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- well as the polycrystalline films used in today's FeRAM. This leads to an upper bound in film thickness of about 1000 Å. The thinness of the ferroelectric film is also constrained. First, there is an intrinsic finite-size effect in which the T_c begins to decrease at a thickness of about 100 Å (17, 22–24) and eventually vanishes for thicknesses in the 10 to 30 Å range (23, 24). The second reason is that extrinsic effects (pinholes and nonuniform thickness over the capacitor area) lead to unacceptably high leakage currents for FeRAM device operation.
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Materials and Methods
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Cation Exchange Reactions in Ionic Nanocrystals

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Cation exchange has been investigated in a wide range of nanocrystals of varying composition, size, and shape. Complete and fully reversible exchange occurs, and the rates of the reactions are much faster than in bulk cation exchange processes. A critical size has been identified below which the shapes of complex nanocrystals evolve toward the equilibrium shape with lowest energy during the exchange reaction. Above the critical size, the anion sublattice remains intact and the basic shapes of the initial nanocrystals are retained throughout the cation exchange. The size-dependent shape change can also be used to infer features of the microscopic mechanism.

Chemical transformations from one solid to another via insertion and exchange of atoms can be used to modify the properties of crystalline materials (1). Recent developments have enabled the production of many technologically important crystalline materials in nanometer sizes, with a wide range of size- and shape-tunable properties (2–8). Of particular interest is the creation of nanocrystals with nonequilibrium shapes and with higher structural and compositional complexity (9–13). In extended solids, reactions involving chemical transformation are in general very slow because of high activation energies for the diffusion of atoms and ions in the solid. For this reason, typical solid-phase reactions require very high temperatures or pressures (14–16) and therefore would seem to be incompatible with kinetically controlled nonequilibrium nanostructures.

However, in crystals only a few nanometers in size, both the thermodynamics and kinetics of reactions can change with size. For example, a large surface-to-volume ratio

can be accompanied by a lowering of phase transition temperatures (17, 18). With the decrease in the volume, statistical averaging of the kinetics and mechanisms over a distribution of heterogeneous reaction sites intrinsic to the bulk solid is also reduced, leading to more homogeneous molecule-like reaction kinetics and even different reaction mechanisms in nanocrystals (19). The optimal use of various chemical transformation methods to broaden the range of nanocrystalline materials depends on an understanding of how chemical transformations in a crystalline solid will be affected by a reduction in size. We show that cation exchange reactions can occur completely and reversibly in ionic nanocrystals at room temperature with unusually fast reaction rates. We also show that the crystal structure and morphology of the reaction products are strongly dependent on the size and shape of the nanocrystals.

The prototypical semiconductor nanocrystal system of CdSe reacts with Ag⁺ ions to yield Ag₂Se nanocrystals by the forward cation exchange reaction, and vice versa for the reverse cation exchange reaction. We chose to work with CdSe nanocrystals because of the high degree of control over size and shape that has been achieved (2, 3). The conversion to Ag₂Se is strongly favored by a thermodynamic driving force of about

–1000 kJ/mol in the bulk (20, 21). Ag₂Se also exhibits an interesting temperature-dependent polymorphism: The superionic conducting phase transition occurs at a relatively low temperature of 133°C in the bulk phase (22). Thus, it may be possible to prepare Ag₂Se with unusually high cation mobility. These two factors favor complete cation exchange in nanocrystals and may prove sufficient to overcome the fact that the exchange reaction is completely kinetically hindered at ambient temperature and pressure in the bulk.

