Soft X-ray absorption spectroscopy of aqueous dispersions of nanoparticles in the water window

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Measuring the electronic structure of photocatalytic nanoparticles directly in aqueous solution is highly relevant since their applications generally necessitate aqueous environment. Soft X-ray absorption spectroscopy (XAS) is highly sensitive to the chemical environment, however XAS measurement in aqueous environment remains challenging, especially in the water window (below 535 eV), required to probe the core level of light elements (C, N, O) and the Ti L edge. The characterization of TiO_2- and carbon-based photocatalysts close to real conditions therefore requires the development of new methods for applications of XAS in liquid in this energy region.

We introduce here a new approach to measure fluorescence yield XAS (FY-XAS) of nanoparticles in water using a holey membrane flow cell.[1] To isolate the aqueous dispersion from the vacuum, silicon nitride membranes with small holes (~750 nm) are used instead of solid membranes to ensure enhanced X-ray transmission, especially in the water window. The small size of the holes ensure good vacuum conditions due to liquid surface tension. This method was applied to anatase TiO_2 nanoparticles aqueous dispersions with two different sizes.

XAS of TiO_2 nanoparticles at the titanium L edge and at the oxygen K edge were successfully measured with a holey membrane-based flow cell at the synchrotron BESSY II. Modifications of the XA spectra, probably induced by hydration, were observed for dispersed samples compared to solid references. In addition, formation of an amorphous ice layer at the liquid water-vacuum interface in the holey area was evidenced and will be discussed.

The use of holey membrane enables new perspectives for the characterization of nanoparticles in liquid with XAS in the water window. This method will be compared to other alternatives for XAS in liquid such as FY-XAS based on standard flow cell or microjet, transmission XAS or the recently introduced total ionic yield XAS.[2] We believe that these methods will facilitate the *in situ* characterization of new photocatalytic nanomaterials with XAS in the soft X-ray region and can contribute to the development of more efficient photocatalysts.

[1] Petit et al, "X-Ray Absorption Spectroscopy of TiO_2 Nanoparticles in Water Using a Holey Membrane-Based Flow Cell", *Adv. Mater. Interfaces* **2017**, 4 (23), 1700755.
[2] Schön et al, "Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells", *J. Phys. Chem. Lett.* **2017**, 8 (9), pp 2087-2092.

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