Angewandte Chemie International Edition

International Edition: DOI: 10.1002/anie.201507263
German Edition: DOI: 10.1002/ange.201507263

Solid-State Chemistry on the Nanoscale: Ion Transport through Interstitial Sites or Vacancies?

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Abstract: *How can ion-exchange process occur in nanocrystals without the size and shape changing and why is the ion transport much faster than in classical interdiffusion processes in macrocrystalline solids? We have investigated these processes at the molecular level by means of high-resolution and analytical electron microscopy in temperature-dependent kinetic experiments for several model reactions. The results clearly show a diffusion process that proceeds exclusively through the interstitial lattice positions with a subsequent "kick out" to remove individual ions from lattice sites without the formation of vacancies. This mechanism has not been observed in nanocrystalline systems before.*

Nanocrystals are perfectly suited to study solid-state reactions. This is not only because of the large surface to volume ratio determining the thermodynamic properties, but also because state-of-the-art syntheses lead to very homogeneous ensembles. This enables the use of experimental techniques as used in homogeneous solution and has already led to impressive results starting from the initial work in the 1990s. For example, it was possible to experimentally confirm the pressure-induced transformation from hexagonal CdSe nanocrystals to the high-pressure cubic CdSe phase[1,2] or to demonstrate the size-dependence of the nanoparticles' melting point.[3,4]

Very current topics in chemistry on the nanoscale are ion-exchange reactions. Based on the pioneering work to synthesize onion-like CdS–HgS–CdS core–shell–shell nanoparticles by ion exchange,[5–8] several reactions have been reported in which a partial or complete cation exchange yields a new class of nanoparticles while retaining the original shape. This process enables nanostructures to be prepared that are very difficult to synthesize directly. However, the ion-exchange mechanism itself is still subject of lively debate. Especially whether the ion transport and exchange is mediated by vacancies or interstitials is a topic of controversy. To resolve this issue, we present three model systems which we believe represent especially interesting scenarios. In particular, Reactions (1)–(3) were investigated.

$$\mathrm{PbSe} + \mathrm{Cd}^{2+} \rightarrow \mathrm{CdSe} + \mathrm{Pb}^{2+} \qquad (1)$$

$$\mathrm{ZnSe} + \mathrm{Cd}^{2+} \rightarrow \mathrm{CdSe} + \mathrm{Zn}^{2+} \qquad (2)$$

$$\mathrm{ZnSe} + \mathrm{Pb}^{2+} \rightarrow \mathrm{PbSe} + \mathrm{Zn}^{2+} \qquad (3)$$

The exchange in Reaction (1) was performed on two different-sized spherical nanoparticle samples ("dots", 5 nm and 10 nm in diameter, respectively) and on elongated nanoparticles ("rods", aspect ratio 4.5). The exchanges in Equations (2) and (3) were performed on ZnSe nanoparticles with 5 nm diameter. Figure 1 displays the 5 nm diameter nanoparticles used for in the Reactions (1)–(3) before and after the cation-exchange reaction.

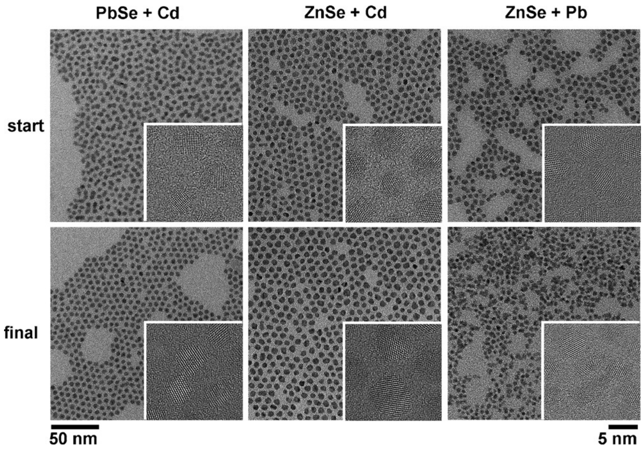

Figure 1. TEM and HRTEM (inset) micrographs of spherical nanoparticles before (start) and after (final) the cation exchange.

