

Effects of I_2 on $Cu_{2-x}S$ Nanoparticles: Enabling Cation Exchange but Complicating Plasmonics

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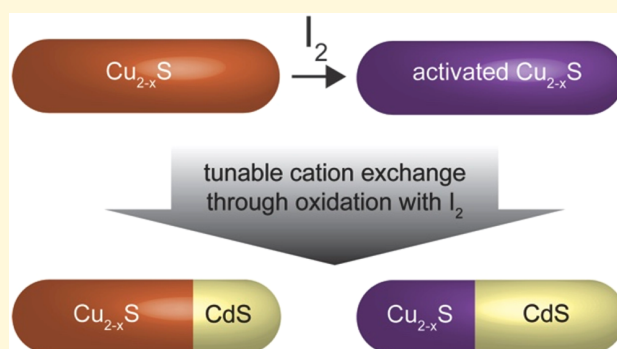


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Supporting Information

ABSTRACT: The effects of I_2 oxidation on the behavior of $Cu_{2-x}S$ nanoparticles—their long-term localized-surface plasmon resonance (LSPR), crystal structure, composition, and ability to undergo cation exchange—were explored. I_2 has been known to induce a blue shift in the LSPR of $Cu_{2-x}S$ nanoparticles due to the increase in the hole concentration through the removal of Cu^+ ions. An unexpected red shift is observed in I_2 -exposed $Cu_{2-x}S$ nanoparticles over the longer times required for cation exchange. Despite this complication of the LSPR behavior, the process of cation exchange from Cu^+ to Cd^{2+} is modulated by the exposure of the $Cu_{2-x}S$ nanoparticle precursor to elemental iodide, I_2 . This is consistent with the promotion of cation exchange through increased vacancy concentration. Treatment with I_2 induces a greater extent of cation exchange than in controls. Increasing I_2 exposure results in a greater extent of exchange and exchange at lower temperatures. The increased mobility of sulfide ions to which the red shift in LSPR is attributed also affects the resultant CdS crystal structure. Zinc-blende CdS , which has an altered anion network, is observed upon increased I_2 exposure or extended cation-exchange reaction times. This work offers insights into the mechanism of cation exchange and the modulation of the LSPR of plasmonic semiconductors.



Ion exchange is a powerful technique for transforming the composition of nanostructures.^{1–3} Not only can it afford single-phase particles with sizes, morphologies, and phases that cannot be attained through direct synthesis,^{4–12} but also it enables the creation of extraordinarily complex nanoheterostructures through multiple partial exchanges.^{13,14} Cu^+ ions are readily exchanged due to their high mobility, and thus copper sulfides,^{7,13,15} selenides,^{16–19} tellurides,^{20,21} and even phosphides²² are widely employed as synthons in cation-exchange schemes. This has been used to great effect in creating multicomponent particles in which the $Cu_{2-x}S$ component exchanges preferentially.^{13,23} An intriguing finding that sheds light on the mechanism of cation exchange is that the facility and extent of exchange of Cu^+ for Cd^{2+} or Zn^{2+} can be modulated based on the Cu^+ vacancy concentration in $Cu_{2-x}S$ nanoparticles.²⁴ This suggests that cation vacancies enable the introduction of new cations into a crystal lattice, which is necessary for ion exchange to occur.

The variation of Cu^+ vacancies in copper chalcogenide nanoparticles has been intensively studied because the resultant alteration in the hole concentration induces a shift in the localized surface plasmon resonance (LSPR) of particles.²⁵ Many post-synthetic routes shift the plasmon

band of copper chalcogenide nanoparticles; most, but not all, do so by the removal of Cu^+ . Oxidation with ferrocenium triflate increases hole concentrations but leaves the $Cu:S$ ratio unchanged,²⁶ as likely does electrochemical oxidation.²⁷ Species such as O_2 , Ce^{4+} , and I_2 , in comparison, generate more Cu -deficient phases.^{26,28–30} This process can be reversed through reduction with an accompanying reversal of the LSPR shift.³⁰ A similar reversible interconversion occurs between covellite (CuS) and chalcocite ($Cu_{2-x}S$), using dodecanthiol to enrich Cu and a sulfur–oleylamine complex to deplete it.³¹

Given the ready modulation of Cu^+ vacancy concentrations in copper chalcogenide nanoparticles through exposure to redox-active species,^{26,28,30} copper sulfide might be viewed as a species that could be “protected” or “deprotected” towards cation exchange by analogy to organic synthesis. The ability to modulate the susceptibility of copper sulfide to cation exchange with a simple solution treatment may enable the

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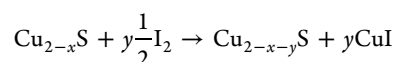
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design of even more complex nanoheterostructures by switching cation exchange on and off. Depending on the degree to which vacancies affect the rate, a significant difference in reaction temperature may be required for full conversion. This could lead to the selective exchange of high-vacancy particles at lower temperatures.

