

Stringing up the Pearls: Self-Assembly, Optical and Electronic Properties of CdSe– and Au–LiMo₃Se₃ Nanoparticle–Nanowire Composites

Frank E. Osterloh,* Jason S. Martino, Hiroki Hiramatsu, and Daniel P. Hewitt

Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616

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ABSTRACT

Chevrel-type LiMo₃Se₃ nanowires dissolved in dimethyl sulfoxide were decorated with 13 nm citrate ligated Au particles (water) and 6 nm trioctylphosphineoxide ligated CdSe particles (tetrahydrofuran) by combining the respective solutions at room temperature, followed by mild acidification with hydrochloric acid in the case of Au. The morphology of the formed nanostructured Au–LiMo₃Se₃ and CdSe–LiMo₃Se₃ aggregates depends on stoichiometry and reaction conditions. While the UV/vis spectra of the aggregates are largely the sum of the subspectra of the building blocks, the emission spectra of the CdSe–LiMo₃Se₃ material reveal quenching of CdSe based photoluminescence. The electrical conductance of 5 nm thick films obtained by drying solutions of the composites decreases with increasing temperature, which shows that the nanowires remain metallic after binding of the nanoparticles.

Electrically conducting organic or inorganic nanowires are generally regarded as crucial building blocks of future microelectronics.¹ Of the many known varieties, LiMo₃Se₃ nanowires² obtained after cation exchange and exfoliation of the Chevrel compound InMo₃Se₃³ are remarkable in several respects: As condensation polymers of triangular Mo₃Se₃ units, these molecular wires have a diameter of only 0.85 nm (from crystal data),⁴ which makes them smaller than single (1–2 nm) and multiwalled (2–25 nm) carbon nanotubes.⁵ Bundles of LiMo₃Se₃ wires possess metallic conductivity^{6,7} and are soluble in polar organic solvents, which enables a solution manipulation of the wires using soft chemistry methods. The successful incorporation of LiMo₃Se₃ nanowires into an organic polymer was reported in 1995 by DiSalvo's group.⁸ Later, Yang and co-workers encapsulated LiMo₃Se₃ wires with organic surfactants to yield organic–inorganic hybrid materials,⁹ and very recently the same group also employed the wires as sacrificial templates for the synthesis of gold nanowires.¹⁰ Here, we report a solution phase method for using LiMo₃Se₃ nanowires to “wire up” metallic Au and semiconducting CdSe nanoparticles. The resultant nanostructured composites are soluble in organic solvents and form electrically conducting films when deposited from solution. The integration of nanoparticles into conducting networks is of great technological interest; potential applications for these and related inorganic composites exist in areas ranging from photochemical cells^{11,12} and batteries to nanowire based chemical sensors^{13–15} and electrochemical catalysts.

Syntheses were carried out at room temperature in a nitrogen glovebox in degassed and/or dried solvents. Aqueous solutions of citrate ligated gold particles were prepared as previously described,¹⁶ diluted with ultrapure water ($R > 18 \text{ M}\Omega$) to a gold content of $0.50 \times 10^{-3} \text{ mol/L}$, and purged with nitrogen before use. Trioctylphosphineoxide (TOPO) ligated CdSe particles (6 nm) were synthesized according to Peng's method.¹⁷ InMo₃Se₃ was prepared and cation-exchanged with LiI according to DiSalvo.⁴ A $1.73 \times 10^{-3} \text{ M}$ stock solution of LiMo₃Se₃ was prepared by dissolving 23 mg of LiMo₃Se₃ in 25 mL of dimethyl sulfoxide (DMSO) with sonication. Optical measurements were performed in sealed quartz ampules, using Hewlett-Packard 8450A UV/vis and Perkin-Elmer LS50B luminescence spectrometers. Samples for electron microscopy (SEM, FEI XL30-SFEG; TEM, Hitachi H-600) were prepared using silicon wafers or holey carbon coated TEM grids as supports.

