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ESRF	**Experiment title: Anomalous SAXS/WAXS study of bimetallic Cu/Ru nanoparticles**	**Experiment number**: 02-01-835
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Shifts:	**Local contact(s)**: MARET Mireille	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

GERGAUD Patrice (*) , CEA-LETI DTSA/SCMC Grenoble

ARQUILLIERE Philippe, ESCPE, Lab. Chimie Organométallique de Surface Lyon

SANTINI Catherine, ESCPE, Lab. Chimie Organométallique de Surface Lyon

Report:

To characterize the core-shell structure of Ru/Cu nanoparticles (NPs) embedded in [C_1C_4Im][NTf_2] ionic liquid (IL), anomalous SAXS measurements were performed below the Ru-K edge (22.117keV) on the CRG-BM02 beamline; the operating mode of the storage ring was 16 bunch filling. The NPs were prepared from the decomposition of two organometallic precursors Ru(COD)(COT) and Cu(Mes) in [C_1C_4Im][NTf_2] ionic liquid under H_2 [1]. The NPs embedded in IL were contained in quartz capillaries of 1.5mm diameter and 10cm length with wall thickness of 10µm. The capillaries sealed under argon were mounted perpendicularly on a multiple sample holder. Accurate positioning of capillaries in the beam was ensured by two stepping motors(Y,Z). A distance of 425mm between the sample and CCD camera has allowed us to measure up to the first peak of the IL structure factor. The size of the beam focused on the CCD camera was 100 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 mica windows which produce negligible scattering compared to kapton foils. 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.

Three samples containing NPs with atomic fractions of Cu, x_{Cu}, equal to 0.1, 0.75 and 0.9, respectively were measured at five energies: 21.6, 21.94, 22.06, 22.1 and 22.11keV. Nps with x_{Cu}=0.1 can be considered as pure Ru NPs and those with x_{cu}=0.75 and 0.9 are expected to be core-shell Ru/Cu NPs. The density of NPs in IL decreases from to $1x10^{-4}$ to $2x10^{-5}$ NPs/nm^3 with increasing the Cu content, corresponding to a volume fraction of NPs about $4.2x10^{-4}$. The SAXS images were corrected from dark current and flatfield. Since the scattered intensities are isotropic, radial averaging was done. Figure 1 shows the radial intensities for the pure IL (I_{IL} :red curve) and the NPs of Cu9Ru1 dispersed in IL (I_{IL+NPs} :black curve). Above $3nm^{-1}$ the signal is thus dominated by the structure factor of IL, while the scattered intensity of NPs is located between 0.4 to $3nm^{-1}$.

[1]. P.P. Arquillère, I.S. Helgadottir, C.C. Santini, P.-H. Haumesser, M. Aouine, L. Massin, J.-L. Rousset, Top Catal DOI 10.1007/s11244-013-0085-3, under press.

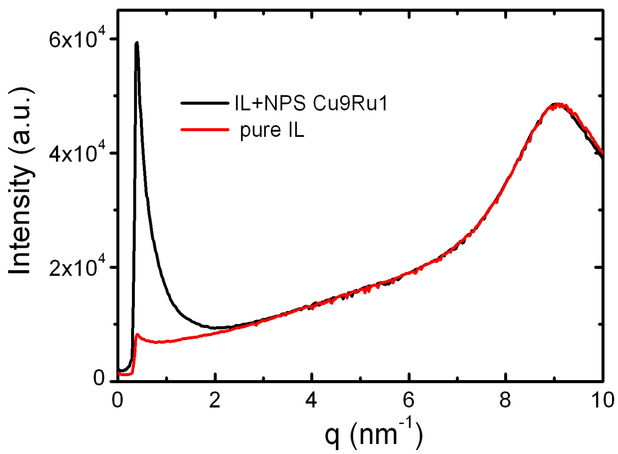

Figure 1: Radial SAXS intensities as a function of the scattering vector,q, measured at 22.10keV (counting time=150s)

The scattered intensity coming from the NPs, I_{NPs} (green curve) was then deduced from I_{IL+NPs} and I_{IL} corrected for transmission factors and monitoring.

For each energy, we have thus measured successively I_{IL+NPs} , I_{IL} and I_{bg} (background) and the corresponding transmissions. For all NPs, a decrease of I_{NPs} was observed by increasing the photon energy attributed to a decrease of the contrast between NPs and IL. Figures 2a and 2b show the intensities I_{NPs} measured at 22.1keV for Ru NPs (x_{Cu}=0.1) and Ru/Cu NPs(x_{Cu}=0.9) as well as the differences:

$\Delta I = I_{NPs}$ (E=21.6keV)-I_{NPs} (E=22.1keV) renormalized with respect to I_{NPs}.

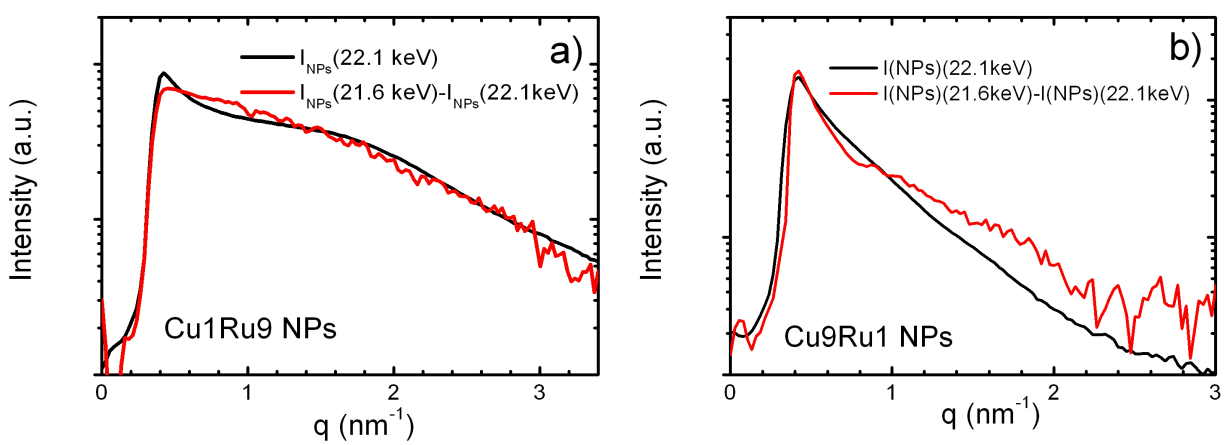

Figure 2: Radial intensities measured at 22.10keV and differential intensities for NPs with: (a) x_{Cu}=0.1 (Ru Nps) and (b) x_{Cu}=0.9 (core-shell Ru/Cu NPs)

For Ru NPs, the decreases of I and ΔI with q are similar, while for the core-shell NPs the decreaseof ΔI with q is much slower than the one of I. As a matter of fact, ΔI is the sum of the partial structure factors S_{RuRu}(q) and S_{CuRu}(q) weighted by the scattering contrast between metal atoms and the ionic liquid. Therefore ΔI is dominated by the core of NPs, showing thus a slower decrease in agreement with the smaller diameter of the core.

Finally, the AGISAXS measurements have allowed us to reveal the core-shell morphology of Cu-rich NPs. However, due to the strong contribution of IL, only the first oscillation of the form factor of NPS is observed, preventing to determine the size dispersion.