Single-atom detection of light elements: Imaging or spectroscopy?

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1. Introduction

Since Dalton’s atomic theory, scientists have dreamed of the direct ‘imaging’ and ‘identification’ of individual atoms. With respect to ‘imaging’, single heavy atoms on a thin C film were observed by scanning electron microscopy by Crewe in 1970 [1]. Then, owing to several important developments in aberration correction [2–5], atomically resolved crystal images were successfully obtained by both transmission electron microscopy (TEM) [6] and scanning TEM (STEM) [7–9]. On the other hand, single-atom ‘identification’ by electron energy-loss spectroscopy (EELS) was theoretically predicted in the 1970s [10]. However, experimental verification had been lacking until the 1990s because of the absence of ideal samples. The possibility of single-atom detection by EELS was discussed by Krivanek et al. in 1991 by demonstrating EELS quantification for small Th clusters on a thin C film [11]. However, the unambiguous demonstration of single-atom identification was never carried out until 2000 when Gd atoms inside fullerene cages were clearly imaged in an EELS map [12].

Thereafter, STEM-EELS has served as the most powerful tool for material characterisations at the atomic level [13–16]. In particular, since a ~1 Å probe at lower accelerating voltages (30–60 kV) is now routinely available with the latest aberration correctors [17–19], nanomaterials such as graphene or carbon nanotubes, which are easily damaged by electron beams at higher acceleration voltages (> 80–120 kV), can be also observed at the atomic level [20–23]. In addition, EELS is capable of examining the detailed chemical states of probed atoms using energy-loss near-edge fine structures (ELNESs). For instance, the ELNES of the C K-edge, which has rich information regarding its chemical bonds, can discriminate singly, doubly, and triply coordinated carbon atoms at the graphene edge with atomic resolution [23]. Moreover, the spin states of single transition-metal atoms (Fe, Cr) doped in a graphene lattice have been also successfully extracted using a white line analysis [24].

In such experiments, the operators usually start by finding the typical places with specific atomic configurations of interest such as defects in materials by annular dark-field (ADF) images and then perform spectroscopy at the target atom. This means that the STEM-EELS analysis so far is based on the fact that the targeted atoms are ‘visible’ according to the ADF images. Thus, the following question arises: if atoms are ‘invisible’ according to the ADF images, how can we find them?

Since the ADF contrast is related to the cross section of elastic scattering and proportional to the square of the atomic number, the location of heavier atoms in a matrix of lighter elements can be straightforwardly recognised by ADF images. In the other case where the target materials are only composed of elements which are located close to each other in the periodic table, e.g. single N (Z=7) or O (Z=8) atoms doped in a graphene lattice (carbon: Z=6), even light atoms can be identified by means of a quantitative analysis of the ADF contrast recorded under the proper conditions (middle-angular ADF (MAADF) conditions in a typical case) [21]. However, for a more complex system such as a crystal with a wide variety of light and heavy elements, the ADF images are not fully adequate for identifying elements atom-by-atom because no specific elemental signals can be obtained. In particular, extremely light atoms such as Li or H are quite difficult to visualise as single atoms when they are located in the vicinities of some other heavier elements because of their significantly higher scattering power, which could smear out the contrast of the light elements.
Although single atomic columns of light elements in thick crystals were visualised by annular bright-field (ABF) contrast [25], several tens of identical atoms contribute to the ABF column images through a channelling effect. If the target is only a single atom thick, the ABF contrast is not advantageous over the ADF because no channelling effect is expected. Therefore, another approach is needed to identify the location of such single invisible atoms of light elements instead of ADF/ABF.
images. Here, we show how to use the EELS contrast for the visualisation of these light atoms. Indeed, EELS is greatly advantageous because its contrast does not correspond to the atomic number but is related to the inelastic cross section, which is sufficiently high to discriminate a single light atom such as Li [26]. In addition, the absorption edges detected by EELS are specific for each element and therefore hardly buried in the signals of other neighbouring atoms as long as the target absorption edges are well isolated from the others in the spectra. Furthermore, the spatial resolution of the EELS contrast is normally sufficiently good to resolve individual atoms [27], although EELS signal delocalisation should be considered [28–31].

In this study, we mainly focus on one-dimensional materials, in which various atoms including both heavier and lighter elements are aligned in a row inside a carbon nanotube (Fig. 1). Since the basic structures and properties of the atomic chains are reported in Ref’s. [26] and [32], we discuss how to characterise non-periodic structures such as vacancies or substitutions of other elements from the ADF images only. Therefore, chemical assignment of these defects by means of EELS is absolutely necessary. Conclusively, the atomic chain in Fig. 2(a) has two defective sites substituted by single K and Cl atoms, while the two defective sites in Fig. 2(b) are expected to be vacancies. Fig. 2(c) and (d) show the elemental map and EELS spectrum taken from the atomic chain in Fig. 2(a). A Cl atom is clearly visible at the I site at the right-side defect in the elemental map constructed from the Cl L-edge around ~200 eV (Fig. 2(c) bottom).

