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Letter to the Editor

Impregnation of carbon black for the examination of colloids using TEM

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ABSTRACT

Nanoparticles are frequently synthesised as colloids, dispersed in solvents such as water, hexane or ethanol. For their characterisation by transmission electron microscopy (TEM), a drop of colloid is typically deposited on a carbon support and the solvent allowed to evaporate. However, this method of supporting the nanoparticles reduces the visibility of fine atomic details, particularly for carbonaceous species, due to interference from the 2-dimensional carbon support at most viewing angles. We propose here the impregnation of a 3 dimensional carbon black matrix that has been previously deposited on a carbon film as an alternative means of supporting colloidal nanoparticles, and show examples of the application of this method to advanced TEM techniques in the analysis of monometallic, core@shell and hybrid nanoparticles with carbon-based shells.

Nanoparticles represent one of the most studied structures in nanotechnology and nanoscience because of the wide range of applications arising from their unique optical, physical and chemical properties [1]. Often they have core@shell structures, or are coated with organic molecules. Nanoparticle functionality is largely affected by the specific configuration of the outer surface atoms. For example, in heterogeneous catalysis activity and selectivity are mostly determined by the type of atomic defects present at the surface of metallic nanoparticles, and in the field of biomedicine the surface coating of hybrid (inorganic core@organic shell) nanoparticles regulates their stability, solubility and targeting.

Nanoparticles are frequently synthesised using solution techniques that yield colloids, i.e., a solid–liquid mixture containing solid particles that are dispersed to various degrees in a liquid medium; most frequently water, ethanol or hexane. Colloid characterisation generally employs a variety of techniques to establish understanding and control over nanoparticle synthesis and properties. Electron microscopy in transmission mode (TEM) and in scanning transmission mode (STEM) are widely used for particle characterisation, and advances in these techniques mean that it is now routinely possible to resolve single atoms at the surfaces of nanoparticles using aberration-corrected microscopes, to elucidate

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the three-dimensional shapes of nanoparticles using electron tomography, and to enhance the contrast in very low density materials (e.g., carbonaceous materials) using electron holography [2,3]. However, the significant potential of these (S)TEM techniques is ultimately limited by the sample and the techniques available for sample preparation.

Typically, examination by (S)TEM requires that a nanoparticulate sample be prepared by depositing a drop of colloid on a thin, electron-transparent support. It is usual that an amorphous carbon film, silicon nitride film or graphene layers deposited on a copper grid constitute the support [4]. Crucially, these sample preparation techniques suffer from the major limitation that the contrast from the support often shadows atomic details at the particle surface. Moreover, it has been established that the thinnest supports can degrade under electron-beam irradiation, affecting particle stability [5], and also that hydrocarbon contamination can be an issue [6]. The most widely used commercially available TEM support is holey carbon, which comprises of a perforated carbon thin film. In this case, sample preparation aims to locate at least some of the nanoparticles of interest at the edges of the perforations. However, the concave nature of the holes means that solvent contaminants tend to accumulate preferentially at these sites. Moreover, if the TEM sample holder is tilted a particle attached to the edge of a hole is very likely to be shadowed by the carbon film. Taken together, these drawbacks significantly limit the application of techniques such as electron tomography [6].

We propose here a method of circumventing some of these fundamental problems by developing a technique for mounting nanoparticulate samples using a carbon matrix that is inspired by the way samples used in electrocatalysis are prepared [7]. Fig. 1 shows an image of a typical Pt-based electrocatalyst supported on carbon black as used in proton-electron membrane fuels cells, and which consists of Pt nanoparticles formed by calcination of a carbon black impregnated with a solution of salt precursor. Carbon black is a low-grade form of graphite, which is composed of nanocrystallites and no long-range order [8]. In Fig. 1 the carbon black is Vulcan XC-72R, which is widely used as a catalyst support in fuel cells because it provides high electrical conductivity, good reactant gas access, adequate water handling and good corrosion resistance, whilst allowing high dispersion of the particles. In electrocatalyst samples it is common to find particles, like the 5 nm Pt particle shown in Fig. 1, attached strongly to the surface of the support and viewed edge-on against a vacuum so as to provide optimal conditions for high-resolution TEM (HRTEM). Fig. 1B is a quantitative phase image of a Pt particle obtained from a defocus series of 20 images at intervals of 5 nm acquired in a FEGTEM JEOL 2020 at 200 kV with spherical aberration of −30 μm and applying the exit-wave restoration technique [2]. The contrast between details of the particle finestructure is very high compared to conventional HRTEM images, and details such as the presence of monoatomic carbon ribbons surrounding the particle can be seen.

