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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 highly active and low-cost carbon electrocatalysts by activating petroleum coke for electrochemical reduction of CO_2 into value-added fuels, targeting the creation of a green route to reusing waste byproduct of oil refining. Our hypothesis is that the combination of engineering atomic-level electronic properties of dopants and constructing meso-scale porous carbon structures can enhance the overall performance for CO_2 reduction reaction (CO_2RR). Within the first year, we mainly focused on the exploration of active sites and catalytic mechanisms of carbon-based catalysts for CO_2RR. Guided by obtained results, we have also started the functionalization of petroleum coke to prepare CO_2RR catalysts. Here, we report the main achievements and progress achieved in the first year, described as follows:

1. Identification of champion transition metals centers in metal and nitrogen co-doped carbon (M-N-C) catalysts for CO_2 reduction

M-N-C is a promising generation catalyst for CO_2RR. However, among various popular transition metals (Cr, Mn, Fe, Co, Ni), the champion metal center is not clear. To do this, we synthesized M/N-doped carbon nanosheets as model catalysts by thermal treatment of citric acid, urea, and metal nitrate at 900 °C under Ar atmosphere. We calculated the maximum achievable Faradaic efficiency (FE) and turnover frequency (TOF) for CO generation at corresponding overpotentials to gauge the reactivity order of these five transition metals. As shown in **Figure 1**, Fe-N-C showed the lowest overpotential of 0.38 V to reach maximum FE of 87 % and Ni-N-C showed the highest FE of 96% and the highest TOF of 1060 h^{-1} at a moderate overpotential of 0.64 V, which are much better than others. It is thus concluded that Fe and Ni are intrinsically efficient metals in M-N-C for the reduction of CO_2 to CO, while Mn, Co, and Cr possess lower properties in catalyzing CO_2 reduction. This work was published in *Applied Catalysis B: Environmental*, 2018, 226, 463-472.
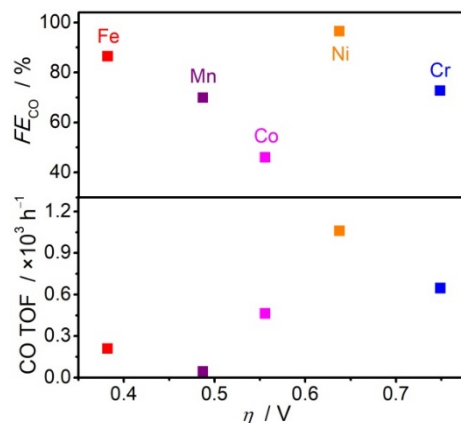
Figure 1. Summary of maximum CO FEs and CO TOFs at corresponding overpotentials over M-N-C.

2. Unveiling active sites of CO_2 reduction on N coordinated single atomic Fe and Co catalysts

The catalytic nature and structure of active sites on M-N-C was also not well-understood because M-N-C commonly have mixed phases of M−N and metallic aggregates, which makes it difficult to accurately reveal catalytic reactivity of M−N. We thus investigated the reactivity and catalytic sites structure of M−N (M=Fe or Co) for CO_2 reduction through a combination of experimental and theoretical approach, i.e. the synthesis of isolated Fe−N_4 or Co−N_4 structures and the theoretical identification of active M−N_4 configuration by first-principles DFT calculations. The atomically dispersed M-N-C catalysts (**Figure 2**) with well-defined M−N_4 sites were prepared by thermal activation of Fe or Co-doped zeolitic imidazolate
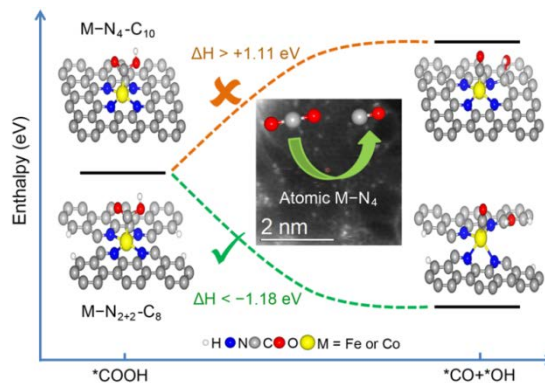
frameworks (ZIF). Activity tests revealed that Fe−N_4 is intrinsically more active than Co−N_4 for CO_2 reduction to CO. In addition, the edge-hosted M−N_{2+2}-C_8 bridging two armchair-like graphitic layers was computationally identified to be the active moiety for the cleavage of COOH intermediate to generate CO; however, the traditionally proposed bulk-hosted M−N_4-C_{10} moiety with M−N_4 embedded compactly in a graphitic layer is not active. This work was published in *ACS Catalysis*, 2018, 8, 3116-3122.

Figure 2. The dissociation of COOH on M−N_{2+2}-C_8 and M−N_4-C_{10}.

3. Constructing carbon nanotube/carbon nanosheet architecture for efficient CO_2 reduction
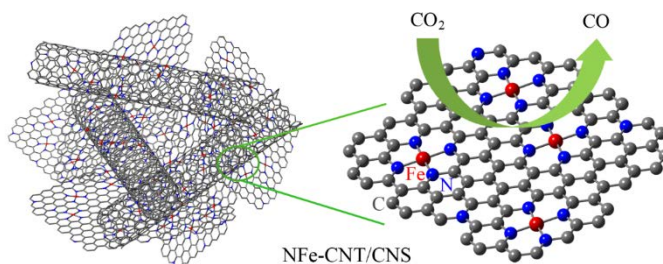
M-N-C architecture and dopants distribution are important factors determining catalytic CO_2 activity. We proposed that the integration of favorable carbon architecture and dense dispersion of N/Fe dopants in carbon frameworks with enhanced synergetic effects could accelerate the electrocatalytic CO_2RR activity. We thus prepared a novel electrocatalyst featuring carbon nanotube (CNT)/carbon nanosheet (CNS) architecture decorated with N/Fe dopants (NFe-CNT/CNS) via a silica-protected calcination method.

NFe-CNT/CNS has substantially enriched density of Fe−N complex and N defects providing numerous active sites, and the 3D architecture between CNT and CNS not only affords enhanced electrical conductivity but also facilitates mass transfer. These integrated advantages endow FeN-CNT/CNS with high electrocatalytic activity for CO_2RR with a low onset overpotential of 0.19 V. This work was published in *Electrochimica Acta*, 2018, 273, 154-161.

Figure 3. The proposed structure of NFe-CNT/CNS for CO_2 reduction.

Finally, we have published a review paper in *Engineered Science*, 2018, 1, 21-32. In this Review, recent advances of designing and synthesizing nitrogen coordinated single atomic transition metals supported on nanocarbons (M−NX-C; M=Fe, Ni, Co) as electrocatalysts for CO2RR are reviewed from both experimental and computational aspects. The catalytic mechanisms and design principles are highlighted, and the correlations of catalyst synthesis-structure-performance relationships are discussed. Based on our experimental results and literature review, we proposed that the doping of carbon with Fe and/or Ni and the construction of micropores to create high-density M−N_{2+2}-C_8 structures could make carbon more efficient for the reduction of CO_2 to CO, which is being used as guidelines to activate petroleum coke for the preparation of low-cost carbon catalysts for CO_2RR application. In the second year, we will focus on developing petroleum coke based catalysts for efficient CO2RR.

This ACS-PRF New Direction Award has enabled the PI to explore a new field of electrochemical CO_2 reduction. The fund has been used to partially support and train two postdoctoral fellows.