New approaches to nanoparticle sample fabrication for atom probe tomography

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Abstract:

Due to their unique properties, nano-sized materials such as nanoparticles and nanowires are receiving considerable attention. However, little data is available about their chemical makeup at the atomic scale, especially in three dimensions (3D). Atom probe tomography is able to answer many important questions about these materials if the challenge of producing a suitable sample can be overcome.

In order to achieve this, the nanomaterial needs to be positioned within the end of a tip and fixed there so the sample possesses sufficient structural integrity for analysis. Here we provide a detailed description of various techniques that have been used to position nanoparticles on substrates for atom probe analysis. In some of the approaches, this is combined with deposition techniques to incorporate the particles into a solid matrix, and focused ion beam processing is then used to fabricate atom probe samples from this composite. Using these approaches, data has been achieved from 10 - 20 nm core-shell nanoparticles that were extracted directly from suspension (i.e. with no chemical modification) with a resolution of better than +/- 1 nm.

Keywords:

Atom probe tomography; nanoparticles; sample preparation; focussed ion beam;

Introduction:

Nanoparticles and other nanometer sized materials display unique properties, which are often size and shape dependent. They are heavily researched for applications in data storage [1], solar cells [2], catalysis [3] and many other applications. However, little is known about their chemical make-up at the atomic scale, owing to the difficulty of analysing individual particles [4]. Atom probe tomography [5] is an atomic-resolution 3D mass spectrometry method that can provide key information to answer questions around nanoparticles such as: What is the composition and the atomic arrangement of the surface? Does the particle form a solid solution or is there partitioning between the

elements? Are there residual elements present from the synthesis? These are all questions that have been answered for bulk materials by atom probe for a number of years now, so the extension to nanomaterials including nano-particles is a logical step. However, the fabrication of samples from such materials poses a great challenge, and gradual progress has been made by several researchers over the years.

In order to access atomic scale structural information from nanoparticles, Lovall et al. [6] used a field ion microscope, which is a high-field technique that is closely related to APT and uses field ionized gas atoms to image surfaces. They developed a setup capable of capturing single Au clusters from a metal cluster source in the size range up to 20 nm onto pre-sharpened tips, by detecting the resulting field electron emission. Using this method, samples that are very clean and would be guaranteed to only contain a single particle could be produced.

A different direction that was pursued for the analysis of nanoparticles in dispersions is the drying of droplets on flat surfaces with subsequent FIB – lift-out after coating with a matrix material (fig. 1 b). Isheim et al. [7] performed experiments on pre-solar nanodiamonds, which they dispersed in a water – isopropanol mixture. After drying a droplet of the dispersion on a Pt coated substrate, they used an SEM to locate a region of suitable nanoparticle density and incorporated the nanoparticles into a layer of electron-beam-assisted deposition (EBAD) of Pt(C) from $(C_5H_4)CH_3Pt(CH_3)_3$. This Pt, which contains between 40-60% C [8], shows quite uneven field evaporation [9] and therefore does not allow for high resolution data and compositional accuracy. In a later publication, they improved upon this technique (Heck et al. [10]) by sandwiching the nano-diamonds in between layers of Pt produced by atomic layer deposition. A similar approach was chosen by Mouttanbir et al. [11] to capture the Al growth catalyst of a thin Si nanowire (~20 nm diameter), together with the nanowire. They have coated the top region of the nanowire with Ni, providing a stable matrix for the atom probe experiment.

A full incorporation of the nanoparticles into a ‘bulk’ matrix was achieved by Folcke et al. [12]. They used an apparatus where they incorporated FePt nanoparticles from inert gas condensation into a Cr matrix during RF sputtering. Even though this promises high quality data, data interpretability was limited due to local magnification effects caused by the evaporation field differences between matrix and particles. Since the particles were very small (< 5 nm), these local magnification effects affected the entire volume of the particles. This is expected to be less of an issue for particle/matrix combinations with matching evaporation fields. The method was also limited to particles that are produced in the apparatus.