Here we set out to investigate the degree to which the oxidation of Cu_{2-x}S with I_2 could be utilized to accelerate cation exchange, whether it can truly “turn on” cation exchange, and how this acceleration influences the nanoheterostructures produced. The substantive knowledge of how I_2 influences LSPR^{26,28} provides a solid foundation on which to build an understanding of its effect on cation exchange. Unlike other well-investigated Cu-extracting agents like trioctylphosphine and dodecanethiol, I_2 is not used in either the nanoparticle synthesis or cation-exchange procedures. This allows for a more straightforward comparison with controls. Ensuring that I_2 was removed before cation exchange ensures that effects on cation exchange are due to the particles themselves, not the residual Cu-extracting agent. Following the procedures of Hartstein et al.,²⁶ we sought to alter the hole and Cu^+ vacancy concentrations of Cu_{2-x}S nanorods using I_2 and to determine the effect on partial cation exchange with Cd^{2+} as well as Zn^{2+} . While exploring the effect of I_2 oxidation on cation exchange, we discovered that the oxidation of Cu_{2-x}S nanoparticles with I_2 has surprisingly complicated effects on the LSPR and the nanoparticle structure. These effects have materials design implications. We investigated the effects of varying degrees of I_2 exposure on the LSPR behavior, elemental composition, and crystal structure. We further relate the extent of I_2 exposure to the rate of conversion of Cu_{2-x}S to CdS or ZnS by stopping the reactions before completion and measuring the extent using powder X-ray diffraction (PXRD), energy-dispersive X-ray spectroscopy (EDS) mapping, and inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and by measuring the extent of conversion at different temperatures. This behavior was compared with that of roxbyite nanoplatelets.

The effects of I_2 on Cu_{2-x}S nanoparticles have been explored in detail by Jain et al.²⁸ and Hartstein et al.,²⁶ and thus we were surprised when our implementation on roxbyite ($\text{Cu}_{1.8}\text{S}$) nanoparticles revealed new aspects of chemical and plasmonic behavior. These behaviors may have cast doubt on the hypothesis that I_2 exposure would accelerate cation exchange through the increase in the concentration of Cu^+ vacancies, so we examined them carefully. The most notable difference regarding our implementation is that after I_2 exposure, particles were obtained as a solid and washed, and their properties were explored over a longer time period. Washing with methanol or ethanol was essential to remove the CuI that formed through the following reaction



Without this washing step, CuI was observed in the PXRD of I_2 -treated particles (Figure S2), and iodine was significant in the EDS (Figure S3).

Prior reports of in situ oxidation of Cu_{2-x}S with I_2 show a Burstein–Moss effect, which is also apparent here at short times.³² The removal of Cu^+ ions results in more holes and fewer states at the conduction band edge. This greater hole concentration shifts the LSPR frequency to the near-infrared (NIR) region, whereas the change in the concentration of

states shifts the band gap.^{26,28} Jain and coworkers²⁸ first reported that the maximum in the LSPR of Cu_2S particles blue-shifts from <0.5 to ~ 1 eV during in situ spectroscopic measurements in which I_2 in increasing amounts was added directly to the cuvette. Under in situ conditions, a similar behavior was observed here with roxbyite ($\text{Cu}_{1.8}\text{S}$) nanorods (Figure S1a). An initial LSPR with a peak below 0.85 eV is visible due to the copper-deficient starting material (roxbyite $\text{Cu}_{1.8}\text{S}$) versus stoichiometric chalcocite (Cu_2S).³³ The structural similarity of the roxbyite and α -chalcocite phases is illustrated in Figure 1d. With increasing I_2 addition, a blue shift

