MMo_3Se_3 ($M = Li^+, Na^+, Rb^+, Cs^+, NMe_4^+$) Nanowire Formation via Cation Exchange in Organic Solution

Jae Hee Song, Benjamin Messer, Yiying Wu,
Hannes Kind, and Peidong Yang*

Department of Chemistry
University of California
Berkeley, California 94720

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Currently, there is intensive research driving toward developing suitable one-dimensional (1D) conducting molecular wires because of their potential use as building blocks for molecular-scale electronic devices.[1] One appealing approach for obtaining molecular wires is the disassembly of quasi-1D crystals[2,3] such as $LiMo_3Se_3$ into structurally and electronically identical molecular wires. These linear chain compounds display a unique variety of physical properties including highly anisotropic conductivity, superconductivity and semiconducting behavior, depending on the identity of the interstitial cation separating the molecular chains $[Mo_3Se_3^-]_\infty$.[4] Therefore $[Mo_3Se_3^-]_\infty$ nanowires with different cations represent a collection of different 1D building blocks for molecular devices. Unfortunately, due to the high-temperature nature of traditional solid-state cation-exchange processes, most MMo_3Se_3 ($M = Na^+, Rb^+, Cs^+, Tl^+$) are prepared as single crystals and are insoluble in any polar solvent.[2] Only $LiMo_3Se_3$ is accessible in the nanowire/molecular wire form due to its solubility in polar solvents.[2a] Recently, we have demonstrated surfactant-induced self-assembly of these inorganic $LiMo_3Se_3$ molecular units into different mesophases.[5] Herein we report the formation of MMo_3Se_3 nanowires of different cations M using low-temperature *chimie douce* solution chemistry. X-ray diffraction, transmission electron microscopy studies, and elemental analysis on these nanowires indicate that different cations have been successfully intercalated into the nanowires.

$LiMo_3Se_3$ crystals and 12-crown-4 were dissolved in propylene carbonate (PC), and the solution was sonicated for 1 h for complete dissolution of $LiMo_3Se_3$. Appropriate amounts of alkali iodide (M = Na, K, Rb, Cs) and NMe_4Cl were dissolved in 10 mL of PC and mixed with the $LiMo_3Se_3$ in PC solution. The mixture was stirred for 5 h at 135−145 °C. The resulting reddish product was centrifuged down, collected, and dried under vacuum for X-ray diffraction (XRD) analysis.

X-ray diffraction taken on the exchanged sample indicates that the parent $LiMo_3Se_3$ structure[2] is maintained after the reaction. Figure 1a shows the XRD patterns for the starting $LiMo_3Se_3$ nanowires and the resulting MMo_3Se_3 product. Upon cation exchange, the (100) peak shifts to lower angles, indicating an expansion of the interwire spacing. Figure 1b shows the lattice constant *a* obtained from the XRD for samples prepared using cations of different radius. It was found that the *a* lattice spacing is linearly correlated to the ionic radius of the exchanged cations within a given periodic group, while NMe_4^+ yields the largest interwire spacing (11 Å).[6] That the *a* spacing to ionic radius ratio for NMe_4^+ is not collinear with the alkali counterions is not surprising, given the nonspherical shape of the ion and the resulting decrease in registry between the counterion and the surface of the $[Mo_3Se_3^-]_\infty$ frame.

