

# Division of Synthetic Chemistry – Advanced Inorganic Synthesis –

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



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## Scope of Research

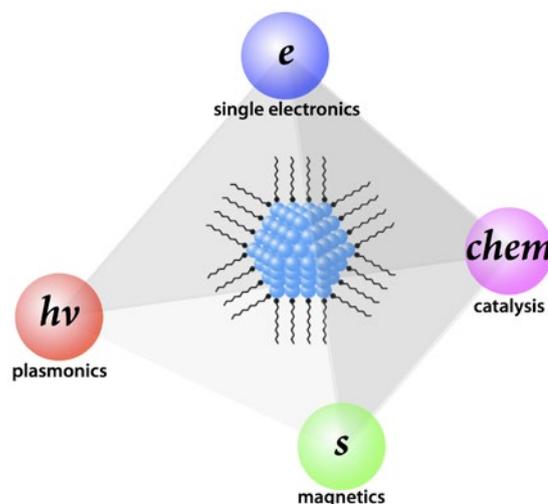
We are focusing on the precise synthesis of inorganic nanoparticles by controlling the primary (size, shape, composition, etc.) and secondary (spatial arrangement) structures to tune properties such as electron confinement, carrier oscillation, spin, and catalysis. These high-quality inorganic nanoparticles 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  
Nanocomposite Magnet

Single Electronics  
Photocatalysts

Plasmonics



## Selected Publications

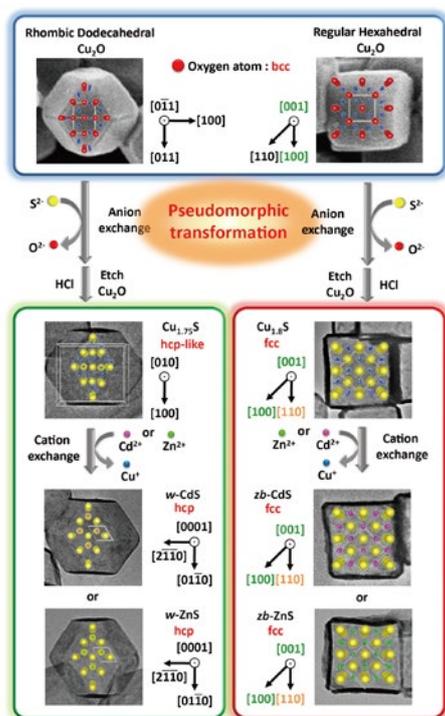
Sakamoto, M.; Inoue, K.; Okano, M.; Saruyama, M.; Kim, S.; So, Y.-G.; Kimoto, K.; Kanemitsu, Y.; Teranishi, T., Light-Stimulated Carrier Dynamics of CuInS<sub>2</sub>/CdS Heterotetrapod Nanocrystals, *Nanoscale*, **8**, 9517-9520 (2016).

Wu, H.-L.; Sato, R.; Yamaguchi, A.; Kimura, M.; Haruta, M.; Kurata, H.; Teranishi, T., Formation of Pseudomorphic Nanocages from Cu<sub>2</sub>O Nanocrystals through Anion Exchange Reactions, *Science*, **351**, 1306-1310 (2016).

## Nano-pseudomorphic Chemistry: Anionic Frameworks Dictate Crystal Systems in Sequential Ion Exchange Reactions

Ionic crystals have been widely used as photo-functional materials such as photocatalysts and photoelectric conversion materials, which are determined by the constituent elements, morphologies, and crystal structures. Because the stable crystal structures of the ionic crystals follow their phase diagrams, it has been difficult to chemically synthesize the high-temperature stable phases. In contrast to the bulk form, chemical conversion of ionic nanocrystals (NCs) via ion exchange reactions can overcome the difficulties associated with controlling the size, shape, chemical composition, and crystal structure in conventional syntheses. In our research, we discovered that the retained shape of the parent-NCs in sequential ion exchange reactions provided an opportunity to obtain non-equilibrium unique structures and even new structures of ionic NCs, these morphologically retained products being known as “pseudomorphs”.

