Multimodal chemical and crystallographic characterisation of carbon nanotube encapsulated metal particles

Introduction

Carbon nanotubes, with both single wall and multiwall types, are of significant research interest as they display a large Youngs modulus, superconducting or semiconducting electrical behaviour, and have the ability to be chemically modified. They have been investigated for potential applications as catalyst supports, nano-sensors, structural composites, and semiconductor components.

Carbon nanotube encapsulation is a process wherein nanoparticles are synthesised or formed within the hollow structure of a carbon nanotube, and has many potential applications including:

- Lithium-ion battery cathodes, where the metal nanoparticle encapsulated within the tube changes the electron density of the nanotube and aids in efficient dissociation of Li_2O_2 at the cathode surface.
- Medical therapeutic delivery systems, where magnetic particles used for thermal tumour treatment can be transported by the nanotube, and be protected from the human body before being heated with an applied magnetic field at targeted locations.
- Nuclear waste remediation, where the nanotube is used to absorb, encapsulate and isolate dissolved active materials from waste streams at generation or decommissioning sites.

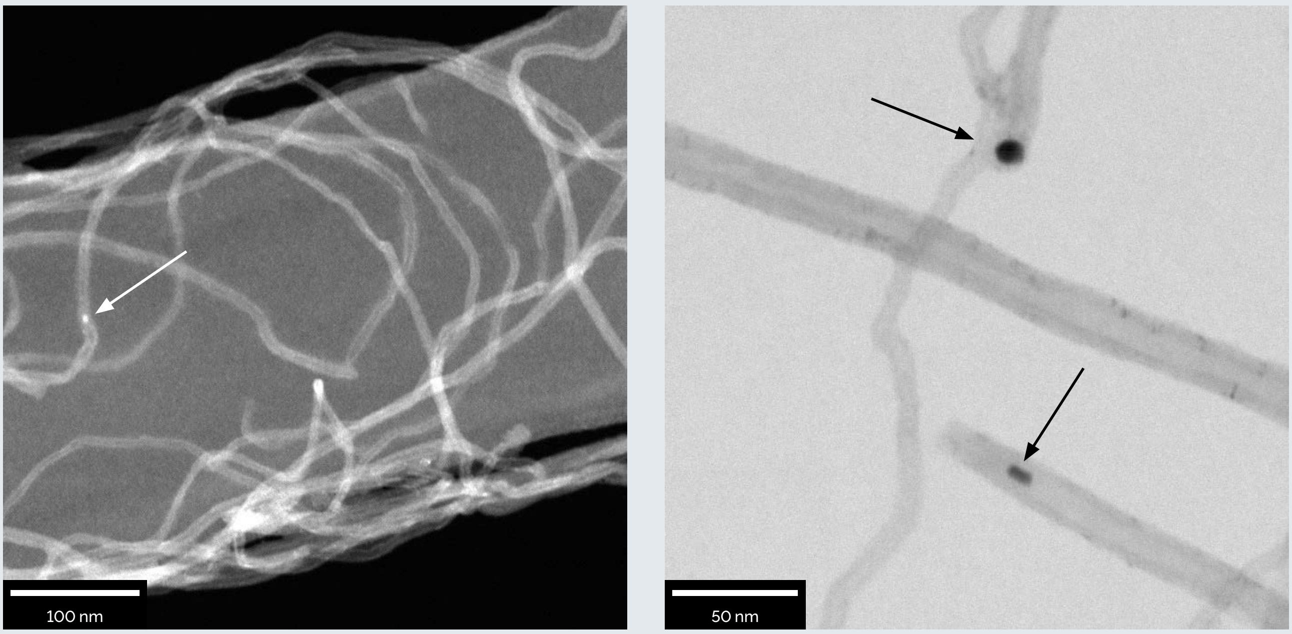


Figure 1: – ADF and BF-STEM images of carbon nanotubes, potentially encapsulated particles are indicated witharrowsdicated with arrows