In the current paper, we provide details of techniques that have been used by the authors in a variety of other publications. Here we focus on providing the necessary detail for the reader to carry out similar the experiments, which was beyond the scope of the earlier publications. We will first discuss the electrophoresis technique used by

Tedsree et al. [13]. It works by using an electric field to attract particles in dispersion to a metal tip, which serves as the substrate for field evaporation (schematic in fig. 1a). This method yielded results on a variety of different nanoparticles [13-16] showing the composition of individual particles and even the partitioning between a core and a shell in the case of Ag@Pd nanoparticles. We then move on to a technique used by Felfer et al. in [17], where CoCuMn particles in agglomerated powder form were used as the starting material. Particle agglomerates were lifted out and solidified using EBAD (fig. 1c). Finally, we will describe the incubation / lift-out technique used by Felfer et al. in [18] (fig. 1b) on Au@Ag core-shell nanoparticles, where a Si substrate was incubated with particles and sputter coated with Cr to produce a solid matrix.

Fig. 1: experimental pathways for the fabrication of atom probe samples from nanoparticles.

Materials and Methods:

The atom probe experiments on the samples prepared by electrophoresis were carried out on a Cameca LEAP 3000X HR instrument [19, 20] by laser pulsing at a base temperature of 55 K using a green laser with 532 nm wavelength. The pulse frequency is 250 kHz and a typical pulse energy was 0.45 nJ, in a $\sim 10 \mu\text{m}$ spot. The DC voltage necessary to evaporate the specimen (evaporation rate) was regulated to evaporate an atom in 1 % of the pulses. The detection efficiency of this system is approx. 35 %.

For the FIB – lift-out we used a Zeiss Auriga® FIB – SEM system equipped with micro-manipulation capabilities. A micro-manipulator (Kleindiek MM3E®) was used for the FIB – lift-out of the solid samples, and a micro-gripper / piezo sub-stage combination (Kleindiek lift-out shuttle®) was used to perform the powder lift-out. The samples prepared by powder agglomeration and lift-out were analysed in a Cameca LEAP 4000X Si instrument at 50 K with laser-assisted field evaporation. The instrument is equipped with a 355 nm UV laser with a spot size of approx. $2 \mu\text{m}$ and a 2D delay line detector with $\sim 55 \%$ detection efficiency. The laser was operated at a pulse frequency of 500 kHz with a typical pulse energy of 90 pJ. The evaporation rate was 1 %.

Results and Discussion:

Sample preparation by (di)electrophoresis:

The first approach to be used to create successful atom probe samples from nanoparticles was electrophoresis, used in refs. [13-16]. Electrophoresis is the physical effect of motion of charged particles in a medium, induced by an electric field [21, 22]. Nanoparticles often possess a surface charge in a medium, which can be positive or negative depending on the combination of particle and medium. This charge is significant enough to attract the particles to a surface of opposite charge due to their small size. Since the particles move in the direction of the electric field (or opposite if they are negatively charged) this effect can be used to attract nanoparticles to a metal tip, which serves as the substrate for the atom probe experiment. In principle any conductive material can be used for the tip as long as the tip apex is sharp enough to be used as an atom probe sample. One could also use multiple tips at the same time (e.g. by using a sharpened TEM half grid [23] or microtip array [24]) to increase throughput.

Fig. 2 a shows a schematic of the experimental setup. A metal tip is dipped into a dispersion of the nanoparticles and a voltage is applied between a counter electrode and the metal tip, with the tip at bias of -3V. This produces an electric field within the liquid that attracts the particles to the tip. Since the field strength is highest at the apex of the tip, the particles are preferentially attracted to this region, where they are suitably positioned for analysis. The use of an actual force also makes it possible to use very dilute solutions, minimizing the potential for the particles to form agglomerates even without the use of surfactants. The physisorbed particles are then bonded to the surface strongly enough to allow for field evaporation in the atom probe even without further steps such as coating.

Fig. 2: Atom probe sample fabrication by dielectrophoresis. (a) Shows the principle setup of the particle deposition unit. (b) nanoparticle distribution on a pre-electropolished Pt-Ru tip after electrophoresis step using identical voltages (3V) but different deposition times. (c) Atom probe results from Pt@Ru particles deposited on a Pt – Rh tip, showing partitioning between Pt rich and Ru rich areas.