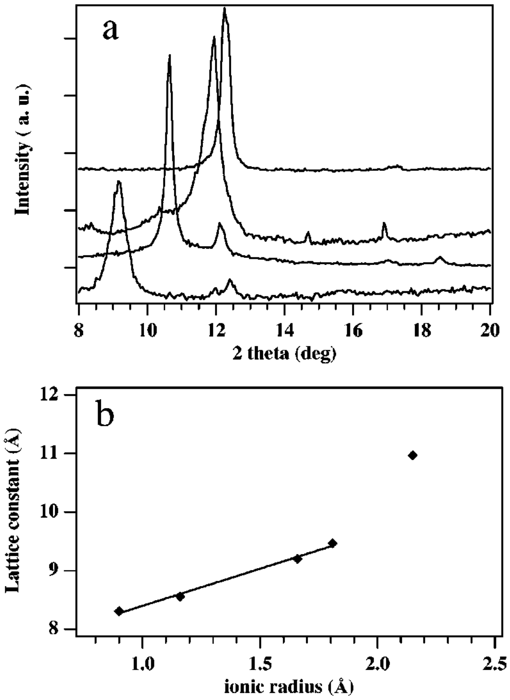

Figure 1. (a). X-ray diffraction patterns for the exchanged nanowire samples, from top to bottom, Li^+, Na^+, Cs^+, NMe_4^+. (b). Lattice constant *a* of the exchanged MMo_3Se_3 sample ($M = Li^+, Na^+, Rb^+, Cs^+, NMe_4^+$) vs the ionic radius of the exchanged ions.

Cross-polarized optical microscopy studies indicate that the products consist of well-aligned microscopic fiber bundles. This is also clearly shown in the field emission scanning electron microscope (FESEM). Figure 2a shows one such image recorded on the $CsMo_3Se_3$ sample. We found that the molecular wires form nanowire bundles with diameters of 10−200 nm. These molecular wire bundles were deposited on copper grids and examined using a transmission electron microscope (TEM). It was found that the individual molecular wires are aligned along the bundle axis and are evenly spaced (Figure 2b). The observed interwire spacing matches well with the XRD data. Similar results have been obtained in the systems of Rb^+, Cs^+, NMe_4^+.

In addition, elemental analysis was carried out for these exchanged compounds. It was found that the exchange is complete in most cases with the notable exception of the K^+ system. For example, the composition of $Li_x(NMe_4)_{1-x}Mo_3Se_3$ was obtained, with $x = 0.07$.

It was reported in an early paper that no cation exchange was observed via the simple addition of an alkali metal halide to a DMSO solution of $LiMo_3Se_3$.[2a] We have observed the same results when no 12-crown-4 is present in the solution. This observation clearly indicates the importance of the addition of 12-crown-4 to the current *chimie douce* reaction. The 12-crown-4 molecules could complex with Li ions in the PC solvent and effectively shield their positive charge, consequently reducing the electrostatic interaction between the negatively charged $[Mo_3Se_3^-]_\infty$ backbone with these Li ions. Cations of different sizes can then associate

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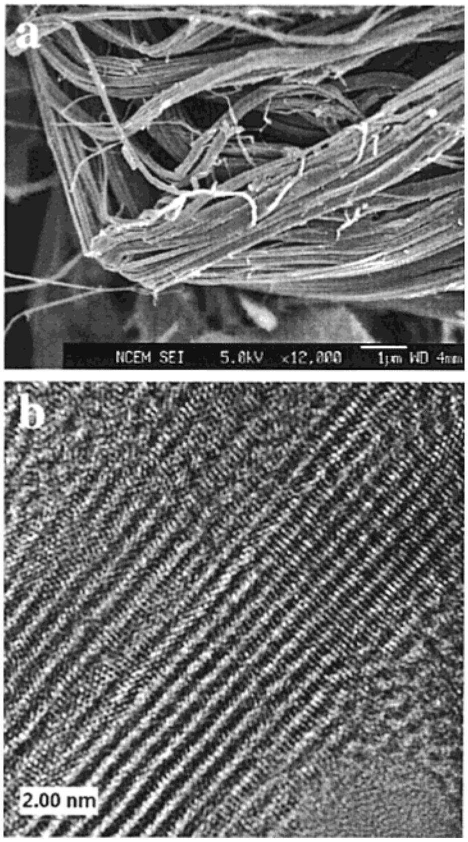

Figure 2. SEM and TEM images of (a) $CsMo_3Se_3$ (b) $NaMo_3Se_3$ nanowire bundles obtained by the cation-exchange process.

to the backbone, and the molecular wires can reassemble into nanowire bundles, but with different interstitial cations.[7] The reason this reaction scheme fails for the K^+ system is that 12-crown-4 also forms a fairly stable sandwich complex with K^+ to form $K(12\text{-crown-}4)_2{}^+$,[6] making the K^+ unfavorable for intercalation with the molecular chain.

