

The Role of the Crystal Structure in Cation Exchange Reactions Involving Colloidal Cu₂Se Nanocrystals

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Stoichiometric Cu₂Se nanocrystals were synthesized in either cubic or hexagonal (metastable) crystal structures and used as the host material in cation exchange reactions with Pb²⁺ ions. Even if the final product of the exchange, in both cases, was rock-salt PbSe nanocrystals, we found that the crystal structure of the starting nanocrystals had a strong influence on the exchange pathway. The exposure of cubic Cu₂Se nanocrystals to Pb²⁺ cations led to the initial formation of PbSe unselectively on the overall surface of the host nanocrystals, generating Cu₂Se@PbSe core@shell nano-heterostructures. The formation of such intermediates was attributed to the low diffusivity of Pb²⁺ ions inside the host lattice and to the absence of preferred entry points in cubic Cu₂Se. On the other hand, in hexagonal Cu₂Se nanocrystals, the entrance of Pb²⁺ ions generated PbSe stripes “sandwiched” in between hexagonal Cu₂Se domains. These peculiar heterostructures formed as a consequence of the preferential diffusion of Pb²⁺ ions through specific (*a*, *b*) planes of the hexagonal Cu₂Se structure, which are characterized by almost empty octahedral sites.

