Supporting information

Construction of Highly Active $FeN_4@Fe_x(OH)_x$ (x=0, 4, 8, 12) Clusters Composite Sites for Oxygen Reduction Reaction and Oxygen Evolution Reaction

Yulin Zhang[1]; Xihao Chen[2]; Siyu Gan[5]; Yu Hu[3,4]; Yi Tian[1]; Shiyu Wang[1]; Long Chen[1] ; Junping Xiao[6,*] and Ning Wang[5,*]

1. School of New Energy Materials and Chemistry, Leshan Normal University, Leshan, Sichuan 614000, China.
2. School of Materials Science and Engineering, Chongqing University of Arts and Sciences, Chongqing, 402160, China
3. Leshan West Silicon Materials Photovoltaic and New Energy Industry Technology Research Institute, Leshan, Sichuan 614000, China.
4. Material Corrosion and Protection Key Laboratory of Sichuan Province, Zigong, Sichuan 643000, China.
5. School of Science, Key Laboratory of High Performance Scientific Computation, Xihua University, Chengdu 610039, Sichuan, China
6. College of Physics and Electronic Information, Baicheng Normal University, Baicheng, Jilin 137000, China

*Correspondence: djtc999@163.com (Junping Xiao); ningwang0213@163.com (Ning Wang)

Computational details

For FeN_4@Fe_4, FeN_4@Fe_8, and FeN_4@Fe_{12}, we calculate how much OH species needs to be adsorbed on the Fe_x cluster before it can be adsorbed on the FeN_4 site. The calculation steps are as 1) The adsorption strength of one OH at various sites (including FeN_4 and Fe atoms of the Fe_x cluster) is calculated, and the strongest adsorption site is obtained; 2) Based on the first step, the adsorption strength of the second OH on the other sites is calculated to determine the strongest site; 3) …… The results indicate that the OH can only start to absorb on the FeN_4 site after there is full OH absorbed on the Fe_x cluster.

The solvation effect by water on ORR/OER activity is calculated using DFT calculations as an implemented implicit method in VASPsol. The adsorption energy in the water solvent environment is calculated as:

$$E_{\text{ads-solv}} = E_{\text{a}} + (E_{\text{solvent}} - E_{\text{vac}})$$

where E_{a} is the adsorption energy in the vacuum, E_{solvent} is the total energy of adsorbate on the catalyst by an implicit solvent model, and E_{vac} is the total energy of adsorbate on the catalyst under a vacuum environment.

