Effect of Additives on LiMo₃Se₃ Nanowire Film Chemical Sensors

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Here we investigate the effect of lithium iodide and cetyltrimethylammonium (CTA) bromide additives on the ability of LiMo₃Se₃ nanowire film sensors to bind and detect organic solvents electrically. Both additives decrease the electrical conductivity of the films. Lithium iodide increases the response of the films to both polar and nonpolar analytes. CTA increases the response of the films to nonpolar analytes but reduces the response to polar analytes. Quartz crystal microbalance measurements show that the modified electrical sensitivities of the films are due to altered analyte adsorption abilities of the films. These results show that the Li⁺ ions are involved in analyte binding in native LiMo₃Se₃ films and that a programming of LiMo₃Se₃ nanowire film sensors is possible by replacing lithium cations with other receptors.

Introduction

Chemical sensors based on the electrical response of nanowires to molecular or ionic analytes have been shown to exhibit ultralow detection limits combined with fast response.[1–9] An additional advantage of these devices is the ability to program them by chemical attachment of receptors to the nanowire surfaces, which makes it possible to detect even complex analytes.[7,10,11] Apart from a few exceptions,[9,12] the majority of known nanowire sensors employ semiconducting materials. We recently discovered that efficient chemical sensors can also be realized with metallic nanowires derived from the Chevrel phase LiMo₃Se₃. Bundles of several tens of LiMo₃Se₃ nanowires (Figure 1a,b) can be obtained by dissolving LiMo₃Se₃ in water or in dimethyl sulfoxide.[13,14] Drop-coating the nanowire solutions onto solid substrates followed by solvent evaporation produces nanometer-thick metallic films that react to chemical analytes with an increase of their electrical resistance.[15] Multichannel chemiresistor arrays can easily be fabricated with this simple approach (Figure 1c,d) by depositing nanowire films on patterned indium tin oxide electrode arrays. Previous work in our laboratory suggests that
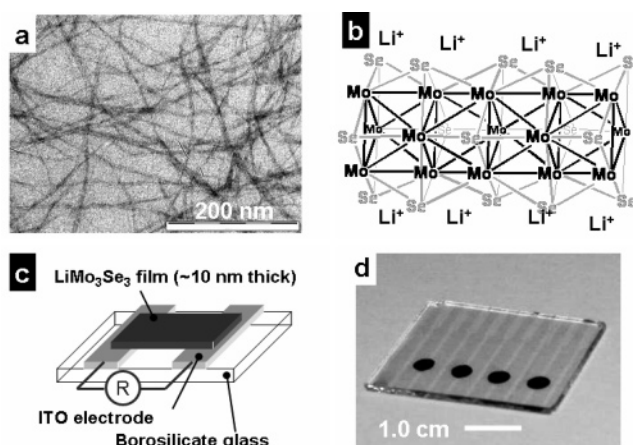

Figure 1. (a) TEM micrograph of LiMo₃Se₃ nanowire bundles from dimethyl sulfoxide. (b) Schematic structure of a single LiMo₃-Se₃ nanowire. (c) Schematic design of a nanowire film chemiresistor. (d) Photo of the device with four nanowire chemiresistors.

the resistance changes of LiMo₃Se₃ nanowire films are at least in part due to changes in the interwire charge transport resulting from analyte-induced swelling of the films.[16] The following are open questions that surround these devices: (a) How do analytes bind to the nanowires (to their Mo, Se, or Li portions)? (b) Is there an *intrinsic* resistance change of the nanowires? (c) Is it possible to program the nanowire film sensors to detect specific analytes? Here, we address questions a and c by studying the mass adsorption and electrical resistance behavior of nanowire films that were chemically altered by incorporation of lithium iodide and cetyltrimethylammonium bromide (CTAB). As we will show, this "doping" affects the response of the sensors to polar and nonpolar analytes. Our analysis further reveals that the Li⁺ ions in the native nanowire films are analyte adsorption sites and that a programming of the chemiresistors is possible by introducing other receptors into the nanowire films.

