Metal-Like Molecule for Stable Oxygen-Evolution: Natural Mimic by Integrating Co_4O_4 Cubane into Polypyrrole

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Exploration of efficient and stable water oxidation catalysts based on polynuclear metal-oxo clusters remains the primary challenge in conversion of renewable energy sources into fuels. The cubic $\{Co_4O_4\}$ complexes, inspired by the natural inorganic core of photosystem II (PSII), have continuously attracted interest as molecular water oxidation catalysts combining features of both heterogeneous and homogeneous catalysis. However, further application remains impeded by the instability during oxygen evolution reaction (OER) and missing knowledge of the design concept in molecular level. Photosystem II (PSII), as a protein complex, shows asymmetric structure and ligand-protein environment for stabilizing the catalytic cubic core. Here, we present a molecular synthetic strategy for stabilization of the Co_4O_4 cubane oxo by both the asymmetric design and the integration with conjugated polypyrrole, thus avoiding the intermolecular aggregation during the OER process. The asymmetric design not only prevents the catalyst decomposition, but also increases the catalytic efficiency by providing the directed cofacial dihydroxide motif. In addition to the protection, polypyrrole is a p-type conducting polymer that promotes the holes transfer during the OER process, resulting in a high turnover frequency (TOF) to the $\{Co_4O_4\}$ molecular catalyst. By a combination of experimental and theoretical results, different oxygen evolution pathways, affected by intramolecular hydrogen bond (IHB), are proposed. This study follows the natural feature and provides an elegant design concept for stabilizing the polynuclear oxo and improving the efficiency of $\{Co_4O_4\}$ cubane for long-term OER.