Experimental Section

Synthesis of CdSe·TOPO/LiMo₃Se₃. (a) A stock solution of trioctylphosphineoxide (TOPO) ligated CdSe particles (6 nm) was prepared by dissolving 75 mg of solid CdSe·TOPO in 20 mL of THF. A 0.4 mL volume of this solution was added with stirring to 0.75 mL of the $1.73 \times 10^{-3} \text{ M}$ LiMo₃Se₃ stock solution in dimethyl sulfoxide (DMSO). The clear brown-red solution was sonicated for 30 s, and the product precipitated by adding 3 mL of ether. The brown precipitate was centrifuged off, washed with tetrahydrofuran (THF), and then dispersed in 2 mL of THF with sonication. (b) For the

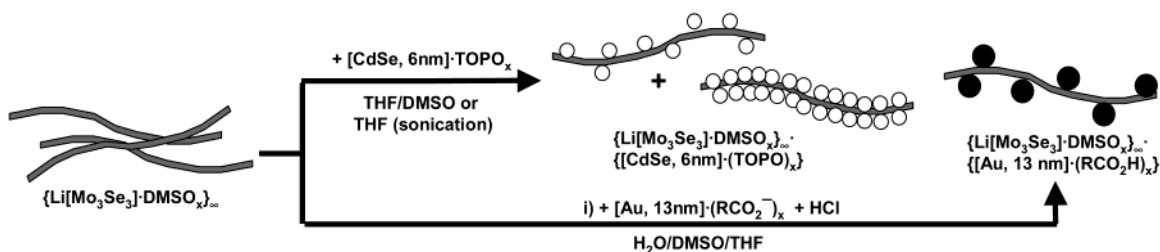


Figure 1. Synthesis of the composites.

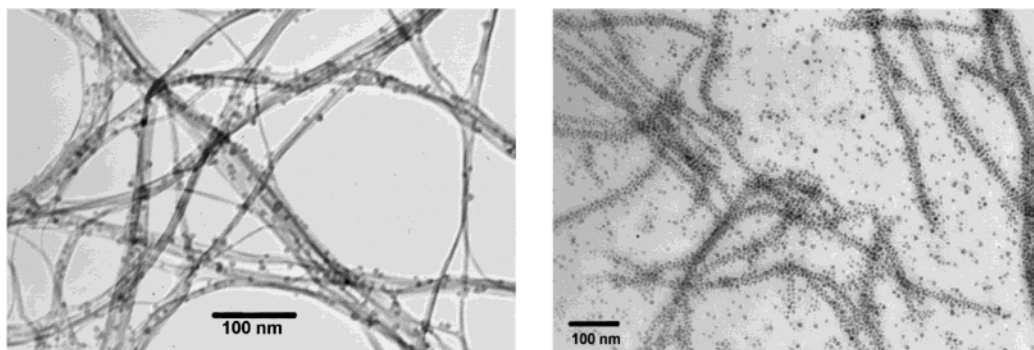


Figure 2. Transmission electron micrographs of two samples of CdSe·LiMo₃Se₃ synthesized according to methods (a) and (b) (Experimental Section).

photoluminescence measurements, a DMSO-free batch of CdSe·TOPO/LiMo₃Se₃ was prepared in THF, because the PL of CdSe·TOPO particles is partially quenched in the presence of high concentrations of DMSO. LiMo₃Se₃ nanowires were first precipitated by combining 0.5 mL of the stock solution with 4 mL of THF, and washed three times with 4 mL of THF to remove any unbound DMSO. The wires were suspended in 4.0 mL of THF and 1.0 mL of the CdSe·TOPO stock solution in THF was added. The suspension was sonicated (5 min) until a homogeneous mixture was formed. The solid was isolated by centrifugation, washed two times with THF, and dispersed in THF (for PL spectrum) or MeOH (to make a film).

