

学位論文の要約

題目 Development of Nickel-based Nanoparticle Catalysts toward Efficient Water Splitting
(高効率水分解のためのニッケル化合物ナノ粒子触媒の開発)

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序論

In recent decades, there has been a continuous need to replace fossil fuels with environmental-friendly and sustainable alternative sources of energy. One of the attractive solutions to replace fossil fuels would be the photoenergy conversion from sunlight to high-value-added chemicals like hydrogen gas by the photocatalytic reaction. These molecular fuels can be stored and consumed on demand using a light weight fuel cell device to efficiently generate electricity with few harmful byproducts. Though many materials are capable of photocatalytically producing hydrogen and oxygen, noble metal groups (Pt, Ir, and Ru) have been used as favorable electrocatalyst due to their high activities and chemical inertness. Recently, the Ni-based electrocatalysts gained attention for high activity due to similar chemical properties compared to Pt in same group number in periodic table. Although the Ni-based electrocatalyst system has showed low onset potential and overpotential for water splitting, they have practical limit associated with bulk like morphologies. The catalytic system based on nanocrystals is one of the promising methodologies owing to their large specific surface areas. In addition, homogeneous dispersion of catalyst nanocrystals in solvent can be used to modify the various electrodes and photocatalysts by simple deposition or coating methods. However, it remained challenging issue to synthesize uniformly structured nanocrystals with high electrocatalytic activity. In this thesis, the author has investigated selective synthesis of monodisperse nanoparticles (spinel Ni_3S_4 , heterostructured cubic-spinel $\text{Cu}_{2-x}\text{Se-Ni}_3\text{Se}_4$, spine Ni_3Se_4 , and phase-segregated $\text{NiP}_x@\text{FeP}_y\text{O}_z$ core@shell) and systematically demonstrated their hydrogen and oxygen evolution reaction.

In the first paper, the author describe the ligand exchange and layer-by-layer deposition method onto electrode for ligand-free nanoparticle (Ni_3S_4) electrocatalyst films for hydrogen evolution reaction in neutral condition. In this work, the author shows layer-by-layer assembly process could be applicable to forming ligand-free and robust nanoparticle films for many types of

photoelectrodes without deteriorating their optical properties. In the second paper, the author describes the possibility of synthesizing novel heterostructure ($\text{Cu}_{2-x}\text{Se-Ni}_3\text{Se}_4$), metastable crystal structure (Ni_3Se_4) by cation exchange reaction and their effective water oxidation properties in alkaline condition. In this work, the author shows possibility of our results for fabricating nanostructures with crystal phases that are not easily accessed by the direct chemical synthesis. In the third paper, the author describes the novel $\text{NiP}_x\text{@FeP}_y\text{O}_z$ nanoparticles without any post-treatment and in situ activation for effective water oxidation properties in alkaline conditions. In this work, the author shows possibility of phase-segregated structures could be transformed into homogeneous active phases, suggesting a new way to design efficient nanostructured catalysts.

Formation of Layer-by-Layer Assembled Cocatalyst Film of S^{2-} -Stabilized Ni_3S_4 Nanoparticles for Electrochemical Hydrogen Evolution Reaction

Metal sulfide nanoparticles are potential candidates for catalyst in water splitting system; however, their poor electrocatalytic activity, owing to the presence of surface ligands, is an obstacle to practical use in that system. In this work, the author selectively synthesizes oleylamine (OLAm)-stabilized Ni_3S_4 ($\text{Ni}_3\text{S}_4/\text{OLAm}$) nanoparticles by hot-injection method. The insulating ligands were exchanged with S^{2-} and loaded on electrodes by a layer-by-layer assembly method with several kinds of metal cation linkers (Cd^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+}). The enhanced catalytic properties were confirmed by electrochemical measurements. A layer-by-layer assembled film with Ni^{2+} as a linker (11 cycles) showed an overpotential of $555\text{ mV}@-4\text{ mA/cm}^2$ at pH 6.8 and a higher and stable current density for 12 h. The activation was attributed to a structural transformation of Ni_3S_4 into $\text{Ni}(\text{PO}_x)_y$, during the hydrogen evolution, which contributed to the high and stable (photo)current densities of the layer-by-layer assembled films. In addition, when this layer-by-layer assembly method was applied to a $\text{CdS}/\text{Cu}(\text{In,Ga})\text{Se}_2$ photocatalyst electrode, the resulting photoelectrode showed an enhanced photocurrent compared with that of the $\text{Ni}_3\text{S}_4/\text{OLAm}$ nanoparticles-spin coated and bare photoelectrodes. These results indicate the versatility of layer-by-layer assembly for fabrication of ligand-free nanoparticle electrocatalyst films.

