

( 続紙 1 )

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論文題目	Transformative Inorganic Nanocrystals during Cation Exchange Reaction (陽イオン交換反応で変態可能な無機ナノ結晶)		
(論文内容の要旨)			
<p>Inorganic colloidal nanocrystals (NCs) are usually defined as the nanometer-sized (1–100 nm) inorganic particles coated with surfactants. The fine-tuning of size, shape, composition, phase, and surfactants can control the electric, optical, magnetic, and chemical properties of colloidal NCs. These features make colloidal NCs attractive and promising building blocks for advanced materials and devices, which are not achieved by the bulk counterparts. Tremendous efforts have been made to develop versatile synthesis methods of colloidal NCs based on chemistry. However, the synthesis of NCs with desired size, shape, composition and crystal structure is still a significant challenge. Access to the sophisticated nanoscale structures is essential to develop highly functional colloidal NCs. Besides the direct chemical synthetic methods, various strategies have been developed to prepare colloidal NCs with complicated structures. Post-synthetic treatment of NCs is the effective methodology, such as ion exchange reaction, galvanic replacement, pressure-induced transformation, and temperature-induced phase transformation. Among them, ion exchange reaction has been widely regarded as a facile and efficient way to obtain well-designed NCs to build novel electronic, magnetic, and photonic devices. Objectives of this doctoral thesis are to study the mechanism of crystal structure transformation and morphology evolution process of ionic NCs during the cation exchange reaction and develop the novel environmentally-friendly cocatalyst for photocatalytic overall water splitting.</p> <p><b>Chapter 2. Crystal Structure Transformation of Ionic Nanocrystals in Cation Exchange Reactions</b></p> <p>Ion exchange reactions are a promising route for overcoming current limits imposed by direct synthetic routes to NCs and for increasing the library of available crystal structures. Generally, incoming cations expel the original cations and preserve the robust anion sublattice because the smaller cations diffuse much faster than larger anions and the overall morphology and crystal system of a NC are retained. In particular, crystal structure transformations derived from anion sublattice deformation through cation exchange without changing the overall host NC morphology are rare. In chapter 2, determinants of the crystal structure transformation of ionic NCs during the cation exchange reaction was investigated. It was discovered the height</p>			

of hexagonal-prism  $\text{Cu}_{1.8}\text{S}$  NCs with a distorted hcp  $\text{S}^{2-}$  sublattice determines the final crystal phase of the cation-exchanged products with  $\text{Co}^{2+}$  ( $\text{CoS}$  with hcp  $\text{S}^{2-}$ , and/or  $\text{Co}_9\text{S}_8$  with ccp  $\text{S}^{2-}$ ) through chemical synthesis and computational modeling. Thermodynamic instability of exposed planes drives reconstruction of anion frameworks under mild reaction conditions. Other incoming cations ( $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ ) modulate crystal structure transformation during the cation exchange reactions by various factors, such as volume, thermodynamic stability, and coordination environment.

### **Chapter 3. Morphological Evolution of $\text{Cu}_{1.8}\text{S}$ -MnS Heterostructured Nanoplatelets during Cations Exchange Reaction**

It has been believed that the cation exchange reactions hardly transform the shape of host NCs because the original anion framework is quite stable. Some studies reported the cation exchange-induced shape transformation of host ionic NCs, but the shape transformation process and the stability of the atypical intermediates during the cation exchange reaction have not yet thoroughly investigated. In chapter 3, a unique morphological evolution process of shape memory behavior during the cation exchange of  $\text{Cu}_{1.8}\text{S}$  NPLs with  $\text{Mn}^{2+}$  was demonstrated. The hexagonal  $\text{Cu}_{1.8}\text{S}$  NPLs evolved to incomplete bow-shaped  $\text{Cu}_{1.8}\text{S}$ -MnS NPLs and then grew back to complete hexagonal MnS NPLs. We found the  $\text{Cl}^-$  from the Mn precursor plays an important role in the decomposition of  $\text{Cu}_{1.8}\text{S}$ . This shape memory behavior was also proved for the Mn cation exchange with rod-shaped and spherical host  $\text{Cu}_{1.8}\text{S}$  NCs. This discovery gives a new aspect to the morphological change during the cation exchange reaction and paves a way to synthesize more complicated heterostructured NCs.

