Structure-property relationship of oxygen-containing graphene: spectroscopic and theoretical characterisation

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Graphene is an outstanding material both thanks to its properties, such as excellent electrical conductivity and optical transparency, and because of its ability to give rise to a variety of new materials through structural modification, e.g. forming graphene oxide, reduced graphene oxide and graphene aerogels. These chemical modifications change the optoelectronic properties of graphene. Therefore, it is important to understand the relationship between the structures and electronic and optical properties of functionalised graphene-based materials. In this collaborative study, oxygen-containing graphene aerogels were produced by detonation of acetylene with oxygen and characterised using transmission electron microscopy, X-ray photoemission spectroscopy and UV-Vis absorption spectroscopy, and using first-principles theoretical modelling. The materials produced were found to contain up to 9% oxygen; the increase in the oxygen content was accompanied by morphological changes and broadening of the optical absorption spectra.Density-functional theory calculations were used to rationalise the structure-property relationship of oxygenated graphene and graphene aerogels, by modelling flat and curved graphene sheets containing epoxide and hydroxyl groups and substitutional oxygen at different concentrations (1-12% oxygen). Curvature was found to have little effect on the electronic properties of graphene: curved graphenes remained semimetallic, and their optical absorption spectra were similar to graphene. However, oxygenation had significant effects on the properties. Graphenes containing substitutional oxygen had new states at the Fermi level, while graphenes containing hydroxyl and epoxide functional groups showed band gap opening at oxygen content above 6%. Moreover, additional peaks appeared in the simulated optical absorption spectra of oxygen-containing graphenes. These results show that morphologically disordered graphene aerogels have electronic properties similar to graphene, while oxygenation significantly changes these materials' optical and electronic properties, leading to new applications in electronics and sensors.