Probing the behavior of single atoms, molecules and 2D layers using electron energy loss spectroscopy with low energy (30 keV and 60 keV) electrons

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1. INTRODUCTION

The understanding of the behavior of small systems is fundamental for the design of material. In the limit, the properties of individual atoms and molecules will needed to be known and controlled. In view of the great advances of electron optics in the previous decades, electron spectro-microscopy is particularly well posed to probe these intrinsically small objects.

In this contribution, we will describe three groups of experiments involving materials with increasingly larger dimensionality. In particular, we will focus on the benefits of using lower energy electrons to perform EELS. We will start by showing how electron energy loss spectroscopy (EELS) can be used to probe the valence of individual Eu atoms exposed to oxygen. After, we will describe how the fine structure of core-loss EELS allows the distinction of fullerenes of different sizes confined in carbon nanotubes. Finally, we will discuss the use of low-loss EELS to map excitons in 2D dichalcogenides.

2. RESULTS

2.1 Experimental apparatus

For these experiments two microscopes have been used. 1) A JEOL 2100F equipped with a cold Field Emission Gun (FEG), two dodecapoles aberration correctors, a low energy GIF-Quantum spectrometer. This first microscope, operated at 30 keV and 60 keV, was used for single atom and molecules identification. 2) A JEOL ARM200 equipped with a Schottky FEG, a double Wien filter monochromator, a dodecapole aberration corrector and a modified low energy GIF-Quantum spectrometer. This microscope, operated at 30 keV, was used to map excitons in single layer dichalcogenides in experiments with the sample at 150 K.

2.2 Single atom valence measurements

We have used core-loss EELS to map the valence state of individual Eu atoms in atomic chains confined inside carbon nanotubes (Fig. 1). By following the energy position of the Eu M_4 edge we have been able to identify a valence change of individual atoms (2.5 eV energy shift) when oxygen enters the carbon nanotubes [1]. More interestingly, we have been able to identify atoms which change continuously between two valence states, possibly due to the small concentration of available O atoms.

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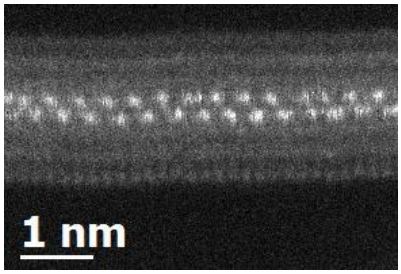

Figure 1. Eu chain inside a triple wall carbon nanotube. The bright spots are individual Eu atoms. The less bright spots below are carbon atoms in the outer carbon nanotube.

2.3 Single molecule identification

Single distinct fullerenes (C_{60} and C_{70}, stored in carbon nanotubes) have been identified using core-loss EELS spectroscopy using 30 keV electrons [2]. This has been done by observing the carbon *K* edge fine-structure. We have used fullerenes crystals as references for single molecule identification. We have also estimated the damaged induced by 30 keV and 60 keV electrons in large C_{60} crystals. Our results indicate that single fullerene spectroscopy is only possible using 30 keV electrons.

2.4 Excitons in single layer $MoS_2/MoSe_2$ interfaces

We have used a focused 30 keV electron beam to map excitons in a $MoS_2/MoSe_2$ interface with a spatial resolution far below that of the wavelength of light emitted by these excitons (hundreds of nanometers) [3]. This has been achieved by using a 1 nm wide, monochromated, electron beam (typical zero-loss full width at half maximum between 20 meV and 50 meV). These excitons appear in the 1.6 eV to 1.8 eV range. We have been able to identify spectral changes between regions separated by about 10 nm.

3. CONCLUSION

We have explored the use of low energy electrons in core-loss and low-loss electron energy loss experiments to probe different properties of low dimensional materials.

REFERENCES

[1] L. H. G. Tizei, et al, *submitted* (2015).
[2] L. H. G. Tizei et al, *Phys. Rev. Lett.*, **113**, 185502 (2014).
[3] L. H. G. Tizei, et al, *Phys. Rev. Lett.*, accepted for publication (2015).