We investigated the reaction by mixing a solution of CdSe nanocrystals (diameter 4.2 nm) in toluene with a small amount of methanolic solution of AgNO₃ under ambient conditions. The volume fraction of methanol in the solution mixture is about 1%; the solution contains Ag⁺ ion in a slightly larger amount than necessary to replace all the Cd²⁺ ions in the nanocrystals. Methanol more strongly binds to any free binary cations in solution and thus favors the forward reaction. A rapid (<<1 s) change of solution color and complete disappearance of fluorescence is observed upon mixing the solutions. Measurements of the x-ray diffraction (XRD) patterns and optical absorption spectra confirm that the reaction product is Ag₂Se (Fig. 1). The reverse reaction is done under ambient conditions by mixing Ag₂Se nanocrystals with an excess amount (typically 50 to 100 times the initial Cd²⁺ content) of Cd(NO₃)₂ in a mixture of toluene and methanol in the presence of tributylphosphine (volume fraction <3%). A slower color change back to that of CdSe nanocrystals and the reappearance of fluorescence are observed over a period of 1 min. XRD patterns, optical absorption, and fluorescence spectra all indicate that CdSe is recovered from the reverse cation exchange. The XRD linewidths of the initial and recovered case are nearly identical. Moreover, the absorption and fluorescence peak positions, which show strong size dependence due to the quantum confinement effect (2), are also nearly identical for the initial and recovered CdSe nanocrystals. Finally, transmission electron micrograph (TEM) images of the initial and recovered

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CdSe (Fig. 1, A and C) also indicate that the size and shape are preserved. This remarkable preservation of volume over multiple complete exchange cycles demonstrates a fundamental feature of cation exchange reactions in nanocrystals: The number of anions per nanocrystal is invariant over multiple cycles (23).

The speed and reversibility of the reaction at room temperature in the nanocrystals is surprising. In a separate experiment with micrometer-sized powders of CdSe, we found the cation exchange to be virtually prohibited under similar experimental conditions over a period of weeks (24). In the bulk phase, these materials were typically subjected to molten salts at very high temperatures to effect the exchange of cations (14). The reaction time for the forward cation exchange reaction ($\ll 1$ s) is much shorter than can be deduced from the reaction time obtained in related systems of larger size [e.g., ~ 10 hours for ~ 100 -nm CdS wire (25)] on the basis of simple scaling of the size in diffusion-controlled reaction schemes, where the reaction time is roughly proportional to the square of the size (26).

This indicates that the effective reaction barrier is much lower in nanometer-sized crystals than in larger systems, therefore also facilitating molecule-like dynamic equilibrium between the reactant and product phases.

High-resolution TEM images of the recovered CdSe spheres indicate that the wurtzite structure of the initial CdSe nanocrystal is not necessarily preserved in the recovered sample. Figure 1G shows an example of the recovered CdSe nanocrystals without noticeable structural defects; Fig. 1H shows one with stacking faults. Moreover, although it is observed much less frequently, a coagulated crystal formed from the merging of two smaller initial nanocrystals (Fig. 1I) can be found, which shows a distinct boundary between two different crystal domains. This raises an important question about whether the cation exchange reaction is topotaxial, where the structural rigidity of the anion sublattice is maintained, or whether substantial morphological reorganization accompanies the reaction.

To obtain a more conclusive answer to this question, we performed cation exchange reactions on nanocrystals with highly aniso-

tropic nonequilibrium shapes, such as rods, tetrapods, and hollow spheres (3, 7, 9). Figure 2 shows TEM images of the initial CdSe nanorods of different sizes and their transformed Ag_2Se nanocrystals. It is readily apparent that thinner nanorods (Fig. 2A) reorganize to the equilibrium spherical shape during the forward reaction, which indicates that the anion sublattice is completely disrupted during the reaction (Fig. 2B). Thicker nanorods maintain their nonequilibrium shapes (Fig. 2, E, F, I, and J). The degree of size control in this system is sufficiently high that it is possible to capture intermediate cases (Fig. 2, C, D, G, and H) where the shape partially anneals, yielding Ag_2Se of rather irregular shape. Thus, there exists a certain size limit below which the structural rigidity of the anion sublattice is not maintained during the cation exchange reaction. The width and length dependence of the morphology changes we observed (e.g., compare Fig. 2, E and F, with Fig. 2, G and H) also suggest that nanorod thickness

