PRF# 58740-UR6
Project Title: Computational Design of Single-Atom Active Sites on Porous Surface for Natural Gas to Liquid Fuel Conversion
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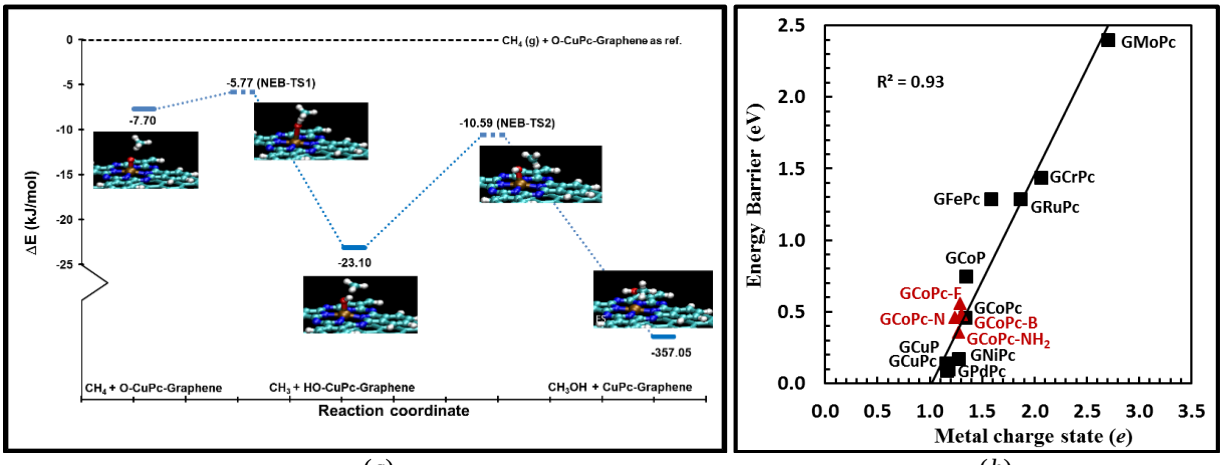
Progress Report:
We have extensively used the financial support from ACS-PRF award No. 58740-UR6 in the previous year for the methane to methanol conversion process on a single-atom active catalyst based on metal phthalocyanines and porphyrins materials. It was a very productive period. We aim to continue the current work and to train undergraduate students to motivate further for their higher study and research for the workforce. In this project, four undergraduate students were recruited and received highly interdisciplinary training in the increasingly competitive and fast-moving area of nanoscience and nanotechnology research. Three students were directly involved in computational work and one student was involved in experimental work to verify some of the theoretical results. All the undergraduate students supported by this grant have graduated with their BS degree in Chemical Engineering. One student is pursuing towards his PhD degree in another University, two undergraduate students are continuing towards their MS degree at New Mexico Tech, and the fourth student is preparing himself after completion his BS degree for his aspiration to get into Harvard University. The financial support from this grant has helped my research group to continue the current project, which will guide the future development of single-metal atom based catalysts by providing not only the choice of catalysts but also the reaction conditions for complete methane to methanol conversion processes at mild conditions. The financial support has also helped the group to explore new research area such as bi-functional catalysts development for OER/ORR based on Perovskite materials. The results obtained from this new research area on OER/ORR from my group helped me to submit a new NSF proposal in the new direction.

Scientific Achievement:
1. Methane to methanol chemistry on metal phthalocyanines and porphyrins functionalized graphene
We have studied the methane chemistry on metal phthalocyanine and porphyrin surfaces and our results indicate that the strong C-H bond (in CH_4) can be activated on both the surfaces. These surfaces could be very promising catalyst for selective conversion of methane to methanol at low temperature. In this work, single-metal active site based on 10 different phthalocyanine/porphyrin functionalized graphene materials have been screened and characterized for the C–H bond activation of methane to methanol conversion process using ab initio density functional theory (DFT) calculations. The results show that a radical mechanism is the predominant mechanism for the C–H bond activation process of methane for these type of materials as shown in **Figure 1(*a*)**. An inverse correlation between the metal-oxo species formation energy and the C–H bond activation energy was observed and both of them have a nice correlation with an electronic descriptor known as metal charge state of the metal-oxo species of these materials as shown in **Figure 1(*b*)**. The catalytic activity of this system can further be tuned by controlling the metal charge state of metal via both substrate doping and ligand exchange. Some of the results were already presented by undergraduate students in both national and local conferences. Now, the results are also considered for publication in peer reviewed journal article. [1]