The main drawback is a size separation that results from different nanoparticle mobilities on the tip. The mobility u_0 of a particle in a medium in which an electric field exists, being defined as the velocity v of the particle divided by the electric field E the particle is subjected to, is proportional to the charge Q of the particle and inversely proportional to the viscosity η of the medium and the particle's radius r (eq. 1, [22]).

$$u_0 = v/E = Q / 6 \pi r \eta \quad (\text{eq. 1})$$

This results in a higher mobility for smaller particles, so smaller particles arrive at the tip first. This effect is often exploited for nanoparticle size (and shape) separation [25] and may lead to an atom probe sample in which smaller particles are overrepresented.

If the particles are not charged, the effect of dielectrophoresis [26] still allows for particles to be attracted to a metal tip. This is due to the fact that the induced charge in an electric field with a field gradient produces a net force on the particle in the direction of the electric field gradient. Due to the fact that the force is not dependent on the direction of the field itself, both AC and DC can be used.

Even though (di)electrophoresis is a well understood phenomenon, determining the experimental parameters that lead to the desired spread of particles on the atom probe tip is experimentally challenging. This is attributed to the fact that the particle distribution produced by a specific setting needs to be verified using a transmission electron microscope (TEM), a process that must be carried out multiple times for each set of experimental parameters. The effect of the varying the period for which the voltage is applied is shown in fig. 2 b for the distribution of Ru@Pt particles on Pt – Rh tips. A voltage of 3V DC was used in both experiments, but changing the period for which voltage was applied from 2 s to 8 s led to vastly different results. After 2 s, the particles are well separated, spaced approx. 50 nm apart, which is ideal for an atom probe experiment. However, after applying the voltage for 8 s, the entire tip is covered by a layer of particles. This leads to limited interpretability of the data produced, since signals from the individual particles become indistinguishable in the atom probe reconstruction.

This method was successfully used to acquire chemical information from a number of different particles [13-16]. In the example in fig. 2 c, Pt@Ru nanoparticles were investigated to clarify whether they occur as a solid solution or if some degree of separation is present. Even though the fidelity of the atom probe data (fig. 2 c) is limited, it is nevertheless able to show that there are regions within these particles that are Pt rich and others that are Ru rich.

The practical advantage of using electrophoresis is the simplicity of the experimental setup. As a result, if experimental parameters can be established that allow for the reproducible production of the desired spread of nanoparticles, this method offers great potential for high throughput, e.g. for process monitoring. Additionally, no ion beam processing is used, eliminating ion damage as a potential source of artefacts. Even without further coating, the yield in these experiments was about 30%, based on the amount of samples where a particle was confirmed to be located on the tip apex by TEM. However, for some particles, namely CeO₂ nanoparticles, no atom probe data could be obtained, even when the presence of particles was confirmed by TEM. Presently, the main aspect that can be improved is the data quality. All of the published results using electrophoresis examined the particles by simply attaching them onto the

substrate and field evaporating them. An increase in data quality might be possible if the particles are incorporated into a matrix by thin film deposition or if pre-field-evaporated substrates, which would possess a cleaner and more regularly shaped tip apex are used.

Sample preparation by powder lift-out:

Nanoparticles often exist in the form of a powder. In this state, the particles tend to form agglomerates. This was used in ref. [17] to create atom probe samples by incorporating them into a solid matrix produced by electron beam deposition of a gaseous precursor. We have used this approach to perform atom probe experiments on Co – Cu and Co – Cu – Mn catalyst nanoparticles (approx. 20 – 50 nm in size), with the results published in [17].

For this purpose, we used a micro-gripper in the FIB-SEM. The particle agglomerate is dispersed onto a standard SEM stub, from which it can be picked up and manipulated onto a Mo TEM grid (fig. 3 a) that was cut in half and electro-polished to form sharp pins [23]. In principle, any sharp needle with a radius at the order of an atom probe tip or slightly blunter can be used. We chose Mo (and later also W) due to the robustness for general handling. We have not used substrates with micron sized flat areas (e.g. Si micro-tip arrays or ion beam cut needles), since good penetration of precursor gas and electron beam is needed for good bonding in the later steps. The procedure starts by choosing a small piece of agglomerate (~2-3 μm) of appropriate size that can be held by the micro-gripper (fig. 3 b). We used an in-situ micro-gripping system mounted on a piezo sub-stage (Kleindiek Lift-out Shuttle). After every change of particle sample, we used the ion beam to remove any particles remaining on the micro-gripper. This ensures that no cross-contamination of samples is taking place.

