Electrically driven cation exchange for \textit{in situ} fabrication of individual nanostructures

Qiubo Zhang$^{1,*}$, Kuibo Yin$^{1,*}$, Hui Dong$^{1}$, Yilong Zhou$^{1}$, Xiaodong Tan$^{1}$, Kaihao Yu$^{1}$, Xiaohui Hu$^{1,2}$, Tao Xu$^{1}$, Chao Zhu$^{1}$, Weiwei Xia$^{1}$, Feng Xu$^{1}$, Haimei Zheng$^{3,4}$ & Litao Sun$^{1,5}$

Cation exchange (CE) has been recognized as a particularly powerful tool for the synthesis of heterogeneous nanocrystals. At present, CE can be divided into two categories, namely ion solvation-driven CE reaction and thermally activated CE reaction. Here we report an electrically driven CE reaction to prepare individual nanostructures inside a transmission electron microscope. During the process, Cd is eliminated due to Ohmic heating, whereas Cu$^{+}$ migrates into the crystal driven by the electrical field force. Contrast experiments reveal that the feasibility of electrically driven CE is determined by the structural similarity of the sulfur sublattices between the initial and final phases, and the standard electrode potentials of the active electrodes. Our experimental results demonstrate a strategy for the selective growth of individual nanocrystals and provide crucial insights into understanding of the microscopic pathways leading to the formation of heterogeneous structures.
Cation exchange (CE) reactions, in which one type of cation ligated within an intact anion sublattice are substituted by another kind of cation, have been regarded as a particularly powerful approach for the growth of heterogeneous structures that are not easily obtained using direct synthesis techniques1–3. The feasibility and the rates of CE processes depend both on the solubility product constant and the nature of the intervening activation barriers during reaction4,5.

Depending on the nature of the strategy adopted to create a thermodynamic imbalance (TDI), CE methods can be divided into two categories6. One is based on CE activated by the ion solvation (Supplementary Fig. 1a), in which the TDI in the system is caused by the selective binding of the liquid ligand environment (LLE) to different sets of ions8,14 and the effect of heat is to reduce the activation barriers4. Here, the direction and rates of CE can be controlled by adjusting the LLE and the reaction temperature4. However, the very dynamic nature of the liquid reaction environment makes it difficult to directly observe the evolution process with a high resolution6. In addition, due to the volume limitations in the LLE, it is not suitable for the selective preparation of individual nanostructures. The second category of CE is based on thermal activation (Supplementary Fig. 1b), in which the TDI in the reaction is caused by vacancies induced by evaporation6,8–10. The effect of heat is both to reduce the intervening activation barriers, as well as to cause the evaporation of ions8. This process can take place in the solid state, which allows us to easily monitor the CE process6. On the other hand, in such a system, it is difficult to selectively synthesize individual NCs due to the lack of appropriate sources for migrating ions. Furthermore, the thermally activated CE is random and uncontrollable, in that the free ingoing ion species randomly diffuse over the inert substrate. Therefore, up to now, this method has not been widely adopted.

Herein, we report an in situ electrically driven CE process for fabrication of an individual sulfide nanostructure inside a scanning tunnelling microscopic–transmission electron microscope (TEM) system, where the entire reaction process was monitored at the atomic scale in real time. Using this method (Supplementary Fig. 1c), it is possible to completely control the CE process and to selectively fabricate individual nanocrystals by applying an electric bias. Thus, it is possible to make more complicated nanostructures with controlled specific structures. We study the formation process and reaction dynamics of the individual heterogeneous nanostructures in detail.

**Results**

**Construction of the experimental setup.** CdS nanowires (NWs) were synthesized by a previously reported solvothermal method11 and were characterized by means of TEM, powder X-ray diffraction, energy-dispersive X-ray spectroscopy and electron energy-loss spectroscopy (EELS) (see Supplementary Fig. 2). The as-prepared CdS NWs have an average diameter of ~40 nm (Supplementary Fig. 2b, f) and were up to several micrometres long (Supplementary Fig. 2a). The NWs are single crystals with the wurtzite (WZ) structure, oriented in the ⟨0002⟩ growth direction, as shown in Supplementary Fig. 2d.e. Supplementary Fig. 2g.h show that the as-prepared CdS NWs have no impurity element doping and the presence of Ni (Supplementary Fig. 2g) arises from the Ni support grid. The CdS NWs enable the facile evaporation of Cd by sublimation. Hence, we have chosen these NWs as precursors for the CE reaction8,10.