Interestingly, shape changes do not occur for Reactions (1) and (2), while the particle morphology is significantly different after performing Reaction (3). We explain this observation with different diffusion and exchange

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507263.

mechanisms, resulting from different ionic radii (Zn^{2+}: 60 pm, Cd^{2+}: 78 pm, Pb^{2+}: 119 pm)[9] and resulting lattice constants. While the difference between the PbSe ($a = 6.1213$ Å) and the CdSe lattice constant ($a = 6.077$ Å) is below 1%, the difference to ZnSe ($a = 5.618$ Å) is more significant, about 9%. Thus, because of their large sizes, lead ions cannot occupy octahedral interstitial sites in the ZnSe lattice. An ion exchange with lead ions is only possible via the surface. If Pb ions enter the crystals, driven by a high Pb excess and higher binding energies (ZnSe 136 kJ mol^{-1},[10] PbSe 302 kJ mol^{-1}[11]), the crystals dissolve.

We performed all further studies on the exchange Reactions (1) and (2). Despite the size and shape preservation in Reactions (1) and (2), they still result in different products. Electron diffraction and Raman spectroscopy (Figure 2, Figure S12,S13 in the Supporting Information) demonstrate this clearly. In case of Reaction (1) the electron diffraction peaks as well as the longitudinal optical (LO) Raman bands of PbSe and CdSe remain separated and only change in relative intensity during the exchange. This is a clear indication of having a core–shell structure with growing shell size in favor of the core dimensions.[12] The core–shell configuration is also visible in the TEM analysis with EDX element mapping of spherical (10 nm) PbSe nanoparticles (Figure 2e,f). In contrast, the continuous shift of the diffraction peaks and the LO frequencies in the case of Reaction (2) is a clear indication of the formation of mixed crystals with a homogeneous alloy composition.[13]

To solve the question of the transport mechanism within the nanocrystal lattice, a discussion of the respective crystal structures is helpful. As demonstrated with electron diffraction and Raman spectroscopy, Reaction (1) results in a phase transition from cubic PbSe in rocksalt structure (coordination number six) to cubic CdSe in zinc blende structure (coordination number four), whereas Reaction (2) occurs with the cubic zinc blende lattice being retained.

The corresponding lattice structures are shown in Figure 3. For Reaction (1), the interstitial sites of the PbSe lattice form the lattice sites of the developing CdSe crystal. For Reaction (2), the exchange has to be performed on the existing lattice sites. The literature describes the cation exchange by a diffusion via vacancies, for the exchange of PbSe with cadmium ions[14,15] as well as for ZnSe with cadmium ions.[16,17] But short diffusion pathways and the resulting reorganization lead to a low vacancy concentration

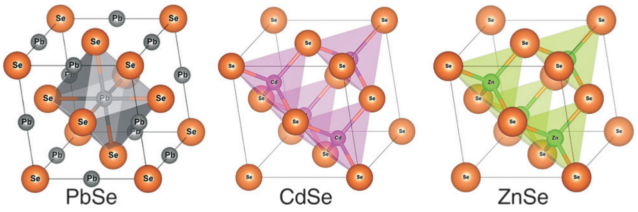


Figure 3. The employed lattice structures.

