Cu₂Se and Cu Nanocrystals as Local Sources of Copper in Thermally Activated In Situ Cation Exchange

Alberto Casu,†‡△ Alessandro Genovese,†‡△ Liberato Manna,*‡† Paolo Longo,⊥ Joka Buha,† Gianluigi A. Botton,∥ Sorin Lazar,∥§ Mousumi Upadhyay Kahaly,§ Udo Schwingenschloegl,§ Mirko Prato,† Hongbo Li,†,# Sandeep Ghosh,† Francisco Palazon,† Francesco De Donato,† Sergio Lentijo Mozo,‡ Efisio Zuddas,‡ and Andrea Falqui*‡

†Department of Nanochemistry, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
‡NABLA Lab, Biological and Environmental Sciences and Engineering (BESE) Division and §Physical Sciences and Engineering (PSE) Division, King Abdullah University for Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia
⊥Gatan, Inc., 5794 W Las Positas Boulevard, Pleasanton, California 94588, United States
∥Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L8, Canada
¶FEI Electron Optics, Achtseweg Noord 5, Eindhoven 5600 KA, The Netherlands
#Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Supporting Information

ABSTRACT: Among the different synthesis approaches to colloidal nanocrystals, a recently developed toolkit is represented by cation exchange reactions, where the use of template nanocrystals gives access to materials that would be hardly attainable via direct synthesis. Besides, postsynthetic treatments, such as thermally activated solid-state reactions, represent a further flourishing route to promote finely controlled cation exchange. Here, we report that, upon in situ heating in a transmission electron microscope, Cu₂Se or Cu nanocrystals deposited on an amorphous solid substrate undergo partial loss of Cu atoms, which are then engaged in local cation exchange reactions with Cu⁺⁺⁺⁺ acceptor phases represented by rod- and wire-shaped CdSe nanocrystals. This thermal treatment slowly transforms the initial CdSe nanocrystals into Cu₂−xSe nanocrystals, through the complete sublimation of Cd and the partial sublimation of Se atoms. Both Cu⁺⁺⁺⁺ donor and acceptor particles were not always in direct contact with each other; hence, the gradual transfer of Cu species from Cu₂Se or metallic Cu to CdSe nanocrystals was mediated by the substrate and depended on the distance between the donor and acceptor nanostructures. Differently from what happens in the comparably faster cation exchange reactions performed in liquid solution, this study shows that slow cation exchange reactions can be performed at the solid state and helps to shed light on the intermediate steps involved in such reactions.

KEYWORDS: in situ transmission electron microscopy, cation exchange, scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy, electron energy loss spectroscopy, energy-filtered transmission electron microscopy

Cation exchange (CE) reactions in ionic crystals involve the partial or the complete replacement of the cation sublattice, while the anion sublattice remains in place and is essentially preserved in the transformation, giving access to materials that would be otherwise difficult to synthesize through a direct synthesis. This kind of process is generally based on the fast direct reactions between inorganic colloidal nanocrystals (NCs) and cationic species, both dispersed in the same liquid phase. In such a system, the very dynamic nature of the reaction environment makes direct monitoring of the process very difficult and, at present, certainly not suitable to single-particle tracking with high spatial resolution. Classical NC systems on which CE reactions have been tested extensively belong to copper chalcogenides and to the II−VI and IV−VI classes of semiconductors. Copper chalcogenides are particularly prone to CE reactions because in

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In particular, copper selenide (Cu$_2$Se) transforms at high temperature into a Cu-depleted superionic Cu$_2$Se phase, characterized by a liquid-like behavior of the Cu cations within a rigid Se sublattice having face-centered cubic (fcc) structure. Here, we aimed to assess whether Cu$_2$Se NCs do lose a measurable fraction of Cu atoms from their lattice once deposited on a substrate and annealed above a certain threshold temperature. If so, our next goal was to clarify if the expelled Cu species could engage in “dry” CE reactions, involving NCs of another ionic material deposited on the same substrate, in our case either CdSe nanorods (NRs) or CdSe nanowires (NWs). To perform this study, we made extensive use of state-of-the-art in situ transmission electron microscopy (TEM) and related spectroscopic techniques. By these means, we were able to both trigger the CE process and follow it with the highest spatial and temporal resolution.

