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Defect density engineering for better graphene performance

Graphenes are emerging electrode materials used in many technologies such as electronics, sensors, as well as energy conversion and storage. The pristine graphenes, due to the elimination of density of states (DOS) at/near the Dirac point (Fermi level), have limited activities for charge transfer and storage. Fortunately, introduction of structural defects and disorders in graphenes can increase the DOS near the Fermi level by forming mid-gap and/or defect states, similar to that in silicon and other semiconducting materials. This improvement significantly promoted the application of pristine graphenes in electrochemical sensing and energy devices. In addition, defects related electronic structure variations in graphenes provides novel opportunity in studying the electrochemical structure-property relationship [1]. However, the delicate control over the defect-related electronic structures and precise correlation between the electrochemical activity and defect density remain challenging. Researchers led by Prof. Dongping Zhan and Prof. Bin Ren in Xiamen University have made significant advance in this field.

In their recent work published in *J. Am. Chem. Soc.* [2], the authors demonstrated that the density of vacancy defects in a graphene sheet can be precisely controlled through Ar^+ irradiation. They prepared patterns of different defect densities on a single-layer graphene sheet, and simultaneously mapped the defect density and the heterogeneous electron transfer (ET) rate of hydroxymethylferrocene (FcMeOH) oxidation over the same patterned graphene sheet (Figure 1), using Raman spectroscopy and the so-called scanning electrochemical microscopy. This new approach allowed them to quantitatively correlate the defect density in graphenes with the electrochemical activity for the heterogeneous ET reactions. The experimental results showed that the ET activity of graphene can be improved by increasing the density of vacancy defects. In addition, they obtained an optimal ET rate of FcMeOH oxidation over a graphene sheet with a moderate defect density. At such an optimal state, a balance between the increase of Fermi DOS and the decrease of sheet conductivity due to increasing the defect density was achieved, so that the whole graphene sheet not only becomes electrochemically activated, but also maintains structural integrity. According to their density functional theory calculations, the vacancy defect can induce mid-gap states in graphene. Because multiple electronic levels and states are involved in the heterogeneous ET between a solid electrode and redox molecules, the corresponding ET rates become proportional to the electronic overlap integral between the electrode and the redox molecules [1]. The introduction of mid-gap states should be able to enlarge the overlap between the DOS distribution of graphene and the redox molecules. The work by Zhan and coworkers represents an elegant example in tailoring the structure and property of graphene through defect density engineering.

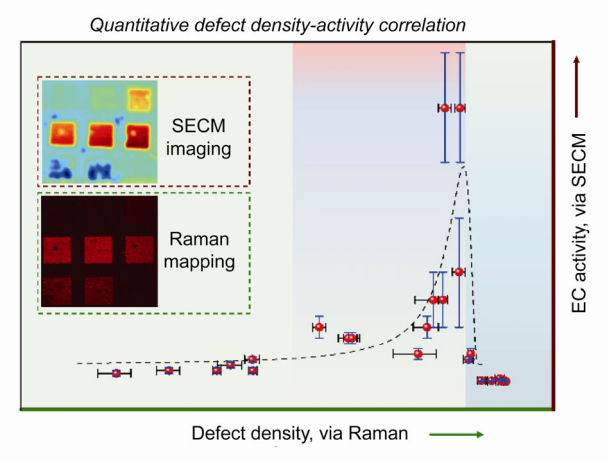

Figure 1 Defect density dependent electrochemical activity of single layer graphene [2].

Shengli Chen
College of Chemistry and Molecular Sciences,
Wuhan University

1 Chen SL, Liu YW, Chen JX. Heterogeneous electron transfer at nanoscopic electrodes: importance of electronic structures and electric double layers. *Chem Soc Rev*, 2014, 43: 5372–5386
2 Zhong J-H, Zhang J, Jin X, Liu J-Y, Li QY, Li M-H, Cai WW, Wu D-Y, Zhan DP, Ren B. Quantitative correlation between defect density and heterogeneous electron transfer rate of single layer graphene. *J Am Chem Soc*, 2014, 136: 16609–16617