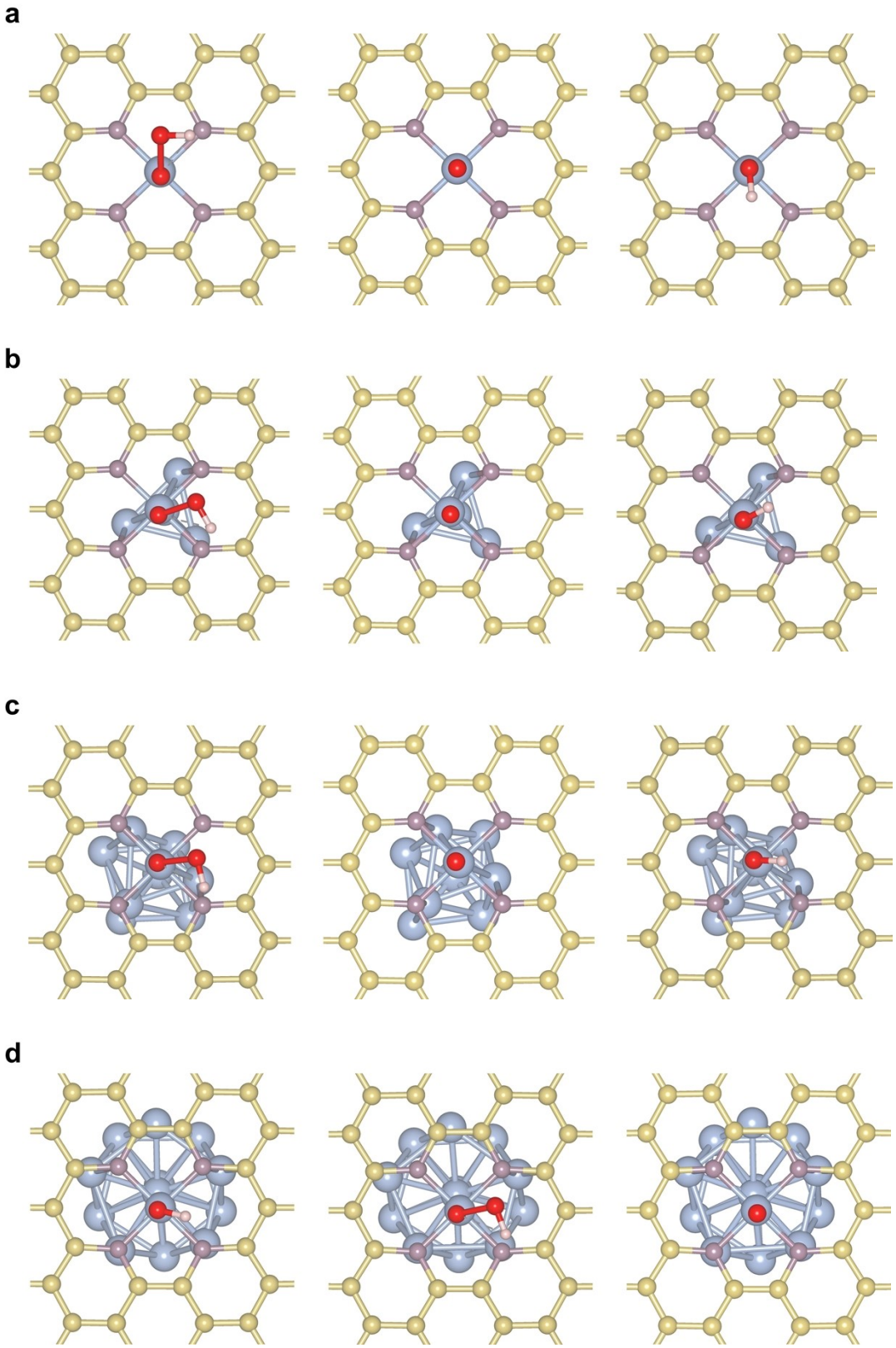

Fig. S1. The optimized structures of reaction intermediates adsorbed on (a) FeN_4, (b) $FeN_4@Fe_4$, (c) $FeN_4@Fe_8$, and (d) $FeN_4@Fe_{12}$, respectively.

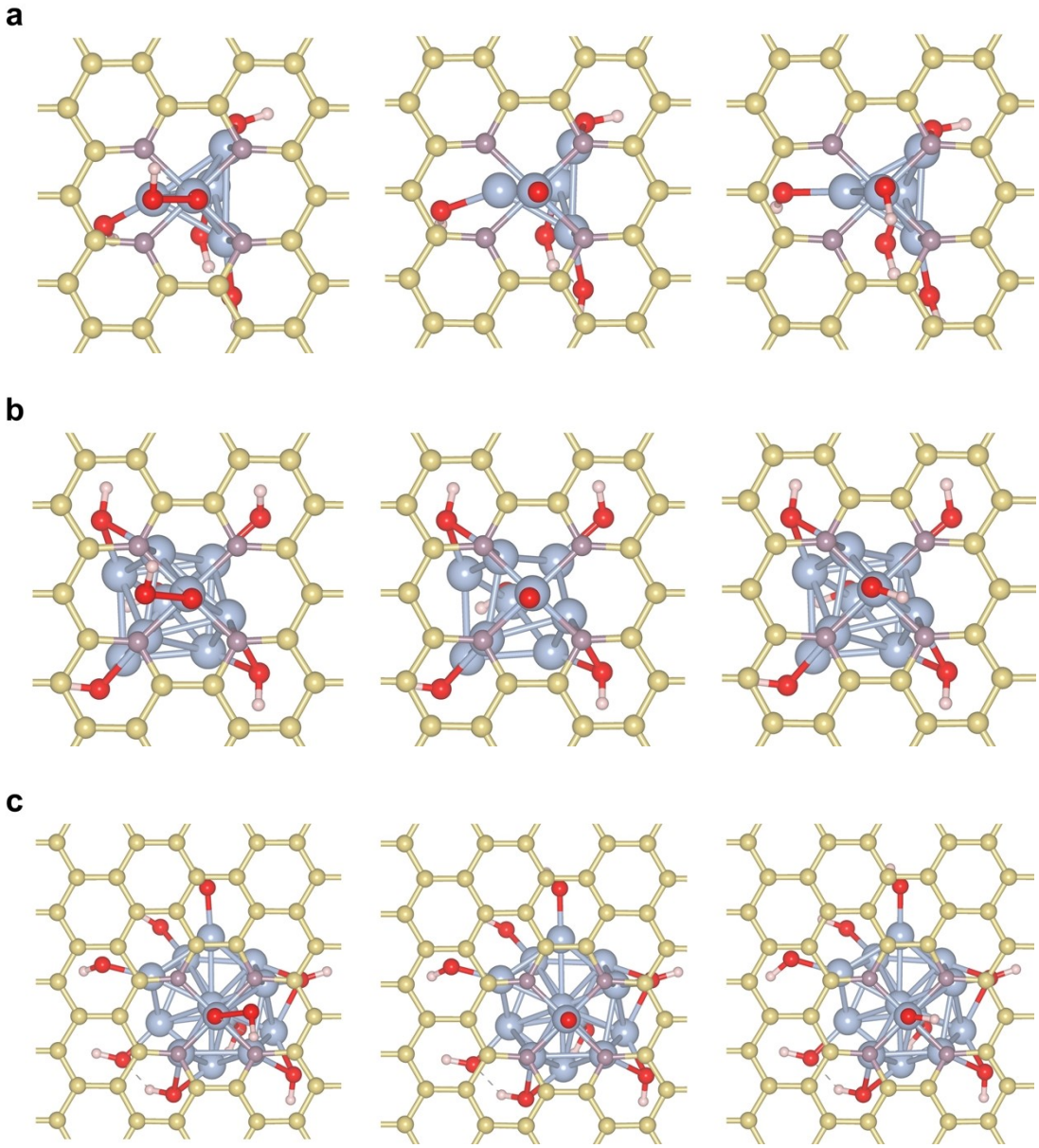

Fig. S2. The optimized structures of reaction intermediates adsorbed on (a) $FeN_4@Fe_4(OH)_4$, (b) $FeN_4@Fe_8(OH)_6$, and (c) $FeN_4@Fe_{12}(OH)_8$, respectively.