Synthesis of Au·cit/LiMo₃Se₃. To 0.2 mL of the LiMo₃Se₃ nanowire stock solution in DMSO was added 3 mL of an aqueous solution of 13 nm gold colloid (0.50×10^{-3} mol Au/L) with stirring to yield a clear red solution. The mixture was sonicated for 30 s, and 0.1 mL (150 equiv of HCl per mole of LiMo₃Se₃) of a 0.6 M HCl solution in THF was then slowly added with stirring. The red precipitate was centrifuged off, and the colorless supernatant was discarded. The product was dispersed in 2 mL of MeOH with sonication to yield an optically clear red solution that was stable for several minutes, depending on concentration of the composite. Stable solutions of the composite form in DMSO or water.

Results and Discussion

CdSe·TOPO–LiMo₃Se₃ composites of varying compositions were synthesized (Figure 1) by combining solutions of trioctylphosphine (TOPO) ligated cadmium selenide particles (6 nm in THF)¹⁷ with a solution of exfoliated LiMo₃Se₃ nanowires in DMSO, or by sonicating a mixture of CdSe·TOPO in THF with LiMo₃Se₃ freshly precipitated from

DMSO by addition of THF. These reactions afford CdSe–LiMo₃Se₃ composites as brown-red solids that can easily be dissolved in methanol or THF to give optically clear solutions.

Gold–LiMo₃Se₃ nanowire composites were similarly synthesized by mixing citrate ligated gold particles (13 nm in water)¹⁶ and LiMo₃Se₃ in DMSO and after adding 60 μmol of hydrochloric acid (150 mole equiv based on LiMo₃Se₃), dissolved in THF. The role of the acid is to reduce the negative charges on both wires and gold particles via protonation, to eliminate repulsive Coulomb forces which do inhibit the formation of a composite. The gold–LiMo₃Se₃ composite forms stable red solutions in polar solvents such as DMSO or water.

The morphology of the CdSe–wire composites depends on the method of synthesis and on their composition. Transmission electron micrographs of samples synthesized in homogeneous and in heterogeneous reactions are shown in Figure 2. When the CdSe content is low, the network formed by bundles of the LiMo₃Se₃ polymer remains mostly intact. Most of the wire bundles in the network are 3–4 nm thick (measured by AFM, see Supporting Information) and contain 7–13 LiMo₃Se₃ strands (assuming hdp of LiMo₃Se₃ molecular chains). The CdSe particles are randomly scattered over this wire network, mostly as individual particles but occasionally in the form of clusters. The CdSe–LiMo₃Se₃ composite synthesized in the heterogeneous reaction with an excess of CdSe nanoparticles contains LiMo₃Se₃ wires that are entirely and uniformly covered with CdSe particles (Figure 2b). Here the nanowires can be viewed as structural templates for the anisotropic aggregation of the CdSe particles.

The morphology of the gold-wire composite (Figure 3), resembles the low-coverage CdSe–LiMo₃Se₃ composite.

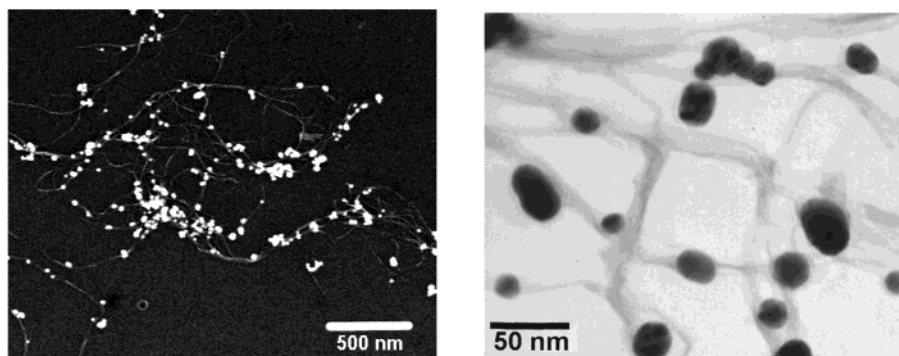


Figure 3. Scanning electron (a) and transmission electron micrographs (b) of Au-LiMo₃Se₃ composite.