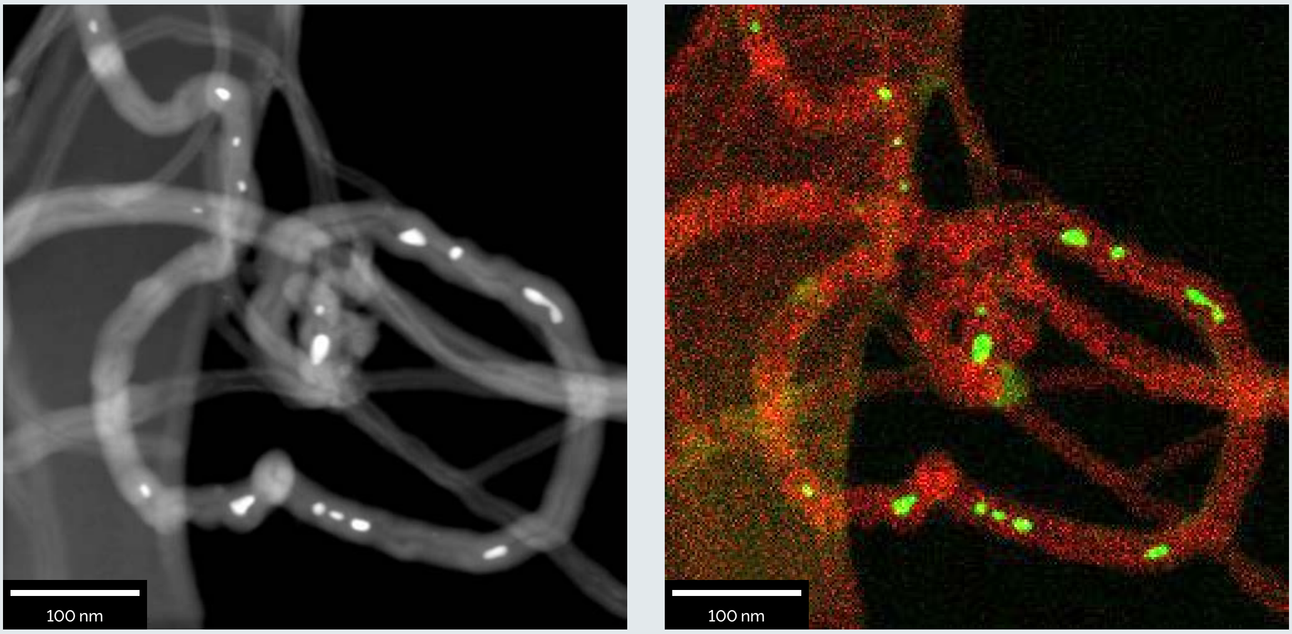
The crystallisation behaviour of these metal nanoparticles can be altered by the carbon nanotubes, providing a unique environment for nucleation and growth studies. To build up an understanding of how the nanotubes affect the crystallisation and stability of these encapsulated nanoparticles, it is necessary to investigate the distribution, composition, and structure of the metal particles within nanotubes.

The TESCAN TENSOR analytical 4D-STEM offers an unparalleled characterisation platform for multimodal chemical and crystallographic studies on individual nanoparticles. The large 2 steradian EDX detector system, fast direct detector camera with 4D-STEM and crystal orientation analysis capability and automated alignments allow for rapid and reliable nanoanalysis in an automation centered package.

This short application note will demonstrate how the TESCAN TENSOR can be used for rapid combined chemical and structural characterisation of carbon nanotube encapsulated metal particles at the individual particle scale.

Methods

A combined approach of STEM imaging, EDX mapping, 4D-STEM and phase contrast imaging was used to identify and characterise metal particles encapsulated within nanotubes. For STEM imaging, a convergence semi-angle of 6.5 mrad and a probe current of 100 pA was used. EDX mapping used a 10 nA probe current in a 1 nm probe with a total acquisition time of 600 s. 4D-STEM datasets were acquired using a 2 mrad probe convergence semi-angle, 250 pA probe current, 2 ms dwell time, and a 2.5 nm pixel size. High resolution phase contrast imaging was performed with a 10 mrad convergence semi-angle and a 65 pA probe current.



▲ **Figure 2:** HAADF STEM and EDX map of carbon nanotubes and metal nanoparticles, carbon is shown in red and iron in green.

Results

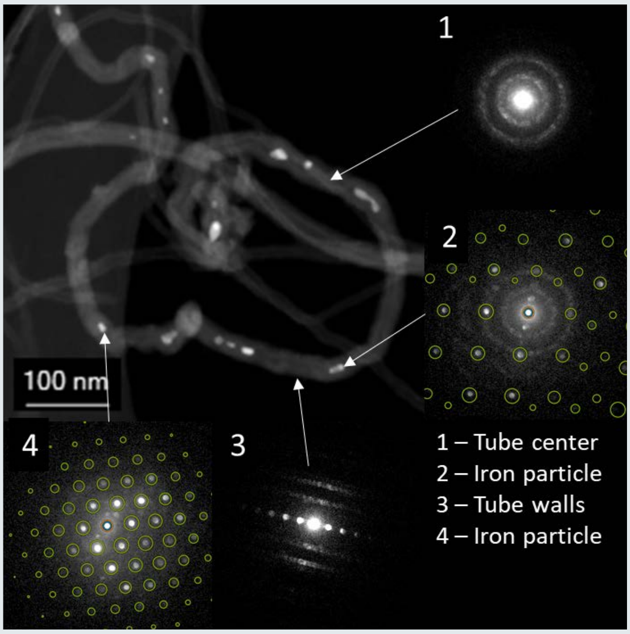
From STEM imaging, it is possible to distinguish nanotubes with embedded nanoparticles, these metal particles occur solely within the tubes, with no external attachments observed. An example can be seen in Figure 1, where the embedded particles are marked with arrows.

