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UO_2 Particle Standards: Synthesis, Purification & Planchet Preparation

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1.0 Summary

The IAEA has previously indicated its desire for reliable provision of suitable reference materials in support of environmental sample analysis and sustained advancement at the Department of Safeguards, as laid out in the Long Term R&D plan (LTRD 10.1 & 10.2). In a recent meeting between NPAC, the IAEA and PNNL, this pressing need was directly outlined by the IAEA as having two main objectives. The first pertains to current operations, such as instrument calibrations and evaluation of bias across the Network of Analytical Laboratories and requires particles on the order of 300-500 nm in diameter. The second need for particle reference material would directly support the IAEA's ongoing R&D efforts and calls for smaller particles ranging from 50 -100 nm in size. As such, the IAEA has expressed a great deal of interest in the newly established synthesis capabilities at PNNL, initially cultivated through a PNNL LDRD project to address the particle-standards shortcomings for uranium oxide material. The joint meeting concluded with a request by the IAEA for 1-2 planchet samples containing PNNL's UO_2 particulate material, to be delivered in the near-term. This report outlines the steps taken to meet that request and includes some basic characteristics of the samples sent to the IAEA.

The primary deliverable outlined in the approved statement of work was as follows:

Task: Planchet Preparation with UO_2 *Particles*

"Using batches of colloidal material previously prepared under the framework of a PNNL LDRD program, deposition and analysis of UO_2 *particles on vitreous carbon planchets will be conducted. A need for non-agglomerated, localized particles on a surface was stressed by the IAEA. With this in mind, drop-casting, spray deposition and spin coating will be evaluated using SEM analysis, in addition to single particle manipulation, all of which hold potential as viable methods of sample preparation. Prior to deposition, DLS and zeta-potential measurements will also be used to verify particle size distributions."*

2.0 UO_2 Particle Synthesis & Purification

A facile hydrothermal route to phase-controlled synthesis of micron-sized uranium oxide was selected for generation of particles in the range of 300-500 nm. The technique can be described as a batch reaction, which offers greater batch-to-batch repeatability and can be easily scaled for higher yields of material. This approach uses organic amines as both reducing agents and structure-directing ligands, further simplifying the synthesis procedure.

In a typical preparation of UO_2 particles, 0.5 mmol (0.22 g) $UO_2(OAc)_2 \cdot 2H_2O$ and deionized water (15 mL, 0.833 mol) were mixed to form a homogeneous solution under vigorous stirring. To this solution was added ethylenediamine (5 mL, 0.075 mol) at room temperature and under continuous stirring for 10 min. The resulting mixture was sealed in a 25 ml Teflon-lined, stainless-steel autoclave and heated at 160°C for 48 hours. The system was then allowed to cool to ambient temperature, and the final product was washed with ethanol and deionized water several times before being collected by centrifugation (4000 rpm). At a minimum, 5-7 washing steps are required to remove trace amounts of schoepite, a hydrated species of uranyl oxide. It's characteristically flat morphology its very distinct when compared to the spherical shape of the UO_2 particles. An example of this can be seen in the SEM images of Figure 1(a,b), where darker colored schoepite platelets can be seen co-deposited with UO_2 particles. Schoepite can also be removed more rapidly by first filtering the uranium samples and then rinsing the collected material with dilute acetic acid (1-2 M).

