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Single Atom Spectroscopy in Low-Dimensional Materials using Low-voltage STEM

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In this presentation, single atom spectroscopy by means of EELS and EDX will be demonstrated to discriminate individual atoms in low-dimensional materials. It has remained a challenge for scientists to see and identify individual atoms since Dalton first proposed distinct atoms in his atomic theory [1]. It is emphasized here that information on the bonding/electronic states has become accessible for single atoms through the EELS fine-structure analysis as well as the spin state. Such analysis was not possible until recently because of an intrinsic limitation, namely, the inevitable irradiation damage due to the huge number of electrons required to realize a high enough signal-to-noise ratio for fine-structure analysis from a single atom.

Elemental analysis down to the single atom limit was demonstrated in 2000 with a successful detection of Gd dopant atoms in carbon nano-peapods [2]. A fully digitized STEM-EELS system enabling the recording of spectrum-image was used for statistical data analysis to convince the single atom detection. Specimen damage due to the high dose of the incident electron beam at 100kV required to isolate the signals from individual atoms was an intrinsic problem in such highly delicate analysis. Although the single atom detection by means of EELS had been anticipated by Isaacson and Johnson [3], their assumption did not consider the atomic movements induced by the incident electron probe itself. The most important point for realizing single atom spectroscopy is in fact to prevent the atoms from being kicked out during observations. If the atoms were completely immobile under the electron probe, any measurement of single atom properties would be possible. In order to reduce the atomic movements and also to enhance the EELS contrast, a lower accelerating voltage is preferred for single atom detection. In this presentation, I would like to emphasize the advantages of the low voltage STEM on three points, namely (i) less knock-on probability, (ii) higher EELS/EDX contrast [4], and (iii) less pronounced delocalization effect. Examples for non-destructive chemical analysis of single molecules [5], bonding state identification of individual nitrogen atoms [6], successful detection of individual light element atoms (Li, Z=3) [7], single-atom spin-state discrimination of transition metal (TM) [8], and direct estimation of X-ray fluorescence yield [9] will be presented.

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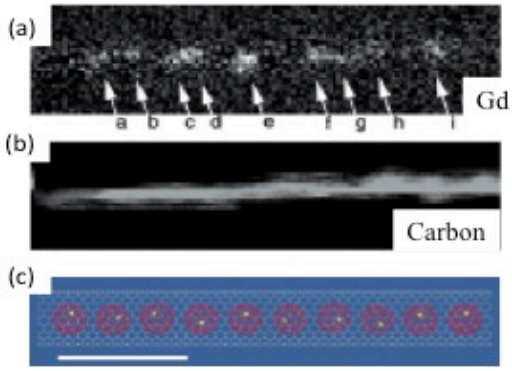

Figure 1. Spectrum-image of Gd peapods obtained using a 100kV electron beam [2]. Massive damage of nanocarbon structure was an issue.

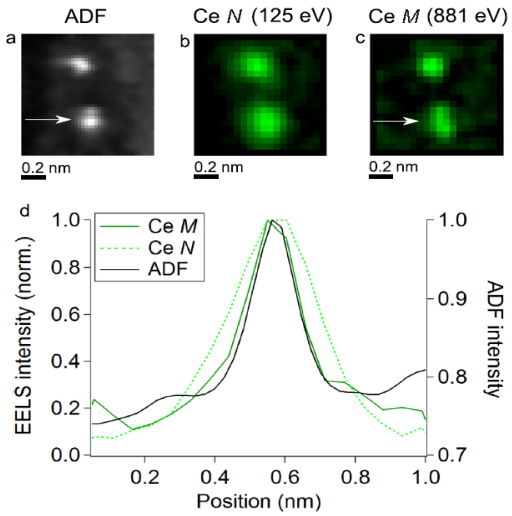

Figure 2. (a–c) ADF and chemical maps at two different energy losses (125 eV and 881 eV) for two Ce atoms. The EELS maps have been made close to the threshold energy for the N and M edges of Ce. Note that the spatial resolution in (c) is similar to that in (a). The broadening in (b) happens due to inelastic scattering delocalization. (d) Comparison of the ADF, Ce N and Ce M signals at 60 keV. The difference in delocalization at two energy losses is clearly seen in (d). (a–c) have been smoothed.

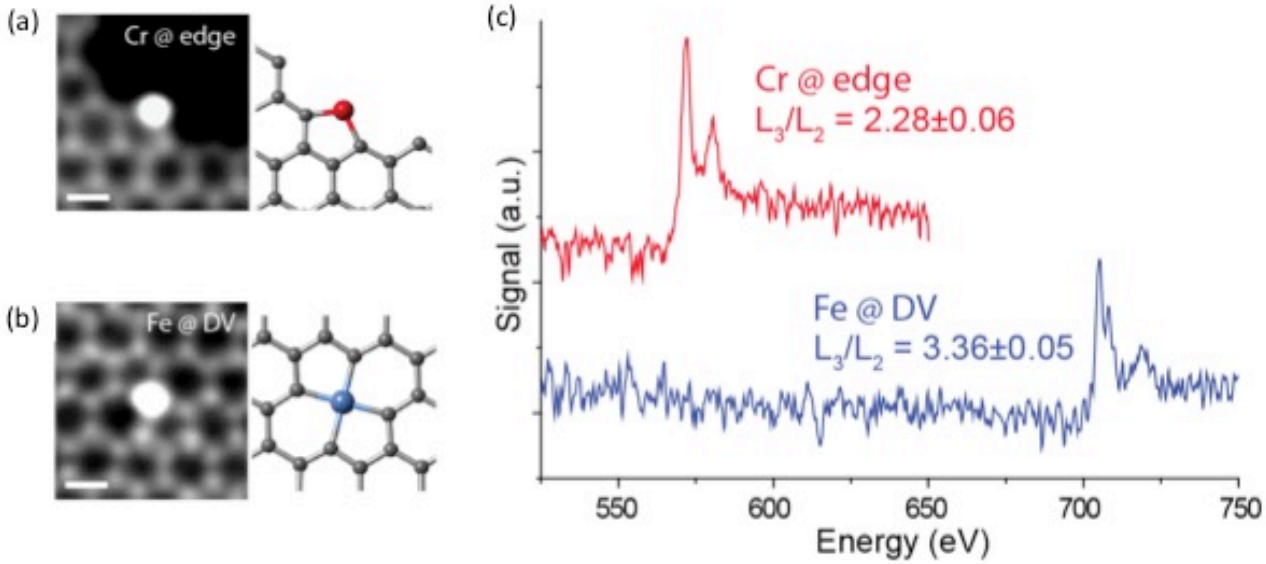

Figure 3. Single atom spin-stage spectroscopy [6]. (a)(b) Experimental ADF images and atomic structures of the Cr atom at the graphene edge (Cr@edge) and the Fe atom at divacancy (Fe@DV), respectively. (c) The EEL spectra of single TM atoms, Cr@edge, and Fe@DV. These two single TM atoms all exhibit a high-spin state based on the analysis of the L_3/L_2 branching ratio.

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