

Advanced Energy Materials Comprised of Non-Natural Nanocrystal Polymorphs

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The cations of a chalcogenide-based (MX, where X = S, Se, Te) nanocrystals can be easily replaced by foreign cations in a topotactic manner such that the anionic sub-lattice is largely preserved. This cation exchange reaction is fast becoming a template-based alternative to the hot-injection synthesis of nanocrystals. A wide range of semiconductor nanostructures of controlled morphology and complex compositions have been prepared using the method, leading to the expansion of the “nanochemistry periodic table”. Cation exchange has also served as a model system for the study of atomistic mechanisms of solid-state transformations. Our recent studies have found some cation exchange reactions to involve co-operativity and a phase transition-like nature, overturning long-held assumptions about reactions in the solid-state.

More recently, in our laboratory, cation exchange is finding a special role not just as a method of synthesis but one of materials discovery. Due to the topotactic nature of the transformation, often the product of an exchange reaction is obtained in a crystal polymorph that is either metastable or in a form absent from the known bulk phase diagram. These polymorphs have fascinating, surprising attributes that can be exploited for energy research. I will provide three examples. The first involves copper selenide clusters prepared by the cation exchange of magic-sized (CdSe)_{33,34} clusters. The clusters have significant lattice strain due to which they exhibit a crystallographic structure that deviates significantly from bulk copper selenide. In particular, the clusters exist in a room-temperature super-ionic phase, wherein the Cu⁺ sub-lattice is effectively “liquid-like”. The fast-ion transport characteristics of these clusters make them suitable candidates for solid electrolytes for batteries. The second example involves mercury-cadmium selenide alloys made by partial cation exchange of wurtzite cadmium selenide nanocrystals. These alloys exhibit both a non-trivial band structure and a band-gap, imparting them attributes of a 3D topological insulator. As a third and final example, I will describe how cation exchange reactions have advanced the field of plasmonic quantum dots.

In summary, these examples highlight the wide-open space for the discovery of new materials and phenomena with the aid of nanocrystal exchange reactions.