sp-hybridized nitrogen atoms doped graphdiyne for oxygen reduction reaction

With the support by the National Natural Science Foundation of China and the Chinese Academy of Sciences, the research team led by Prof. Wang Dan (王丹) at the State Key Laboratory of Biochemical Engineering, CAS Center for Excellence in Nanoscience, Institute of Process Engineering, Chinese Academy of Sciences, uncovered the sp-hybridized nitrogen atoms doped into the defined sites of graphdiyne, which was published in *Nature Chemistry* (2018, 10(9): 924—931).

The research attention on ORR catalysts has been diverted from platinum-based materials to metal-free electrocatalysts, especially carbon-based catalysts due to the high cost and scarcity of platinum. Doping carbon materials with heteroatoms, especially the nitrogen atom, has proved to be an effective activation method, which can enhance the electronic density of states, electrical conductivity and surface hydrophilicity.

However, in previous studies, the doping on traditional carbon nanomaterials, which consist of sp^2-hybridized carbon atoms, only took place at defect sites or edges, thus it is hard to control. Wisely, by designing a pericyclic reaction on the sp-hybridized carbon atoms in graphdiyne, N atoms were site-selectively introduced into carbon nanomaterials and the doping proportions were naturally controlled. The following TG-DTA-MS, XANES and XPS characterization all proved their proposed mechanism, and the sp-hybridized nitrogen atoms, the novel doping form of nitrogen atoms, were induced into graphdiyne.

Additionally, due to the larger negative charge density of the sp-hybridized N atoms, the sp-N-doped graphdiyne presented the best comprehensive ORR performance among the reported metal-free electrocatalysts, and its catalytic activity superior to that of Pt/C in alkaline solution, as well as better stability and methanol resistance than Pt/C in both alkaline and acidic solutions.

Their doping strategy to incorporate sp-N atoms into carbon nanomaterials in a controllable way, and the understanding of the doping mechanism, may open new opportunities for site-specific doping of sp-N atoms into other catalysts and thereby broaden the scope of their applications.

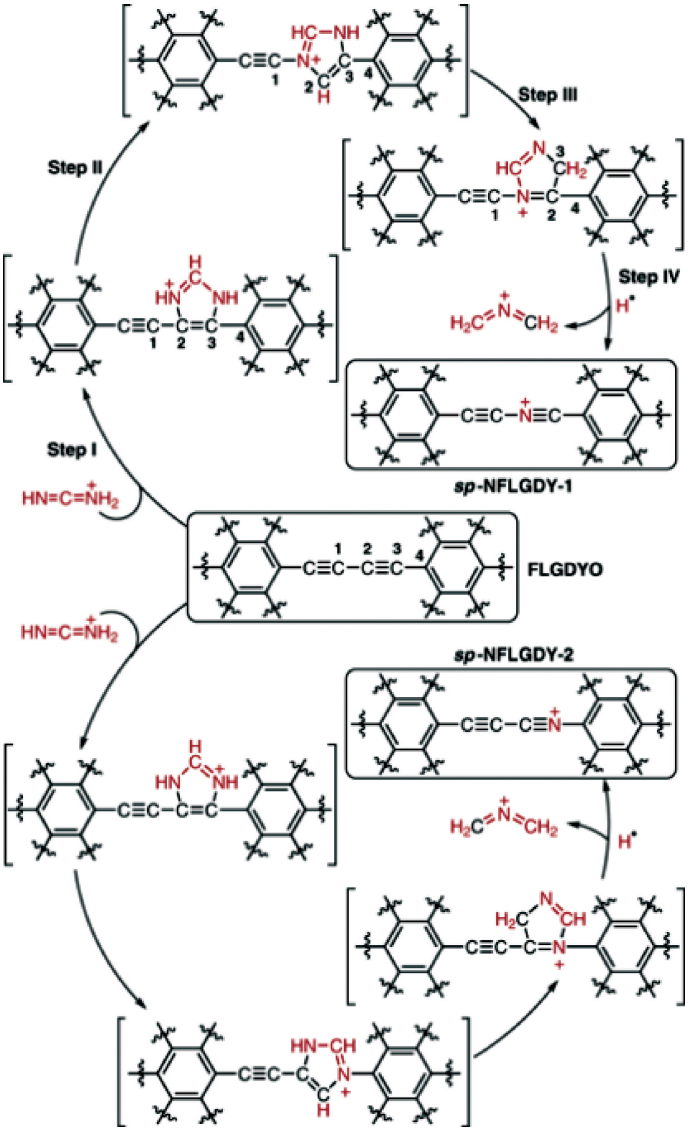

Figure The synthesis of sp-hybridized nitrogen doped graphdiyne.