

Determinants of Crystal Structure Transformation of Ionic Nanocrystals in Cation Exchange Reactions

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Abstract:

Changes in the crystal system of an ionic nanocrystal during a cation exchange reaction are unusual yet remain to be systematically investigated. In this study, chemical synthesis and computational modeling demonstrated that the height of hexagonal-prism roxbyite ($\text{Cu}_{1.8}\text{S}$) nanocrystals with a distorted hexagonal close-packed sulfide (S^{2-}) sublattice determines the final crystal phase of the cation-exchanged products with Co^{2+} [wurtzite cobalt sulfide (CoS) with hexagonal close-packed S^{2-} and/or cobalt pentlandite (Co_9S_8) with cubic close-packed S^{2-}]. Thermodynamic instability of exposed planes drives reconstruction of anion frameworks under mild reaction conditions. Other incoming cations (Mn^{2+} , Zn^{2+} , and Ni^{2+}) modulate crystal structure transformation during cation exchange reactions by various means, such as volume, thermodynamic stability, and coordination environment.

One Sentence Summary:

The morphology of ionic nanocrystals determines the corresponding crystal structure after cation exchange reactions.

Main Text:

Crystallographic control expands available routes to tuning the physical and chemical properties of colloidal ionic nanocrystals (NCs), which researchers have conventionally determined by size, shape, and composition (*1-4*). Ion exchange reactions are a promising route for overcoming current limits imposed by direct synthetic routes to NCs and for increasing the library of available crystal structures (*5-10*). Generally, incoming cations expel the original cations and preserve the robust anion sublattice because the smaller cations diffuse much faster than larger anions and the overall morphology and crystal system of a NC are retained (*11-13*). For example, the cation exchange of hexagonal close-packed (hcp) wurtzite (*w*)-CdSe NCs with Cu^+ affords hcp Cu_2Se NCs in which the hcp Se^{2-} sublattice framework is maintained, despite the hcp Cu_2Se phase being thermodynamically metastable in the copper selenide family, indicating that the kinetic stability for maintaining the Se^{2-} sublattice is preferred (*14*). Because anion sublattice deformation is usually hindered, only a few cation exchange reactions transform the crystal structure (*15-17*). In particular, crystal structure transformations derived from anion sublattice deformation through cation exchange without changing the overall host NC morphology are rare—for example transformations from tetragonal Cu_3Se_2 to *w*-CdSe, and from chalcocite Cu_2S to rocksalt-PbS (*18, 19*).

Anion sublattice rearrangement during cation exchange appears to be material-dependent, but the mechanism of lattice reconstruction has been poorly understood given the lack of systematic studies focusing on crystal structure transformation during the cation exchange reaction. An understanding of the critical factors that govern crystal structure transformation is needed to expand the synthetic range of ionic nanomaterials (*20*).

Here, we demonstrate that the crystal structure of cation-exchanged NCs strongly depends on the shape of the host NCs. In this work, we used $\text{Cu}_{1.8}\text{S}$ NCs with 16 hexagonal-prism shapes—from rod to plate—as host ionic NCs for a cation exchange reaction with Co^{2+} (*21-23*). The crystal structure of the cation-exchanged CoS_x NCs strongly depended on the height (length of the *a*-axis) of the host hexagonal-prism $\text{Cu}_{1.8}\text{S}$ NCs. Comprehensive experiments and theoretical calculations indicated a morphology-dependent kinetic barrier for unconventional anion sublattice reconstruction from hcp to cubic close-packed (ccp). In the case of other incoming cations, cation-dependent factors determined the crystal structures of cation-exchanged NCs.

We chose roxbyite $\text{Cu}_{1.8}\text{S}$ NCs with a distorted hcp S^{2-} anion sublattice for cation exchange with various cations (Co^{2+} , Mn^{2+} , Zn^{2+} , and Ni^{2+}) because of fast Cu^+ diffusion in non-stoichiometric Cu_{2-x}S NCs (24-27). Furthermore, facile control over the size and shape of roxbyite $\text{Cu}_{1.8}\text{S}$ NCs allowed investigation of the effects of NC morphology in various applications (21, 28). We first applied the cation exchange reaction with Co^{2+} to $\text{Cu}_{1.8}\text{S}$ nanoplates (NPLs) and nanorods (NRs). We injected a dispersion of $\text{Cu}_{1.8}\text{S}$ NCs in tri-*n*-octylphosphine into a 100°C solution containing Co^{2+} , oleylamine, and 1-octadecene; and maintained the temperature at 100°C for 5 min (29). Energy-dispersive x-ray (EDX) spectroscopy confirmed that the cation exchange was nearly complete ($\text{Cu}/\text{Co} < 3$ mol %) within 5 min.

The host $\text{Cu}_{1.8}\text{S}$ NPLs were 61.3 ± 3.2 nm in width and 5.2 ± 0.4 nm in height (Fig. 1, A and B); and the (400) and (008) planes were in the longitudinal and lateral directions of the plate, respectively (Fig. 1, C and D). After cation exchange of the $\text{Cu}_{1.8}\text{S}$ NPLs with Co^{2+} , the hexagonal plate shape was maintained whereas the size decreased to 57.2 ± 3.1 by 5.0 ± 0.4 nm (width by height) (Fig. 1E). Non-uniform contrast in individual NPLs in TEM images arises from the residual strain by the lattice volume change. The x-ray diffraction (XRD) pattern and high-resolution transmission electron microscopy (HRTEM) indicated that the resulting NPLs had the *w*-CoS phase (Fig. 1F), and the (002) and (110) planes aligned in the longitudinal and lateral directions, respectively, of the NPL (Fig. 1, G and H). Thus, the *w*-CoS NPLs retained the hcp S^{2-} sublattice from the host hcp $\text{Cu}_{1.8}\text{S}$ NPLs. The *w*-CoS phase was thermodynamically metastable in the cobalt sulfide family, as confirmed by theoretical calculations of the formation energy (table S1). Formation of a thermodynamically metastable phase through the cation exchange reaction has often been observed because of the preferable retention of the anion sublattice of host NCs versus deformation into a more stable phase (11, 12).

Next, we synthesized $\text{Cu}_{1.8}\text{S}$ NRs, with a width of 14.9 ± 1.0 nm and a height of 26.9 ± 3.2 nm, as the host NCs (Fig. 1, I and J). HRTEM images showed that the (400) and (008) planes aligned in the longitudinal and lateral directions, respectively (Fig. 1, K and L), confirming that the NRs have a larger number of smaller basal (400) planes stacking in the [100] direction than do NPLs. After cation exchange with Co^{2+} , the original rod shape was slightly distorted but roughly maintained while the size decreased to 13.0 ± 1.5 by 24.6 ± 2.8 nm (width by height) (Fig. 1M). Notably, the XRD pattern of the resulting NRs was in accordance with the distorted ccp pentlandite-type Co_9S_8 phase (Fig. 1N) (30), where the S^{2-} sublattice framework was completely

different from that of the host hcp $\text{Cu}_{1.8}\text{S}$. HRTEM images showed that the (222) and (440) planes aligned in longitudinal and lateral directions, respectively, in the Co_9S_8 NRs (Fig. 1, O and P). These results demonstrate that the shape of a host NC determines the final crystal structure of a cation-exchanged product.

Both $\text{Cu}_{1.8}\text{S}$ and $w\text{-CoS}$ phases are composed of hexagonally packed S^{2-} monolayers (MLs) (fig. S1) stacking in a zigzag ABABAB... manner along the [100] and [001] directions, respectively. The ccp Co_9S_8 phase has similar hexagonally packed S^{2-} MLs, but the stacking is in a triplicate ABCABC... manner along the [111] direction (fig. S2). Transformation from hcp to ccp by sliding the A and B layers in the [010] direction of hcp $\text{Cu}_{1.8}\text{S}$ is unusual but possible (fig. S2B) (31). The lattice volume per S^{2-} anion decreased by 32% from $\text{Cu}_{1.8}\text{S}$ to Co_9S_8 in the cation exchange (table S2). This large change in volume likely allowed the S^{2-} anions to move extensively, resulting in the formation of corresponding stable phase (32). HRTEM images in fig. S3 showed that the [111] stacking direction of the Co_9S_8 phase tilted by 19.5° to the long axis in Co_9S_8 NRs, which could be explained by sliding the S^{2-} MLs of the $\text{Cu}_{1.8}\text{S}$ phase into the same direction. Another possible rearrangement is to slide only the A layer in the [010] direction of the hcp $\text{Cu}_{1.8}\text{S}$ phase to form the ccp arrangement with an ABCBA twin boundary (fig. S2C), which we observed in Co_9S_8 NRs (fig. S3).

To understand the determining factor in shape-dependent crystal structure transformation during cation exchange reactions, we studied cation exchanges between Co^{2+} and 16 types of hexagonal prism-shaped roxbyite $\text{Cu}_{1.8}\text{S}$ NCs with different widths and heights (Fig. 2A, fig. S4, and table S3). We synthesized these various-shaped $\text{Cu}_{1.8}\text{S}$ NCs by systematically modulating the $\text{Cu}(\text{NO}_3)_2/\text{CuCl}_2$ precursor molar ratio (table S4) (28), which we named $\text{Cu}_{1.8}\text{S-S1}$ to $\text{Cu}_{1.8}\text{S-S16}$ in descending order of height (table S3). The XRD patterns of all of the $\text{Cu}_{1.8}\text{S}$ NCs corresponded to the roxbyite phase (fig. S5), yet the relative peak intensities varied because of the anisotropic shape effect. HRTEM images of representative $\text{Cu}_{1.8}\text{S}$ NCs showed the [100] direction aligned to the height (fig. S6).

After cation exchange with Co^{2+} , the overall morphologies of the host NCs were pseudomorphically retained with some distortions for all of the cation-exchanged NCs (Fig. 2B and fig. S7). On the basis of their XRD patterns, the cation-exchanged NCs from $\text{Cu}_{1.8}\text{S-S1}$ to $\text{Cu}_{1.8}\text{S-S7}$ (larger height: >13.6 nm) exhibited the Co_9S_8 phase, whereas those from $\text{Cu}_{1.8}\text{S-S11}$ to

Cu_{1.8}S-S16 (smaller height: <7.1 nm) exhibited the *w*-CoS phase (Fig. 2C and fig. S8). The HRTEM images of representative CoS_x NCs indicated that (222) and (002) planes stacked along the height of Co₉S₈ and *w*-CoS NCs, respectively (fig. S9). Notably, the XRD patterns of the products obtained from Cu_{1.8}S-S8 to Cu_{1.8}S-S10 (medium height: 9.6 to 12.5 nm) exhibited a mixture of both Co₉S₈ and *w*-CoS phases (Fig. 2C and fig. S8). The HRTEM images of NCs from Cu_{1.8}S-S9 (Co₉S₈ + *w*-CoS) also confirmed that the individual NC has either a *w*-CoS or Co₉S₈ phase rather than both phases (Fig. 2D and fig. S10), indicating that the Cu_{1.8}S-S8 to Cu_{1.8}S-S10 NCs with medium height transformed to either Co₉S₈ NCs or *w*-CoS NCs.

Figure 2E summarizes the relation between the dimensions of the host NCs and the crystal phase of the cation-exchanged NCs, which indicated the boundary of the crystal structure transformation at a height of ~ 9 to 13 nm containing Cu_{1.8}S-S8 to Cu_{1.8}S-S10 NCs. Without exception, Cu_{1.8}S NCs larger or smaller than this intermediate height region were transformed into Co₉S₈ (*w*-CoS) NCs, respectively. However, we found no correlation between the width of the host NCs and the crystal phase of the cation-exchanged NCs. For example, long rods (S2, 19.5-nm width by 67.2-nm height) and small plates (S15, 18.8-nm width by 5.4-nm height) were transformed into Co₉S₈ and *w*-CoS NCs, respectively (fig. S11, A and B). Likewise, wide rods (S1, 60.5-nm width by 90.4-nm height) and large plates (S16, 61.3-nm width by 5.2-nm height) were transformed into Co₉S₈ and *w*-CoS NCs, respectively (fig. S11, C and D), suggesting the importance of the height of the host NCs for crystal structure transformation. Further plots of aspect ratio or volume versus height of the host Cu_{1.8}S NCs also indicated that only the height of the NCs was a critical factor in the crystal structure of cation-exchanged products (fig. S12). This rule was valid regardless of the presence of angled facets truncating corners of the hexagonal prism Cu_{1.8}S NCs (fig. S13).

Other factors could influence the structure of cation-exchanged products. Specifically, the TOP molecules have been reported to induce the structural change of Cu_{2-x}S NCs by extracting S²⁻ before the cation exchange (33). In our study, both the sonication of Cu_{1.8}S NCs in TOP for 30 min to prepare the injection solution and the control experiments without Co²⁺ did not cause serious change in their morphologies and crystal structures (fig. S14). In addition, the volumes of the resulting CoS_x NCs calculated from their sizes were close to those expected by the theoretical lattice shrinkage from the corresponding Cu_{1.8}S NC (fig. S15). These results indicate that TOP did

not cause severe dissolution and phase transformation but served to accelerate the cation exchange reaction.

To understand these phenomena, we considered the cation exchange mechanism to be dependent on the shape of the NCs. The shape of the host NCs often determines the initial reaction site where the cation exchange starts because the surface energy, ligand density, and Cu^+ defect density depend on the exposed crystal planes (34). Moreover, the directional cation diffusion in NCs might affect anion lattice reconstruction. To confirm the effect of cation exchange on the crystal phase of the products, we compared the cation exchange processes of three types of $\text{Cu}_{1.8}\text{S}$ NCs—long rods (S2), thick plates (S5), and thin plates (S16)—by observing partially cation-exchanged NCs as intermediate products.

