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

Broad Section D

Title of Project : Supercritical hydrothermal synthesis of High-entropy nanoceramics

ADSCHIRI Tadafumi
(Tohoku University, Advanced Institute for Materials Research, Professor)

Research Project Number : 21H05010 Researcher Number : 60182995
Term of Project : FY2021-2025 Budget Allocation : 144,300 Thousand Yen
Keyword : supercritical water, strain, nanoparticles, ionic conductivity

【Purpose and Background of the Research】

New material synthesis is possible by performing material synthesis in the "supercritical phase," but has traditionally been accomplished in the gas, liquid, and solid phases in the industrial sector. Nanoparticles with extremely high strain and large defects can be synthesized in the supercritical phase. This unique structure affords a different electronic state and increases the oxygen ion conductivity by at least three orders of magnitude at low temperatures. It is expected that high-speed chemical reactions at low temperatures, which were not possible in the past, can be performed. This phenomenon can have a significant impact in the field of chemistry, which is comparable to that of “high-temperature superconductivity” in physics.

The principle of the peculiar structure formation in the supercritical process including the surface stabilization effect of organic molecules in the supercritical reaction and quenching of the metastable phase (Ostwald's step rule) will be elucidated. Furthermore, the principle of the new chemical function (super ionic conductivity) owing to the high disordered strain and large defects of the formed organic–inorganic hybrid nanoparticles will be elucidated. Based on these, the applications of the unique chemical phenomena to the chemical processes (contribution to society) such as low-temperature reforming, chemical recycling, CO_2 fixation catalytic reaction, and photocatalytic reaction employing the unique electronic state will be investigated.

【Research Methods】

1) Generations of mechanism high-entropy nanoceramics (Strain/defect control process)

The formation mechanisms of strain and defects will be clarified by monitoring the changes in the microstructures (strained structures) immediately after nucleation (order of milliseconds) by experimental measurements employing synchrotron radiation, rapid quenching device, and computational analysis. This can lead to the controlled synthesis of high-entropy nanoceramics with high strain structures through rapid quenching.

2) Principle of high disordered strain and expression of new functions (Creation of new science)

Adschiri group provides nanomaterials with different strains/defects. In addition to correlating the ultra-high-performance electron microscopy data with large-scale computational studies, the ionic and electronic state measurements will be performed using synchrotron radiation and photoelectron spectroscopy. As a result, a correlation between the high-concentration defects/strain and physical properties can be established. By incorporating the discrete geometry of WPI-AIMR (persistent homology) that can allow the description of disordered structures, the correlation between the disordered structure and function will be clarified.

3) Application of High-Entropy Nanoceramic Chemistry (New technology for the society)

For various high-entropy nanoceramics (different strains/defects) provided by Adschiri, the oxygen carrier capabilities and catalytic functions will be evaluated. New technologies based on the high-entropy nanoceramic chemistry will be developed for a green society including the utilization of low-temperature waste heat for H_2 production, CO_2 fixation, and photo catalysis.

【Expected Research Achievements and Scientific Significance】

In this study, the formation mechanism of these highly disordered nanoparticles with high strain and large defects (high-entropy nanoceramics) in the supercritical state is elucidated, and a synthesis method (via strain control) is developed. In addition, the mechanistic principle of the high oxygen ion conductivity of high-entropy nanoceramics is elucidated using a combination of atomic observation technology, synchrotron radiation, photoelectric measurements, and computational studies. By introducing state-of-the-art mathematics, i.e., discrete geometry (homology), this disordered structure will be described, thereby affording the structure–function correlation. Based on these results, new chemical processes that utilize this unique characteristic will be developed. Particularly, with the aim of building a CO_2-free chemical cycle in the environment, new methods for hydrogen production will be developed using low-temperature waste heat, CO_2-free waste chemical cycle, photocatalysis, and environmental catalytic reaction employing the specific electronic states.

【Publications Relevant to the Project】

· Zhang, J., et al., "Extra-low-temperature oxygen storage capacity of CeO_2 nanocrystals with cubic facets" Nano Letters, 11(2), 361–364 (2011).
· Hao, X., et al., "Atomic-Scale Valence State Distribution inside Ultrafine CeO_2 Nanocubes and Its Size Dependence" Small, 14(42), 1802915/1–8 (2018).

【Homepage Address and Other Contact Information】

https://www.wpi-aimr.tohoku.ac.jp/ajiri_labo/index.html