Experimental Section

All preparations and conductivity measurements were carried out in a nitrogen glovebox with an oxygen level of less than 1 ppm. Degassed solvents of reagent grade (dimethyl sulfoxide (DMSO),

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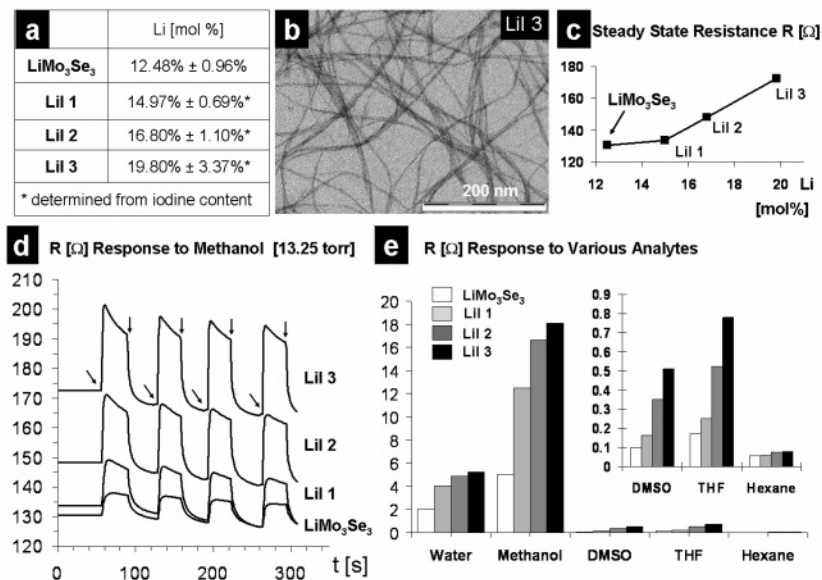

Figure 2. Properties of LiI-doped LiMo₃Se₃ nanowire films: (a) Li content and labeling scheme (molar percentages are given according to [Li]/([Li] + [Mo] + [Se]) × 100); (b) TEM micrograph of LiI/LiMo₃Se₃ (LiI 2); (c) steady-state resistance data; (d) methanol (13.25 Torr) induced resistance data (addition and removal of analyte are shown with arrows); (e) resistance response of several LiI/LiMo₃Se₃ films to vapors of water (1.23 Torr), methanol (13.25 Torr), DMSO (0.04 Torr), THF (7.60 Torr), and hexane (7.55 Torr).

99.7%; tetrahydrofuran (THF), 99.9%; ethanol, 99.9%; methanol, 99.9%; hexane, 99.9%) were used as test analytes. Indium tin oxide (ITO) substrates (120−160 nm thick ITO on 1.1 mm thick alumosilicate glass with a resistance of 5−15 Ω/cm) were purchased from Delta Technologies and patterned into electrode arrays (Figure 1d, 0.1 mm nonconductive gap) using standard photolithography techniques.

Preparation of LiMo₃Se₃ Stock Solution. A 25 mg sample of LiMo₃Se₃ powder was first dissolved in 20 mL of DMSO solvent, by stirring the mixture for 5 min and sonicating it for 5 min at room temperature. The precipitate was centrifuged off, and the concentration of the stock solution was calculated by subtracting the mass of the remaining dry solute. The final concentration of the solution was calculated to be 1.75 mM.

Preparation of LiI/LiMo₃Se₃ Nanowire Films. Three solutions containing increasing concentrations of Li⁺ ions were prepared by dissolving 7.0, 14.0, and 21.0 mg of LiI in 1.0 mL of water and by adding these solutions to three 2.0 mL batches of the LiMo₃Se₃ stock solution. LiI-doped nanowire films were obtained by drying one drop of each solution on an ITO-coated glass substrate in a vacuum for 120 min.