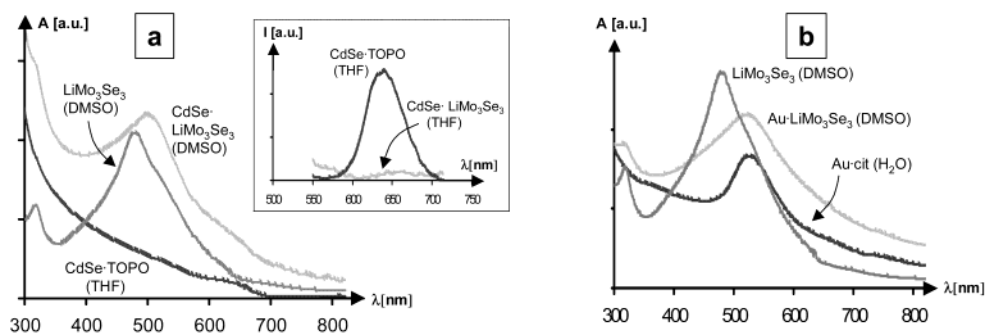


Figure 4. Electronic spectra and PL spectra (insert) of (a) CdSe-LiMo₃Se₃ and (b) Au-LiMo₃Se₃ composites in the indicated solvents.

However, the LiMo₃Se₃ network is less regular, probably because of the larger structure directing influence of the 13 nm Au particles, whose surface area is about five times that of the 6 nm CdSe particles. As a result of the stronger wire-particle bonding, gold particles are partially incorporated into bundles (Figure 3b), causing the observed morphology changes of the wire network.

Repeated washings of the composites with THF (CdSe-LiMo₃Se₃) and methanol or water (Au-LiMo₃Se₃) have no effect on the composition of the materials. The notions that CdSe-TOPO and LiMo₃Se₃ lack bridging ligands, and further, that Lewis-hard Fe(II,III) ions of bare Fe₃O₄ nanoparticles do not bind to the wires (unpublished results), are in support of a covalent bonding model. Strong covalent bonds can be formed by the Lewis-Soft couples cadmium(II)/selenide and Au(I) ions/selenide. The LiMo₃Se₃ strands in the bundles, on the other hand, are held together electrostatically as in crystalline LiMo₃Se₃.

UV/vis spectra of the composites and their pure components are shown in Figure 4. The electronic spectra of both composites are mainly a superposition of the spectra of the separate building blocks. This suggests that LiMo₃Se₃ nanowires and CdSe and Au particles remain intact after formation of the composite. The red color of the CdSe-LiMo₃Se₃ and Au-LiMo₃Se₃ composites originates from intense bands at 498 and 522 nm, respectively. For the pure wires, this weakly solvent-dependent band appears at 480 nm in DMSO, at 470 nm in H₂O, and at 486 nm in propylenecarbonate. The shoulder at 640 nm in the CdSe-LiMo₃Se₃ composite corresponds to the band gap excitation of CdSe nanoparticles (1.93 eV); its width reflects the size distribution of the 6 nm CdSe nanoparticles. In the UV/vis spectrum of the Au-LiMo₃Se₃ composite, this feature is

replaced with the surface plasmon band of the gold particles, which occurs at 526 nm for the pure gold colloid in water.

Photoluminescence spectra of CdSe-TOPO particles and of the CdSe-LiMo₃Se₃ composite, prepared in THF, are shown in the inset of Figure 4a. When excited at 380 nm, solutions of TOPO-ligated CdSe particles in THF emit at 640 nm. Upon binding to the wires, this photoluminescence is quenched completely. Quenching can result from either TOPO removal (which allows surface redox processes to occur),¹⁸ from injection of the photoexcited electrons into the LiMo₃Se₃ polymer, or from dipolar coupling between nanoparticles and wires (Förster transfer).¹⁹ Based on IR-spectroscopy, the first possibility can be ruled out. IR spectra of the composite (Supporting Information) clearly contain bands (2921 [CH₂], 2854 [CH₃] cm⁻¹) characteristic of the TOPO ligands, the majority of which remain coordinated to the CdSe particles upon formation of the composite. Further measurements are required in order to determine the exact nature of the quenching in these systems.

