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Editorial

Preface to Special Issue on Water Splitting, from Molecular to Material

Water splitting produces hydrogen (H_2) as a green energy carrier, delivering new rooms for the usage of renewable but transient energy, such as solar and wind energy. The development is of fundamental significance to deal with environmental issues and to build carbon-neutral society. Oxygen evolution reaction (OER) in anode and hydrogen evolution reaction (HER) in cathode occur during the process. Both of these two half reactions involve the transfer of multiple electrons and protons and also the significant rearrangement of several atoms, leading to sluggish kinetics for these processes. Therefore, catalysts are required to accelerate these two reactions. Water-splitting catalysts can be divided into two branches, namely molecular and material catalysts. Molecular catalysts possess clear and systematically regulatable structures, which are favorable for mechanism and structure-function relationship investigations. Material catalysts with dense and high-exposure active sites, as well as great conductivity, are typically efficient and stable. More importantly, mutual learning between these two systems encourages further design of water-splitting catalysts, like rational regulation of active site electronic structures for material catalysts, and immobilization of molecular catalysts. These key scientific challenges for large-scale applications of water splitting technology motivate us to organize the special issue of “water splitting, from molecular to material”. The issue contains 16 papers, including 9 articles, 2 communications and 5 reviews, which cover main frontiers and most of research aspects of water splitting catalysis. A brief description is delivered below, serving as an outline favorable for further reading.

Molecular catalyst possesses plenty of advantages, partially including well-defined and precisely tunable structures, clear active sites and catalytic mechanisms, designed high intrinsic activity, great selectivity, and high metal-atom economy. These features of molecular catalysis attract a broad of research interests. Nam, Fukuzumi and Lee summarized recent progresses in producing hydrogen peroxide by solar-light-driven oxidation of water by dioxygen and its usage

as a green oxidant and fuel. Cao and co-workers reviewed the evolution of metal-oxygen species during transition metal-catalyzed water oxidation, focusing on discussing the feasible O–O bond formation mechanisms during OER over synthetic molecular catalysts. Dey and co-workers demonstrated an iron porphyrin having triazole containing 2nd sphere hydrogen bonding residues appended with redox active ferrocene moieties (α_4 -tetra-2-(3-ferrocenyl-1,2,3-triazolyl) phenylporphyrin ($FeFc_4$)) as a catalyst for selective proton reduction at the Fe^0 state, paving the way for selective proton reduction in the presence of oxygen. Zhang and co-workers investigated the redox properties of a Cu^{III} complex with a redox-active macrocyclic ligand and examined its reactivity, unclosing buffer anion effects in the case of Cu^{III} complexes for water oxidation catalysis. On the bases of mechanism investigation, Wang and co-workers integrated porphyrin-Pt into a light-harvesting metal-organic framework, boosting the activity by ~830 times for visible light-driven hydrogen production. Sun, Li and co-workers reported dye-sensitized photoanodes decorated with pyridine additives towards efficient solar water oxidation.

Materials see a great progress recently for the construction of water splitting catalysts, especially in mechanism-based material design. The review by Wei, Huang and co-workers summarized the recent progress in the construction of single-atom catalysts (SACs) for OER and HER applications, including alloy-based SACs, carbon-based SACs and SACs supported on other compounds. Zhang, Yu and co-workers reviewed the recent advances in amorphous electrocatalysts for water splitting. Amorphous nanomaterials with short-range order and long-range disorder features have recently shown superior activity compared to their crystalline counterparts in water electrolysis. The review article by Wang and co-workers provided an overview of the nanoarchitectures and surface physicochemical properties of nanocarbons, which affect the electrocatalytic performance for polymer electrolyte membrane fuel cells, with an emphasis on both physical characteristics, including pore structures, chemical properties,

heteroatom doping, and functional carbon-based supports. Apfel and co-workers presented the synthesis, characterization and electrocatalytic investigation of ternary metal-rich sulfide composites $\text{Fe}_x\text{Co}_{9-x}\text{S}_8$ and $\text{Ni}_y\text{Co}_{9-y}\text{S}_8$, which possess pentlandite-type structures. Ni/Co compounds generally tend to show higher catalytic activities towards HER than their respective Fe/Co compounds. Xu and co-workers reported an effective strategy for the *in-situ* chemical transformation of Fe-based bimetallic MIL-88 metal-organic frameworks into corresponding bimetallic hydroxides towards efficient electrocatalytic OER, which are composed of amorphous ultrasmall nanoparticles and afford an abundance of catalytically active sites. Zhang, Fang and co-workers reported an odd-membered cyclic hetero-polyoxotitanate nanoclusters with high stability and activity towards photocatalytic H_2 evolution. Lu, Lu and co-workers synthesized a new nickel boron oxide/graphdiyne hybrid catalyst with low metal valence states by a facile *in-situ* synthetic approach, which displayed high photocatalytic and electrocatalytic H_2 evolution rates. Gong and co-workers investigated the effect of the transition-metal electrocatalysts on photoelectrochemical OER using Si-based photoanodes. Hu, Liu and co-workers developed an etching-assisted synthesis approach to integrate highly active NiFe_2O_4 nanoparticles with a robust and active NiOOH scaffold on commercial stainless steel, which exhibits excellent activity and stability for electrocatalytic OER. Sun, Liu and co-workers combined molecular design and material construction for electrocatalytic oxygen reduction, which is the reverse reaction of OER, using different iron phthalocyanines adsorbed on carbon nanotubes as catalysts. It is revealed that

electron-deficient iron phthalocyanine catalysts are more favorable for electrocatalytic oxygen reduction.

As guest editors, we appreciate all the authors for their great contributions to this special issue, and also we thank the editorial staffs of *Chin. J. Catal.* for their massive help. We hope that the topic of the special issue would inspire the development of water splitting technologies, and also be enlightening to other energy systems.

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