**RESULTS AND DISCUSSION**

**In Situ TEM Annealing of sole Cu$_2$Se Nanocrystals.** As a starting experiment, colloidally synthesized Cu$_2$Se NCs were placed on a TEM carbon-coated grid. Using a TEM heating holder, careful morphostructural and chemical analyses of the NCs were performed at room temperature (RT), before and after in situ heating. Such a heating step consisted of keeping the holder at a target temperature for a given time. We found a threshold temperature of 400 °C and a heating time of about 60 min as parameters for a detectable Cu depletion in the NCs. High-resolution TEM (HRTEM) of individual NCs and electron diffraction (ED) analysis on groups of NCs (after annealing, in order to avoid any lattice thermal expansion effect) indicated that, while the cubic structure of the initial NCs was preserved, their lattice had slightly contracted (Figure 1A,B). In particular, linear integrated ED profiles displayed a slight shift of the diffraction peaks toward higher nm$^{-1}$ values in the reciprocal space, with respect to the nonannealed NCs (Figure 1C). The main (220) diffraction peak shifted from...
to the agreement with the experimental data, providing ample support for the structure of the NCs.

The modeled EEL spectrum (Figure 1 G) was in good agreement with the density functional theory (DFT) calculations using the random phase approximation (see Materials and Methods for further details). A second set of experiments was then aimed at assessing if the expelled Cu species could activate CE reactions of other nanostructures equally arranged on the same substrate. The natural choice fell on CdSe, as NCs of this material have been shown to undergo rapid CE in solution even at RT. In this case, spherical Cu2Se NCs (whose transformation upon annealing was reported in the first paragraph) were deposited on the TEM grid’s carbon film together with CdSe NRs. The different morphologies of NCs made their two populations easily distinguishable, as shown by the high-angle annular dark-field scanning TEM (HAADF-STEM) image reported in Figure 2A,B.

Before annealing, the sample was analyzed by mapping various regions of the grid in order to rule out any structural or compositional evolution taking place already at RT. Chemical analysis of single NCs, performed in STEM mode via energy-dispersive X-ray spectroscopy (STEM-EDX), yielded Cu2Se and CdSe stoichiometries for the two types of nanostructures, respectively. Indexing of the linear integrated ED patterns, obtained from the same regions, confirmed the stable coexistence of both cubic antifluorite Cu2Se and hexagonal wurtzite CdSe, as displayed in Figure 2C,D.

In the present work, each set of EFTEM maps recorded during the annealing experiments was treated according to an apriori noise-normalizing approach with the aim to minimize the human-based biasing effects, control the background, and improve the signal-to-noise ratio within the data set. Hence, this approach, once applied to the thermally sensitive Cu2Se–CdSe system, allowed discriminating and comparing more clearly the faint signals of chemical species involved in CE reactions over time. Normalized energy-filtered TEM (EFTEM) elemental mapping then proved the spatial localization of Cu and Cd in the two different types of NCs (Figure 2E). Annealing was performed using the same temperature ramps of the first experiment, and after 60 min at 400 °C, the

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4.868 to 4.921 nm, indicating a decrease of about 3% of the unit cell volume that can be ascribed to a partial loss of Cu (see Supporting Information for further details). These data were corroborated by chemical quantification via high-resolution electron energy loss spectroscopy (HR-EELS) using a monochromated scanning TEM (STEM) of several NCs (Figure 1D), which indicated a decrease in the Cu/Se atomic ratio from 2.01:1 of the pristine NCs to 1.91:1 in the annealed NC (Figure S1). Furthermore, HR-EELS analysis of the same Cu1.91Se NCs points to a change in the electronic band structure due to Cu depletion suffered by the crystal lattice: while in the low loss region of the Cu2Se NCs no feature was detected (Figure 1E), an additional feature appeared in the same region at 1.1 eV of the EELS spectrum as a consequence of the copper depletion, as shown in Figure 1F,G and Figure S2. This was previously interpreted as directly correlated to a near-infrared absorption band in the range from 900 to 1600 nm and arising from a LSPR due to the presence of Cu vacancies.

HR-EEL Spectrum’s Density Functional Theory Simulations of the Cu2Se Nanocrystals after Annealing. To further confirm that the feature observed in the low loss EEL spectrum at 1.1 eV was due to copper depletion, we modeled a HR-EEL spectrum of a Cu2−xSe finite crystal via density functional theory (DFT) calculations using the random phase approximation (see Materials and Methods for further details). The modeled EEL spectrum (Figure 1G) was in good agreement with the experimental data, providing ample support to the influence of the loss of Cu atoms on the electronic band structure of the NCs.

