Development of a method for spontaneous generation of nano catalyst particles for hydrogen production

- Professor Bong-Joong Kim's team extracted all highly doped metal catalysts from oxide substrates without causing structural damage to the substrate and firmly bonded them to the substrate... Presenting a new avenue for catalyst exsolution technology that has reached its limits.
- Expanding the horizons of nano catalyst technology, expected groundbreaking improvements in electric vehicles, gas sensors, and gas reforming... Published in 「Small」, a renowned international academic journal in the nano field

▲ School of Materials Science and Engineering Professor Bong-Joong Kim

At the Gwangju Institute of Science and Technology (GIST, President Kichul Lim), Professor Bong-Joong Kim's research team in the School of Materials Science and Engineering extracted all highly doped metal catalyst particles from an oxide substrate without causing structural defects in the substrate and announced that they have developed a new concept of Exsolution⋆ technology that is partially embedded in the substrate and firmly bonded.

⋆ ex-solution: ⋆ Ex-solution: When given a high temperature reducing atmosphere (over 700-800 degrees Celsius, hydrogen atmosphere), a phenomenon in which a specific metal component is separated from a specific oxide substrate or support (mainly perovskite-structured oxide material, e.g. ABO3) and comes out to the surface of the substrate. Mainly noble or highly active metals substituted at the B atom site come out to the surface of the substrate and form particles.

The research team also used real-time transmission electron microscopy⋆ to identify the principles of generation and control of size, density, and distribution of ‘exsolved’ metal catalyst particles.

⋆ transmission electron microscope: A microscope that shoots a high-voltage electron beam to penetrate thin materials and allows observation at hundreds of thousands of times magnification.

The exsolution phenomenon of metal catalyst particles using an oxide support causes the catalyst particles to be embedded in the surface of the support, so coarsening⋆ does not occur even at high temperatures, making it possible for high-temperature catalytic reactions (e.g. gas sensors, etc.) and renewable energy (e.g. gas reforming, fuel) and is considered very important in applications such as batteries.

The exsolution phenomenon occurs through high-temperature heat treatment in a reducing environment after doping a solid oxide substrate with a metal element. In this existing method, only a small portion of the metal element escapes due to the slow diffusion rate of the metal element within the solid* substrate, making it difficult to generate a large amount of catalyst particles on the substrate. The escaped metal elements cause structural defects (e.g. oxygen vacancies*) in the oxide substrate. Due to these problems, the activity and durability of the utilized devices have drastically decreased, which has been pointed out as a limitation of catalyst technology.

* solid phase: A solid state in which molecules or ions are arranged in fixed positions and have a certain shape and volume.

* coarsening: A phenomenon in which the size and density of catalyst particles change instantaneously as atoms move from nanocatalyst particles with high chemical potential energy and small particle size to nanocatalyst particles with low chemical potential energy and large particle size.

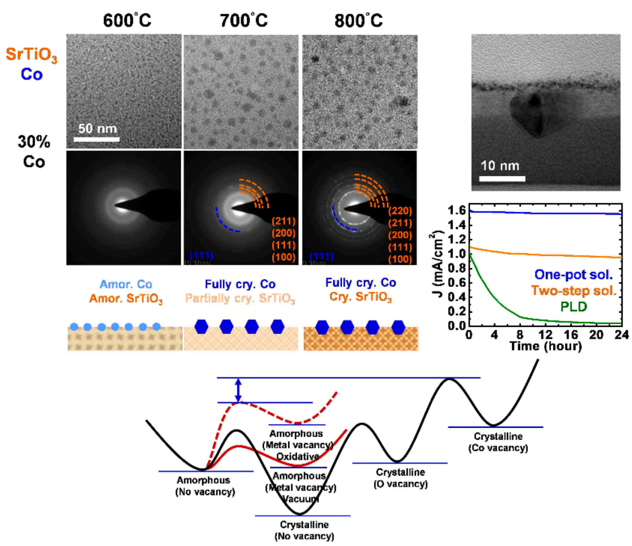
* vacancy: A state in which there are no atoms in the original position in the lattice. When the vacancy concentration increases, a change in the lattice structure may occur.