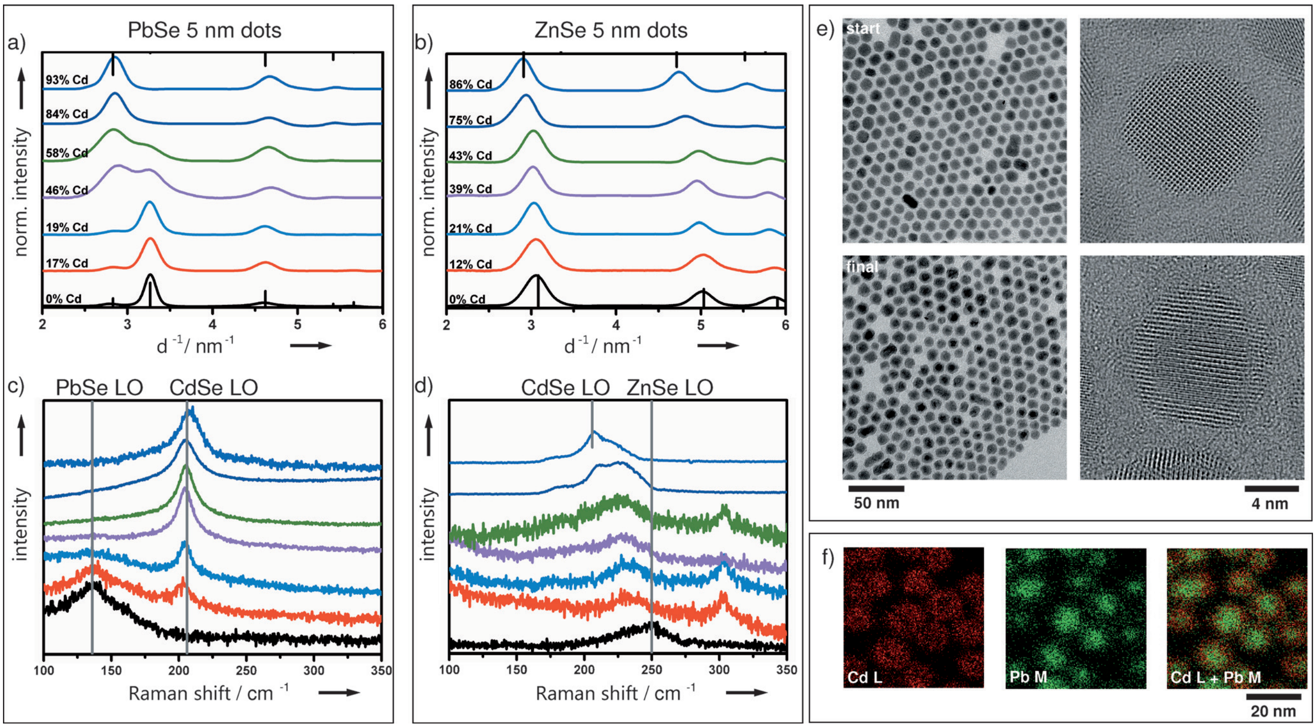


Figure 2. PbSe and ZnSe nanoparticles. Electron diffraction rotation profiles of 5 nm PbSe nanoparticles with Cd^{2+} ions (a) and 5 nm ZnSe nanoparticles with Cd^{2+} ions (b). Raman spectra of 5 nm PbSe nanoparticles with Cd^{2+} ions (c) and 5 nm ZnSe nanoparticles with Cd^{2+} ions (d). The Raman band at 300 cm^{-1} results from the Si substrate. ZnSe nanoparticles with a high cation exchange ratio were measured under different conditions because of the strong luminescence. The order of the spectra is the same for electron diffraction and Raman spectroscopy. e) TEM and HRTEM micrographs of 10 nm PbSe nanoparticles before (start) an after (final) the cation exchange. f) EDX element mapping Pb M and Cd L and their superposition for PbSe nanocrystals after the cation exchange.

in nanocrystals.[18–20] Thus, a diffusion via vacancies is not probable. Furthermore, a solid-state reaction by vacancy creation would require activation energies in the 10^2 kJ mol^{-1} regime, whereas the activation energies of an exchange without vacancy creation are at least an order of magnitude smaller.[21,23] Because of this difference, the estimation of the activation energies for the cation exchange Reactions (1) and (2) allows the explanation of the diffusion and exchange mechanisms.

