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| | **Experiment title:**<br>Structural characterization of plutonium oxide nanomaterials | **Experiment number**: |
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**Report:**

We performed structural characterization of the $PuO_2$ nanoparticles, prepared by various synthetic methods. Prior the studies, we synthesized several types of $PuO_2$ NPs, using environmentally and waste storage relevant conditions, *i.e.* varying the pH (*e.g.* pH 8 and pH 12) and the precursor (Pu(III), Pu(IV), Pu(V)) – six samples in total, which were investigated by the High energy X-ray scattering (HEXS) data at ID15A beamline.

Data were collected at room temperature. An incident energy of 120 keV was selected in order to be below the Pu K-edge at 121.79 keV and to minimize absorption. The K-edge XANES spectrum was measured to verify the incident energy. Data was collected up to 30 $Å^{-1}$ using a Dectris CdTe 2M pixel detector. Patterns were corrected for detector geometry, response and transparency, and integrated using a locally modified version of pyFAI[1] with outlier filtering. F(q) and G(r) were calculated from the resulting powder diffraction patterns using modules from DIFFPY-CMI[2] and locally developed cleaning algorithms. The full profile real-space refinement of crystal structures based on the pair distribution functions (PDFs) was made using PDFgui software.[3] PDFgui performs a least-squares refinement of the structural model to the G(r). The parameters refined for the NPs series were lattice parameter *a*, particle diameter for PDF shape damping function (spdiameter)

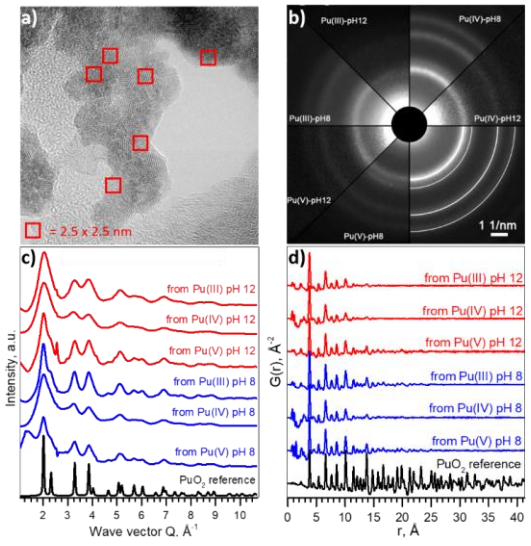


Fig.1 **. Size and structure information of $PuO_2$ NPs. a)** HRTEM images of Pu(V) pH 8 NPs, **b)** SAED patterns of particles, white lines indicate peak positions for $PuO_2$ standard, **c)** Intensity profiles of the 2D diffraction of Pu samples **d)** the corresponding reduced pair distribution functions (PDFs) G(r) obtained by Fourier transformation (FT) of the data with $Q_{max}$ = 26.0 $Å^{-1}$

and the data scale factor (delta2). Parameters such as the PDF Gaussian dampening envelope due to limited Q-resolution and isotropic atomic displacement parameters (ADPs) were obtained from the fit of the experimental data of the $PuO_2$ reference and fixed at these values for the refinements of the NP experimental sets, in order to minimize the number of refinable parameters and to obtain the most robust values for the coherent domain size. Water model was used in order to reproduce the contribution of water at the short-range order. All samples were fitted in the range from 1.7 to 20 Å and the maximum wave vector Q of the data used for the generation of PDF was settled to 26 $Å^{-1}$. The $R_w$ value is goodness of fit measure to show the agreement between calculated and experimental data.

It turns out that HEXS is very powerful experimental method for the investigating nano-sealed materials, as it can provide a fingerprint of the nanoparticle size and discriminate between short range order (represented by finite non-random displacements from the ideal crystal structure) and random thermal displacements. The intensity profiles of the 2D diffraction for six investigated samples of $PuO_2$ NPs and a $PuO_2$ reference are shown in Fig. 1c. For the comparison we show here the HRTEM data (Fig. 1a) which confirms that similar NPs are formed (with respect to the size distribution and crystallinity), regardless of different precursors and pH conditions. A comparison of selected area electron diffraction (SAED, Fig. 1b) patterns with bulk $PuO_2$ is shown. In Fig.1b the diffraction patterns from $PuO_2$ NPs are similar, with the NPs having the same long-range structure as the $PuO_2$ reference, even though local structural deviations from the bulk should normally be observed in the nanosize materials with HEXS. The peaks are broader in the case of NPs, illustrating the effect of the nanosized coherent domains. The peak appearing at Q ~ 2.40 $Å^{-1}$ comes from the background (*i.e.* kapton capillary) and for most samples can be successfully substracted using the measurement of the empty capillary. The corresponding reduced pair distribution function (PDFs) (G(r)) are shown in Fig. 1d. Peaks from short-range correlations in $PuO_2$ NPs have the same sharpness as peaks of the $PuO_2$ reference, indicating that the short-range order is identical. The intensity of the oscillations drastically decreases with increasing r, nearly disappearing after r = 20-25 Å; an indication of the coherence length of the $PuO_2$ particles. The damping of the G(r) can be refined in order to extract the average particle size, confirming the direct observation that the NP diameters are in the range of 1.3 - 2.6 nm, in a good agreement with HRTEM and XRD estimations. The results of the full profile structural refinements are shown in Fig. 2 for all $PuO_2$ NP samples and for the $PuO_2$ reference, where bulk $PuO_2$ (space group $Fm\bar{3}m$) was used as the structure model. Those results are part of the paper, recently submitted for publication[4].

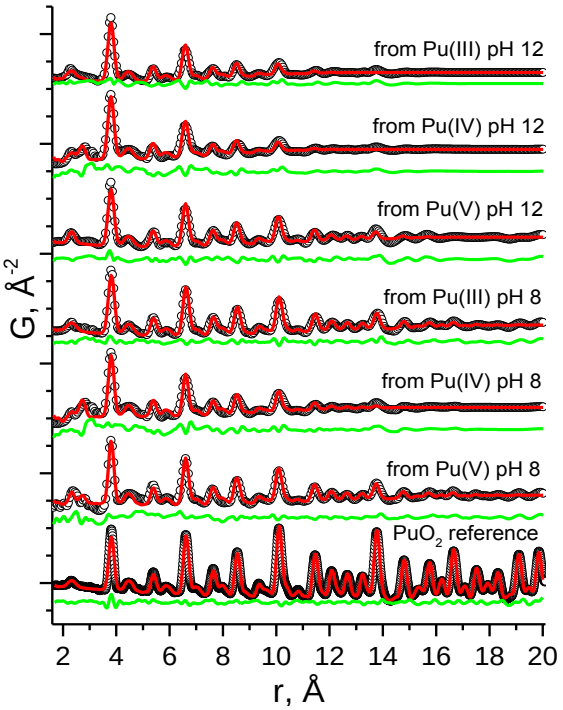


Fig.2. **The results of the pair distribution functions (PDFs) fits from all samples and $PuO_2$ reference.** The experimental reduced (PDFs) G(r) obtained by Fourier transformation (FT) of the data with $Q_{max}$ = 26.0 $Å^{-1}$ (black dots), calculated PDFs from the refined structural model (red line) and the difference curve (green line).

References:


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