In Situ TEM Simultaneous Heating of Cu2Se Nanocrystals and CdSe Nanorods. A second set of experiments was then aimed at assessing if the expelled Cu species could activate CE reactions of other nanostructures equally arranged on the same substrate. The natural choice fell on CdSe, as NCs of this material have been shown to undergo rapid CE in solution even at RT. In this case, spherical Cu2Se NCs (whose transformation upon annealing was reported in the first paragraph) were deposited on the TEM grid’s carbon film together with CdSe NRs. The different morphologies of NCs made their two populations easily distinguishable, as shown by the high-angle annular dark-field scanning TEM (HAADF-STEM) image reported in Figure 2A,B.

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Cu$_{1.85}$Se NCs exhibited a stable Cu$_{1.85}$Se stoichiometry, revealing therefore a loss of Cu from their lattice. Moreover, Cd was no longer present in the rods, whose composition had become Cu$_{1.96}$Se, as assessed by STEM-EDX analysis. As no secondary nucleation of Cd-rich phases was observed on the carbon film, we concluded that the Cd species had sublimated under the high-temperature and vacuum conditions (see Table S2). Normalized EFTEM mapping confirmed the absence of Cd and the diffusion of Cu into the initial CdSe NCs (Figure 2F), while differences in intensity observed between Cu$_{1.85}$Se NCs and Cu$_{1.96}$Se nanorods should be attributed to the consistent differences in mean thicknesses of the two populations (i.e., ~7 nm for the nanorods and ~12 nm for the NCs). Linear integrated ED pattern profiles of ensembles of NCs were indexed according to the cubic Cu$_{1.85}$Se phase alone, denoting the complete transformation of the initial hexagonal wurtzite CdSe phase (Figure 2C,D). Annealing caused shrinkage in volume of both the Cu$_2$Se and CdSe NCs. However, while the Cu$_{1.85}$Se NCs suffered only a small variation in average diameter, the starting CdSe NRs underwent a remarkable decrease in their mean length, from 34.8 to 21.9 nm, and a minor decrease in diameter, from 7.6 to 7.2 nm (Figure 2B). This corresponded to an average decrease in rods volume of 44%, estimated by approximating their shape to that of small cylinders, well above the theoretically volume contraction (12%) expected in going from wurtzite CdSe to antifluorite Cu$_2$Se, if a complete preservation of the Se anions would be assumed. Therefore, during the Cd $\rightarrow$ Cu CE reaction, part of the Se sublattice of CdSe sublimated, causing an additional volume loss of 36%, and that could be ascribed to concomitant causes, as discussed in the following. First, the binding energy of atoms on the apical facets is generally lower than that of the atoms inside the crystal lattice. This aspect, along with the change of crystal potential, due to cationic substitution and structural transition at high temperature, may promote the partial Se sublimation from the tips of NRs under the high-vacuum conditions of the TEM, also taking into account the very high vapor pressure of both Cd and Se, which moreover scales with the temperature, as reported in Table S2 of the Supporting Information. Second, this occurrence should be also attributed to the case-to-case availability of Cu$_2$Se NCs acting as Cu donors for the CdSe nanorods. Once the threshold temperature for CE has been crossed and the CE reaction has started, if the quantity of locally available depleted Cu is not sufficient for a complete Cd-to-Cu substitution, a partial sublimation of Se from the anionic sublattice is triggered in order to preserve the electroneutrality of the nanorod structure. Similarly to the case of the Cd species, we concluded that the depleted Se sublimated under the high-temperature and vacuum conditions. As reported in detail in the Supporting Information, this allowed us to roughly calculate the free energy variation ($\Delta$G) of the corresponding overall reaction: this is negative ($-138.6 \times 10^3$ kj) and indicates that the exchange is thermodynamically favored under the experimental conditions.

Notably, neither reshaping nor shrinkage was observed in CdSe NCs annealed under the same conditions but in the absence of Cu$_{1.85}$Se NCs, which supports our hypothesis that the sublimation of Cd from the CdSe NCs was triggered by Cu atoms and partially destabilized the Se atoms, too, as clearly shown in Figure S3.

The evolution in the composition of the CdSe nanorods during the annealing from RT to 400 °C was studied by normalized EFTEM mapping, and the relevant results are reported in Figure 3. Here, the normalized EFTEM maps displayed an incipient onset of the exchange reaction at 350 °C, with Cu substituting Cd in the nanorods, as confirmed by the yellow zones in the map, which indicate local superimposition of Cd and Cu maps. At this temperature, we expected the start of Cd and Se sublimation and the consequent volume shrinkage of NRs. At 400 °C, the conversion of the nanorods from CdSe to Cu$_{1.96}$Se was complete, with almost complete sublimation of Cd.