After the addition of the to-be-exchanged ions we monitored the reactions with TEM, EDX (Figure S1–S5), and UV/Vis spectroscopy. The optical properties, absorption and fluorescence, change significantly with the changing composition during the cation exchange (Figure S6–S8).

For the exchange experiments, a twofold Cd^{2+} excess relative to the Pb^{2+}content and a fivefold Cd^{2+} excess relative to the Zn^{2+} content was used. Dependencies on the Cd^{2+} ion concentration were not observed, as long as Cd was used in excess. Monitoring the reaction conversion with time reveals two distinct phases (Figure S9–S11). Within the first minutes, a fast conversion up to 30% is observed and the reaction slows down drastically afterwards. The initial, fast conversion can be assigned to surface reactions as the relative contribution of this process depends on the nanoparticle size and is consistent with the estimated number of surface sites. The slow component of the conversion allows the diffusion rate of the cation exchange to be estimated. To obtain numerical values, the conversion after 30 min was estimated for different temperatures. After subtracting the surface-related component, the first-order rate constant[22] can be calculated, Equation (S2).

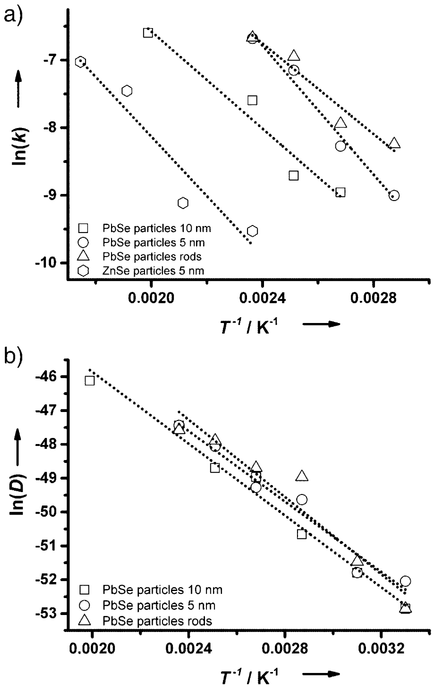
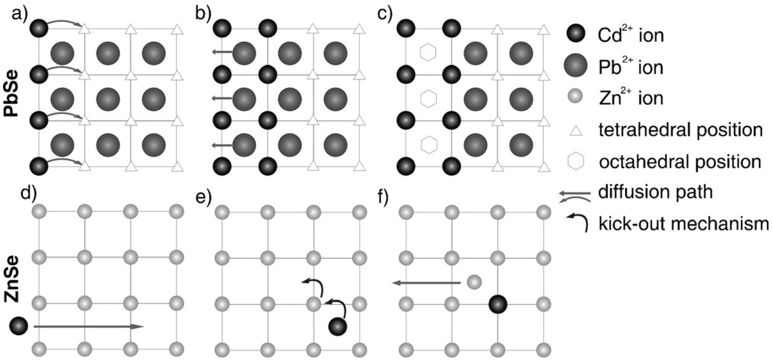


Figure 4. Arrhenius plot of a) velocity rate and b) diffusion constants ($m^2 s^{-1}$) an linear fit.



Scheme 1. Exchange mechanism for the cation exchange with cadmium in a) PbSe nanoparticles and b) ZnSe nanoparticles.

The resulting Arrhenius plots (Figure 4a) look different for each sample. However, the activation energies are in the 30 to 40 kJ mol^{-1} regime throughout. These values are characteristic for an ion exchange without a vacancy creation.[23]

In the case of the exchange of Pb^{2+} with Cd^{2+}, the developing core–shell composition enables a further way to obtain the diffusion coefficients. We estimated the shell size by TEM and the reaction conversion after the complete conversion of Reaction (1). This thickness corresponds to half the total distance the Cd^{2+} and Pb^{2+} ions have to travel through the crystal. Because of the defined interface between pure PbSe and CdSe, the diffusion length is known, too. The diffusion coefficient can simply be calculated following the 2nd Ficks' law [Eq. (S3)].[22,24] Temperature-dependent experiments result in activation energies around 43–48 kJ mol^{-1} for all PbSe samples (Figure 4b), which agrees very well with the values from the kinetic investigations.