Fig. 3: Fabrication of atom probe samples from agglomerates of CoCu nanoparticles. (a) The experimental setup inside the FIB – SEM system. (b) Small particle agglomerate. (c) Particle agglomerate, lifted out and attached to Mo grid. (d) The sample after initial Pt(C) deposition, pyramid and annular Ga⁺ milling

combined with deposition of Pt(C). (e) Final atom probe tip, imaged in SEM (SE) and TEM. Two larger particles are marked in the image. (f) Typical shape of a fractured atom probe sample produced by this technique.

Once the agglomerate has been picked up and successfully transferred to the electro-polished Mo grid, it is impaled onto the sharp end of a grid post (fig. 3 c). The agglomerate is then held in this position by an initial layer of electron beam assisted deposition (EBAD) and shaped into a pyramid for further annular milling (fig. 3 d, [23]). This way, preferential milling of the not-yet solidified particle agglomerate is effectively avoided. For the deposition, we used Pt from $(C_5H_4)CH_3Pt(CH_3)_3$, a common EBAD precursor. Annular milling is carried out at a low accelerating voltage (< 10 kV, to minimize ion induced damage) under a constant stream of precursor gas, while simultaneously imaging the tip with the electron beam at a high accelerating voltage (30 kV) and a high beam current (~ 10 nA). This way, during milling, Pt is deposited into the voids between the particles, producing a solid matrix for the specimen. By using a high accelerating voltage for the electron beam, the electrons possess a high enough penetration depth into the agglomerate to produce secondary electrons in the entire volume between the particles. These secondary electrons trigger the decomposition of the CVD process gas and lead to the formation of a solid matrix within the entire volume of the atom probe tip, rather than just an outer shell. The progress is monitored by using a detector for the transmitted electrons in the SEM. A schematic of this setup is provided in the supplementary material.

The result of this process is shown in fig. 3 e. The left image shows the surface of the sample, recorded in secondary electron imaging mode in the SEM with an in lens detector. It shows that the surface is smooth and free of voids. The right hand image in fig. 3 e shows the same tip imaged in a dedicated 120 kV TEM. Two larger particles (20 - 30 nm) are marked in the image. The presence of smaller particles (< 10 nm), even though confirmed to be present by atom probe, is not obvious in the image, since the Pt(C) deposit is also comprised of small particles of similar size. Interestingly, the individual particles do not touch each other, but are separated by approx. 50 nm. This thought to be the result of the formation of the matrix during the EBAD process.

This process can be used on powder materials, is very fast (~ 10 -20 min per atom probe tip, from picking up the agglomerate to finished tip) and produces usable atom probe data (fig. 3 e)]. However, the need to produce a matrix with sufficient adherence in between the particles has posed a challenge that has not yet been fully resolved. There are two main challenges, both of which are related to the choice of matrix material. Firstly, the use of $(C_5H_4)CH_3Pt(CH_3)_3$ to produce the matrix leaves a lot of carbonaceous material within the matrix. This is to be expected, since reported values of C in electron or ion beam assisted deposition of Pt from this precursor range from 40 – 60 % [8]. The C in the matrix leads to both a deterioration in the spatial quality of the data and the

formation of a large number of decomposition products during field evaporation. These decomposition products significantly complicate the interpretation of the mass spectrum, and the peaks frequently overlap with those of the species of interest. Aside from the data quality aspect, also the amount of data collected per particle was relatively low. This is attributed to poor adhesion between the particles and matrix, which leads to sample fracture when the particles are ripped out by the electrostatic forces present during the experiment (fig. 3 f).