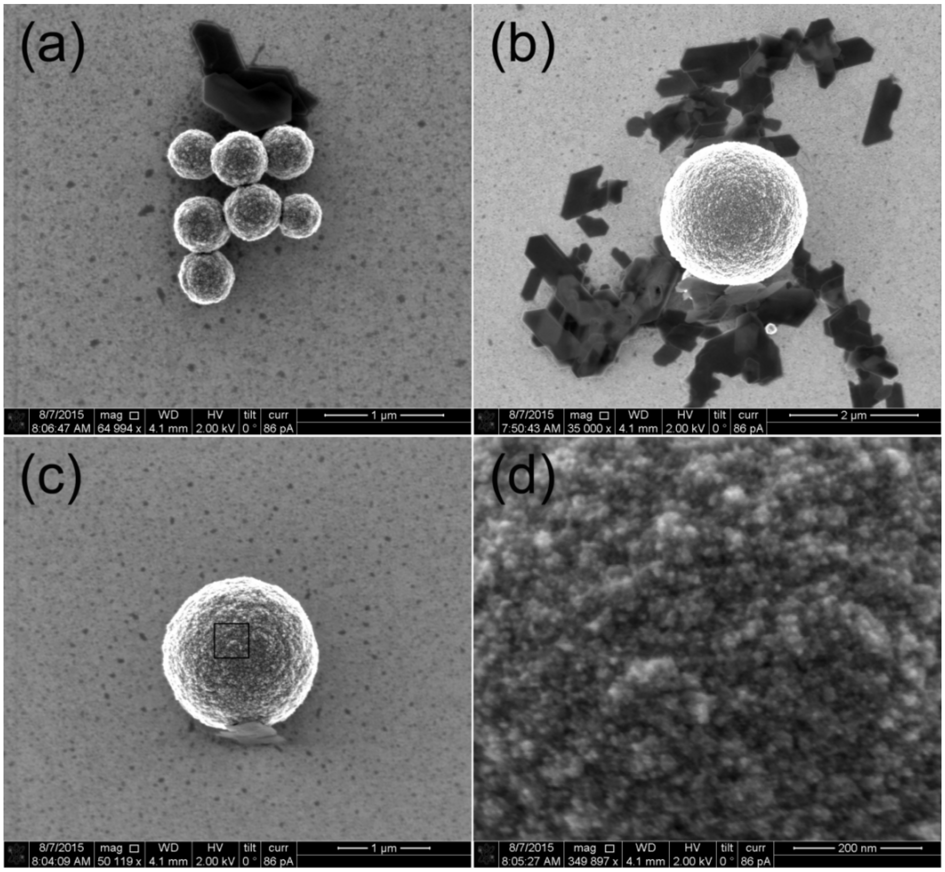

Figure 1. SEM images of UO_2 and schoepite crystals deposited across a gold-coated silicon substrate.

It was confirmed through XRD analysis that the samples of uranium particles exhibit a fluorite crystal structure, indicative of UO_2. However, the broadened peaks of a representative diffraction pattern shown in Figure 2, seem to point towards smaller, nano-sized crystallites, in contrast to the micron-sized particles evidenced by SEM. This observation lead to the conclusion that the mechanism for UO_2 particle formation and growth in a hydrothermal environment occurs as a result of orientated attachment. This process of crystal growth begins with the nucleation of nano-sized crystallites, which proceed to coalesce along energetically favorable facets, forming larger, polycrystalline structures. The grainy appearance of the final micron-sized particles formed in this way is clearly visible from high resolution SEM image of Figure 1(d), taken from the surface of a particle shown in Figure 1(c).

Batches of UO_2 particles prepared with this method were found to have an initial broad size distribution range that scaled from 200 nm to 3 µm. Stoichiometric optimization of the reaction conditions and the use of more strongly coordinated capping ligands would likely reduce the overall size variation in as-synthesized material. However, given the task constrains, it was decided to use size selective precipitation to narrow the particle diameter to 300-500 nm with previously synthesized particles. To do this, samples of washed UO_2 particles were treated with an additional acetic acid (3-4 M) rinse, enhancing the hydrophilic nature of the particles surface chemistry. The more stable colloidal dispersions were then subjected to 30 minute centrifuge cycles with sequentially increasing speeds of 1000 rpm. The supernatant was decanted after each cycle and the precipitate collected and redispersed in fresh deionized water. By using centripetal force, particles of different sizes were fractionated based on their total mass. It should be noted that for best results with selective precipitation, dilute colloid dispersions are preferable to avoid premature precipitation due to agglomeration.