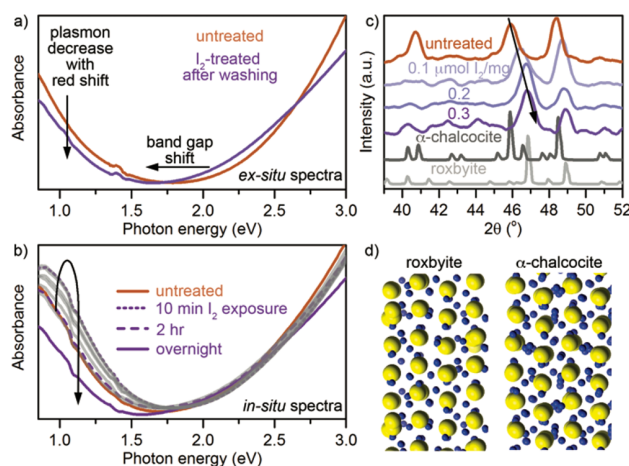


Figure 1. (a) UV–vis/NIR spectra of I_2 -treated roxbyite nanoplatelets post-isolation compared with the original particles, showing a red shift of the LSPR. (b) In situ UV–vis/NIR spectra of I_2 -treated roxbyite nanoplatelets showing the variation in LSPR over time. (c) PXRD of nanorods exposed to varying amounts of I_2 , revealing a continuous shift towards greater copper deficiency. ICDD references for roxbyite $\text{Cu}_{1.8}\text{S}$ (00-023-0958) and α -chalcocite Cu_2S (00-023-0961) are provided. (d) Fragments of the crystal structures of roxbyite (ICSD 185807) and α -chalcocite (ICSD 100333), demonstrating their structural similarity.

in the band gap due to Cu^+ removal is seen. The minimum between the band-gap absorption and the LSPR onset shifts from 1.7 to 1.3 eV, and the LSPR peaks increase. When particles were treated with I_2 , precipitated, thoroughly washed, and then resuspended (the ex situ condition, Figure 1a and Figure S1b), however, the band-gap onset red-shifted with respect to the untreated particles, and the LSPR decreased. This behavior was unexpected; if anything, we predicted that additional oxygen exposure might have induced further oxidation and a blue shift in the LSPR. Typically, oxygen exposure that would occur on aging induces blue shifts in LSPR in chalcocite (Cu_2S),^{28,33,34} although roxbyite ($\text{Cu}_{1.8}\text{S}$) is less sensitive to a spontaneous increase in the copper deficiency because it is already non-stoichiometric.

We examined the LSPR over time after in situ I_2 exposure (Figure 1b, Figure S1c) to gain insight into the origin of the red shift observed in ex situ roxbyite particles after I_2 exposure (Figure 1a). Hypotheses were that this might be due to the washing/precipitation processes or due to the evolution of LSPR over time. I_2 solution was injected into suspended roxbyite particles, and the evolution of the visible–NIR light absorption spectrum over time was monitored (Figure 1b). Hartstein and coworkers similarly watched the alteration in the LSPR due to I_2 exposure on α -chalcocite over time.²⁶ They

observed that the initial large blue shift rapidly relaxed over ~ 10 min but remained blue-shifted even 45 min after exposure. At these longer times, the slope of the line depicting the relaxation of the LSPR continued to decrease slightly. We observed the same initial increase in intensity and blue shift of the plasmon peak at from below 0.85 eV to 0.90 eV. This blue shift maximized at 10 min; then, the intensity began to fall, and the peak position shifted back to the red. By 2 h, the spectrum was nearly identical to that of the particles prior to injection of I_2 . After reaction overnight, the spectrum of the in situ I_2 -treated particles was comparable to that of the particles post-washing. This could be explained using two possible hypotheses. The first is that the initial increase in Cu^+ vacancies is counteracted over time by some reduction process, which will be discussed in the context of the PXRD and elemental analysis (vide infra). An alternative proposal is that with longer reaction times, the surface chemistry of the particles is altered. The surface chemistry could alter the dielectric constant at the surface and thereby the LSPR.²⁵ Changes in the surface functionality through ligand exchange have also been shown to influence the copper deficiency of copper sulfides.^{35,36} Particles in solution with I_2 show the same red shift in the band gap and the LSPR as particles that were dried and exposed to ambient conditions overnight. This consistency seems to rule out surface ligands as the cause of the shift. The large and constant size of the nanorods rules out size-induced LSPR shifts as seen by Wang and coworkers.³⁷ Overall, the reversal of the blue shift in the LSPR over longer times has implications for the use of plasmonic copper chalcogenides in optical applications such as photothermal therapy.^{38,39} To obtain the strong NIR absorption necessary for photothermal therapy, highly copper-deficient particles are needed. Whereas O_2 -induced blue shifts in LSPR can be maintained long-term, these more controllable I_2 -induced blue shifts are not. This suggests that other systems that alter LSPR in copper chalcogenides should be evaluated over long time periods. Short-term in situ measurements of LSPR may be insufficient to guide the design of plasmonic devices and applications.

