PRF # 58633-DNI6
Project Title: Computational Modeling of High Temperature Water-Gas Shift Reaction over Iron Oxide Catalysts
Directed by: Dr. Peilin Liao

***In the first year of the grant, we have made progress in the following projects:***

1. High temperature water-gas shift reaction over iron oxide catalysts

We have been investigating the reaction mechanism of high temperature water-gas shift reaction over iron oxide catalysts. We applied first principles DFT+U calculations to study the (111) surface of $Fe_3O_4$. We identified the stable termination under experimental conditions (Figure 1) and started to study how the surface catalyzes the water-gas shift reaction. The complexed $Fe_3O_4$ (111) surfaces give rise to several possible pathways for water dissociation and CO oxidation. We are investigating how various surface sites affect the reaction energetics and preparing a manuscript on our findings.

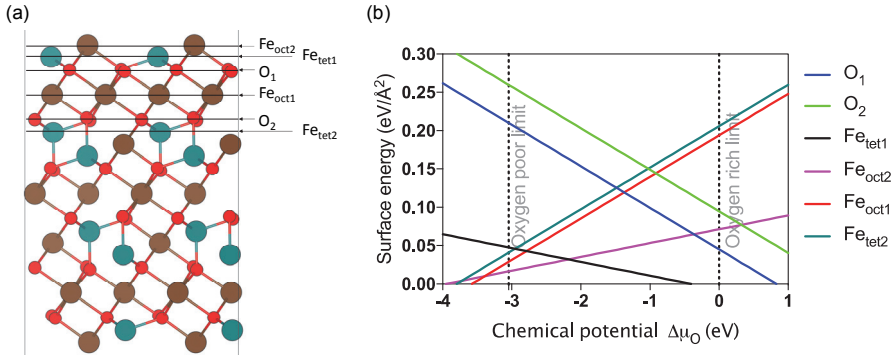


**Figure 1.** (a) Illustration of possible surface terminations for $Fe_3O_4$ (111) surface. (b) Surface energy calculated for different terminations.

2. Hydrogen evolution reaction (HER) on Ni and $Ni_3N$ interface

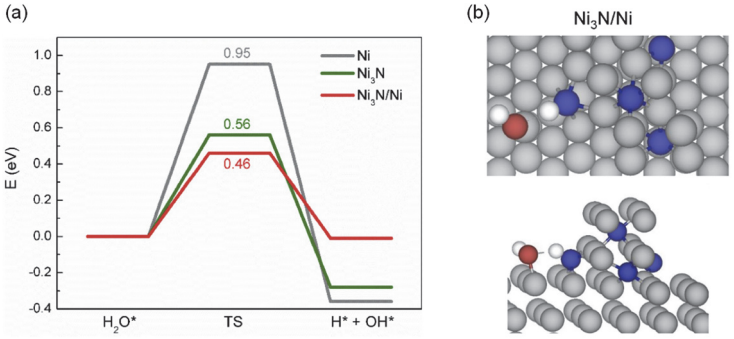


**Figure 2.** (a) Energy barrier for water dissociation on Ni, $Ni_3N$, and $Ni_3N$/Ni. (b) Transition state structures for water dissociation over $Ni_3N$/Ni. Color code: Ni: grey; N: blue; H: white.

We investigated the hydrogen evolution reaction on pure Ni, pure $Ni_3N$ and $Ni_3N$/Ni interface. We studied hydrogen adsorption, water adsorption and water dissociation on the three catalysts. The interfacial N site and Ni hollow site of $Ni_3N$/Ni interface give close to zero Gibbs free energy of hydrogen adsorption, 0.01 eV and -0.07 eV, respectively, which indicates promising reaction sites for HER. To further investigate the HER activity under neutral and alkaline conditions which is a lack of free protons, we simulated the water adsorption and dissociation on the interfacial structure. The water adsorption results shows a strong surface-

water attraction with an adsorption energy as -0.33 eV. Furthermore, the $Ni_3N$/Ni interfacial structure gives a significantly lower barrier of 0.46 eV in water dissociation reaction, compared to 0.95 eV for pure Ni and 0.56 eV for $Ni_3N$ (Figure 2). Our calculations support and explain excellent performance of the hybrid catalysts synthesized by our collaborators. These results have been published in *Nat. Commun.* 9, 4531 (2018).