Based on these values we conclude that the ion exchange in both Reactions, (1) and (2) works without creating vacancies. As Reaction (1) results in a core–shell structure and Reaction (2) in an alloy, the reaction mechanisms must still differ (Scheme 1). For Reaction (1), the diffusion of cadmium ions happens via tetrahedral interstitial sites in the PbSe lattice. Because of the almost equal lattice constants, the tetrahedral interstitial sites have ideal dimensions for cadmium ions, while the octahedral sites are occupied with lead ions. During the process, the lattice changes from rocksalt to zinc blende, while the lead ions diffuse out of the nanocrystal through interstitials (octahedral sites) in the developing zinc blende lattice. Even though it is small, the contraction of the lattice further hinders a backward diffusion of lead ions into the newly formed lattice. The mechanism leads to the observed core–shell structures, in which the CdSe shell grows around a shrinking PbSe core with overall size and shape preservation. Clearly, this process is controlled by diffusion, the activation energies are thus the ones for the diffusion through the interstitial sites.

For Reaction (2), the exchange does not result in a change of the lattice structure. Both, ZnSe and CdSe are in zinc blende structure. Cadmium ions can diffuse into the nanocrystal through interstitials (octahedral and unoccupied tetrahedral sites) of the zinc blende lattice. The cadmium ions then replace zinc ions from their respective lattice sites by a kick-out mechanism.[25,26] Zinc ions, now occupying interstitials, will then leave the crystal by diffusion through interstitials. The formation of the homogeneous alloy requires an equal distribution of cadmium ions in the ZnSe lattice before the real exchange occurs. Thus, the rate determining step is not diffusion, but the ion exchange. The estimated activation energy is the one of the cation exchange. The fact that this value is rather small can only be explained with a kick-out mechanism without vacancy creation.[23,25,26] In this process, the developing vacancy is filled by the exchanging ion in a cooperative process, which lowers the activation energy of this exergonic process significantly compared to typical vacancy creation.

Thus, we were able to demonstrate that an excess of exchange ions in solution results in a diffusion into the nanocrystal even without vacancies for the ion transport being present. The transport is solely mediated by the interstitial sites. Other work has shown that a direct introduction of dopant atoms results in no diffusion of these atoms (trapped dopant).[18,27] Furthermore, Sung et al. observed an activation energy of $152\,\mathrm{kJ\,mol^{-1}}$ for the interdiffusion of CdSe–ZnSe core–shell particles.[28] However, their experiments were performed on readily prepared core–shell particles without cation excess in solution. Therefore, a vacancy has to be created to enable diffusion via intermediate lattice sites. Because of the related high activation energies, this process does almost not happen at room temperature. This also explains why core–shell particles are stable at room temperature for years and do not form alloys with time.

In summary, the investigation of solid-state reactions in nanocrystals enables a detailed view on the underlying processes on the atomic scale. Owing to the strong spatial confinement, the lack of intrinsic vacancies, and the short diffusion pathways, the kick-out mechanism in nanocrystals can be clearly demonstrated. This mechanism was postulated for macroscopic crystals to explain differences in the diffusion profiles of dopant atoms. In nanocrystals, this process is the key to understand ion exchange processes.

Acknowledgements

The authors acknowledge financial support from the German Research Foundation (DFG) via the Cluster of Excellence “Centre for Ultrafast Imaging” (CUI).

Keywords: cation exchange · nanoparticles · PbSe · reaction kinetics · ZnSe

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 14183–14186
Angew. Chem. **2015**, *127*, 14389–14393

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Received: August 4, 2015