ESRF	**Anomalous SAXS study of bimetallic Ru-Ta nanoparticles**	**Experiment number**: MA-2231
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Report:

To characterize the core-shell structure of Ru/Ta nanoparticles (NPs) embedded in $[C_1C_6Im][NTf2]$ ionic liquid (IL), anomalous SAXS measurements were performed below the Ru-K edge (22.117 keV) and the Ta-L_{III} edge (9.881 keV) on the CRG-BM02 beamline. The Ru and Ta NPs were prepared from the decomposition of two organometallic precursors Ta $=CHCMe_3$ and Ru(COD)(COT) in $[C_1C_6Im][NTf_2]$ IL under H_2. Bimetallic NPs were prepared by successive decomposition of the precursors: (i) decomposition of the Ru (resp Ta) precursor, (ii) addition of a solution of the Ta (resp Ru) precursor, (iii) decomposition under H_2. In both cases, Ru content was 20% of total metal content. Therefore, these bimetallic NPs are labelled Ru2Ta8 (decomposition of Ru on TaNPs) and Ta8Ru2 (decomposition of Ta on RuNPs). The NPs embedded in IL were contained in quartz capillaries of 10 cm length with wall thickness of 10 µm. Their diameters were equal to 1 and 1.5 mm for the measurements performed respectively at the Ta and Ru edges. The capillaries sealed under argon were mounted perpendicularly on a multiple sample holder. Accurate positioning in the beam was ensured by two stepping motors(Y,Z). The sample-CCD camera distances of 900 mm (Ta edge) and 1900 mm (Ru edge) were chosen allowing measurements up to 2.5 nm^{-1}, i.e.well below the first peak of the IL structure factor around 9 nm^{-1} .The size of the beam focused on the CCD camera was 140 µm high and 150µm wide. The SAXS set-up was under primary vacuum excepted around the sample holder. The tubes before and after the sample holder were closed by kapton windows. A photomultiplier (PM) with a removable kapton foil was mounted after the samples for sample alignement and transmission measurements. The direct beam was stopped by a Pb disk of 2mm diameter centered on a kapton foil placed inside the beam-stop chamber just before the CCD camera.

The ASAXS measurements were done at five energies: at the Ru-K edge (21.6, 21.94, 22.05, 22.09 and 22.106 keV) and the Ta-L_{III} edge (9.68, 9.78, 9.844, 9.862 and 9.872 keV). At each energy, five capillaries containing pure IL, IL+Ru NPs, IL+Ta NPs, IL+Ta8Ru2 NPs and IL+Ru2Ta8 NPs were successively measured as well as the background for the determination of transmissions.

In Figure 1a, the scattered intensities of only the nanoparticles were obtained by subtracting the IL contribution (black curve) taking into account the transmissions of IL and IL+NPs. The curves obtained for E=21.6 keV reveal a strong increase of the intensity below 0.4 nm^{-1} for the particles containing Ta. Such effect stems from the agglomeration of nanoparticles and is not taken into consideration in the analysis of the morphology of the bimetallic particles, which relies on the anomalous variation of the scattered intensities with energy. Compared to pure Ru NPs (red curve), the intensities for pure Ta and bimetallic NPs are much larger and decrease more rapidly with q between 0.5 and 2 nm^{-1}, indicating the presence of larger particles. Moreover, the intensity for the Ru2Ta8 sample is similar to the Ta signal for q smaller than 1.25 nm^{-1} and to the Ru signal above, revealing two populations of Ru and Ta NPs. From Guinier plots a linear behaviour is

found only for the Ru NPs leading to an average diameter of 2.3 nm ± 0.2 nm. For the Ta and Ta8Ru2 NPs, a broad distribution of diameters ranging from 2 to 4 nm is found depending on the q-range.
For theTa8Ru2 NPs, Figure 1b shows the variation of the radial intensity when approaching the Ru K-edge.

