

## Unlocking Catalytic Powers of Nonprecious Nanomaterials

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### Abstract

Although the precious metal-based materials are widely recognized as superior catalysts for clean energy applications, their large-scale commercial use has been hindered by their expensive and scarcity nature. The development of high performance, plentiful and cheap nonprecious materials based catalysts is therefore vital for the commercial viability of clean energy future. Unfortunately, the most of nonprecious materials in their pristine forms possess little or no catalytic activity. As such, unlocking the catalytic activities of nonprecious materials has become an important scientific task, but highly challenging.

This presentation reports a number of broadly applicable approaches to unlock the catalytic activities of nonprecious nanostructured materials. A number of examples from our recent investigations will be used to demonstrate the effectiveness and applicability of such approaches.

Materials science is an inherently interdisciplinary research field, which involves physics, chemistry, and biology. The research of materials science emphasizes understanding a material's structure, and thus its properties and performance, through multiple capabilities ranging from synthesis, processing, and characterization to theory. As materials are the basic substances that make up all everyday objects, materials science is so important to nearly every aspect of science and technology in human existence and social life.

Non-precious-metal single atom (NPM-SA) confined nanomaterials with maximum metal atom utilization have recently attracted particular interest, providing opportunities for exploiting novel heterogeneous electrocatalysts with low cost and high efficiency. The applications of non-precious-metal single-atom catalysts (NPM-SACs) have been extensively developed in electrochemical energy technologies such as fuel cells, metal-air batteries, and hydrogen production via water splitting. NPM-SACs can be confined on substrates with various structures and dimensions from 1D to 3D. However, the role of the structural dimensions of substrates has not been critically summarized. In

this review, recent advances in NPM-SACs such as facile synthesis, characterization, performance in catalyzing oxygen redox reactions, and related applications are highlighted through a focus on different dimensional substrates (1D, 2D, and 3D). The general fabrication strategies and the catalytic mechanism of NPM-SACs in the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are extensively discussed. Moreover, the opportunities and challenges in this emerging field are presented on the basis of its current development.

It remains elusive as to how exactly the site-specific atom in a catalyst can induce a chemical reaction mainly due to the observed catalytic performance from an ensemble average of all active atoms in the catalyst. In this work, we have reported the catalytic properties of four metal clusters (namely, Au<sub>8</sub>Pd, Au<sub>9</sub>, Au<sub>24</sub>Pd and Au<sub>25</sub>) for the oxidation of benzyl alcohol. It was found that the Pd atom in the Au<sub>8</sub>Pd cluster is likely to be a key to catalyze the oxidation reaction, in which the Pd atom can provide an active site to adsorb and activate O<sub>2</sub>. Our calculation study suggests that the high catalytic activity of the Au<sub>8</sub>Pd cluster is due to the unique ability of Au<sub>8</sub>Pd to mediate the electrons and holes of the adsorbates. This work provides a feasible strategy to enable highly efficient chemical processes via precisely doping foreign atoms into catalysts with atomic precision.

CO<sub>2</sub> and sustainably produced hydrogen have the potential to serve as an ingredient for converting electrical power generated by windmills or solar panels into a gas fuel. This 'power-to-gas' concept can solve two problems at once: it reduces CO<sub>2</sub> emissions while creating more flexible applications of sustainable energy. However, profitable conversion of CO<sub>2</sub> would require an extremely effective catalyst. Researchers from Utrecht University have found a way to study the conversion process in detail and to determine the perfect size for the catalytic nickel nanoparticles. The researchers will publish their results in *Nature Catalysis* on Monday, 29 January.

Lead author Charlotte Vogt explains: "When we make metal nanoparticles smaller and smaller, they start to show very different properties to what we expect and understand from classical physics and chemistry". Together with colleagues Florian Meirer and Bert Weckhuysen from Utrecht University and researchers from chemical company BASF, Vogt found that nickel

particles exhibit optimal catalytic activity at a size of 2.5 nanometres, about 40,000 times smaller than a human hair. The researchers also found that a specific architecture of these tiny nickel particles facilitates the activation of CO<sub>2</sub>.

Catalysis, as a key and enabling technology, plays an increasingly important role in fields ranging from energy, environment and agriculture to health care. Rational design and synthesis of highly efficient catalysts has become the ultimate goal of catalysis research. Thanks to the rapid development of nanoscience and nanotechnology, and in particular a theoretical understanding of the tuning of electronic structure in nanoscale systems, this element of design is becoming possible via precise control of nanoparticles' composition, morphology, structure and electronic states. At the same time, it is important to develop tools for in situ characterization of nanocatalysts under realistic reaction conditions, and for monitoring the dynamics of catalysis with high spatial, temporal and energy resolution. In this review, we discuss confinement effects in nanocatalysis, a concept that our group has put forward and developed over several years. Taking the confined catalytic systems of carbon

nanotubes, metal-confined nano-oxides and 2D layered nanocatalysts as examples, we summarize and analyze the fundamental concepts, the research methods and some of the key scientific issues involved in nanocatalysis. Moreover, we present a perspective on the challenges and opportunities in future research on nanocatalysis from the aspects of: (1) controlled synthesis of nanocatalysts and rational design of catalytically active centers; (2) in situ characterization of nanocatalysts and dynamics of catalytic processes; (3) computational chemistry with a complexity approximating that of experiments; and (4) scale-up and commercialization of nanocatalysts.

Sulfur hexafluoride (SF<sub>6</sub>) is a refractory greenhouse gas. Catalytic decomposition of SF<sub>6</sub> was seldom reported. In this work, we synthesized novel multi-metal containing catalysts from heavy-metal solid wastes, and applied them in green catalytic decomposition of SF<sub>6</sub> for the first time. As a result, the waste-derived catalysts, which mainly contained Cr, Cu and Fe oxides, remarkably removed SF<sub>6</sub> at a capacity of 1.10 mmol/g at 600°C. This active temperature was 100-200°C lower than that of phosphate catalyst, but much lower than 5000 K by electrical arc reported elsewhere. XRD analysis showed that the solid phase transformed from metal oxides (e.g. Fe<sub>2</sub>O<sub>3</sub>) to fluorides (e.g. FeF<sub>3</sub>) with the consumption of SiO<sub>2</sub>. At the same time, on-line FTIR analysis detected that the