Design of Nanostructured Catalysts for Sustainable Energy and Environmental Uses

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Significance and Relevance

The precise structural control of special reaction fields, such as the nanopores of zeolites, mesoporous silica, MOFs, and thin film interfaces, was achieved. This led to the successful precise design of single-site photocatalysts (isolated metal ions, photo-functional metal complexes), ultra-fine particle semiconductor photocatalysts, plasmonic catalysts, high-entropy alloy particle catalysts, and porous metal catalysts with unique structures distinct from conventional ones. These nano-designed high-activity catalysts were extended to environment-friendly reactions such as hydrogen cycling reactions (hydrogen production from water and hydrogen carrier molecules, hydrogen peroxide synthesis), carbon dioxide reduction reactions (synthesis of CO, formic acid, methanol, methane), and air-water purification, revolutionizing catalyst development.

Introduction and Motivations

Designs of “active sites", "reaction fields" and “energy injection” are important for catalyst development. In the nanospace of zeolite, mesoporous silica and MOF, it is possible to control the structure of catalytic active sites in forms of fine particles, clusters, molecules, and atomic moieties, and also possible to control the reaction fields with unique properties such as hydrophobicity and electrostatic fields. Ultrafine semiconductor photocatalysts, single-site photo-catalysts, plasmonic catalysts, nano-alloy catalysts, Yolk-shell catalysts, and MOF photocatalysts, can be designed for H_2 production, CO_2 fixation, H_2O_2 synthesis, and various selective reactions.

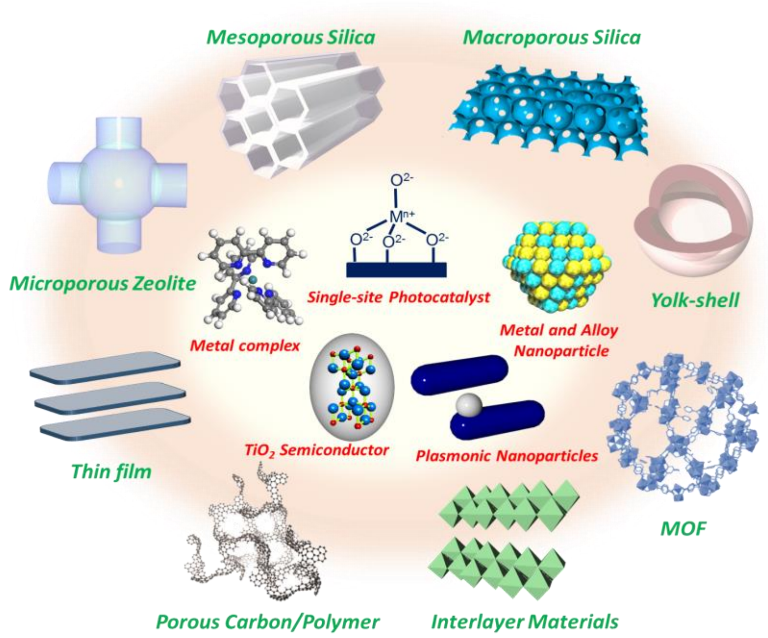

Figure 1 Design of mesostructured catalysts and photocatalysts using porous materials.

Results and Discussion

Design of Single-Site/Ultra-Fine Particle Photocatalysts in Nanospaces:

The focus was made on the ability of nanoporous materials such as zeolites to fuse metal ions in an isolated state, leading to the development of "single-site photocatalysts" with structures and properties significantly different from conventional photocatalysts by introducing metal ions into pores and frameworks. Applications to CO_2 reduction and NO_X decomposition were attempted, clarifying the importance of surface coordination unsaturated sites (tetra-coordinated titanium oxide, bi-coordinate copper ions, etc.). Furthermore, high functionality was achieved by fixing photo-functional metal complexes as single-site photocatalysts in nanospaces, applied to hydrogen production from water. On the other hand, the hybrid of ultra-fine semiconductor particles and nanoporous materials was conducted, modifying pore surfaces (with hydrocarbon, fluorine, apatite, graphene, etc.) and improving spatial characteristics (hydrophilicity/hydrophobicity, electrostatic field, spatial volume) to achieve reactant concentration and reaction efficiency. Unique higher-order nanostructures such as macro/mesoporous structures, core-shell structures, and yolk-shell (hollow space) structures were developed, leading to further activity improvements. Particularly, high-efficiency CO_2 reduction was enabled by integrating basic polymers capable of concentrating CO_2 with CO_2 reduction catalysts in hollow spaces.

Design of Plasmonic/MOF Photocatalysts Utilizing Nanostructures:

Based on single-site photocatalysts, well-defined metal nanocatalysts were prepared and utilized for H_2O_2 synthesis and VOC combustion. Furthermore, by using rapid uniform heating via microwave heating and the regulated spaces of mesoporous materials, metal nanoparticles (Ag, PdAu, etc.) with precisely controlled shape, size, and color were prepared, leading to the development of plasmonic catalysts that can exhibit localized surface plasmon resonance under visible light irradiation and significantly enhance catalytic performance. Additionally, the design of metal-organic framework (MOF) photocatalysts aimed at H_2O_2 generation was conducted, creating reaction fields that inhibit the decomposition of generated H_2O_2 by hydrophobizing MOF surfaces. Furthermore, a two phases reaction system of water-organic solutions was developed, enabling the high-concentration production of H_2O_2.

Design of New Catalytic Materials Utilizing Hydrogen Spillover Phenomena:

A catalyst preparation method has been developed utilizing the "hydrogen spillover phenomena," in which hydrogen molecules diffuse as atomic hydrogen on the surface of oxides through metals. Whether hydrogen diffuses on the surface of the support or is doped into the support depends on the basicity, surface functional groups, oxygen defects, and crystal phase of the oxide support. On Mo oxide, hydrogen activated by Pt spills over and is doped into the Mo oxide in large quantities, resulting in the preparation of reduced H_XMoO_{3-y} with numerous oxygen defects, demonstrating high activity for CO_2 reduction by functioning as a photothermal conversion catalyst under visible light irradiation. On the other hand, on oxides such as CeO_2, active hydrogen diffuses on the surface through hydrogen spillover, allowing the low-temperature rapid reduction and alloying of adjacent base metal ions. This phenomenon was utilized to develop a method for easily preparing high-entropy alloys and non-equilibrium alloy particles, designing catalysts that show high performance for CO_2 reduction, NOX decomposition, and hydrogen production from hydrogen carrier molecules.

References

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