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Editorial for special issue on metal-based materials for energy catalysis

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We are so honored to present a special issue on the topic of "metal-based materials for energy catalysis" as Guest Editors of the journal *Rare Metals*. It showcases most recent research advances on metal-based energy catalysis and provides review and outlook for this area. The exhaustion of fossil energy drives the ongoing development of renewable energy conversion and storage. Featured by many intrinsic advantages, metal-based catalysts are key to the development of energy conversion and storage devices and have been at the center of extensive and intensive studies in the past few decades. Researches on metal-based catalysts have spanned from metallic alloys to oxides and nitrides, from nanoparticles to nanowires, nanosheets and frame-like morphologies, from porous structure to core/shell structure, etc. Still, there are a wide variety of challenges in terms of scientific fundamentals and practical application *yet* to be solved.

The *Rare Metals* special issue presents a collection of reviews and research articles focusing on metal-based materials for energy catalysis. It includes two reviews and nine research articles dedicated to the frontiers of metal-based catalysis, from rational design of various highly active catalysts to mechanistic analysis of structure–performance relationship. It is right time to launch a single issue centering on catalysis by noble metal and transition metal-based materials. The comprehensive reviews as well as insightful original researches will offer new path to resolving challenging questions and open up new possibilities for emerging and interesting research areas.

Porous materials with high surface area and hierarchically ordered structure have proven to be beneficial for heterogeneous catalysis. One review discussed in detail four typical kinds of metal catalysts, i.e., metal oxides, porous metals, metal nanoparticles supported on metal–organic frameworks (MOFs) and zeolites from the aspects of synthetic approaches and catalytic applications [1]. The other review focused on single nanoparticle–nanoscale shell structures including core–shell and yolk–shell, and multiple nanoparticles embedded in nanoscale shells [2]. Nanoscale shell layers with tunable physicochemical properties are advantageous in that they are able to inhibit thermal sintering and particle aggregation, and that they improve reaction kinetics by facilitating diffusion of molecules.

In order to address the drawback of corrosion of carbon black support that usually leads to the activity decay of Pt catalyst, one article presented the hybrid support consisting of TiN nanoparticles with good chemical stability and carbon nanotubes (CNTs) with good electronic conductivity [3]. The atomic layer deposition (ALD) approach was employed to deposit TiN nanoparticles onto CNTs; the hybrid support was then used to load Pt nanoparticles to obtain Pt@TiN/CNTs catalyst. The strong electron transfer as well as chemical coupling between Pt and TiN was

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shown to promote oxygen reduction reaction (ORR) activity and stability of Pt@TiN/CNTs relative to Pt/C.

Pd-based catalysts are the topic of considerable research as well. One report focused on electrocatalysis of ethanol oxidation reaction (EOR) by $PdPb_3$ nanochains [4]. The exceptional EOR performances of $PdPb_3$ nanochains relative to Pd/C were ascribed to the tuning of reaction intermediates via the introduction of second metal (Pb) to modulate Pd electronic structure. Meanwhile, the introduction of Pb as an oxophilic metal generates adsorbed OH species on the adjacent Pd and thus facilitates the oxidative removal of CO intermediates. Two reports featured Pd/CeO_2 catalysts for CO oxidation [5, 6]. One of them reported the influence of Pd chemical states on catalytic activity [5]. The Pd species exist in the form of PdO and $Pd_xCe_{1-x}O_2$, the latter of which is formed as a transition layer between PdO and CeO_2 to accelerate the transport of active oxygen species. The valence states are 2 and between 2 and 4 for PdO and $Pd_xCe_{1-x}O_2$, respectively. The ascending trend of catalytic activity of CO oxidation is well in accordance with surface concentration of $Pd_xCe_{1-x}O_2$. The other report presented electroless chemical deposition of Pd species onto reduced CeO_2 nanorods [6]. During the synthesis of uniform Pd nanoparticles (NPs) on CeO_2 (Pd NPs/CeO_2-ECD), the reduced CeO_2 nanorods with high concentration of Ce^{3+} and oxygen vacancy facilitate electron transfer to Pd precursors to enable nucleation and growth of Pd NPs. The prominent electronic metal–support interaction (EMSI) effect and the absence of chloride ions endow Pd NPs/CeO_2-ECD with remarkable CO oxidation activity as compared to Pd NPs/CeO_2 prepared by impregnation. The strong EMSI effect was manifested by the propensity for the oxygen species located at the Pd NPs/CeO_2 interfaces to be reduced and by the higher anti-sintering capability of Pd NPs/CeO_2-ECD.