The XRD pattern of partially cation-exchanged NCs of $\text{Cu}_{1.8}\text{S}$ -S2 NRs ($\text{Co/Cu} = 46/54$ mol/mol by EDX) showed coexistence of $\text{Cu}_{1.8}\text{S}$ and Co_9S_8 phases (Fig. 3, A and B). Scanning TEM (STEM)–EDX spectroscopy mapping showed that the elements Cu and Co were located at different ends of the NRs and formed a heterointerface of $\text{Cu}_{1.8}\text{S}$ (400)// Co_9S_8 (222), suggesting that cation exchange started from one tip of the rod (Fig. 3, C to F) (35, 36). A partially cation-exchanged product of $\text{Cu}_{1.8}\text{S}$ -S5 thick NPLs ($\text{Co/Cu} = 35/65$ mol/mol by EDX) also had both $\text{Cu}_{1.8}\text{S}$ and Co_9S_8 phases (Fig. 3, G and H), although the $\text{Cu}_{1.8}\text{S}$ and Co_9S_8 phases shared the same crystal plane, as shown by STEM–EDX spectroscopy (Fig. 3, I and J). This result indicated that cation exchange started from one edge of the $\text{Cu}_{1.8}\text{S}$ -S5 NPL and propagated in an in-plane direction, resulting in the formation of a heterointerfacial plane of $\text{Cu}_{1.8}\text{S}$ (008)// Co_9S_8 ($4\bar{4}0$), tilted 90° with respect to that of S2 NRs (Fig. 3, K and L). Thus, the Co_9S_8 phase can form regardless of the cation exchange starting plane and the progressing direction.

However, partial cation exchange of $\text{Cu}_{1.8}\text{S}$ -S16 thin NPLs ($\text{Co/Cu} = 48/52$ mol/mol by EDX) yielded NPLs consisting of $\text{Cu}_{1.8}\text{S}$ and $w\text{-CoS}$ phases (Fig. 3, M and N). The element Co was located at six corners of the hexagonal plate, indicating that cation exchange started at the peripheral corners of $\text{Cu}_{1.8}\text{S}$ -S16 NPLs (Fig. 3, O to R) (22). Although both thin and thick NPLs had an in-plane cation exchange propagation path, the corresponding CoS_x phases were completely different, strongly indicating that the cation exchange route did not determine the crystal structure of CoS_x NCs. We attributed the different exchange routes to the difference in reactivity of the crystal planes of $\text{Cu}_{1.8}\text{S}$ NCs (27, 37). Because the reactive surface area is minimized in

equilibrium shape (38), the tip $\{100\}$ and side $\{010\}/\{001\}$ facets were preferentially reactive owing to the intrinsically unfavorable atomic arrangement and/or less ligand coverage in NRs and NPLs, respectively, even though both NCs had the same roxbyite phase.

In the partial cation-exchanged products, the XRD peaks assigned to roxbyite $\text{Cu}_{1.8}\text{S}$ phase shifted and approached those of djurleite $\text{Cu}_{1.94}\text{S}$, which was probably induced by the strain at the heterointerface (fig. S16, A to C) (39). Thus, the $\text{Cu}_{1.8}\text{S}$ phase could be slightly changed in this cation exchange process. However, the strain effect had little impact on the shape-dependent phase transformation, because the XRD peak shift took place regardless of the shape of NCs and the hcp S^{2-} structure in Cu_{2-x}S phase preserved the hcp structure during the cation exchange reaction (fig. S16D).

We next investigated the thermodynamic stability of the CoS_x phases. The w - CoS phase is reported to be thermodynamically unstable but kinetically stabilized by the high robustness of the S^{2-} anion framework during the cation exchange reaction (13). However, our results indicated that stabilization by the anion framework was unlikely to work for cation-exchanged NCs with a large height. In other words, the activation energy for the S^{2-} framework reconstruction from hcp to ccp greatly depended on the height of the cation-exchanged NCs. Considering the difference in the formation energies between the w - CoS and Co_9S_8 phases, applying thermal energy to the w - CoS phase should induce a phase transition, even for thin NPLs (table S1). Thus, to confirm the thermal energy effect, we varied the reaction temperature (over the range from 60° to 150°C) in a cation exchange reaction of $\text{Cu}_{1.8}\text{S}$ -S16 thin NPLs. As the temperature increased, the phase fraction of the Co_9S_8 increased (nearly reached 100% at 150°C), and the overall plate shape was retained (fig. S17). Thus, the S^{2-} anion framework was relatively fragile in cation exchange with Co^{2+} , given the thermodynamic instability of the w - CoS phase. Furthermore, in the case of NRs, decreasing the reaction temperature did not change the crystal phase of cation-exchanged NCs; for example, Co_9S_8 NRs formed even at 60°C (fig. S18). Thus, the kinetic barrier for S^{2-} anion framework reconstruction of NRs was substantially lower than that of NPLs. This shape-dependent crystal structure transformation at various temperatures can rule out the effect of diffusion rate of cations on the phase transformation (40).

We considered why anion sublattice reconstruction occurred in cation exchange of larger-height $\text{Cu}_{1.8}\text{S}$ NCs regardless of the reaction temperature. Surface energy is an important factor for

linking the crystal structure and morphology of NCs. In general, a specific crystal plane with high surface energy is covered by more-stable planes in the equilibrium shape (38). In the present cation exchange reaction, which pseudomorphically retained the overall shape, phase transformation would be the only route to lower the surface energy. Theoretical calculations of representative exposed planes of *w*-CoS showed that the surface energies of the side planes, (100) and (110), were higher than those of the basal plane (001), suggesting that exposure of such side planes was strongly disfavored (table S5).

Because the side surface area increased as the height of the NCs increased, we hypothesize that the thermodynamic instability of large-height *w*-CoS NCs triggers reconstruction of their S^{2-} sublattices. However, further theoretical insights are required to quantitatively explain the threshold height of $Cu_{1.8}S$ NCs that induces crystal structure transformation. We conclude that kinetic stabilization of a metastable phase during the cation exchange reaction depends on the overall shape of the NCs. A large deviation from the intrinsic equilibrium stable shape with a metastable phase is likely to decrease the kinetic barrier to anion sublattice reconstruction, thereby leading to the thermodynamically stable phase.

Whether the crystal structure transformation occurred was related to how the hcp crystal phase of the cation-exchanged products was stabilized. Because the difference in the formation energies between hcp and the other phases depended on the type of metal sulfide, other metal cations used in the cation exchange reaction should have different determining factors than that of the CoS_x case (i.e., factors other than the height of the host NCs). We used three cations (Mn^{2+} , Ni^{2+} , and Zn^{2+}) for cation exchange of $Cu_{1.8}S$ -S4 NRs and $Cu_{1.8}S$ -S16 NPLs. Cation exchange of $Cu_{1.8}S$ -S4 NRs with Mn^{2+} and Zn^{2+} resulted in formation of *w*-MnS and *w*-ZnS NRs, respectively (Fig. 4, A to H), unlike in the Co^{2+} case. When using Ni^{2+} as an incoming cation, we obtained Ni_3S_4 NRs with a distorted ccp S^{2-} framework, where the (222) plane aligns along the longitudinal direction in the Ni_3S_4 NRs, as observed in the Co_9S_8 -S4 NRs (Fig. 4, I to L). However, cation exchange of $Cu_{1.8}S$ -S16 NPLs with Mn^{2+} and Zn^{2+} formed of *w*-MnS and *w*-ZnS NPLs, respectively (Fig. 4, M to T). Notably, when we used Ni^{2+} as an incoming cation, we also obtained slightly distorted NPLs with a Ni_3S_4 phase (Fig. 4, U and V), indicating that the S^{2-} sublattice was reconstructed even in thin NPLs (Fig. 4, W and X).

Both MnS and ZnS have two typical phases: wurtzite (hcp) and zincblende (zb, ccp) structures.

Because the trend of the formation energy difference between the *w*-MnS and *zb*-MnS phases was similar to that between the *w*-CoS and Co₉S₈ phases (table S1), we expected a similar crystal structure transformation of *w*-Cu_{1.8}S NRs into *zb*-MnS. However, the volume change from Cu_{1.8}S NCs to MnS NCs with either phase was too small (< 2%) to reconstruct the S²⁻ anion sublattice during cation exchange, in contrast with large volume change (> 15%) in the CoS_x case (table S2 and fig. S19). In fact, cation exchange with large volume change triggered the drastic anion sublattice reconstruction (32). For ZnS, both phases had nearly the same formation energies (table S1), suggesting that a driving force for the crystal structure transformation was small, and the hcp S²⁻ framework was retained despite the volume change during the cation exchange reaction reaching ~10% (table S2 and fig. S19).

For cation-exchanged NCs with Ni²⁺, NiAs-type NiS is a representative hcp NiS_x phase, but it was quite difficult to form this phase by cation exchange of Cu_{1.8}S NCs because octahedral coordination of Ni²⁺ in NiS was unlikely to result from roxbyite Cu_{1.8}S with a trigonal or tetrahedral coordination of cations (13). Although we expected *w*-NiS to form through cation exchange of Cu_{1.8}S NCs with Ni²⁺, *w*-NiS NCs appear to not have been reported. Thus, a critical factor inhibited formation. Furthermore, the volume change of the lattice was quite large (>28%) in the context of transformation from Cu_{1.8}S to any NiS_x phase (table S2), offering an opportunity for S²⁻ sublattice reconstruction. These considerations may account for the drastic phase transformation to stable ccp-Ni₃S₄ from any shape of host Cu_{1.8}S NCs.

References and Notes:

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Supplementary Materials:

Materials and Methods

Figs. S1 to S19

Tables S1 to S5

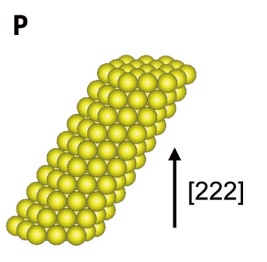
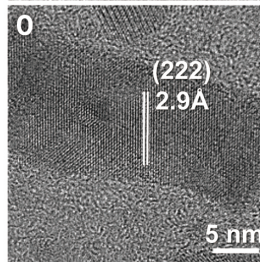
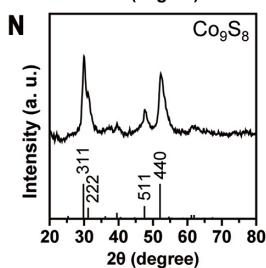
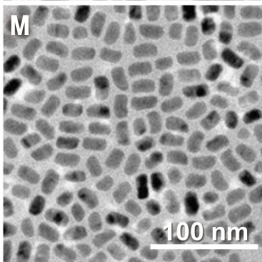
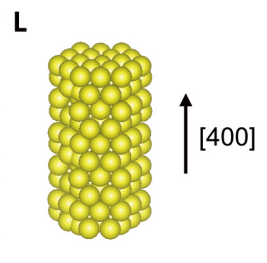
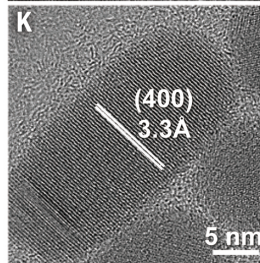
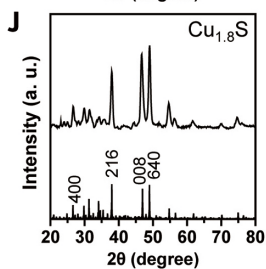
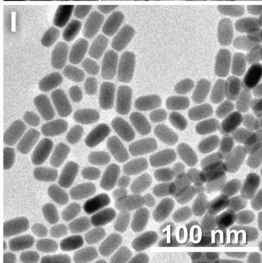
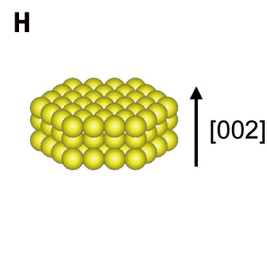
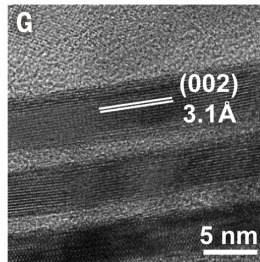
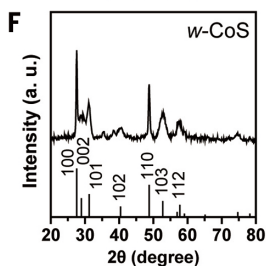
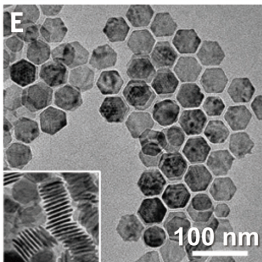
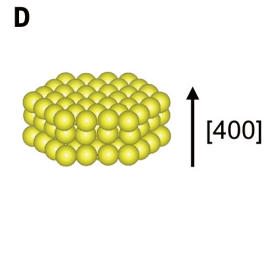
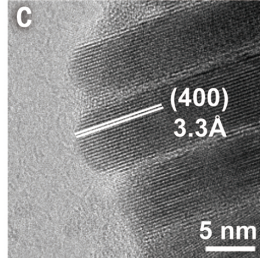
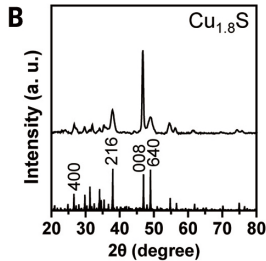
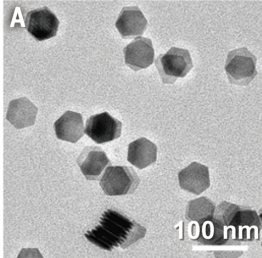
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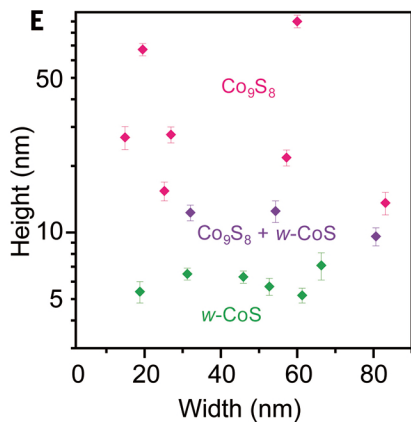
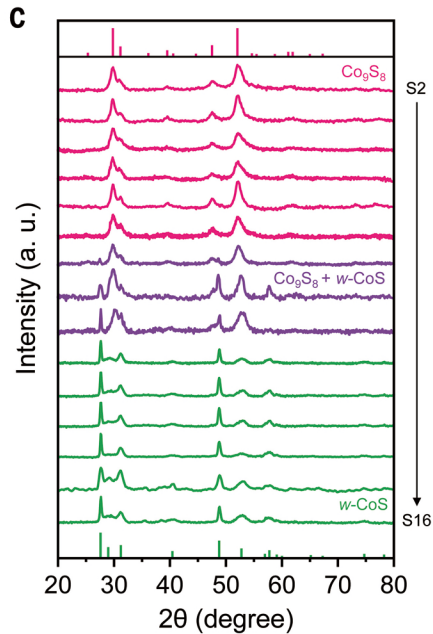
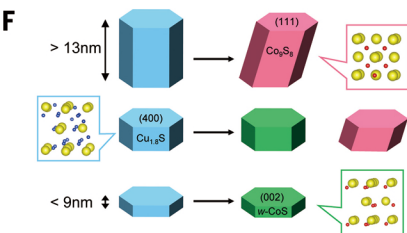
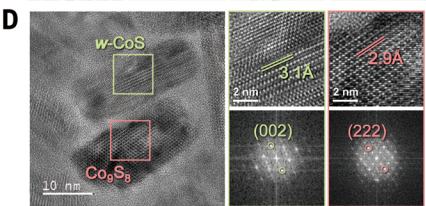
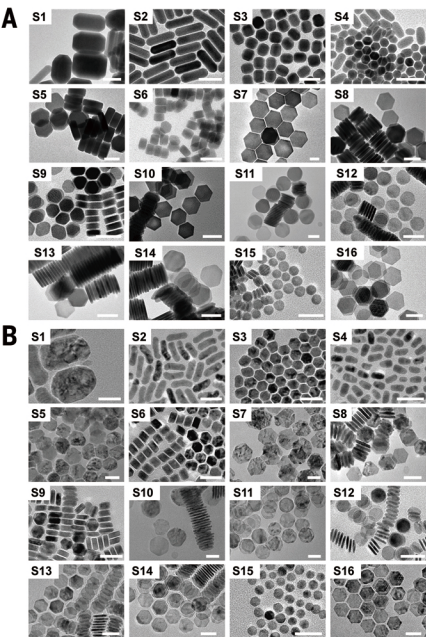
Fig. 1. Cation exchange reactions of Cu_{1.8}S NPLs and NRs with Co²⁺. TEM images, XRD patterns, HRTEM images, and S²⁻ sublattice models of (A to D) Cu_{1.8}S NPLs, (E to H) *w*-CoS NPLs, (I to L) Cu_{1.8}S NRs, and (M to P) Co₉S₈ NRs. Reference XRD patterns: roxbyite Cu_{1.8}S [International Centre for Diffraction Data (ICCD) number 00-064-0278], pentlandite Co₉S₈ (ICCD 00-056-0002), and simulated *w*-CoS (12). a.u., arbitrary units.

