DEVELOPMENT OF NEW ACTINIDE-BASED HYBRID MATERIALS

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In the nuclear industry, materials and more particularly those based on actinides are omnipresent. To increase our knowledge of this type of materials, it seems essential to develop new simple and effective synthetic strategies for the production of model materials or precursors of model materials. In this context, actinide-based hybrid materials appear to be good candidates presenting modular physico-chemical properties. This project deals with the conception of new structured actinide-based hybrid materials, which can display unusual properties with respect to the bulk inorganic counterpart. In this way, we are focused our attention on the development of new bottom-up synthesis strategies.

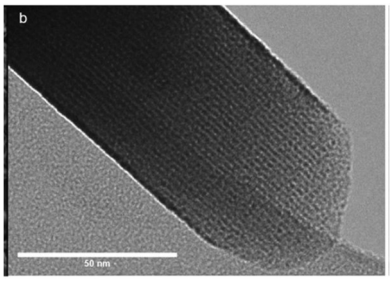


Figure 1. TEM image of actinide-based nano-sheet

Table 1 d_{U-U} calculations and interlamellar distances measured by TEM and SAXS of nanohybrids formed with different linkers

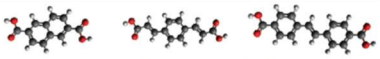
	Naphthalene-2,6-dicarboxylic acid	1,4-Phenylene diacrylic acid	4,4′-Stilbene dicarboxylic acid
Molecules			
d_{U-U} (nm)	1.37	1.62	1.81
TEM (nm)	1.65	1.83	1.90
SAXS (nm)	1.60	1.88	1.94

Table 1. Table of inter nano-lamellae distances

First, we developed a one-pot approach in order to control the nano-structure of the material.[1] Using a ternary molecular system (dicarboxylic acid, oleylamine, dibenzyl ether), it is possible to obtained nano-sheets displaying an intern nanometric structuration in which UOx nano-lamellae (around 1 nm) are separated by organic linkers (Figure 1). In the nano-sheets, the inter-UOx nano-lamellae distance could be adjusted in accordance with the length of the employed dicarboxylic acid linker (Table 1). Moreover, the stacking distance between two nano-sheets could be modulated by adjustment of the synthesis temperature. Using this synthesis methodology, it is possible to modulate the structure of materials at the nanometric scale by adjusting some parameters intrinsic to the reaction. This approach is currently developed in the team for the synthesis of new NMC (Ni/Mn/Co) hybrid materials for Li-ion batteries.[2]

A second strategy, based on the self-assembly of functionalized nanoparticles, is developed. [3] This strategy starts with the well-known synthesis of metal-oxide nanocrystals (UO_2, ThO_2 or MO_x) stabilized with oleic acid.[4] This method permits to obtain well-defined monodisperse nanoparticles with an average size of 4.5 nm for UO_2 and 3.5 nm for ThO_2 (Figure 2 top). Then, the surface of the pre-synthesized nanoparticles is modified using capping agents having reactive pendant functionality (alkyne, azide, ionic moiety) without modification of the morphology of the nanoparticles. To obtain the final materials, the crosslinking of modified nanocrystals could be operated through a click-chemistry step catalyzed by Cu(I) or electrostatic interactions (Figure 2 bottom). The final goal consists in the formation and the characterization of heterometallic nano-hybrid superlattices.

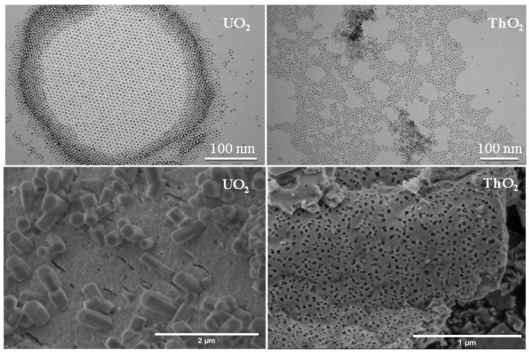


Figure 2. Top: TEM images of UO_2 (left) and ThO_2 (right) nanocrystals / Bottom: SEM images of functionalized nanoparticles self-assemblies (UO_2 (left) and ThO_2 (right))

The third strategy is developed with the goal to produce actinide-based hybrid materials using complex organic phases from liquid-liquid extraction processes. Currently, in the spent fuel cycle, the liquid-liquid extraction step is followed by stripping one. To avoid this latter, it could be interesting to induce direct controlled precipitation in the complex organic phase (metal ions + extractant + dodecane), using simple ditopic organic linkers (as oxalic acid or 2,5-dihydroxi-1,4-benzoquinone) to promote the formation of coordination polymers or MOF potentially having adjustable properties (structure, morphology, texture, robustness). These materials could be envisaged as new precursors for the preparation of actinide-based oxide materials used in the nuclear fuel cycle.

[1] Elisa Re, Xavier Le Goff, Guillaume Toquer, Jerome Maynadie and Daniel Meyer, "**Linker-assisted structuration of tunable uranium-based hybrid lamellar nanomaterials**"; *New J. Chem.*, **2020**, 44, 8463.

[2] Thèse T. Riant.

[3] Thèse E. Ré.

[4] Damien Hudry, Christos Apostolidis, Olaf Walter, Thomas Gouder, Eglantine Courtois, Christian Kübel and Daniel Meyer, "**Non-aqueous synthesis of isotropic and anisotropic actinide oxide nanocrystals**"; *Chem. Eur. J.*, **2012**, 18, 8245.