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Metal Nanowire Formation Using $Mo_3Se_3^-$ as Reducing and Sacrificing Templates

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Recent research in the field of nanometer-scale electronics has focused on two fundamental issues: the operating principles of small-scale devices[1] and schemes that lead to their realization and eventual integration into useful circuits.[2] The availability of a nanoscale toolbox is the key for this field of research. Among the many potential building blocks within this nanoscale toolbox, nanowires are considered one of the key components because they can be used as interconnects and other functional devices in nanoelectronics.[3] Unfortunately, although several processes have been developed for the syntheses of semiconductor nanowires,[4] few methods have been developed for preparing free-standing, uniform metal nanowires. Among them, template synthesis (in porous matrixes such as porous Al_2O_3 films[5] and mesoporous silica[6]) and step-edge decoration[7] are considered as effective approaches. The step-edge decoration method was recently employed to produce Mo nanowires of 100 nm thickness.[7] Metal nanowires have also been prepared by using DNA[8] and carbon nanotubes as templates.[9] Herein we report a simple chemical process for synthesizing long, free-standing metal nanowires. $LiMo_3Se_3$ nanowires are used as both reducing agents and sacrificial templates in this study to yield continuous metal nanowires. The metal nanowires generally have diameters of 10−100 nm and lengths of several micrometers. These metal nanowires display small ohmic resistances at room temperature, indicating that these wires could prove useful as interconnects in nanoelectronic circuits.

Previously, DNA has been used as a biotemplate for making metallic nanowires,[8] although the continuity of the resulting metal nanowires has been problematic. Since DNA itself does not possess any reducing/oxidizing capability, the synthesis generally is a two-step process, which involves metal activation followed by chemical reduction. Nevertheless, the construction of electronic circuits based only on native DNA remains problematic, mainly due to the high resistance of DNA that limits its potential applications in this regard. Recently, Braun and co-workers presented a new approach by fixing DNA between two contacts and utilizing it as a template for the construction of a silver nanowire.[8] This technique uses the molecular recognition properties of the molecule for the defined buildup of a nanostructure and installs its electrical functionality by the directed construction of a metallic wire on the biotemplate. However, the reported 100 nm thick silver wires displayed a nonconducting gap for small bias voltages.

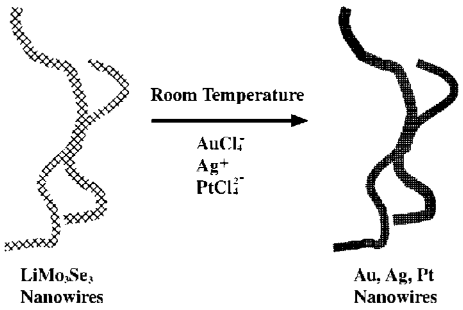

Figure 1. Schematic illustration of metal nanowire templating reaction between $LiMo_3Se_3$ nanowires and metal ions.

In this study, we choose $[Mo_3Se_3^-]_\infty$ molecular chains as our experimental system for two important reasons. First, these molecular chains are obtained by dissolution of crystals of quasi-1D materials $LiMo_3Se_3$ in polar solvent.[10] Each chain is made of staggered stacks of triangular Mo_3Se_3 with a diameter of 0.5 nm. The molecular chain itself is a reducing agent and can be readily oxidized. Second, these individual molecular wires form uniform nanowire bundles with diameters of 2−100 nm in certain polar solvents such as methanol and DMSO. Hence, these nanowires possess dual functionalities, being reductive one-dimensional templates. In fact, the redox chemistry of $LiMo_3Se_3$ was previously studied by Tarascon, and it was demonstrated that insertion and extraction of Li/Mo_6Se_6 is reversible.[11]

To form uniform metal nanowires, a redox reaction is carried out using $LiMo_3Se_3$ nanowires as the reducing agents to reduce aqueous metal ions (e.g., $AuCl_4^-$, Ag^+, $PdCl_4^{2-}$, $PtCl_4^{2-}$). Metal ions are reduced and deposited directly on the nanowire templates, while the nanowire templates are oxidized into Mo_3Se_3 and eventually dissolve in water (Figure 1). Consequently, metal nanowires with diameters of 2−100 nm can be obtained through this cooperative chemical templating process. Metal nanowires of Au, Ag, Pt, and Pd can be readily synthesized.

In a typical experiment, a $LiMo_3Se_3$ solution was prepared by dissolving 5 mg of $LiMo_3Se_3$ in 20 mL of DMSO. A 2 mL drop of metal ion solution (0.005 wt %) was added to this DMSO solution. Using the Au nanowire system as an example, evidence of the reaction is apparent immediately after the solution mixing. The overall solution color develops a pink tint, and a peak at 526 nm appears in the UV−vis absorption spectra, indicating that Au nanocluster nucleation and growth has occurred.