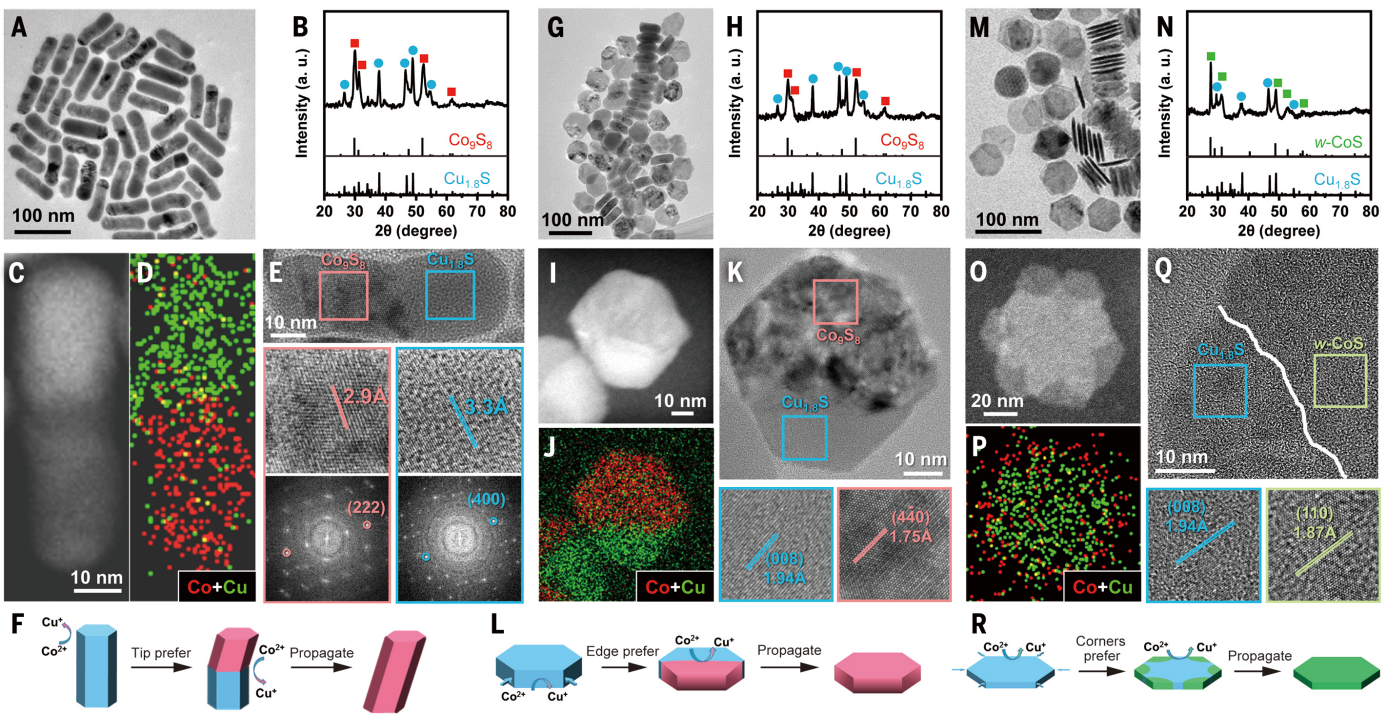
Fig. 2. Cation exchange reactions of Cu_{1.8}S NCs with 16 kinds of morphologies with Co²⁺. TEM images (50-nm scale bars) of (A) 16 types of hexagonal prism-shaped Cu_{1.8}S NCs and (B) cation-exchanged CoS_x NCs. (C) XRD patterns of CoS_x-S2 to CoS_x-S16 NCs. (D) HRTEM images of NCs from Cu_{1.8}S-S9 (Co₉S₈ + *w*-CoS). (E) Height–width plots of host Cu_{1.8}S NCs and corresponding CoS_x phases after the cation exchange. (b) Schematics of height-dependent phase transformation of NCs during the cation exchange. Reference XRD patterns in (C) correspond to pentlandite Co₉S₈ (pink, ICCD 00-056-0002) and simulated *w*-CoS (green).

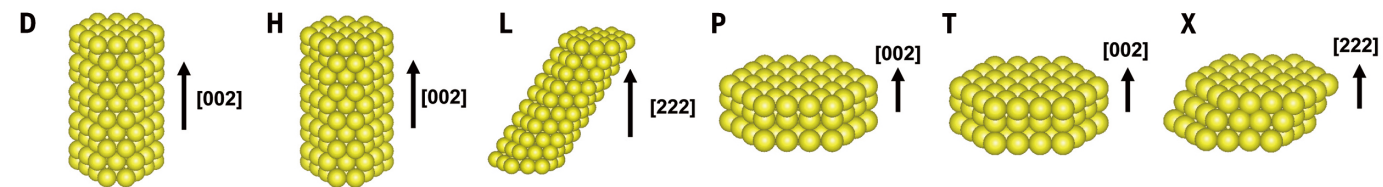
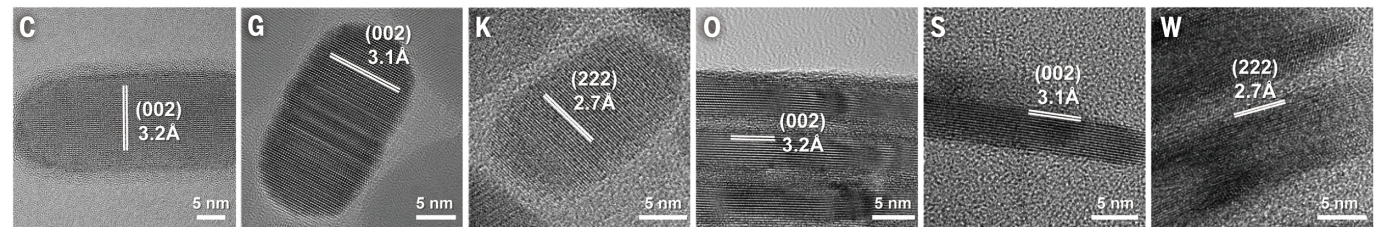
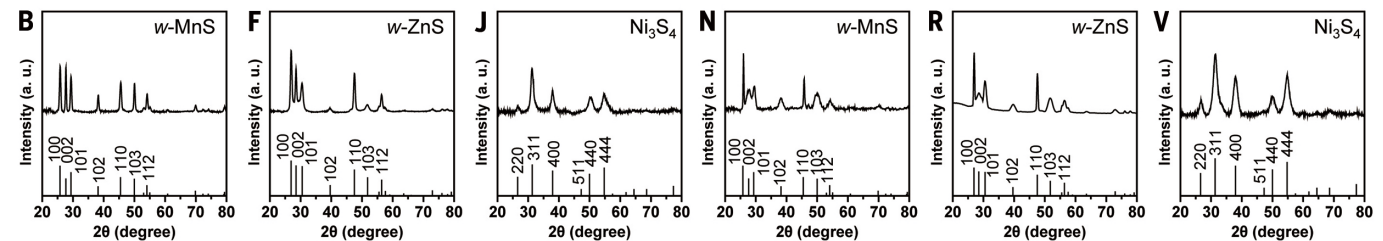
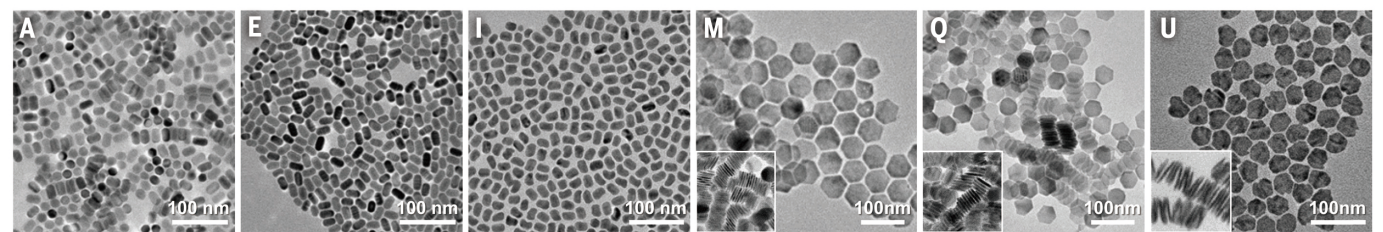
Fig. 3. Partial cation exchange reactions of Cu_{1.8}S-S2, S5, and S16 NCs with Co²⁺. (A, G, and M) TEM images; (B, H, and N) XRD patterns; (C, I, and O) STEM–high-angle annular dark field images; (D, J, and P) STEM-EDX spectroscopy mapping images; (E, K, and Q) HRTEM images; and (F, L, and R) schematics of cation exchange of partially cation-exchanged NCs: [(A) to (F)] Cu_{1.8}S/Co₉S₈-S2 NRs, [(G) to (L)] Cu_{1.8}S/Co₉S₈-S5 NPLs, and [(M) to (R)] Cu_{1.8}S/*w*-CoS-S16 NPLs.

Fig. 4. Cation exchange reactions of Cu_{1.8}S NRs and NPLs with Mn²⁺, Zn²⁺, and Ni²⁺. TEM images, XRD patterns, HRTEM images, and crystallographic structure of S²⁻ sublattice, respectively, of (A to D) *w*-MnS NRs, (E to H) *w*-ZnS NRs, (I to L) Ni₃S₄ NRs, (M to P) *w*-MnS NPLs, (Q to T) *w*-ZnS NPLs, and (U to X) Ni₃S₄ NPLs. Reference XRD patterns: *w*-MnS (ICCD 01-089-4089), *w*-ZnS (ICCD 01-079-2201), and polydymite Ni₃S₄ (ICCD 00-043-1469).