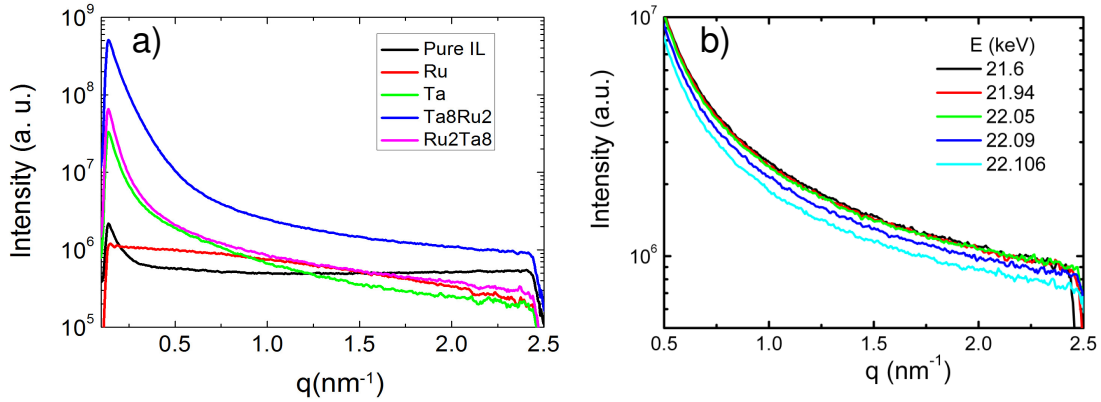

Figure 1: a) Radial SAXS intensities as a function of the scattering vector, q, measured at E=21.6 keV for pure IL, pure Ta and Ru NPs and two bimetallic NPs (for preparation see text). b) For Ta8Ru2 NPs, variation of the radial intensity with photon energy (K-Ru edge)

The intensity of a spherical particle with a Ru-core/Ta-shell structure is given by:
$I(q) \approx [3V_c(\xi_{Ru}-\xi_{Ta})J(qr_c))/qr_c + 3V_s(\xi_{Ta}-\xi_{IL})J(qr_s))/qr_s]^2$ (1),
where $r_s=r_c+t_s$. r_c is the core radius and t_s is the shell thickness, V_c and V_s are the volumes of the Ru core and the whole particle, respectively, ξ_i (i=Ru,Ta, IL) are the electronic densities and $j(x)=(\sin x-x\cos x)/x^2$.
The observed decrease with E is mostly due to the decrease of the cross-term $(\xi_{Ru}-\xi_{Ta})*(\xi_{Ta}-\xi_{IL})*J(qr_c)*J(qr_s)$. Using a core radius of 1.15 nm and a shell thickness of 0.55 nm (i.e. 2 Ml of Ta), the intensities calculated from the expression (1) for the different energies and integrated over a narrow q-range (1, 1.25 nm^{-1}) lead to a variation between the two extreme energies of 6% and this figure holds for a monodisperse suspension. The experimental curves (Fig. 1b) would lead to a variation of the integrated intensity of 26%, i.e. much larger than 6%, but also larger than the value corresponding to a shell consisting of only one monolayer of Ta atoms equal to 9%. However, as shown in Fig1b, the decrease of the scattered intensity becomes more important from 22.09 keV. In contrast, the change in intensity between the three first energies is weaker and its magnitude order is in a relatively good agreement with the model assuming 2 Ml of Ta. The pronounced decrease of the scattered intensity above 22.05 keV can be attributed to a decrease of the number of particles in the beam. Indeed such effect was also observed at the Ta edge leading to an increase of the scattered intensity when approaching the Ta edge while a decrease is expected. A small change in the nanoparticles number in the beam is emphasized in capillary of 1 mm. Consequently no confirmation of the core-shell morphology can be brought by the Ta-edge measurements.

In summary, a core-shell morphology for the Ta8Ru2 nanoparticles is probable relying on the integrated intensities obtained at the Ru edge. As already shown for the Ru-Cu nanoparticles [1] the differential intensity between I(E=21.6) and I(E=22.05) proportional to the cross-term would decrease more slowly than the total intensity dominated by the term $(3V_s(\xi_{Ta}-\xi_{IL})J(qr_s))/qr_s)^2$.

*[1] Helgadottir et al, Nanoscale, 2014, **6**, 14856.*