HRTEM observations revealed that, upon CE, the hexagonal close-packed (hcp) sublattice of Se anions in the initial CdSe NCs was reorganized into a cubic (fcc) sublattice. The lattice transformation preserved the closepacking direction, namely,
[0001]hcp in the initial wurtzite CdSe and [111]fcc in the final antifluorite Cu2-xSe rods (Figure 4A–C). Moreover, by performing fast HRTEM analysis while annealing the sample, we could visualize (Figure 4D,E) a gradual modification of the CdSe crystal structure, already at 350 °C, with the formation of sequential extrinsic stacking faults along the initial [0001]hcp direction of the CdSe rods. The formation of these structural defects therefore changed the local strain field at the nanoscale within the crystal lattice, as assessed via peak pairs analysis (PPA)25 (see Materials and Methods) reported in Figure 4D,E. Here, the shear strain field in the right region of the nanorod was almost unchanged from 350 to 400 °C, as in this temperature range the rod was able to retain the wurtzite CdSe structure, while compressive shear zones (blue) were compatible with the occurrence of intrinsic planar stacking faults. Conversely, the shear strain field in the left region exhibited a significant increase combined with a growth of tensile shear zones (red and yellow) from 350 to 400 °C, as shown by the integrated shear strain line profiles. This might be correlated to the formation of pervasive extrinsic planar stacking faults, due to the transformation of the Se crystal sublattice from wurtzite CdSe to antifluorite Cu2−xSe, namely, from the hexagonal ABABAB to the final cubic ABCABCABC close-pack, during Cu cation exchange and Cd sublimation reactions.

In Situ TEM Simultaneous Heating of Cu2Se Nanocrystals and CdSe Nanowires. We carried out additional experiments in which wurtzite CdSe NWs instead of rod-shaped NCs were used as Cu acceptors. They gave rise to the same CE reaction observed with the CdSe rods. In this direction, the normalized EFTEM maps acquired under different thermal conditions (Figure 5B,E,H) indicated the occurrence of CE reactions and the evolution of the Cu signal with increasing temperature. While the Cu signal in the RT map was localized only on the Cu2Se NCs, an additional faint Cu signal was discriminated over the carbon film already at 350 °C. HRTEM characterization confirmed the transformation from hexagonal hcp CdSe NWs into the corresponding cubic fcc Cu2Se (Figure 5C,F,I). In such a case, CdSe NWs at RT exhibit the main {0002} and {1120} lattice planes of an hcp structure in perpendicular vector orientation, as confirmed by Fourier analysis (FT inset of Figure 5C) compatible with the [1100] zone axis projection. At 350 °C, the NWs exhibited a cubic structure characterized by evident {111} and {110} lattice planes forming an angle of 70° and pervasive {111} planar stacking faults crossing the lattice. The corresponding Fourier analysis, compatible with the [011] zone axis projection of a fcc structure, revealed accordingly a strong linear streak consistent with this type of defective structure (FT inset of Figure 5F). Finally, at 400 °C, the totally exchanged NWs evidenced only lattice sets of cubic fcc Cu2−xSe. In particular, Figure S1 and the FT inset display the [011] HRTEM zone axis projection of an exchanged NW exhibiting the typical {111} and {110} lattice planes of a fcc structure forming an angle of 70°, as depicted in the Fourier analysis.

Moreover, the use of few CdSe nanowires, surrounded by many Cu2Se NCs, enabled us to observe the Cu CE fronts moving along the length of the wires, as shown in Figure S4, and revealed the two-dimensional diffusion of Cu species on the substrate over time. In regard to this, the EFTEM maps, acquired under different thermal conditions (Figure 5B,E,H) and normalized according to the method reported in ref 22, exhibited an evolution of the Cu signal with increasing temperature.

In Situ TEM Simultaneous Heating of Metal Cu Nanocrystals and CdSe Nanorods. In order to confirm the role of the copper source in the CE reaction mechanism observed between Cu2Se NCs and CdSe NRs, further experiments were performed using metal Cu NCs as copper donors. The concentration of Cu NCs was lowered with

