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Pre-doped oxygenated defects activate nitrogen-doped graphene for the oxygen reduction reaction

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Abstract

The presence of defects and chemical dopants in metal-free carbon materials plays important roles in the electrocatalysis of the oxygen reduction reaction (ORR). The precise control and design of defects and dopants in carbon electrodes will allow the fundamental understanding of activity-structure correlations for tailoring catalytic performance of carbon-based, most particularly graphene-based electrode materials. Herein, we adopted monolayer graphene – a model carbon-based electrode – for systematical introduction of nitrogen and oxygen dopants, together with vacancy defects, and studied their roles in catalyzing ORR. Compared to pristine graphene, nitrogen doping exhibited a limited effect on ORR activity. In contrast, nitrogen doping in graphene pre-doped with vacancy defects or oxygen enhanced the activities by 3.7 and 6.8 times, respectively. The optimal activity was achieved for nitrogen doping in graphene functionalized with oxygenated defects – 4.6 times more than nitrogen-doped and 7.3 times more than pristine graphene. More importantly, oxygenated defects is highly related to the 4e− pathway instead of nitrogen dopants. This work indicates a non-negligible contribution of oxygen and especially oxygenated vacancy defects for the catalytic activity of nitrogen doped graphene.[1-4]

References

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Figures

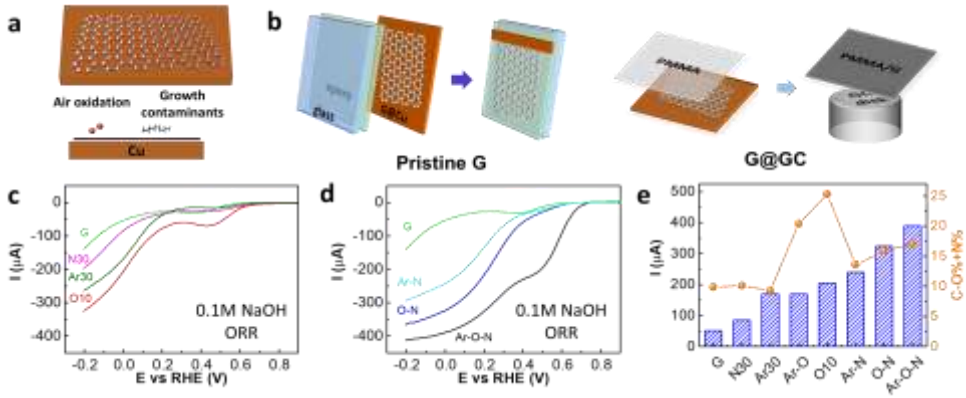

Figure 1: a) Illustration of air-face and copper-face of graphene. b) Preparation of pristine G supported by an epoxy substrate using the copper-face and G@GC using the air-face. c) LSV curves of G, N30, Ar30 and O10 samples at a rotation speed of 800 rpm. N30 represents 30 s nitrogenation, Ar30 for 30 s of argon plasma treatment, O10 for 10 s of oxygen plasma treatment. d) LSV curves of G, Ar-N, O-N and Ar-O-N samples. Ar-N represents graphene co-doped with Ar30 and N30, O-N for O10-N30, Ar-O-N for Ar30, O10 and N30 treated graphene. e) ORR activities correlate with atom % of carbon-oxygen and carbon-nitrogen (C-O%+N%) for non-, single- and dual-doped graphene samples.