The microscope used in this study is a JEOL Triple CS1 microscope that consists of a cold FEG (capable of operating at different accelerating voltages of 15, 30, and 60 kV), delta-type Cs correctors for TEM/STEM, and a GATAN quantum GIF spectrometer dedicated to low voltages. The details of the sample preparation for the atomic chains inside the carbon nanotubes or the metallofullerene peapods are described in Ref.[26].

2. Single dopant atoms and mono-vacancies in atomic chains

Fig. 2(a) and (b) show STEM-ADF images of CsI atomic chains inside double-walled carbon nanotubes (DWNTs) [32], both of which show some defective sites. The convergence and collection angles for the ADF imaging are 48 and 79 mrad, respectively (high-angular ADF (HAADF) condition). The specimen was intentionally doped with K and Cl by a vapour-phase method. It is extremely difficult to ascertain the nature of the defects–vacancies or substitutions of other elements–from the ADF images only. Therefore, chemical assignment of these defects by means of EELS is absolutely necessary. Consequently, the atomic chain in Fig. 2(a) has two defective sites substituted by single K and Cl atoms, while the two defective sites in Fig. 2(b) are expected to be vacancies. Fig. 2(c) and (d) show the elemental map and EELS spectrum taken from the atomic chain in Fig. 2(a). A Cl atom is clearly visible at the I site at the right-side defect in the elemental map constructed from the Cl L-edge around ~200 eV (Fig. 2(c) bottom).
Although the K elemental map is quite noisy and it is difficult to extract the K $L$-edge intensity precisely because it just overlaps the C $K$-edge, the maximum of the K $L$-edge intensity extracted by subtraction of C $K$-edge does coincide with a Cs lattice site on the left side. On the other hand, from the vacancy sites in Fig. 2(b), no signal related to possible dopant/impurity atoms was observed under our experimental conditions (Li, O, F, Na, Cl, and K). Note that we cannot completely ignore the possibility of H atoms doped at these defective sites because we still do not have an effective way to detect single H atoms, as discussed later. That is, we cannot distinguish whether this defect is a vacancy or H substitution site, although the latter is unlikely to occur considering the shorter I–H bond length expected, which does not fit the atomic distance observed.

3. Substitution of an O atom at a F site in an atomic chain of CsF

Fig. 3 shows two sequential EELS maps of a CsF atomic chain inside a DWNT. Similar to the case of Cl or K in Fig. 2, a F ($Z=9$) atom is difficult to visualise in the ADF image (Fig. 3(a) (left)). However, the EELS chemical maps taken during the first scan (Fig. 3(a)) clearly show that the trace of a F atom reasonably exists between two Cs atoms to form a CsF chain. Surprisingly, a Cl atom is also found at a F site, which was probably doped unintentionally during the growth process. The Cl impurity is located at the bottom F site. More interestingly, from the second scan (Fig. 3(b)), the upper two F atoms are suddenly substituted with O atoms, and the bottom F atom is simply gone. Consequently, the distance between two Cs atoms is considerably expanded, as shown in the line profiles of the ADF contrast along the chain (Fig. 3(c) and (d)). Although the mechanism of this phenomenon is still unclear, the following scenario can be assumed: F atoms are basically quite unstable in the presence of the electron beam and tend to be quickly ejected. These ejected F atoms are highly reactive, interact with the surrounding DWNT, and create holes in the walls. Then, O atoms enter through these holes and fill the vacancy sites where the F atoms were initially located. Indeed, O atom insertion into carbon nanotubes was also reported in the case of Eu chains inside a carbon nanotube [33]. The most important implication of the experiment is that simple STEM/TEM imaging is unable to discern which element causes such a phenomenon if no chemical information is available. A simultaneous EELS analysis is indispensable for corroborating unexpected phenomena with unexpected impurities.