Figure 4. HRTEM investigation of a CdSe nanorod during thermally activated solid state CE. (A) CdSe nanorod at the preheating stage (RT), with a length of 34 nm and exhibiting wurtzite structure, with mutually perpendicular (0002) and [1010] lattice planes and with [0002] and [1012] crystal directions forming an angle of about 43° (FT inset). (B) After thermal activation of CE, the nanorod was slightly reduced in length (29 nm) due to the Se loss. The rod exhibited the cubic symmetry of the antifluorite structure of the Cu2−xSe phase with mutually perpendicular [111] and [220] lattice planes and [111] and [311] crystal directions forming an angle of about 58° (FT inset). Right panels of both (A) and (B) show the corresponding Fourier transforms, consistent with hexagonal [0110] and cubic [112] zone axes, respectively. (C) Structural sketch representing the NRs’ hcp and fcc Se sublattices (yellow spheres) of wurtzite CdSe (preannealing) and cubic antifluorite Cu2Se (postannealing). (D,E) HRTEM images with planar stacking faults (white and black arrows) and the corresponding shear strain maps of a nanorod at 350 and 400 °C with the integrated shear strain line profiles (white dotted lines).
same directionality was maintained between the exchanged and the previous experiments, as the CE reaction progressed, the structurally transformed and exchanged rods. In analogy with HRTEM revealed examples of both partially and fully (Figure S5B). In particular, detailed characterization by elastic-

respect to the experiments involving Cu$_2$Se NCs in order to verify whether full or partial CE could still be observed by decreasing the net amount of copper available to the reaction. The results, summarized in Figures 6 and S5, indicate that CE takes place in the CdSe NRs, with the concomitant structural and chemical transformation to Cu$_2$Se. The CE was also found to be dependent on the local surface density and proximity of the Cu NCs deposited on the TEM substrate. The Cu NCs, visible as coarse cuboidal nanoparticles among the CdSe rods in Figure 6A,B, underwent partial dissolution during heating, and the released copper was engaged in CE with the adjacent CdSe NRs, as indicated in Figure 6C,D. The CE was always found to progress from the rods’ end, along the c-axis (Figure S5B). In particular, detailed characterization by HRTEM revealed examples of both partially and fully structurally transformed and exchanged rods. In analogy with the previous experiments, as the CE reaction progressed, the same directionality was maintained between the exchanged and unexchanged parts of the NRs; that is, [0001]$_{Cu}$ was converted into [111]$_{Cu_2Se}$ (Figure S5), with an epitaxial interface between the exchanged and unexchanged parts of the rod and with the orientation relationship $\langle 0110 \rangle_{Cu_2Se}/\langle 0001 \rangle_{CdSe}/\langle 011 \rangle_{Cu_2Se}$. This, along with the preferential shrinking also observed in the case of Cu$_2$Se//CdSe CE reactions indicates that the c-axis of the nanorods offers a preferential direction of CE front in the CdSe lattice. The EFTEM images acquired after annealing at 400 °C for 90 min and displayed in Figure 6E,F also show that CdSe NRs in close proximity to the Cu NCs underwent CE, while other CdSe NRs that were isolated and flanked by other NRs underwent partial or no CE and retained most of the Cd in their structure, as confirmed by an EDX compositional analysis of individual NRs. This supports our hypothesis that the Cd expulsion from the rods is driven by copper in-diffusion and CE in the rods, rather than being only an annealing effect. In particular, Figure 6G,H shows that an isolated cluster of CdSe rods more than 300 nm away from the copper source (in such a case an array of Cu NCs) also underwent CE, confirming the very high mobility of the Cu species diffusing on the substrate at 400 °C. In order to
eliminate a possible electron beam effect during the CE in the presence of Cu NCs, solid-state CE annealing experiments were performed ex situ in a furnace under conditions similar to those in the TEM column: similar chemical CE and structural transformation were observed here, as well.

Our experiments indicate that the free Cu species, once expelled from their original and local source, reach the acceptor particles and there give rise to a thermally activated CE reaction. One potential mechanism for distributing such free Cu species over the CdSe NRs/NWs (and therefore enable CE) is via vapor phase diffusion. In such case, the expelled Cu should recondense from the vapor phase on the hot TEM grid. However, this appears unlikely for a series of reasons. First, the sample was heated under high and dynamic vacuum and with a cryogenic trap located in close proximity to the sample that should promptly adsorb any chemical released by the sample by sublimation. Second, in the unlikely event of recondensation of copper from the vapor phase, then under the high-vacuum conditions in which the experiment is performed, such Cu should have recondensed uniformly and isotropically over the whole substrate and enabled CE also on NRs/NWs that were far from any Cu₅Se/Cu NC. This is contrary to our observation of a locality effect in CE, as more distal NRs/NWs were less affected by CE or were not exchanged at all. Finally, if Cu was able to recondense on the substrate, a similar fate should have occurred to the sublimated Cd and (in part) Se species. Then, we should have been able to map the presence of Cd and Se in regions that were not initially occupied by CdSe NRs/NWs.

