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Special Issue of Single-atom Catalysis

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Single-atom catalysts(SACs) are a new type of heterogeneous catalysts formed by isolated metal atoms anchored on kinds of substrates. SACs are distinctly distinguished from traditional catalysts by characterizing with unique electronic structure, quantum size effect and unsaturated coordination environment, etc., which brought subverted effects on traditional catalytic fields once upon the emergence. The unique chemical and physical properties impart SACs with outstanding catalytic performance, embodying nearly 100% atom utilization, high catalytic activity and excellent durability. SACs invariably have been the “hotspot” in catalysis research field during the last decade, shining brilliantly in applications of electro-, photo- and thermal catalysis. In particular, the advent of SACs points towards a possibility of the substantial cost reduction of precious metal catalysts in the future. This themed issue selected advanced studies on design, synthesis, characterization, and application of SACs, dedicating to assisting readers in a comprehensively and in-depth understanding of SACs.

This special issue collects 8 reviews, 1 perspective and 14 original research articles. The first review part provides a series summary of SACs supported on different substrates concerning their synthetic strategies, reaction mechanism, structural characterizations, and their applications in electrocatalysis, photocatalysis and liquid phase hydrogenation, etc. The review by Liu and colleagues explicitly illuminated the difference between SAC and single site catalyst(SSC) in terms of their goals, synthetic methods, coordination structures, and support choice of corresponding catalysts, and introduced the surface organometallic chemistry method for synthesizing SSC. Yan *et al.* emphasized the applications of SACs in a variety of

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electrocatalytic reactions, including hydrogen evolution reaction(HER), oxygen reduction reaction(ORR), oxygen evolution reaction(OER), CO_2 reduction reaction(CO_2RR), and nitrogen reduction reaction(NRR). Zhang *et al.* reviewed the recent progress on covalent organic frameworks based SSCs towards synthesis procedures, compositions, structures, performances, and mechanisms. The review by Liu and colleagues introduced the applications of different types of SACs mainly in liquid phase selective hydrogenation reactions. Su *et al.* summarized recent advances of TiO_2-supported SACs, including synthetic strategies, structure elucidation, and catalytic applications, and deeply interpreted their fabrication tips, structure-reactivity relationships, and mechanistic insights. The review by Sui and colleagues introduced recent studies on using advanced transmission electron microscope(TEM) for the characterization of carbon- and metal-based-substrate supported SACs, where not only atomic dispersion of single atoms can be studied, but also the distribution of elements and the valence state with local coordination can be resolved. Shao *et al.* comprehensively summarized the research progress of SACs based on layered double hydroxides and discussed in detail on the preparation strategies, characteristics and extensive applications. Han *et al.* presented the recent progress in the synthesis, reaction mechanism and applications of the C_3N_4-based SACs for CO_2RR to C_1 products.

The second perspective part includes one paper. Teng *et al.* elaborated the effects of single-atom sites on the charge dynamics and reaction kinetics of polymer-based photocatalysts and discussed the opportunities and challenges in the rational design of single-atom dispersed polymer photocatalysts.

The third original research part includes 14 advanced studies, involving innovative synthesis approaches, detailed theoretical calculations, profound mechanism discussions as well as breakthrough progress in catalytic performance for SACs. Zhang *et al.* reported a metal-organic framework(MOFs)-assisted approach to synthesizing indium-based materials as catalysts for the electroreduction of CO_2. Wei *et al.* provided a facile solution to synthesize well-aligned titanium dioxide nanorods by using hydrothermal reaction. By calcining the materials under different atmospheres and temperatures, a batch of titanium dioxides with excellent OER catalytic efficiency were obtained. Wu *et al.* reported a facile, low-temperature strategy to

prepare a supported Pd liquid metal(PdLM) catalyst, where a galinstan liquid alloy was taken as the support to replace Pd ion and dissolve Pd metal. Meanwhile, large droplets of liquid metal were turned into microparticles, which gives a larger specific surface area. The liquid support facilitates the atomic dispersion of metal to obtain fully exposed active sites, resulting in superior activity, stability, and methanol tolerance. Chen *et al.* reported the fabrication of ultrahigh loading Cu SACs in a nitrogen-rich carbon matrix(Cu-N-C, 14.5%, mass fraction) by the pyrolysis of Cu precursor. Li *et al.* demonstrated that competitive coordination of zirconium nodes in a typical metal-organic framework known as MOF-545 with monocarboxylate modulator over H_2TCPP is an effective way to modulate the electronic state and steric environment of active zirconium sites for achieving Lewis acid catalysis with high performance. Ge *et al.* studied the effect of Nafion ionomer content on the structure and catalytic performance of direct CO polymer electrolyte membrane fuel cells by using Rh-N-C SACs as the anode catalyst layers. Shen *et al.* reported single Ni atoms successfully anchored onto carbon-vacant PCN nanosheets(CCN-SANi) *via* a two-step ammonia thermal treatment and photo-deposition process. Theoretical calculations and experimental results demonstrated that the optical absorption property and the charge transfer ability of CCN-SANi have been significantly improved with the introduction of single Ni atoms to form $Ni\text{-}N_3$ sites. He *et al.* successfully prepared zeolitic imidazolate framework-8 derived nitrogen-doped carbon-supported cerium SACs by ball milling method, and the Ce_1/NC catalyst exhibited exceptional catalytic performance in the selective oxidation of saturated C—H bonds in aromatic compounds. Liu *et al.* developed a comprehensive full-metal-species quantification method for dispersion quantification of metal-supported catalysts that consist of diverse species to discern the source of catalytic activity by quantifying the fractions of metal species with the evolution of catalytic performance based on atomic accuracy statistics over massive TEM images data. Zhang *et al.* prepared SACs of FeN_4 coupled with Fe_3C on the N-doped carbon by one-step pyrolysis method. The FeN_4 and Fe_3C synergistically catalyze the polysulfide conversion when the N-doped carbon provides the high conductive three-dimensional skeleton in Li-S batteries. Tang *et al.* successfully synthesized novel Pt group metal-free catalysts based on porous Fe-N-C materials as catalysts with high activity and durability for the cathode ORR. Wang *et al.* Cu/Fe SACs with weak/strong oxygen affinity to clarify the effect of dual-atom configuration on ORR performance based on density functional theory(DFT) calculations. Mu *et al.*

fabricated Fe SACs by selecting Co_3S_4 nanosheets with rich defects as ideal support to enhance the OER activity. Wang *et al.* employed DFT calculations to investigate NRR on molybdenum disulfide monolayer supported Fe_2-dimer catalyst by imitating the Fe-S structure of nitrogenase.

In summary, this special issue presented some recent developments of SACs in different aspects including design, synthesis, characterization, theoretical calculations, mechanism discussion and a variety of catalytic applications. We expect more readers could be attracted to explore SACs by this issue and promote the progress of the related studies. It has been a great honor for us to serve as guest editors for this issue.