To determine the temperature-dependent electrical conductivity, films of the nanocomposites and of the pure nanowires were made by drop-coating 0.1–0.16 mL of the respective sample solutions (from methanol) onto a four-probe gold microelectrode array on borosilicate glass (gold leads: 5 μm (w) × 3 mm (l) × 110 nm (d); gaps: 5 μm), followed by evaporation of the solvent. This yielded films of 5 nm thickness, based on SEM (Figure 5) and AFM (Supporting Information) measurements.

Figure 6 shows plots of the electrical conductivities of the films versus temperature. Apart from the material with the highest CdSe content, all nanocomposites exhibit room-temperature conductivities on the order of 10³ Ω⁻¹ cm⁻¹, which agrees with theoretical calculations for exfoliated

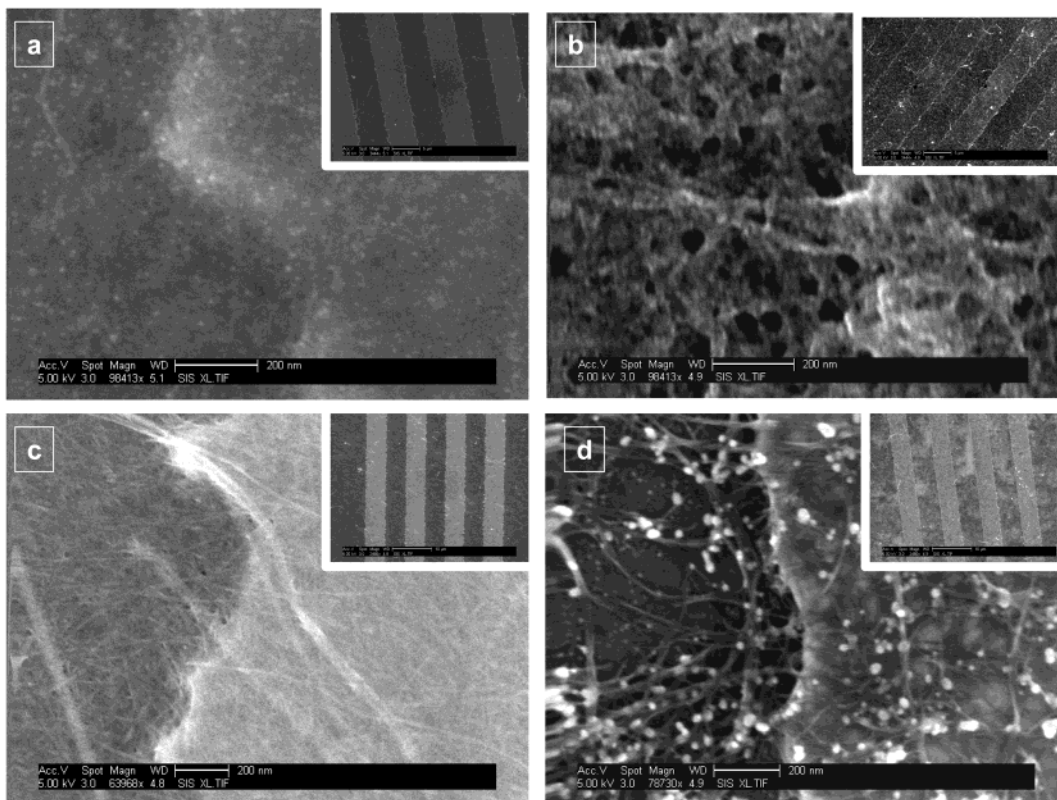


Figure 5. Scanning electron micrographs of composite films on the gold microelectrode array (low magnification images are shown as insets; scale bars are 5–10 μm). The gold microelectrodes (on right side in each micrograph) are elevated by 110 nm over the borosilicate glass substrate. (a) CdSe–LiMo₃Se₃ composites with low and (b) with high CdSe content, (c) pure LiMo₃Se₃ nanowires, and (d) Au–LiMo₃Se₃ composite (all from methanol).