The CE experiments were conducted inside a Cs-corrected TEM (FEI Titan 80–300). The schematic diagram of the in situ experimental setup integrated into the TEM is illustrated in Fig. 1a. On the left side, the chemically active Cu electrode, which supported the vertically oriented CdS NWs (diameters about 40 nm) and was the source of Cu cations12, was glued to an Au rod using conductive epoxy (Chemtronics, CW2400). On the right side, a W tip was fixed onto a piezo manipulator and functioned as a movable and chemically inert electrode12.

**Electrically driven CE.** During an in situ TEM experiment, the W tip was manipulated to touch one of the CdS NWs following which a positive voltage of 1.0 V was applied to the Cu electrode against the W tip for 1 s. The electron beam was blocked during biasing, to avoid the influence of the electron beam irradiation effects. Figure 1b–k show respectively, the characteristics of the NW before and after biasing. Figure 1b shows the low-magnification TEM image of the CdS NW before biasing. In this
Figure 2 | Detailed characterization of a CdS/Cu2S core-shell structured NW. (a) High-resolution TEM pseudo colour image of the CdS-Cu2S heterostructure NW showing stacking faults in the CdS core indicated by red arrows. The purple area represents CdS core and the gold area represents Cu2S shell. Scale bar, 10 nm. (b) High-resolution image of the region included by the red dotted square in (a). The region under the yellow dotted line (the reaction zone) has a width of ~1 nm. Scale bar, 2 nm. (c,d) The FFT images on the left-hand side (c) and the right-hand side (d) of the interface in the CdS/Cu2S heterostructure at the Cu2S \{002\}/[100] CdS interface. (e) Schematic diagram of the CdS-Cu2S heterostructure, corresponding to (b).

image, the CdS NW is seen sandwiched between the Cu grid and the W tip, forming a metal–semiconductor–metal structure. Selected-area electron diffraction (SAED) pattern of a CdS NW (Fig. 1c) shows that the pristine CdS NW is a single crystal with WZ structure and EELS mapping (Fig. 1e,f) confirms that sulfur and cadmium are distributed uniformly. The I–V curve and equivalent circuit of the metal–semiconductor–metal CdS/Cu2S heterostructure at the Cu2S interface. (f) Curve and the equivalent circuit for this device. It is clear that an Ohmic contact is formed at the Cu-Cu2S interface, which is in accordance with previous reports. If the Schottky barrier of CdS-W interface is too high, the Cu-Cu2S/CdS-W system would not be conductive at a positive voltage. This suggests that the Schottky barrier reduces at the end of the reaction, on which more will be discussed later in this study. In general, CdS is an n-type semiconductor due to sulfur deficiency, whereas Cu2S is a p-type semiconductor due to the presence of copper vacancies. Therefore, we conclude that the observed unidirectional rectifying behaviour originates from both Cu2S/CdS interface and CdS/W interface.