Supplementary Materials for

**Determinants of Crystal Structure Transformation of Ionic
Nanocrystals in Cation Exchange Reactions**

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Materials and Methods

Chemicals

Oleylamine (OLAM, 90%, Aldrich), 1-octadecene (ODE, 90%, Aldrich), tri-*n*-octylphosphine oxide (TOPO, $\geq 90\%$, Aldrich), *tert*-dodecanethiol (*t*-DDT, 98.5%, Aldrich), 1-dodecanethiol (DDT, $\geq 98\%$, Aldrich), tri-*n*-octylphosphine (TOP, 99%, Aldrich), copper(II) chloride (CuCl_2 , 99%, Aldrich), copper(II) nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%, TCI], copper(I) thiocyanate (CuSCN , 99%, Aldrich), manganese(II) chloride (MnCl_2 , 99%, Aldrich), nickel(II) chloride (NiCl_2 , 98%, Aldrich), zinc(II) chloride (ZnCl_2 , 99%, Aldrich), and cobalt(II) chloride (CoCl_2 , 99%, Aldrich) were used as received without further purification. All solvents [hexane, isopropanol (IPA), toluene, and acetone] were of analytical grade and were used as received without further purification.

Synthesis

Synthesis of $\text{Cu}_{1.8}\text{S}$ NCs ($\text{Cu}_{1.8}\text{S-S1-S3}$, S5, S6, and S8-S16) (28):

CuCl_2 (x mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($1.5 - x$ mmol), OLAM (2.46 mL), and ODE (15 mL) were combined in a three-neck round-bottom flask equipped with a Schlenk line. The system was vacuumed for 30 min at 80°C . The flask was purged with N_2 and was heated to 180°C at a rate of $20^\circ\text{C min}^{-1}$. When the temperature of the reaction solution reached 120°C , *t*-DDT (6 mL) was rapidly injected. The reaction system was maintained at 180°C for desired time and then cooled to room temperature with a water bath. The reaction product was collected by centrifuging $2\times$ with an acetone/IPA mixed solvent. The final black precipitate was resuspended in hexane for further use. The shape of $\text{Cu}_{1.8}\text{S}$ NCs was modulated via the $\text{Cu}(\text{NO}_3)_2/\text{CuCl}_2$ mole ratio and reaction time. Table S4 summarizes the reaction conditions.

Synthesis of $\text{Cu}_{1.8}\text{S-S4}$ NRs (28):

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (281 mg), TOPO (2.9 g), and ODE (15 mL) were combined in a three-neck round-bottom flask equipped with a Schlenk line. The system was vacuumed for 30 min at 80°C . The flask was purged with N_2 and was then heated to 180°C at a rate of $20^\circ\text{C min}^{-1}$. When the reaction solution reached 120°C , a *t*-DDT:DDT mixture (volume ratio 10:1; 7.5 mL) was rapidly injected. The reaction system was maintained at 180°C for 5 min and then cooled to room temperature with a water bath. The product NRs were collected by centrifuging $2\times$ with an acetone/IPA mixed solvent. The final black precipitate was resuspended in hexane for further use.

Synthesis of $\text{Cu}_{1.8}\text{S-S7}$ NPLs (41):

CuSCN (60.8 mg) and OLAM (10 mL) were combined in a three-neck round-bottom flask equipped with a Schlenk line. After the system was vacuumed for 30 min at 80°C , the solution was purged with N_2 . Then, the reaction system was heated to 240°C and

maintained at that temperature for 30 min. After cooling to room temperature, the reaction product was collected by centrifuging 2× with an acetone/IPA mixed solvent and resuspended in hexane for further use.

Cation exchange reactions:

Cation exchange reactions were performed based on a published procedure (42). Typically, CoCl₂ (0.4 mmol), OLAM (4 mL), and ODE (10 mL) were added to a three-neck round-bottom flask equipped with a Schlenk line. The solution was heated to 100°C under vacuum for 30 min, and then the flask was purged with N₂. The mixture was heated to 180°C and maintained at that temperature for 30 min to form a Co-OLAM complex, followed by cooling to 100°C. In a separate vial, a mixture of Cu_{1.8}S NCs (containing 0.1 mmol S) and TOP (3 mL) was sonicated for 30 min and degassed under vacuum for 30 min. The Cu_{1.8}S NCs/TOP suspension was rapidly injected into the Co-OLAM solution at 100°C and the reaction proceeded for 5 min. Finally, the reaction solution was cooled to room temperature. The final product was collected by centrifuging 2× with an acetone/IPA mixed solvent and resuspended in hexane. The partial cation exchange products of Cu_{1.8}S/CoS_x NCs were synthesized using a smaller quantity of CoCl₂ (Co:S=1:2 mol:mol) in otherwise the same reaction conditions. Mn, Zn, and Ni cation exchange were conducted through the same procedure except using MnCl₂, ZnCl₂, and NiCl₂, respectively.

Characterization

Transmission electron microscopy (TEM) observations were performed on a JEM1011 (JEOL) at an accelerating voltage of 100 kV. High-resolution TEM (HRTEM), high-angle annular dark field-scanning TEM (HAADF-STEM), and energy-dispersive X-ray (EDX) spectroscopy elemental mapping images were collected with a JEM-ARM200F (JEOL) at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were measured on PANalytical X'Pert Pro MPD powder diffractometer with CuK α radiation ($\lambda = 1.542 \text{ \AA}$) under 40 mA and 45 kV.

Calculation details

We performed first-principles calculations within density functional theory for *w*-CoS, *w*-MnS, *w*-NiS, and *w*-ZnS, *zb*-MnS and *zb*-ZnS, cobaltpentlandite-type d-ccp Co₉S₈, and spinel-type d-ccp Ni₃S₄. We used the computational code OpenMX which is based on optimized pseudopotentials and pseudo-atomic-orbital basis functions (43). The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof is selected for an exchange-correlation functional (44).

1. The configuration of basis sets was *s3p3d2f1* for all elements in these systems.
2. The cutoff radius was 8.0 atomic units (a.u.) for S and 6.0 a.u. for Co, Mn, Ni, and Zn.

3. The cut-off energy was chosen as 500 Ry, and k -point meshes were $20 \times 20 \times 20$ for the cubic systems and $30 \times 30 \times 18$ for the hexagonal systems.
4. The lattice parameters and atomic positions in the systems were optimized until the calculations satisfied the convergence criteria which were 1.0×10^{-7} Hartree for the total energy and 1.0×10^{-4} Hartree/Bohr for the maximum force on each atom, respectively.
5. The calculations for three CoS-surface systems terminated at the (100), (001), and (110) planes were also performed in the same manner.
6. These model surface systems have 10~15 layers and a 10 Å blank area at each terminated plane in order to represent surface regions.

Obtained calculation results are at zero Kelvin and we do not consider the reaction paths of how these systems are fabricated because of the limitation of first-principles calculations.

Calculation result

We calculated the formation energies (E_{form}) of these systems by using the following equation;

$$E_{\text{form}} = E_{\text{bulk}} - (\alpha\mu[X] + \beta\mu[S])$$

Here, E_{bulk} are the total energies of bulk cubic and hexagonal systems, and $\mu[X]$ and $\mu[S]$ are the chemical potentials of X and S, which are the equivalent to the total energies of these ground states, respectively. X represents Co, Mn, Ni, and Zn, and α and β can take any positive integers depending on how many X and S exist in a bulk system.

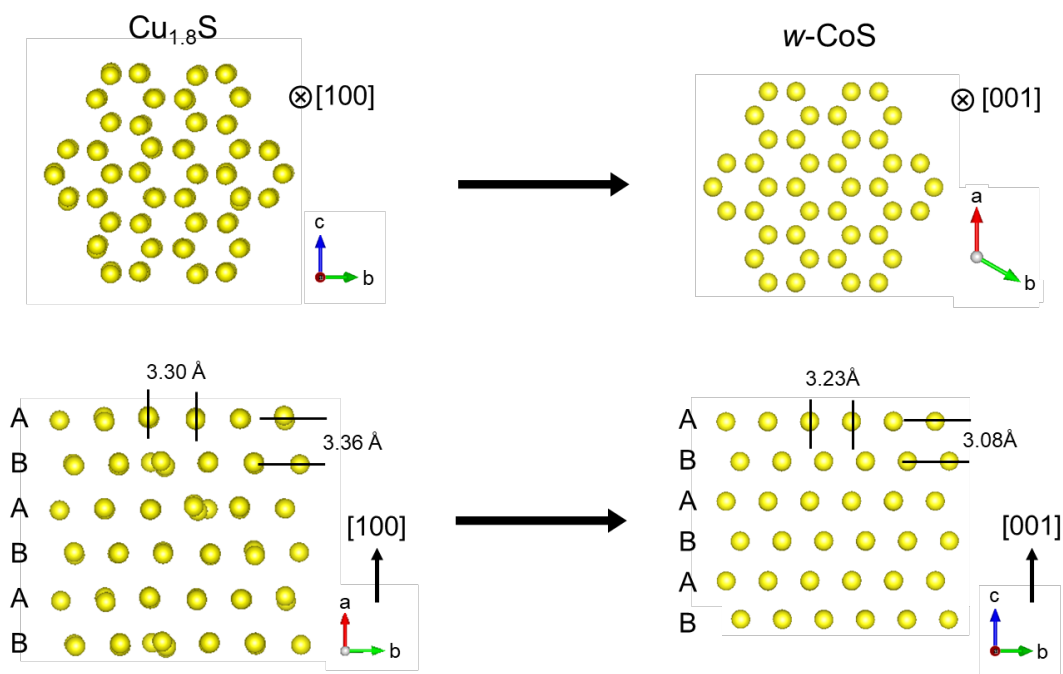


Fig. S1.
Schematic of S^{2-} lattice change from $\text{Cu}_{1.8}\text{S}$ to $w\text{-CoS}$.

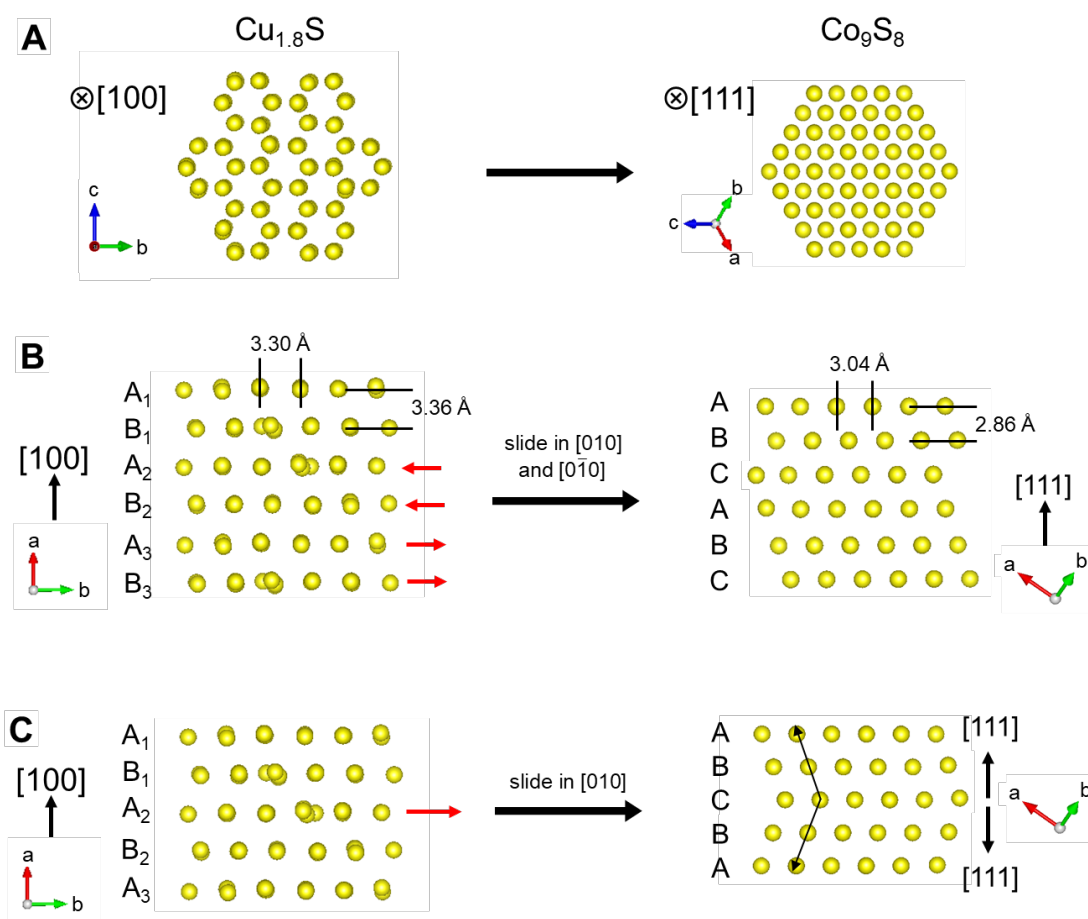


Fig. S2.

Schematic of S^{2-} lattice change from $\text{Cu}_{1.8}\text{S}$ to Co_9S_8 . (A) View from vertical direction of $\text{Cu}_{1.8}\text{S}$ and Co_9S_8 . (B) Normal and (C) faulty reconstruction processes.