The ability to synthesize MMo_3Se_3 of different intercalated cations provides a source of nanowire building blocks for a variety of different transport properties. For example, $I-V$ measurement was carried out on individual $LiMo_3Se_3$ nanowires using a four-probe configuration. During the measurement, $LiMo_3Se_3$ nanowires were dispersed on prefabricated Au electrodes. Linear $I-V$ data clearly indicates that these nanowires remain metallic down to 20 K (Figure 3a), which is consistent with the early STM studies on this particular system.[8] The resistance of the nanowire decreases with the decreasing of the temperature and plateaus off around 20 K, which may be considered as an indication of a Peirels distortion leading to a semiconducting ground state, which is common in quasi-1D materials, or to disorder-induced electron localization.[2,4,9]

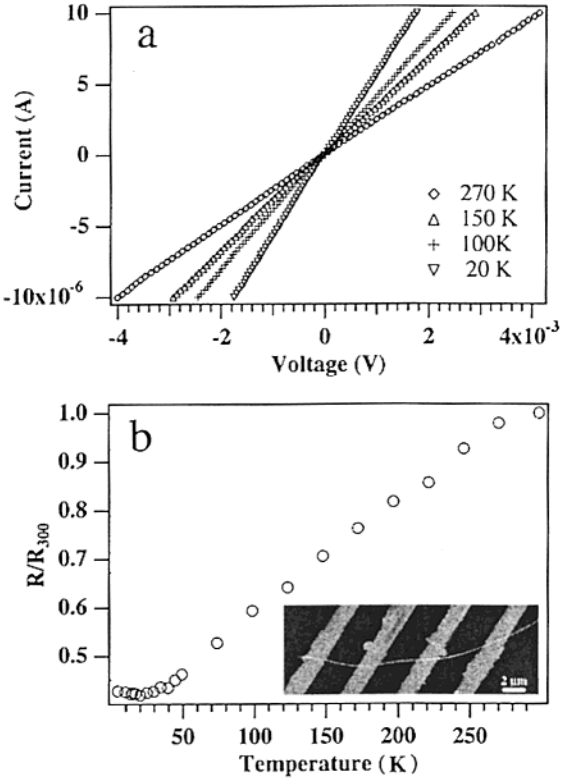

Figure 3. (a). $I-V$ curves taken on a $LiMo_3Se_3$ nanowire at different temperature. (b). R/R_{300} vs temperature, R is the nanowire resistance at different temperatures, R_{300} is the nanowire resistance at 300 K. Inset shows the $LiMo_3Se_3$ nanowire (~90 nm in diameter) with four Au electrodes.

In conclusion, we have demonstrated a simple *chimie douce* solution process for making MMo_3Se_3 nanowires of different cations M. The cation-exchange process occurs at low temperature and is greatly facilitated by the addition of 12-crown-4, which efficiently extracts the Li cations from the starting materials. It offers a facile approach to modifying the electrical properties of the $[Mo_3Se_3{}^-]_\infty$ nanowires by exchanging the intercalated cations.[9]

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(7) In the recent reported $(MoS_2)-I_x$ single-wall nanotube bundles, iodine is intercalated between MoS_2 nanotubes in a similar fashion, although their preparation is carried out in gas phase. (Remskar, M.; Mrzel, A.; Skraba, Z.; Jesih, A.; Ceh, M.; Demsar, J.; Stadelmann, P.; Levy, F.; Mihailovic, D. *Science* **2001**, *292*, 479).

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(9) Preliminary electron transport and magnetization measurement on these MMo_3Se_3 nanowires with different cations indeed show different electrical properties including semiconducting, metallic, and superconducting.