Due to the short time spent preparing a sample, the high reproducibility and the guaranteed high density of nanoparticles within the dataset, this approach remains very attractive if the problem of matrix material properties can be solved. This might be achieved by the use of different pre-cursors. Attractive candidates are metal carbonyls ($\text{Fe}(\text{CO})_5$ [27], $\text{Co}_2(\text{CO})_8$ [28], $\text{W}(\text{CO})_6$ [29]) which tend to have purities around 85% after deposition. They decompose in an autocatalytic reaction, which may increase deposition efficiency in regions that the electron beam is not able to fully penetrate. Another possibility is the use of tungsten fluoride (WF_6) [30] where purities of 98% are readily achieved. The attractiveness of the above precursors arises from the fact that they can potentially be used in current FIB-SEM setups.

Sample preparation by dispersion application / coating:

The method with which the highest quality data so far has been achieved is a coating – lift-out approach [18]. In this method, particles are distributed on a flat substrate and coated with a matrix material. The so-fashioned thin film can then be lifted out using standard APT lift-out techniques [23]. Like electrophoresis, this method is suitable for the analysis of particles in dispersion but it is not necessarily limited to that. We have successfully applied it to the analysis of the surface distribution of Ag on Au@Ag nanoparticles prepared by citrate reduction [31] with a size of 10-20 nm [18].

To achieve this, we have created a suitable particle distribution by applying a nanoparticle dispersion to a surface and so that particles, through Brownian motion, hit the surface remain attached to it [32]. After a certain amount of time, the excess dispersion is removed. This was done using a pipette. No other means such as compressed nitrogen were used, mainly due to safety concerns regarding the nanoparticle solution. This has the advantage over drying that no ‘coffee stain’ patterns form, leading to a generally much more uniform distribution of the particles on the substrate.

We have found that the most crucial factor to achieving a suitable particle distribution is the choice of substrate material and its structure. A very clean substrate surface is desirable since contaminants such as oxides and carbonaceous residues may impact data quality. Through trial and error, we found that Si, freshly cleaved along {1 1 1} planes, is a suitable substrate. The cleaved Si substrate is mounted onto an SEM stub and loaded with the Au@Ag nanoparticles (fig. 4 a), which were dispersed in ultra high purity water (MilliQ®). In order to achieve a suitable particle distribution on the surface,

we systematically carried out experiments on different cleaving facets and structure. The most suitable distribution was achieved by cleaving the wafer such that small cleaving steps, 30 – 50 μm in width (fig. 4 b) are exposed to the nanoparticle solution for approximately 1 min. Since Si rapidly produces a layer of oxide on the surface in air [33] this step is carried out immediately after cleaving the surface. Once the liquid is removed, the substrate is moved into the thin film deposition chamber where a high vacuum is present, thus preventing any further oxidation. The resulting distribution of nanoparticles is depicted in fig. 4 c. This approach may need to be adapted depending on the type of particle and the type of solvent and substrate to be used.

Fig 4: Fabrication of atom probe samples from a dispersion of Au@Ag nanoparticles. (a) The experimental setup for the nanoparticle incubation. (b) Part of the Si wafer with cleaving steps. (c) An image showing the nanoparticle distribution. (d) The surface of a wafer step after deposition of 200 nm of Cr and a strip of ~400 nm of Pt(C). (e) Lifting out a bar of material, which is sliced into individual atom probe samples. (f) An individual sample on a Mo grid post, ready for final milling.

Once a suitable distribution of particles is produced (fig. 4 c), the particles are incorporated into a solid matrix by coating. The function of this matrix is to facilitate even field evaporation thus increasing the quality of the reconstructed data. If possible, a material with similar field evaporation properties to the particles should be chosen. We used sputter deposition of Cr in a Dynavac Xenosput® sputter coater (evaporation field: approx. 30 V/nm [5, 34]) as the matrix for the Au@Ag (evaporation field of Au: 35 V/nm, [35]). Although shadowing during deposition may be expected to produce voids around the particles that would negatively impact the mechanical integrity of the samples, we saw no evidence of this in the resulting data for these specimens.

Once the particles are incorporated into a matrix, a lift-out procedure, similar to the ones described in refs. [23, 24] is used to produce the atom probe tips (also see the supplementary movie). Initially, a strip of material is deposited using electron beam

assisted CVD (EBAD, fig. 4 d). The purpose of this strip is purely to protect the specimen during milling, and it does not form part of the actual atom probe sample, so the type of material to be used does not play an important role.

