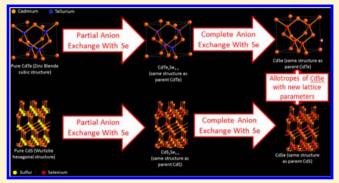


Anion Exchange in II-VI Semiconducting Nanostructures via Atomic **Templating**

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Supporting Information

ABSTRACT: Controlled chemical transformation of nanostructures is a promising technique to obtain precisely designed novel materials, which are difficult to synthesize otherwise. We report high-temperature vapor-phase anionexchange reactions to chemically transform II-VI semiconductor nanostructures (100-300 nm length scale) while retaining the single crystallinity, crystal structure, morphology, and even defect distribution of the parent material via atomic templating. The concept of atomic templating is employed to obtain kinetically controlled, thermodynamically metastable structural phases such as zincblende CdSe and CdS from zincblende CdTe upon complete chemical replacement of Te with Se or S. The underlying transformation mechanisms are



explained through first-principles density functional theory calculations. Atomic templating is a unique path to independently tune materials' phase and composition at the nanoscale, allowing the synthesis of novel materials.

KEYWORDS: Nanostructures, nanowire, nanobelt, anion exchange, atomic template, CdS, Wurtzite, Zincblende, chemical transformation

on-exchange reactions, i.e., selective chemical substitution of ions in ionic materials, have been utilized as an effective route for the chemical transformation of nanostructures to design novel materials with unique physical, chemical, and structural properties and also to understand the distinctive transformation mechanisms at the nanoscale. However, most ion-exchange studies in nanostructures have focused on cation exchange in sub-10 nm crystals via solution-phase chemistries; these studies have provided important insights about cation-replacement reactions at these small length scales, but have limited the scope in understanding chemical transformations in intermediate length scale nanostructures (100-300 nm) such as nanowires (NWs) and nanobelts (NBs), with critical dimensions in this size scale. We previously reported a cation exchange in CdS NWs with diameters in the 10-300 nm range with Zn, via high-temperature vapor-phase reactions. This enables kinetically controlled and size-dependent chemical transformation products ranging from alloyed NWs to metal-semiconductor heterostructures, underscoring the importance of chemical transformations in nanostructures for the synthesis of novel materials. 15 Anion-exchange reactions, on the other hand, are kinetically quite challenging in comparison to cation exchange because anions are usually much bigger than their cationic counterparts in a compound. Anions form the structural framework in crystals of predominantly ionic materials such as II-VI semiconductors

and are therefore more difficult to dislodge without upsetting the structural integrity of the material.¹⁶ Anions possess sluggish diffusivity owing to their large size, which renders their replacement with another anion and subsequent ejection from the material kinetically unfavorable. Therefore, there are limited reported studies on anion-exchange reactions in nanostructures, and much of the work has been accomplished through solution-phase ion-exchange routes. 17-27 The thermal energy of solution-phase chemical reactions is only capable of supporting diffusion over very short distances (<50 nm) in typical laboratory experiment time frames, and hence, this is not the preferred route to effect chemical transformations in larger (100-300 nm) nanostructures. Therefore, one needs to develop alternate routes to replace anions in nanostructures over longer length scales, which would require higher temperatures and better control over reactant delivery to precisely control the rate of exchange reactions. Proper control over reaction rates via temperature and reactant control is essential because very rapid exchange processes would destroy the structural integrity of the sample, and very low reaction rates (typically at lower temperatures) may not be adequate to

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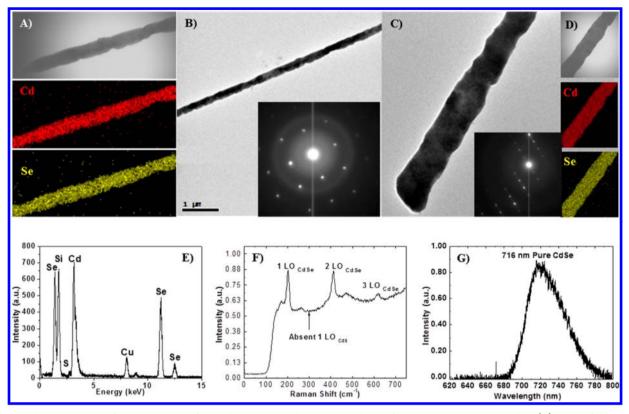


