Title:

Precise Manipulation of Iron Spin States for A Near 100% Selectivity of Singlet Oxygen Production

Authors & affiliations:

Na Lu[1,2], and Fu Liu[*1,2]*

[1]Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China;
[2]University of Chinese Academy of Sciences, Beijing, China.

Abstract:

Singlet oxygen ($^1O_2$) is a long life non-radical reactive oxygen specie (ROS) with attracting properties such as strong electrophilicity, high selectivity, wide pH tolerance and high-salty resistance comparing with radicals (•OH and $SO_4^{\bullet-}$). The regulation of atomic coordination structure of single-atom catalysts (SACs) is an excellent strategy for promoting $^1O_2$ generation selectivity by peroxymonosulfate (PMS) activation. However, the current methods to regulate the type and form of coordination atoms are complex and uncertain, so developing a simple and effective method to regulate the atomic structure of SACs is necessary. Here, melamine, cyanuric acid and Fe were uniformly complexed to form supramolecular aggregates, following with the thermal polymerization process to prepare Fe single-atom carbon-nitride catalyst (Fe-CN). We manipulated the coordination environment of Fe-CN through simply changing the heating rate (e.g. 2, 3, 4 ºC/min, respectively) to precisely control the spin state of the iron. As indicated by experiment and density functional theory (DFT) calculations, FeON6, FeON4, FeN6 were active sites under different heating rates, and $^1O_2$ generation proportion was 67.0%, 78.0%, 98.5%, respectively. The adsorption, electron transfer and dissociation of PMS on higher-spin FeN6 were all more favorable than those on the atomic structures containing Fe-O bond at the vertical direction of CN surface. The generated $^1O_2$ degraded organic pollutants with high efficiency across high salinity and broad pH range, and the assembled membrane exhibited a high catalytic degradation rate of 4224 min^{-1}, beyond most of state-of-the-art catalytic materials. The modulation of temperature rise process and further design of coordination environment during catalysts preparation can be considered as a novel design principle for SACs toward PMS activation. This work provides a new idea for improving the $^1O_2$ generation selectivity of SACs.

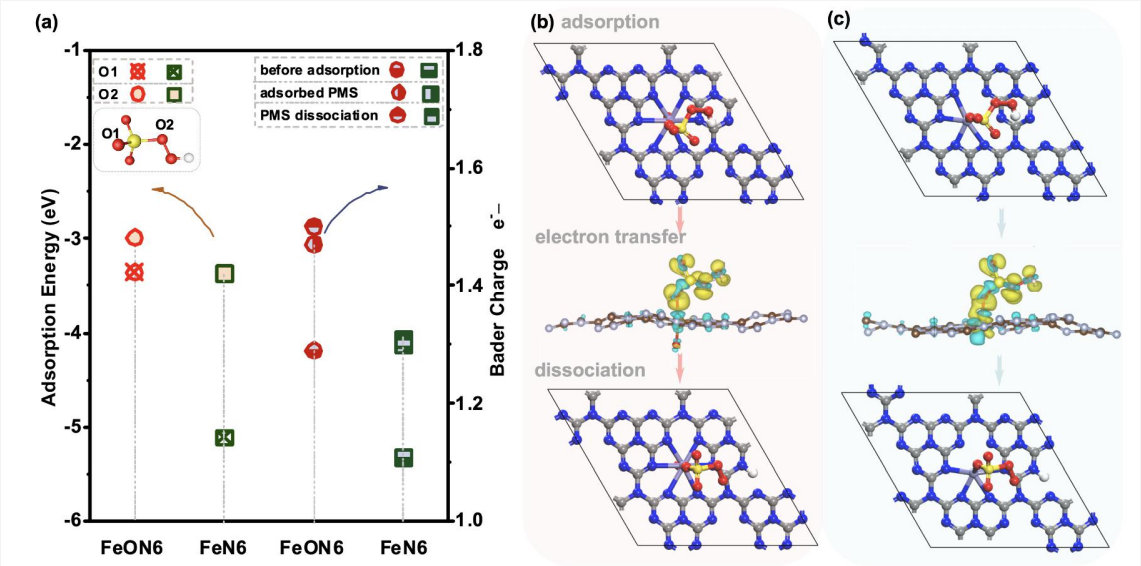

Figure. DFT calculations.