Magnetic Nanowires

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Magnetic-Dipolar-Interaction-Induced Self-Assembly Affords Wires of Hollow Nanocrystals of Cobalt Selenide**

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Self-assembly, an attractive and practical methodology, allows the formation of a wide range of nanostructures for promising applications—for example, nanoparticle arrays for new optical band-gap materials[1] or high-density magnetic recording media,[2] self-assembled monolayers (SAM) for nanometer-thick films on a variety of substrates,[3] and nanofibers of self-organized small molecules or oligopeptides for drug delivery and tissue engineering.[4] Hydrogen bonding and/or van der Waals interactions are usually the driving forces that result in self-assembly at the nanoscale.[5] Despite extensive investigation, it is still difficult to control and predict the nanostructures resulting from these two types of forces. Although several recent reports have shown that magnetic dipolar interactions induce rather predictable nanoassemblies,[6,7] methods for maintaining these assemblies when the magnetic force decreases or vanishes have been less thoroughly investigated. Therefore, we decided to use the magnetic dipoles inherently associated with magnetic nanoparticles[8] to form 1D assemblies of hollow nanocrystals of semiconductors.[9]

We chose to make wires of hollow nanocrystals of $CoSe_2$ to demonstrate the concept, because 1) the isolation of a nanonecklace of cobalt nanocrystals on a substrate from a dispersion after removal of the solvent[7] indicated that magnetic dipolar interactions are sufficient to maintain 1D assemblies of nanocrystals in solution; 2) the recently reported formation of hollow CoSe nanocrystals from cobalt nanocrystals through the Kirkendall effect[10] suggested that a similar process could be used to generate hollow $CoSe_2$ nanocrystals from 1D assemblies of cobalt nanocrystals; 3) hollow nanostructures have received considerable attention because they exhibit properties that differ from their solid counterparts;[11] and 4) nanowires of hollow nanocrystals of $CoSe_2$ are unknown. Herein, we show that when their sizes reach approximately 20 nm cobalt nanocrystals self-assemble into wires in solution at temperatures as high as 455 K. Through the nanoscale Kirkendall effect,[10,12] wires of hollow $CoSe_2$ nanocrystals form without loss of the preassembled nanostructure induced by the magnetic dipolar interactions of the cobalt nanocrystals. In control experiments, when the size of the cobalt nanocrystals is 6 nm, or when 20-nm cobalt nanocrystals are in an alternating magnetic field, no wires of hollow $CoSe_2$ nanocrystals form. These observations confirm that the magnetic interaction plays a key role in the formation of the nanowires of hollow $CoSe_2$ crystals. Several types of ferromagnetic metallic nanocrystals (iron, cobalt, nickel, FePt, or CoPt) can be prepared readily, and their self-assembly depends on the magnetic dipolar interactions of particles of a certain size. Therefore, the method shown herein should be a general route to 1D assemblies of hollow nanocrystals.

The synthesis of wires of hollow $CoSe_2$ nanocrystals is easy and straightforward. Cobalt nanocrystals of approximately 20 nm in diameter were prepared according to a modified literature procedure[13] and then dispersed in a solvent (for example, 1,2-dichlorobenzene) by using trioctylphosphine oxide (TOPO) as a surfactant. The injection of a dichlorobenzene solution of selenium into the dispersion of cobalt nanocrystals under reflux at 455 K resulted in a black dispersion of $CoSe_2$ nanocrystals after approximately 30 min. Transmission electron microscope (TEM) images reveal that the $CoSe_2$ nanocrystals form wires of intercon-

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nected hollow spheres (Figure 1a). High-resolution TEM images (inset, Figure 1a) and analysis of the electron diffraction pattern of the sample suggest that these hollow spheres are crystalline. Scanning electron microscope (SEM)