Figure 1. Characterization of nanostructures after undergoing complete anion exchange from WZ CdS into WZ CdSe. (A) Bright-field scanning TEM (BF-STEM) micrograph and EDS map scan of a ≈200 nm diameter NW after complete chemical transformation from CdS into CdSe. (B) BF-TEM micrograph of the same NW confirming morphological integrity along the entire length after anion exchange. Inset: SAED pattern corresponding to single-crystalline WZ CdSe. (C) BF-TEM micrograph of a NB after undergoing complete chemical transformation. Inset: SAED pattern corresponding to single-crystalline WZ CdSe. (D) BF-STEM micrograph and EDS map of the same CdSe NB showing a uniform chemical transformation. (E) EDS point scan from the same NB confirming complete chemical transformation from CdS to CdSe with no residual S. (F) Raman spectrum of a completely transformed CdSe nanostructure showing LO phonon peaks corresponding to the Cd−Se bond. The large background is due to the photoluminescence (PL) emission due to 532 nm laser excitation. (G) PL spectrum of a completely transformed CdSe nanostructure showing a band-edge emission corresponding to pure CdSe.

replace anions deeper in the structure. Here, via hightemperature vapor-phase chemical reactions, we report anionexchange reactions in II-VI semiconducting NWs and NBs, structures that are excellent systems to access a variety of length scales and morphologies along with significant ionicity to study their transformation properties. The II-VI nanostructures are also important due to their interesting physical properties and potential nanoelectronic and nanophotonic applications.^{28–33} In our studies, we achieve complete anion exchange in a variety of nanostructures of different sizes while retaining the atomic template of the parent compound in the form of its crystal structure, defect distribution, and morphology. These observations can enable precise engineering of well-known semiconductor compositions in new and previously unobserved kinetically controlled phases, which are difficult to obtain otherwise, leading to the synthesis of new materials with novel properties.

To explore the potential of anion exchange for the chemical transformation of nanostructures and to study the accompanying evolution in the crystal structure and physical properties, single-crystalline wurtzite (WZ) CdS nanostructures were synthesized via the vapor—liquid—solid (VLS) method in a tube furnace setup,³¹ and anion exchange was performed on asgrown CdS nanostructures with Se vapor. (See the Supporting Information for experimental details.) The experimental conditions were optimized after extensive trials involving

variation of precursor type, quantity, reaction temperature, and time, and it was observed that for a reaction time of approximately 1 h, the temperature was the most important factor that determined the final product. Overheating (>625 °C) caused excessive sublimation of the parent nanostructure, and underheating (<575 °C) led to a negligible chemical transformation. The anion-exchange reaction at 600 °C for 1 h was observed to be optimal to obtain the complete chemical transformation of CdS into CdSe while retaining the singlecrystalline WZ structure, the morphology, and the growth orientation of the parent nanostructure (Figure 1A-E). The results were reproduced for a wide range of sizes and morphologies of WZ CdS ranging from sub-100 nm diameter NWs to 500 nm wide NBs. The observed surface roughness of the nanostructures can be attributed to ≈4% lattice expansion upon transformation from WZ CdS to WZ CdSe, some material deposition on the surface at a high temperature, and vacancies and possibly dislocations induced by the anionexchange reaction, due to which observation of lattice planes via HRTEM was challenging. A better choice of reactants along with their controlled delivery and along with more fine-tuning of the reaction temperature can further improve the morphology of the transformed products. Raman spectroscopy of a completely transformed CdSe nanostructure shows that longitudinal optical (LO) phonon peaks corresponding to pure CdSe³⁴ were present while those corresponding to pure CdS³⁵