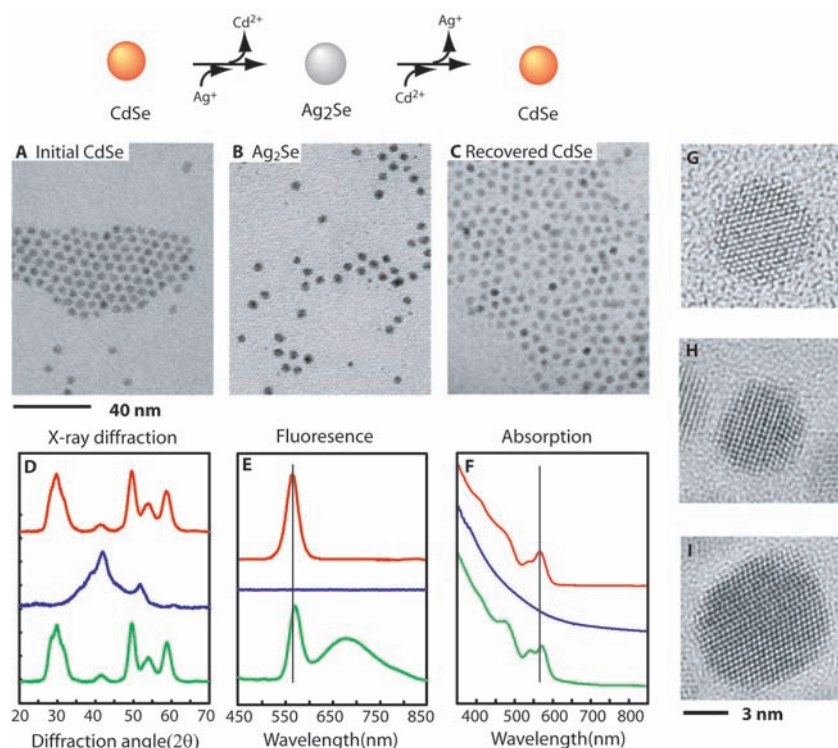


Fig. 1. TEM images of (A) initial CdSe (diameter 4.2 nm), (B) Ag_2Se transformed from the forward cation exchange reaction, and (C) recovered CdSe nanocrystals from the reverse cation exchange reaction. (D to F) XRD patterns, fluorescence emission, and optical absorption spectra of initial CdSe (red), Ag_2Se (blue), and recovered CdSe (green) nanocrystals, respectively. In the recovered CdSe, the peak positions of the emission and absorption show a slight redshift from those of the initial CdSe, which becomes negligible for nanospheres larger than 6 nm in diameter. An additional fluorescence emission feature near 700 nm seen in the recovered CdSe (E) is due to the increased surface trap emission. Vertical lines in (E) and (F) are a guide for the comparison of peak positions. (G to I) High-resolution TEM images of the recovered CdSe nanocrystals without structural defects (G), nanocrystals with stacking faults (H), and a large coagulated nanocrystal formed by merging of two 6-nm nanocrystals (I). The distinct boundary of the different structures is clearly visible.

