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Functionalized holders for 3D S/TEM imaging and analysis of nanoparticles

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The unique structure-property relationships of nanoparticles are driving the continuing the development of new microscopy techniques. Recent advances in STEM/TEM instrumentation are allowing for the three-dimensional characterization of materials [1]. However traditional sample preparation techniques are not ideally suited for characterizing particles with diameters of much less than a micron. Depending upon their size, charge and chemistry it can be difficult to evenly disperse and adhere nano particles on conventional TEM grids. Furthermore, if the grid or sample holder is in the beam path it can convolute both the imaging, EDS and EELS signals. A technique for functionalizing sample holders has been developed to facilitate the 360 degree STEM/TEM imaging and analysis of particles much less than a micron in size. This three-step technique is used to customize both the shape and the surface-chemistry of needle stubs, which are used in FIB-STEM/TEM compatible rotation holders [1]. In one example reported here, this technique was used for the 360 degree characterization of silica coated gold particles that are used for DNA labeling [2]. The instruments used in this example are a Hitachi FB-2100 FIB and a Hitachi HD-2300 dedicated 200kV FE-STEM.

In the first step, a FIB is used to customize the geometry of the brass needle stub. The needle stub holders offer a combination of three orientations (α = +90, 0 and -90), and 360°(β) of rotation, while the FIB stage offers an additional +-60° (α) of tilt. Using a combination of holder and stage positions it is possible to mill almost any desired shape from the 30μm end-radius of a stub. It is also possible to use the FIB microsampling technique [3] to attach a particular material to the end of the needle stub for use as a substrate. In the second step a coater or deposition system is used to coat the FIB shaped stub with a material suited to act as a substrate for the nanoparticles of interest. Ideally this coating can be selected to control the adhesion and dispersion of the nanoparticles. SiO_2 was chosen as a substrate for the SiO_2/Au particles. The third and final step for preparing the sample holders is to chemically treat the surface to enhance adhesion of the nanoparticles and a wide range of chemical treatments are available [4], [5]. In most cases this three step process can be accomplished in much less than one day.

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With the careful selection of geometry, surface material and terminal group chemistry, this technique yields a nearly optimal sample holder for 360 degree imaging and analysis of sub-micron particles. A sub-set of STEM HAADF images acquired during the 360 degree rotation of a single SiO_2/Au particle is shown in Figure 2. The SiO_2 shell of this particle ranges from 125 to 150nm in diameter, and it contains two 20nm Au particles. The functionalized needle stub makes it possible to image and analyze this nanoparticle over the entire 360 degree range with a minimum of shadowing and no substrate effects. In this particular example some tilt was used during the rotation to optimize the viewing angle and further minimize the shadowing, as seen in the changing angle between the Au cores. It is also worth noting that the presence of the ligands leads to a dramatic increase in the beam-induced contamination rate. This data set demonstrates that the three-step process for functionalizing holders can facilitate the 3D S/TEM imaging and analysis of sub-micron particles by addressing the geometric, materials and chemical requirements of this special class of materials.

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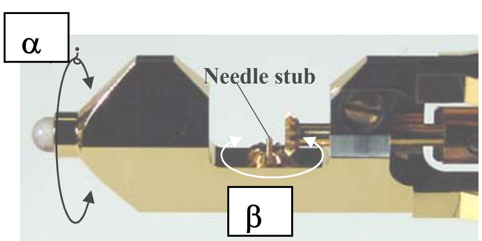

FIG.1 A FIB-STEM/TEM compatible specimen rotation holder, and needle stub (α = tilt, β = rotation).

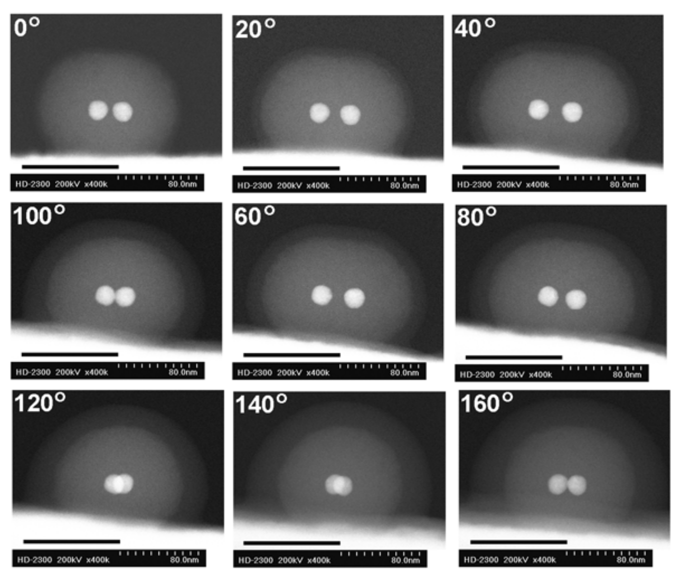

FIG.2 A sub-set of the HAADF STEM images taken while rotating a single 150nm SiO_2/Au nanoparticle 360 degrees. The rotation axis is centered on the particle and normal to the substrate in this view. (scale marker = 100nm).

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