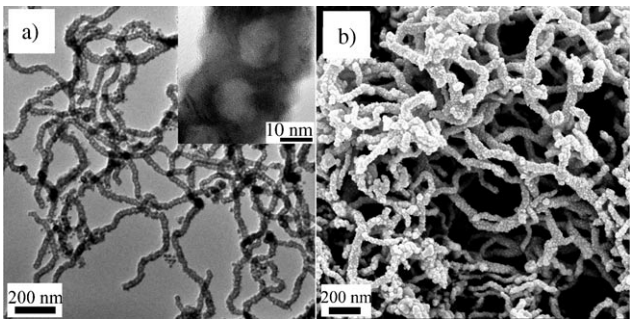


Figure 1. a) TEM image (inset: HR-TEM image), and b) SEM image of the wires of hollow $CoSe_2$ nanocrystals.

images indicate that the wires of hollow $CoSe_2$ nanocrystals are the major nanostructure formed (Figure 1b). This observation suggests that the wires form in high yield, which may allow large-scale production. The X-ray diffraction (XRD) pattern of the $CoSe_2$ nanocrystals (Figure 2) matches that of

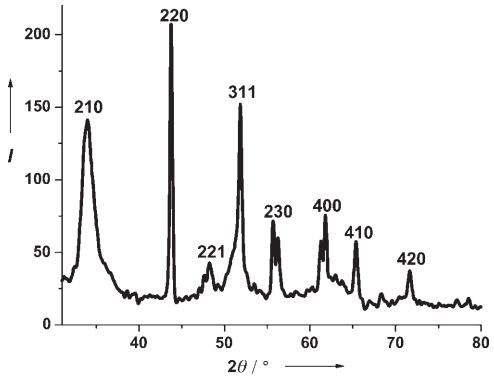
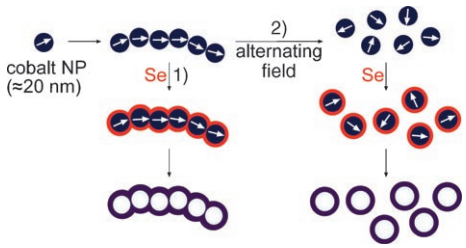


Figure 2. XRD pattern of the wires of hollow $CoSe_2$ nanocrystals.

the primitive cubic phase of $CoSe_2$ (Powder Diffraction File #090234). The X-ray photoelectron spectrum (XPS) of the $CoSe_2$ nanocrystals shows peaks at 778.7 and 54.4 eV, corresponding to the binding energies of the cobalt $2p_{3/2}$ and selenium $3d_{5/2}$ states.[14] In addition, X-ray fluorescence (XRF) analysis indicates that the ratio of Co:Se in the sample is approximately 1:1.80, which suggests that other cobalt selenide phases (for example, CoSe and Co_3Se_4) may be present in small amounts.[15]

Additional TEM analysis of the dispersion of cobalt nanocrystals prior to the addition of selenium showed that the cobalt nanocrystals assemble into wires (see Supporting Information), which are similar to the assemblies of hollow $CoSe_2$ nanocrystals. We also observed a small amount of necklace structures in both the samples of cobalt nanocrystals and hollow $CoSe_2$ nanocrystals (see Supporting Information). Furthermore, the sizes and alignment of the holes of the hollow $CoSe_2$ nanocrystals match with the sizes and alignment of the cobalt nanocrystals in the 1D assembly. These results lead to the proposed mechanism for the formation of wires of hollow $CoSe_2$ nanocrystals (Scheme 1). Each cobalt nano-



Scheme 1. Formation of hollow $CoSe_2$ nanocrystals from cobalt nanoparticles (NP) in the 1) absence and 2) presence of an alternating magnetic field.

crystal behaves as a single magnetic dipole, and the cobalt nanocrystals form chains or necklaces in solution because of strong magnetic dipolar interactions. After being added into the dispersion, selenium reacts with cobalt, and a thin layer of selenium or $CoSe_2$ grows around the wires of cobalt nanocrystals, without disintegration of the wires. Further reaction between selenium and cobalt through the nanoscale Kirkendall process maintains the preassembled nanostructures and affords a 1D assembly of hollow $CoSe_2$ nanocrystals. According to this mechanism, disruption (process 2) in Scheme 1) or reduction of the magnetic dipolar interactions before the addition of selenium should prevent the formation of the wires of hollow $CoSe_2$ nanocrystals. To illustrate this point, we conducted the two following control experiments.

