# Preparation of Atom Probe Specimens Containing Individual Nanoparticles

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Atom probe tomography (APT) combines sub-nanometer resolution, three-dimensional chemical and isotopic imaging, and a combined ionization + detection efficiency as high as 80 %. In principle, other forms of mass spectrometry would require an analysis volume roughly an order of magnitude larger to achieve a comparable level of analytical precision. APT is thus an attractive option for analyzing nanoparticles, and several such experiments have been conducted and published to date [1-4]. However, few of these experiments have sought to analyze specific, isolated nanoparticles [5]. In this work, we present a straightforward method for creating atom probe specimens from individual nanoparticles of interest on a solid substrate, using a dual beam FIB-SEM instrument equipped with an in-situ nano-manipulator. The primary limitation of this technique is the size of the nanoparticle must be large enough to allow for manipulation, which is ultimately determined by the sharpness of the manipulator needle and the positioning precision of the nano-manipulator.

Dilute solutions of commercially available nanoparticles dispersed in ethanol were created, agitated using an ultrasonic probe, and then drop cast onto silicon substrates. The particles used in the study were primarily $Bi_2O_3$ and $TiO_2$, ranging in size from approximately 80 nm to 200 nm. The in-situ nano-manipulator was used to pick specific particles from the substrate and place them onto an APT specimen support post of a commercially available flat-top-post array coupon, without the use of any in-situ platinum deposition. A variety of pick-and-place techniques were explored, including pre-sharpening the flat top post with the ion beam, milling a small dimple into the top of the post for the particle to rest in, and using an electron beam-curable adhesive on top of the post. After placing the particles atop the posts, as shown in Figure 1(a), a sputter-coating system was used to deposit approximately 150 nm of cobalt onto the coupon. Cobalt was chosen for its favorable field evaporation behavior and lack of isobaric peak overlaps with the elements of interest. While the deposition is not conformal enough to fully encapsulate the particle sample, the film does provide a sufficient capping layer to allow final tip shaping in the FIB, shown in Figure 1(b), relying on redeposition to fill in any gaps underneath the particle. However, the film is still thin enough to permit the location of the buried particle to be readily identified. This is particularly important as the particle size is nearly the same as the diameter of the finished tip, and any off-center misalignment can result in some, or all, of the nanoparticle being accidentally milled away. EDS mapping throughout the FIB milling process can aid in ensuring the particle remains centered in the tip. An EDS map of a finished APT specimen is shown in Figure 1(c).

Multiple experiments were conducted in the atom probe to find suitable run conditions (e.g., laser pulse energy, detection rate, etc.). This is complicated by the fact that the capping material and the particle may exhibit different field evaporation behavior, a common problem in APT experiments. Figure 2(a) shows a portion of a mass spectrum from a specimen tip prepared from a 100 nm diameter $TiO_2$ particle, clearly indicating the presence of the $TiO^{1+}$ ion family peaks between 62 Da and 66 Da, and Figure 2(b) is a 3D reconstruction showing the relative locations of the Co capping layer (blue) and the $TiO_2$ particle (red).

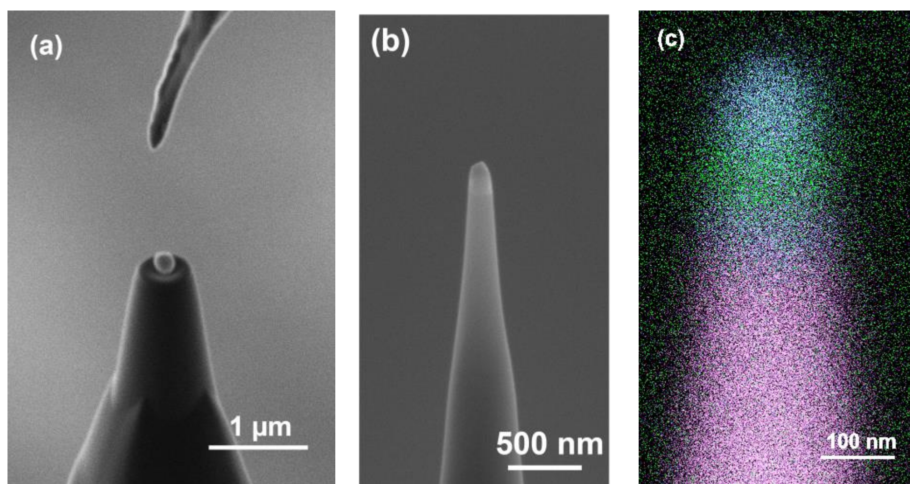


**Figure 1.** (a) $Bi_2O_3$ nanoparticle placed on top of pre-shaped and dimpled post. Manipulator needle is shown retracted from the post to illustrate desired sharpness and orientation. (b) Final shaped tip containing a single $TiO_2$ nanoparticle. (c) EDS map of a finished tip showing the location of Ti, contained in the $TiO_2$ nanoparticle (green) underneath the cobalt capping layer (blue), on top of the silicon post (pink).

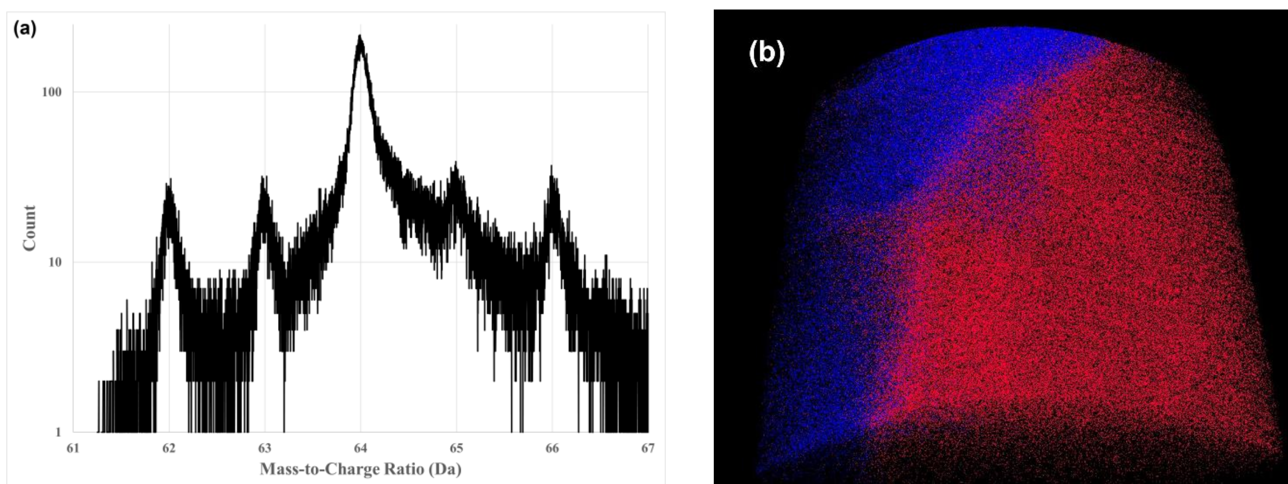


**Figure 2.** (a) Mass spectrum showing $TiO^{1+}$ family of peaks ranging from 62 Da to 66 Da. (b) 3D reconstruction showing interface between Co capping layer (blue) and $TiO_2$ nanoparticle (red).

References:

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