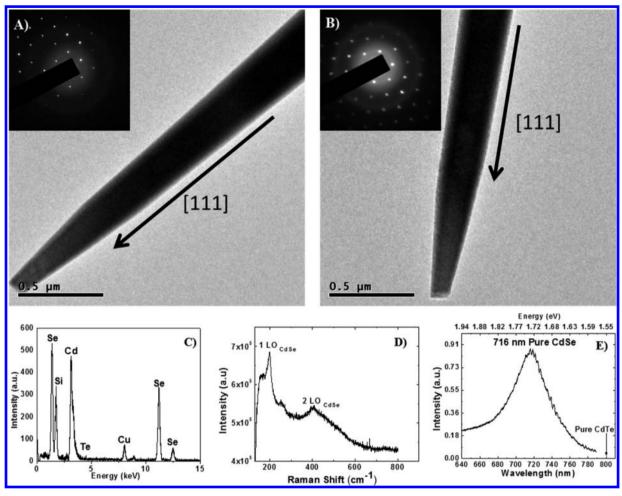


Figure 2. Characterization of NW after undergoing complete anion exchange from ZB CdTe into ZB CdSe. (A) Bright-field TEM micrograph of a ZB CdTe NW before anion exchange. Inset: SAED pattern confirming the ZB crystal structure and <111> growth axis. (B) Bright-field TEM micrograph of the same CdTe NW after complete anion exchange into CdSe. Inset: SAED pattern confirming retention of the ZB crystal structure and <111> growth axis with lattice parameters matching pure ZB CdSe. (C) EDS point scan of the same NW, confirming complete chemical transformation into CdSe with no residual Te. (D) The Raman spectrum also confirms complete chemical transformation with the presence of only Cd—Se LO phonon peaks. (E) PL spectrum displaying band-edge emission corresponding to pure CdSe.

or CdS_xSe_{1-x} alloys³⁶ were absent, confirming the presence of only Cd-Se bonds in the transformed product (Figure 1F). Photoluminescence (PL) spectroscopy of a completely transformed CdSe NW indicates band-edge emission corresponding to pure CdSe³⁷ (≈716 nm) (Figure 1G), further confirming that the band gap of the anion-exchanged material matched WZ CdSe. Achieving complete chemical anion exchange in large nanostructures while retaining the structural integrity of the parent material is a surprising result, which we attribute to a controlled high-temperature vapor-phase reaction that enabled a large-scale atomic diffusion and substitution reaction, while maintaining relatively slow reaction rates to not collapse the structure. It is important to note that, while the anions, which are the structural pillars of the lattice, were being replaced, the cations remained in their positions, thereby retaining the singlecrystalline structure of the parent compound. Although the chemical transformation of CdS into CdSe is thermodynamically unfavorable³⁸ (Supporting Information), the high-temperature and the vapor-phase Se reactant succeeded in kinetically driving forward this reaction. The exact mechanism of this chemical substitution process will be described in detail later.

Motivated by the evidence that the anion lattice framework can be preserved during the anion-exchange reaction in WZ

CdS, the concept was further explored in other phases of II-VI semiconductors with the idea of independently engineering the crystal structure and chemical composition of the material. For example, CdTe is thermodynamically stable in the zincblende (ZB) crystal structure, whereas CdS is stable in the WZ crystal structure at room temperature and atmospheric pressure. 39,40 However, the CdSe crystal structural stability at ambient conditions is size-dependent; typically, <10 nm diameter CdSe nanocrystals can exist in the ZB phase, whereas larger crystals stabilize in the WZ phase. 41-50 Therefore, it is challenging to obtain larger (>100 nm) crystals (NWs and NBs) of CdSe in the zincblende (ZB) phase via conventional synthesis techniques. Since the anion framework can be maintained during the replacement reactions, we performed experiments in order to obtain metastable crystal structures (e.g., CdSe in ZB phase). The anion-exchange reaction was performed in ZB CdTe NWs and NBs of different sizes (>100 nm diameter, thickness, and widths) with vapor-phase transport of Se vapor at 450 °C. The transformation of CdSe from CdTe requires a lower temperature (450 °C) in comparison to CdSe from CdS (600 °C) owing to lower bond energy of Cd–Te than Cd–S, as also reflected by their respective melting temperatures. 34,35 In order to understand the evolution of crystal structure upon

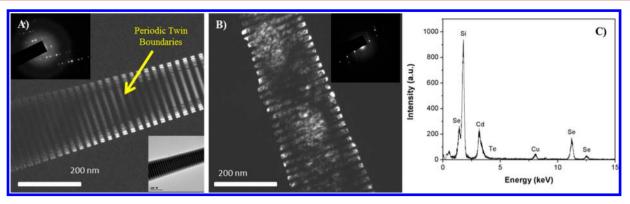


Figure 3. Characterization of a twinned NW after undergoing complete anion exchange from ZB CdTe into ZB CdSe. (A) Dark-field TEM micrograph of a periodically twinned CdTe NW before anion exchange. Upper left inset: SAED pattern confirming the ZB crystal structure, twinning, and <111> growth axis. Bottom right inset: bright-field TEM micrograph of the same NW. (B) Dark-field TEM micrograph of the same NW after complete anion exchange into CdSe. Upper right inset: SAED pattern confirming retention of the ZB crystal structure, twinning, and <111> growth axis with lattice parameters matching pure ZB CdSe. (C) EDS point scan of the same NW confirming complete chemical transformation into CdSe with no residual Te.

