

学位論文の要約

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)

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序論

Colloidal nanocrystals have received increasing attention because the controllable physical and optical properties of a wide range of nanocrystals of fine-tune composition, size, and shape. Cation exchange reaction of colloidal nanocrystals is a promising route for overcoming current limits imposed by direct synthetic routes to nanocrystals and for increasing the library of available crystal structures and morphologies. By using the cation exchange reaction, the fine-tuning of the phase and shape of nanocrystals can be synthesized under mild conditions, which can not only overcome the limit of structures of nanocrystals in the conventional bottom-up approaches, but also adjust the physical and optical properties of the HNCs for advanced optoelectronic and catalytic applications. Moreover, photocatalytic water-splitting is a promising technology for sustainable hydrogen. Developing efficient and non-hazardous cocatalysts for existing best Al-doped SrTiO₃ photocatalyst is desirable for improving photocatalytic water-splitting activity.

Determinants of crystal structure transformation of ionic nanocrystals in cation exchange reactions

Changes in the crystal system of an ionic nanocrystal during a cation exchange reaction are unusual, and yet remain to be systematically investigated. Here, it was discovered that the height of hexagonal-prism roxbyite Cu_{1.8}S nanocrystals with a distorted hexagonal close-packed sulfide anion (S²⁻) sublattice determines the final crystal phase of the cation-exchanged products with Co²⁺ [wurtzite cobalt sulfide (CoS) with hexagonal close-packed S²⁻ and/or cobalt pentlandite (Co₉S₈) with ccp S²⁻]. Computational modeling demonstrated thermodynamic instability of exposed planes drives reconstruction of anion frameworks under mild reaction conditions. Other incoming cations (Mn²⁺, Zn²⁺, and Ni²⁺) modulate crystal structure

transformation during cation exchange reactions by various means, such as volume, thermodynamic stability, and coordination environment.

Morphological evolution of Cu_{1.8}S-MnS heterostructured nanoplatelets during Mn cations exchange with Cu_{1.8}S nanoplatelets

Shape transformation during a cation exchange reaction are rare and the stability of the atypical intermediates have not yet systematically and thoroughly investigated. Here, an unexpected shape change of ionic NCs was discovered during the cation exchange of Cu_{1.8}S nanoplatelets with Mn²⁺. The hexagonal-shaped Cu_{1.8}S nanoplatelets evolved to bow-shaped Cu_{1.8}S-MnS nanoplatelets through the partial decomposition of Cu_{1.8}S. It was found that the Cl⁻ from Mn²⁺ precursor (MnCl₂) caused the decomposition of Cu_{1.8}S part. Moreover, the bow-shaped Cu_{1.8}S-MnS nanoplatelets grow back to complete hexagonal MnS nanoplatelets through the growth of MnS from the broken part after supplying an adequate amount of Mn²⁺ precursor. This shape memory-like behavior was also applicable to Cu_{1.8}S NCs with other morphologies such as rod and sphere. This discovery gives a new way to control overall morphology of ionic NCs and synthesize more structurally sophisticated HNCs under mild conditions.

Self-activated Rh-Zr mixed oxide as a nonhazardous cocatalyst for photocatalytic hydrogen evolution

Photocatalytic water-splitting is a promising technology for sustainable hydrogen production and Al-doped SrTiO₃ (STOA) photocatalyst is regarded as the best water-splitting photocatalyst under UV irradiation to date. Developing suitable cocatalysts for STOA is desirable for improving photocatalytic water-splitting activity. Here, we demonstrated the Rh-Zr mixed oxide works as an efficient, non-hazardous cocatalyst for photocatalytic overall water-splitting. Impregnation of Zr and Rh precursors formed RhZrO_x cocatalyst particles on STOA, which exhibited 31 times higher photocatalytic water-splitting activity than a RhO_x cocatalyst. Electrochemical analysis revealed the backward reaction of water-splitting was dramatically suppressed on RhZrO_x. Our nonhazardous Zr-based cocatalyst will be useful for large-scale applications to photocatalytic water splitting.