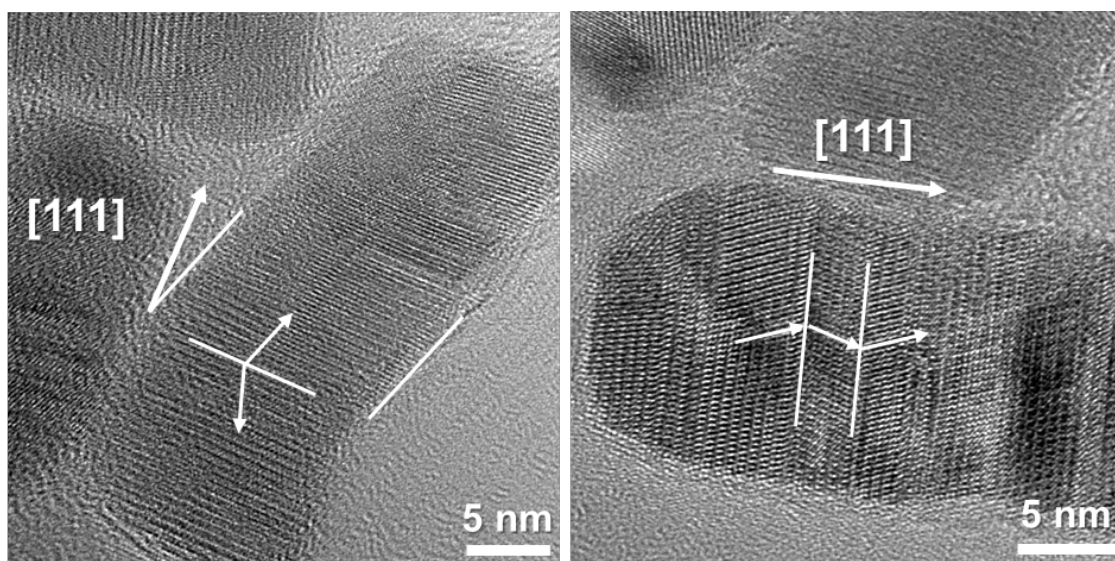


Fig. S3.
HRTEM images of Co₉S₈ NRs with twin boundaries.

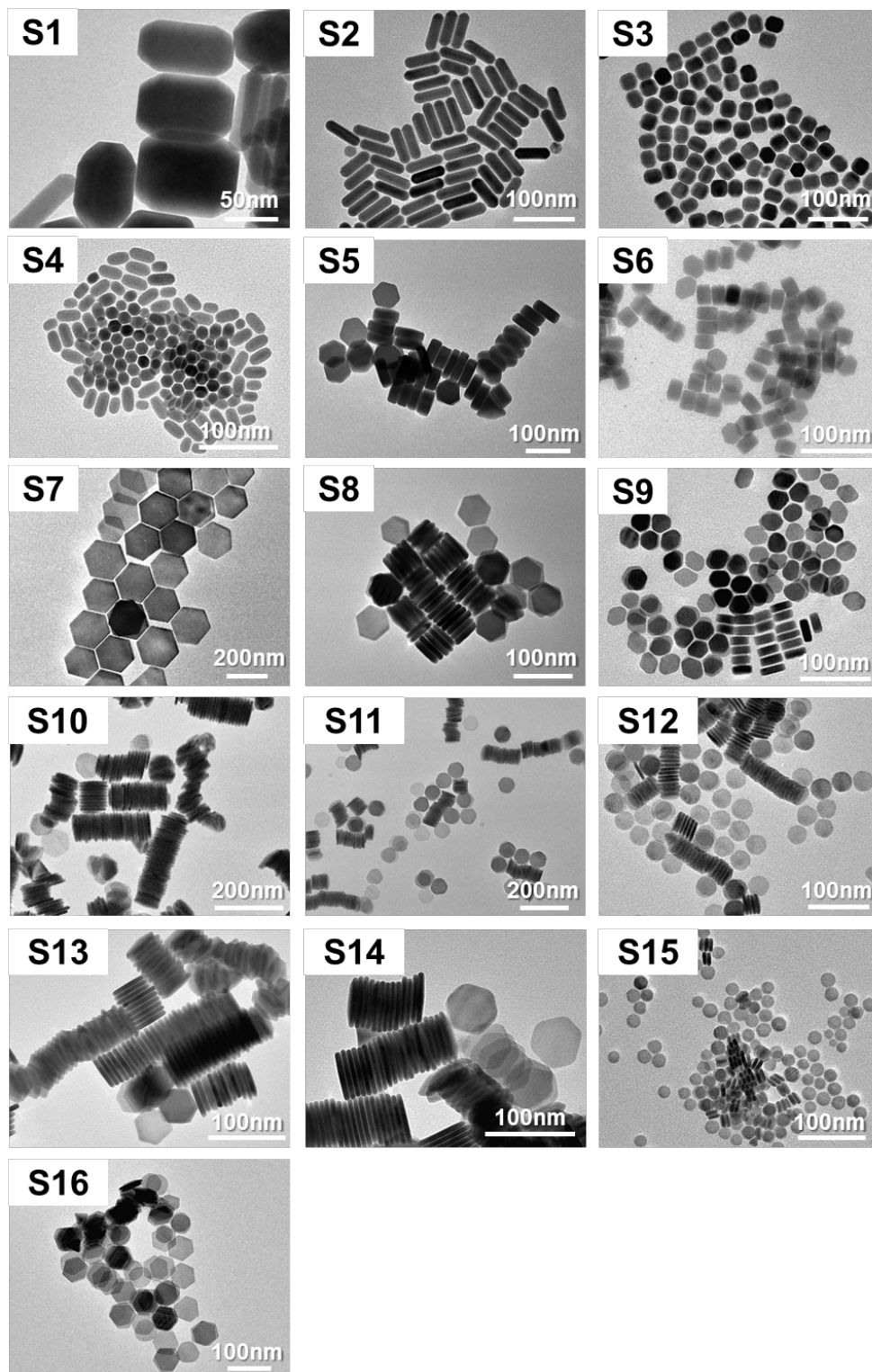


Fig. S4.
Enlarged TEM images of host $\text{Cu}_{1.8}\text{S}$ NCs.

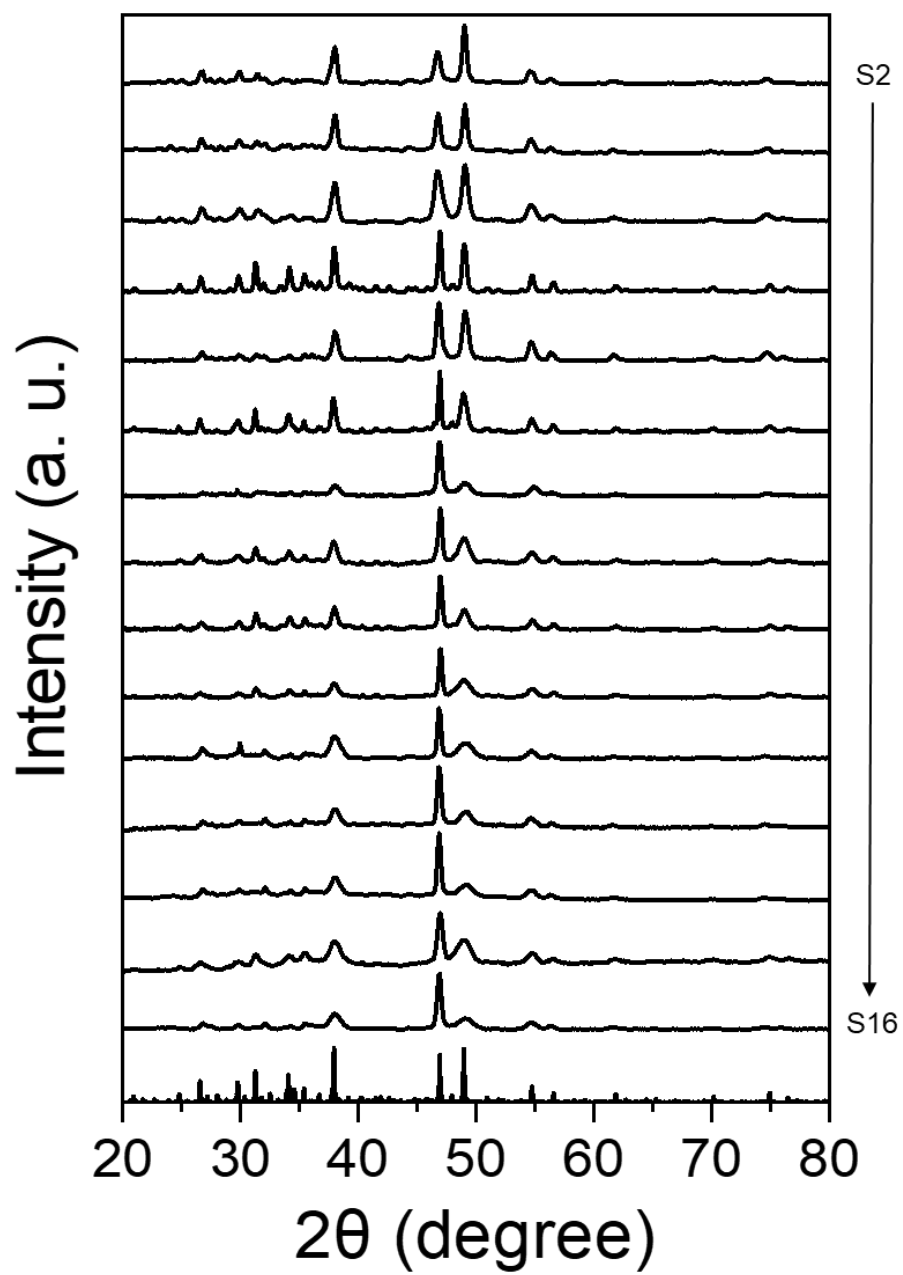


Fig. S5.

XRD patterns of Cu_{1.8}S NCs. Reference pattern at the bottom is roxbyite Cu_{1.8}S.

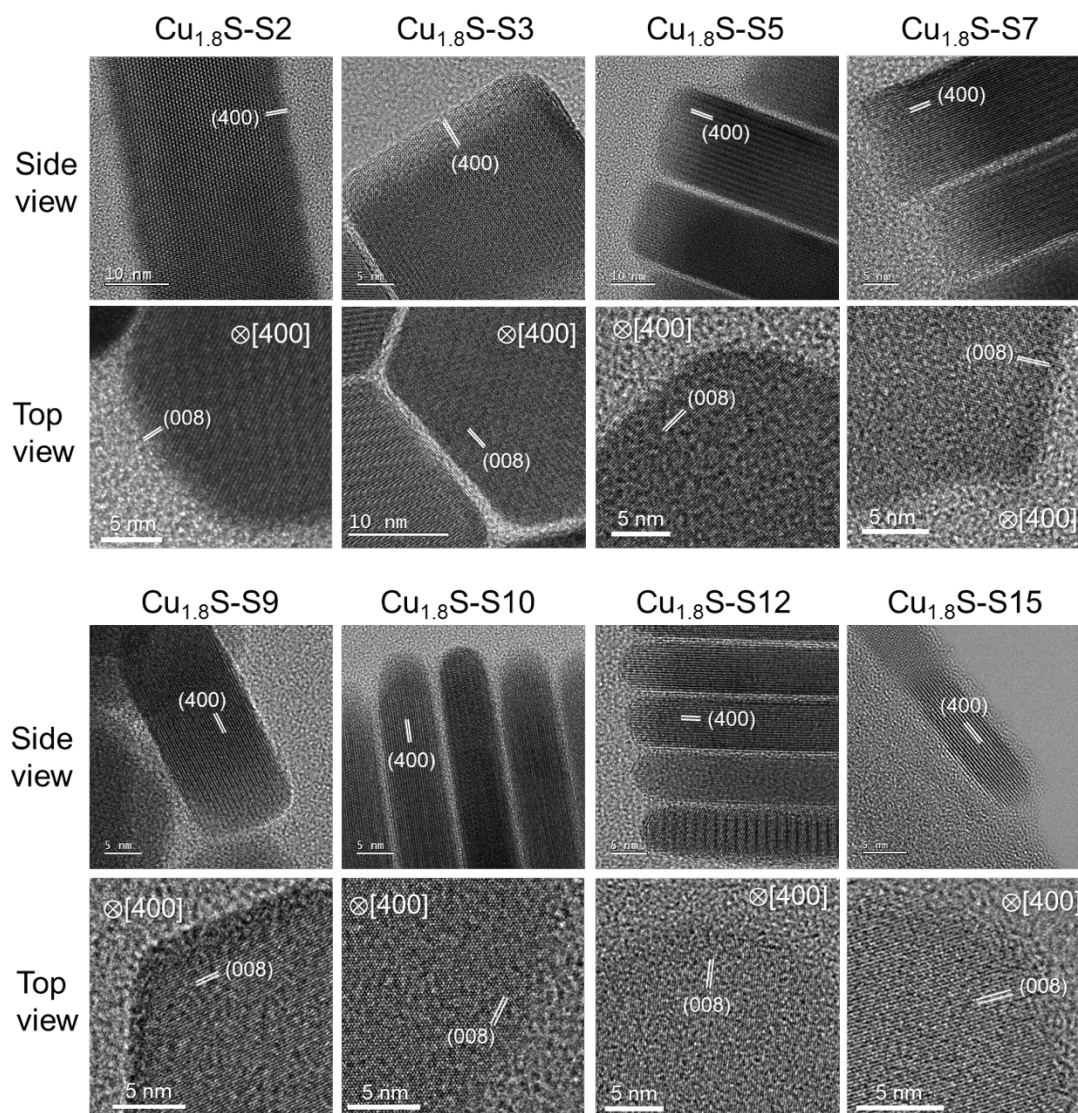


Fig. S6.

HRTEM images of representative host $\text{Cu}_{1.8}\text{S}$ NCs from the side and top view.

