Direct visualization of the spatial distribution of functional groups in graphene oxide

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Graphene oxide (GO) is of great interest for both fundamental research and applications as a result of its great mechanical strength and flexibility and ability to be modified (functionalized) by chemical means to tailor its electronic properties. It can also be used to produce graphene. The chemical structure of GO depends on the synthesis method used [1,2] and is still incompletely understood, despite previous studies aimed at the direct identification and visualization of functional groups using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) [3] and aberration corrected transmission electron microscopy (TEM) [4]. It is generally accepted that GO contains carboxylic groups, ketones, quinones, epoxides, lactones and hydroxyl groups in different proportions. The lack of information about its detailed structure is not only limited to the functional groups that are present but also to how they are distributed spatially. As chemical functionalization (modification) provides control over the solubility, band gap and mechanical properties of GO, direct information about the types of functional groups and their distribution is of great importance [5].

Here we use different approaches for the synthesis and modification of GO and provide preliminary results from the atomic resolution structural and electronic characterization of GO by means of electron energy loss spectroscopy (EELS) and energy-filtered TEM (EFTEM).

GO was synthesized by the method of Hummers and Offeman [6]. In order to remove traces of remaining metal ions, the product was treated with an aqueous solution of ethylenediaminetetraacetic acid (EDTA) in a basic medium and then purified by dialysis against ultrapure water. Finally, a proportion of the product was subjected to dialysis against HCl. In order to determine the location and spatial distribution of the functional groups in the GO we prepared GO samples "doped" with different metal ions (Ca, Hg, Ba).

TEM experiments were performed at 80 kV in an FEI Titan G2 60-300 TEM. This is a fourth generation field emission gun TEM, which contains a monochromator and allows both spherical and chromatic aberration of the objective lens to be corrected.

The EEL spectra acquired from different samples of GO (not shown) indicate that the Ca content varies depending on the synthesis route.

Using HAADF STEM, we observe that the Hg is in the form of nanoparticles, while Ba and Ca are more evenly distributed, presumably on the atomic scale.

Fig. 1 shows results from graphene oxide containing Ba. The HREM image in Fig. 1a contains dark spots showing the distribution of Ba atoms. The EEL spectra (Fig. 1b) shows that O and Ba are present and elemental maps of these elements are shown in Figs. 1c & 1d.

The image shown in Fig.1a and the EEL spectrum shown in Fig.1b were acquired after recording the Ba map. Our study shows that at 80 kV radiation damage occurs, as shown by the inset in Figure 1a. However it is possible to minimise the damage by reducing the dose rate.

In both the images and the elemental maps, local variations in intensity are visible on the same spatial scale. These results are consistent with both Ba and O containing groups not being uniformly distributed on the GO membrane.

Our results suggest that it is possible to record the spatial distribution of functional groups on graphene oxide using chromatic aberration corrected EFTEM [7].

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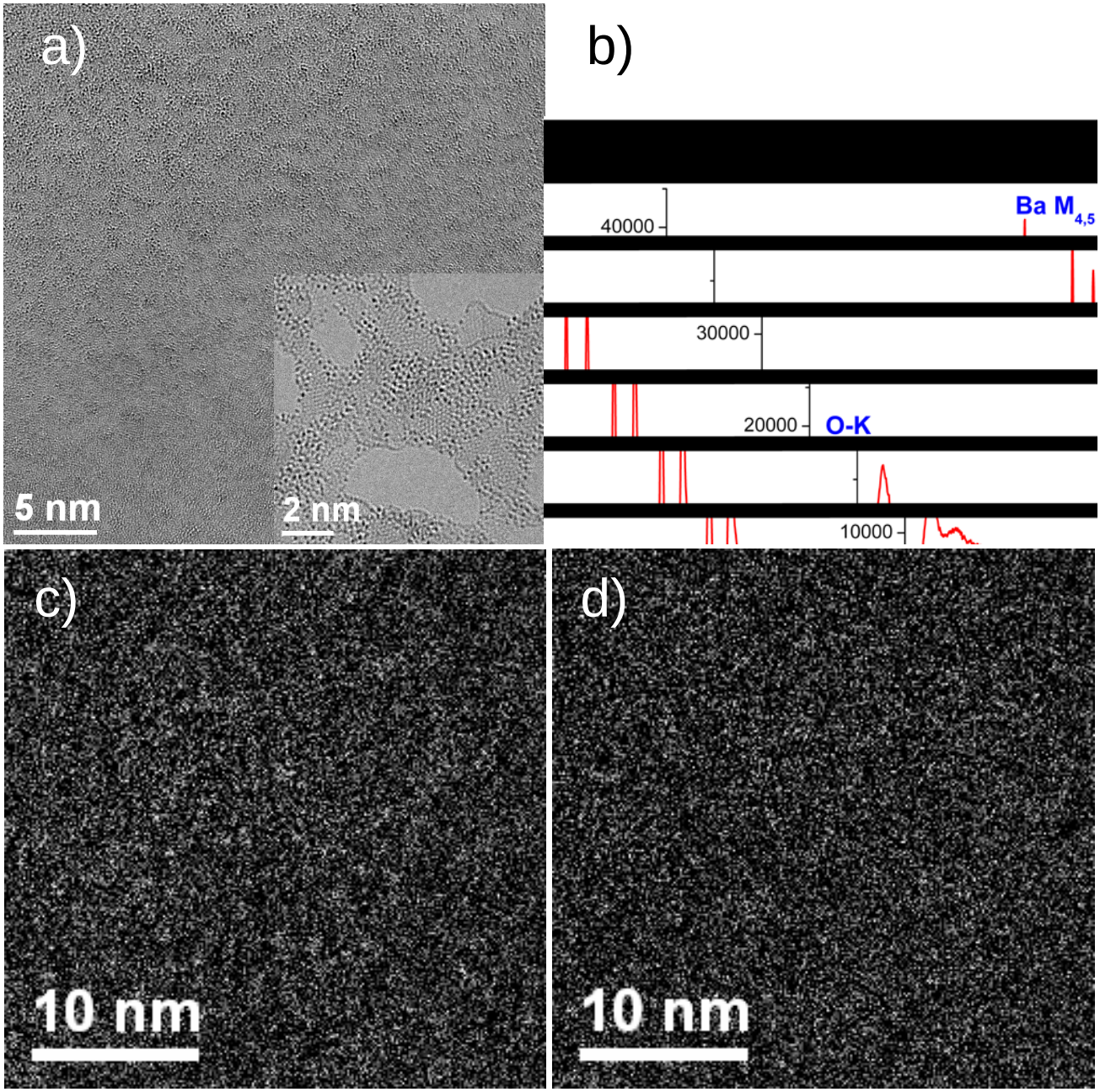

Figure 1. *a) Chromatic aberration corrected high-resolution TEM image of GO recorded at 80kV after energy-filtered TEM. The inset shows damaged GO after prolonged electron irradiation. b) EEL spectrum showing the O K edge and the Ba $M_{4,5}$ edges. c) Oxygen map and d) Ba map.*