To investigate the CE from CdS to Cu2S at the atomic scale, we took high-resolution TEM images. As shown in Fig. 2a, the CdS (purple colour) and Cu2S (golden colour) are both crystalline with core-shell (CdS/Cu2S) structure. A few stacking faults are observed in CdS (Fig. 2a) as highlighted by red arrows. They may be introduced in the process of the preparation of CdS NWs, such as the stacking faults in Supplementary Fig. 2c. Figure 2b shows the CdS/Cu2S interface wherein the reaction zone can be clearly identified. The reaction zone (area enclosed by the yellow dotted lines) spans several atomic layers (about 1 nm) and it was critical for the solid-phase CE reaction. For nanocrystals, the width of reaction zone determines the morphological stability of reaction precursors. Within reaction zone, the crystal is in a structurally non-equilibrium state where both the cations and anions are mobile. If the reaction zone spans the whole width of the crystal, the morphology of crystal prefers the thermodynamic more stable shape (sphere-like) before all the ions reach the final equilibrium positions. The LC Cu2S (200) lattice fringes begin to appear along the NW shell instead of the WZ -CdS (001) lattice fringes, as verified from the fast Fourier transformation (FFT) patterns shown in Fig. 2c,d. The schematic diagram of CdS-Cu2S heterostructure shown in Fig. 2e corresponds to the structure in Fig. 2b. From these images, we can also identify the
The physical mechanism of electrically driven CE. The formation of CdS/Cu$_2$S core-shell structured NW was also studied using STEM–EELS mapping, where Cd maps represent CdS and Cu maps represent Cu$_2$S, as the S sub-lattice in the NW is intact during the whole exchange process. Before biasing (Fig. 3a), the starting template CdS NW is oriented in the <001> growth direction. During biasing, the following changes occur. First, sublimation of Cd resulting in cation vacancies at the CdS surface due to Ohmic heating, while the inner Cd ions diffuse to the surface leaving cation vacancies at the subsurface. Second, electro-dissolution of the Cu electrode in accordance with the equation, $\text{Cu} \rightarrow \text{Cu}^{2+} + e^-$, after which the Cu$^{2+}$ ions migrate along the subsurface of the NW towards the W electrode driven by the external electric field to react with the sulfide ions according to the equation, $2\text{Cu}^{2+} + S^{2-} \rightarrow \text{Cu}_2\text{S}$ (Fig. 3b). Next, Cu$^{2+}$ ions reach the other end of the NW forming CdS/Cu$_2$S core-shell structure with one end closed (Fig. 3c). Finally, Cu$^{2+}$ continues to migrate forming CdS/Cu$_2$S core-shell structure with both ends closed (Fig. 3d). With continued biasing (Supplementary Fig. 4), the inward diffusion of Cu$^{2+}$ will push Cd$^{2+}$ out of the cation locations and the expelled Cd$^{2+}$ will tend to escape through the weakest sites in the shell (marked by a blue arrow in Supplementary Fig. 4d).

Cd sublimation of heterogeneous NCs was previously observed in colloidal CdSe, CdSe/Cu$_{x}$P/CdSe NCs, NCs and CdSe/PhSe NCs. The sublimation temperatures are as low as 450 K (ref. 8). When a constant bias is applied, the CdS NW’s temperature will rise due to Ohmic heating until it reaches a thermal equilibrium state. We simulated the temperature distribution of a CdS NW in thermal equilibrium state by finite element method and found that the temperature raised by Joule heating is enough to induce sublimation of Cd (Supplementary Fig. 6).

In this process, high chalcocite (HC) Cu$_2$S, which is the high-temperature phase of stoichiometric Cu$_2$S, is not only a reaction product but also functions as a channel for cation transport. This is due to the fact that there is a greater number of possible occupation sites with similar energy than the number of Cu atoms in the HC orientation relationship of CdS/[100]/[100]Cu$_2$S, which is in accordance with the previous observations on similar structures reported in the literature.

Using this synthesis technique, it is possible not only to grow CdS/Cu$_2$S core-shell structure with one end closed, but also to fabricate core-shell structures with both ends closed, as shown in Supplementary Fig. 4a–d. In addition, the degree of heterogeneity can be controlled by adjusting the biasing time. We applied a 0.5 V positive voltage on another NW and the EELS mapping data were obtained every 10 s. Results (Supplementary Fig. 4b–d) show that during the whole biasing process, the sulfide anion sublattice remains intact, and that the Cu$_2$S zone at the top end of the NW increases with biasing time. Supplementary Fig. 4e shows the lengths of the Cu$_2$S zones grown at the top end of the NW after biasing for different time. The growth rate of Cu$_2$S (marked by white two-way arrows) slows down with time, because it is increasingly harder for Cd ions to be replaced in the NW as the CE reaction progresses. Further biasing of partially cation-exchanged NWs will lead to deformation of the NWs before the total replacement of Cd ions (Supplementary Fig. 5a,b and Supplementary Movie 1) due to the high temperature raised by Ohmic heating.
ions tend to migrate more along the [001] direction under the action of electric field force. As a result, the reaction proceeds along [001] direction later.