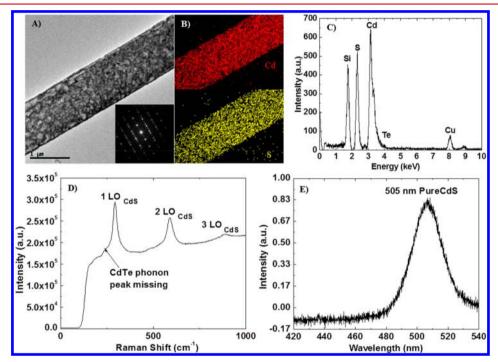


Figure 4. Characterization of a NB after undergoing complete anion exchange from ZB CdTe into ZB CdS. (A) Bright-field TEM micrograph of a ZB CdS NB after undergoing complete chemical transformation from ZB CdTe. Inset: SAED pattern of the NB confirming retention of ZB crystal structure, twinning, and <112> growth axis. The transformed NB is a single crystal. (B) EDS map scan of the NB showing uniform chemical transformation into CdS. (C) EDS point scan of the NB confirming complete chemical transformation. (D) Raman spectrum displaying LO phonon peaks corresponding only to Cd—S bonds, thereby confirming complete chemical transformation. (E) PL spectrum displaying band-edge emission corresponding to pure CdS.

chemical transformation, the same nanostructure assembled on e-beam transparent SiN_x membrane was identified and characterized in detail via TEM studies before and after the replacement reaction. In agreement with our expectations, we obtained CdSe nanostructures in the ZB phase upon anion exchange of Te by Se in ZB CdTe, and the resulting materials retained the morphology, the single crystallinity, and most interestingly, the ZB crystal structure of parent CdTe upon complete chemical transformation (Figure 2A–C). The lattice constant of ZB CdSe was measured to be $\approx\!6.1$ Å, which closely matches the calculated value for ZB CdSe, assuming that ZB and WZ have similar Cd–Se bond distances of $\approx\!2.6$ Å. (See the Supporting Information for calculations.) Raman and PL

spectroscopy also confirmed complete chemical transformation by displaying LO phonon and band-edge emission PL peaks corresponding to pure CdSe^{51,52} (Figure 2D,E). Single-crystalline ZB CdSe formation from ZB CdTe indicates that high-temperature vapor-phase anion-exchange reactions can preserve the atomic template of the parent nanostructure.

If anion exchange is truly atomic template preserving, it must also retain the nature and location of extended lattice defects in a nanostructure upon chemical transformation, assuming that the reaction temperature does not exceed the defect annealing temperature itself. To validate this hypothesis, ZB CdTe nanostructures synthesized via the VLS mechanism, 33 which naturally possess planar growth defects such as twin