Examination of the LSPR over time presented a seeming disconnect between two data sets. Cu^+ vacancies seemed to increase based on the detectable formation of CuI and the blue shift in the plasmon resonance. Over time, however, the shift in the LSPR reverses to suggest a reduction process. To disentangle this behavior, the effect of I_2 exposure on elemental compositions (Figure S4) and the crystal structure (Figure 1c and Figure S5) were investigated. Inductively coupled plasma–optical emission spectrometry (ICP-AES) measurements of digested particles showed increases in the Cu/S mole ratios from 1.38 ± 0.05 to 1.8 ± 0.1 after moderate I_2 exposure, not the decreases that would be consistent with the removal of Cu^+ ions. Whereas stripping of the sulfur-containing dodecanethiol surface ligands during the I_2 -treatment process certainly contributes to this behavior, a similar increase is observed upon I_2 exposure of oleylamine-terminated roxbyite nanoplatelets. In platelets, a pre- I_2 Cu/S ratio of 1.78 ± 0.03 increases to 2.18 ± 0.07 upon I_2 exposure. TEM analysis of nanorods and nanoplatelets at this extent of exposure shows no change in the particle size, distribution, or morphology upon treatment with $0.20 \mu\text{mol}$ of I_2 per milligram of nanorods (Figure 2a,b and Figure S7). This static behavior eliminates the possibility of the drastic rearrangement of the sulfide anion lattice of the crystals. High-resolution transmission electron

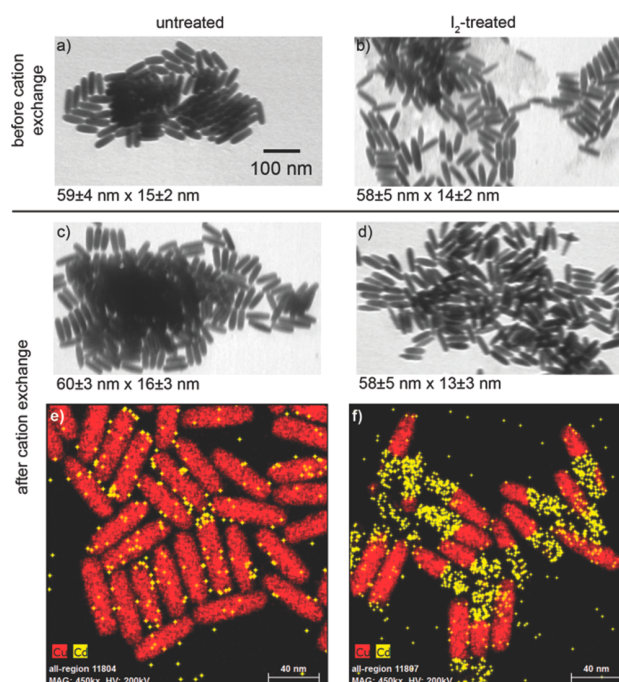


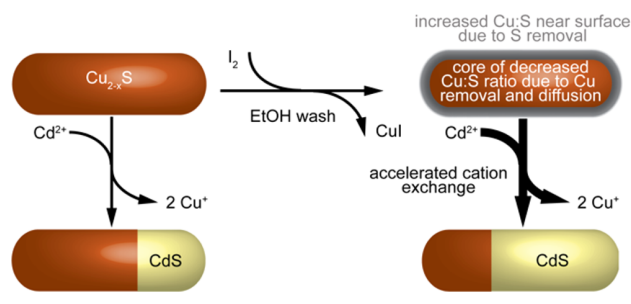
Figure 2. (top) TEM images of I_2 -treated ($10 \mu\text{L}$ of $20.0 \text{ mM } I_2/\text{mg}$ of $Cu_{1.8}S$ particles) (right) and untreated (left) roxbyite nanorods before (top) and after (bottom) Cd^{2+} cation exchange, showing that the particle sizes and shapes are altered neither by I_2 exposure nor by cation exchange. (bottom) EDS mapping of Cu (red) and Cd (yellow) shows significant cation exchange only on the I_2 -treated particles.

