Atomic Imaging and Spectroscopy of Single Layered Materials with Interrupted Periodicities

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The interrupted periodicities (atomic defects or edge structures) are quite important especially in low-dimensional crystals since they strongly affect their physical and/or chemical properties. In bulk crystals electron microscopes have been widely used to examine structural defects such as dislocations and grain boundaries, which are regarded as one- and two-dimensional structural defects, respectively. In contrast, the individual point defects (zero-dimensional defects, such as mono-vacancies, impurity/dopant atoms) were believed to be difficult to investigate. Both atomic sensitivity and atomic resolution are required in the analytical techniques.

After a monovacancy was first observed by TEM and proved to be stable even in low-dimensional carbon structures [1], studies of point defects in mono-layered materials have become very popular among scientists. Vacancies and topological defects in graphene are commonly examined at atomic level [2, 3, 4]. Defects and edge structures in hexagonal boron nitride (h-BN) are also a hot topic among physicists [5, 6, 7, 8]. Recently, mono-vacancies have been successfully identified in WS_2 nano-ribbons [9].

Here we show how HR-TEM and spatially resolved EELS can be applied to the studies of various single-layered materials with the interrupted periodicities. Atomic defects and edge structures can be unambiguously identified with the elemental assignment. The inevitable delocalization of EELS signals is suggested to practically limit the achievement of using EELS for chemical mapping with atomic resolution. The boron monovacancy (V_B) is assigned as a typical point defect by ADF imaging and EELS, and energy-loss near edge fine structure (ELNES) is used to investigate the electronic states of nitrogen atoms around the point defect. The work provides an example of spectroscopic imaging based on the scanning transmission electron microscopy (STEM)-EELS techniques to demonstrate the possibilities of exploring the electronic states with single atom sensitivity. A JEM-2100F equipped with a delta corrector and cold field emission gun was operated at 60kV for these spectroscopy experiments [10, 11]. A fast Frourier transform (FFT) of the typical ADF image shows that the microscope can resolve 0.108 nm in the STEM mode (not shown). The probe current was ~ 40 pA.

Fig. 1 shows an example of atomic defects in CVD graphene. The model structure involves pentagons and heptagons located at the boundary to accommodate the small angle boundary. A monovacancy in h-BN is examined by STEM-EELS (Fig. 2). The core-level spectroscopy on the nitrogen atoms at the vicinity of boron vacancy is successfully made [12].

References

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Figures

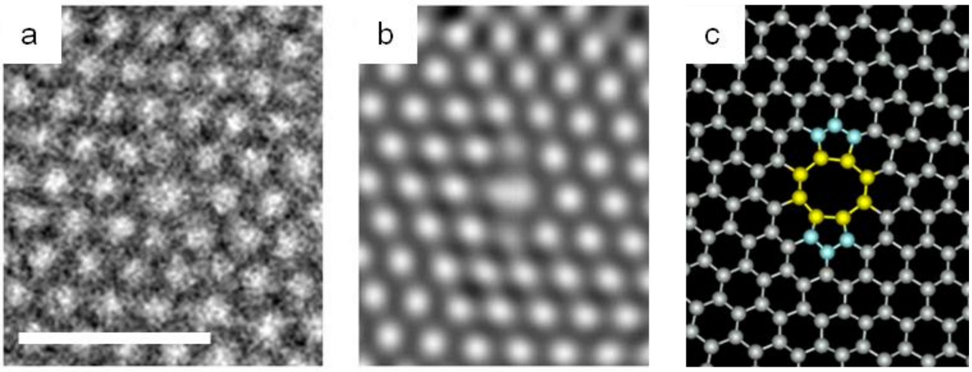

Fig. 1 An example of 5-8-5 defect in graphene. (a) HR-TEM BF image, taken at 120kV. Octagon is almost at centar between two pentagons at up and down side (b) simulated TEM image and (c) relaxed atomic model. Octagon with yellow color and pentagon with blue color. Bar = 1nm. JEM 2010F with the CEOS corrector operated at 120kV.

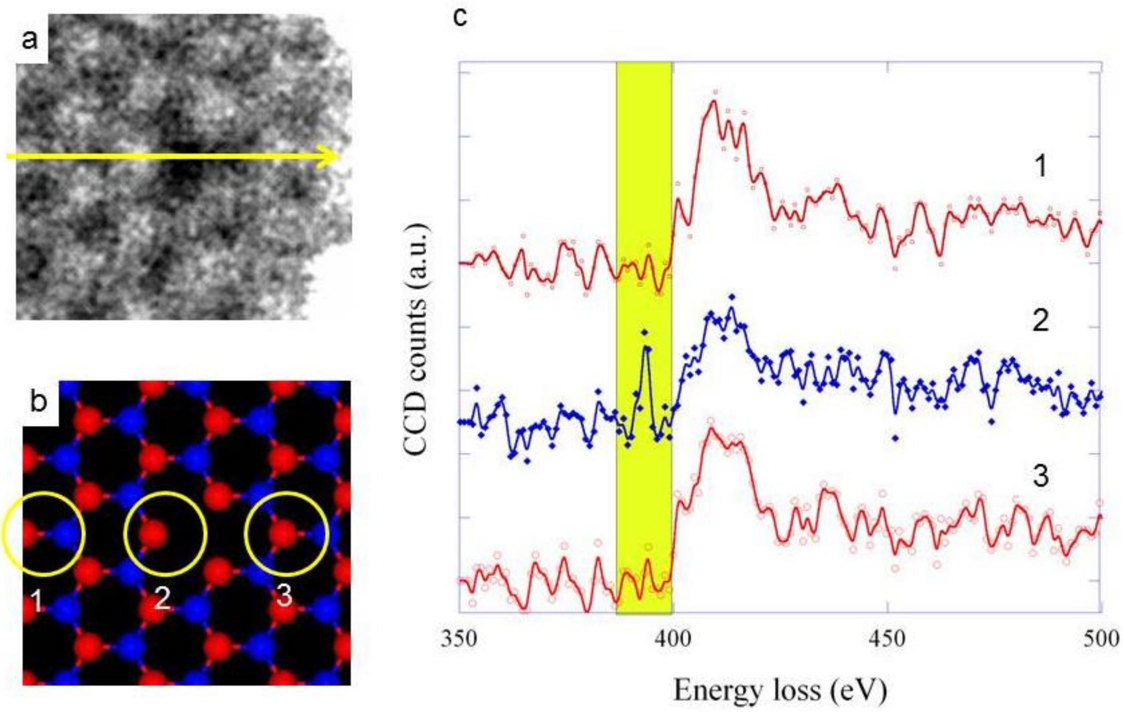

Fig. 2 Monovacancy in h-BN layer [13]. (a) ADF image shows a monovacacny in a single layer h-BN. Line-spectrum was recorded along the yellow line. (b) Schematic presentation (red: nitrogen, blue: boron) of boron monovacancy. (c) Nitrogen K-edge fine structures extracted from the line-spectrum. Each of three approximately corresponds to the probe positions marked in (b). A prominent prepeak in the nitrogen K-edge can be found at 392 eV in the spectrum recorded at the position 2, i.e., near the boron vacancy site.