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## Unraveling Iron Oxide Nanoparticle Reactivity via Integrated Experimental and Computational Approaches

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With the increasing urgency to mitigate environmental degradation, the promotion of sustainable, eco-friendly industrial processes is imperative. In this context, enzyme-mimicking nanomaterials, or nanozymes, have emerged as promising alternatives, offering high stability and reusability. Among these, iron oxide nanoparticles (NPs) exhibit intrinsic peroxidase-like catalytic activity, efficiently decomposing  $\text{H}_2\text{O}_2$  and oxidizing organic compounds. Despite extensive research on their catalytic properties, the precise reaction mechanisms governing their activity remain unresolved, particularly with respect to their structural characteristics and the influence of the surrounding medium.

This study focuses on nanozymes composed of  $\text{Fe}_3\text{O}_4$  (magnetite) and  $\text{Fe}_2\text{O}_3$  (hematite) nanoparticles. Using density functional theory (DFT) and classical molecular dynamics simulations, we explore the chemical reactivity of these materials in both vacuum and under microsolvation by water. The climbing image nudged elastic band (CI-NEB) method is employed to locate transition state structures, enabling the determination of thermodynamic feasibility and kinetic barriers of the  $\text{H}_2\text{O}_2$  decomposition reaction. We analyze the (001) surface of both materials and relate our findings to experimental data, including electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM) results.

Our simulations reveal key insights into the differences in reactivity between  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , particularly in the production of OH and OOH radicals, as observed experimentally. While both surfaces predominantly expose  $\text{Fe}^{3+}$  ions,  $\text{Fe}_3\text{O}_4$  nanozymes exhibit significantly higher OH radical production. We have analyzed in the first place possible  $\text{H}_2\text{O}_2$  decomposition mechanisms in the surfaces. We then performed classical MD simulations for understanding water solvation patterns. This allowed us to extract the most populated solvent conformations, and include a few water molecules directly interacting with the surface in the electronic structure calculations. By examining the electronic structure and charge transfer mechanisms, we elucidate the influence of water microsolvation and provide a comprehensive explanation for the experimentally observed catalytic differences between these materials.