microscopy (HR-TEM) (Figure S6) shows that single crystallinity is maintained after I_2 exposure but that some surface roughening occurs. Increased I_2 exposure, however, induces a further decrease in Cu/S ratio to 0.82 ± 0.03 (Figure S4) and in the crystallinity of the PXRD pattern (Figure S5), indicating that there is a threshold above which large-scale reorganization does occur. Given evidence that Cu is removed, we hypothesize that sulfur anions are also etched from the surface to an extent that does not noticeably affect the particle size (Figure 2a) but that is observable in the Cu/S molar ratio. The decrease in Cu/S ratio observed in the elemental composition data is consistent with a red shift in the LSPR. This suggests that the longer-term shift in LSPR is due to an actual decrease in the hole concentration. Such a decrease could result from fewer surface Cu^+ vacancies upon I_2 exposure if there was a concomitant depletion of sulfide ions. The observed surface roughening shows that the I_2 exposure can make the surface sulfides mobile. PXRD, on the contrary, suggests the increase in Cu^+ vacancies upon I_2 exposure (Figure 1c and Figure S5). Upon the treatment of particles with an increasing quantity of I_2 , the crystal structures move toward a more copper-deficient phase. We observed this both for particles that were initially roxbyite and, more prominently, for a set of particles that were initially α -chalcocite (Figure 1d). Roxbyite and α -chalcocite share a distorted hexagonally close-packed sulfide anion lattice, with variations in the highly complex cation ordering (Figure 1d), with roxbyite being more Cu-deficient than α -chalcocite. In the untreated sample, peaks at 41 , 46 , and $48.5^\circ 2\theta$ match that of the α -chalcocite reference (ICDD 00-023-0961) but not that of roxbyite (ICDD 00-023-0958). When increasing amounts of I_2 are added, the

reflections due to the sulfide sublattice gradually shift from those of α -chalcopyrite to those of roxbyite. As the quantity of I_2 is increased from 0.1 $\mu\text{mol } I_2/\text{mg}$ of particles to 0.3 $\mu\text{mol } I_2/\text{mg}$ of particles, the 46 and 48.5° 2 θ peaks gradually shift to larger values, indicative of a shrinking in d spacing due to the removal and rearrangement of Cu^+ . Similar behavior was reported by Hartstein and coworkers and attributed to the increase in the concentration of Cu vacancies that accompanies the removal of Cu^+ through the reaction with I_2 .²⁶ The removal of Cu^+ from djurleitite¹⁰ using trioctylphosphine results in the contraction of the lattice, and the reflection shifts to larger 2 θ while inducing phase changes in the Cu_2Se system.²⁴

The removal of Cu to form CuI could affect both the copper and sulfide ions, and the effect could be different for the surfaces versus the nanorod cores (Scheme 1). Such an

Scheme 1. Depiction of I_2 Exposure and Its Proposed Effects on Cu_{2-x}S Nanorods and the Resultant Cation Exchange



interpretation can reconcile the later LSPR shifts and elemental composition with the conflicting short-time LSPR behavior and PXRD. Initially, Cu^+ ions migrate to the surface, increasing the hole concentration across the whole particle, thereby inducing a blue shift of the LSPR. Later, some Cu^+ ions are redistributed throughout the rod, resulting in the observed relaxation of the LSPR. Such an argument has previously been invoked to explain the relaxation of LSPR in copper chalcogenides.^{10,30} If this were the only effect, then it would be predicted that the LSPR of the treated particles would remain slightly blue-shifted due to the net removal of Cu^+ , and that the overall Cu/S ratio would decrease. Instead, we observe a slight red shift and an increase in the Cu/S molar ratio. Our interpretation is, then, that sulfide ions are dissolved from the surface due to structural destabilization. This would increase the overall Cu/S ratio by depleting sulfur at the surface. This occurs while preserving the Cu-deficient crystalline phase within the core of the particle. Such an interpretation complicates the argument that simply removing Cu^+ ions should accelerate the cation-exchange process. Given the importance of empty surface sites for promoting cation exchange,⁴⁰ an enrichment of Cu^+ ions at the surface could, perhaps, block Cd^{2+} binding sites, actually decreasing the rate of cation exchange. The impact of exposing roxbyite nanorods and nanoplatelets to I_2 on cation exchange thus warrants a more in-depth investigation.