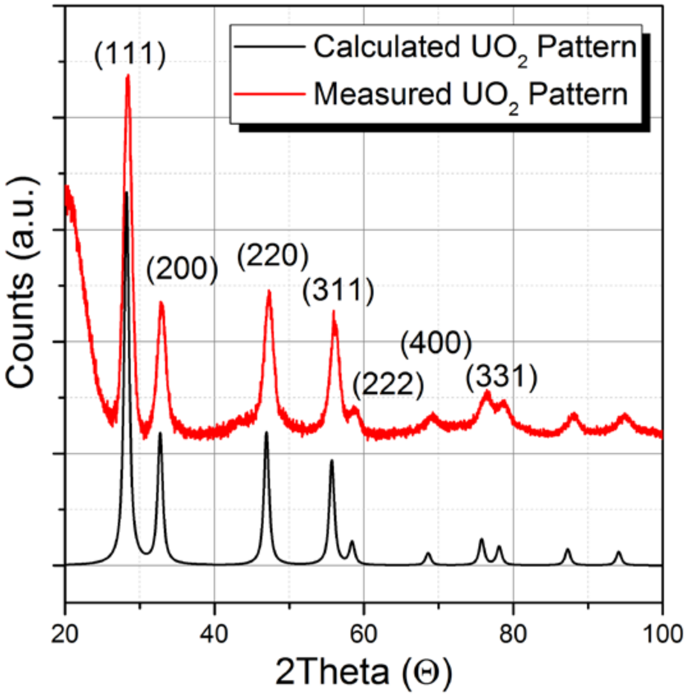

Figure 2. X-ray diffraction pattern collected from a sample of UO_2 particles.

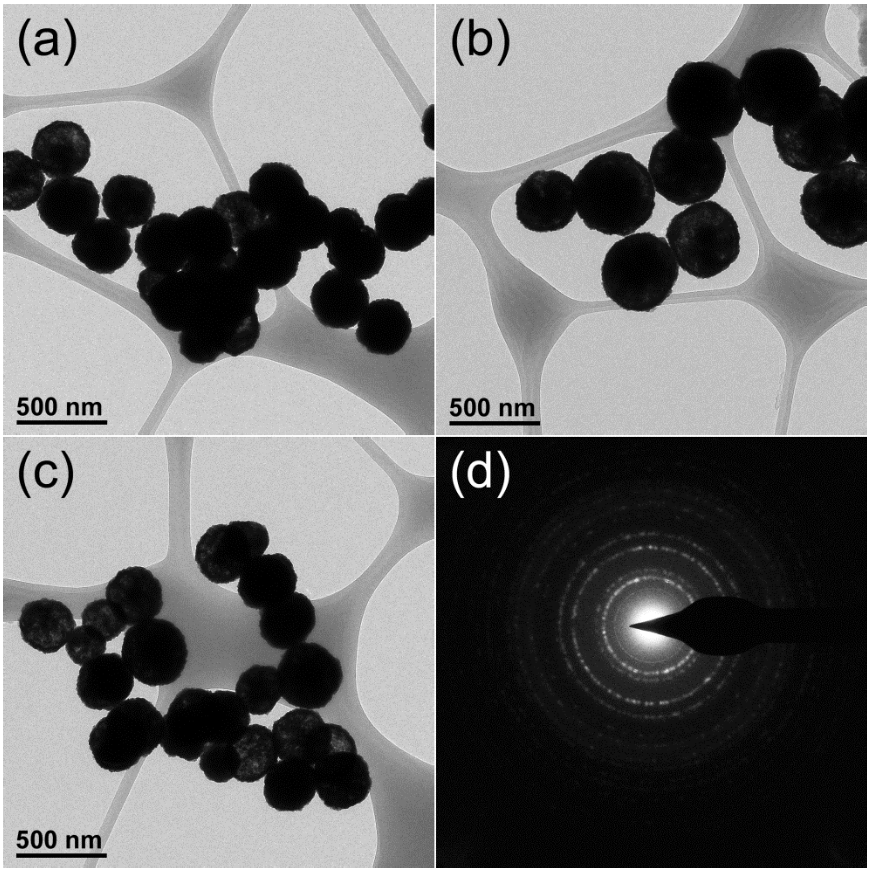

Figure 3. TEM and SAED of UO_2 particles following purification and selective precipitation treatments.

