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Analysis of few-nm sized metal nanoparticles on carbon nanostructures

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Abstract. HAADF-STEM tomography has been used to analyse the size and distribution of encapsulated gold nanoparticles (NPs) in hollow graphitised carbon nanofibres. HAADF combined with a rolling-ball filter allows few-nm sized metallic NPs to be imaged with sufficient contrast against the higher volume carbon support structures to enable tomographic reconstruction.

1. Introduction

There has been increasing interest in hybrid metal nanoparticle (NP)/carbon nanostructures over the past decade [1-3]. For such materials, information on the distribution of the NPs on, or encapsulated within, the carbon structure is of particular importance. In most cases, the metal NPs are formed in situ, e.g. during arc discharge growth of the carbon nanostructure, complicating control of the size, shape and dispersion of the NPs. Where pre-formed NPs are encapsulated [4,5], the relative orientations of NPs within the nanostructure and the distances between the NPs become the main factors of interest.

Tilt-series TEM is the most suitable analytical technique for investigating the location of metal NPs adsorbed on the exterior or encapsulated within a three-dimensional (3D) carbon nanostructure. For particle size distribution analysis and tomographic reconstruction, it is particularly important to quickly and reproducibly separate the contributions to the signal from the metal NPs and the carbon support structure. While elementally sensitive techniques such as EDX mapping may produce a lower contribution to the signal from the carbon content, the additional acquisition time per frame required makes this approach inconvenient in terms of total time requirements, whilst increasing the potential to alter the sample, e.g. by the beam induced coalescence and ripening of metastable metal NPs.

Traditional Bragg diffraction contrast bright-field and dark-field TEM analysis of such structures can be difficult due to the significantly large volume of the carbon structure compared to the metal NPs, particularly for few-nm sized NPs. Conversely, high angle annular dark field (HAADF) STEM provides for atomic number contrast, and increases the metal NPs’ relative contribution to the signal.

In this work, we apply HAADF-STEM imaging to Au-NPs encapsulated in hollow graphitised carbon nanofibres (GNF). These nanofibres comprise graphene layers, forming a herringbone stack at an angle to the main axis, and thus have a corrugated interior [6]. Consequently, the interaction
between encapsulated NPs and the GNF is potentially more significant than the NP-NP interaction, in terms of positioning and aggregation [7].

2. Experimental
Samples consisting of dodecanethiolate-stabilised AuNPs were inserted into GNFs in supercritical CO₂ [7]. TEM analysis was performed using a JEOL 2100F FEGTEM, equipped with a Gatan Orius camera for conventional imaging and a JEOL digital STEM system for annular dark field imaging. TEM specimens were deposited onto copper grid mounted holey carbon films from methanolic solution and dried under a stream of nitrogen. Acquisition of HAADF tilt series was performed using a Gatan 916 tomography holder, with a tilt range of -55 to +55 degrees, with one image taken per degree. Post acquisition filtering of the tilt series was performed using ImageJ software. Tomographic reconstructions were produced using IMOD 3.13.2 software.

3. Results and discussion
With conventional diffraction contrast imaging (figure 1), ‘large’ (i.e. > 5 nm) NPs are clearly discernible, but smaller NPs, particularly when viewed along the edge of the inside of the hollow GNF, are difficult to identify.

![Figure 1: Conventional bright field image of Au NPs encapsulated in a graphitic nanofibre (scale bar = 50 nm).](image)

The contrast between the metal NPs and the carbon of the nanofibre is greatly improved by using the Z-contrast sensitivity of HAADF imaging (figure 2). Such images allow the locations of NPs to be identified unambiguously, relative to the structure of the GNF, particularly as part of a tilt series. Comparison of the original zero-tilt image before tilt series acquisition with that at the end indicated that no discernable ripening of the NPs had occurred during tilt-series acquisition. However, even though the NPs are now clear enough to be identified, the contrast levels between the metal NPs and carbon structure remains problematic for tomographic reconstruction.
Figure 2 Unfiltered HAADF STEM images of Au NPs encapsulated in a graphitic nanofibre, tilted at -42, 0, +42 degrees. (Scale bars = 20 nm.)

To further enhance the contrast for reconstruction from such tilt series, a number of filters were tested, to remove the large scale carbon background from the image. It was found that a 50 pixel rolling ball filter produced clear results (figure 3), although some contrast from the graphitic nanofibre remained at positions where the walls were viewed edge on. The size of the rolling ball filter in this case was chosen to avoid losing signal from any of the NPs, rather than to minimise the contribution from the carbon at the expense of losing NP information.

As some contribution from the carbon material is still clearly visible, careful thresholding of the subsequent reconstruction was required to optimise the final 3D model, in terms of identifying the location of NPs on the inside and outside surfaces of the GNF. Tomographic reconstruction of this sample (figure 4) confirmed the presence of metal NPs on both the exterior and interior surfaces of the hollow GNF in this instance.

Figure 3 HAADF STEM image after applying a 50 pixel rolling ball filtered image (1 pixel = 0.113nm). Scale bar = 20nm
Figure 4 Tomographic reconstruction from rolling ball filtered HAADF STEM images of Au NPs on the inner and outer surfaces of a hollow graphitic nanofibre, viewed (a) edge on and (b) down the long axis. Scale bar = 20nm

4. Conclusion
The Z-contrast sensitivity of HAADF imaging combined with post-acquisition image rolling-ball filtering has been used to extract information on the localisation of metal NPs encapsulated in graphitic nanofibres, with minimised signal contribution from the carbon support.

References