Bimetallene advances oxygen electrocatalysis

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Electrocatalysis lies at the heart of electrochemical devices that enable the efficient conversion and storage of renewable energy, ultimately having a capability to promote a sustainable society. Therefore, the exploration and development of high-performing electrocatalysts—generally at nanoscale or even at atomic scale to maximize the active surface/volume ratio typically such as two-dimensional catalysts—has been one of the hottest research topics in the past decade [1–3]. A typical example is the search for suitable electrocatalysts for oxygen reduction reaction (ORR), which hinders the widespread adoption of fuel cells and metal-air batteries due to sluggish kinetic-induced large overpotential and high platinum loading. Through rationally structural engineering, advanced platinum group metals (PGMs)-based electrocatalysts with high mass activities (activity in terms of PMGs mass) in acidic electrolytes have been rapidly emerging; however, much less success has been witnessed for PGMs-based electrocatalysts in alkaline environment probably due to the challenges in optimizing the oxygen binding energy in the massive presence of hydroxide.

Recently, Guo and co-workers [4] developed a class of palladium-molybdenum nanosheets featured with sub-nanometer thickness and highly curved geometry (due to the structural analogy with graphene, it is then denoted as "metallene") [5], which showed a record ORR activity in terms of both mass activity and specific activity in alkaline electrolyte with outstanding stability. PdMo "bimetallene" also showed promising performance when it was being used as a cathode in metal-air batteries (both Zn-air and Li-air

batteries).

Previous fundamental studies have established that the ORR activity of PGMs-based materials could be fine-tuned by downshifting/upshifting the d-band center of corresponding PGMs sites through the ligand and/or strain effect. In this case, the authors deliberately introduced and combined several beneficial structural properties into a single material, i.e., PdMo "bimetallene" (Figure 1). First, the four-atomic-layer thickness enables over half of the Pd atoms being exposed on the surface, resulting in an ultrahigh electrochemical active surface area of 138 m^2/g_{Pd}. Secondly, alloying Pd with Mo significantly changed the electronic structure of the former and thus optimized the oxygen
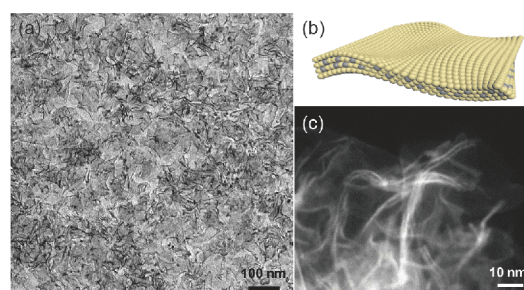
Structure — performance correlation:
- Two dimension — high stability, multiple anchoring sites
- Sub-nanometer thickness — High surface area, quantum size effect
- Highly curved geometry — tensile strain effect

Figure 1 (a) Transmission electron microscopy (TEM) image; (b) scheme and (c) high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image of the PdMo bimetallene catalysts, along with the analysis of corresponding structure-performance correlation [4] (color online).

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binding strength on Pd. Thirdly, the combination of buried Mo and curved geometry induced a tensile strain, which not only stabilized the ultrathin structure by lowering the free energy (as verified by molecular dynamics simulation) but also moving the oxygen binding energy closer to the optimized one. Lastly, the authors innovatively proposed the quantum size effect in tuning the oxygen adsorption strength on PGMs for enhanced ORR activity, which provides useful insights into the development of high-performance catalytic system.

In summary, the "metallene" materials proposed and investigated by Guo and co-workers are a promising type of electrocatalysts for the emerging renewable energy field. I anticipate that this work will raise vast research enthusiasm being devoted into the "metallene" and other two-dimensional electrocatalysts, and we shall witness more advances in terms of fundamental understanding and practical application in the near future.

Conflict of interest   The author declares no conflict of interest.

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