Instead of using the existing method, the research team coated the substrate with a strontium titanate (SrTiO3) sol-gel solution heavily doped with cobalt (Co) and heat-treated it in vacuum.

When observed with increasing temperature using a real-time transmission electron microscope technique, the coated thin film underwent a phase change from an amorphous* solid to a crystalline* solid starting at 700 degrees Celsius. In particular, the entire amount of cobalt element doped at 30% in the amorphous state was ‘exsolved’ onto the substrate, and the substrate then crystallized at high temperature.

* amorphous: A solid state made up of randomly arranged atoms or molecules without a regular crystal structure.

* crystalline: A solid state in which atoms or molecules are arranged in a regular and repetitive pattern.



▲ Real-time observation of kobold particle exsolution in amorphous and photoelectrochemical cell reaction
(1) Real-time transmission electron microscopy imaging and diffraction analysis of Co exsolution phenomenon on sol-gel coated $SrTi_{0.7}Co_{0.3}O_3$ amorphous substrate (2) Transmission electron microscope image showing Co particles embedded in the substrate (3) J-t plot of photoelectrochemical cell (4) Thermodynamic free energy landscape for analyzing amorphous exsolution

The size and distribution of the 'exsolved' cobalt element were very small, uniform, and partially embedded in the substrate, maximizing the activity and lifespan of the photoelectrochemical cell for water splitting.

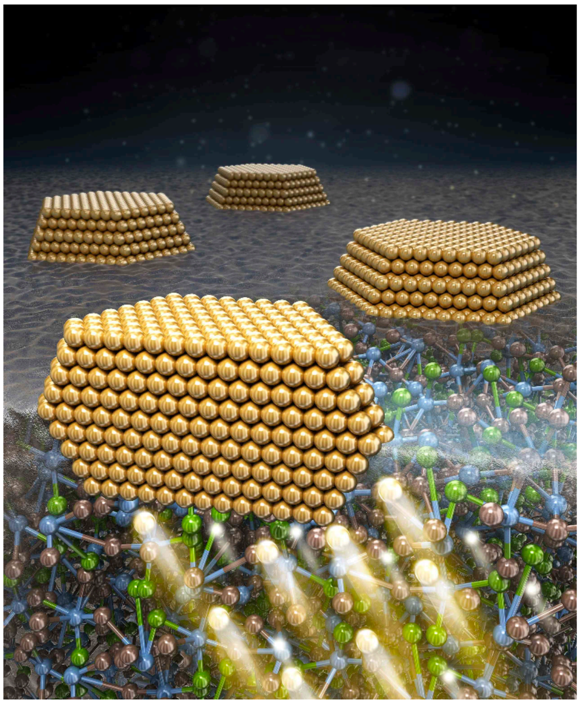
Compared to cell performance through solid-phase exsolution under the same conditions, the activity increased by about 50% and maintained almost the same activity for 24 hours. On the other hand, in the case of cells through solid-phase exsolution, the activity was completely lost within about 8 hours.

The research team additionally confirmed through first-principles calculations* that this phenomenon is due to the low vacancy generation energy of cobalt element in amorphous solids.

* first-principles calculation: A method of calculating the electronic structure and properties of materials without empirical parameters or experimental data, based on the basic laws of physics.

Professor Bong-Joong Kim said, "This research outcome is significant in that it suggests a new way forward for catalytic exsolution technology, which has reached its limits, and is expected to bring about groundbreaking improvements in fields such as electric vehicles, gas sensors, and gas reforming in the future."

This research, led by Professor Bong-Joong Kim (corresponding author) of GIST's School of Materials Science and Engineering, was conducted with support from the National Research Foundation of Korea's Researcher Support Project and the GIST-MIT International Joint Research Project, and the results of this research were published in 'Small', an authoritative journal in the nano field and was selected as the inside back cover of the print edition.



▲ Selected as 'Small' cover paper (Inside Back Cover) in recognition of excellence

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