A more plausible scenario is that the copper species expelled by the Cu₅Se/Cu NCs diffuse over the amorphous substrate that constitutes the mechanical support for the nanostructures in the TEM grid. Two pieces of experimental evidence support this second scenario. First, our normalization approach to the whole set of EFTEM images collected at the different samples' temperatures allowed us to make them coherent in terms of signal-to-background discrimination, permitting then to attribute the increase in the Cu signal (observed on the amorphous substrate already at 350 °C) to the out-diffusion of the Cu species expelled from Cu₅Se/Cu NCs, which could then reach the CdSe particles, as expected for a simple thermal diffusion process over an amorphous substrate. Second, there is a proximity effect on Cu depletion of the NCs acting as copper sources, which is strongly in favor of a surface diffusion process. After annealing, the chemical composition of the original Cu₅Se NCs, acquired via STEM-EDX, showed a variation in Cu depletion of the NCs that depended on their distance (D) from the CdSe NWs: the composition of the NCs ranged from Cu₁₁₃Se (when D < 100 nm) to Cu₁₉₉Se (when 100 nm < D < 500 nm). An analogous effect was observed also when Cu NCs were used instead of Cu₅Se as local sources of copper for the in situ CE reaction. In this case, the Cu content in the partially or fully exchanged CdSe NRs markedly depended on the proximity of the copper source, the Cu NCs, and the presence of other Cu scavengers on the substrate along the diffusion path (other CdSe NRs), ranging from Cu₅Se in close proximity to the cluster of Cu NCs to Cu₁₃₅Se further away from the copper source. Finally, as expected, we observed that—once the activation energy to start the CE reaction had been reached by crossing the threshold temperature—its kinetics, that is, the rate of CE reaction, increased with increasing temperature. Besides, we also noticed that such a rate depends on the type of cation donor species. Even if elucidating the reasons for these differences is beyond the main aim of this paper, further experimental studies and theoretical simulations are currently being performed in our groups to shed more light on such issue.

Since the exchange was observed not only on CdSe NCs directly in contact with Cu₅Se NCs but also on those several nanometers apart, this leads us to discuss a second and fundamental point, the latter concerning the migration mechanism followed by the copper expelled by the NCs acting as its sources: which was its oxidation state during the diffusion on the substrate? In this case, it would be unlikely for the Cu species to leave the Cu₅Se NCs as charged ions and thermally diffuse on the substrate. A more plausible explanation is that thermal annealing causes a release of Cu species from the Cu₅Se NCs as zerovalent (Cu⁰) atoms that can move randomly on the amorphous carbon film, similarly to the two-dimensional diffusion process of metallic atom species over a substrate. Also, it is unlikely that the amorphous nature of the carbon film could allow the expelled Cu⁰ atoms to follow any favored migration paths and therefore to self-organize into clusters along certain preferential directions. Since both species involved in the exchange (Cu and Cd) exist as cations only when they are in the NCs, and as the NCs evolve from CdSe to Cu₁.₉₆Se, this chemical and structural transformation can be considered as a CE reaction mediated by an intermediate step with migrating Cu⁰ free atoms. Furthermore, this Cu⁰-mediated process was corroborated by the thermally driven CE reaction occurring in CdSe when metallic copper NCs instead of Cu₅Se NCs were used as Cu donor nanospecies.

The cation exchange reactions observed in all the experiments were triggered solely by annealing. We found indeed that the thermal CE between CdSe and Cu₅Se took place also in those areas that were never directly exposed to the electron beam irradiation, occurring even in samples heated at 400 °C in the TEM with the beam blanked (Figure S6), as well as in the CdSe rods in the presence of Cu NCs on a TEM grid heated ex situ. We additionally tested a Si₃N₄ support as a different type of amorphous substrate, and also in this case CE took place at 400 °C (Figure S7), indicating that the unreactive chemical nature of the substrates does not affect the migration of the copper and the consequent in situ CE reaction. We finally carried out additional experiments outside the electron microscope, by annealing similar CdSe and Cu₅Se samples in the high-vacuum prechamber of an X-ray photoelectron spectrometer (XPS), followed by their immediate XPS analysis at different temperatures with no air exposure (Figure S8). These experiments confirmed our previous findings and ruled out any role of electron irradiation in the CE reactions.

