

# 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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## 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

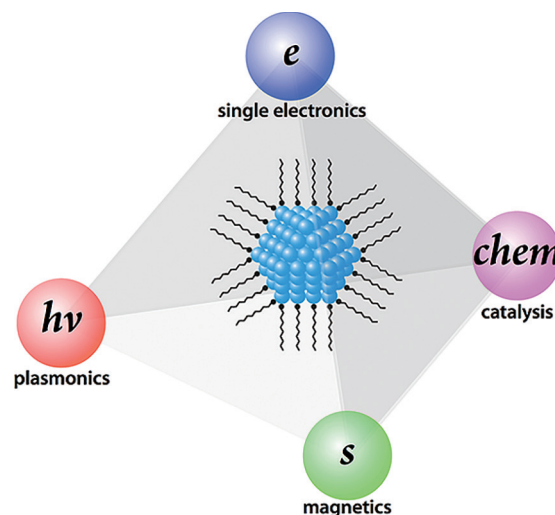
Inorganic Nanomaterials

Quantum Dots

Plasmonics

Oxidation Reduction Reactions

Photocatalysts



## Recent Selected Publications

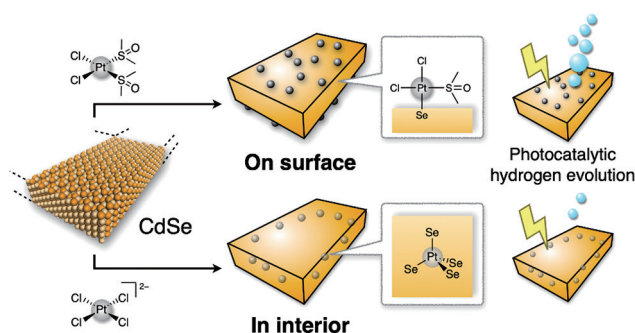
Endo E.; Saruyama M.; Teranishi T., Location-Selective Immobilisation of Single-Atom Catalysts on the Surface or within the Interior of Ionic Nanocrystals Using Coordination Chemistry, *Nat. Commun.*, **14**, 4241 (2023).

Chiga Y.; Takahata R.; Suzuki W.; Mizuhata Y.; Tokitoh N.; Teranishi T., Isomer-Selective Conversion of Au Clusters by Au(I)-Thiolate Insertion. *Inorg. Chem.*, **62**, 10049-10053 (2023).

Suzuki W.; Takahata R.; Chiga Y.; Kikkawa S.; Yamazoe S.; Mizuhata Y.; Tokitoh N.; Teranishi T., Control over Ligand-Exchange Positions of Thiolate-Protected Gold Nanoclusters Using Steric Repulsion of Protecting Ligands, *J. Am. Chem. Soc.*, **144**, 12310-12320 (2022).

## Location-Selective Immobilization of Single-Atom Catalysts on the Surface or Within the Interior of Ionic Nanocrystals Using Coordination Chemistry

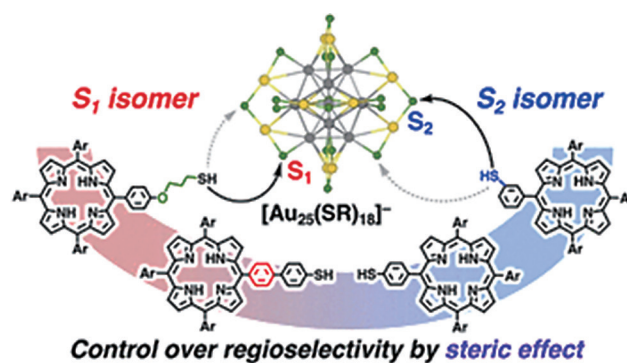
Single-atom catalysts dispersed on support materials show excellent heterogeneous catalytic properties that can be tuned using the interactions between the single atoms and the support. Such interactions depend on whether the single atoms are located on the surface or within the interior of the support. However, little is known about immobilising single atoms on the surface or within the interior of supports deliberately and selectively. Herein, such location-selective placement of single atoms is achieved through the choice of metal complex precursor, solvent, and work-up procedure. (Figure 1) Using CdSe nanoplatelets as a support, a  $\text{cis-[PtCl}_2(\text{SO}(\text{CH}_3)_2)_2]$  precursor in an aprotic solvent exclusively attaches single Pt atoms on the surface of the support. In contrast, a  $[\text{PtCl}_4]_2^-$  precursor in a protic solvent followed by amine treatment places 60% of the single Pt atoms inside the support by cation substitution. The surface-adsorbed single Pt atoms show higher stability in photocatalytic hydrogen evolution than the substituted ones, and the preclusion of substitution as internal Pt maximises the activity. Thus, this study provides a viable strategy for the structurally precise synthesis and design of single-atom catalysts.



**Figure 1.** Location-selective immobilization of Pt single atoms on the surface or within the interior of CdSe nanocrystals and its effects on photocatalytic hydrogen evolution.

## Control over Ligand-Exchange Positions of Thiolate-Protected Gold Nanoclusters Using Steric Repulsion of Protecting Ligands

Organic ligands on gold nanoclusters play important roles in regulating the structures of gold cores. However, the impact of the number and positions of the protecting ligands on gold-core structures remains unclear. We isolated thiolate-protected  $\text{Au}_{25}$  cluster anions,  $[\text{Au}_{25}(\text{SC}_2\text{Ph})_{17}(\text{Por})_1]^-$  and  $[\text{Au}_{25}(\text{SC}_2\text{Ph})_{16}(\text{Por})_2]^-$  ( $\text{SC}_2\text{Ph}$  = 2-phenylethanethiolate), obtained by ligand exchange of  $[\text{Au}_{25}(\text{SC}_2\text{Ph})_{18}]^-$  with one or two porphyrin-thiolate (Por) ligands as mixtures of regioisomers. (Figure 2) The ratio of two regioisomers in  $[\text{Au}_{25}(\text{SC}_2\text{Ph})_{17}(\text{Por})_1]^-$  as measured by  $^1\text{H}$  NMR spectroscopy revealed that the selectivity could be controlled by the steric hindrance of the incoming thiols. Extended X-ray absorption fine structure studies of a series of porphyrin-coordinated gold nanoclusters clarified that the  $\text{Au}_{13}$  icosahedral core in the  $\text{Au}_{25}$  cluster was distorted through steric repulsion between porphyrin thiolates and phenylethanethiolates. This study reveals interesting insights into the importance of the steric structures of protecting ligands for control over core structures in gold nanoclusters.



**Figure 2.** Strategy for control over regioselectivity of  $[\text{Au}_{25}\text{SR}_{18}]^-$  by steric effect.