

Iron Dopants in Cobalt Oxide on Au(111): Structural Insight into Synergistic Effects in Mixed Metal Oxides

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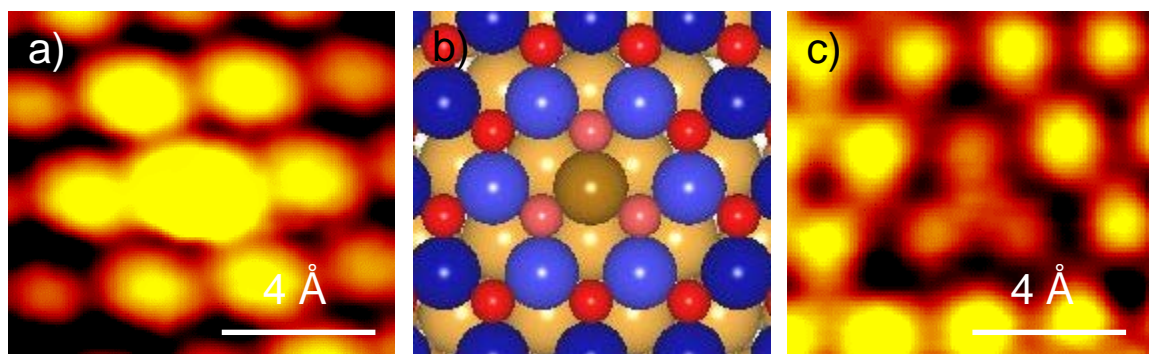
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Transition metal oxides have emerged as promising candidates for oxygen evolution reaction (OER) catalysts due to their earth-abundance and high theoretical catalytic activity [1]. Compared to simple unary oxides, mixed metal oxides, as catalysts for OER, have attracted much attention due to their significant synergistic effects [2]. However, the mechanism of such synergistic effects, especially the link between the atomic-scale structures and their interesting chemical properties, is poorly understood.

Here, aiming to associate the synergistic effects with the structural properties, we have synthesized iron doped cobalt bilayer oxide on a single crystal Au(111) substrate. By means of atom-resolved tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) in combination with density functional theory (DFT) modeling, the as-synthesized iron-cobalt oxide are compared with the corresponding unary iron and cobalt bilayer oxide, respectively.

STM and XPS results reveal that iron species embed in a facile way into the cobalt bilayer oxide resulting electronically modification of the cobalt oxide matrix. DFT modeling and fingerprint from XPS spectrum indicate the iron dopants possess a higher oxidation state than in the structurally corresponding unary bilayer oxide. Further atomic-scale analysis suggests the substituted iron atoms are structurally displaced further away from the substrate than the metal in either of the corresponding unary oxides. Both nearby oxygen and cobalt atoms in the nearest coordination shell are geometrically and electronically perturbed. Through chemical modification and DFT calculations, high-symmetry domains are assigned to the moiré-structured nanoislands. Moiré-related properties of the iron dopants, such as appearance and statistical distribution, are analyzed. Our results indicate that the chemical environment of oxygen at the doping sites would be modified by the iron species reciprocally and our findings may enable a better understanding of the synergistic effects of mixed metal oxides in catalytic applications.



References:

[1] Man, Isabela C., Hai-Yan Su, et al., *ChemCatChem* 3(7), 1159-1165 (2011).

[2] Morales-Guio, Carlos G., et al., *J. Am. Chem. Soc.* 138(28), 8946-8957 (2016).