Inspired by this method of preparing electrocatalysts, we now propose the use of carbon black as a matrix that can be easily impregnated with as-prepared colloids prior to examination of the resultantly supported nanoparticles by TEM. Fig. 2A shows schematically the technically simple and cost-effective impregnation procedure. Starting from a TEM grid with holey carbon film, the process involves: (i) dry impregnation of the grid with an ultrafine powder of carbon black – in our experiments we used Vulcan XC-72R, which represents an industrial standard for conductive carbon black and which is readily commercially available from suppliers like Graphene Supermarket or Cabot Corporation, (ii) wetting of the grid with a drop of colloid, (iii) drying, and optionally (iv) very short Argon plasma cleaning for reducing hydrocarbon contamination (20–30 s). Fig. 2B shows an image acquired using a scanning electron microscope (SEM) of a TEM grid with holey carbon film and carbon black powder. Fig. 3 shows a typical bright-field TEM

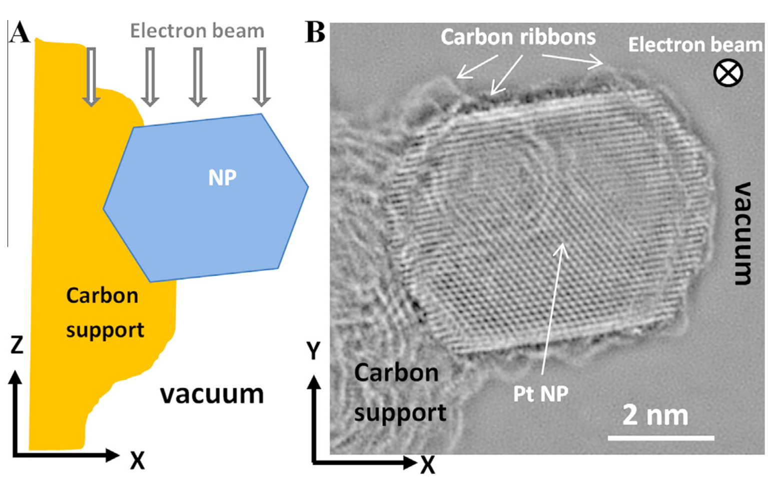

Fig. 1 – (A) Schematic of a single nanoparticle (NP) attached to the surface of a carbon black support, in edge view in vacuum. These conditions optimise the visibility of the details of the nanoparticle. (B) Phase image of a Pt nanoparticle on carbon black obtained using through-focal series restoration. Surface roughness and carbon ribbons surrounding the particle are clearly visible. (A colour version of this figure can be viewed online.)

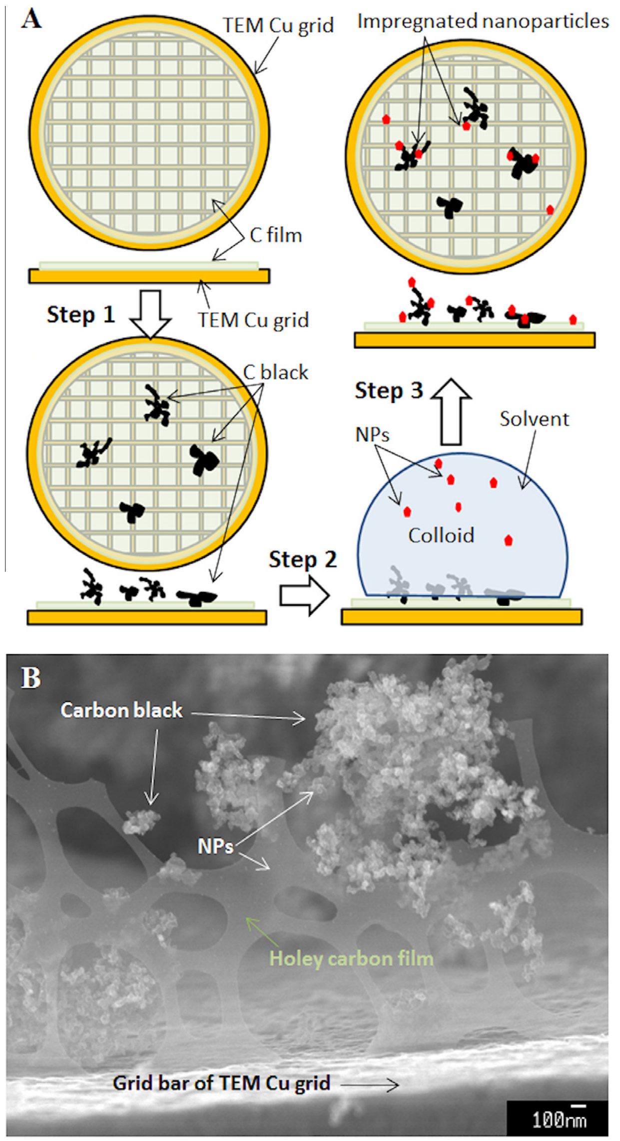

Fig. 2 – (A) Multistep impregnation method for treating a holey carbon TEM grid with carbon black first and colloid afterwards. (B) Low-magnification image of a TEM copper grid with holey carbon film and carbon black powder impregnated onto it. Subsequently drop-cast NPs reside on both the carbon film and the carbon black. (A colour version of this figure can be viewed online.)