I_2 exposure of roxbyite nanorods speeds Cd^{2+} cation exchange versus the same, untreated roxbyite nanorods, to the point that conditions can be found in which cation exchange is “turned off” without I_2 . TEM of a set of roxbyite nanorods (Figure 2c,d and Figure S7) shows that the nanorod aspect ratio and size were unchanged in either process,

suggesting that in both oxidation and cation replacement, the S^{2-} anion lattice remained broadly intact. Control and I_2 -exposed roxbyite nanorods were exposed to a $\text{Cd}(\text{oleate})_2$ solution under identical time and temperature conditions simultaneously (45 °C and 30 min; see the Supporting information for more details). EDS mapping (Figure 2e,f and Figure S7) shows that the nanorods exposed to I_2 before cation exchange have significant amounts of Cd^{2+} at the end of the rods, whereas the particles that were not I_2 -treated showed very little evidence of cation exchange under the conditions used for this sample. The spatial positioning of Cd is consistent with cation exchange. The segregation of Cd at the end of the rods is due to both the minimization of interfaces⁴¹ and the better coincidence of the CdS and Cu_{2-x}S crystal lattices along the length of the rods.¹³ Not all rods reacted to the same extent, suggesting that ion replacement takes place at slightly different rates in different particles, despite a 45 min exposure to trioctylphosphine proposed to clean and homogenize the surface.¹⁰ Without this step, however, the reproducibility of the cation exchange was problematic.

Variation in the amount of I_2 added modulated the extent of exchange (Figure 3a). The Cu_{2-x}S nanorods exposed to

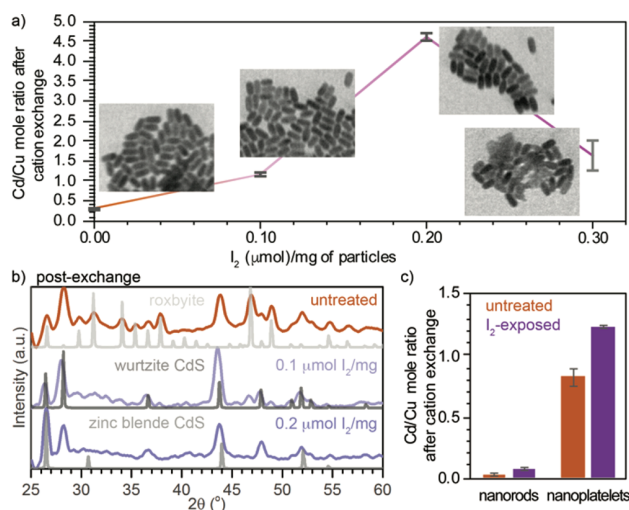


Figure 3. (a) Extent of Cd^{2+} cation exchange, measured by the ICP-determined Cd/Cu mole ratio, for Cu_{2-x}S nanorods with various I_2 exposures. Insets show the particles post-exchange. Error bars give the standard deviation of ICP-AES measurements. **(b)** PXRD of post-cation-exchanged nanorods. Overlays emphasize the evolution of the crystalline phase. For the untreated sample (top), a large signal due to roxbyite $\text{Cu}_{1.8}\text{S}$ is present with wurtzite CdS. For the 0.1 $\mu\text{mol } I_2/\text{mg}$ sample (center), the wurtzite crystalline phase dominates. With increased I_2 exposure (bottom), significant zinc-blende character is observed. **(c)** Extent of exchange for control and I_2 -exposed Cu_{2-x}S nanorods versus nanoplatelets under identical conditions of I_2 treatment and Cd^{2+} exchange based on ICP-AES measurements.

varying amounts of I_2 were then simultaneously exposed to the $\text{Cd}(\text{oleate})_2$ solution to induce cation exchange using the identical time and temperature conditions (50 °C for 1 h). The resultant Cd/Cu mole ratio was measured by ICP-AES after acid digestion of particles. To monitor for processes other than cation exchange, like the dissolution of roxbyite nanorods or the growth of separate CdS particles, the morphology was measured for every sample. The aspect ratio and size of the