Figure 3(a-c) shows several micrographs captured from UO_2 particles that were synthesized, cleaned and collected at 8000 rpm. The particles were then drop-cast to lacey carbon-coated copper TEM grids with an ultra-thin (3 nm) carbon film for size evaluation. As is illustrated, the mean particle diameter measured for this sample fell within a range of 300-500 nm. A representative selected area electron diffraction (SAED) pattern from one of these particles (Figure 3(d)) was indexed to the cubic fluorite crystal structure of UO_2. The polycrystalline nature of the pattern would seem to confirm earlier conclusions of individual nanocrystalline domains within the larger, micron-sized particles. TEM analysis was used to evaluate colloid samples after each purification step and aided in the final size screening of each mass fraction. Following particle treatment steps, it was confirmed with a high level of confidence that almost all traces of schoepite or other amorphous material had been separated from the colloid dispersion to be used in planchet preparation. Dynamic light scattering measurements (DLS), shown in Figure 4, were also used to gauge the average particle size in solution. Based on DLS analysis, the mean diameter for the final sample of UO_2 particles was calculated at 338.17, ±63 nm. Bulk analysis like DLS, as opposed to discrete analysis by SEM or TEM, can be a better indicator of true particle size distribution but its broader range of values are often caused by inherent particle agglomeration, necessitating stable colloid dispersions.

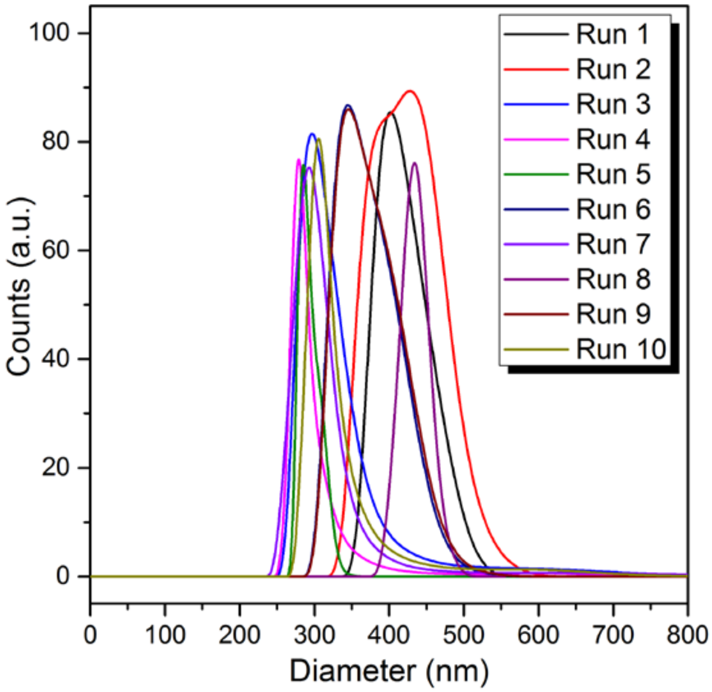

Figure 4. DLS measurements taken from a solution of UO_2 particles following selective precipitation.

3.0 Planchet Preparation

When approaching the deposition of UO_2 particles on vitreous carbon planchets it was decided to use particle separation as a key stipulation to quickly down select potential techniques. Apart from drop-casting, spin-coating and spray deposition were also considered. As-received planchets were first cleaned with the use of a solvent series and bath sonication. The general procedure that was followed required sonicating planchets in different solutions with the following order: acetone, methanol, IPA, water, IPA and then drying the planchets with pressurized nitrogen. Planchets were then inspected with an optical microscope and if necessary, the cleaning process was repeated until all visible dust particulate and grease had been removed. Initial attempts of spin-coating colloid samples presented a number of disadvantages. On average, the majority of sample being applied to the planchets is quickly spun off, and while this in itself can be a limiting factor for trace quantities of material, it also results in the contamination of the spin-coater, which in turn presents the possibility for cross-contamination of different samples. When spin-coated planchets were analyzed by SEM almost no particles appeared to have deposited on the sample, with the few particles being found mostly located at the edges of the substrate. Faced with the growing list of challenges with this approach, spin-coating was quickly dropped as a viable option for planchet preparation.

