

# 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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\*New Research Field  
Development Project

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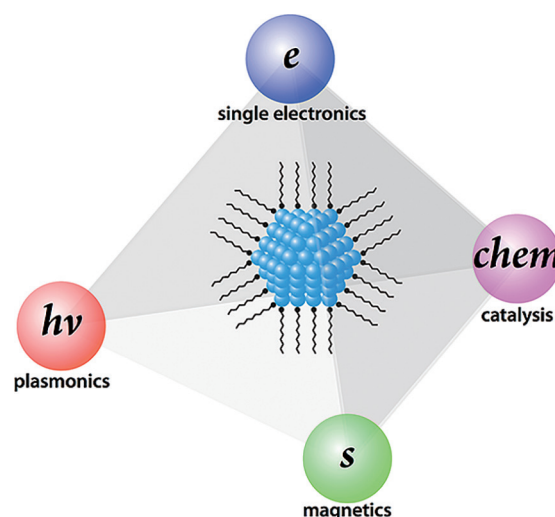
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## Scope of Research

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



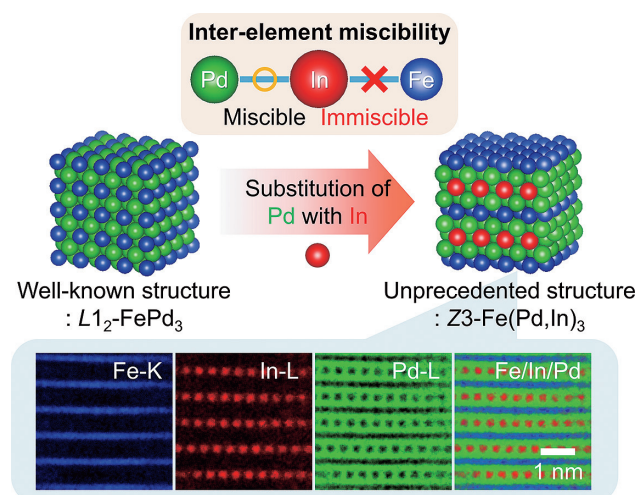
## Recent Selected Publications

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).

## Inter-Element Miscibility Driven Stabilization of Ordered Pseudo-Binary Alloy

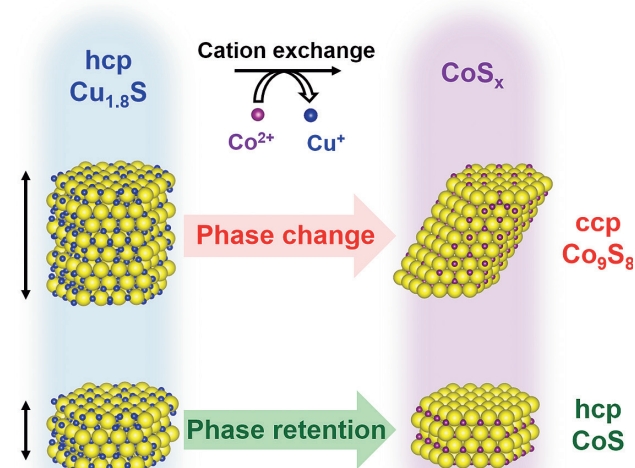
The crystal structure is a crucial factor for determining the physical and chemical properties, which indicates that an exploration of new-type crystal structures can give us a chance for the development of well-known properties or the discovery of new functions. An infinite number of crystal structures in a multicomponent alloy with a specific atomic ratio can be geometrically possible, although only thermodynamically-stable phases can be formed. For instance, in the case of the  $\text{FePd}_3$  alloy system, only  $L1_2$  ( $\text{Cu}_3\text{Au}$ -type) phase and  $A1$  ( $fcc$ -type solid-solution) phase have been experimentally obtained. Therefore, a synthetic strategy of stabilizing new-type crystal structures is deserved. Here, we experimentally showed the first example of a layer-structured pseudo-binary alloy, theoretically called  $Z3\text{-FePd}_3$ . This  $Z3$  structure is achieved by adding a small amount of  $\text{In}$ , which is immiscible with  $\text{Fe}$  but miscible with  $\text{Pd}$  and consists of an alternate  $L1_0$  ( $\text{CuAu}$ -type)- $\text{PdFePd}$  trilayer and  $\text{Pd-In}$  ordered alloy monolayer along the  $c$  axis (Figure 1). First-principles calculations strongly support that the specific inter-element miscibility of  $\text{In}$  atoms stabilizes the thermodynamically-unstable  $Z3\text{-FePd}_3$  phase without significantly changing the original density of states of the  $Z3\text{-FePd}_3$  phase. Our results demonstrate that the specific inter-element miscibility can switch stable structures and manipulate the material nature with a slight composition change.



**Figure 1.** (a) Model of the phase change from well-known ( $L1_2$ ) to unprecedented ( $Z3$ ) structures driven by the specific inter-element miscibility of  $\text{In}$  atoms and atomic-resolution energy dispersive X-ray spectroscopy (EDX) elemental maps of  $Z3$ -type  $\text{Fe}(\text{Pd},\text{In})_3$ .

## 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.