The I–V curves of NWs at different stages of the reaction (Fig. 3a–d) are shown in Fig. 3j. The curve in Fig. 3a indicates that Schottky-type contacts are formed at both Cu-CdS and CdS-W interfaces in accordance with the energy band diagram of the original Cu–CdS–W structure (Fig. 3e). The unidirectional rectifying behaviour of these structures shown in Fig. 3b,c can be explained on the basis of energy band diagram of Cu-Cu2S/CdS–W system (Fig. 3f) and the origin of the bidirectional conductance of the structure in Fig. 3d can be traced back to the energy band diagram of the Cu-Cu2S–W system (Fig. 3g). The electrical properties of the NW depend on the extent of CE and can therefore be tuned to meet the needs of special functional devices. It is worth noting that the Schottky barrier of the CdS/W interface in Fig. 3e reduces upon biasing (Fig. 3f). Though the work function of W (4.55 eV) is lower than the Fermi level of n-type CdS (about 5.7 eV), it is still a Schottky contact at the CdS/W interface at the beginning (Fig. 3b) because of the Fermi level pinning effect. The diffusion of Cu+ will force the inclusion of a fraction of the Cd2+ ions into the crystal lattice of the n-type CdS semiconductor, leading to heavy cation doping as shown in Fig. 3i (ref. 22). Positively charged Cd ions can provide an additional potential (Fig. 3i), thereby reducing both the built-in potential and the depletion width to maintain the Fermi energy balance between W and CdS22. Therefore, the Schottky barrier at the CdS/W interface reduces.

**Discussion**

To confirm that this type of CE is electrically driven (including an electric field force and Ohmic heating), an equal negative voltage in the reverse direction (the direction of the electric field is from W tip to the Cu grid) was applied on the CdS NW to simulate a temperature distribution that is similar to the bias condition from the Cu grid to the W tip. The result of this simulation revealed that the CdS NW was not transformed into Cu2S/CdS alloys, whereas the reaction was similar to the lithiation of a conversion materials anode.

In view of its much lower boiling point (765°C) than copper (2561.5°C)20, all other conditions being the same, Cd is easier to sublimate. It should be emphasized that in the early stages of this process, the migration of Cu+ is along the sub-surface rather than on the surface of the NW. Normally, Cu+, is expected to move preferentially along the surface as compared with the bulk due to the smaller barrier12. However, the electro-dissolution of Cu is slower than the evaporation of Cd. As a result of Ohmic heating, Cd on the surface evaporates first following which the bulk Cd2+ will migrate to the surface leaving behind cation vacancies in the subsurface. Under these conditions, it is easier for Cu+ to migrate along the subsurface.

From Fig. 3 and Supplementary Fig. 4, we find that the reaction dominantly starts along [100] direction and then proceeds along [001] direction. According to the above analysis, the reaction is carried out on the premise of Cd sublimation. The Cu/CdS contact position has a higher temperature than other positions (Supplementary Fig. 6), so evaporation of Cd (resulting in Cd vacancies) starts at Cu/CdS interface first. It has been found that the interface CdS(001)/Cu2S(001) has a lower formation energy than the attachment of Cu2S to the CdS (100) facet18. Thus, the reaction prefers to start along the [100] direction. Once Cd vacancies formed at the surface of the CdS NW, the ingoing Cu

\[
2\text{Cu}^+ + \text{CdS} + 2e^- \rightarrow \text{Cd} \uparrow + \text{Cu}_2\text{S}
\]
We tried to replace copper by several other metals (for example, gold, silver, platinum, aluminum, molybdenum, nickel and lithium) to produce similar heterostructures of NWs using this method. The results are shown in Fig. 4a. The metals marked by spheres denote those that cannot react with CdS and those marked by stars are metals that can replace Cd²⁺ in CdS NWs. After an analysis of the results, we find that the following necessary conditions need to be fulfilled for the formation of heterostructures. First, the initial phase (hexagonal CdS) and the final phase (for example, Au₄S₄, Ag₂S, Cu₂S and Li₂S) should have similar S sublattices to allow for a kinetically facile transformation. Furthermore, as the reaction product (HC phase Cu₂S) is a super ionic conductor, this would be as a faster transport path to supply Cu ions for subsequent reactions along the axial direction. Finally, a Cu₅S₄/CdS core-shell structure is formed. For Li ion exchange, the driving forces include chemical affinity in addition to electric field force and Ohmic heating, because Li ions show a much stronger interaction (ΔG°(Li₂S) = −225.0 kJ mol⁻¹) with sulfide anions when compared with Cd ions (ΔG°(CdS) = −156.5 kJ mol⁻¹). Hence, Li ions are more likely to diffuse inward and displace Cd ions. The reaction between Li and CdS may take place even without assistance from Ohmic heating. However, the ionic diffusivity of Li in Li₂S is very poor as a result of which most of the Li ions migrate along the NW surface as demonstrated by the presence of a thin shell of Li on the NW surface (Supplementary Fig. 9e). This leads to the transformation of the NW into a mixed heterostructure at the end of reaction.