CONCLUSIONS

We showed how thermally activated cation exchange reactions involving different kinds of NCs deposited on the same substrate can occur and be studied by an in situ TEM approach. Besides, we showed that such CE reactions, when performed in a solid state, took tens of minutes to be completed: their kinetics is much slower than in the liquid phase, where they often take only a fraction of a second to reach completion. This calls for further investigations aimed at understanding whether the observed phenomena can take place even when both the donor and acceptor species (Cu₅Se/Cu and CdSe NCs, respectively) are assembled as extended aggregates and, consequently, how the NC aggregation state (i.e., the possible degree of order/assembly of the NCs) could influence the thermally driven solid-state CE reaction. Our in situ TEM
approach to the study of the solid-state exchange reactions could then open interesting perspectives in identifying the intermediate states of such transformations and could be applicable to many other combinations of materials. It could additionally pave the way to methods for the modification of chemical composition, crystal structure, and physicochemical properties of materials at a local scale.

MATERIALS AND METHODS

Synthesis of NCs. Syntheses were carried out following standard published procedures. All details on synthesis and processing of the NCs are reported in the Supporting Information.

In Situ TEM Thermal Heating Experiments. In situ thermal heating experiments were performed within the TEM column, that is, under high-vacuum conditions (pressure $P \sim 1.5 \times 10^{-7} \text{ Pa}$), using a dedicated single tilt heating holder capable of reaching a maximum temperature of 800 °C. In those experiments that required the concomitant presence of both copper cation donor ($\text{Cu}_2\text{Se}$ NCs or Cu NCs) and acceptor ($\text{CdSe}$ rods or CdSe wires) species on the ultrathin carbon-coated gold TEM grid, these species were not deposited on the grid from a common solution. Instead, two sequential depositions of the respective solutions were made on the TEM grid. This procedure was followed in order to minimize as much as possible any cation exchange reaction already in the solution phase, that is, prior to deposition and annealing.

Before the in situ experiments were performed, these samples were cleaned with ethanol and heated at 130 °C in a pumping station ($P \sim 10^{-3}--10^{-4} \text{ Pa}$) in order to eliminate the residuals of excess surfactants. Note that this treatment should not remove quantitatively the surfactants bound to the surface of the NCs. In situ thermal treatment of all samples was carried out according to a common protocol: the system was initially heated from room temperature to 300 °C at a heating rate of 5 °C min$^{-1}$ and afterward up to a reaction temperature of 400 °C at a heating rate of 2.5 °C min$^{-1}$. This helped to minimize thermal drift and enabled monitoring the exchange reaction over time after its thermal activation.

Transmission Electron Microscopy Characterizations. HR-EELS Analysis. This was performed in STEM mode with a FEI Titan 80-300 Cube with double spherical aberration correction of both condenser and objective lens, working at an accelerating voltage of 300 kV and equipped with an ultra-bright-field emission gun (XFEG), an electron monochromator, and a GIF Quantum ERS energy spectrometer, with a final energy resolution of 0.10 eV (at KAUST, Thuwal, Saudi Arabia) for the Cu$_2$Se NCs and of 0.07 eV (at McMaster University, Hamilton, Ontario, Canada) for the Cu$_2$Se NCs. In both experiments, HR-EELS analysis was carried out in single range mode, focusing on the low loss energy region from 0 to 20 eV and with an exposure time of 1 ms per pixel on an area of 0.1 μm$^2$, yielding a total exposure time of 75 s per investigated region. Detailed chemical analysis via EELS was carried out in TEM and STEM mode (spectrometry imaging) using a FEI Tecnai G2 F20 microscope, working at 200 kV, equipped with field emission electron source, a GIF Quantum ER energy filter, and a Gatan K2-Summit direct detection camera (at Gatan Inc., Pleasanton, CA, USA). The EELS spectra were acquired from 300 to 2300 eV energy range in order to detect an energy variation in the energy profile of the Cd M-edge (404 eV), Cu L-edge (931 eV), and Se L-edge (1436 eV), with an exposure time of 8 ms per pixel on an area of 0.25 μm$^2$, yielding a total exposure time of a few minutes per investigated region.

HRTEM, HAADF-STEM, STEM-EDX, and EFTFM Analysis. These measurements were performed by a JEOL JEM-2200FS microscope, working at 200 kV, equipped with a Schottky electron source, a CEDOS spherical aberration corrector of the objective lens, an in-column Omega energy filter, and a Gatan US1000 CCD camera (at Istituto Italiano di Tecnologia, Genova, Italy). Spatially resolved chemical analysis of NCs was performed in STEM mode via EDX using a Bruker Quantax 400 XFlash 6T silicon drift detector (SDD) with an area of 60 mm$^2$. STEM-EDX analyses were carried out at room temperature before and after the heating experiments in order to avoid saturation of the SDD detector due to infrared thermal emission of the heated TEM holder. Elemental maps via EFTFM imaging were acquired using a contrast aperture of about 10 μm to reduce aberrations, mostly chromatic, and using the three-window method (one post- and two pre-edge) to extract the background. The elastic (zero loss) image was acquired as reference with a 10 eV wide energy slit; the elemental maps using Cu L-edge (931 eV) and Cd M-edge (404 eV) were acquired on the same area of zero loss with energy slits of 50 and 30 eV, respectively, and normalized according to the method reported in ref 22.

