alignments of the sheathed nanowires, several examples show cross-bar arrangements.

2. 3D wiring by Crystal Growth

Recently, some molecules are known to store information written by electronic recording, which is called molecular memory. An apparent advantage of molecular memory is its high information density expected from its extremely small size. However, such a high density can only be achieved after technologies for the arrangement and wiring of these molecules are established. In this regard, none of existing 2D or 3D wiring technology is effective in realizing large-scale molecular wiring for the moment.

Scheme 1 shows a classification of known conducting nanowires that might be suitable for wiring molecular memories. Most of the nanowires are independent and do not form a long-range ordered periodic structure as in the cases of carbon nanotube (CNT) or semiconductor nanowires (upper branches). On the other hand, some organometallic complexes, inorganic 1D materials, and organic cation radical species can form conducting nanowires aligned by crystallographic periodicity (lower branches). Some of them are associated with insulating sheath, so that the anisotropy in the conductivity can be very high. In order to make these nanowires practically effective in wiring the molecular devices, issues listed below should be addressed. (1) the number of strands in one nanowire should be multiplied in order to avoid serious disconnection due to a lattice defect (2) the insulation resistance of the sheath should become high enough to avoid cross-talks (3) the nanowires should be arranged orthogonally in a layer-by-layer stacking as shown in Figure 1 (4) molecular devices should be allocated at each inter-connection of the nanowire system. Strategies to overcome these obstacles will be discussed.



Scheme. 1 Classification of conducting nanowires. Most of the nanowires do not form a crystalline entities, but some of them can be aligned in a periodic pattern with crystallographic symmetry. Among them, alchemist's gold, $(cation)_xPt_3(CO)_6$, and Pu_3Zn_{22} show 3D cross-bar arrangements. (from ref. 1)

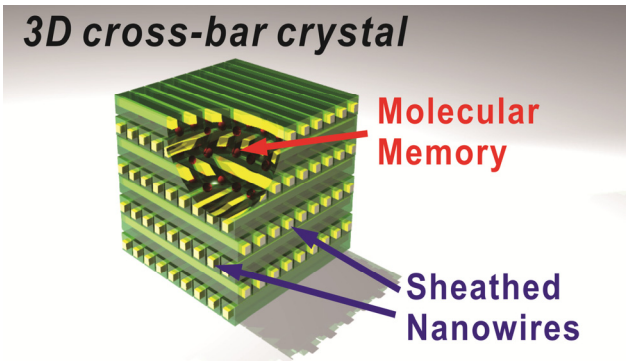


Fig. 1 Graphical image for 3D cross-bar wiring in a nanowire crystal. Red sphere, yellow bar, green cover represent molecular memory, conducting wire, and insulating sheath, respectively.

3. Molecular Nanowires Sheathed by Insulating Cover

Platinum Nanowires and Related Organometallic Compounds

Platinum atom is very likely to form a stable 1D chain with high conductivity. The most famous and oldest example is so-called KCP ($K_2[Pt(CN)_4]X_{\delta}{\cdot}yH_2O$, where X = Cl or Br, $\delta \approx 0.3$, and $y \approx 2.5$). The 1D platinum atomic chain in KCP exhibits conductivity more than 100 Scm^{-1}. It is surrounded by insulating cyanide sheath, which makes its conduction anisotropy more than 10,000. This anisotropy is fairly good as a single chemical compound, but still is not sufficient to prevent current leakage between the wires. Indeed, the bulk conductivity is known to be governed by the hopping resistance between the wires even when the measurement is done along the wire direction. This is because the wire is cut into pieces by the lattice defects in the real crystal system. The average length of the platinum wire seems less than 100 nm. In order to expand the chemical variety of the platinum nanowire, it is possible to exchange the ligands from cyanide to organic anions, although better physical property has not been obtained as yet. Another possibility is to use anionic platinum instead of using cationic platinum (as in KCP). In this case, $(cation)_xPt_3(CO)_6$ can form a cross-bar arrangement of nanowires that comprise platinum tri-nuclear complexes. $Pt_3(CO)_6$ can even form a cubic nanowire arrangement where the nanowires are running in three different directions.

Similarly to platinum, atomic mercury is known to form a 1D conducting chain in a cationic form. In addition, it is possible to form a cross-bar arrangement, too, in the crystal structure of Alchemist's gold ($Hg_{3-\delta}AsF_6$), although the wires are not sheathed. Silver atoms also form a 1D nanowire, probably in a neutrally charged condition.

Molecular Nanowires Sheathed by Halogen-Bonded Network

The author's group has developed a sheathed nanowire system where 1D stack of conducting organic molecules is covered with an insulating supramolecular network. The insulating 3D network is made of halide ions and iodine-containing molecules, between which a strong intermolecular interaction called 'halogen bonding' is playing a role of glue. Because all the components are organic molecules, our system has good degree of designing in the material development. The highest conductivity along the nanowire direction to date is 65 Scm^{-1} and the highest anisotropy of conductivity is about 100,000,000. Figure 2 shows the crystal structure of nanowires with such a high anisotropy, where conducting π-radicals (TSF) are stacked to form 1D chain while insulating 'Teflon-like' molecule (HFTIEB) covers those chains. It has been also possible to obtain double-stranded nanowire covered with an insulating sheath (ref. 2). Although no nanowire is stuffed inside, we have also succeeded in constructing a cross-bar channel structure in an insulating halogen-bonded network as shown in Figure 3 (ref. 3).

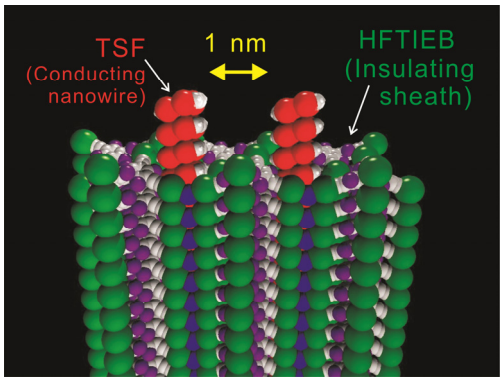


Fig. 2 Structure of supramolecular nanowire crystal comprising TSF and HFTIEB. The separating distance between two adjacent TSF nanowires is more than 1 nm, so that the insulation resistance between the wires is very high. (from ref. 2)

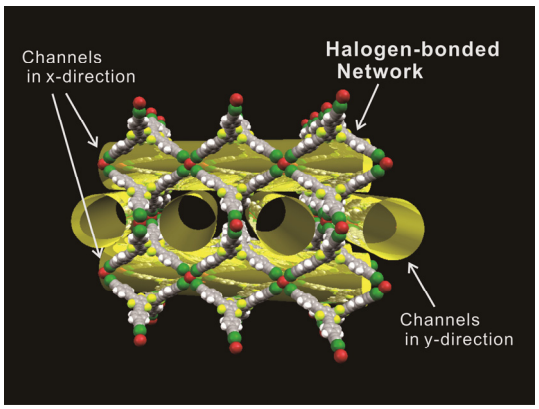


Fig. 3 One example of halogen-bonded network that exhibits cross-bar arrangement of 1D channels. For the moment, these channels are only prototypes and are not filled with nanowires (from ref. 3)

3. Conclusions

By making tremendous efforts, it has been possible to improve the arrangements and structures of nanowires with insulating sheath. Further improvement might require modelling by computation because of its complexity. Such efforts are worth making because of the expected high-density of the molecular memory that should be more than 1 peta-byte/cm^{-3}.

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