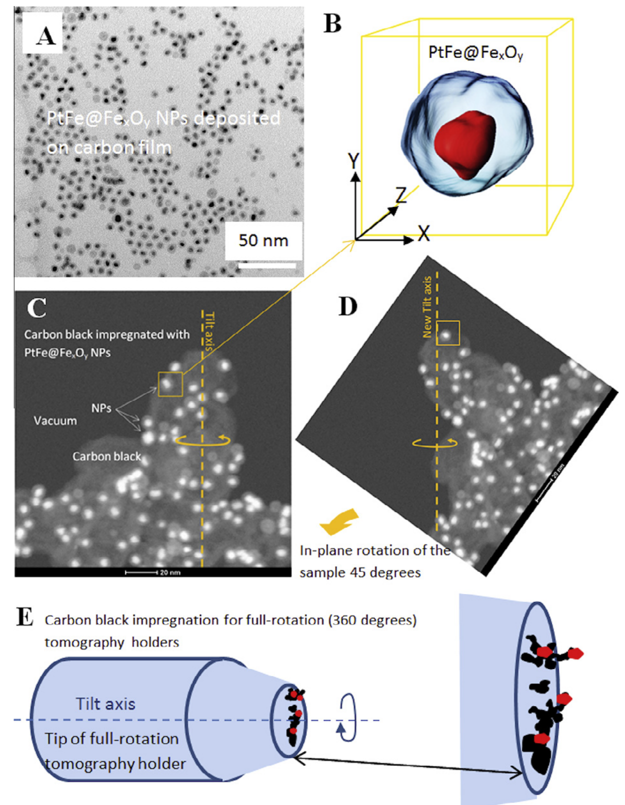

Fig. 3 – (A) Conventional bright-field TEM image of $PtFe@Fe_xO_y$ nanoparticles deposited on carbon film. (B) Three-dimensional isosurface visualisation of one $PtFe@Fe_xO_y$ nanoparticle after tomographic reconstruction. (C) HAADF STEM image of the same sample as shown in (A) after impregnation into carbon black. Many particles are now visible at the edge of the carbon. The image is one of many from a series of images acquired at different tilt angles between −70 and +75 degrees for the application of electron tomography as shown in (B). The tilt axis is the dashed line. (D) Using dual-axis tomography holders the tilt axis can be optimised to enable specific particles to be viewed without there being a carbonaceous background. (E) Carbon black impregnation can be used also on the tip of a full-rotation tomography holder for the application of electron tomography without there being any missing wedges. (A colour version of this figure can be viewed online.)

image of $PtFe@Fe_xO_y$ core@shell nanoparticles deposited directly onto the carbon film of a TEM grid following hexane evaporation. Fig. 3B shows the isosurface visualisation of the three-dimensional shape of one $PtFe@Fe_xO_y$ nanoparticle after the application of HAADF STEM tomography using the method of carbon black impregnation. Fig. 3C is one of many from a series of images acquired at different tilt angles between −70 and +75 degrees for the application of electron tomography as shown in Fig. 3B. Importantly, using carbon black it is possible to achieve excellent particle dispersion. Because of the complex surface morphology and thus high surface-to-volume ratio of carbon black the probability of being able to view a surface-attached particle against the background vacuum is much larger, making the application of TEM techniques such as electron tomography more effective [8]. For example, using a dual-axis tomography holder (e.g., *Model 2040 of Fischione Instruments*) the tilt axis can be optimised for specific particles, rotating the sample in order to enable a selected particle or region of particles to be viewed against a vacuum (e.g., the highlighted particle in Fig. 3D), hence improving the tomographic reconstruction. Moreover, when a sample supported on a 3-dimensional carbon black matrix is tilted to high angles, overlapping between particles out of the field of view is minimised relative to what is observed using a conventional 2-dimensional carbon support. In contrast to