First chemical synthesis of spinel Ni_3Se_4 and Janus $\text{Cu}_{2-x}\text{Se-Ni}_3\text{Se}_4$ nanocrystals with excellent catalytic activity for oxygen evolution reaction

The cation exchange reaction is an emerging area in nanocrystal research, because the substitution of original cations with different ones enables us to synthesize metastable nanocrystals that could not be accessible by one-pot synthesis. In this work, for the first time, the author has discovered that the

synthesis of monodisperse spinel Ni₃Se₄ nanocrystals using the cation exchange reaction. In this work, using cubic berzelianite Cu_{2-x}Se nanocrystals as a starting template, the author succeeded to replace Cu⁺ to Ni²⁺ and finely tune the molar ratio of Ni:Cu in nanocrystals. The important points of the work are as follows. Firstly, the metastable spinel Ni₃Se₄ is obtained by the cation exchange reaction, because both Cu_{2-x}Se and spinel Ni₃Se₄ contain face centered cubic Se anion sub-lattice, which makes the formation of spinel Ni₃Se₄ possible with retention of Se framework in Cu_{2-x}Se structure. Secondly, partially cation exchanged nanocrystals showed Janus type heterostructure composed of cubic Cu_{2-x}Se and spinel Ni₃Se₄ domains due to the large lattice mismatch and immiscibility of two phases. Thirdly, the Ni cation exchanged Cu_{2-x}Se nanocrystals showed large active sites and low charge transfer resistance, thus leading to efficient electrocatalytic activity. Especially, the heterostructure of Cu_{2-x}Se-Ni₃Se₄ nanocrystals exhibited a lower overpotential of 230 mV@mA/cm² in 0.1 M KOH than Cu_{2-x}Se (568 mV@mA/cm²) and Ni₃Se₄ nanocrystals (250 mV@mA/cm²). Our work not only provides the synthetic pathways to the novel phased nanocrystals but also expands to the modulating method for constructing high-performance energy conversion catalyst.

Phase-segregated NiP_x@FeP_yO_z core@shell nanoparticles: ready-to-use nanocatalysts for electro- and photo-catalytic water oxidation

The high overpotential of the oxygen evolution reaction is a critical issue to be overcome to realize efficient overall water splitting and enable hydrogen generation powered by sunlight. Homogeneous and stable nanoparticles dispersed in solvents are useful as both electrocatalysts and cocatalysts of photocatalysts for the electro- and photo-catalytic oxygen evolution reaction, respectively, through their adsorption on various electrode substrates. In this work, phase-segregated NiP_x@FeP_yO_z core@shell nanoparticles are selectively synthesized by the reaction of Fe(CO)₅ with amorphous NiP_x seed-nanoparticles. The NiP_x@FeP_yO_z nanoparticles on conductive substrates exhibit higher electrocatalytic activity in the oxygen evolution reaction than those of other metal phosphide-based catalysts. The NiP_x@FeP_yO_z nanoparticles can also be used as a cocatalyst of an anodic BiVO₄ photocatalyst to boost the photocatalytic water oxidation reaction. The excellent catalytic activity and high stability of the NiP_x@FeP_yO_z nanoparticles without any post-treatment are derived from in situ activation through both the structural transformation of NiP_x@FeP_yO_z into mixed hydroxide species, (Ni, Fe)O_xH_y, and the spontaneous removal of the insulating organic ligands from nanoparticles to form a smooth and robust (Ni, Fe)O_xH_y substrate heterointerface during the oxygen evolution reaction.