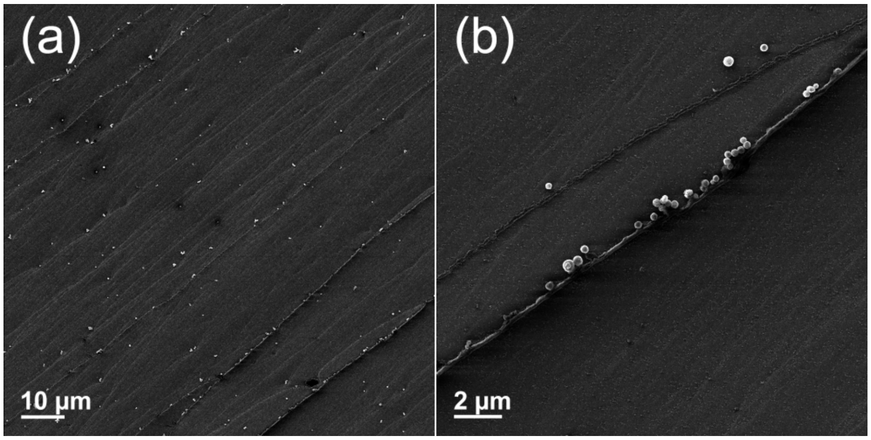

Figure 5. He-ion micrographs showing UO_2 particles drop-cast from an aqueous solution.

Drop-casting is the most basic form of sample preparation spanning SEM, TEM and SIMS. However, this relatively facile approach is prone to particle agglomeration and what is referred to as the "coffee-stain effect". As the term implies, rings of material are deposited across the surface of a substrate as the solvent evaporates and retreats to sequentially smaller areas. An example of this can be seen in the He-ion images of Figure 5, where UO_2 particles are clearly deposited in rows, left by the retreating aqueous solution. A possible way of mitigating this effect is to use a solvent that readily wets the underlying substrate, while also slowing the rate of evaporation. In this way, a much more even evaporation occurs, propagating down to a thin film of solvent, spread out across the entire substrate surface, which ultimately maximizes the area for particle deposition.

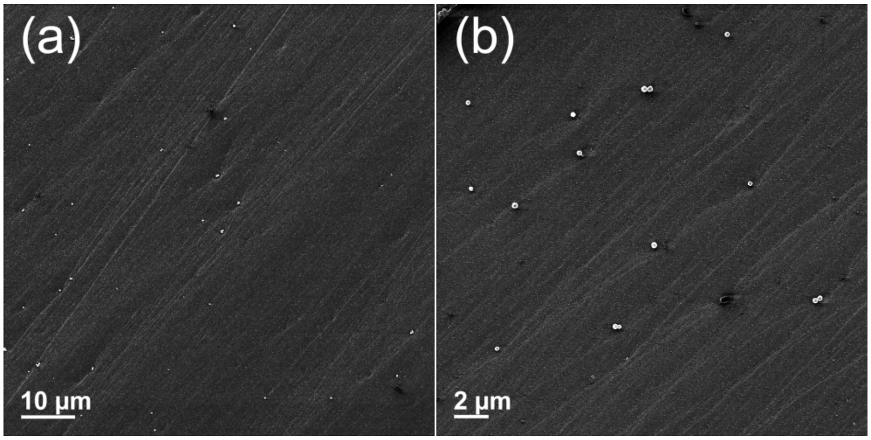

Figure 6. He-ion images of UO_2 particles drop-cast from an IPA solution with controlled evaporation.

