学位論文の要約

題目

Synthesis of Solid-Solution Alloy Nanoparticles and Investigation of their Electrocatalytic Properties

（固溶体ナノ粒子の合成及び電極触媒特性の研究）

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序論

Solid-solution alloy nanoparticles (NPs) have widely been studied because they show synergetic properties derived from each constituent metal and are promising to be used in electrocatalytic clean energy conversion. However, as it stands now, we cannot always obtain solid-solution alloys with any kind of metal combination because a lot of metal combinations are immiscible in bulk states. It is still challenging to synthesis the solid-solution alloy NPs, especially for which have a large gap of reduction potential between the constituent metals because concurrent reduction of metal ions is the key point for the syntheses of solid-solution alloy NPs. In addition, the functional properties of the solid-solution alloy NPs are determined by their size, shape, composition and crystal structure. Up to now, the size, shape and composition has extensively been studied for controlling the property of the solid-solution alloy NPs. While, the crystal structure is rarely used to tune the property of the solid-solution alloy NPs, because the crystal structure control for solid-solution alloy NPs is unavailable. Therefore, the purpose of this thesis is to create novel immiscible solid-solution alloy NPs and control the crystal structure of the alloy NPs and further to investigate their electrocatalytic performance.

1. Solid-Solution Alloy Nanoparticles of the Combination of Immiscible Au and Ru with Large Gap of Reduction Potential and their Enhanced Performance for Oxygen Evolution Reaction

We report on novel solid-solution alloy nanoparticles (NPs) of Au and Ru over the whole composition range, although Au and Ru are a totally immiscible couple of elements in bulk state and have the largest gap of reduction potentials in noble metals. Powder X-ray diffraction, scanning transmission electron microscopy, and energy-dispersive X-ray measurements demonstrated that Au and Ru atoms are homogenously distributed in the alloy NPs. We investigate the catalytic performance of Au_xRu_{1-x} NPs for oxygen evolution reaction, for which Ru is well known as one of the best monometallic catalysts, and find that even only 10% Au in the alloy could greatly enhance the catalytic performance.

2. Selective Control of fcc and hcp Crystal Structures in Au–Ru Solid-Solution Alloy Nanoparticles through Chemical Reduction Method

We propose a new approach for the selective control of the crystal structure in solid-solution alloys by using a chemical reduction method. By precisely tuning the reduction speed of the metal precursors, we succeeded in selectively synthesizing face-centered cubic (fcc) and hexagonal close-packed (hcp) AuRu solid-solution alloy nanoparticles (NPs) at a Au:Ru ratio of 1:3. The structures of the obtained NPs were confirmed by using synchrotron powder X-ray diffraction analysis, scanning transmission electron microscopy (STEM), energy-dispersive X-ray measurements and atomic resolution STEM. In addition, the mechanism of crystal structure control was confirmed by using the results of UV-Vis spectral and electrochemical analyses.

3. Crystal Structure-Dependent Thermal Stability and Catalytic Performance of $AuRu_3$ Solid-Solution Alloy Nanoparticles

The influence of the crystal structure of $AuRu_3$ alloy nanoparticles (NPs) on their thermal stability was investigated by using in situ synchrotron PXRD analysis. The hexagonal close-packed (hcp)-$AuRu_3$ alloy NPs show better thermal stability than the face-centered cubic (fcc)-$AuRu_3$ alloy NPs. The influence of the crystal structure on the catalytic performance of $AuRu_3$ alloy NPs was investigated through the oxygen evolution reaction. Both fcc- and hcp-$AuRu_3$ alloy NPs show onset potentials comparable to Ru NPs. However, the hcp alloy NPs show higher durability than the fcc alloy NPs.