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| | **Experiment title:** Local structure of $PuO_{2\pm x}$ nanoparticles together with its analogues $CeO_{2-x}$ and $ThO_2$ | **Experiment number**: |
| **Beamline**: **BM20** | **Date of experiment**: from: 03.05.2017 to: 09.05.2017 from: 23.01.2018 to: 03.02.2018 | **Date of report**: 01.03.2018 |
| **Shifts:** 18 + 30 | **Local contact(s)**: Kristina Kvashnina, BM20, ESRF | *Received at ESRF:* |


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## Report:

Plutonium, cerium and thorium oxide nanoparticles (NPs) in different size were prepared by rapid chemical precipitation and were the objects of these studies. At the first stage of the experiment (03.05.2017-09.05.2017) only cerium and thorium NPs were studied. Second stage of the experiment (23.01.2018-03.02.2018) was fully devoted to plutonium NPs.

1) $CeO_2$

NPs of $CeO_2$ with tree different sizes (2, 5 and 8 nm) were studied by Ce $L_3$-edge high energy resolution fluorescence detected (HERFD) XANES. Pre-edge structure (formed by the 2p-4f quadrupole transitions) for the three types of nanoparticles (2-8 nm) reveals the presence of the Ce(IV) oxidation state and confirms the absence of Ce(III) inside $CeO_2$ NPs even for the NPs with a very small size of 2 nm (fig. 1a). However, the main edge Ce L3 edge transitions (due to the 2p-5d electronic excitations) show different shapes (fig.1b). We found that peaks in the absorption spectra of 2nm size $CeO_2$ are essentially developing and became wider for compare to 5nm, 8nm and bulk $CeO_2$, which might lead to the electron delocalization over the surface of nanoparticles, and hence decreasing the probability of the discrete electron transfer from 2p to the 5d orbital.

To study the effect of thermal treatment on NPs electronic structure, ceria NPs with 2, 5 or 8 nm sizes were dried for 24 hours at 40 °C or 150 °C in air. We found a strong evidence of different spectral shape while investigating the electronic structure of as-prepared and dried $CeO_2$ nanoparticles at the Ce L3 edge HERFD spectra (fig.1b). The biggest effect has been observed for the smallest NPs (2nm).

2) $ThO_2$

The ThO2 NPs with different sizes (from 2 to 30 nm) were studied by Th L3-edge HERFD XANES and EXAFS. Similar to ceria NPs, the influence of size and post synthetic thermal treatment of the sample on the electronic structure was observed. Decrease of the $ThO_2$ NPs size leads to changes of HERFD spectra (fig.2). The same tendency was observed in EXAFS spectra (fig.2c)

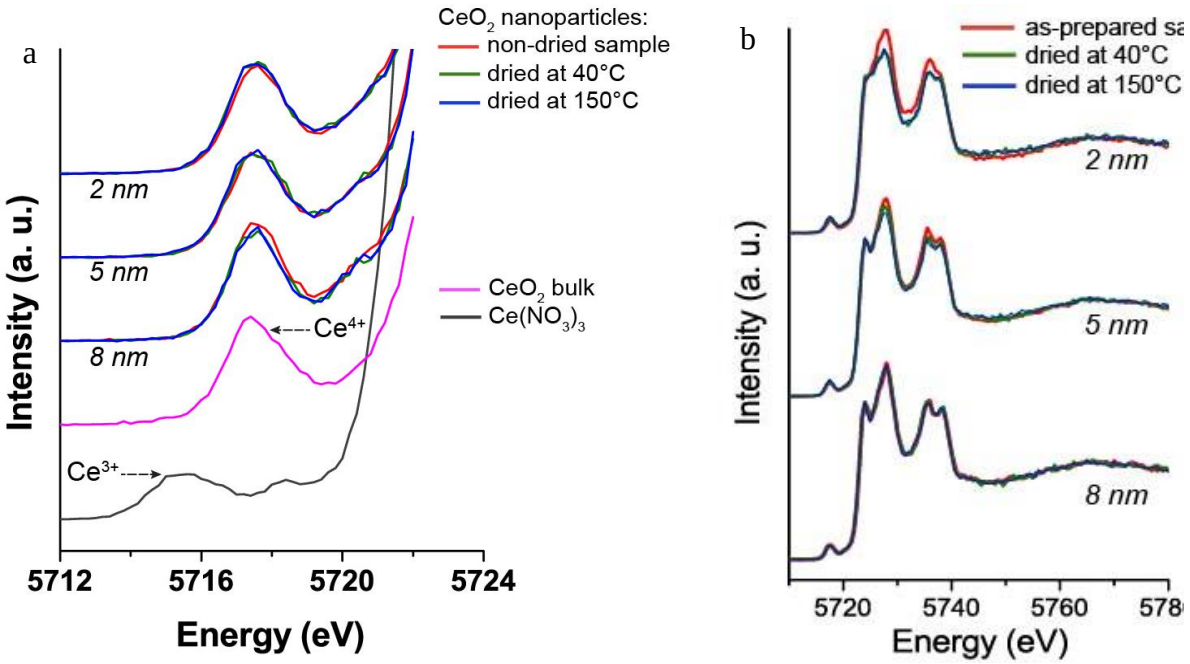


Figure 1. (a) Pre-edge HERFD spectra of $CeO_2$ NPs and bulk material and cerium(III) nitrate; (b) HERFD spectra recorded for 2nm; 5nm; 8nm of $CeO_2$ NPs after different thermal treatment.

