

## Single Cu–N<sub>4</sub> Sites Enable Atomic Fe Clusters with High-Performance Oxygen Reduction Reaction

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**Abstract :** Atomically dispersed Fe–N<sub>4</sub> catalysts are proven as promising alternatives to commercial Pt/C for the oxygen reduction reaction. Most reported Fe–N<sub>4</sub> catalysts suffer from inferior O–O bond-breaking capability due to superoxo-like O<sub>2</sub> adsorption, though the isolated dual-atomic metal sites strategy is extensively adopted. Atomic Fe clusters hold greater promise for promoting O–O bond cleavage by forming peroxy-like O<sub>2</sub> adsorption. However, the excessively strong binding strength between Fe clusters and oxygenated intermediates sacrifices the activity. Here, we first report a Fe<sub>x</sub>/Cu–N@CF catalyst with atomic Fe clusters functionalized by adjacent single Cu–N<sub>4</sub> sites anchoring on a porous carbon nanofiber membrane. The theoretical calculation indicates that the single Cu–N<sub>4</sub> sites can modulate the electronic configuration of Fe clusters to reduce O<sub>2</sub>\* protonation reaction free energy, which ultimately enhances the electrocatalytic performance. Particularly, the Cu–N<sub>4</sub> sites can increase the overlaps between the d orbitals of Fe and p orbitals of O to accelerate O–O cleavage in OOH\*. As a result, this unique atomic catalyst exhibits a half potential (E<sub>1/2</sub>) of 0.944 V in an alkaline medium exceeding that of commercial Pt/C, whereas acidic performance E<sub>1/2</sub> = 0.815 V is comparable to Pt/C. This work shows the great potential of single atoms for improvements in atomic cluster catalysts.

**Keywords :** Hierarchical porous fibers, atomic Fe clusters, Cu single atoms, oxygen reduction reaction; O-O bond cleavage

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