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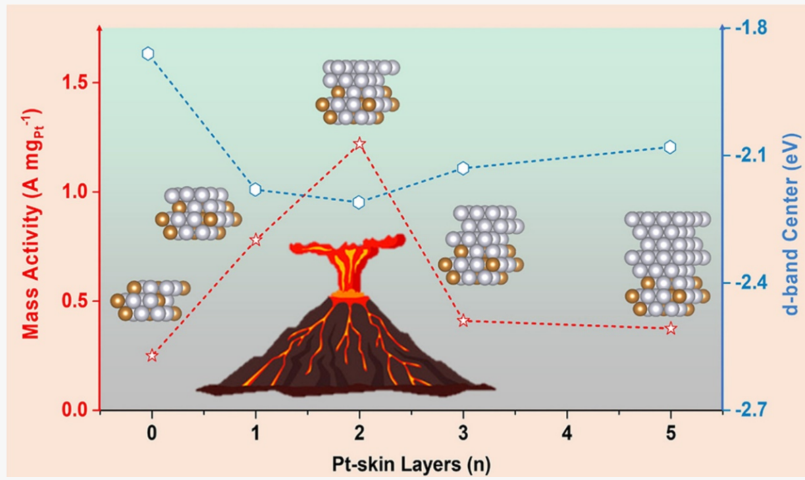
Engineered Pt-skin layers unlock record oxygen-reduction catalysis



Volcano-Shaped Relationship Between Pt-Skin Thickness and ORR Activity.

FAYETTEVILLE, GA, UNITED STATES, December 22, 2025 / EINPresswire.com/ -- Scientists have developed a way to precisely tune atomic-scale platinum “skin” layers on porous PtCu nanodendrites—revealing how these ultrathin shells reshape catalytic behavior in fuel cells. By gradually thickening or thinning the Pt shell, the team uncovered a striking parabolic shift in the d-band center, showing how geometric strain and electron transfer interplay to govern reaction kinetics. At the heart of this curve lies a sweet spot: a two-layer Pt-skin that delivers the fastest oxygen reduction, exceptional durability, and record-high activity. This work not only pinpoints why this configuration excels but also establishes a roadmap for constructing more efficient, low-Pt catalysts for clean energy systems.

Fuel cells rely on platinum-based catalysts to accelerate the oxygen reduction reaction (ORR), a slow step that restricts efficiency and increases system cost. Although alloying Pt with transition metals and designing porous nanostructures have improved performance, researchers still lack fine control over the Pt-skin—the outermost atomic layers that directly govern catalytic behavior. These layers determine the balance of surface strain, adsorption strength, and electronic interactions, yet their impact remains difficult to probe experimentally. Traditional deposition techniques rarely achieve atomic precision, leaving the fundamental structure–activity relationship largely unresolved. Due to these challenges, there is a pressing need to deeply investigate how Pt-skin thickness shapes ORR activity.

A research team from Shanghai University and Wuhan University reported (DOI: 10.1016/j.esci.2025.100396) on September, 2025, in eScience, a breakthrough synthesis that enables atomically precise control of Pt-skin layers on dendritic PtCu nanospheres. By modulating reduction conditions, the team constructed catalysts with zero to five Pt layers and systematically mapped how structural strain, electron redistribution, and d-band energetics evolve with shell thickness. Their findings reveal that a two-layer Pt-skin achieves the most favorable electronic configuration, leading to outstanding ORR performance in both half-cell tests and H_2–O_2 proton exchange membrane fuel cells.

Using sodium citrate and citrate as reduction modulators, the researchers synthesized a full library of PtCu@PtnL nanospheres with finely tuned Pt-skin thicknesses from 0 to 5 layers. High-resolution microscopy and spectroscopy confirmed uniform porous dendritic structures, ~30 nm in size, with Pt layers precisely wrapped around the PtCu alloy core. XRD patterns indicated identical alloy phases, while XPS revealed systematic shifts in Pt 4f binding energies reflecting layer-dependent electron transfer.

Density functional theory and Pt valence-band measurements uncovered a concave parabolic evolution of the d-band center across the series—evidence that geometric compressive strain and electron redistribution vary nonlinearly with skin thickness. The two-layer Pt-skin exhibited the lowest d-band center, providing the optimal binding energy for ORR intermediates. Free-energy calculations further confirmed that this configuration delivers the smallest overpotential and fastest reaction kinetics.

Electrochemically, PtCu@Pt_2L outperformed all other variants, achieving a mass activity of 1.22 A $mgPt^{-1}$ and a specific activity of 2.14 mA cm^{-2}, far exceeding commercial Pt/C. Durability testing over 30,000 cycles preserved both structure and performance, while single-cell tests reached a peak power density of 1.61 W cm^{-2}, beating Pt/C by 39%.

An independent expert in electrocatalysis noted that the study “offers one of the clearest mechanistic maps yet for designing Pt-based catalysts with atomic precision.” The expert emphasized that identifying a volcano-type relationship between Pt-skin thickness and ORR performance fills a long-standing knowledge gap in fuel-cell science. “This work doesn’t just find a better catalyst—it explains why it is better,” the expert said. “The ability to disentangle strain and electronic effects at the atomic level will accelerate the rational design of high-performance, low-platinum systems across the clean-energy sector.”

The discovery of the optimal two-layer Pt-skin configuration provides a powerful new design principle for next-generation fuel-cell catalysts. With high power density, excellent durability, and lower Pt usage, PtCu@Pt_2L nanostructures could significantly reduce fuel-cell costs in electric vehicles, portable power units, and stationary energy systems. The synthesis is also scalable—demonstrated at gram level—and adaptable to other Pt-based alloys, enabling broader industrial application. More broadly, the mechanistic insights gained here offer a blueprint for tuning atomic interfaces in a wide range of electrocatalysts, supporting the transition toward efficient, affordable clean-energy technologies.

References
DOI
10.1016/j.esci.2025.100396

Original Source URL
https://doi.org/10.1016/j.esci.2025.100396

Funding Information
This work was supported by the Natural Science Foundation of Shanghai (Grant No. 23ZR1423900) and National Natural Science Foundation of China (Grant No. 22272105).

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