Graphene Oxide-Derived Non-Precious Metal Oxygen Reduction Catalysts

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One particular potential application of graphene in the area of advanced energy materials is to use it as a catalyst for oxygen reduction reaction (ORR)–an important electrochemical reaction, crucial to a variety of electrochemical energy storage and conversion processes (*e.g.* fuel cells and metal-air batteries).[1] The attractive properties of graphene in the context of electrocatalysis are high surface area (theoretical value: ~2630 m^2 g^{-1}), good chemical stability, excellent conductivity, unique graphitic basal plane structure, and the amenability to functionalization.[2]

Chemical doping with heteroatoms (*e.g.*, N, B, P, or S) into graphene planes can tune the electronic properties, provide more active sites, and enhance the interaction between carbon structure and oxygen molecules. Among various heteroatoms, nitrogen doping plays a critical role in modifying graphene materials due to comparable atomic size of nitrogen and carbon, as well as the presence of five valence electrons in the nitrogen atoms to form a strong covalent bond with carbon atoms. It was experimentally found that the nitrogen atoms can be incorporated into the graphene basal plane, replacing carbon atoms at different locations and leading to the formation of various defects.[3,4] Theoretical studies have shown that nitrogen can be viewed as an *n*-type carbon dopant that assists in the formation of disordered carbon nanostructures and donates electrons to carbon, thus facilitating the ORR.[5] In addition, a recent $\Delta\mu$ X-ray absorption spectroscopy (XAS) study has found that divacant defects (cavities) in the carbon support may serve as the anchors for N-doping and allow coordination of the central metal atoms (Fe or Co).[6]

These results imply that the maximum number of active centers, consisting of metal centers stabilized by nitrogen-containing ligands, is limited by the total number of defects in the supporting material. Compared to other type of carbon materials, a significant advantage of using graphene as a catalyst support is that more N-doped sites containing defect pockets/vacancies for coordination of metal ions are available.[7] Nitrogen-doped graphene structures have been found to be dominant in highly-active and durable ORR catalysts.[8-12] Thus, the presence of graphene seems important in the synthesis of active catalysts toward the ORR.

Graphene oxide (GO) is one of the main precursors of graphene-based materials. It was demonstrated that a complete reduction process for GO can lead to an effective restoration of the π-conjugated structure and result in highly conductive graphene materials, possibly making GO one of the most promising materials with controlled defects/vacancies *via* chemical oxidation process. Subsequent reduction can lead to the restoration of the π-conjugated structure, generating highly conductive graphene catalysts from GO.

We expect to prepare GO-based catalysts with designed doping location and coordination environment between metal and nitrogen or carbon. This may lead to an increase in the density in graphene of active sites with desirable binding structures.[7] In the preliminary experiments, we have prepared a GO-derived graphene catalyst using different nitrogen precursors (*e.g*

ethylenedimine-EDA, melamine-Me and polyaniline-PANI). Their corresponding ORR activity in acidic and alkaline electrolytes is shown in **Figures 1a** and **1b**, respectively. The potential advantages of using graphene oxide to prepare non-precious metal catalysts will be discussed and the correlation between synthesis-morphology-performance will be established for these GO-based ORR catalysts.
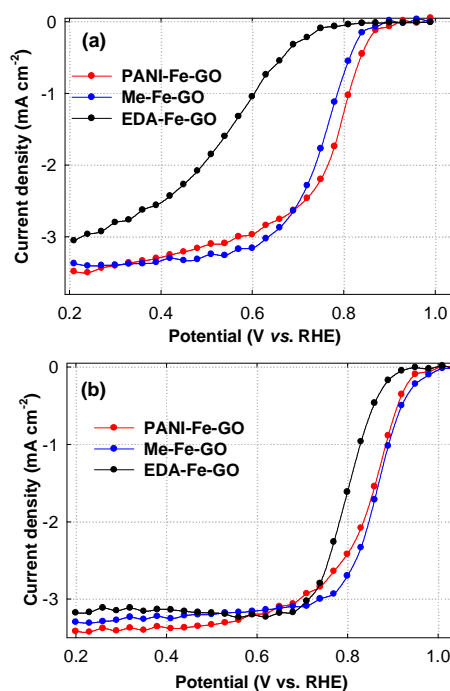

Fig. 1 ORR activity on graphene oxide based catalysts in (a) acidic and (b) alkaline media

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