### **Chapter 4. Self-activated Rh-Zr Mixed Oxide as a Nonhazardous Cocatalyst for Photocatalytic Hydrogen Evolution**

Platinum group metals are widely used for the hydrogen evolution reaction; they reduce  $\text{H}_2\text{O}$  because of the metals' high activity and stability. However, these metals also catalyze backward reactions, such as  $\text{O}_2$  photoreduction and  $\text{H}_2\text{O}$  formation, from evolved  $\text{H}_2$  and  $\text{O}_2$ . In chapter 4,  $\text{RhZrO}_x$  was found to be an effective, robust and environmentally friendly cocatalyst. Zr and Rh precursors with a certain ratio ( $\text{Zr/Rh} = 5 \text{ wt/wt}\%$ ) formed  $\text{RhZrO}_x$  cocatalyst particles on STOA exhibited a higher photocatalytic water-splitting activity ( $31\times$ ) than a  $\text{RhO}_x$  cocatalyst. The dissociation of  $\text{Cl}^-$  ions from preformed Rh-Cl-Zr-O solid led to formation of the active phase of  $\text{RhZrO}_x$ . Additional  $\text{CoO}_x$  loading as an oxygen evolution cocatalyst further improved the activity by 120%, resulting in an apparent quantum yield of 33 ( $\pm 4$ )% at 365 nm and a long durability of 60 h. Our discovery could help scale up photocatalytic hydrogen production.

(続紙 2)

(論文審査の結果の要旨)

イオン交換反応は、イオン性ナノ結晶の結晶構造ライブラリを増やすための有望な手法である。陽イオンのイオン半径は陰イオンよりはるかに小さいため、一般に、陽イオン交換時の陰イオン副格子変形に由来する結晶構造変態はまれである。李展召氏は、陽イオン交換反応中のイオン性ナノ結晶の結晶構造変態の決定要因を検討した結果、歪んだ hcp  $S^{2-}$  副格子をもつ六角柱  $Cu_{1.8}S$  ナノ結晶の高さが、 $Co^{2+}$  とのカチオン交換生成物の最終結晶相 (hcp  $S^{2-}$  をもつ  $CoS$ 、または、ccp  $S^{2-}$  をもつ  $Co_9S_8$ ) を決定することを発見し、露出結晶面の熱力学的不安定性が、穏和な反応条件下で陰イオンフレームワークの再構築を促進することが原因であることを明らかにした。他の陽イオン ( $Mn^{2+}$ 、 $Zn^{2+}$ 、 $Ni^{2+}$ ) では、体積、熱力学的安定性、配位環境などのさまざまな要因によって、陽イオン交換生成物の結晶構造変換が決まることも実証した。

イオン性ナノ結晶の陰イオン骨格は非常に安定なため、陽イオン交換反応は親ナノ結晶の形状をほとんど変化させないと考えられてきた。李展召氏は、六角柱状  $Cu_{1.8}S$  ナノ結晶と  $Mn^{2+}$  の陽イオン交換において、形状記憶挙動を示すユニークな形態変化プロセスがあることを発見した。六角柱状  $Cu_{1.8}S$  ナノ結晶は、不完全な弓形の  $Cu_{1.8}S$ - $MnS$  ナノ結晶に変形後、完全な六角柱状  $MnS$  ナノ結晶に構造が回復することが分かり、 $Mn$  前駆体の塩化物イオンが  $Cu_{1.8}S$  の分解に重要な役割を果たしていることを明らかにした。この形状記憶挙動は、ロッド状および球状の宿主  $Cu_{1.8}S$  ナノ結晶との  $Mn^{2+}$  陽イオン交換でも証明された。この発見は、陽イオン交換反応における形態変化に新たな観点を与え、本手法のより複雑なヘテロ構造ナノ結晶合成への展開が期待される。

よって、本論文は博士（理学）の学位論文として価値あるものと認める。また、令和 3 年 1 1 月 1 2 日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。

なお、本論文は、京都大学学位規程第 1 4 条第 2 項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める。

要旨公表可能日： \_\_\_\_\_ 年 \_\_\_\_\_ 月 \_\_\_\_\_ 日以降