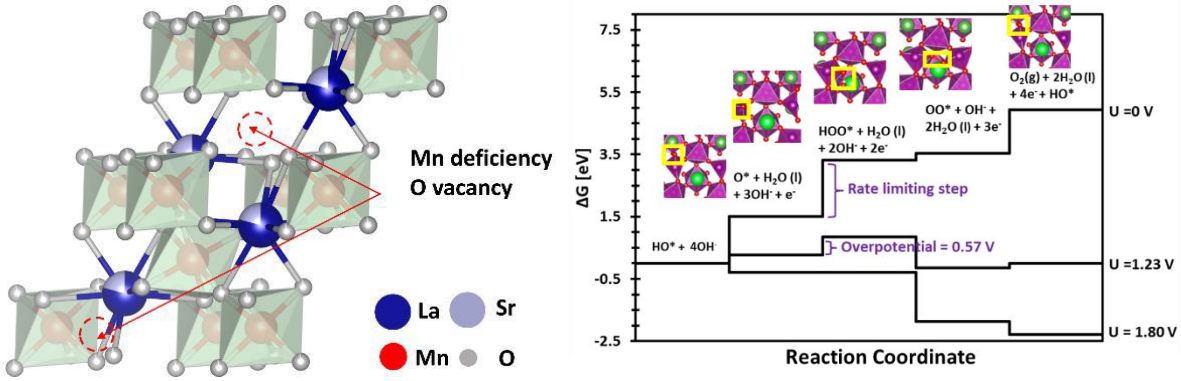


(*a*) (*b*)

Figure 1. (*a*) Reaction energy profile for the reaction of CH_4 with pre-adsorbed O atom on CuPc functionalized graphene surface *via* radical mechanism. (*b*) Metal charge state of catalyst explored as a descriptor of C−H bond activation energy. Black square represents the GMPc−O systems and red triangles represents the GCoPc−O system with graphene substrate modified with N and B doping, and CoPc with NH_2 and F ligands.

2. OER/ORR Perovskite Catalysts

We have also leveraged the financial support from ACS-PRF and recruited one undergraduate student to work on newly improved perovskite oxides materials, bifunctional oxygen electrocatalysts for oxygen evolution/reduction reactions, have major implications to energy conversion devices such as fuel cells and rechargeable metal-air batteries. For the first time, we have shown that OER/ORR performance can be improved of A-site excess of $La_{1-x}Sr_xMnO_3$ (LSM) Perovskite, and it can be attributed to transition metal *d*-band center upshift and oxygen *p*-band center approaching Fermi level. Some of the works have already been published in ACS Catalysis [2]. The undergraduate student is now continuing the same work for his MS degree.



(*a*) (*b*)

Figure 2. (*a*) $La_{1-x}Sr_xMnO_3$ (LSM) Perovskite with Mn and O deficiency. (b) Free energy diagram of a four-step OER mechanism on $La_{1-x}Sr_xMnO_3$ (LSM) (001) surface in alkali medium. In all schematics, each purple ball is Mn, fluorescent green ball is Sr, green ball is La, red ball is O and white ball is H.

Peer reviewed journal articles:

1. Filonowich, D.; Luna, M.; Quinn, T. and Choudhury, P. "Electronic Descriptor of Single Metal-Oxo Species on Phthalocyanine and Porphyrin Functionalized Graphene Towards Methane Activation Process." (2019) (under review).
2. Xu, W.; Apodaca, N.; Wang, H.; Yan, L.; Chen, G.; Zhou, M.; Ding, D.; Choudhury, P. and Luo, H. "A-site Excessive (La0.8Sr0.2)1+xMnO3 Perovskite Oxides for Bifunctional Oxygen Catalyst in Alkaline Media." ACS Catalysis 9, 5074 (2019).

Technical (oral/poster) presentations:

- Apodaca, N. and Choudhury, P. "Density Functional Theory Study of Oxygen Evolution Reaction on Specific Terminated Facets of Perovskite Oxides." *AIChE Annual Meeting*, 2018, Pittsburgh, PA.
- Luna, M.; Quinn, T.; Kerwin, J.; Headrick, S.; Mussel, S. and Choudhury, P. "Computational Screening and Characterization of Single-Atom Catalysts for Natural Gas to Liquid Feedstock Conversion Process." *AIChE Annual Meeting*, 2018, Pittsburgh, PA.
- Mantos, P.; Chowdhury, S. and Choudhury, P. "The Screening of Single-Atom Active Sites on Two-Dimensional Material for Methane to Methanol Conversion." *AIChE Annual Meeting*, 2018, Pittsburgh, PA.
- Choudhury, P.; Luna, M.; Stalcup, M.; Filonowich, D. "Computational Screening and Characterization of Single-Atom Active Site for Methane to Methanol Conversion Process." *NM-AVS*, 2018, Albuquerque, NM.
- Stalcup, M. and Choudhury, P. "Computational Screening and Characterization of Heterogeneous Catalysts for Natural Gas to Liquid Feedstock Conversion Process." *SRS* 2018, Socorro, NM.