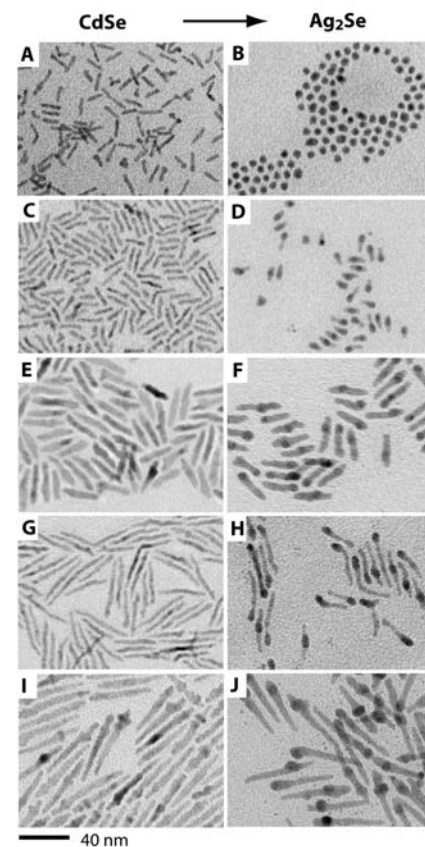


Fig. 2. TEM images of CdSe nanorods of different sizes (A, C, E, G, and I) and their transformed Ag_2Se crystals (B, D, F, H, and J). The average dimensions (width \times length) of CdSe nanorods are (A) 3.2 nm \times 15 nm, (C) 3.4 nm \times 17 nm, (E) 5.3 nm \times 29 nm, (G) 3.6 nm \times 37 nm, and (I) 5.6 nm \times 58 nm. As the nanorods become thicker from (A) to (I), the shape change during the cation exchange reaction is suppressed.

is a more relevant variable than nanorod length in determining the shape change.

Other even more complex and high-energy nonequilibrium shapes of nanocrystals, such as hollow spheres and branched tetrapods (9, 12), maintain their overall shapes throughout complete cation exchange cycles, provided they have a dimension thicker than ~ 5 nm (Fig. 3). CdS hollow spheres maintain overall morphology during the cation exchange, although a smoothing of the rough surface and a small increase in volume are observed. In the case of CdTe tetrapods, slight expansion ($\sim 5\%$) of the width of each branch is observed after the transformation to Ag_2Te .

The observed changes in size can be accounted for by changes in the crystal unit cell symmetry and lattice parameters during the transformation. In Fig. 4A, the structures of Se^{2-} sublattices in wurtzite CdSe and various phases of Ag_2Se are presented to show the topotaxial relationship between the reactant and product phases and associated changes in dimension. Small increases in the width observed in the transformation of thicker CdSe rods to tetragonal Ag_2Se rods (Fig. 2, F and J) reflect the changes in dimension upon change of the crystal structure as shown in Fig. 4A. These observations reveal a second fundamental feature of cation exchange in nanocrystals: The anion sublattice connectivity is preserved during exchange in large nanocrystals.

There are two possible explanations for the crossover of morphology change at widths of 4 to 5 nm observed in CdSe nanorods. First, the structure of the reaction product is progressively changing from a cubic to a tetragonal phase and eventually adopts an orthorhombic phase in the bulk material in crystals of larger size. For small spheres and thin, short rods of CdSe, like those in Figs. 1 and 2A, the Ag_2Se product is cubic. For thicker rods such as those in Fig. 2, E and J, the Ag_2Se is tetragonal (fig. S1). The cubic phase of Ag_2Se is a superionic conductor, with a diffusion coefficient for Ag^+ ions similar to that in liquid solvent ($\sim 10^{-5}$ cm²/s), unlike in other phases of Ag_2Se (22, 27). Because the smaller CdSe nanocrystals are those that form the cubic phase of Ag_2Se and lose structural rigidity, it is conceivable that the high mobility of the Ag^+ ions influences the morphology of the crystal during the reaction. However, we consider this unlikely, because it is the anion sublattice that forms the structural framework of the crystal in the cation exchange reaction, and this should occur regardless of the degree of cation mobility.

A more likely explanation arises when we consider that 4 to 5 nm is comparable to the best available estimates of the width of the reaction zone. Solid-state reactions and the associated phase transformation and microscopic morphology changes in the bulk have been considered extensively. The evolution of the reaction front