Preparation of CTAB/LiMo₃Se₃ Films. LiMo₃Se₃ nanowire films were prepared by depositing one drop of the stock solution onto the ITO electrode array and by drying it in vacuo for 1 h. The nanowire films were then fully covered with 0.1 mL of aqueous solutions of variable CTAB concentrations (1.22, 1.75, and 2.62 mM) in a N₂ atmosphere. After 2.5 h the films were rinsed with water to remove unreacted CTAB and dried in vacuo for 2 h.

Conductivity Measurements. ITO electrode arrays with LiMo₃Se₃ nanowire films were mounted in a homemade chamber (∼20 mL) and placed under a vacuum (<100 mTorr). After 30 min, 1.0 mL of saturated analyte vapor (in nitrogen gas) at ∼25 °C was injected into the chamber, and the consequent resistance increase was monitored and recorded by a computer-controlled Keithley 7200 multimeter using a two-probe configuration.

Other Measurements. Elementary analyses were performed on a Cameca SX-100 electron microprobe instrument, with scan sizes ranging from 1 to 10 μm. TEM images of LiMo₃Se₃ nanowire samples were recorded on a Philips CM12 transmission electron microscope.

Results and Discussion

Lithium iodide-doped nanowire film chemiresistors were obtained by drop-coating a mixture of LiMo₃Se₃ and LiI in DMSO/water on an ITO-patterned glass substrate, followed by drying in a vacuum. LiI doping levels were adjusted with the stoichiometric ratio of the reagents. The compositions and other properties of native and three separate doped LiMo₃Se₃ nanowire films obtained in this fashion are summarized in Figure 2. According to energy dispersive spectroscopy, the molar Li concentrations in the doped samples range from 15% to 19.8% (the untreated nanowires contain 12.5% Li⁺ cations as LiMo₃-Se₃). TEM data of the sample labeled as LiI 2 (Figure 2b) show that LiI doping has no effect on the diameter of the nanowire bundles. The diameters of the doped nanowires (mean value 5.0 ± 0.6 nm) remain the same as those of the native nanowires from water (Figure 1a, 5.4 ± 0.6 nm). Two-probe measurements of the lateral conductance of the films reveal that increasing the LiI content leads to an increase of the electrical resistance of the films (Figure 1c). This is expected because of the small conductivity of LiI (∼10⁻⁷ Ω^{-1} cm⁻¹ at 100 °C)[17] compared to LiMo₃Se₃ (10³ Ω^{-1} cm⁻¹).[13]

The time-dependent resistance traces for the nanowire films in response to methanol vapor (13.25 Torr) are shown in Figure 2d.

Upon injection of the vapor, the nanowire film resistance increases and then returns to the base value when a vacuum is applied to the film. When the test is performed in a nitrogen atmosphere where the films are protected from air oxidation, this behavior is entirely reversible. Figure 2d also shows that the sensor response ΔR increases with increasing LiI concentration in the film. This also holds true for vapors of water, dimethyl sulfoxide (DMSO), tetrahydrofuran, and hexane. The responses of the sensors to these analytes are summarized in Figure 2e. Comparing non- and fully-doped films, the increase in response is most pronounced for DMSO (5.1×) and THF (4.6×), intermediate for methanol (3.6×) and water (2.6×), and smallest for hexane (1.4×). These results indicate that LiI functions as a sensitizer for the nanowire film. In agreement with previous observations,[15] the overall sensitivity of the sensors increases in the order of increasing polarity of the analytes.