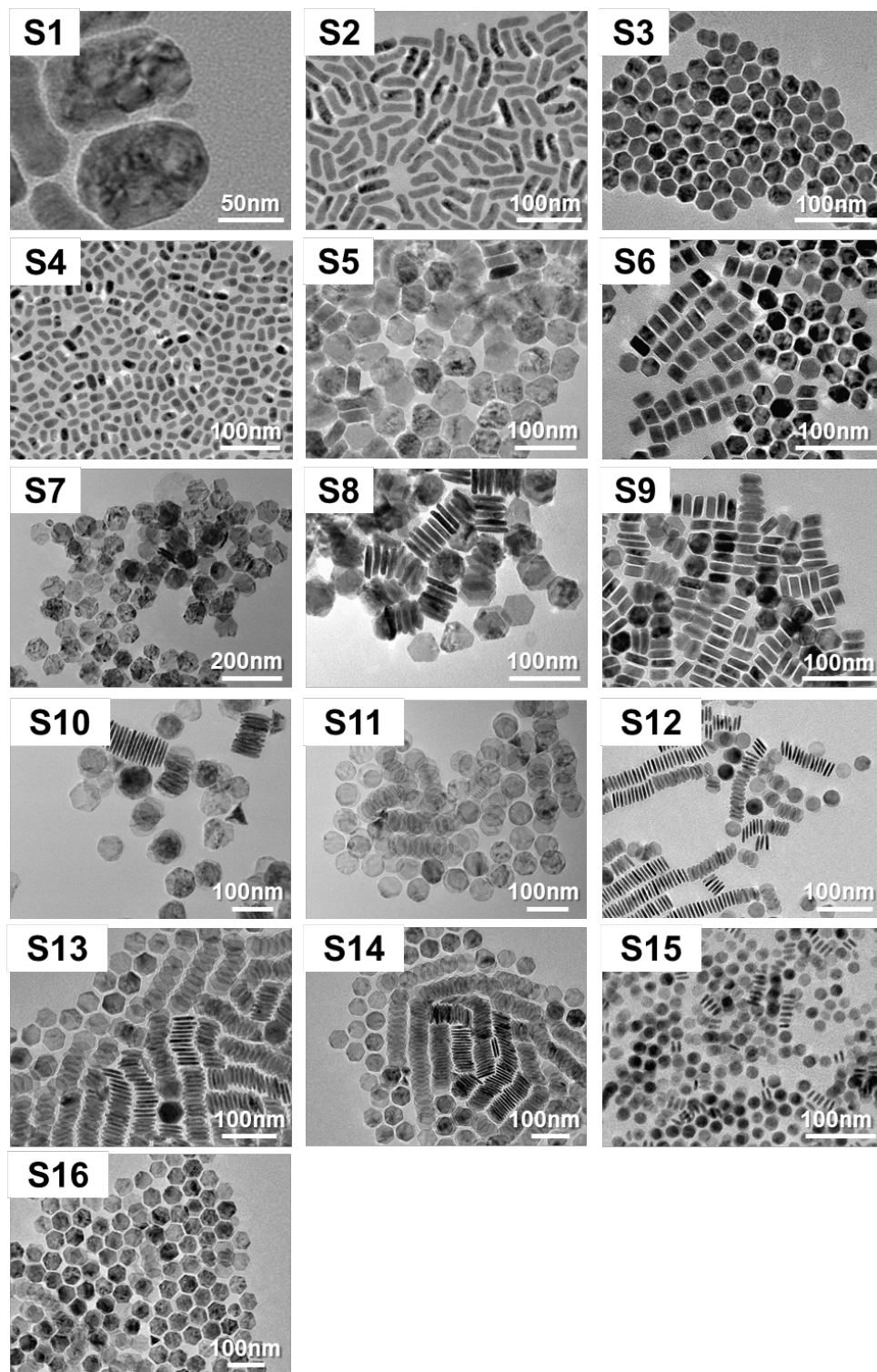


Fig. S7.
Enlarged TEM images of CoS_x NCs.

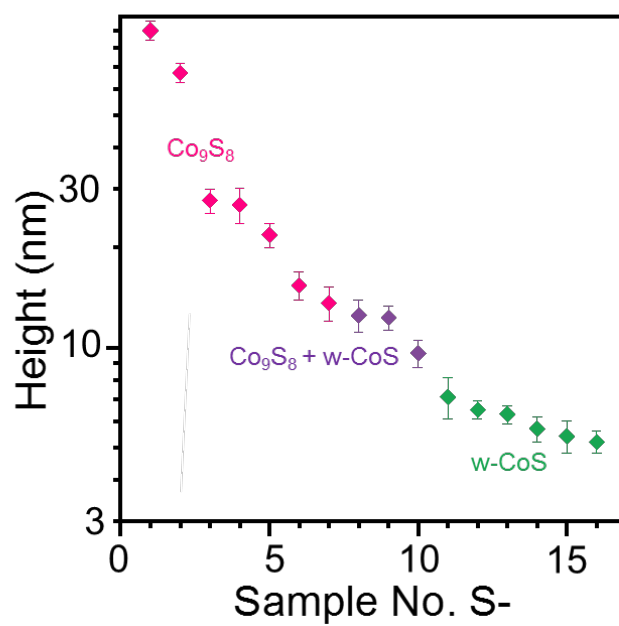


Fig. S8.

Sample number–height plots of $\text{Cu}_{1.8}\text{S}$ NCs and corresponding CoS_x crystal structure after cation exchange.

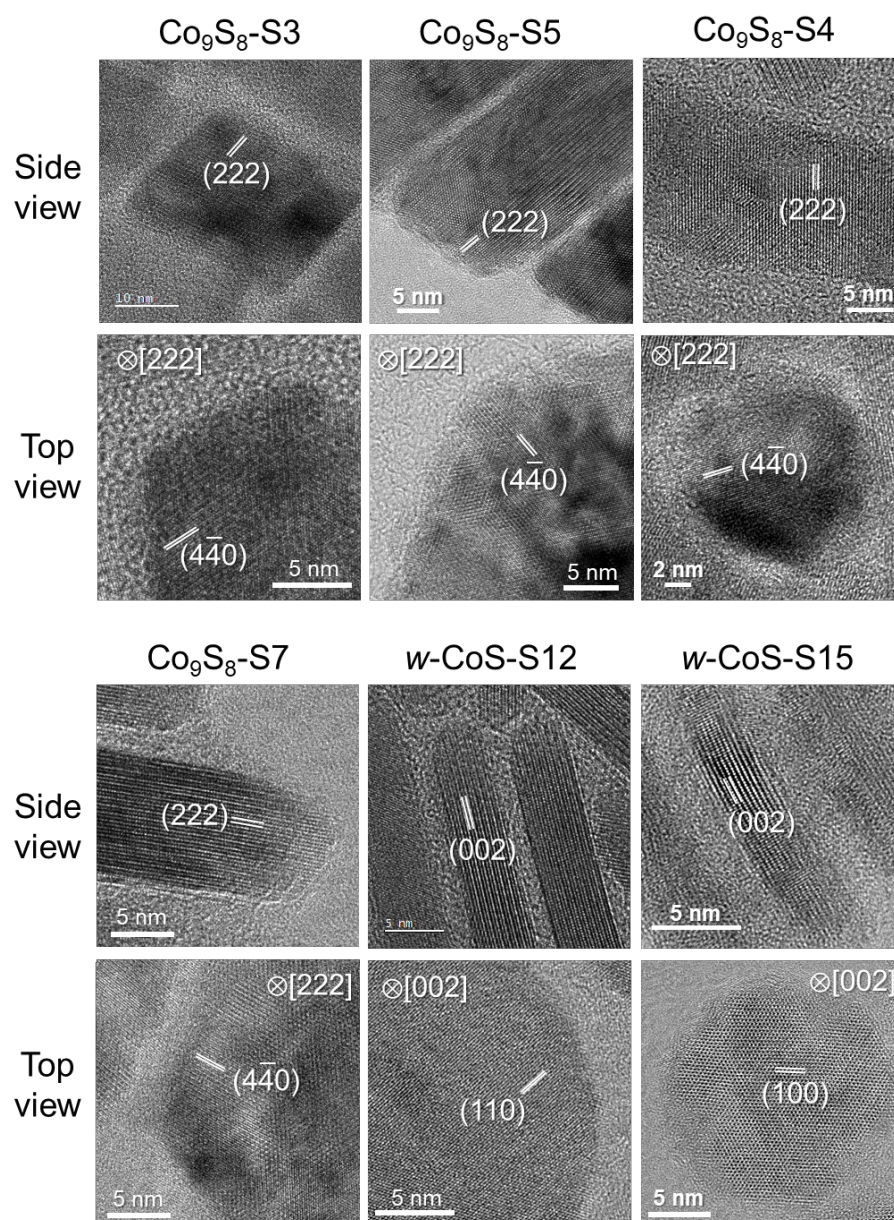


Fig. S9.

HRTEM images of representative CoS_x NCs from side and top view.

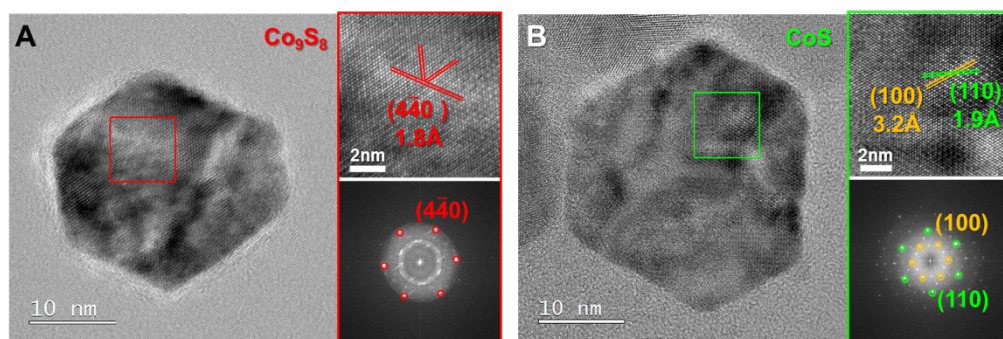


Fig. S10.

HRTEM images and corresponding fast Fourier-transform (FFT) analysis images in the facial direction of (A) Co_9S_8 -S9 and (B) $w\text{-CoS}$ -S9 NCs.

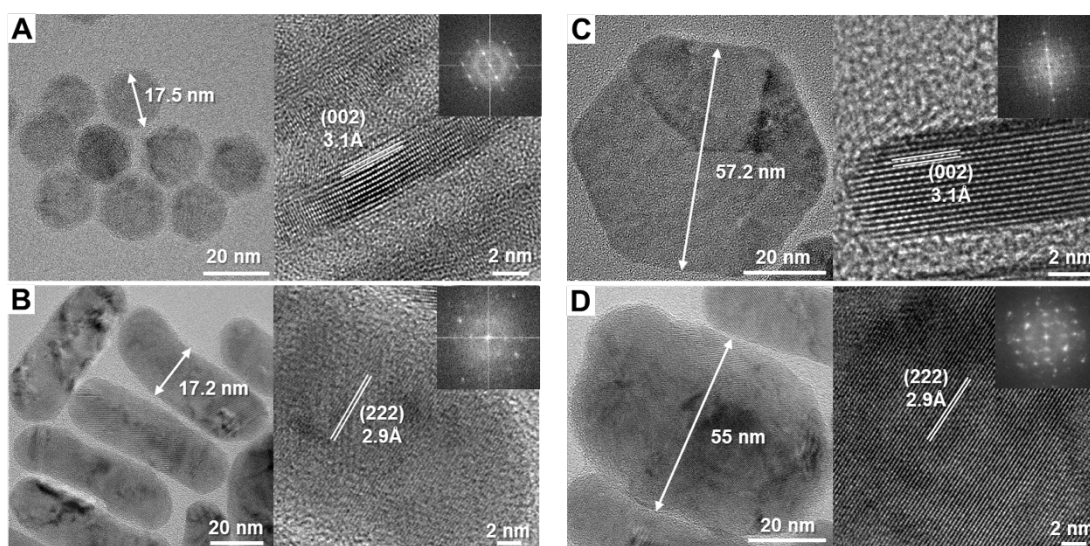


Fig. S11.

TEM, HRTEM, and FFT images of (A) *w*-CoS-S15, (B) Co₉S₈-S2, (C) *w*-CoS-S16, and (D) Co₉S₈-S1 NCs.

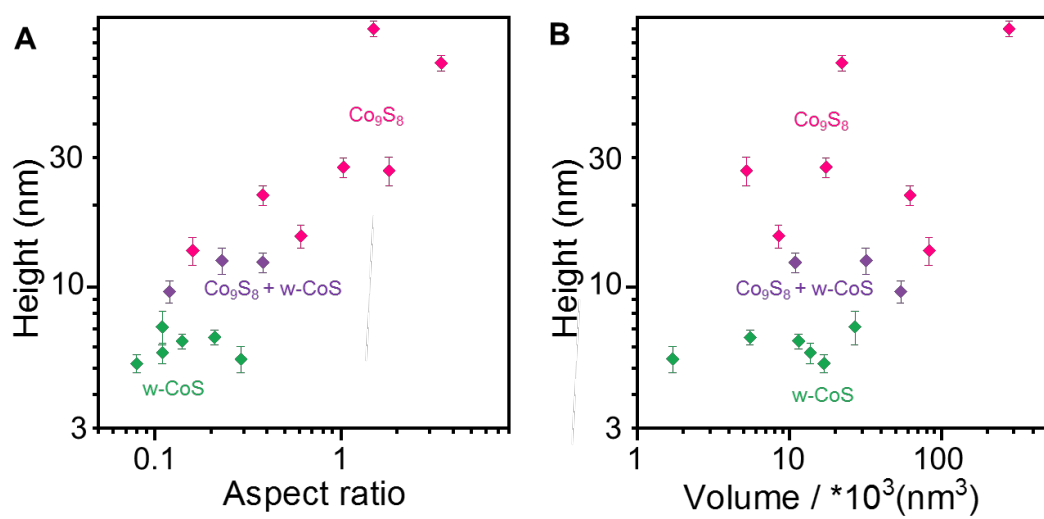


Fig. S12.