4. Single Li-atom detection

Figs. 4 and 5 show the unambiguous detection of individual Li atoms [26]. In Fig. 4, we used the ‘peapod method’, in which individual Li atoms are captured in fullerene cages. This is the standard and most effective approach for capturing single atoms. Commercially available Li@C$_{60}$ molecules are further encapsulated in an SWNT to form a Li@C$_{60}$ peapod (Fig. 4(a)). In the ADF image (Fig. 4(b)), the round shape of the C$_{60}$ molecules inside the SWNT is clearly visible, but no obvious contrast for the Li atoms was initially located. Indeed, O atom insertion into carbon nanotubes was also reported in the case of Eu chains inside a carbon nanotube [33]. For comparison, another peapod consisting of La@C$_{82}$ and Ce@C$_{82}$ is also shown in Fig. 4(e-h) [34]. In this case, the La and Ce atoms are visible even in the ADF contrast as brighter spots (Fig. 4(f)). The sizes of these brighter spots in ADF image reflect the atomic positions including ‘atomic motion’ such as the thermal vibration or the
fluctuation caused by the electron beam as well as the effect of the electron probe tail. On the other hand, the atomic position displayed in the EELS chemical maps (Fig. 4(g)) further involves the effect of EELS signal delocalisation as well as the above two factors. From classical theory, EELS signal delocalisation is inversely proportional to the absorption energy\cite{28}. The expected EELS signal delocalisation for the La and Ce N-edges located around 120 eV can be estimated as 0.2 nm at 30 kV. This is the reason why the EELS chemical maps (Fig. 4(g)) indicate that the atomic size is relatively larger than that in the ADF image (Fig. 4(f)) \cite{27}. For the Li case, the atomic position indicated by the EELS chemical map, which is comparable to the size of the fullerene cage, does involve a large EELS signal delocalisation for the Li K-edge estimated as ~0.7 nm at 30 kV in addition to the atomic motion within the fullerene cage and the effect of electron probe tail. The key to successfully image Li atoms in an EELS chemical map is that the Li atoms are caged so that the Li atom cannot escape, even when the electron beam tries to eject it. It is important to choose the right accelerating voltage to avoid damaging the carbon cage; then, the Li atoms will remain inside the cage, and the e-beam can detect the Li atoms if within the delocalisation distance.

Li atoms can be also trapped in a CNT as a ladder structure of a LiI crystal (Fig. 5). In this case, only I atoms are visible inside the DWNT as brighter spots in the ADF image (Fig. 5(a)). However, the zigzag configuration of 1 atoms implies the presence of counter ions. Indeed, the alternative zigzag configuration of Li atoms is clearly displayed in the EELS chemical map constructed by using the Li K-edge (Fig. 5(c)).

Interestingly, the spatial distribution of the Li signal in this chemical map is much smaller than that for a Li atom inside a C60 molecule in Fig. 4(c). A simple reason for this discrepancy is the difference in the atomic motion. Light elements in atomic chains are more confined (0.4 nm) because of the robust ionic interaction between neighbouring counter ions, while a Li atom inside a C60 molecule moves rather freely in a larger space (0.7 nm). The strong screening effect of the heavier atoms within the atomic chains can be also considered as the reason for the reduction in the delocalisation effect. Such relatively localised EELS signals are advantageous to perceive the location of such invisible light atoms, while a higher spatial resolution for EELS images is needed for a more detailed atomic structural analysis.

In addition, the peak position and shape of the Li K-edge vary depending on the atomic configuration or bonding nature; therefore, the chemical states of the Li atoms can be also predicted \cite{26}, although the signal obtained from a single Li atom is very weak to discuss the detailed fine structures.

5. Conclusion

We have demonstrated the great potential of atom-by-atom EELS, which can be used to investigate the spatial distributions of individual light atoms such as Li, which are hardly visible in conventional STEM/TEM imaging. Tracking the movements of Li atoms in sequential EELS images will be a great milestone in the near future because it would accelerate some emerging material research such as the development of

Fig. 5. Detection of Li atoms in a ladder structure of a LiI crystal. (a) ADF image of a ladder structure of a LiI crystal and (b) its contrast intensity map. In the ADF image, only the I atomic positions, which exhibit a zigzag configuration, can be seen. However, the Li chemical map in (c) composed by the Li K-edge in (d) obtained from the chain in (a) clearly indicates that the Li atoms are aligned in a zigzag pattern between the I atoms. The expected model of this LiI chain is shown in (e). The EELS elemental map in (c) is smoothed by the convolution of a 3×3 pixel matrix. The images are adapted from Ref. \cite{26}. The experiments were performed at 60 kV.
electrodes for Li-ion batteries or novel low-dimensional materials doped with light elements.

The detection of single H atoms still remains a challenge. The H K-edge appears around 15 eV, at which large plasmon signals appear and easily hamper the detection of H K-edge in such a huge background. In addition, this lightest atom is more likely to escape from the electron beam. Therefore, the detection of single H atoms would not be easily possible unless one could fix them in vacuum. Another possible approach for detection of H atoms which has been recently discussed often is the usage of vibrational spectroscopy [35]. However, this is unfortunately unrealistic for the detection of single H atoms.

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Appendix A. Supplementary information

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References