Electron Diffraction Analysis. Selected area electron diffraction patterns (SAEDPs) were acquired using a FEI Tecnai G2 F20 microscope working at 200 kV, equipped with a Schottky electron source and Gatan US1000 CCD camera with a high-sensitive thick scintillator (at Istituto Italiano di Tecnologia, Genova, Italy). Cubic Cu$_2$Se and hexagonal CdSe SAEDPs were indexed using ICSD card no. 67050 and no. 41491, respectively.

Strain Field Analysis. The strain field was measured using the peak pairs analysis starting from the HRTEM images. Strain maps, displaying the in-plane components of the symmetric strain tensors, were generated by considering the deformation stored in the rod lattice. Within the PPA method, the structural displacements, $u_i$, of the atomic columns were used to calculate the in-plane shear strain tensor, $\varepsilon_{xy} = \frac{1}{2} (\frac{u_x}{a} + \frac{u_y}{b})$, considering as the lattice basis vectors the 0002 and 1010 "structural reflections". The coordinates of $u_i$ displacements were chosen such that the $x$-axis was parallel to the [001] crystal axis, corresponding to the rod elongation, as well.

DFT Simulations of the Low Loss EEL Spectrum. The low loss EEL spectrum was modeled via DFT using the random phase approximation (Vienna Ab Initio Simulation Package). The projector-augmented-wave method (plane wave cutoff energy of 800 eV) was employed, together with the generalized gradient approximation for the exchange-correlation functional in the Perdew–Burke–Erzerhof flavor. Both Cu$_2$Se and Cu$_{2-x}$Se were optimized up to an energy convergence of $10^{-5}$ eV and a force convergence of 4 meVÅ. Monkhorst–Pack $k$-meshes of $8 \times 8 \times 8$ (structure relaxation) and $16 \times 16 \times 16$ (optical calculations) points were used for Brillouin zone integrations. The DFT simulations were carried out considering a stoichiometric Cu$_2$Se crystal and a virtual Cu-depleted Cu$_{2-x}$Se crystal, both with fcc antifluorite structure and a $\sqrt{2} \times \sqrt{2} \times 1$ unit cell size. The Cu-depleted Cu$_{2-x}$Se crystal was obtained by removing one atom of Cu from the total 16 Cu and 8 Se atoms. This removal, due to the cubic symmetry of antifluorite phase, generates 6.25% vacancies of Cu in the crystal lattice corresponding to Cu$_{10.56}$ stoichiometry (which is a close estimate of the vacancy concentration that was measured experimentally). The imaginary part of the frequency-dependent dielectric tensor was obtained from the first-principles eigenstates and afterward the real part by means of the Kramers–Kronig relations. Thus, the EEL spectrum was determined in the random phase approximation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b07219.

Details on the chemical synthesis of nanocrystals; structural characterization of Cu$_2$Se nanocrystals via electron diffraction at pre- and post-heating conditions; element quantification of Cu$_{2-x}$Se nanocrystals via EELS post-heating conditions; HR-EELS analysis; structural and thermodynamic details on the chemical and crystal structure transformation of nanorods from wurtzite CdSe to antifluorite Cu$_{2-x}$Se; annealing experiment on CdSe nanorods alone; normalized element mapping via EFTFM of CdSe nanowires and Cu$_2$Se nanocrystals; in situ TEM simultaneous heating of metal Cu nanocrystals.
and CdSe nanorods; HRTEM images of partially and completely exchanged CdSe nanorods; element mapping via EFTEM of CdSe nanowires and Cu$_2$Se nanocrystals annealed in beam-blanked conditions; element mapping via normalized EFTEM of CdSe nanorods and Cu$_2$Se nanocrystals on a Si$_3$N$_4$ TEM grid; and X-ray photoelectron spectroscopy characterization (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: liberato.manna@iit.it.
*E-mail: andrea.falqui@kaust.edu.sa.

**Author Contributions**

△A.C. and A.G. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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