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MS-2-O-3121 Imaging functional groups in graphene oxide at atomic resolution

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Graphene oxide is a form of graphene with its surface modified by the addition of functional groups such as carboxylic groups, ketones and hydroxyl. The structure and distribution of the functional groups depends on the synthesis method used and they affect its chemical, electrical and mechanical properties. Of particular interest is the chemical composition and spatial distribution of these functional groups. Direct identification of the groups by high-resolution imaging is not possible at present, but they can be made visible by bonding heavy atoms, such as Ba, to selected groups and imaging the distribution of the heavy atoms.
High-resolution images of Ba doped graphene oxide taken at 80kV in a Cs and Cc corrected transmission electron microscope (TEM) show the structure of the graphene oxide with minimal electron beam damage but are not able to identify the Ba atoms. We attempted to use energy-filtered electron microscopy to image the Ba M_5 and M_4 edges at 781eV but radiation damage over the long exposures required prevented location of the Ba atoms to better than a few nm. Compositions measured using energy loss spectroscopy (EELS) revealed a progressive loss of O with increasing temperature and that 1% O is retained at 800°C.
High-resolution scanning transmission electron microscopy (STEM) at room temperature proved to be impossible due to contamination from migration of the functional groups on the graphene surface. Contamination was overcome by imaging with the graphene oxide above 400°C in a stable heating holder.
Simultaneous STEM energy-loss spectrum images (SI) and high-angle annular dark-field (HAADF) and bright-field (BF) images acquired at a specimen temperature of 800°C allowed us to correlate the location of the Ba atoms with features in the high-angle dark-field images at atomic resolution.
Simultaneously acquired HAADF and BF-STEM images (Fig. 1) show bright and dark dots at the same positions. These bright dots are identified as Ba atoms by EELS as shown in Fig. 2a. The corresponding elemental maps extracted from the SI are shown in Fig. 2b-d. The maps also show that Ca and O occur together and that Ba is not associated with a significant concentration of O. The positions of Ba atoms attached to functional groups on graphene oxide can therefore be mapped with atomic spatial resolution by using a combination of STEM and TEM techniques. The fact that Ca was observed to correlate strongly with O suggests that it could be used as a marker for the positions of the O-containing groups.

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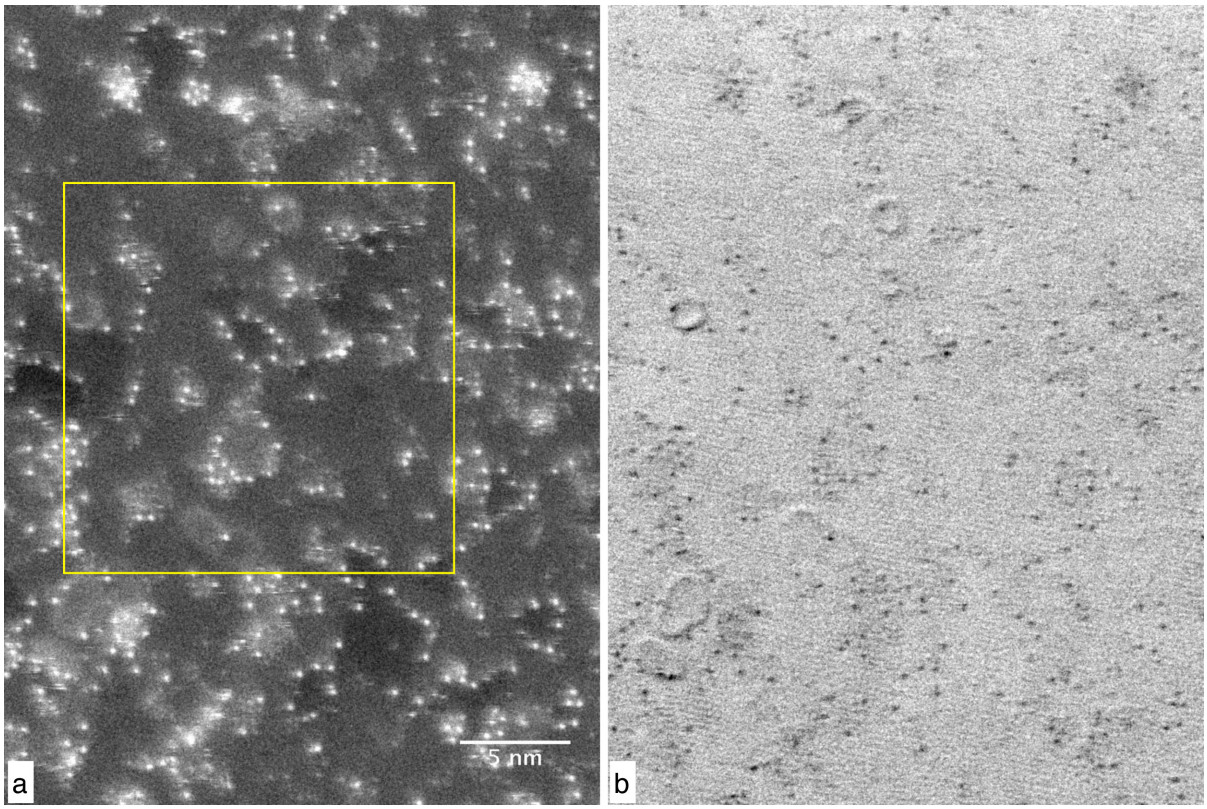