(A) Aspect ratio–height plots and (B) volume–height plots of Cu_{1.8}S NCs and corresponding CoS_x crystal structure after cation exchange.

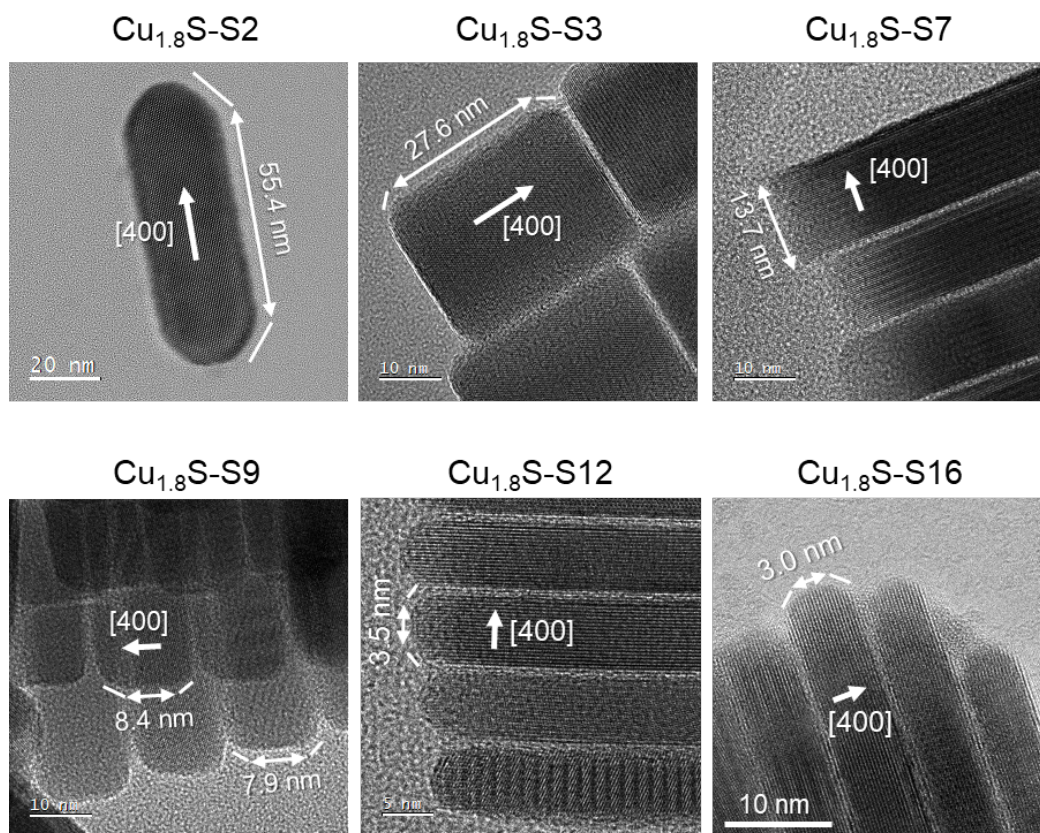


Fig. S13.

HRTEM images of representative host $\text{Cu}_{1.8}\text{S}$ NCs to show the angled facets from the side-view.

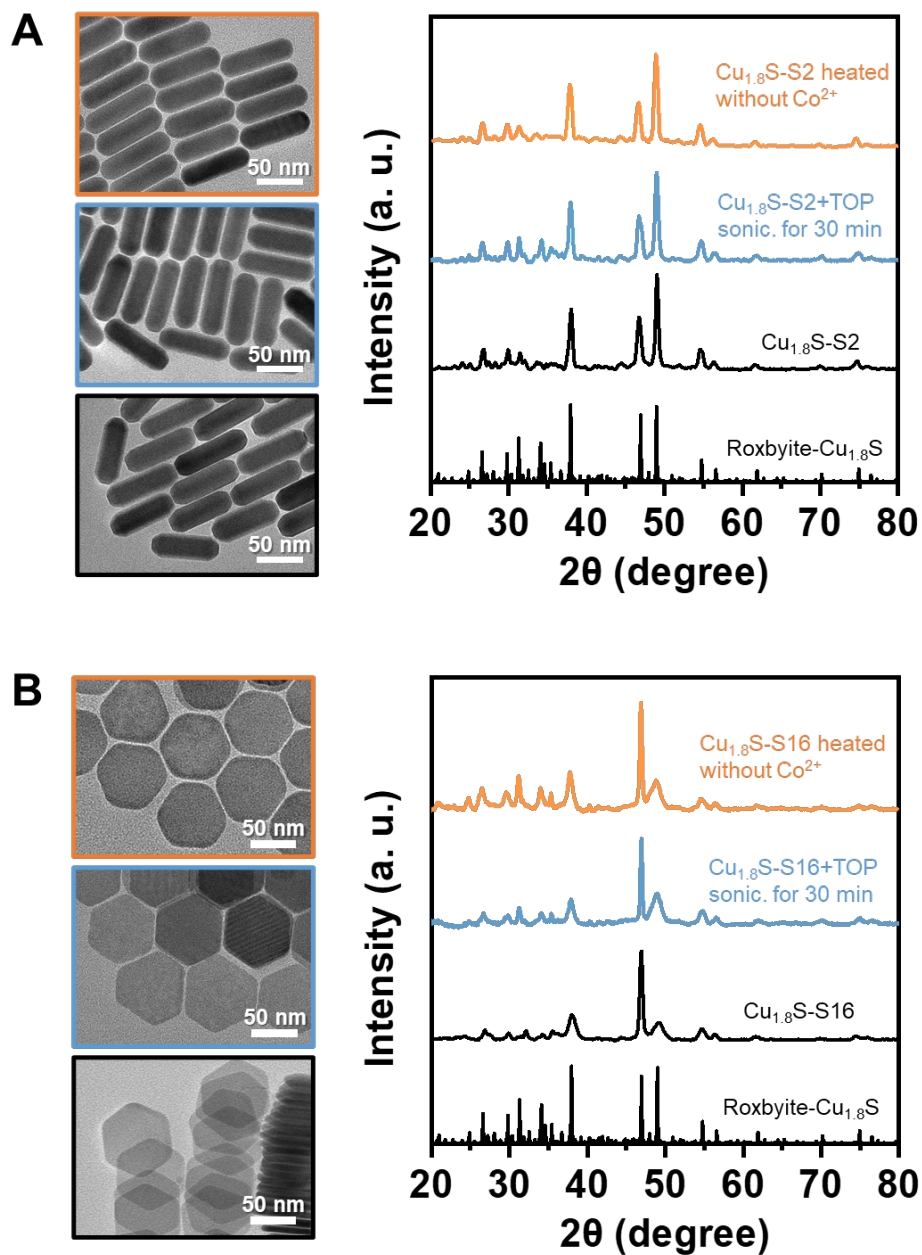


Fig. S14.

TEM and XRD patterns of host $\text{Cu}_{1.8}\text{S}$ (A) NRs (S2) and (B) NPLs (S16): (black) as-synthesized, (blue) after sonication in TOP for 30 min, and (orange) after heating at 100°C for 5 min in the presence of TOP and OLAM in ODE without Co^{2+} .

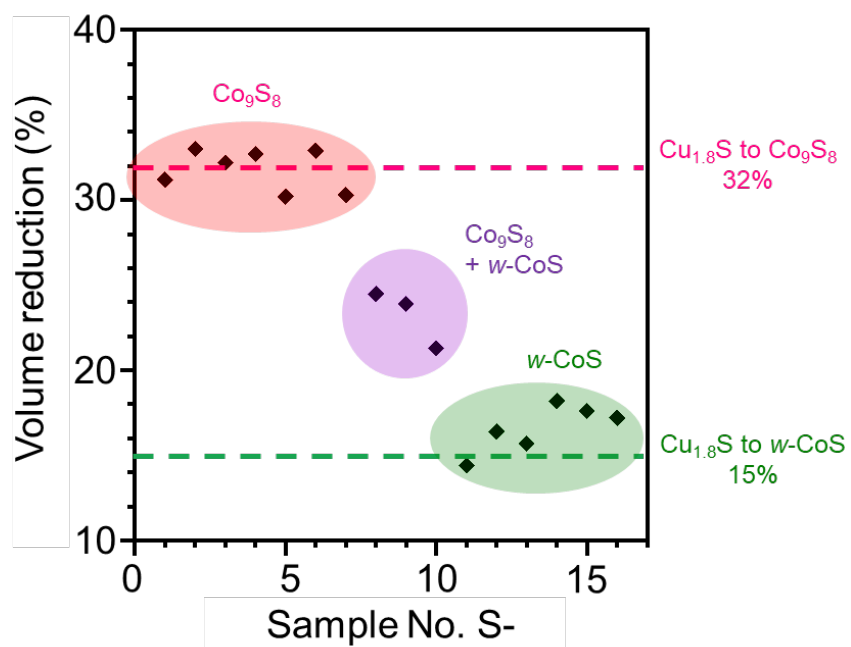


Fig. S15.

Volume reduction of NC in the cation exchange reaction with Co^{2+} estimated from their sizes. Theoretical volume reduction from host $\text{Cu}_{1.8}\text{S}$ to Co_9S_8 or $w\text{-CoS}$ was calculated to be 32% (pink broken line) or 15% (green broken line), respectively.

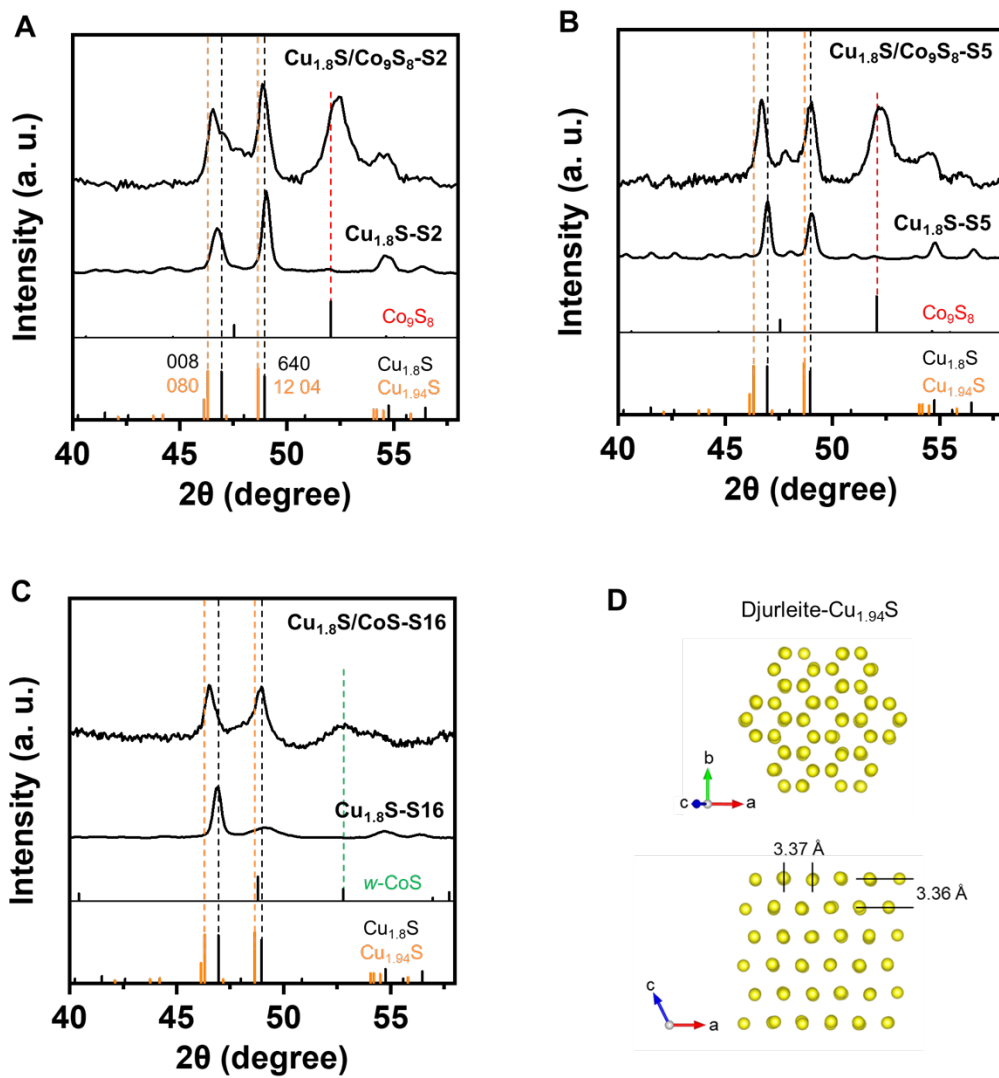


Fig. S16.

Comparison of XRD patterns of host Cu_{1.8}S NCs and Co²⁺ partial cation exchanged Cu_{1.8}S/CoS_x NCs for (A) S2, (B) S5, and (C) S16 samples. (D) Hcp S²⁻ lattice of djurleite-Cu_{1.94}S.