3. Hydrogen evolution reaction (HER) on Co and $Co_2N$ interface

We also studied the HER on pure Co, pure $Co_2N$ and $Co_2N$/Co interface. The $Co_2N$/Co exhibits the strongest water adsorption among the three models, and the optimal water adsorption site is located at the interface of $Co_2N$/Co with one of the H atoms in water approaching the edge N in $Co_2N$ through hydrogen bond interaction. The critical transition state of water dissociation has the lowest energy on $Co_2N$/Co. In addition, the free energy changes of hydrogen adsorption at two interfacial sites of $Co_2N$/Co were calculated to be merely -0.02 and -0.04 eV, very close to the ideal value of 0 eV (Figure 3). In contrast, both $Co_2N$ and Co exhibit strong hydrogen affinity (-0.27 to -0.40 eV). Collectively, these DFT computational results demonstrate that the interfacial sites of $Co_2N$/Co can enhance water adsorption, facilitate water dissociation, and also exhibit optimal hydrogen adsorption energy, all of which contribute to its extraordinary HER activity. These results have been published in *ACS Energy Lett*. 4, 1594 (2019).

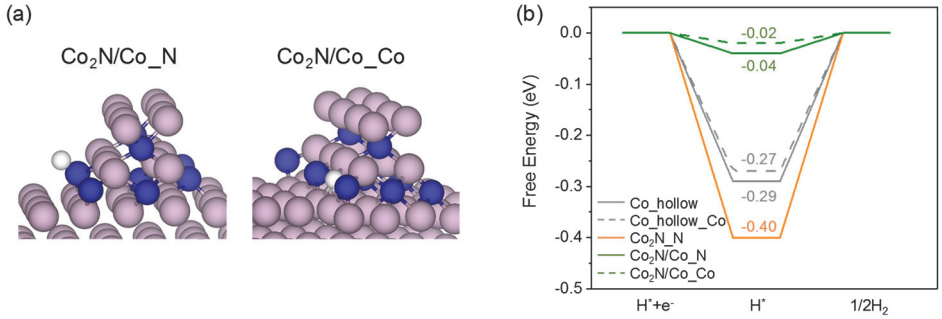


**Figure 3.** (a) $Co_2N$/Co interfacial structures showing two different sites for hydrogen adsorption. Color code: Co: light purple; N: blue; H: white. (b) Hydrogen adsorption free energy on pure Co, pure $Co_2N$, and $Co_2N$/Co interface.

***The impact of research on PI's career and the students***

1) The ACS PRF award allows the PI to support her graduate students to perform fundamental studies on iron oxide catalysis, develop new collaborations, and travel to numerous conferences and meetings for presenting their work and networking with researchers in the field.

2) Three graduate students (Pilsun Yoo, Jiaqi Yang, Shukai Yao) have been trained on this project and published peer-reviewed papers. Pilsun and Jiaqi have presented their work at the NAM 26 (2019 North American Catalysis Society Meeting).

***Publications that acknowledged this grant***

1. F. Song, W. Li, J. Yang, G. Han, T. Yan, X. Liu, Y. Rao,* P. Liao,* Z. Cao,* Y. Sun,* "Interfacial sites between cobalt nitride and cobalt act as superior bifunctional catalysts for hydrogen electrochemistry," *ACS Energy Lett*. 4, 1594 (2019).
2. F. Song, W. Li, J. Yang, G. Han, P. Liao,* Y. Sun,* "Interfacing nickel nitride and nickel boosts both electrocatalytic hydrogen evolution and oxidation reactions," *Nat. Commun.* 9, 4531 (2018).