Fig. 1: Simultaneously acquired (a) HAADF and (b) bright-field STEM images at a specimen temperature of 800°C after recording the spectrum image (Fig.2), whose approximate area is marked by the box in (a). The bright dots in the HAADF image (a) correspond to the dark dots in the bright-field STEM image (b).

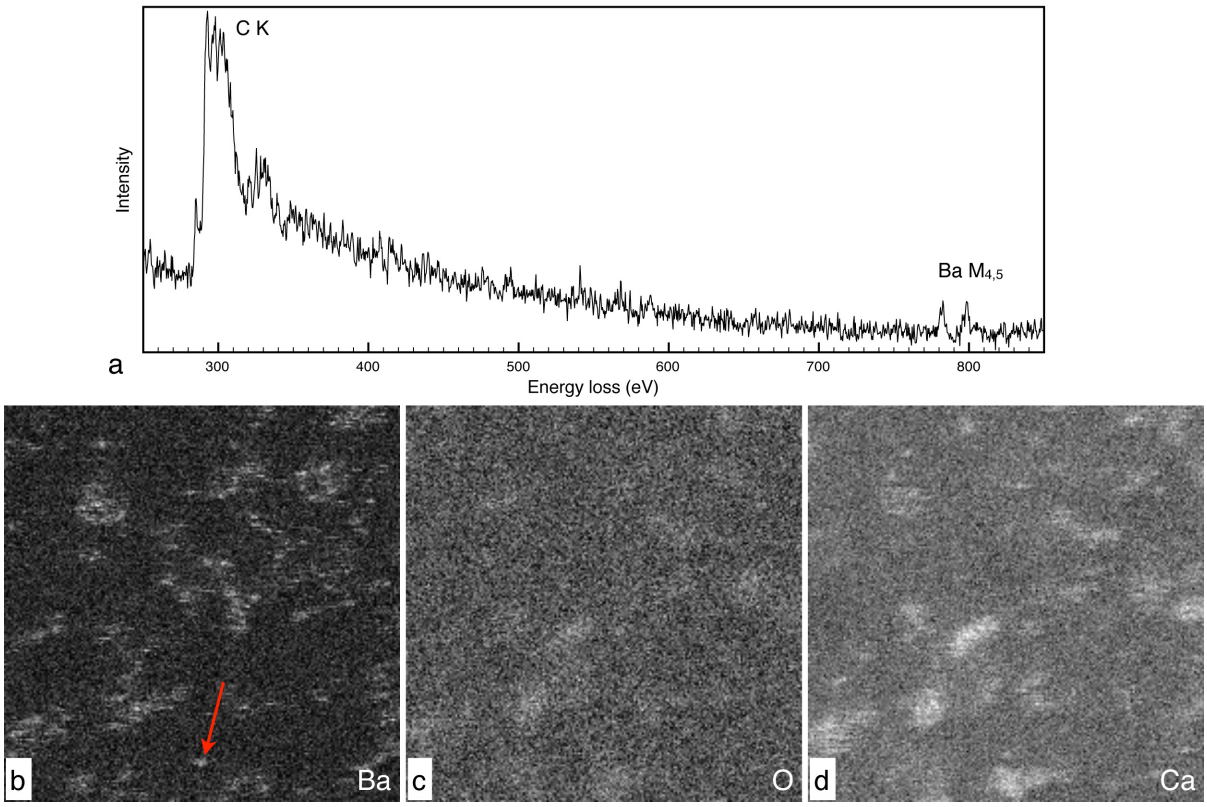

Fig. 2: (a) EEL spectrum extracted from a 3x3 pixel (0.25x0.25 nm) part of the spectrum image centred on a single Ba atom marked by the arrow in (b). (b-d) Elemental maps of the Ba $M_{4,5}$, O K and Ca $L_{2,3}$ edges obtained from the SI (200x200 spectra, dwell time 0.02s per spectrum, after VCA processing).