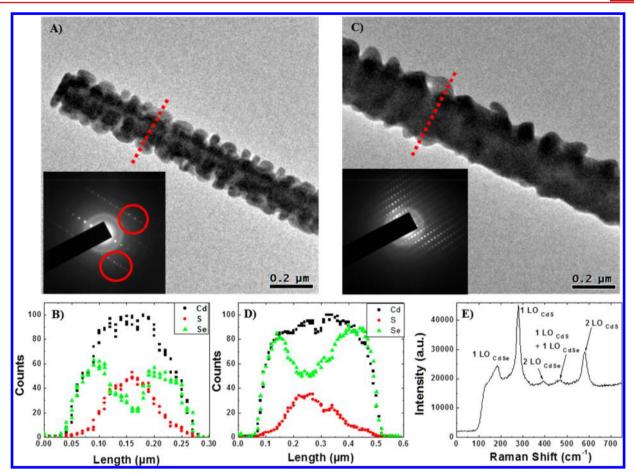


Figure 5. Characterization of nanostructures after undergoing partial anion exchange from CdS to CdS_xSe_{1-x} . (A) Bright-field TEM micrograph of CdS_xSe_{1-x} NW after anion exchange at 300 °C. Inset: SAED pattern of the NW confirming single-crystalline WZ structure with split and elongated spots (red circles). (B) EDS line scan of the same NW confirming the core—shell morphology of the alloyed NW (along the dotted line in A). (C) Bright-field TEM micrograph of CdS_xSe_{1-x} NW after anion exchange at 450 °C. Inset: SAED pattern of the NW confirming single-crystalline WZ structure of CdS_xSe_{1-x} . (D) EDS line scan of the same NW confirming the core—shell morphology of the alloyed NW (taken along the dotted line in C). (E) Raman spectrum of an alloyed CdS_xSe_{1-x} NW showing LO phonon peaks corresponding to both Cd—S and Cd—Se bonds.

boundaries⁵⁴ (characterization details in Supporting Information), were chosen for an anion-exchange reaction with Se (reaction temperature, 450 °C). The same nanostructure was characterized before and after the anion-exchange reaction to study the evolution of defects and their distribution upon chemical transformation (Figure 3A). Supporting our hypothesis of atomic templating, the resulting NW not only retained the single-crystalline ZB crystal structure but also the periodic twin boundaries of the parent material upon undergoing complete chemical transformation into CdSe (Figure 3B,C). These results in addition to providing important details about the chemical transformation mechanism (discussed later) show the potential for independently engineering both the chemical composition and structural phase of materials at the nanoscale while preserving the defect distribution of the parent material.

As mentioned earlier, CdS is thermodynamically stable in the WZ crystal structure at room temperature and atmospheric pressure, and it is challenging to synthesize larger nanostructures (>100 nm) of CdS in the ZB phase. Therefore, to obtain large ZB CdS nanostructures, we performed an anion-exchange reaction at 450 °C in ZB CdTe nanostructures with S vapor. Upon performing the reaction, we once again observed complete chemical transformation into single-crystalline ZB CdS while retaining the twin boundaries of the parent CdTe NBs (Figure 4). The lattice constant of ZB CdS was measured

to be \approx 5.8 Å, which closely matches the calculated value for ZB CdS structure, assuming that ZB and WZ have similar Cd–S bond distance of \approx 2.5 Å. (See the Supporting Information for calculations.) Successful chemical transformation of ZB CdTe into ZB CdS while retaining the planar defects is another proof of the lattice preserving nature of the anion-exchange reaction at the nanoscale. The ability to synthesize large nanostructures of CdS and CdSe in ZB phase highlights the role of anion-exchange-based chemical transformation techniques in phase engineering of metastable structures, which are challenging to obtain otherwise.

To understand the mechanism behind the observed lattice-framework-preserving chemical transformation, a series of control experiments were designed to study anion exchange in the WZ CdS model system by introducing Se. The reaction was kinetically controlled by lowering the reaction temperature, thereby decelerating the transformation kinetics while keeping all other experimental conditions the same, to obtain insights into the step-by-step structural and chemical evolution of the nanostructures. Upon performing anion exchange at 300 °C (lowered from 600 °C) in a $\approx\!200$ nm diameter WZ CdS NW for 1 h, we observed that the NW possesses a rough morphology with periodic protrusions on the surface. Selected area electron diffraction (SAED) patterns of the NW reveal a single-crystalline WZ structure with split diffraction spots

corresponding to pure WZ CdS and WZ CdSe (Figure 5A). An EDS line scan along the radial direction indicates that the NW possesses a compositional gradient, with a Se-rich phase on the surface and a S-rich phase toward the core, indicating an incomplete anion-exchange reaction (Figure 5B). However, upon performing anion exchange at 450 °C on another ≈200 nm diameter WZ CdS NW for 1 h, we again observe rough surface morphology (smoother than the experiment at 300 °C but still much coarser than the reaction at 600 °C), but we find a uniform lattice parameter (no observable diffraction spot splitting) throughout the material (Figure 5C). The EDS line scan along the radial direction indicates a compositional gradient. However, the penetration depth of Se toward the core is higher than was obtained via the anion-exchange reaction performed at 300 °C (Figure 5D). Raman spectroscopy of the NW indicates LO phonon peaks corresponding to both Cd–S and Cd–Se bonds in a CdS_xSe_{1-x} -type alloy in addition to a sum frequency peak (\approx 480 cm⁻¹) (Figure 5E) that corresponds to a two-mode behavior from the CdS_xSe_{1-x} alloy.36

