Carbon layers down to a thickness of a single layer have been known to form on metal surfaces for more than 50 years. Graphene on metal surfaces is also known to lead to catalytic deactivation.[1,2] However, it has not yet been recognized that graphene can also offer a level of oxidation protection to individual atoms or small clusters of atoms in/on the graphene layer. Here we will show using annular dark field imaging in a scanning transmission electron microscope and electron energy-loss spectroscopy (EELS) that Si and Fe atoms incorporated in a graphene layer are not oxidized. We further combine the microscopy data with first-principles density-functional calculations of the reaction of the impurity with graphene and the impurity with oxygen. Interestingly, our density-functional theory calculations explain these observations are due to preferential bonding of O to non-incorporated atoms and H-passivation effects.

Figure 1 shows annular dark-field images of a single Si atom segregated to a carbon vacancy and a single Fe atom segregated to a carbon divacancy. Si has also been found in graphene divacancies, but Fe has not been imaged in graphene single vacancy sites. The observed intensities are consistent with there being just a single impurity atom incorporated in the graphene defects, i.e. no additional oxygen. EELS confirms the identification of these impurity atoms as Si and Fe. The spectrum from a Si atom (Fig. 2c) shows an edge onset of about 102 eV which is less than the oxide value and close to the edge onset for Si in of SiC. No oxidation features are apparent in the Si-L2,3 edge and no O-K edge was detectable in the spectrum. The core loss spectrum from a Fe atom (Fig. 2f) not only confirms the identification it also indicates that the Fe atom is not oxidized. The ratio of the Fe L3/L2 edges is lower than any seen for the various forms of Fe oxide. There have been no previously published experimental or theoretical studies on the oxidation resistance of iron or silicon incorporated in graphene to our knowledge. This is a potentially important discovery, Improved resistance to oxidation has important consequences for some catalytic reactions and small devices based on single atoms or small clusters of non-noble metals. Graphene as a substrate appears to protect single atoms and small clusters of atoms from oxidation without completely isolating them.[3]

References

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Fig. 1: ADF images of graphene. The as recorded data (a,b) were corrected to remove noise and probe tail effects (c,d). Images a and c show a Si atom in a C vacancy site. Images b and d show an Fe atom in a C divacancy site. The scale mark on each image corresponds to 0.2 nm. Taken from Ref. 3.

Fig. 2: EEL spectrum image data from single atoms incorporated in graphene. ADF image of a Si atom in graphene (a), Si composition map (b) and spectrum obtained over the Si atom (c). ADF image of an Fe atom (d), Fe composition map (e) and the spectrum obtained over the Fe atom (f). The scale marks correspond to 0.2 nm. Taken from Ref. 3.