Non-noble metal-based bifunctional electrocatalysts with extraordinary catalytic performances toward ORR and oxygen evolution reaction (OER) have emerged as potential candidates for rechargeable Zn–air batteries. Two research articles covered this topic [7, 8]. One report showed the Fe–polyphthalocyanine molecules anchored on carbon black (Fe-PPc@CB) as bifunctional oxygen electrocatalyst [7]. The electrocatalyst was synthesized via melt polymerization approach, where pyromellitic dianhydride formed macromolecules and Fe atoms were situated at the center. The presence of abundant free electrons and atomically dispersed MN_4-type active sites enabled Fe-PPc@CB to exhibit exceptional ORR and OER activities. Another article reported three-dimensional mesh-like $NiCo_2O_4$ nanoparticles coupled with Co–N_x structure formed by annealing treatment of $NiCo_2O_4$ under N_2 [8]. The mesoporous hybrid structure with high-speed mass transfer in conjunction with the substrate materials with high electronic conductivity due to high degree of graphitization endowed $NiCo_2O_4$/CoN_x catalyst with remarkable ORR and OER catalytic activities. What's more, multiple active sites of $NiCo_2O_4$ spinel structure and metal coordination sites of Co–N_x structure facilitate catalytic activity.

Owing to their surface plasmon resonance properties, Au-based nanoparticles are extensively investigated in terms of surface-enhanced Raman scattering (SERS) analysis. The interparticle plasmonic coupling associated with the inhomogeneity of interparticle nanogaps size, however, needs to be avoided due to the resultant attenuation in the reproducibility of Raman signals. The SERS sensitivity and signal reproducibility of bare Au NPs and Au/oxide (Au/SiO_2, Au/TiO_2, Au/Fe_2O_3) heterostructured NPs were compared in one report [9]. It turned out Au NPs were not uniformly distributed on the substrate with obvious particle assembly in some regions, which causes intensity variations of Raman signals. In contrast, no interparticle plasmonic coupling appears for the Au/oxide heterostructured NPs homogeneously distributed on the substrate, indicative of high reproducibility of Raman signals. Moreover, the sensitivity of SERS analysis is dependent upon refractive index of the oxide. For Au/oxide heterostructured NPs, the electromagnetic hotspots become visible at the Au/oxide interface for SERS analysis due to the strong plasmonic coupling. The intensity of Raman signals increases as the refractive index increases, and the sensitivity of SERS analysis is the highest for Au/Fe_2O_3 heterostructured NPs among the three oxides.

Photochemical water splitting as an effective energy conversion device has also garnered increasing research interest in the past years. Rational design of the semiconductor sensitized system, a class of photochemical water splitting systems, is still faced with some challenges such as recombination of electron–hole pairs. One report proposed a novel WO_3/Fe_2O_3 heterojunction structure, grown via chemical vapor deposition, which promotes separation and migration of photogenerated electrons/holes while suppressing recombination of electrons/holes [10]. The photocurrent densities of WO_3/Fe_2O_3 heterojunction are therefore higher than those of WO_3 and Fe_2O_3.

One article in this issue reported the computational fluid dynamics simulation alongside experimental investigation conducted to examine dispersibility and suspensibility of ultrafine powder slurry [11]. The suspension characteristics of the slurry are closely correlated with the impeller type, stirring speed and impeller clearance. The ideal parameters for single-particle dispersibility and suspensibility of ultrafine TiO_2 slurry are implementation of Rushton disk turbine impeller with the stirring speed of 400 $r{\cdot}min^{-1}$ and impeller clearance of 0.32 T.

We would like to express our sincere thanks to all the authors and reviewers for their great contributions to make

the special issue reach out to researchers in this area. We wish this special issue will appeal to broader readership in the future.

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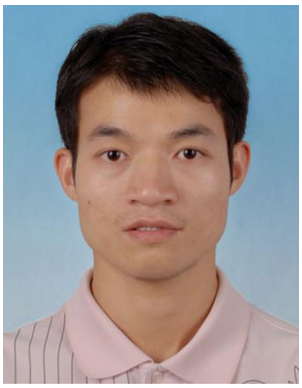

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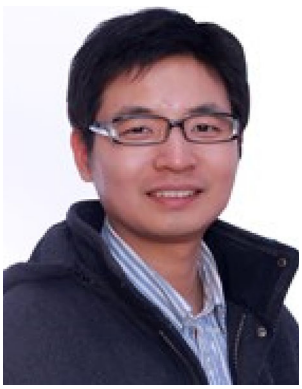

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