On the basis of the results obtained from the partial and complete chemical transformation in WZ CdS with Se, we propose the following mechanism for the observed anionexchange reaction. The reaction temperature influences the rate of the reactant species generated (Se vapor), the kinetic driving force for the anion exchange to proceed and the diffusivity of atoms in the nanostructure, all of which determine the chemical composition and composition distribution of the final product. At a particular reaction temperature, CdS nanostructures (Figure S4A) will be exposed to a constant flux of Se vapor, which will react with CdS at the surface creating domains of a Se-rich CdS_xSe_{1-x} alloy through anion exchange, and the excess vapor will condense as amorphous selenium (a-Se) on top, creating protrusions (Figure S4B). Besides anion exchange, incoming Se atoms can occupy the S vacancies sites in CdS, 5 which is a thermodynamically favorable process. Our firstprinciples DFT calculations (Supporting Information) show that the Gibbs free energy for the reaction involving one Se atom in vapor occupying a single S vacancy in WZ CdS is ΔG = -3.01 eV/vacancy at 600 °C, $P_{Se} = 100$ Torr.

Unlike the thermodynamically highly favorable vacancy occupation reaction, the anion-substitution reaction depends strongly on the reaction conditions. Our calculations show that the excess Se source vapor and high temperature play a major role in driving this reaction. We find that anion substitution proceeds when S is at a much lower partial pressure than Se:

$$WZ CdS + Se(gas) \rightarrow WZ CdSe + S(gas)$$

$$\Delta G_{\rm rxn} = -0.11 \, {\rm eV/unit} \ {\rm cell} \ {\rm at} \ 600 \, {\rm ^{\circ}C}$$

$$P_{\rm Se} = 100 \text{ Torr and } P_{\rm S} = 10^{-4} \text{ Torr}$$

In our experiment, the carrier gas (argon flowing at 15 SCCM) is capable of instantaneously transporting away rejected S vapor, which is a byproduct of the forward anion-exchange reaction, acting as an efficient sink for S. This helps in pushing the reaction forward and minimizing the reverse anion-exchange reaction (CdSe transforming into CdS). On the other hand, at equal partial pressures of Se and S vapors, our calculations predict that the complete transformation of WZ CdS into WZ CdSe at our reaction temperature (600 °C) via anion exchange is thermodynamically unfavorable; $\Delta G_{\rm rxn} = 0.932$ eV/unit cell at 600 °C, $P_{\rm Se} = P_{\rm S} = 100$ Torr. This shows

