

# 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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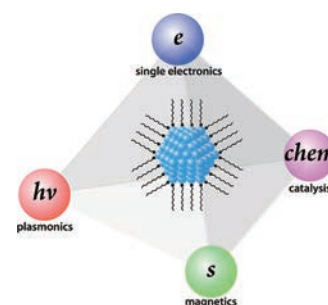
The National University of Ireland – Galway, Spain, 27 November–27 December

## 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



## Selected Publications

Eguchi, D.; Sakamoto, M.; Tanaka, D.; Okamoto, Y.; Teranishi, T., Porphyrin Derivative-Protected Gold Cluster with a Pseudotetrahedral Shape, *J. Phys. Chem. C*, **121**, 10760-10766 (2017).

Kim, S.; Nishino, T.; Saruyama, M.; Sakamoto, M.; Kobayashi, H.; Akiyama, S.; Yamada, T.; Domen, K.; Teranishi, T., Formation of Layer-by-Layer Assembled Cocatalyst Films of S<sup>2-</sup>-stabilized Ni<sub>3</sub>S<sub>4</sub> Nanoparticles for Electrochemical Hydrogen Evolution Reaction, *ChemNanoMat*, **3**, 764-771 (2017).

Eguchi, D.; Sakamoto, M.; Teranishi, T., Ligand Effect on the Catalytic Activity of Gold Clusters in the Electrochemical Hydrogen Evolution Reaction, *Chem. Sci.*, **9**, 261-265 (2018).

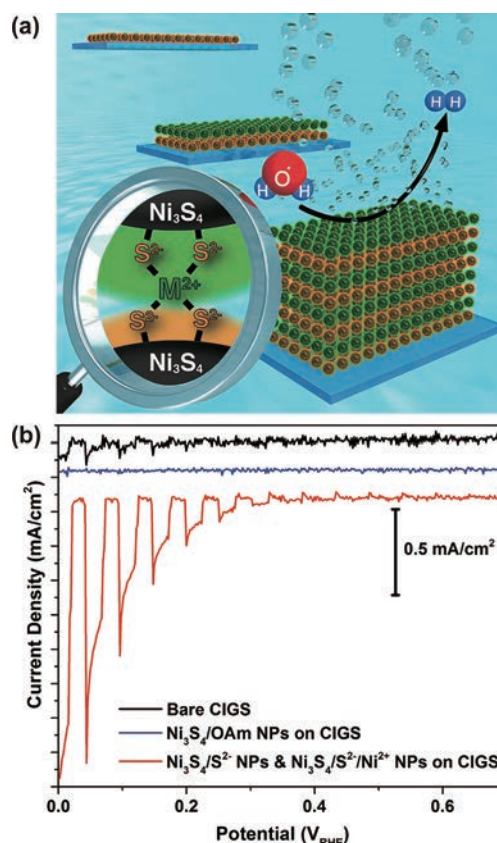
## Formation of Layer-by-Layer Assembled Cocatalyst Films of $S^{2-}$ -Stabilized $Ni_3S_4$ Nanoparticles for Hydrogen Evolution Reaction

Production of hydrogen fuel by electrolysis of water is a promising and sustainable solution to energy problems. In recent years, a number of metal sulfide have been identified as promising candidates for hydrogen evolution reaction (HER) electrocatalysts. Nanoparticle (NP) materials have advantages for fabrication of HER electrodes based on their large surface-to-volume ratios, however, surface organic ligands can hinder electron transfer both from the electrode to the NPs and from the NPs to protons. Recently, ligand-exchange methods have been developed, in which small inorganic ligands are used to replace the original organic ligands. Here, we report the layer-by-layer (LbL) assembly of  $S^{2-}$ -stabilized  $Ni_3S_4$  NPs ( $Ni_3S_4/S^{2-}$ ) and metal cation modified  $Ni_3S_4/S^{2-}$  ( $Ni_3S_4/S^{2-}/M^{2+}$  ( $M = Cd, Ni, Co,$  or  $Zn$ )) NPs to improve electron transfer and increase the electrochemically active surface area (Figure 1a). LbL film of  $Ni_3S_4/S^{2-}$  NPs showed much lower overpotential and higher stability than that of  $Ni_3S_4$  NPs protected by organic ligands. Additionally, this LbL assembly technique could be applied as a HER cocatalyst on the cathodic photocatalyst electrode,  $CdS/Cu(In,Ga)Se_2$ . The photocurrent was enhanced compared with that of organic ligands-stabilized  $Ni_3S_4$  NP-loaded and bare electrodes (Figure 1b). This LbL assembly process could be applicable to forming ligand-free and robust NP films for many types of photoelectrodes without deteriorating their intrinsic optical properties.

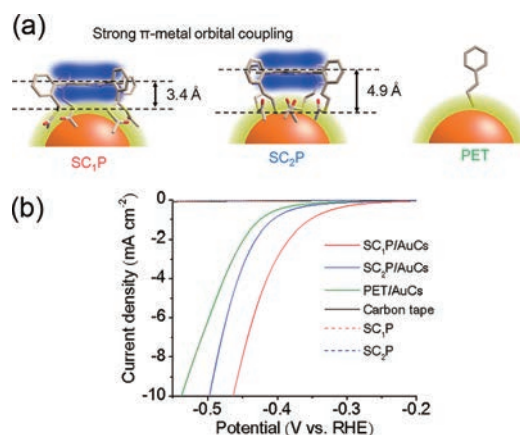
## Ligand Effect on the Catalytic Activity of Porphyrin Protected Gold Clusters in the Electrochemical Hydrogen Evolution Reaction

Metal clusters (MCs) are promising catalysts due to their unique quantized electronic structures and large surface-to-volume ratios. Because of their large surface-to-volume ratios, the electronic structures of MCs should be perturbed by organic ligands. Recently, it was found that the face-on coordination of porphyrin derivatives ( $SC_nP$ ,  $n = 1$  or  $2$ ) with AuCs caused a dramatic perturbation in the electronic structure of the  $SC_nP$ . Therefore, face-coordination of  $SC_nP$  with AuCs could strongly influence their catalytic activity. Here, we systematically studied the ligand effect of  $SC_nP$  on AuCs in the electrochemical hydrogen evolution reaction (Figure 2a), which is a key catalytic reaction for producing clean energy from inexhaustible water. AuCs with face-coordinated  $SC_1P$  show a 460% higher current density

at overpotential of 0.4 V compared with phenylethanethiol (PET)-protected AuCs (Figure 2b). The dramatic catalytic enhancement is attributed to charge migration from the porphyrin to the Au core. This ligand effect provides a novel strategy for enhancing the catalytic activity of MCs.



**Figure 1.** (a) Illustration of LbL assembly of  $Ni_3S_4/S^{2-}$  NPs on an electrode substrate. (b) Photocurrent density vs. potential plots of bare, organic ligand-protected  $Ni_3S_4$  NPs, and  $Ni_3S_4/S^{2-}$  NPs modified  $CdS/Cu(In,Ga)Se_2$  photoelectrodes.



**Figure 2.** (a) Illustration of coordination fashions of  $SC_nP$  and PET on Au surface. (b) HER polarization curves of each AuCs,  $SC_nP$ , and bare carbon paper in 0.5 M phosphate buffer solution (pH 6.7).