doi:10.1017/S1431927620023533
Microsc. Microanal. 26 (Suppl 2), 2020

Atomic-configuration Modulation of Active Sites on Electrocatalysts

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An active site on the surface of a catalyst is the ensemble of atoms that directly catalyzes a reaction, such as carbon dioxide electrochemical reduction (CO_2ECR), nitrogen reduction reaction (NRR), hydrogen evolution, oxygen evolution, oxygen reduction and others.[1-3] Modulating the atomic configurations of active sites is crucial and highly desired for improving the properties of catalysts and controlling catalysis.[4,5] However, it is highly challenging to modulate the atomic configuration of active sites and enable the confident control of active sites at atomic level. In this talk, with the guide of our density functional theory calculations, we have experimentally realized the modulation of the atomic configuration of active sites on MoC nanoparticle surfaces and single-atom catalysts for significant enhanced CO_2ECR and NRR, respectively. This atomic-level modulation is well confirmed by atomic-resolution high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) imaging, high-resolution 3D electron tomography and other techniques.

The modulation adjusts the potential-limiting step of the electrocatalytic reduction of CO_2ECR to CH_4 on the MoC nanoparticles. Consequently, the Faradaic efficiency (FE) of the CO_2ECR to CH_4 is enhanced 5 times in aqueous solutions at ambient conditions. This high FE value fluctuates within a narrow range for 50 hours, indicating high stability. This modulation strategy provides new opportunities to effectively improve the activities of catalysts and eliminate the OH poisoning by precisely decorating metal active sites with heterogeneous atomic patterns. Moreover, the modulated single-atom catalysts for NRR achieved an FE increase by 2 % and an NH_3 yield rate increase by 49.28 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$ at –0.35 V. The enhanced NRR performance is ascribed to their unique geometry and electronic structure, which not only facilitate the adsorption and activation of N_2 molecule but also lower the free energy change of the potential-determining step.

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