To achieve this effect, UO_2 particles were precipitated from aqueous solutions and redispersed in isopropyl alcohol (IPA) with bath sonication. Approximately 100 µl of colloid dispersion was then applied to the surface of a glassy carbon planchet. Wetted planchets were placed in portable desiccator vessels and stored in a refrigerated environment (~5°C) over night. Samples prepared in this manner did not exhibit the characteristic coffee-stains of deposited material. The He-ion images of Figure 6 give a good representation of the type of particle separation observed when using slow rates of evaporation coupled with IPA solvent. Although some areas were found to have two or more particles co-localized, it was decided that this approach still offered an appropriate concentrations and separation of particulate for SEM or SIMS assay.

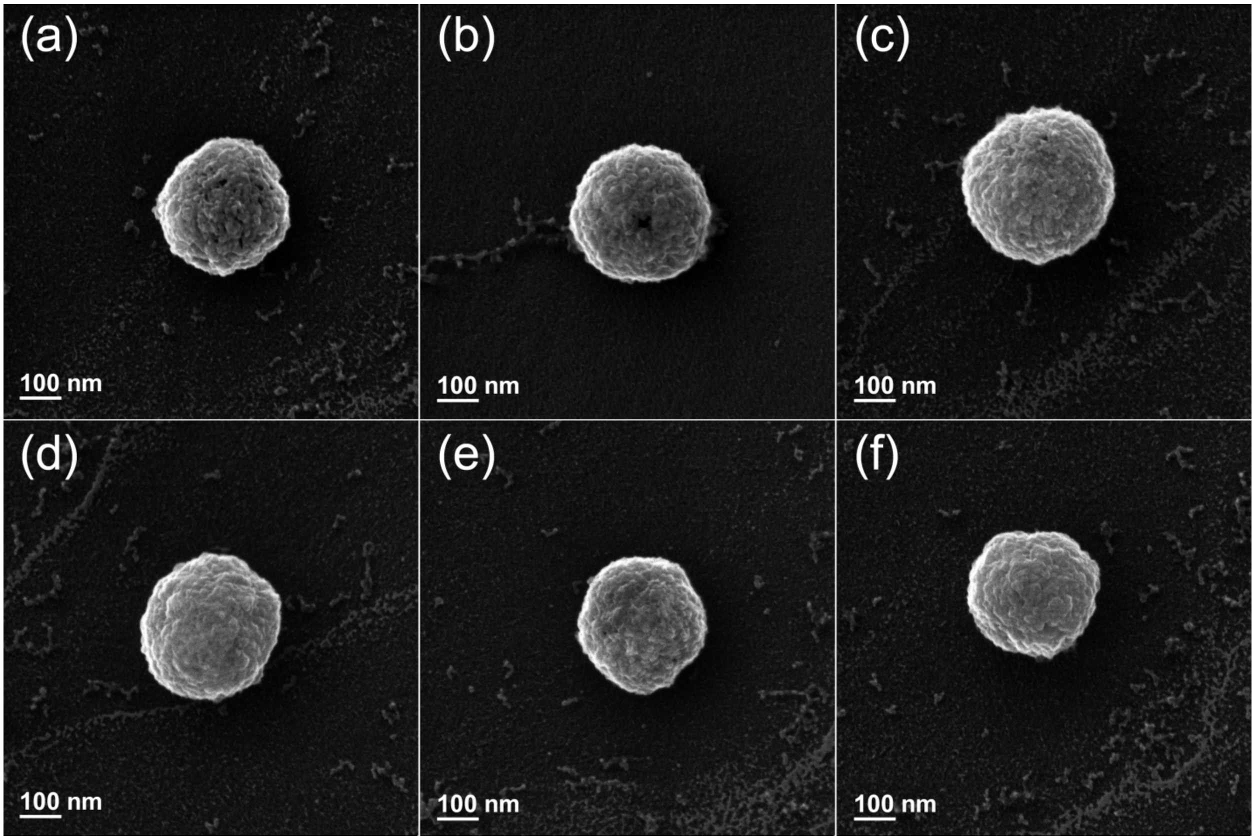

Figure 7. He-ion images of UO_2 particles drop-cast from an IPA solution with controlled evaporation.