EDX analysis was used to find the composition of these particles, which were revealed to contain only iron. EDX mapping of the deposits showed that iron was detected only inside these discrete particles and iron atoms were not dispersed through the nanotube volume. The EDX mapping is shown in Figure 2.

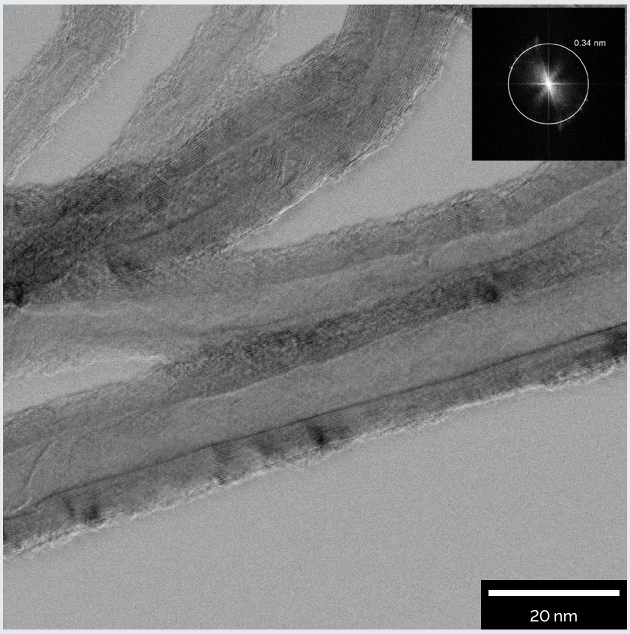
Using the information from EDX, 4D-STEM with automated crystal orientation analysis was used to assess the crystallinity of the iron particles. It was found that in some cases, the iron particle was crystallographically aligned with the carbon nanotube, suggesting that the nanotube had some influence on the crystallization or crystal growth of the iron particle. However, in many cases, there was no crystallographic relationship between the iron particle and the carbon nanotubes. Kinematic diffraction templates were used to index the NBED patterns to observe the crystallographic orientation of the iron particles.

Nanobeam diffraction (~3 nm probe size was used for this study) is well suited to extracting crystallinity information from localised regions, in this case it is possible to identify diffraction coming from only the nanoparticle within the nanotube, and from the nanotube walls separately. This is shown in Figure 3.

The NBED patterns from the tube walls showed several diffraction spots, related to the number of layers present. High resolution phase contrast imaging was used to investigate the number and spacing of the layers in the nanotubes. The lattice image shows a tube wall spacing of approximately 0.34 nm, measured from the spots in the fast Fourier transform image, this is consistent with known values for the spacing of carbon layers in graphite. These high-resolution images showed that the nanotubes did not display a consistent number of layers, ranging from 5 to over 15 layers.



▲ **Figure 3:** Virtual ADF image and NBED patterns from a carbon nanotube with embedded iron nanoparticles, the NBED patterns have been indexed using templates generated using the CIF for iron (COD code 9008537)



▲ **Figure 4:** High-resolution phase contrast STEM image of carbon nanotube with the inset FFT showing 0.34 nm tube wall spacing.

Conclusions

In this application note, combined 4D-STEM and EDX analysis was used to study metal nanoparticles encapsulated within carbon nanotubes, producing insights into the metal nanoparticles crystallography and chemistry. The TESCAN TENSOR analytical 4D-STEM system allowed for rapid characterisation of complex specimens down to the sub-nanometer scale. Multimodal characterisation provides correlated studies into chemistry and structure, opening new insights into engineering materials from the micron scale, down to the atomic scale.

TESCAN ORSAY HOLDING, a. s.
Libušina tř. 21, 623 00 Brno - Kohoutovice / Czech Republic
(phone) +420 530 353 411 / (email) sales@tescan.com / marketing@tescan.com