

# Division of Synthetic Chemistry

## – Advanced Inorganic Synthesis –

[https://www.scl.kyoto-u.ac.jp/~teranisi/index\\_E.html](https://www.scl.kyoto-u.ac.jp/~teranisi/index_E.html)



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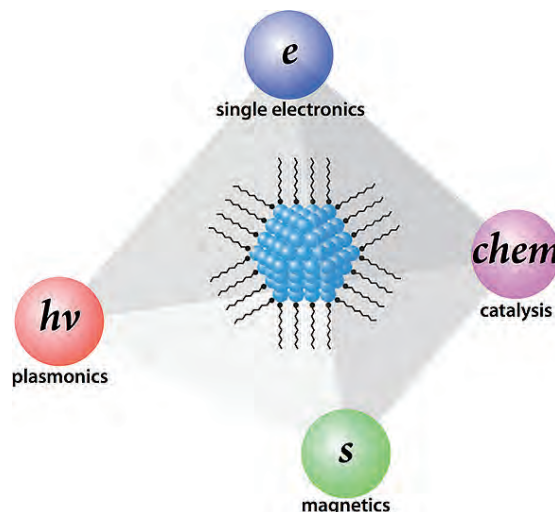
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## Scope of Research

We are focusing on the precise synthesis of inorganic nanoparticles by controlling the primary (size, shape, composition, *etc.*) and secondary (spatial arrangement) structures to tune properties such as electron confinement, carrier oscillation, spin, and catalysis. These high-quality inorganic nanoparticles are applied to both high-performance nanodevices (*e.g.*, single electron transistor, plasmon waveguide, and nanocomposite magnet) and photo-energy conversion materials (*e.g.*, overall water splitting and solar cell).

### KEYWORDS

Inorganic Nanoparticles    Single Electronics    Plasmonics  
Nanocomposite Magnet    Photocatalysts



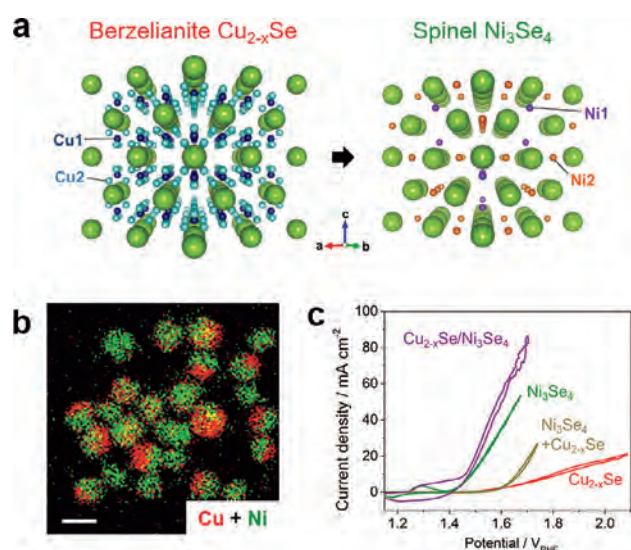
## Recent Selected Publications

Saruyama M.; Sato R.; Teranishi T., Transformations of Ionic Nanocrystals via Full and Partial Ion Exchange Reactions, *Acc. Chem. Res.*, **54**, 765-775 (2021).

Li Z.; Saruyama M.; Asaka T.; Tatetsu Y.; Teranishi T., Determinants of Crystal Structure Transformation of Ionic Nanocrystals in Cation Exchange Reactions, *Science*, **373**, 332-337 (2021).

