【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： Nanoscale Element Replacement Science: Structural Transformation of Nanocrystalline Phases and Development of Novel Functions

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Keyword：Nanoparticle-related Chemistry, Colloid, Material Conversion and Catalyst, Energy Conversion Materials

【Purpose and Background of the Research】

Noble metal nanoparticles (NPs) are excellent functional materials based on the band structures that the d band centers are a few eV lower than the Fermi levels. Therefore, it seems difficult to replace the noble metal NPs with other NPs.

In this study, a series of novel NPs that surpass the performance of noble metal NPs will be generated from theoretical and experimental points of view as follows.

(1) The electronic structures of NPs are largely modulated by the introduction of p-block elements into d-block metal NPs and the alloying by element replacement (galvanic replacement) with base metal ions to achieve the superior physical and chemical properties.

(2) The crystal and electronic structures are modulated by the partial element replacement (ion exchange) to form the ionic crystalline heterostructured NPs, which can convert the whole near infrared light energy.

Through these studies, novel material science called "nanoscale element replacement science" on the basis of the new concept "ground-state electronic structure modulation" will be developed.

【Research Methods】

In this study, two kinds of novel NPs, unprecedented metal NPs and ionic crystalline heterostructured NPs, are designed and synthesized to achieve the superior properties, compared with the noble metal NPs (Fig. 1).

• Synthesis and novel functions of metal compound NPs and unprecedented alloy NPs

A series of metal compound NPs composed of d-block metals and p-block elements are converted into the unprecedented alloy NPs by the pseudo-galvanic replacement of p-block elements with base metal ions. Then, novel physical and chemical properties of these NPs based on the ground-state electronic structure modulation are developed.

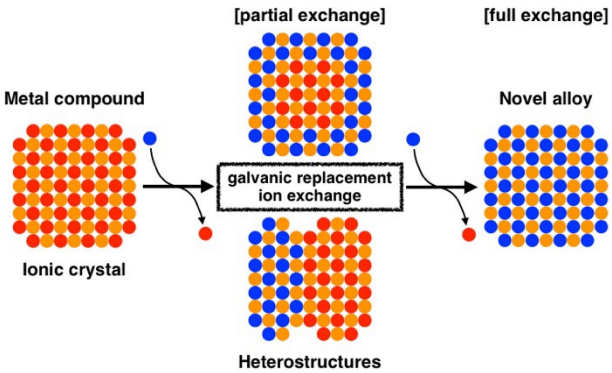

Fig. 1　Formation of novel alloy NPs and heterostructured NPs by using element replacement reactions

• Synthesis of ionic crystalline heterostructured NPs for near-infrared light energy conversion

Ionic crystalline heterostructured NPs are synthesized by ion exchange of heavily doped semiconductor NPs ($Cu_{2-x}S$, ITO, etc.) exhibiting localized surface plasmon resonance in near-infrared region, and used as near-infrared light energy conversion materials.

【Expected Research Achievements and Scientific Significance】

If the crystal structures and electronic structures of inorganic crystal phases could be freely modulated by simple element replacement reactions, rare noble metals would be completely replaced. For example, if the Pt NPs used in the polymer electrolyte fuel cell could be replaced with NiP_x NPs having comparable catalytic ability, the cost of the catalysts would be simply reduced to 1/3000 or less. In addition, if the rod-like Au NPs, which absorb near-infrared light, could be substituted for heavily-doped semiconductor NPs, whole near-infrared light energy would be utilized, which is a great contribution to energy problems.

【Publications Relevant to the Project】

• Z. Lian, T. Teranishi et al., "Plasmonic p-n Junction for Infrared Light to Chemical Energy Conversion", *J. Am. Chem. Soc.*, **141**, 2446–2450 (2019).
• H.-L. Wu, T. Teranishi et al., "Formation of Pseudomorphic Nanocages from Cu_2O Nanocrystals through Anion Exchange Reactions", *Science*, **351**, 1306–1310 (2016).

【Term of Project】

FY2019-2023

【Budget Allocation】

155,100 Thousand Yen

【Homepage Address and Other Contact Information】

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