

**PRF# 58167-ND10**

**Project Title:** Heteroatom-Doped Porous Carbon Derived from Petroleum Coke for Electrocatalytic Conversion of Carbon Dioxide to Fuels

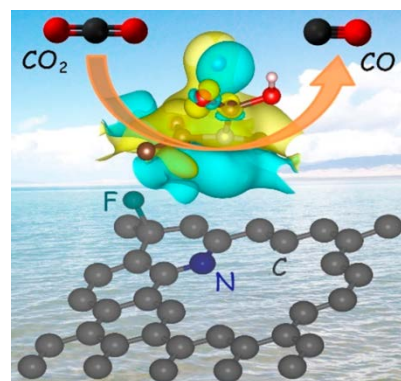
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**Narrative Progress Report**

The goal of this project is to develop a cost-effective heteroatom-doped carbon catalyst from petroleum coke to transfer CO<sub>2</sub> into valuable fuels. In the first year, we mainly focused on the exploration of transition metals active sites and catalytic mechanisms for electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>RR). In the second year, we have explored non-metal heteroatoms (S and F) as catalytic sites for CO<sub>2</sub>RR, where these dopants can be usually found among the impurities of petroleum coke. In addition, we have successfully fabricated an efficient catalyst using petroleum coke as the raw feedstock and demonstrated the possibility of using petroleum coke to replace traditional graphite materials. Here, we report the main achievements and progress achieved in the second year, described as follows:

1. Efficient CO<sub>2</sub> electroreduction by highly dense and active pyridinic nitrogen on holey carbon layers with fluorine engineering

Electrocatalytic CO<sub>2</sub> reduction by nitrogen-doped carbon (N-C) catalysts provides a solution for CO<sub>2</sub> reuse; however, it suffers a large overpotential and poor selectivity due to the low intrinsic reactivity of N dopants. To solve this problem, we promoted CO<sub>2</sub> reduction on N-C by increasing the numbers and inherent catalytic reactivity and selectivity of pyridinic N dopants. We synthesized a 2D nitrogen and fluorine co-doped holey carbon layers (NF-C) by annealing a mixture of sucrose, ammonium fluoride and dicyandiamide at 950 °C. In NF-C, the holey nanostructure can preferentially host dense edge-located pyridinic N, while electron-rich fluorine can activate pyridinic N sites by engineering their electronic properties (**Figure 1**). Consequently, the resultant NF-C exhibited a CO Faradaic efficiency of 90% at a low overpotential of 490 mV for 40 h without decay, significantly surpassing the F-free N-C counterpart. Density functional theory (DFT) calculations reveal that the electron donation from a nearby F atom increases the charge density and delocalizes electronic density of states of pyridinic N. These electronic benefits thus greatly promote the CO<sub>2</sub> activation on the highly dense and active pyridinic N sites by facilitating the electron transfer and strengthening the binding interaction with \*COOH intermediate. This work was published in *ACS Catalysis* **2019**, 9, 2124–2133.



**Figure 1.** Schematic illustration of the holey carbon layers with F engineering.

2. Promoting electrocatalytic CO<sub>2</sub> reduction on nitrogen-doped carbon with sulfur addition

In addition to fluorine (F) engineering to activate N-C, we also explored another dopant, sulfur (S), to improve catalytic CO<sub>2</sub>RR activity of N-C. We prepared N and S co-doped carbon (NS-C) by heating citric acid and thiourea mixture (**Figure 2**). The NS-C exhibited a high CO Faradaic efficiency of 92% and a CO current of 2.63 mA cm<sup>-2</sup> at a low overpotential of 490 mV, much better than that of the S-free N-C counterpart. By correlating dopant configurations with catalytic performance of model catalysts and