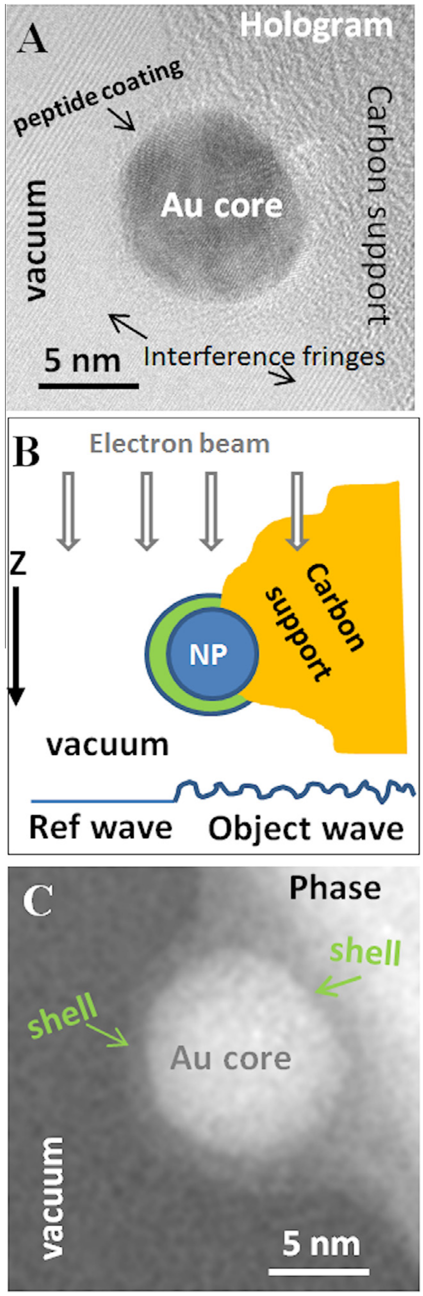

Fig. 4 – (A) Electron hologram of a single nanoparticle after impregnation of carbon black with a colloidal dispersion of Au nanoparticles coated with thiocoraline peptide. The coating is barely visible and is likely amorphised by the electron-dose (25 A/cm^2) and high acceleration voltage (300 kV) used. (B) Schematic showing that the particle at the carbon black edge is optimally located for the application of electron holography because the reference electron wave experiences only a vacuum. (C) Low-resolution phase image of the hybrid nanoparticle obtained from the hologram shown in (A). The low-density organic shell surrounding the whole surface of the nanoparticle is now visible. (A colour version of this figure can be viewed online.)

the latter case, a sample supported on carbon black is surrounded by vacuum for most tilt angles; this improves the quality of the reconstructed volume facilitating its post-processing (e.g., volume segmentation). Indeed, carbon black impregnation could be used also on the tip of a full-rotation tomography holder for the application of electron tomography without there being any missing wedges (see Fig. 3E).

In a third example of the successful use of carbon black as a support, Au nanoparticles coated with organic compounds were interrogated. These have many applications in biomedicine, where their surface is often modified with peptides, proteins, DNA, or polymers [1]. One fundamental difficulty with the TEM analysis of such samples is that the organic coating is composed of molecules that consist mostly of carbon. Staining is a technique used to aid the TEM investigation of organic samples, firstly to protect them against electron radiation damage and secondly to enhance the contrast of the low-density materials. However, this method is not effective for relatively small (<10 nm) hybrid nanoparticles. An interesting alternative for their characterisation is the use of electron holography [3]. Fig. 4 shows an example of the impregnation of carbon black with a colloid of Au nanoparticles coated with peptides for anti-tumoral therapy [9]. Fig. 4A shows an electron hologram of one Au@peptide nanoparticle acquired on a Titan FEGTEM at 300 kV with an electrostatic bi-prism and an electron dose of 25 A/cm^2. The hologram contains encoded information of the phase the electron wave exiting the sample. Electron holography works by inducing interference between the electron wave that permeates the sample with a reference wave ideally from an empty region of space without the sample (i.e. the vacuum). As shown schematically in Fig. 4B, a nanoparticle attached to the edge of the carbon black is ideally situated for the application of holography. The phase image computed in Fig. 4C from the hologram in Fig. 4A is much more sensitive to small changes in composition compared with conventional TEM images and so greatly enhances the contrast of the low-density particle coating without the need for staining.

The present results reveal that the impregnation of the high-surface-to-volume material carbon black with colloids represents a very promising method for facilitating the application of existing advanced TEM techniques to the study of the smallest details of catalysts, core@shell and hybrid nanoparticles with a carbon-based exterior. This simple method shows great promise for extension to other types of non-carbonaceous supports such as metal oxides, and to the examination of other nanostructures, such as nanodiamonds, nanotubes or carbon nanodots [10].

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