Surface Functionalization of HOPG: Unravelling Wet Chemical Oxidation Mechanisms

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For the synthesis of heterogeneous catalysts and semi-conductors, surface functionalization (via area activation) of substrates using a bottom-up approach has gained great interest, due to the increasing control of the engineering surfaces on the atomic scale. This approach enables the creation of well-defined nanostructures otherwise unobtainable through the traditional lithographic (top-down) processes by directing metal or metal oxide deposition to occur at specific active sites, which are obtained through surface functionalization. The investigation of surface functionalization by acid etching of a well-defined graphite surface, as a model 2D material is presented.

In this study, we report the effect of two different acids that produce oxygen containing functional groups on highly oriented pyrolytic graphite (HOPG). The HOPG surface is a pristine and relatively unreactive surface that consists of a sp^2 hybridized network of carbon atoms on the basal plane and naturally occurring defect sites, such as step edges and vacancies. Concentrations of 0.1M-12 M of hydrochloric acid (HCl) and 0.1M-16 M nitric acid (HNO_3) were used to oxidize and functionalize the HOPG surface. X-Ray photoelectron spectroscopy was used to investigate the binding energies and the HOPG surface functionalization. It was found that after oxidation, the HOPG surface produced primarily hydroxy functional groups for both acids. The oxidation of the HOPG surface also greatly affected the surface morphology and this effect was investigated using atomic force microscopy. The topography of the HOPG surface post-etching changed significantly and the differences seen between the surface treated with the two acids increased as the acid concentration used to etch increased. The results showed that below 4 M HCl(aq) or HNO_3(aq), the acid treated surfaces showed similar surface morphologies and functional groups. At high concentrations of HCl(aq) and HNO_3(aq) significantly different morphologies were produced. These studies suggest that understanding the oxidation mechanism on the surface of 2D materials has potential for selective growth of metals/metal oxide nanostructures for new catalyst and semiconductor devices.