nanorods treated with 0.00 to 0.20 $\mu\text{mol I}_2/\text{mg}$ of nanorods were unchanged (Figure 3a). Given the retention of particle shape concomitant with the increase in Cd/Cu mole ratio, the Cd/Cu mole ratio was taken to indicate the extent of exchange. As the amount of I_2 to which the nanorods were exposed before cation exchange was increased from 0.00 to 0.20 $\mu\text{mol I}_2/\text{mg}$ of nanorods, the resultant Cd/Cu mole ratio increased; more Cu^+ vacancies within the crystalline core allowed a faster exchange with Cd^{2+} . Without any I_2 exposure, there was fewer than 1 Cd/100 Cu ions (0.303 ± 0.004 Cd/Cu ratio); exposure to 0.20 $\mu\text{mol I}_2/\text{mg}$ of nanorods yielded a 15-fold increase to 4.58 ± 0.06 . The PXRD of nanorods that were not exposed to I_2 before cation exchange (Figure 3b, top) shows a mixture of roxbyite and wurtzite CdS. This hexagonal CdS is expected for the pseudo-hexagonal roxbyite phase.⁸ The remaining Cu_{2-x}S converted from α -chalcocite to roxbyite. This transition to a more copper-deficient phase is the opposite of what was observed upon Zn^{2+} exchange of roxbyite by Ha et al.⁴² This transformation was attributed to differential rates of interface growth and Cu^+ removal, and such behavior could vary with the Cd^{2+} system. As the amount of I_2 exposure increased to 0.10 $\mu\text{mol I}_2/\text{mg}$ of nanorods, crystalline Cu_{2-x}S was no longer prominent in the PXRD, and the primary phase was wurtzite CdS (Figure 3b, center). As the amount of I_2 exposure before cation exchange increased to 0.20 $\mu\text{mol I}_2/\text{mg}$ of nanorods, wurtzite CdS was still the primary phase. Residual peaks due to roxbyite disappeared, but the relative peak heights at 26.5° and $28^\circ 2\theta$ indicate the formation of zinc-blende CdS (Figure 3b, bottom). Wurtzite CdS, which is both the thermodynamically preferred phase and expected for the hexagonal sulfide lattice, has peaks at both 26.5° and $28^\circ 2\theta$, whereas the metastable zinc-blende CdS phase only has a peak at $26.5^\circ 2\theta$. The increased intensity of $26.5^\circ 2\theta$ suggests that the cubic zinc-blende CdS phase is present. The change in the crystal structure of the resultant CdS from the expected hexagonal phase sheds further light on the effect of I_2 on the sulfide anions and will be discussed in more detail later.

PXRD, TEM, and ICP data show that upon attempting Cd^{2+} cation exchange on nanorods treated with high levels of I_2 exposure, the nanorods are destroyed. Exposure to 0.30 $\mu\text{mol I}_2/\text{mg}$ of nanorods showed a reversal of the trend of increasing the Cd/Cu ratio with more I_2 exposure (Figure 3a), just as the Cu/S ratio of this sample dropped before exchange (Figure S4). Before exchange, the nanorods exposed to 0.30 $\mu\text{mol I}_2/\text{mg}$ of nanorods were intact, maintaining their size and shape despite a large decrease in the Cu/S ratio and an increased signal-to-noise of the PXRD that suggested a reduction in crystallinity (Figure 1c). Upon cation exchange, there was a significant reduction in the Cd/Cu mole ratio that we interpret as a failure of cation exchange (Figure 3a). No reflections were visible in the PXRD, and TEM of post-exchanged particles showed a significant amount of amorphous, non-particulate material with few nanorods (Figure 3, inset). This suggests that enough Cu^+ was removed upon I_2 exposure to destabilize the lattice. The destabilization of a large population of the nanorods is to such a degree that the structural integrity cannot be maintained upon cation exchange.

The influence of I_2 exposure on the crystal phase of the resultant CdS was further explored with roxbyite nanoplatelets. Nanoplatelets were much more responsive to I_2 -promoted cation exchange and showed a greater extent of Cd^{2+} exchange, whether treated or untreated, than nanorods (Figure 3c). The particle size and shape were maintained throughout both

processes, as with the nanorods (Figure S8). Zn^{2+} ions, which would be expected to have the same mechanism of cation exchange as Cd^{2+} ions, are also incorporated to a greater degree in platelets that have been I_2 -activated (Figure S9). So great was the activation toward cation exchange in nanoplatelets that we examined the extent of exchange at room temperature. Some degree of Cd^{2+} cation exchange was expected, even in unoxidized particles,¹³ based on literature reports, but the process is very slow. I_2 exposure sufficiently activated nanoplatelets toward Cd^{2+} cation exchange so that a significant color difference was observable after 2 h (Figure 4a). The spectra below show that after 2 h, the untreated