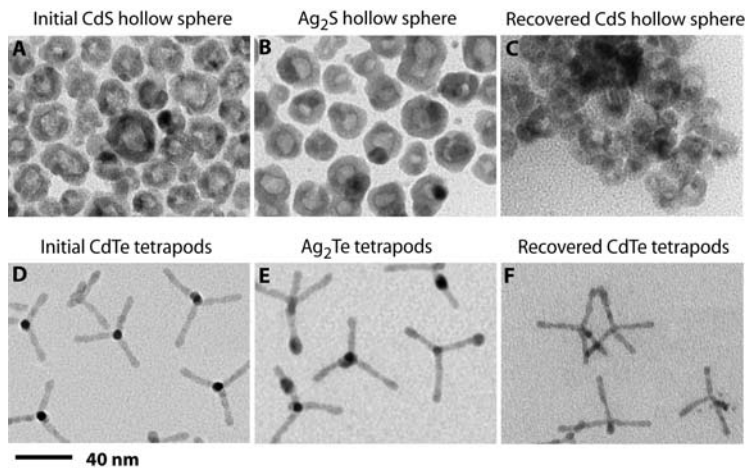


Fig. 3. (A to C) TEM images of (A) initial CdS hollow spheres, (B) Ag_2S hollow spheres produced from cation exchange of CdS, and (C) recovered CdS from the reverse cation exchange reaction. (D to F) TEM images of (D) initial CdTe tetrapods, (E) Ag_2Te tetrapods produced from cation exchange of CdTe, and (F) recovered CdTe from the reverse cation exchange reaction.

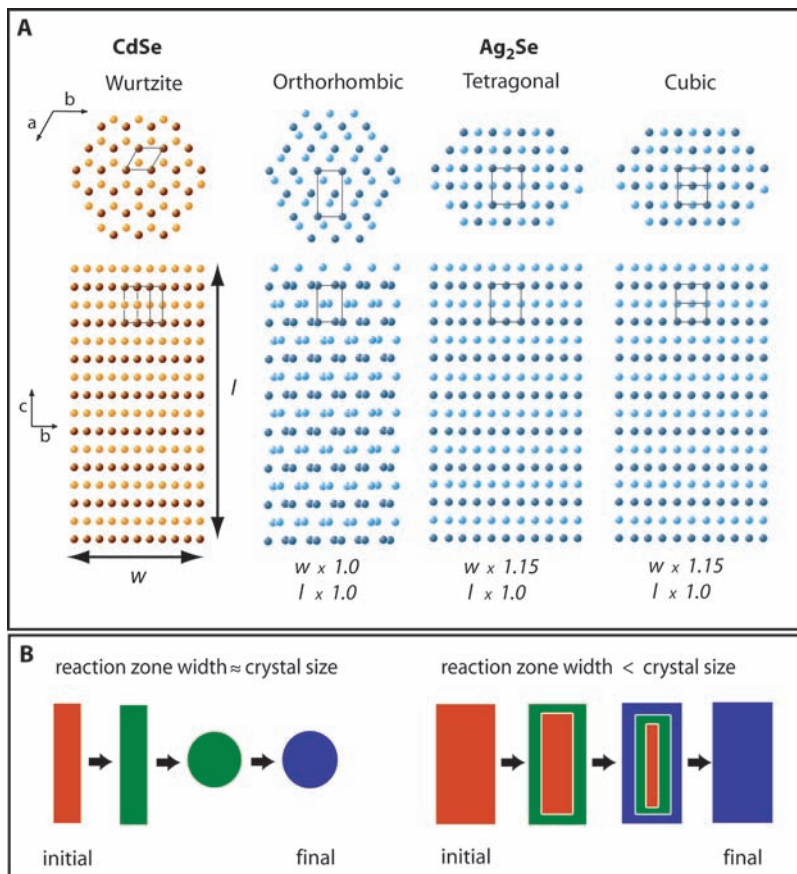


Fig. 4. (A) Comparison of the projection of the selenium anion sublattice in the wurtzite CdSe nanorod and different phases of Ag_2Se nanorods. Dark and light colors are used to distinguish the anions in different atomic layers in the direction corresponding to the long axis of CdSe. Projection of a unit cell is also shown superimposed on the anion sublattice structure to facilitate the comparison. Anion sublattices show simple topotaxial relationships, where the transformation between different structures can be accomplished by movement of ions mostly in the planes perpendicular to the long axis (c axis) of CdSe. (B) Illustration of the size-dependent morphology change during the reaction. Orange and blue colors indicate the regions of initial reactant and final product phase, respectively. The green region indicates the reaction zone where the structural equilibrium is not yet established.

and kinetics can be modeled in a formalism of diffusion kinetics with appropriate chemical and mechanical driving-force fields near the heterogeneous interfaces where the reaction occurs (28). On the nanometer scale, changes in the reaction free energy and the height of the reaction barrier inevitably accompany the well-known increase in vibrational amplitude and diffusion rate (29, 30). This qualitatively changes the picture for the reaction.

