Controlling Ion Exchange Balance and Morphology in Cu^+ –to– In^{3+} Cation Exchange of $Cu_{3-x}P$ Nanoplatelets

Cation exchange reaction is a powerful tool enabling the access to control of morphology and structure of colloidal nanocrystals (NCs). However, a relatively large amount of crystal defects in cation–exchanged NCs is one of the major obstacle for technological application. Here, we demonstrate the controlling of ion exchange balance in Cu+-to– In3+ cation exchange reaction of Cu3-xP nanoplatelets (NPLs) and the consequential morphology change by nanoscale Kirkendall effect. Cation–exchanged NPLs exhibit various morphologies depending on the ligand composition introduced in cation exchange reaction. In particular, cracked morphology appears when solvation of Cu+ overwhelms the stoichiometric desolvation of In3+. Elemental analysis combined with a mathematical description of stoichiometry of Cu3-xP segment enables the effective quantification of cation vacancy concentration which is the origin of Kirkendall void nucleation. Ion solvation energetics of cation exchange reaction turns out to control the balance between cation solvation and desolvation which is responsible for dramatic increase of Cu+vacancies that eventually lead to defect generation.