that lowering the S vapor partial pressure as compared to the Se vapor partial pressure reduces the Gibbs free energy of the products, making the forward reaction thermodynamically favorable by lowering $\Delta G_{\rm rxn}$ from 0.93 to -0.11 eV/unit cell at 600 °C and making the backward reaction kinetically unfavorable by increasing the activation barrier as a result of reducing the Gibbs free energy of products. Upon anion exchange, the initial CdS_xSe_{1-x} domain size will be directly proportional and domain spacing will be inversely proportional to the incoming Se vapor flux, which is dictated by the reaction temperature. Domain growth of CdS_xSe_{1-x} will involve the outward diffusion of Se²⁻ to the S²⁻-rich regions while fresh Se²⁻ is introduced into the system through a constant anion exchange (Figure S4C). In addition, surface diffusion, which is faster than bulk diffusion, will lead to the preferential chemical transformation at the surface before the core of the nanostructure, thereby creating a core-shell-type morphology instead of an axial heterostructure (Figure S4D). Since the source of Se vapor can be assumed to be infinite with respect to the limited nanostructure volume available, the anion-exchange reaction and CdS_xSe_{1-x} domain growth will continue on the surface until heating is stopped (Figure S4E). Therefore, at the lowest reaction temperature (300 °C) for 1 h, pure CdS at the core is preserved and is surrounded by a shell of CdS_xSe_{1-x} alloy, which explains the diffraction spot splitting in a SAED pattern (Figure 5A inset). The rough surface morphology is due to Cd²⁺ diffusing from nearby regions into the accumulated a-Se protrusions, thus creating Se-rich CdS_xSe_{1-x} in the outermost shell. At an intermediate reaction temperature (450 °C) for 1 h, the entire nanostructure transforms into a CdS_xSe_{1-x} alloy with a radial composition gradient, which allows the system to relax to an intermediate lattice parameter between pure CdS and CdSe. The surface roughness is relatively lower, since the a-Se condensation rate will be smaller at higher temperatures, and the deposited a-Se will be consumed at a faster rate through anion exchange. At the highest reaction temperature (600 °C), the reaction front proceeds inward all the way to the core, completely transforming CdS into CdSe with the lowest surface roughness, due to a negligible a-Se deposition on the surface. The most important factor responsible for the observed surface roughness at 600 °C is lattice expansion by \approx 4% as CdS converts into CdSe and also material sublimation due to a large strain and high temperature of the reaction. Since the fully transformed nanostructures show no signature of any residual sulfur, it is believed to diffuse outward to the surface and then sublimate. At reaction temperatures below 300 °C, no anion exchange is observed for a similar reaction duration (1 h) since there is not enough kinetic drive to push forward both the chemical substitution reaction and the atomic diffusion. At reaction temperatures higher than 600 °C, the nanostructures sublimate, possibly owing to a very fast chemical substitution reaction, thereby causing a large-scale bond breaking and thereby destabilizing the anion lattice framework. These experiments demonstrate the utility of vapor-phase anion-exchange reactions in chemically transforming large nanostructures to new single composition or compositionally graded nanomaterials while preserving the lattice framework of the parent material. This enables the synthesis of metastable phases of materials at the nanoscale while preserving the defect density of the parent

To summarize, we have demonstrated vapor-phase anionexchange reactions as a novel chemical transformation route to

independently control materials' structural phase and composition, thereby allowing us to synthesize well-known compounds in metastable stable crystal phases, which can even retain the defect distribution from the parent nanostructure (Figure 6). In the size range studied in our work (<300 nm),

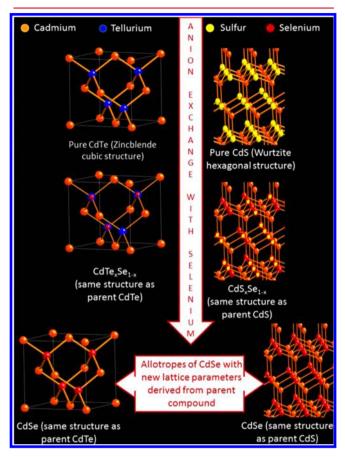


Figure 6. Schematic representation of the concept of atomic templating where, for example, polymorphs (WZ and ZB) of a compound (CdSe) can be produced by performing anion exchange in starting compounds with different crystal structures (WZ CdS versus ZB CdTe).

we did not observe an onset of major defects such as the formation of polycrystalline domains and fracture or destruction of the observed products, which typically occurs in bulk systems. Our work exhibits controlled chemical reactions at the nanoscale while preserving the structural integrity of the material in spite of substituting anions, which are considered structural pillars in a crystal framework. This method, which we call "atomic templating", is a promising tool that can be extended beyond II—VI semiconductors to engineer more exotic materials at the nanoscale for a variety of electronic, optical, and energy harvesting and conversion applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b04424.

TEM, Raman spectroscopy, and photoluminescence spectroscopy experimental details, growth and characterization details of CdTe nanobelts, anion exchange

experimental details, ZB lattice constant calculations for CdSe and CdS, Figures S1–S4, and first-principles calculations using density functional theory (PDF)

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Author Contributions

R.A. and R.A.* conceived and designed the experiments. R.A., N.M.K., and W.L. optimized the growth conditions and synthesized the CdS and CdTe nanostructures. R.A. performed the anion-exchange reaction and the chemical and structural characterization before and after. M-L.R. performed photoluminescence experiments. L.Z.T and A.M.R performed first-principles density functional theory calculations. R.A. and R.A.* interpreted and analyzed the data. R.A., L.Z.T., A.M.R., and R.A.* cowrote this Letter.

Notes

The authors declare no competing financial interest.

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