The high magnification He-ion images of Figure 7 were collected as part of the final evaluation for samples 3 and 4 before being sent to the IAEA. Helium ion microscopy was found to be uniquely suited to imaging UO_2 particles on carbon planchets. The primary reason for this is the sub-pico amps of operating current at which the instrument can image, which is more than an order of magnitude lower than conventional SEM. As the helium ion beam interacts with the sample, it does not suffer from a large excitation volume, and hence provides sharp images with a large depth of field. In this respect, helium ion microscopy proved most useful at identifying even trace amounts of organic residue, which would otherwise have gone unnoticed by SEM. An example of this can be seen by comparing images of UO_2 particles captured by SEM in Figure 8. The same resolution of detail on the particles is not achieved, while the surrounding surface of the vitreous carbon substrate appears almost spotless even at reduced working voltages of just 2 kV.

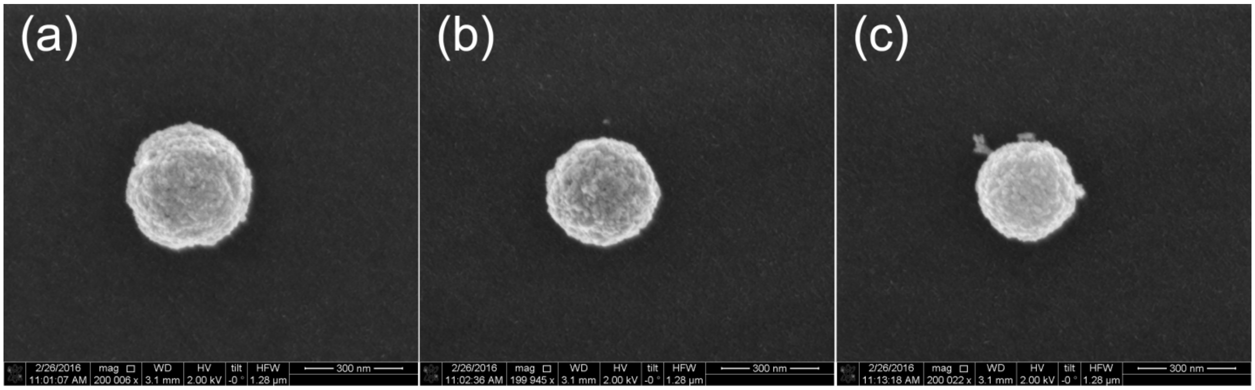

Figure 8. SEM images of UO_2 particles drop-cast from an IPA solution with controlled evaporation.

Particle deposition was also investigated using spray-coating techniques. This was facilitated with the use of a small stencil airbrush connected to filtered nitrogen gas. The technique is best preformed with volatile solvents, which are required to vaporize prior to impacting the target substrate. After a certain amount of trial and error, IPA was again settled upon as the preferred colloid solvent. As this approach essentially removes any solvent induced effects on the process of particle deposition, agglomeration issues were not observed by He-ion analysis. Figure 9 illustrates the type of particle separation seen with the use of spray-coating. In most cases, particles were separated over tens to hundreds of microns, a benefit more applicable to SIMS than SEM/EDX requirements. Total concentration of particles was much lower in these samples but could be increased with successive applications of sprayed material.