In conclusion, we demonstrate an in situ CE process driven by electricity to transform individual NW into heterostructures during TEM imaging. This method can be used not only to finely control the CE process but also to selectively modify individual nanocrystals in an integrated system of NCs. The various reaction steps in the process are identified by observing the growth of CdS/Cu₂S core-shell structure from the CdS NW precursor, which are namely sublimation of Cd, electro-dissolution of Cu, migration of Cu ions and the formation of CdS/Cu₂S core-shell structure. The reaction mechanism strongly supports the fact that the inwardly migrating cations (here, Cu⁺ and Li⁺) originate from metal active electrodes and are driven by the electric field force, whereas the outward migration of cations (here, Cd²⁺) occurs due to evaporation into the gas phase and is actuated by Ohmic heating. Results from contrasting experiments reveal that the structures of the heterogeneous nanocrystals formed depend on both the mobility of the cations within the crystal and the binding energy of the inwardly migrating ions and the sulfur sublattice. Our results open a new perspective to selective CE on individual nanocrystals and also provide critical insights into the microscopic mechanism of solid-state exchange processes.

Methods
CdS NW preparation. CdS NW samples were synthesized via a solvothermal method. In brief, 0.2665 g Cd(CH₃COO)₂ · 2H₂O (99.99%, Aladdin) and 0.0641 g sublimed sulfur (99.95%, Aladdin) were dissolved in 40 ml ethylenediamine (98%, Aladdin) under vigorous stirring and then transferred to a teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 200 °C for 2 h after which it was allowed to cool to room temperature naturally. The yellowish products were isolated by centrifugation at 6,000 r.p.m. for 10 min and washed five times with methanol (certified ACS, Aladdin).

Set up of the in situ TEM experiment. In this work, a half copper grid was glued onto a gold wire with conductive epoxy. The as-prepared CdS NWs were dissolved in ethanol solution to achieve a homogeneous suspension. Then, a drop of solution was casted on the half Cu grid and was dried in the air for 10 min. As a result, some NWs were anchored on the edge of the half grid. The tungsten tips were prepared by electrochemically etching. The etching duration was 2 mol l⁻¹ NaOH and the etching voltage was 2 V with a constant current of 10 mA. All W tips were cleaned by plasma cleaning for 60 S to reduce impurities at the surface for in situ TEM experiments. The structure of the device is shown in Fig. 1a. All the in situ experiments in this work were conducted in vacuum.

Materials characterization and electrical measurements. Powder X-ray diffractograms of the obtained CdS products were measured using an X-ray diffractometer (Rigaku, Ultima III) with Cu Kα radiation as the X-ray source. The reflections were indexed assuming a hexagonal structure for CdS with lattice parameters a = 4.15 Å and c = 10.13 Å. The data was collected using a step size of 0.02° and a scan time of 0.5 s per step. The X-ray diffractograms were analyzed using the high score software to determine the crystal structure of the as-prepared CdS NWs.
TEM characterization and electrical property measurements were carried out using an aberration-corrected TEM (Titan 80–300) equipped with a TEM-scanning tunneling microscopic holder.

**Simulation of temperature gradient.** We supposed that the CdS NW as a one-dimensional system with length L obeys the classical heat equation with Joule heating:

\[ \nabla (k \nabla T) + \frac{\delta V^2}{r^2} = 0 \]  

(2)

where \( V \) is the applied bias, \( L \) is the length of NW, \( k \) is the thermal conductivity, \( \delta \) is the electric conductivity and \( T \) is the temperature. The parameters of \( k \) and \( \delta \) of Cu20.27, CdS28–30 and W20.27 are well-known. Equation (2) was solved by finite element method with appropriate boundary conditions at a given applied bias of 1 V.

**Data availability.** The Cu and W thermal conductivity data that support the findings of this study are available in Lange’s Handbook of Chemistry, https://nist.gov/JPCRD/jpcrdS1Vol3.pdf The CdS thermal conductivity data that support the findings of this study are available in J. Phys. Chem. Ref. data, doi: 10.1063/1.3476469 (ref. 30). The CdS electric conductivity data that support the findings of this study are available in Appl. Phys. Lett. with the identifier 10.1063/1.1900950 (ref. 29).

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