Figure 2 shows transmission electron microscopy images taken before (a) and after (b−d) the templating reaction for the Au nanowire system. Before the reaction, the $LiMo_3Se_3$ molecular chains self-assemble into nanowire bundles of 10−100 nm in diameter. After the redox reaction, Au nanowires of similar diameters and morphology are obtained. These Au nanowires are continuous and polycrystalline. Figure 2d shows a high-resolution TEM image of an individual Au nanowire with diameter of 15 nm. It can be seen that the Au nanocrystalline domains fuse together at the interface and form a continuous and robust

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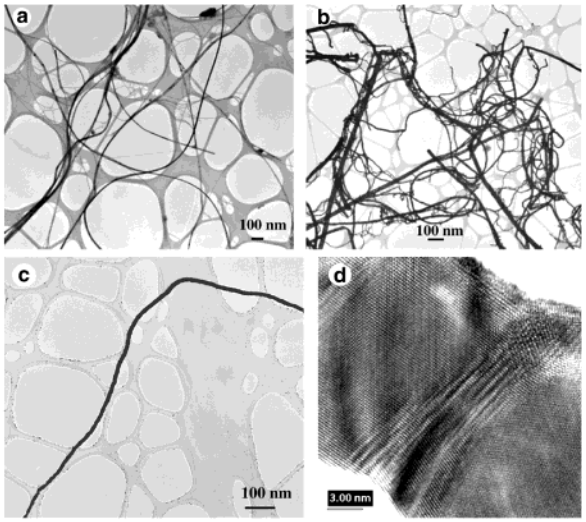

Figure 2. Transmission electron microscopy images of the $LiMo_3Se_3$ nanowires before (a) and after (b−d) the redox reaction with $AuCl_4^-$.

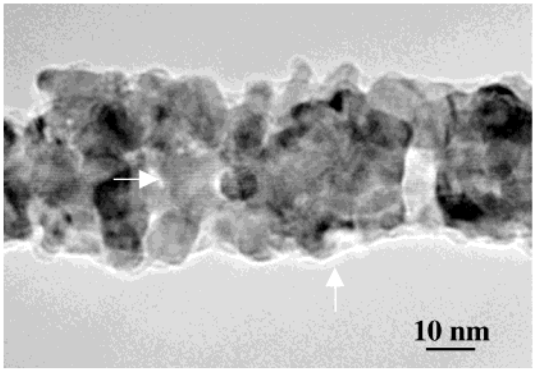

Figure 3. TEM image of an incompletely templated nanowire where both the lattice fringe of $LiMo_3Se_3$ structure (indicated by a horizontal arrow) and Au nanocrystals can be seen (indicated by a vertical arrow).

nanowire. Overall, the redox reaction is as follows (NW = nanowires):

$$3LiMo_3Se_3(NW) + AuCl_4^- \rightarrow Au(NW) + 3Mo_3Se_3 + 3LiCl + Cl^-$$

Since the Mo_3Se_3 products will be further oxidized in H_2O into their corresponding oxides and solvated into water, no solid Mo_3Se_3 components can be observed on the TEM grids after the reaction, evidenced by elemental analysis using energy-dispersive X-ray spectroscopy (EDX). Selected area electron diffraction on the products also indicates that the obtained wires are single-phase Au without residue templates (see the Supporting Information).

The initial stages of the redox reaction for this metal nanowire templating mechanism can be further examined using electron microscopy. Figure 3 shows a transmission electron microscopy image of a partially templated $LiMo_3Se_3$ nanowire bundle. In the center of the nanowire, the individual lattice fringe from the remaining $LiMo_3Se_3$ structure (8.5 Å) can still be seen, while the nanowire itself is decorated with Au nanocrystals formed by the redox reaction.

Since the redox potential for reducing $AuCl_4^-$ in aqueous solution is 1.002 eV, we expect that similar templating chemistry can be readily applied to Ag (E_{re} = 0.80 eV), Pd (E_{re} = 0.6 eV), and Pt (E_{re} = 0.76 eV).[12] Indeed, we have successfully obtained Ag and Pt nanowires with a similar procedure. To the best of our knowledge, this is the first example of redox templating at room temperature to produce metal nanowires. Previously, carbon nanotubes have been used as templates to produce carbide nanowires, but only at very high temperatures. This room-temperature templating procedure provides a simple and useful approach to producing nanowires of different compositions by utilizing template nanowires with reducing or even oxidizing capabilities.

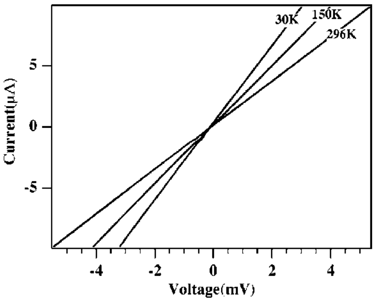

Figure 4. Linear $I-V$ (296, 150, and 30 K) measured on a single Au nanowire with four-probe configuration. The diameter of the wire is ~90 nm.

The templating and simultaneous nucleation of Au nanocrystals on the host matrix invariably yields polycrystalline nanowires. However, since Au nanocrystals fuse together to yield a continuous wire, these metallic nanowires are sufficient for many potential applications, including interconnections in nanoelectronics. Four-probe transport measurements have been carried out on individual Au nanowires. Linear $I-V$ curves were observed at all temperatures, unlike those for metal nanowires templated on DNA. The resistivity of the Au nanowire decreases linearly with decreasing temperature (Figure 4). All samples were observed to have ohmic behavior at room temperature, with resistivity of $\sim 10^{-4}\ \Omega\cdot$cm. This value is 2 orders of magnitude higher than the bulk value, presumably due to the polycrystalline nature of the nanowire.

In summary, a simple redox templating procedure was developed to synthesize continuous metal nanowires 10−100 nm in diameter. $LiMo_3Se_3$ nanowires were used as sacrificing templates with reducing capability. The produced metal nanowires show linear $I-V$ characteristics with low resistivity, making them suitable as interconnects in nanoelectronics.

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Supporting Information Available: EDX spectrum and electron diffraction recorded on Au nanowires (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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