Propagation of the reaction zone at the interface, which typically spans several atomic layers, is central to the description of the solid-phase cation exchange reaction in the bulk (28). In nanocrystals, because of the relatively small number of atomic layers within a few nanometers (typically two or three layers per nanometer), the width of the reaction zone can become a large part of or comparable to the whole width of the crystal. This can have two important consequences for reactions in nanometer-sized crystals. First, the slow propagation of the reaction front, driven by the gradient of the local chemical potential near the reaction zone, may become less important as the rate-limiting process of the reaction. Second, at the early stage of the reaction, the whole crystal can be in a structurally nonequilibrium state where both the cations and anions are mobile (31, 32). This can result in a change of the morphology to the thermodynamically more stable shape before all the ions reach the final equilibrium positions of the product phase. As the crystal becomes thicker, propagation of the reaction front is observed and the morphology is maintained (Fig. 4B). The change of morphology that progressively diminishes with the increase in the width of the nanorods is consistent with the idea that the soft reaction zone has a finite width, which falls within the size range for nanocrystal synthesis.

The cation exchange reaction in nanocrystals, investigated mainly with Ag^+ ion in this study, can easily be extended to exchange with other cations. For example, CdSe nanocrystals can be successfully transformed into CuSe and PbSe nanocrystals through the cation exchange reaction with Cu^{2+} and Pb^{2+} ions, respectively, under ambient conditions (33). On the other hand, attempts to induce anion exchange have not been successful under similar experimental conditions, possibly because of the much larger size of the anions relative to the cations, which makes diffusion more difficult.

Our results show that the cation exchange reaction is a versatile route for expanding the range of nanoscale materials with diverse compositions, structures, and shapes without having to develop new synthetic methods to produce each individual nanostructure. Although the finite width of the reaction zone may impose a limit on the size of the nano-

crystal that can be transformed without loss of the original shape, this may be overcome by using an inert and rigid structural support or matrix. Our study also demonstrates that inorganic nanocrystals may be far more chemically dynamic than previously realized.

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- The maximum number of exchange cycles in this study is two. With repeated exchange cycles, the average volume of the nanocrystals is invariant, whereas the structural imperfection (such as shown in Fig. 1H) may accumulate.
- The XRD pattern of powdered CdSe crystal in contact with saturated methanolic solution of $\text{Cd}(\text{NO}_3)_2$ containing excess $\text{Cd}(\text{NO}_3)_2$ for 2 weeks indicates no sign of compositional or structural change.
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- Supported by the U.S. Department of Energy under contract DE-AC03-76SF00098.

Supporting Online Material

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Figs. S1 and S2

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Hysteretic Adsorption and Desorption of Hydrogen by Nanoporous Metal-Organic Frameworks

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Adsorption and desorption of hydrogen from nanoporous materials, such as activated carbon, is usually fully reversible. We have prepared nanoporous metal-organic framework materials with flexible linkers in which the pore openings, as characterized in the static structures, appear to be too small to allow H_2 to pass. We observe hysteresis in their adsorption and desorption kinetics above the supercritical temperature of H_2 that reflects the dynamical opening of the "windows" between pores. This behavior would allow H_2 to be adsorbed at high pressures but stored at lower pressures.

The widespread use of hydrogen as a fuel is limited by the lack of a convenient, safe, and cost-effective method of H_2 storage. None of the current H_2 storage options (liquefied or high-pressure H_2 gas, metal

hydrides, and adsorption on porous materials) satisfy the criteria of size, recharge kinetics, cost, and safety required for use in transportation (1). An adsorbent material with porosity on the molecular scale could