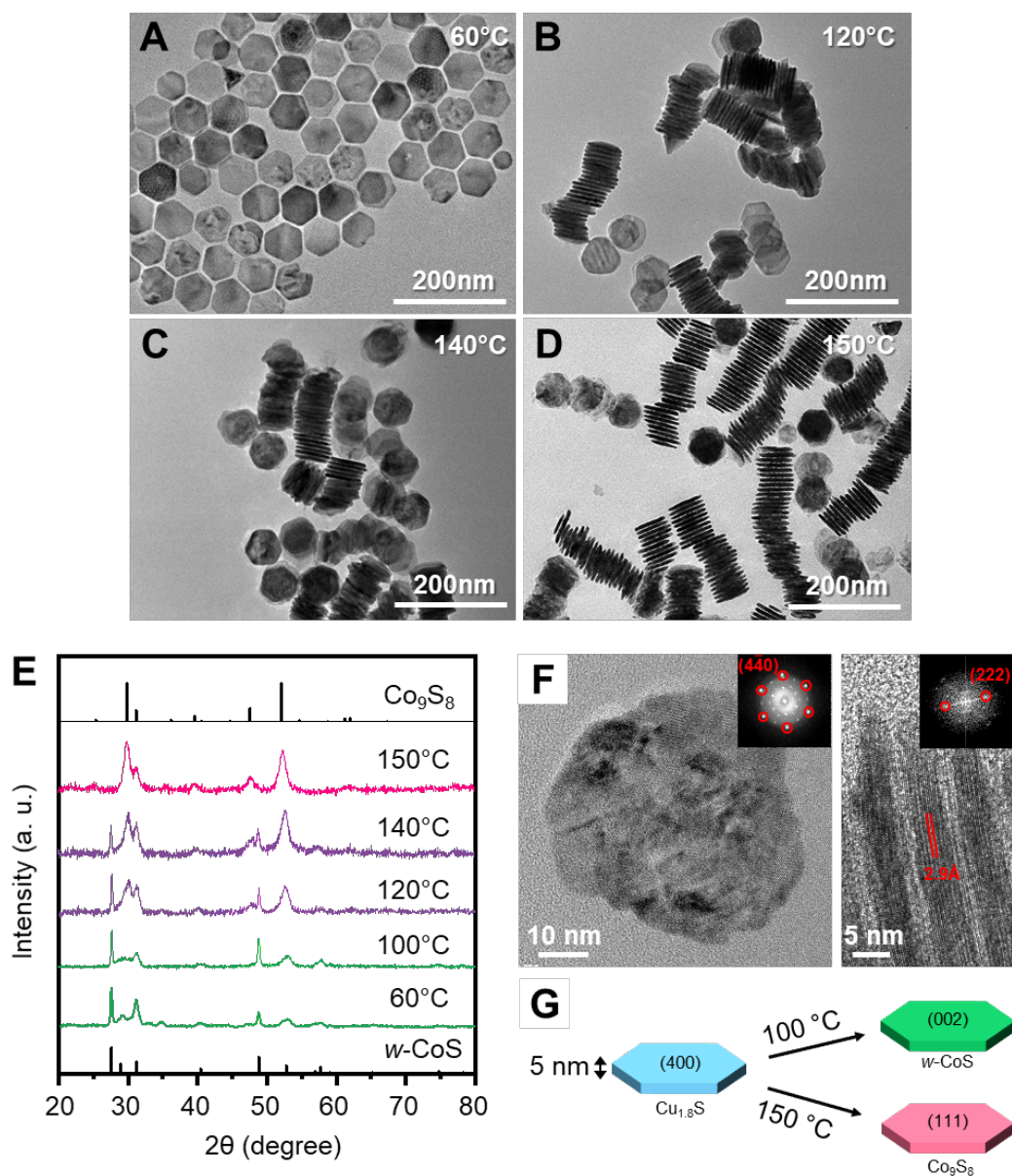


Fig. S17.

TEM images of CoS_x-S16 NPLs prepared at (A) 60°C, (B) 120°C, (C) 140°C, and (D) 150°C. (E) XRD patterns of CoS_x NPLs obtained by cation exchange at 60°C, 100°C, 120°C, 140°C, and 150°C. (F) HRTEM images of Co₉S₈ NPLs obtained by cation exchange at 150°C. Reference XRD patterns: pentlandite Co₉S₈ (ICCD 00-056-0002) and simulated w-CoS. (G) Schematic of phase selective formation of CoS_x NPLs.

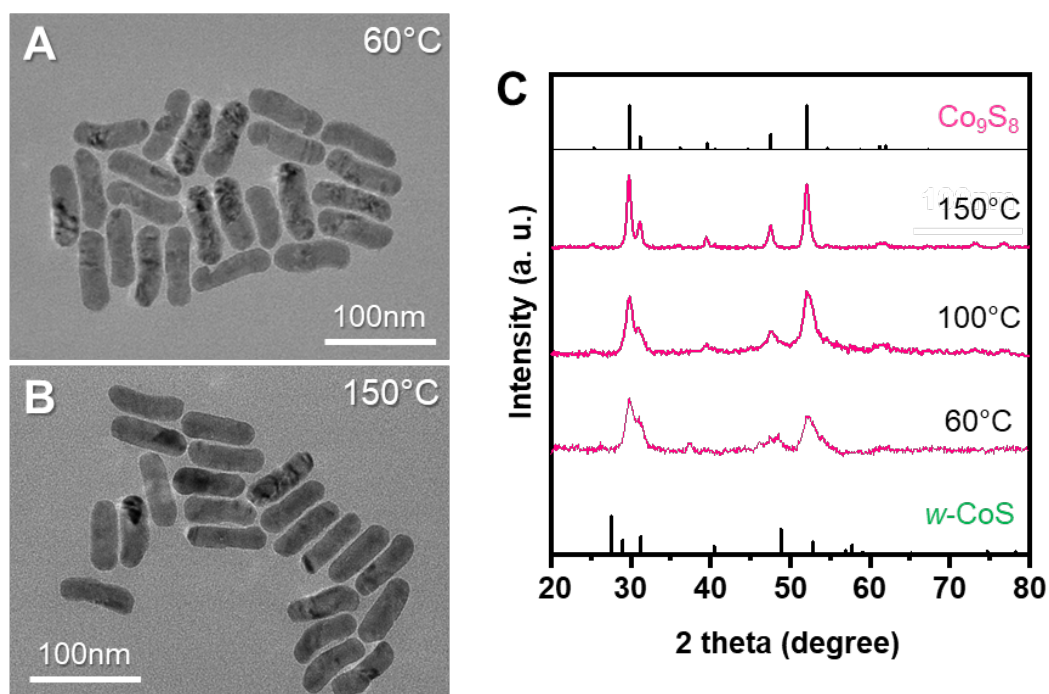


Fig. S18.

TEM images of Co₉S₈-S₂ NRs prepared at (A) 60°C and (B) 150°C. (C) XRD patterns of Co₉S₈-S₂ NRs prepared at 60°C, 100°C, and 150°C.

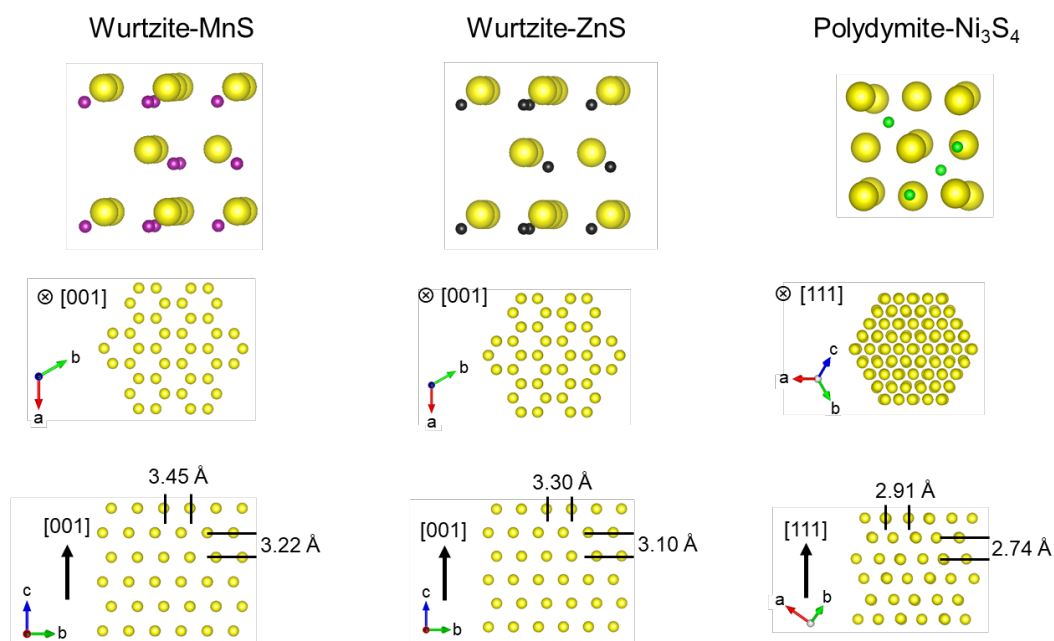


Fig. S19.

(Pseudo) unit cells and S sublattice structures of *w*-MnS, *w*-ZnS, and Ni₃S₄.

Table S1.

Summary of crystal phases of expected cation exchange products and corresponding formation energies.

Compounds	S ²⁻ sublattice structure	Formation energy per S atom (eV)
<i>w</i> -CoS	hcp	−0.535
Co ₉ S ₈	d-ccp	−0.917
<i>w</i> -MnS	hcp	−0.595
<i>zb</i> -MnS	ccp	−1.432
<i>w</i> -ZnS	hcp	−1.699
<i>zb</i> -ZnS	ccp	−1.666
<i>w</i> -NiS	hcp	−0.651
Ni ₃ S ₄	d-ccp	−0.415

Table S2.

Crystal cell volume per S^{2-} anion of roxybite- $Cu_{1.8}S$ and potential cation exchange products. ΔV is the volume change ratio from host $Co_{1.8}S$ NCs.

Compounds	S^{2-} sublattice structure	Volume per S ($\text{\AA}^3$)	ΔV
$Cu_{1.8}S$	d-hcp	43.5	-
<i>w</i> -CoS	hcp	37.1	-15%
Co_9S_8	d-ccp	29.6	-32%
<i>w</i> -MnS	hcp	44.3	+1.8%
<i>zb</i> -MnS	ccp	43.7	+0.5%
<i>w</i> -ZnS	hcp	39.0	-10%
<i>zb</i> -ZnS	ccp	39.4	-9.4%
NiAs-type NiS	hcp	27.3	-37%
<i>w</i> -NiS	hcp	31.2	-28%
Ni_3S_4	d-ccp	26.7	-39%

Table S3.
Morphological details of Cu_{1.8}S NCs.

Sample	S1	S2	S3	S4	S5	S6	S7	S8
Width (nm)	60.5 ± 4.2	19.5 ± 1.5	26.9 ± 2.3	14.9 ± 1.0	57.2 ± 5.4	25.2 ± 2.1	83.1 ± 6.9	54.3 ± 3.9
Height (nm)	90.4 ± 5.9	67.2 ± 4.3	27.7 ± 2.3	26.9 ± 3.2	21.8 ± 1.8	15.4 ± 1.5	13.6 ± 1.6	12.5 ± 1.4
Aspect ratio	1.50	3.45	1.03	1.81	0.38	0.61	0.16	0.23
Volume (*10 ³ nm ³)	280	22.1	17.4	5.2	62.0	8.5	82.9	31.9
CoS _x crystal structure	cubic	cubic	cubic	cubic	cubic	cubic	cubic	cub + hex

Sample	S9	S10	S11	S12	S13	S14	S15	S16
Width (nm)	32.0 ± 3.0	80.6 ± 6.6	66.3 ± 2.6	31.2 ± 2.7	45.9 ± 3.1	52.7 ± 3.1	18.8 ± 1.4	61.3 ± 3.2
Height (nm)	12.3 ± 1.0	9.6 ± 0.9	7.1 ± 1.0	6.5 ± 0.4	6.3 ± 0.4	5.7 ± 0.5	5.4 ± 0.6	5.2 ± 0.4
Aspect ratio	0.38	0.12	0.11	0.21	0.14	0.11	0.29	0.08
Volume (*10 ³ nm ³)	10.9	54.0	27.0	5.5	11.5	13.7	1.7	16.9
CoS ₂ crystal structure	cub + hex	cub + hex	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal

Table S4.

Reaction condition summary [mole ratio of $\text{Cu}(\text{NO}_3)_2$: CuCl_2 and holding time] for $\text{Cu}_{1.8}\text{S}$ NCs preparation in the method reported previously (28). $\text{Cu}_{1.8}\text{S}$ -S4 and S7 NCs were synthesized by different procedure. See Materials and Methods section for details.

S-	$\text{Cu}(\text{NO}_3)_2$	CuCl_2	min
1*	0.75	0.25	5
2	0.75	0.25	5
3	0.5	0.5	5
5	0.2	0.8	5
6	0.3	0.7	1
8	0.275	0.725	1
9	0.25	0.75	1
10	0.1	0.9	5
11	0.05	0.95	5
12	0	1	1
13	0	1	2
14	0	1	3
15	0	1	0.5
16	0	1	5

* $\text{Cu}_{1.8}\text{S}$ -S1 wide NRs were formed as overgrown byproducts of the $\text{Cu}_{1.8}\text{S}$ -S2 sample.

Table S5.

Comparison of surface energies of the (100), (110), and (001) planes of *w*-CoS.

<i>w</i> -CoS	ΔE_{surf} (meV Å ⁻²)
$E_{\text{surf}}(100) - E_{\text{surf}}(001)$	+23.2
$E_{\text{surf}}(110) - E_{\text{surf}}(001)$	+17.6