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

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ABSTRACT

Single-atom imaging and spectroscopy at a lower accelerating voltage (~60 kV) has been largely facilitated by the development of aberration correctors for transmission electron microscopy (TEM)/ scanning TEM (STEM). Such an STEM condition will reduce beam damage and has therefore been demonstrated capable of detecting individual atoms of light elements including B, C, and N in mono-layered materials. However, other light elements such as Li, O, or F are still difficult to visualise as individual atoms by using conventional STEM/TEM imaging because their extremely weak contrast can be often smeared out by the other atoms nearby. In this paper, we demonstrate the successful detection of these 'hardly visible' atoms in the spectroscopy mode.

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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 heav-
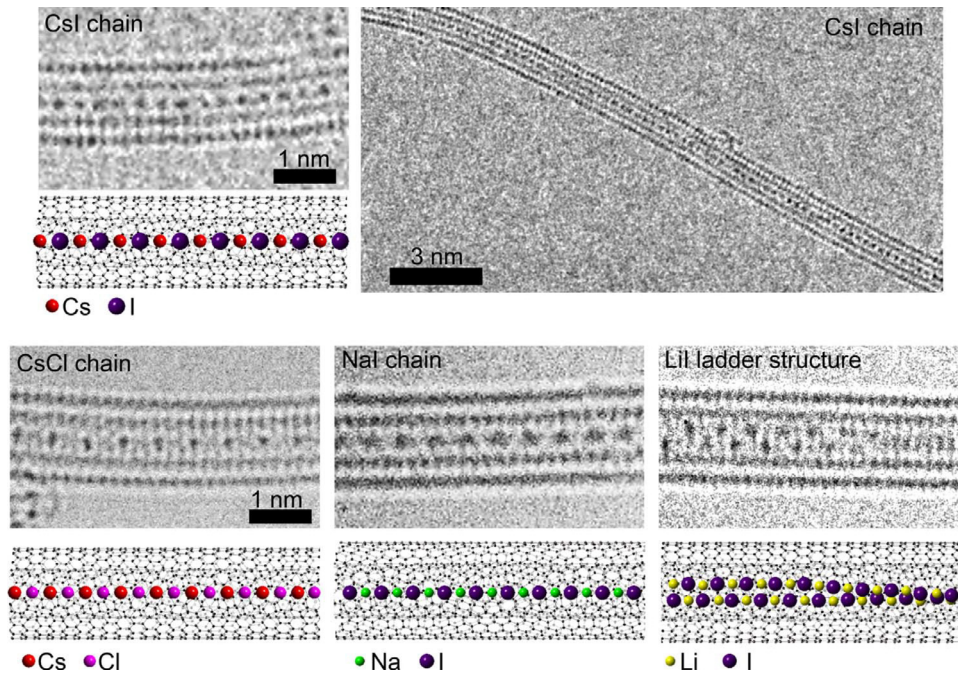
Fig. 1. Examples of 'visible' and 'hardly visible' atoms in conventional TEM images of one-dimensional atomic chains (operated at 60 kV). The upper panels show typical TEM images of a CsI atomic chain inside a DWNT. The Cs and I atoms are alternatively aligned in a row. In this case, both elements are clearly visualised as darker spots between four carbon nanotube walls. The bottom panels show TEM images of CsCl, NaI, and LiI atomic chains inside DWNTs (from left to right). Heavier atoms (Cs and I) presumably show strong contrast, while lighter atoms (Cl, Na, and Li) cannot be identified from the contrast. Note that these light atoms show weak contrast in relatively under focused TEM images when they are almost immobile in a confined space (Supplementary information). The TEM images were taken at 60 kV.
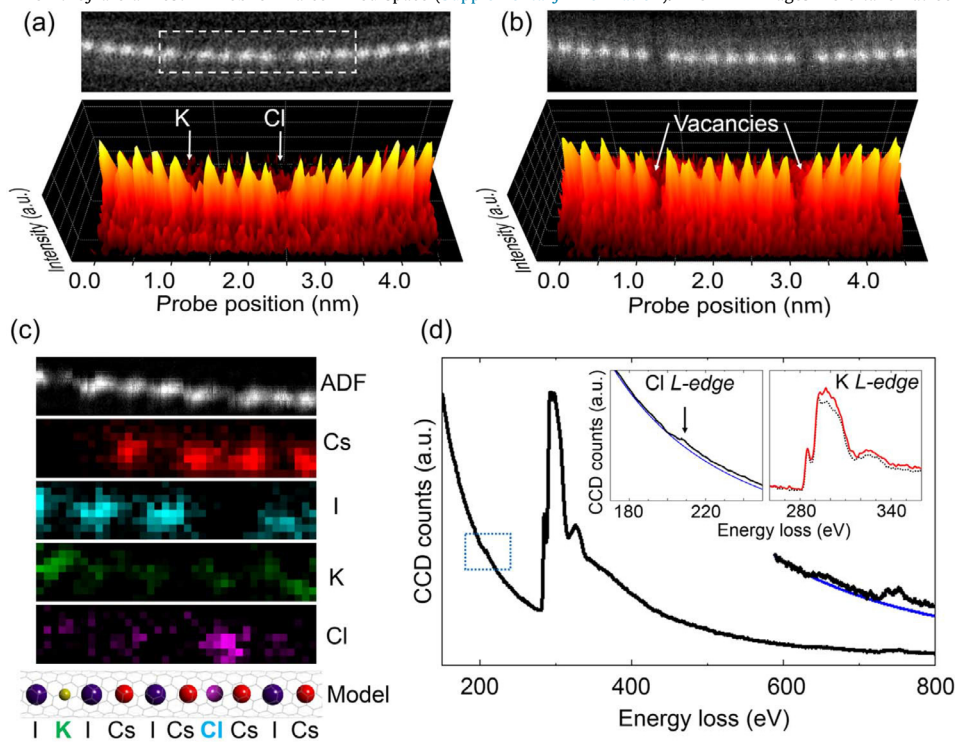
Fig. 2. Detection of single dopant atoms and mono-vacancies in CsI atomic chains co-doped with K and Cl. STEM images (top) and intensity profile maps of the ADF contrast (bottom) for CsI atomic chains involving (a) K and Cl substitutions and (b) two vacancies. (c) EELS chemical map constructed from the EELS spectra shown in (d) collected from the chain in (a) around the dopants. The STEM images were taken at 60 kV. A principal component analysis (PCA) was performed to create the elemental map in (c), although the spectra in (d) are not processed.

ier 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