ESRF	**Experiment title:** X-ray absorption spectroscopy at the nanometer scale under reaction conditions	**Experiment number:** HC2291
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Shifts: 18	**Local contact(s):** Maciej Jankowski	*Received at ESRF:*

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Report:

The ability to obtain spectroscopic information at a nanometer scale could lead to a breakthrough in the understanding of catalysis. Of particular interest is the local chemical state of catalysts *during* operation. Synchrotron X-ray scanning tunneling microscopy (SXSTM) may be able to provide such information. In a SXSTM measurement, the enhancement of the tunneling current induced by X-rays is measured. In vacuum, it was shown that this signal depends so strongly on the local X-ray absorption coefficient that nanometer resolution chemical maps can be obtained[1]. Based on our experiences in HC1754, we developed a methodology to perform SXSTM measurements in a gas environment. In HC2291, we succesfully tested this combined X-ray absortion and scanning tunneling microscopy instrument (see figure 1).

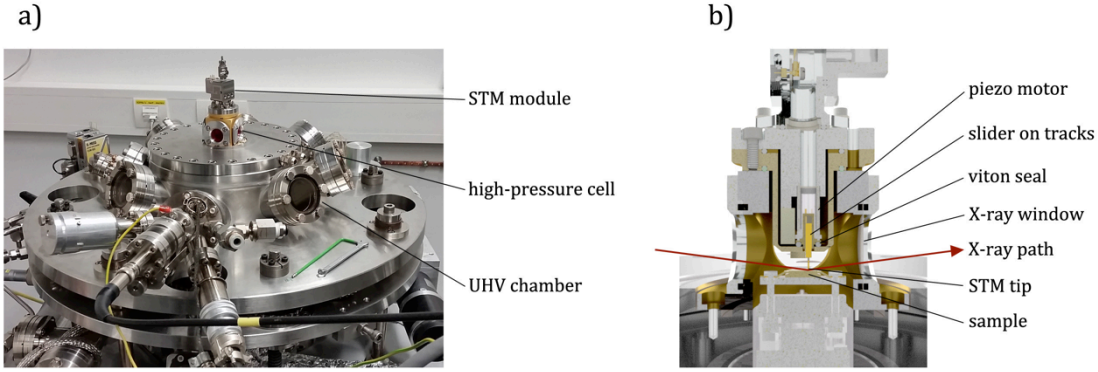

Figure 1: Combined STM X-ray absorption instrument with kapton windows providing high X-ray transmission above 8 keV.