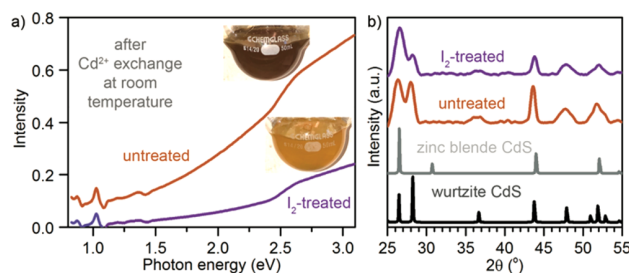


Figure 4. (a) UV-vis/NIR absorption spectra of Cu_{2-x}S nanoplatelets, Cd^{2+} -exchanged for 2 h, with insets showing the solutions after overnight exchange. (b) PXRD of control and I_2 -exposed nanoplatelets that have been Cd^{2+} -exchanged overnight, showing an alteration in the phase mixture of the resultant CdS.

sample shows a considerable signal due to the band-gap onset of copper sulfide at 1.0 eV. This color difference became much more pronounced overnight (Figure 4a, insets). After overnight exchange, both samples showed the formation of CdS. Zinc-blende CdS was more prominent in the I_2 -activated particles (Figure 4b and Figure S10). For comparison, after 5 min of exchange at 50°C , both untreated and I_2 -treated platelets formed the wurtzite phase. This is similar to the formation of zinc-blende CdS for nanorods with higher I_2 exposures. This indicates that both time and I_2 exposure promote the rearrangement of the sulfide lattice.

This work complements a growing, but incomplete, understanding of the mechanism of cation exchange. It supports the report of Lesnyak et al.²⁴ that copper deficiency in copper chalcogenides activates cation exchange. To an extent, this investigation bolsters their explanation that this is due to the increase in the number of vacancies that pair with interstitial cations to form Frenkel pairs that usher ions through a lattice, facilitating the introduction of Cd^{2+} and the removal of Cu^+ . This explanation is complicated here due to the creation of Cu^+ vacancies through the reaction with I_2 and the resultant impacts on the behavior of the sulfide ions. The LSPR and the elemental composition of I_2 -treated particles suggest that an increase in vacancies in one area of the particles is offset by an overall reduction, explicable by the removal of surface sulfide ions. The rearrangement of the sulfide lattice in the exchanged heteronanostructures further suggests mobile sulfide ions. The anion framework is almost perfectly immobile during the interchange of Cd^{2+} and Cu^+ in CdSe:Te/Cd nanorods.^{43,44} This enables phase-selective cation exchange by selecting hexagonal or cubic copper chalcogenide precursors.^{4,8} On the contrary, the anion framework alters dramatically upon the exchange of Cu_{2-x}S to Au_2S .⁴⁵ The situation observed here falls between these two extremes. The increase in Cu^+

vacancies or the removal of sulfides due to I_2 increases the mobility of the anion framework sufficiently to see some rearrangement under more extreme conditions. Although a detailed mechanism for this rearrangement is not available as yet, the surface roughening observed upon I_2 exposure (Figure S6) suggests that the mobility of S^{2-} ions at the surface may play a role. Increased anion mobility could possibly promote ion movement through the nanoparticle, further facilitating cation and anion exchange. This behavior is analogous to the facilitation of cation exchange in CdSe through Ag^+ doping. Here dopants disrupt bonds, allowing Cd^{2+} to be more easily replaced by Pb^{2+} .⁴⁶ Given that copper chalcogenides are distinct in the degree of nonstoichiometry that they afford, further studies will be needed to understand how widely this finding can be applied.

The new insights into the effect of I_2 on the composition, structure, plasmonic behavior, and cation exchange of copper chalcogenide nanoparticles provided here open a multitude of opportunities related to the design of plasmonic and nanoheterostructured colloidal particles. The tuning of LSPR with chemical oxidants has complicated side effects, shifting the LSPR in the opposite direction over time. Such complexities must be further investigated and accounted for in the implementation of plasmonic devices. The identification of conditions in which cation exchange can be “switched on” through I_2 exposure suggests that I_2 could be used as a “protecting/deprotecting” group for $Cu_{2-x}S$ synthons in the rational design of highly complex nanoheterostructures. Such a change might allow switching between cation exchange and shell deposition, like that seen in the exchange with Sn ions.²³ The finding that increased copper vacancies enable greater mobility of both cations and anions means that I_2 may accelerate both cation and anion exchange. Lastly, the ability to controllably modulate the crystal structure of the resultant cation-exchanged product through extended exchange potentially enables the creation of more complex nanoheterostructures.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.9b00402>.

Experimental information and additional data (PDF)

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Notes

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