## Novel Cu–Ni Bimetallic Selenide Nanocrystals Formed via Cation Exchange Reaction for Water Oxidation Catalysis

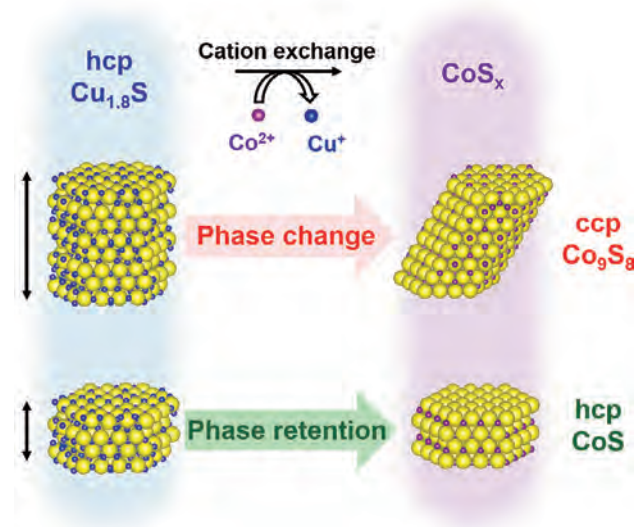
Controlling composition and nanostructure of electrocatalysts is important for dramatic improvement of the catalytic performance. The cation exchange reaction of nanocrystals (NCs) has been considered as facile way to provide unusual crystal structures and sophisticated functional nanostructures that cannot be achieved by conventional direct synthetic procedure. We demonstrated the cation exchange-derived formation of metastable spinel  $\text{Ni}_3\text{Se}_4$  NCs from berzelianite  $\text{Cu}_{2-x}\text{Se}$  NCs, and the formation of novel Cu–Ni selenide NCs as active oxygen evolution reaction (OER) catalysts. A rare spinel  $\text{Ni}_3\text{Se}_4$  phase was formed because the face-centered cubic (fcc)  $\text{Se}^{2-}$  sublattice in  $\text{Cu}_{2-x}\text{Se}$  NCs was kinetically retained throughout the cation exchange process (Figure 1a). Partial cation exchange reaction by tuning the Ni/Cu mole ratio led to the formation of Janus-type  $\text{Cu}_{2-x}\text{Se}/\text{Ni}_3\text{Se}_4$  NCs, exhibiting remarkable catalytic activities in the OER with small overpotentials of 230 mV at  $10 \text{ mA cm}^{-2}$  in 0.1 M KOH. These results imply that the cation exchange reaction could have huge potential for the creation of novel heterostructured NCs showing superior electrocatalytic performance.



**Figure 1.** (a) Retention of fcc Se lattice of  $\text{Cu}_{2-x}\text{Se}$  NCs during  $\text{Cu}^+$  to  $\text{Ni}^{2+}$  cation exchange. (b) STEM-EDS mapping of  $\text{Cu}_{2-x}\text{Se}/\text{Ni}_3\text{Se}_4$  NCs formed via partial cation exchange. (c) CVs of NCs in 0.1 M KOH.

## Revealing the Determinants of Crystal Structure Transformation of Ionic Nanocrystals in Cation Exchange Reactions

Ionic NCs have been widely utilized as photo-functional materials, whose properties are determined by the constituent elements and crystal structures. Cation exchange reaction can easily modulate the composition of ionic NCs to prepare a variety of functional nanomaterials. However, it has been believed that cation exchange hardly changes the crystal structure of parent ionic NCs. We applied the cation exchange reaction to hexagonal-prism-shaped  $\text{Cu}_{1.8}\text{S}$  NCs with 16 kinds of height and width using  $\text{Co}^{2+}$ . It was discovered that crystal system of resultant  $\text{CoS}_x$  NCs depends on the height of parent  $\text{Cu}_{1.8}\text{S}$  NCs, in which the original hexagonal-close-packed (hcp) crystal system of  $\text{Cu}_{1.8}\text{S}$  NCs with thicker or thinner than about 10 nm yielded cubic-close-packed (ccp)  $\text{Co}_9\text{S}_8$  or hcp  $\text{CoS}$  NCs, respectively (Figure 2). The ab-initio calculation revealed the surface energy of side surface is larger than that of basal plane in hcp  $\text{CoS}$ , suggesting unfavored large side surface area of thick hcp  $\text{CoS}$  NCs induced the phase transformation into more stable ccp  $\text{Co}_9\text{S}_8$ . Other incoming cations ( $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ ) modulated the phase transformation trend in cation exchange reactions by various means, such as volume, thermodynamic stability, and coordination environment. This discovery could lead to the phase control of ionic NCs under mild condition, which enables the synthesis of unexplored functional ionic nanomaterials.



**Figure 2.** Height of hexagonal-prism  $\text{Cu}_{1.8}\text{S}$  NCs determines the crystal structure of products after  $\text{Co}^{2+}$  cation exchange.