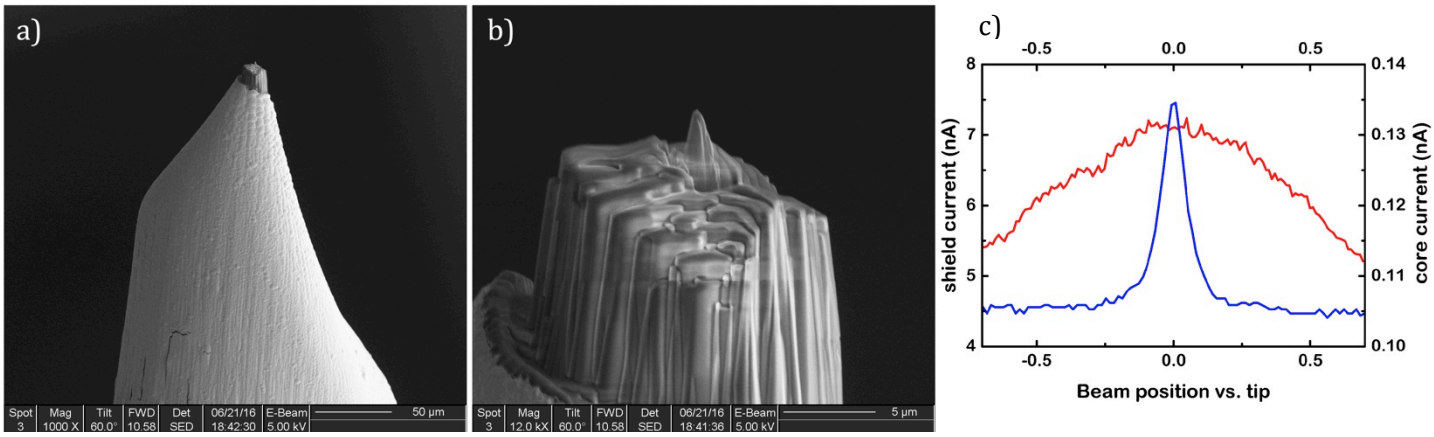

Figure 2: Coaxially coated STM tips used to reduce the ion current collected by the STM tip. a,b) SEM images of the tip apex. c) Current collected on the tip shield and core while scanning the beam across the surface underneath the tip.

To suppress the collection of the ion currents that are generated in the gas phase by photo-electrons, coaxially coated STM tips were used (see figure 2). The conductive outer shield of the coaxial tips can be biased to deflect ions away from the tip core. From figure 2c it is clear that the coaxial coating of the tip largely removes the background current, bringing it to a manageable regime.

In tunneling contact, the X-ray-induced current needs to be separated from the regular topographic tunneling current in order to perform height feedback while obtaining the X-ray-induced signal. As the integration of our STM with ID03's flow chamber does not permit complete electronic shielding and vibrational isolation, the height feedback system needs to have a high-speed response. We have therefore developed a novel X-ray/topo current separation scheme, that allows us to perform stable scanning while obtaining the X-ray-induced current (see figure 3a).

Finally, we have measured the X-ray-induced current on Au(111) in 800 mbar Ar as a function of topographic tunneling current (figure 3b). The clear correlation proves that we are truly sensitive to the X-ray-induced enhancement of the tunneling probability, which is the underlying mechanism that provides local chemical contrast. Thus, our measurements have opened the way to *in situ* chemical mapping of model catalysts. A manuscript based on the results described above is in preparation.

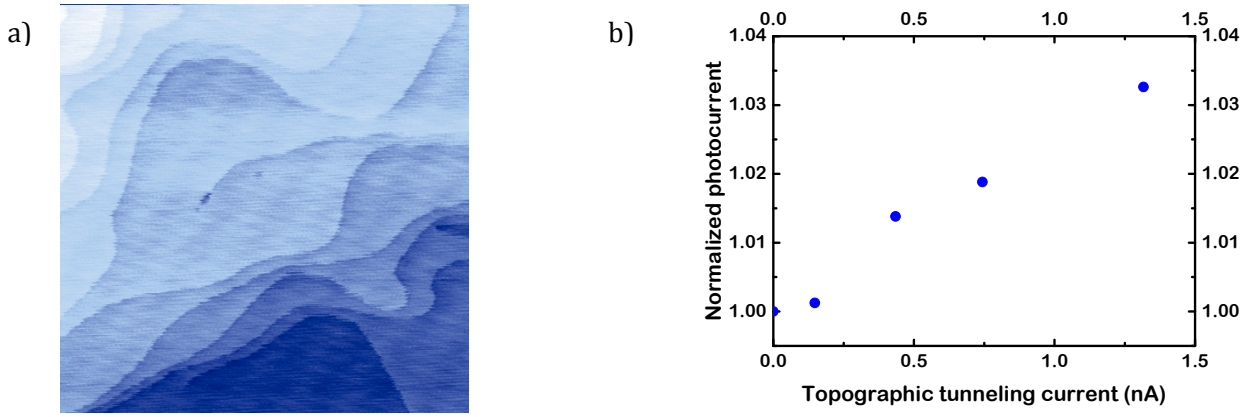

Figure 3: Performance for SXSTM measurements. a) Topographic image of Au(111) in 800 mbar Ar with X-rays on. b) X-ray-induced current versus topographic tunneling current, showing our sensitivity towards enhancement of the tunneling probability.

[1] N. Shirato *et al., Nano Letters* 14, 11, 6499-6504, **2014**
[2] S.L.M Schroeder *et al., Surface Science Letters* 324, L371-L377, **1995**