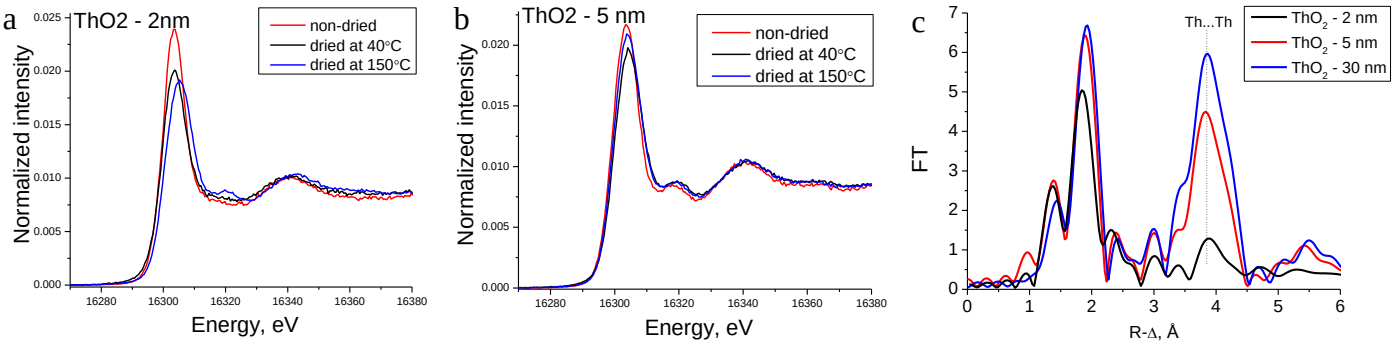


Figure 2. HERFD spectra of (a) 2nm and (b) 5nm $ThO_2$ NPs after different thermal treatment; (c) EXAFS spectra of $ThO_2$ NPs with different particles size.

3) $PuO_2$

Redox chemistry of plutonium is more complicated for compare to cerium and thorium. Plutonium can exist in four oxidation states (Pu(III), Pu(IV), Pu(V) and Pu(VI)) upon environmental conditions and can easily change it. At the same time presence of Pu in different oxidation states in $PuO_2$ NPs structure is still an open question. In this work we studied $PuO_2$ NPs synthesized from different oxidation state of Pu: Pu(III), Pu(IV), Pu(V) and Pu(VI). We used several synchrotron radiation techniques available at ROBL to study $PuO_2$ NPs: Pu $L_3$ edge HERFD,XANES, EXAFS and XRD. HERFD spectra showed the presence of Pu(IV) oxidation state in all NPs , produced from Pu(III), Pu(IV) and Pu(V) (fig.3a). EXAFS spectra at the Pu L3 edge show that size of the particles and their structures are very similar.

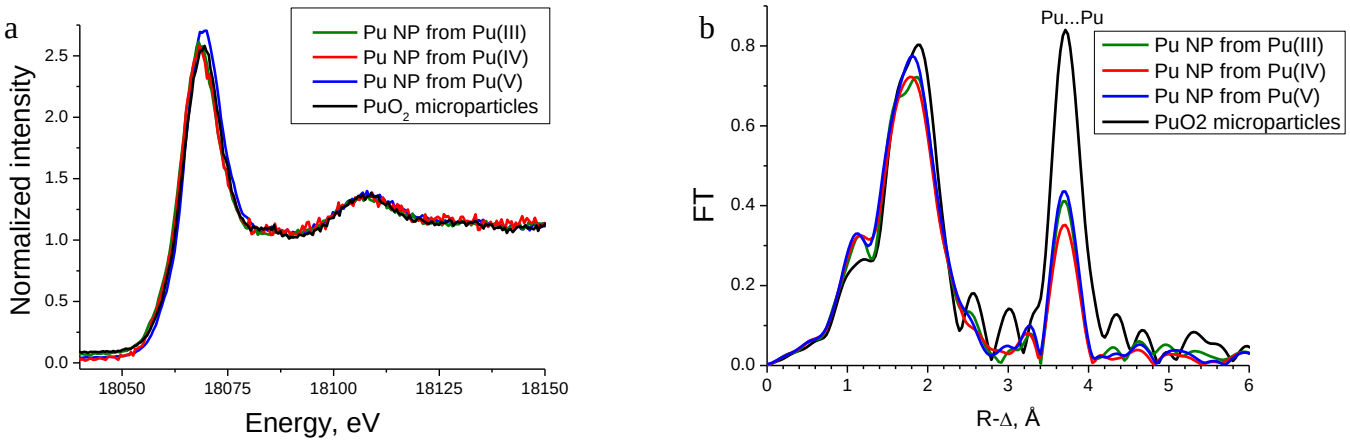


Figure 3. (a) HERFD and (b) EXAFS spectra of Pu NPs synthesized from different Pu oxidation states.