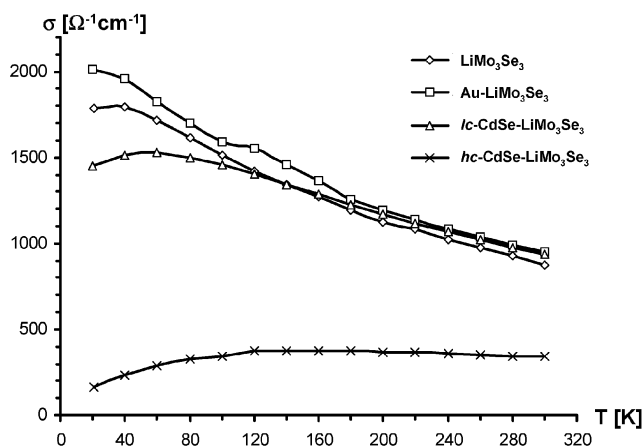


Figure 6. Plots of the film conductance vs temperature. The specific conductivities were calculated based on a lead separation of 5 μm , film length of 1 mm, and film thickness of 5 nm. For the Au–LiMo₃Se₃ a film thickness of 3.5 nm was used in order to correct for the lower density of the film (see Figure 5d). The current was 1 mA. The abbreviations *lc* and *hc* refer to low and high CdSe content. Ohmic behavior was confirmed at all temperatures.

LiMo₃Se₃ wires (100–1000 $\Omega^{-1} \text{cm}^{-1}$).⁸ The electrical conductivity of the composite with high CdSe content is much lower because LiMo₃Se₃ nanowires are entirely coated with a nearly insulating layer of CdSe (0.5 $\Omega^{-1} \text{cm}^{-1}$ for single crystals).²⁰ This layer increases the contact resistance between individual wire fragments in the film (see below).

The temperature behaviors observed for the films fall into two groups. Films of LiMo₃Se₃ and of the Au–LiMo₃Se₃

material are metallic conductors over the entire temperature interval, a behavior that has been previously observed for individual wire bundles.⁷ Films of the CdSe–LiMo₃Se₃ composites, on the other hand, display metallic character only at high temperature, whereas below 60 K (low CdSe content) and 120 K (high CdSe content) the films become semiconducting. The semiconducting behavior indicates that charge transport across the film is limited by thermally activated hopping of electrons between nanoscale components.²¹ This conduction mechanism has been previously observed by Murray et al. in gold nanoparticle films,²² by Heath et al. for films of Ag nanocrystals,²³ and by DiSalvo in LiMo₃Se₃ films, under conditions where the separation of the electrodes was much larger than the mean nanowire length.^{24,25} Thermally activated conduction is most prominent for the CdSe containing films, because the introduction of this bad electrical conductor increases the electron tunneling barriers between separate nanowire bundles. The fact that at $T > 120$ K even the CdSe–LiMo₃Se₃ nanocomposite with the highest CdSe content behaves as a metallic conductor implies that conduction predominantly occurs through LiMo₃Se₃ wire bundles, and not through CdSe nanoparticles.

In conclusion, we have shown that well-defined nanoparticle–nanowire composites can be synthesized in high yield by combining solutions of exfoliated LiMo₃Se₃ nanowires with CdSe and Au colloids. Binding of the nanoparticles does not change the metallic properties of the nanowires, whose specific conductance stays close to the value for the pure

wires. Thus, nanowires of LiMo_3Se_3 are well suited as electrical connects in nanostructured films. Because of its simplicity, the described wiring-up procedure may be of interest for the development of systems in which efficient charge transport to and from nanoparticles is a requirement, e.g., in batteries, solar cells, and microelectronics.

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Supporting Information Available: IR spectra and AFM scans for selected nanocomposites (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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