In situ heating and tomography of gold nanoparticles on carbon structures

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Abstract. A series of thermally mediated dynamic (in situ) experiments in the transmission electron microscope (TEM) have been performed, in order to obtain improved understanding and control of the ripening and migration processes of gold nanoparticles on multi-wall carbon nanotubes (MWNTs). In particular, post-heating tomography was used to appraise the resultant dispersion of the nanoparticles within these three-dimensional (3D) composite structures.

1. Introduction

Supported gold nanoparticles may be used for a wide range of applications, including low temperature catalysis and light absorption [1]. As the functional properties of gold nanoparticles are strongly affected by their size and shape, it is necessary to obtain a full understanding of the thermal stability of supported gold nanoparticles and how it is affected by the material support.

In this work, we performed in-situ heating of gold nanoparticles on a support material, followed by post-anneal tilt analysis to understand the ripening and migration processes of the nanoparticles, and how the relate to the structure of the support material.

The commercial availability of graphene oxide films is advantageous for work of this nature. This substrate has benefits for both the heating and tomographic analysis of these composite materials. Firstly, the substrate provides better heat conductivity than traditional amorphous carbon films, allowing the temperature at the sample to be more reliably calculated from knowledge of the heating holder crucible temperature. Secondly, the low contrast background of the graphene oxide film assists greatly in tomographic reconstruction, producing minimal background to the sample even at high tilt angles.

2. Experimental

Arc-discharge produced multi-wall nanotubes (AD-MWNTs, MER corporation) were treated with nitric acid (16 M for 24 h) at the reflux point and the resulting mixture was then diluted with deionised water (200 mL). This was filtered using a 0.45 μm pore size PTFE membrane filter, washed thoroughly with water until neutral pH and ethanol (50 mL), and dried under vacuum to yield a black
solid (192 mg). 1 mg of Gold nanoparticles were suspended in hexane and mixed, via sonification, with 1 mg of AD-MWNTs [2]. The resultant composite material was again filtered through PTFE and washed with ethanol and acetone. The composite was dispersed in ethanol and spotted onto graphene oxide TEM support films (Graphene Supermarket).

Imaging for in situ heating and tomographic analysis has been performed largely in scanning TEM mode. This rastering mode of imaging reduces beam heating effects [3], ensuring that the ripening of the nanoparticles during in situ heating is predominantly an effect of thermal heating from the support stage, with no observable further ripening occurring during post-heating tomographic analysis. High angle annular dark field (HAADF) imaging is particularly suitable for analysing metal nanoparticles on 3D carbon supports as the atomic number sensitivity makes few-nm sized metallic nanoparticles visible against the background for a significantly greater volume of graphitic material. As the orientation of the crystalline nanoparticles does not strongly affect the intensity of the HAADF image, this mode produces an image series that is particularly suitable for tomographic reconstruction.

TEM investigations were performed using a Jeol 2100F equipped with JEOL and Gatan digital STEM detectors and a Gatan Orius CCD camera for conventional imaging. In situ heating was performed using a Gatan 652 double tilt heating holder. Post-annealing tilt series were acquired using a Gatan 916 room temperature tomography holder. Tilt series acquisitions was performed using SerialEM software, with tomographic reconstruction performed using IMOD 4.3

The relationship between the temperature of the nanoparticles on a graphene oxide film to the recorded temperature of the heating holder crucible was calibrated prior to this work using the evaporation temperature of Ag nanoparticles dispersed onto graphene oxide film, as a reference point [4,5].

3. Results and Discussion

Samples of Au nanoparticles on acid treated MWNTs were first investigated at room temperature to locate a suitable region of the grid and nearby identifying marker features. The size of Au nanoparticles on the structure was found to range from approximately 1.5nm to 6nm in diameter prior to annealing. The holder temperature was then rapidly raised to 500 °C, with the sample location and focus tracked manually using the HAADF STEM mode on high scan rate. Once the temperature had reached 500 °C, images were taken in HAADF STEM mode every five minutes, for a total duration of 150 minutes (Figure 1). The particles had largely reached a stable size after 135 minutes.

After the in-situ heating, the sample was cooled to room temperature in vacuum before transferring to the tomography holder for high-tilt image series acquisition on two axis. A stereogram showing typical images of the post-anneal structure is shown in figure 2. Finally, HRTEM analysis was performed on the exterior gold nanoparticles (figure 3).

Subsequent to annealing, gold nanoparticles within the carbon nanostructure were found to be predominantly between 1 and 2.5nm in diameter. Particles on the exterior of the carbon support ranged from 2nm to 7nm, with a greater number at the higher end of the range than prior to annealing. Coalescence of some gold nanoparticles on the exterior of the support into non-spherical shapes was observed.
Figure 1 HAADF images of Au nanoparticles on acid treated multi-walled carbon nanotubes, annealed in situ at 500 °C for 135 minutes, illustrating the ripening of the nanoparticles. Left: t=0 min, right t=135min.

Figure 2 HAADF stereogram images of gold nanoparticles on multi-walled carbon nanotubes after in situ annealing.
4. Conclusions
From post-heating tilt-series analysis, it can be seen that particles on the exterior of the nanotube exhibit more significant ripening than those encapsulated within the tube, and are located in a linear orientation on the exterior of the nanotubes. Graphene oxide support films are advantageous for this work, providing improved thermal transport in comparison to conventional amorphous carbon films, while also producing a lower background signal.

References
[1] Turba T, Grant Norton M, Niraula I, McIlroy D N, 2009 J Nanopart Res 11, 2137-2143
[2] Brust M, Walker M, Bethell D, Schiffrin D J, Whyman R, 1994 J Chem Soc Chem Commun, 801-804
[3] La Torre A, Giménez-López M C, Fay M W, Rance G A, Solomonsz W A, Chamberlain T W, Brown P D, Khlobystov A N, 2012 ACS Nano 6 2000-2007
[4] Kang S Y, Kim K, 1998 Langmuir 14 226-230
[5] Yonezawaa T, Arai S, Takeuchi H, Kamino T, Kuroda K, 2012 Chem Phys Rev 537, 65-68