The subsequent steps are identical to the steps of conventional lift-out, where a bar of substrate with the thin film on top is lifted out using a micro-manipulator inside the FIB-SEM system. The bar is then attached piece-wise to an electropolished Mo-grid (fig. 4 f) which provides adequate clearance from other atom probe tips during field evaporation in an atom probe with micro-electrode [36, 37] (single, electropolished wires could be used in conventional atom probes with remote counter electrodes). This produces a sample in which the layer of nano-particle/matrix is sandwiched between the substrate and the capping EBAD layer, oriented along the measurement axis. At this orientation, we find that the layer is much less susceptible to fracture during the atom probe experiment, as was also observed by Heck et al. [10]. Fig. 4 f shows such a sample before it is sharpened to a suitable radius for field evaporation. As a sharpening strategy we used 'pyramid milling', where a four (or more) sided pyramid is created by ion milling the sample side-on rather than annular milling on-axis. This strategy is highly beneficial in cases where material combinations are milled that possess greatly different sputter properties, such as Si and EBAD Pt. However, the top of the pyramid must still be transformed into a cone shape by a short annular pattern [23]. Great care has been taken not to introduce any damage from the Ga^+ focused ion beam, which could impact fine scale analysis through ion induced mixing. The ion energies were therefore kept below 10 keV after the lift out, following the technique in ref. [38].

The reconstructions obtained from the coating/lift-out samples exhibited significantly improved quality compared to the data obtained from both electrophoresis, where no matrix material was used and powder solidification, where lower purity matrix material was used. Specimen yield was also good, with the experiments yielding 10 datasets of 5-50 M atoms from 10 tips, 3 of which contained one or more nanoparticles. To obtain a quantitative estimate of the resolution, we used a model of the shell atoms, derived by iteratively fitting a surface to the shell [39]. We then calculated the distance distribution of the shell atoms with respect to that surface. In our data, the Ag atoms are present within a layer around the surface model that exhibits a Gaussian distribution of the atoms in the direction of the surface normals, with the full-width-half-maximum being 0.91 nm. This assumes that all of the Ag is present within one infinitely thin monolayer that is spread out because of the finite resolution of the data, and is therefore only an upper limit for the resolution achieved. This suggests that the best option to study loose, individual nanoparticles, is to incorporate the nanoparticles into a composite sample, where they are sufficiently supported during the field evaporation process, during which the sample is subjected to large forces [40, 41]. This leads to the least artefacts using current reconstruction protocols [42, 43].

The coating/lift-out method is the most experimentally challenging and time-consuming of those presented here. It is also the method that produced the highest quality data.

For its widespread use, it will be necessary to devise methods to easily produce the desired distribution of particles on the substrate surface, rather than the trial and error approach used so far. The distribution must have a sufficient density of nanoparticles that there is a good chance of capturing one or more within an atom probe experiment, but one that is low enough that the particles are not touching each other (producing voids in the subsequent matrix deposition step). Exposing the substrate to the dispersion for a set amount of time and subsequently removing the liquid with e.g. a pipette or by wicking the liquid away, shows potential for this.

Conclusions:

Here we have described three methods that can be used to obtain atom probe data from nanoparticles; electrophoretic deposition of particles on tip – shaped substrates, particle agglomeration and dispersion incubation. Electrophoresis and incubation use dispersions of nanoparticles as the sample, while particle agglomeration can be carried out on samples in powder form.

The three techniques are applicable to different types of particle samples and each one has specific advantages and drawbacks. Electrophoresis and particle agglomeration have a relatively high throughput, and the data quality was sufficient to show partitioning between a core and a shell in the case of core – shell nanoparticles [17]. The best quality data was acquired using an incubation / drying method combined with thin film deposition [18]. All of the techniques still have potential for improvement in both usability and data quality.

In order to produce high quality data, a number of additional challenges remain, mostly related to the ability to reproducibly produce samples with a high yield of particles, the choice of matrix material used and the residues from the solvent if a dispersion was used. If these challenges can be resolved, atom probe tomography promises to become a staple in nanoparticle research, enabling an entirely new approach to the rational design of particles.

Acknowledgements

The authors acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the University of Sydney. This work was performed in part at the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation under NSF award no. ECS-0335765. CNS is part of Harvard University.

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