First, we chose cobalt nanocrystals with a smaller size (6 nm) as starting materials, because they have weaker magnetic dipolar interactions than cobalt nanocrystals with diameters of 20 nm. Under the conditions described above, the reaction between 6-nm cobalt nanocrystals and selenium only affords monodispersed hollow nanocrystals (Figure 3a). No 1D assemblies of nanocrystals are observed, probably because the magnetic dipolar interactions between these small cobalt nanocrystals are too weak to form chain or necklace nanostructures at 455 K. Second, we synthesized hollow $CoSe_2$ nanocrystals in an alternating magnetic field,

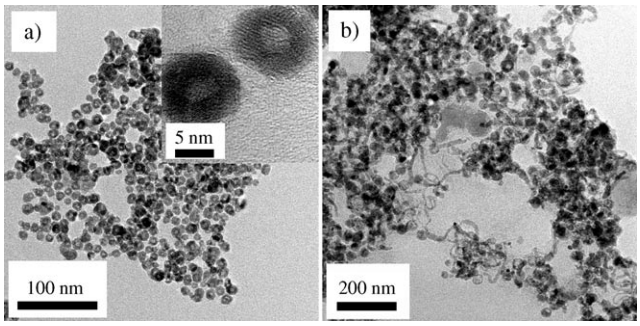


Figure 3. a) TEM image (inset: HR-TEM image) of the monodispersed hollow $CoSe_2$ nanospheres synthesized from 6-nm cobalt nanocrystals; b) TEM image of the hollow $CoSe_2$ nanostructures synthesized in an alternating magnetic field.

$B(t) = B_0 \sin(\omega t)$, where $B_0 = 35$ G and $\omega = 2\pi f$ with $f = 50$ Hz, generated by a Helmholtz coil. In this field, the reaction of 20-nm cobalt nanocrystals with selenium gives only a small number of individual hollow nanocrystals of $CoSe_2$, in addition to a small number of selenium nanowires (Figure 3b).[16] This result is consistent with process 2) proposed in Scheme 1. Because of the head-to-tail arrangement of the magnetic dipoles of the nanoparticles, it is difficult to "switch" all of the dipoles at the same time. The breaking of the chain is due to the vibrational magnetic torque applied, which disrupts the dipolar interactions between the particles. Once the chain is broken, the alternating magnetic torque causes the particles to rotate and prevents them from reconnecting. This mechanism agrees with our observations. These two experiments confirm that magnetic dipolar interactions play a key role in the formation of 1D assemblies of hollow $CoSe_2$ nanocrystals. The use of magnetic dipolar interactions, which can be easily modified through the application of an alternating magnetic field, in the formation of nanostructures provides a useful alternative to the use of electronic dipolar interactions (as applied in the assembly of nanowires of CdSe[5] and PbTe[17]).

To establish the generality of this procedure, we replaced selenium by sulfur or tellurium in the reaction with 20-nm cobalt nanocrystals. As shown in Figure 4, we obtained wires

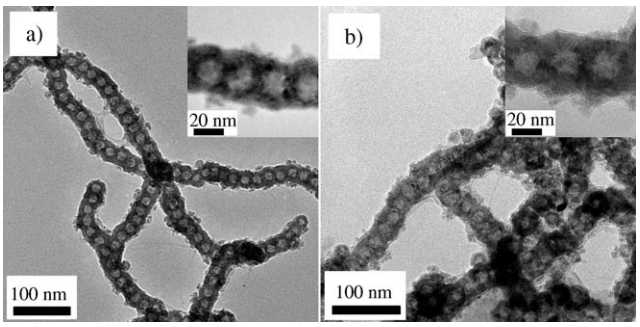


Figure 4. TEM images (insets: HR-TEM images) of the wires of hollow nanocrystals of a) Co_3S_4 and b) CoTe.

of hollow Co_3S_4 and CoTe nanocrystals, which are similar in morphology to the hollow $CoSe_2$ nanocrystals. The XPS of the Co_3S_4 wires shows peaks at 778.9 and 162.2 eV, corresponding to the binding energies of the cobalt $2p_{3/2}$ and sulfur 2p states. XRF analysis indicates that the ratio of Co:S in the sample is 1:1.32, nearly 3:4, which agrees with the ratios of the corresponding precursors. For the CoTe sample, XRF analysis indicates that the ratio of Co:Te is approximately 1:1 (see Supporting Information).