We investigated the crystal structures of the pseudomorphic nanocages, which were formed by the anion exchange ( $O^{2-} \rightarrow S^{2-}$ ) of hexahedral  $Cu_2O$  NCs



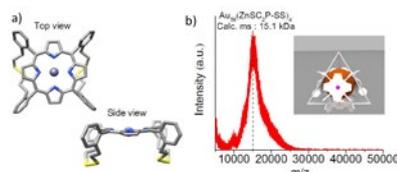
**Figure 1.** (Left hand) The rhombic dodecahedral  $Cu_{1.75}S$  nanocages with a triclinic phase are formed by the anion exchange ( $O^{2-} \rightarrow S^{2-}$ ) and the subsequent etching of rhombic dodecahedral  $Cu_2O$  NCs enclosed with  $\{110\}$  planes at ambient conditions. Further cation exchange ( $Cu^+ \rightarrow Cd^{2+}, Zn^{2+}$ ) gives the hexahedral CdS or ZnS with a hexagonal phase. (Right hand) The hexahedral  $Cu_{1.8}S$  nanocages with a cubic phase are formed by the anion exchange ( $O^{2-} \rightarrow S^{2-}$ ) and the subsequent etching of hexahedral  $Cu_2O$  NCs enclosed with  $\{100\}$  planes at ambient conditions. Further cation exchange ( $Cu^+ \rightarrow Cd^{2+}, Zn^{2+}$ ) gives the hexahedral CdS or ZnS with a cubic phase.

enclosed with  $\{100\}$  planes and rhombic dodecahedral  $Cu_2O$  NCs enclosed with  $\{110\}$  planes at ambient conditions. It was discovered that the shape-dependent anionic framework (surface anion sublattice and stacking pattern) of  $Cu_2O$  NCs determined the crystal system of anion-exchanged products (Figure 1). In other words, the cubic system can transform into not only the cubic system but also the triclinic and hexagonal systems. Furthermore, we found that the resulting nanocages have the multiply-twinned structure. A high-temperature stable phase such as wurtzite ZnS ( $> 1020$  °C) was also obtained with this method at ambient conditions. We envisage that this pseudomorphic transformation method could be applicable to a number of other ionic NCs and thin films at ambient temperatures to find the novel properties and functions.

## Porphyry Derivative-Protected Gold Cluster with a Pseudo-Tetrahedral Shape

The shape of a nanomaterial plays an important role in controlling the packing arrangement and properties of the assembly that it forms. In the case of metal clusters, the shape of the metal core is veiled by a flexible organic ligand with a comparable size to that of the metal core. Here, we controlled the overall shape of ligand-protected gold clusters (AuCs) using a rigid, planar molecule as a ligand by following a simple geometrical relationship between an inscribed sphere and a circumscribed polyhedron.

For the rigid, planar molecule, we synthesized a new porphyrin derivative that could strongly attach to the AuCs in a face-coordination fashion (Figure 2a). We synthesized AuCs face-coordinated by four  $ZnSC_2P$ -SS ligands with a core size of  $1.0 \pm 0.2$  nm. Structural assignment using MALDI-TOF MS, ICP-AES, and UV-vis-NIR absorption spectra indicated that the  $ZnSC_2P$ -SS/AuCs have a pseudo-tetrahedral shape (Figure 2b). Thus, we have demonstrated that a simple geometrical relationship between an inscribed sphere and a circumscribed polyhedron can be applied to control the shape (symmetry) of metal clusters with a size of less than 2 nm. The present results pave the way to a new concept for controlling the pseudo-symmetry of ligand-protected metal clusters.



**Figure 2.** (a) single X-ray crystal structures of  $SC_2P$  and  $ZnSC_2P$ -SS from top view and side view. Hydrogen atoms have been omitted for clarity. (b) MALDI-TOF spectrum of  $ZnSC_2P$ -SS/AuCs. Inset is schematic illustration of the  $ZnSC_2P$ -SS/AuCs with pseudo-tetrahedron shape.