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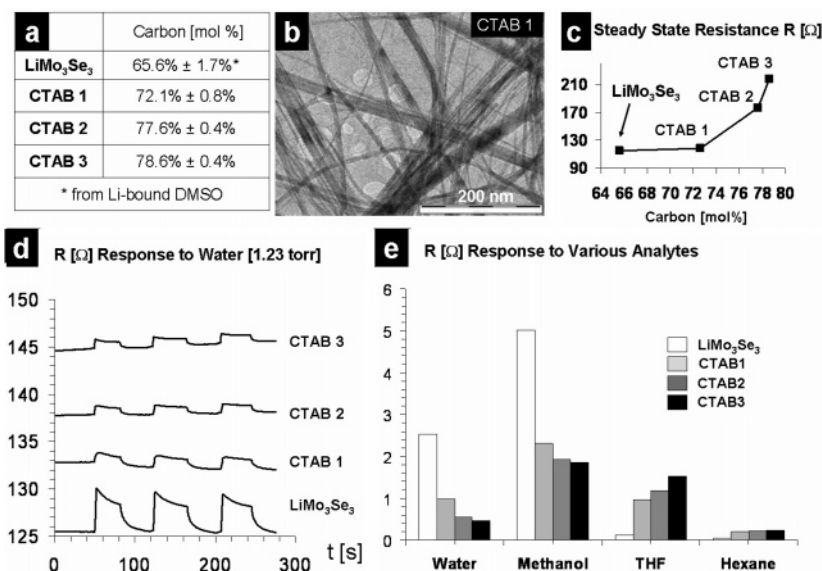
Figure 3. Properties of CTAB-doped LiMo$_3$Se$_3$ nanowire films: (a) molar compositions and sample labeling scheme (molar carbon concentrations are given according to [C]/([C] + [Mo] + [Se]) × 100); (b) TEM micrograph of CTAB/LiMo$_3$Se$_3$ (CTAB 1); (c) steady-state resistance data; (d) temporal resistance of doped and undoped films in response to water vapor (1.23 Torr); (e) resistance response of CTAB/LiMo$_3$Se$_3$ films to four different analytes (partial pressures as in caption of Figure 2).
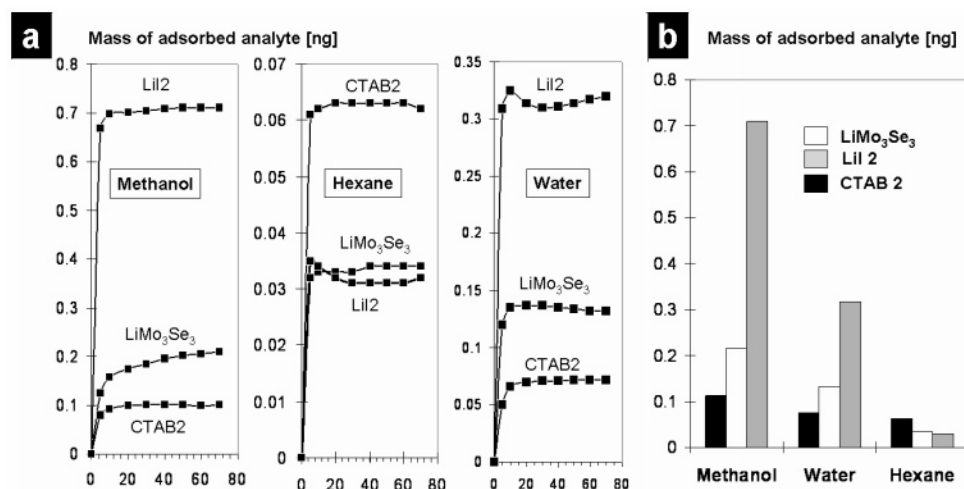

Figure 4. Analyte adsorption to nanowire films: (a) temporal mass increase of LiI/LiMo$_3$Se$_3$, CTAB/LiMo$_3$Se$_3$, and LiMo$_3$Se$_3$ nanowire films exposed to three different analytes at different partial pressures, methanol (13.25 Torr), water (1.23 Torr), hexane (7.6 Torr); (b) comparison of mass increases for different LiMo$_3$Se$_3$ films.