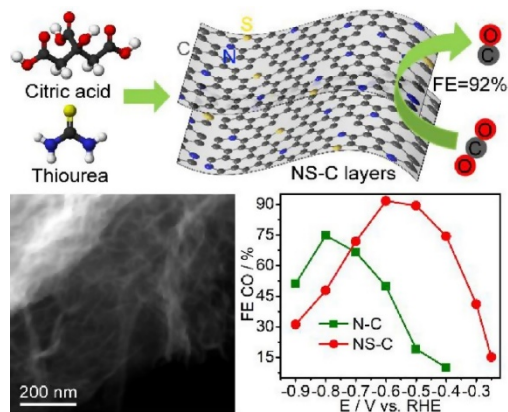
combining theoretical density functional theory (DFT) calculations, we revealed that incorporating S in N-C leads to the generation of a higher density of pyridinic N that serves as the determining active site for CO<sub>2</sub> activation. In addition, S dopants significantly promote the catalytic reactivity and selectivity of both pyridinic and graphitic N by decreasing the free energy barrier for key intermediate \*COOH formation. This work was published in *Applied Catalysis B: Environmental* 2019, 252, 240–249.

### 3. Highly efficient nickel and nitrogen co-doped carbon catalysts derived from industrial waste petroleum coke for electrochemical CO<sub>2</sub> reduction

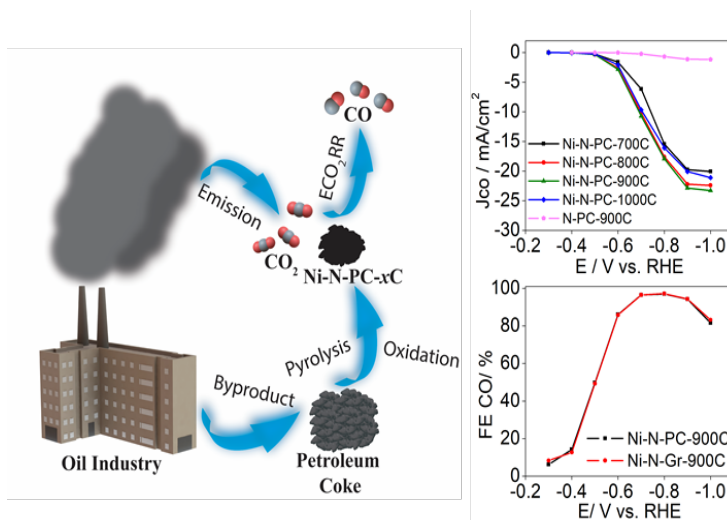
With the understanding that nitrogen-coordinated single atomic nickel sites (Ni-N) is highly selective and active to reduce CO<sub>2</sub> to CO, we prepared a high-performance N and Ni co-doped carbon catalyst with Ni-N sites for CO<sub>2</sub> reduction from petroleum coke. Using petroleum coke, a waste from oil industry as the catalyst building block is one of the major objectives in this ACS-PRF project. We activated petroleum coke by sulfuric acid and potassium permanganate at 55 °C overnight. By mixing it with urea and treating at 900 °C under Ar atmosphere, we prepared a Ni and N co-doped carbon catalyst. As a result, 97% CO faradaic efficiency has been achieved on the co-doped petroleum coke with a current density at about 18mA/cm<sup>2</sup> at -0.8V versus the reversible hydrogen electrode (RHE) (**Figure 3**). Compared to the traditional graphite-based material, petroleum coke provides an alternative solution as a much cheaper and more abundant source in the large-scale application of CO<sub>2</sub>RR while maintaining a similar electrocatalytic performance. This work is being submitted to *ACS Sustainable Chemistry & Engineering*.

In summary, in this two-year project we have advanced the fundamental understanding of catalytic active sites for CO<sub>2</sub> reduction and prepared a petroleum coke-derived highly active catalysts to reduce CO<sub>2</sub> into CO. The concept of beneficial reuse of two waste products (petroleum coke and CO<sub>2</sub>) from petroleum industry has been demonstrated.

This ACS-PRF New Direction Award has enabled the PI to explore a new field of electrochemical CO<sub>2</sub> reduction. The fund has been used to partially support and train two postdoctoral fellows and a PhD student.



**Figure 2.** The illustration of N-doped carbon catalyst preparation, morphology and electrocatalytic performance with S addition.



**Figure 3.** The process of CO<sub>2</sub>RR using petroleum coke as catalyst building block; catalytic performance of petroleum coke based catalysts (Ni-N-PC-xC) in comparison with graphite based catalyst (Ni-N-Gr-900C).