Multifunctional nanoreactors for combined in-operando STEM and synchrotron spectroscopy

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Understanding the function of materials in reactive environments is a crucial issue to advancing several of the world's most pressing energy needs, specifically in the areas of catalysis, energy conversion and energy storage. In most of the cases, much of the current knowledge has been obtained under conditions that largely deviate from those of practical applications of these materials. There is common agreement that information have to be acquired on different lengh scales and that, to this aim, multiple techniques need to be intelligently combined. Much of effort has been made lately in designing new instruments and adapting existing ones to investigate catalysts under *operando* conditions. Another approach has been the use of micro- or nanoreactors that separate the high-pressure volume from the (ultra)high vacuum part via ultrathin walls of an inert material. Very recently, microreactor cells have been developed to integrate the capabilities of ensemble-averaging synchrotron techniques with local probe ones as TEM to analyze the same catalytic process with different instruments [1,2].

We propose here the development of a novel multifunctional microreactor for *operando* low voltage Scanning TEM in a SEM compatible with a broad range of synchrotron techniques. The microreactor is a sealed chamber consisting of two facing membranes with SiN semi-transparent windows allowing transmission of both electrons and X-rays. It allows operation at atmospheric pressure, in presence of reactive gases and at elevated temperatures. The device is designed to be compatible with Grazing Incident Small Angle X-ray Scattering (GISAXS) and Wide-Angle X-ray Scattering (GIWAXS) where extended beam footprint (about 1x10 mm^2) and small penetration of the beam are involved due to the grazing incidence geometry. The entire fabrication protocol has been designed to ensure optimal electron transparency for STEM imaging and to preserve the mechanical resistance of the membranes for GISAXS experiments.

We successfully demonstrated the feasibility of our approach by studying the stability, shape and size evolution of PVP-capped Pd nanocrystals under oxidation/reaction conditions. Information on size, morphology of the nanocrystals obtained at the nanoscale by STEM have been coupled with that concerning their collective behaviour over extended areas such as size, aggregation and cristalline structure by GISAXS/GIWAXS, all in one portable microreactor and under identical reaction conditions.

[1] J.F. Creemer Ultramicroscopy 2008, 108, 993– 998

[2] Shen Zhao ChemCatChem 2015, 7, 3683 – 3691