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Atomic Resolution Vibrational EELS Acquired from an Annular Aperture

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Recently, sub-10 meV resolution of electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) [1] makes the detection of vibrational modes at atomic scale possible. For example, it had already been proved that atomic resolved phonon spectroscopy can be realized by either collecting high-angle scattering in polar material [2], or collecting impact scattering of non-polar material [3]. Alternatively, an annular collecting geometry should significantly improve efficiency of atomic vibrational spectroscopy from the theory [4]. However, such an experiment verification has never been done. Here we present the primary experimental results of atomic resolution vibrational EELS using an annular aperture.

Experiment was performed using Nion U-HERMES 200 operated at 60 kV with 35 mrad convergence semi-angle. Hexagonal-BN(h-BN) sample was exfoliated and dispersed in ethanol by ultrasonic before transferred onto 3 mm carbon TEM grid. Annular EELS aperture was placed before the entrance of EELS magnetic prism. We used annular aperture with 1 mm inner-diameter and 1.4 mm outer-diameter, which corresponds to 25-35 mrad collecting semi-angle in our experimental setting. An illustration of h-BN Brillouin zone and the collection area in reciprocal space was shown in Fig. 1(a). Annular aperture was made from 0.1 mm thick copper foil. Fig. 1(b) is the optical microscopy image of an annular aperture. Fig. 1(c) is the electron microscopy image of the annular aperture.

A representative experimental EELS spectrum collected with the annular aperture from h-BN is shown in Fig. 2(a) with black circles. The zero-loss peak (ZLP) background was fitted using Pearson Ⅶ function, and labeled by a blue dashed line in Fig. 2(a). The background-subtracted EELS signal spectrum is presented in Fig. 2(a) as the red line. There are mainly two features in the signal spectrum, which correspond to the acoustic phonon modes at boundary of Brillouin zone and optical phonon modes respectively. The insets of Fig. 1(a) are sketches of representative atomic vibration modes. The HAADF image is simultaneously collected and presented in Fig. 2(b), in which atomic columns are well resolved. The spectrum image is normalized by the total intensity so as to correct the instability of beam current. Fig. 2(c)-(e) show the maps integrated over energy windows -10→10 meV, 50→140 meV and 140→240 meV, corresponding to the mapping for ZLP, acoustic phonon and optical phonon modes respectively. In each mapping, the atom columns are resolvable.

In the detection of atomic resolution vibrational EELS, the annular aperture plays two roles. Firstly, the annular aperture includes large contribution from the excitation of acoustic phonon at boundary of Brillouin zone. The energy of acoustic phonon can reach as high as 140 meV at zone boundary, enables easy detection of acoustic phonon. Secondly, for optical phonon, annular aperture screens the most of contribution of delocalized dipole scattering at low collection angle, leaving impact scattering dominated large angle signal.

In summary, we achieve the detection of atomic resolution vibrational EELS using annular aperture. Compared with off-axis geometry method, annular aperture method has advantages of high efficiency (estimated to be 2 times higher now and can be optimized), convenience (no need for tuning from normal setting) and generality (no limit on materials). We believe this method will be useful for exploring the vibrational related properties of surface, interface and other structural defects [5].

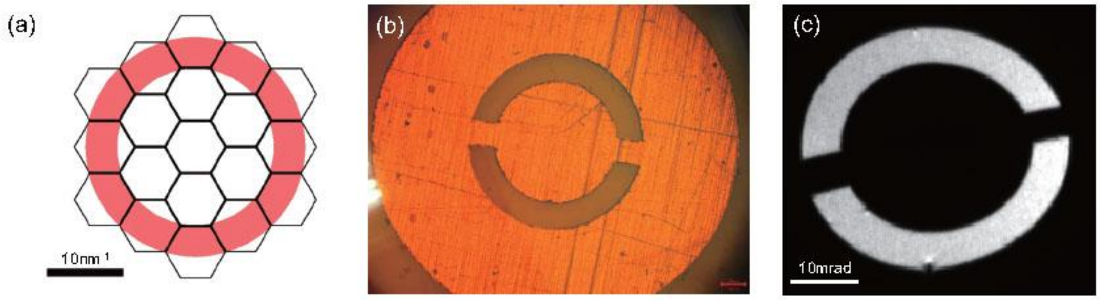

Figure 1. (a) An illustration of h-BN Brillouin zone and the collection area in reciprocal space. (b) The optical microscopy and (c) TEM image of annular aperture.

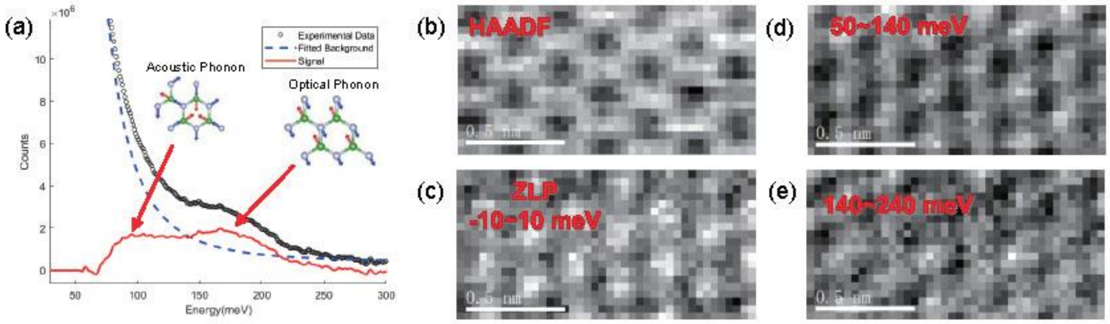

Figure 2. (a) Experimental EELS data (black circles), fitted background (blue dashed line), and EELS signal (red line) of h-BN. The inset show the sketch of two vibration modes. (b) HAADF image and (c-e) simultaneously collected EELS with different integration windows.

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