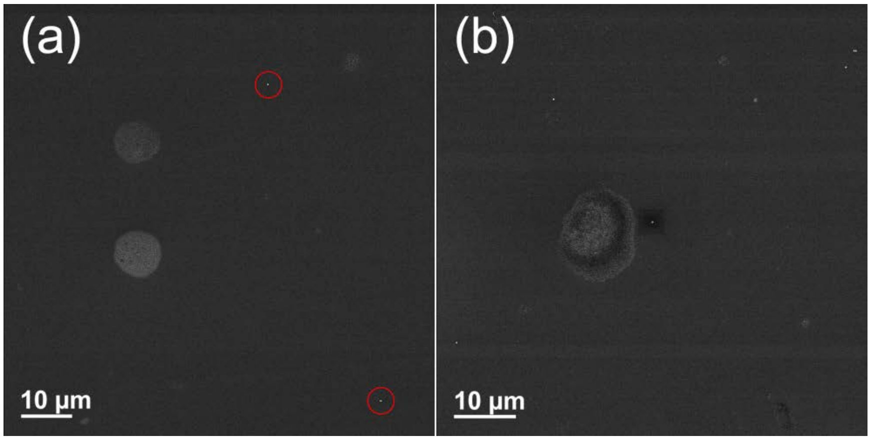

Figure 9. He-ion images of spray-coated UO_2 particles (highlighted by red circles) on vitreous carbon.

The high magnification He-ion images of Figure 10 were collected as part of the final evaluation for samples 1 and 2 before being sent to the IAEA. When directly comparing these images to those shown in Figure 7, a much cleaner surrounding surface is apparent with spray-coated samples. A similarly textured substrate surface was also observed and would seem to be consistent with polished glassy carbon material. It should be noted that spray-coated samples appeared to blacken over time under the He-ion beam, possibly due to a thin film of organic material depositing as carbon. As such, spray-coated planchets were treated with 5 minutes of an argon plasma clean to remove light hydrocarbon material.

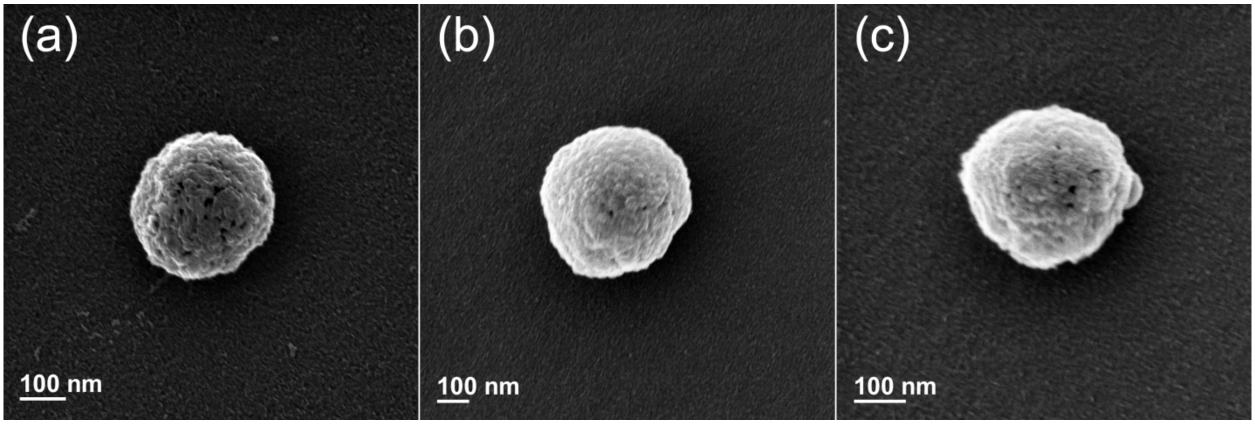

Figure 10. High magnification He-ion images of spray-coated UO_2 particles on glassy carbon planchets.

4.0 Summary

A total of four vitreous carbon planchets, coated with UO_2 particulate, were prepared and sent to the IAEA. The particles were synthesized by hydrothermal decomposition of a uranyl precursor and then purified with a number of different solution washes. UO_2 particle morphology and structure were studied with a combination of techniques including, TEM, SAED, SEM, HeIM, XRD and DLS. On average, the particles were found to have a spherical morphology, comprised of polycrystalline UO_2 material. Size selective precipitation was used to reduce the particle diameter of colloid material to within a range of 300-500 nm. Modify variations of drop-casting and spray-coating were evaluated and refined for the deposition of UO_2 material to carbon planchets. Both approaches showed different strengths and so two samples prepared by drop-casting and two by spray-coating were sent for assessment.