Magnetization measurements indicate that the wires of hollow $CoSe_2$ nanocrystals are ferromagnetic. As shown in Figure 5, the field-dependent magnetization ($M(H)$) of the wires of hollow $CoSe_2$ nanocrystals at 50 K displays hysteresis typical of a ferromagnet. The coercivity (H_c) of the wires of hollow $CoSe_2$ nanocrystals is approximately 600 Oe, roughly half that of the 20-nm cobalt nanocrystals (approximately 1100 Oe; see Supporting Information). Standard zero-field cooling (ZFC) and field cooling (FC) temperature-dependent magnetization ($M(T)$) measurements indicate bulk ferromagnetism. Similar $M(T)$ curves were observed for 20-nm cobalt nanocrystals (see Supporting Information). The magnetic behavior of the wires of hollow $CoSe_2$ nanocrystals suggests that these nanocrystals may actually form a polycrystalline wire with holes. The small peak at 14 K in the ZFC curve (Figure 5, inset) could be due to the unblocking of superparamagnetic $CoSe_2$ nanocrystals, which is evidenced by the FC data from 5 to 30 K. To exclude the possibility that the ferromagnetism solely originates from residual cobalt nanocrystals, we measured the magnetization of the wires of hollow $CoSe_2$ nanocrystals in a 1000-Oe field from 5 to 674 K (Figure 6). We used a SQUID magnetometer to collect the

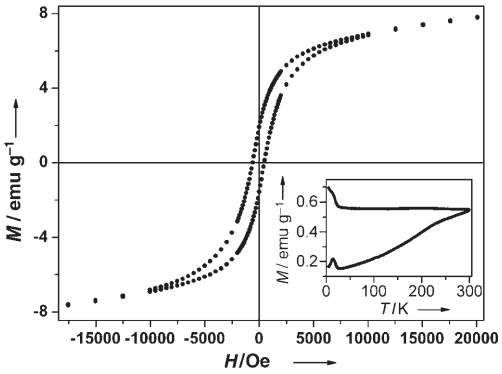


Figure 5. The hysteresis loop for the wires of hollow $CoSe_2$ nanocrystals at 50 K (inset: temperature-dependence of the ZFC (lower) and FC (upper) magnetization of the wires of hollow $CoSe_2$ nanocrystals in a magnetic field of 100 Oe).

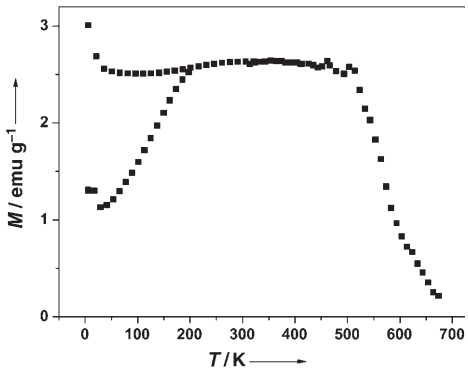


Figure 6. Temperature-dependence of the ZFC (lower) and FC (upper) magnetization of the wires of hollow $CoSe_2$ nanocrystals in a magnetic field of 1000 Oe.

data from 5 to 300 K and a vibrating sample magnetometer to collect the data from 300 to 674 K. The Curie temperature was determined by the position of the maximum of $|dM/dT|$ to be 570 K, which is roughly 1000 K lower than the Curie temperature of cobalt. This result suggests that the ferromagnetism of the wires may arise from $CoSe_2$, although the detailed mechanism has yet to be established.

In summary, we have demonstrated that the nanoscale Kirkendall effect can be applied to a magnetically preassembled nanostructure to form 1D assemblies of hollow nanocrystals of cobalt chalcogenides at elevated temperatures.

This procedure provides an alternative route to nanowires with a unique morphology (interconnected hollow nanocrystals) that is difficult to achieve using other means. This "magnetic-guiding" strategy is also compatible with other methodologies for creating nanostructures.[9,18] In addition, the magnetic nanostructures produced may have potential applications in the fabrication of nanodevice components. We are currently investigating this possibility.

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