To elucidate the role of Li$^+$ cations as possible analyte binding sites, we also manufactured nanowire chemiresistors in which the Li$^+$ ions from LiMo$_3$Se$_3$ were partially replaced with alkylammonium ions. Cetyltrimethylammonium is a quaternary ammonium ion that is known to electrostatically associate with Mo$_3$Se$_3^-$.[18] Treatment of LiMo$_3$Se$_3$ nanowire films with aqueous CTAB solutions followed by washing with water results in formation of (CTA)Mo$_3$Se$_3$ and in elimination of LiBr. The results of microprobe analyses (Table 3a) confirm the absence of bromide in the films and show increasing amounts of carbon, due to increasing CTA concentrations. Significant amounts of C were also detected in the unmodified LiMo$_3$Se$_3$ nanowire films. This carbon is attributed to DMSO that remains coordinated to Li ions. IR spectra of the material (see the Supporting Information in ref 15) show characteristic bands of this molecule, even after prolonged drying of the films in vacuo. From the observed carbon mole fraction of 65.6%, we assume that each Li$^+$ ion is coordinated

by four DMSO molecules, leading to a calculated carbon mole fraction of 57%. According to the transmission electron micrographs (Figure 3b), the nanowires associate into bundles after treatment with the ammonium salt (for comparison, see Figure 1a). The mean diameters of the CTAB-treated bundles (13.8 ± 4.0 nm) are significantly greater than those of native LiMo$_3$Se$_3$ nanowires from water (5.4 ± 0.6 nm). This nanowire association is driven by the hydrophobic effect and by the van der Waals interactions between the neutral (CTA)Mo$_3$Se$_3$ adducts.[18] Steady-state resistances for the films range from 115.0 Ω for the unmodified film to 217.8 Ω for the most doped film (Figure 3c). The increase in resistance with increasing CTA concentration is due to the insulating properties of CTA.

The effect of CTA on the time-dependent sensor response to analytes depends on the nature of the analyte (Figure 3d,e). Increasing CTA concentrations in the film diminish the response of the films to methanol vapor and water. For THF and hexane, on the other hand, increasing concentrations of CTA in the films lead to a stronger resistance increase in the sensors. Compared

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to those of the unmodified nanowire films, the resistance responses of the fully doped films are 11.8 and 4.6 times *stronger* for THF and hexane and 5.4 and 2.7 times *weaker* for water and methanol. This suggests that the hydrophobic nature of CTA increases the adsorption of nonpolar analyte molecules and diminishes the adsorption of polar molecules. To test this hypothesis, a quartz crystal microbalance was employed to determine the amounts of analyte molecules adsorbed onto doped and nondoped films. Time-dependent mass increases for native and LiI- and CTAB-doped nanowire films are shown in Figure 4a.

After injection into the test chamber, all analytes adsorb quickly onto the nanowire films. Generally, 90% of the adsorption is completed within 5 s. Only for the combination of methanol and the nonmodified $LiMo_3Se_3$ nanowire film does the adsorption continue beyond 60 s. This continuing adsorption is probably due to partial dissolution of the nanowire film in the presence of the good solvent methanol at relatively high partial pressure (13.25 Torr). Adsorption also strongly depends on the analyte and on the doping agent in the film (Figure 4b). LiI-doped films adsorb methanol and water more strongly than native and CTAB-doped films. CTAB-doped films on the other hand have a stronger affinity for hexane than for water or methanol. These trends can be explained with a preference of polar analytes for the polar additive LiI and that of nonpolar analytes for the less polar additive CTA.

In conclusion, we have shown that LiI- and CTA-doped nanowire films can be manufactured by mixing the nanowires with LiI in solution or by diffusing CTAB into films. The additives lead to a decrease of the electrical conductivity of the films. However, LiI increases the electrical film response to polar analytes, while CTA increases the electrical film response to nonpolar analytes. Quartz crystal microbalance measurements show that the modified electrical sensitivities of the films are correlated with the adsorption ability of the analytes. The Li^+ and CTA^+ ions act as "receptors" for the binding of polar/nonpolar analytes, respectively. These results suggest that the introduction of other receptors either by direct nanowire modification or via doping of nanowire films can lead to nanowire sensors with specific sensing capabilities. Studies in this direction are under way.