

The ESEM as *In Situ* Platform for the Study of Gas-Solid Interactions

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In order to understand the working principle of functional materials they should, at one point, be studied in their working state. In view of electron microscopy, atomic motion and chemical dynamics can be observed by *in situ* TEM. However, size constrains and the requirement of electron beam transparency impose substantial limitations with respect to dimension, complexity and preparation of a specimen. Furthermore, atomistic details can only be resolved under conditions where atomic scale dynamics are slow compared to the temporal resolution of the detection system. In the case of gas-solid interactions, *in situ* TEM observations are therefore often performed at reduced chemical potential of the reactive gas phase. Due to the strong focus on ultimate spatial resolution, the potential of environmental scanning electron microscopy (ESEM) as a flexible tool for *in situ* studies in the field of material science has recently been overlooked.

In situ experiments performed in the ESEM can be used to complement localized information that is obtained by *in situ* TEM. Instead of atomistic details, it reveals the complexity of hierarchical multi-scale processes in which collective movements of a large number of atoms are involved. Thus, effects related to heat and mass transport are accessible. Compared to the TEM, the ESEM imposes far less restrictions with respect to available space and dimensions of the sample. This opens up the possibility to bridge the “materials gap” between simplified model- and complex real-world system. Similarly, the focus on collective dynamics allows observations at higher chemical potential of the reactive species and thus, a closing of the so-called “pressure gap”. Another important aspect is the reduced areal dose rate and lower kinetic energy of the beam electrons in ESEM. Contributions and extent of various beam induced processes are different and, in most cases, less severe than in the TEM. Furthermore, the ESEM allows fast and efficient screening of the parameter field and facilitates a more efficient use of the *in situ* TEM set-up.

In order to obtain a unique platform for *in situ* studies of gas-solid interactions under controlled atmosphere, we have equipped a commercial ESEM with a home-built gas-feeding station, a heating stage, and a mass spectrometer. For topography and 3D imaging of surface dynamics at temperatures of up to 1000 °C, a newly developed four-quadrant BSE detector was implemented. In addition, a detector for electron beam absorbed current (EBAC) was installed in order to complement the large-field detector with a signal that is independent of gas composition and pressure.

It will be shown how the use of this instrument allows to study the emergence of catalytic function in the interplay between a gas-phase and a metal catalyst [1]. Dynamics of metal catalysts under redox conditions will be presented (Figure 1a, b) as well as the ability to study vapour-liquid-solid growth of semiconductor nanowires (Figure 1c, d) [2]. Due to the high sensitivity of the SE signal, it is even possible to study metal

catalysed chemical vapour deposition of graphene at 1000 °C (Figure 1e) [3,4]. Finally, it will be demonstrated that contrast variations due to different molecular species on the surface of platinum during catalytic NO₂ hydrogenation can be detected (Figure 1f).

References:

[1] M. Greiner *et al*, *Phys.Chem.Chem.Phys.* **17** (2015), p. 25073.

[2] X. Huang *et al*, *Adv. Funct. Mater.* **25** (2015), p. 5979.

[3] Z.-J. Wang *et al*, *ACS Nano* **9** (2015), p. 1506.

[4] Z.-J. Wang *et al*, *Nature Communications* **7** (2016).

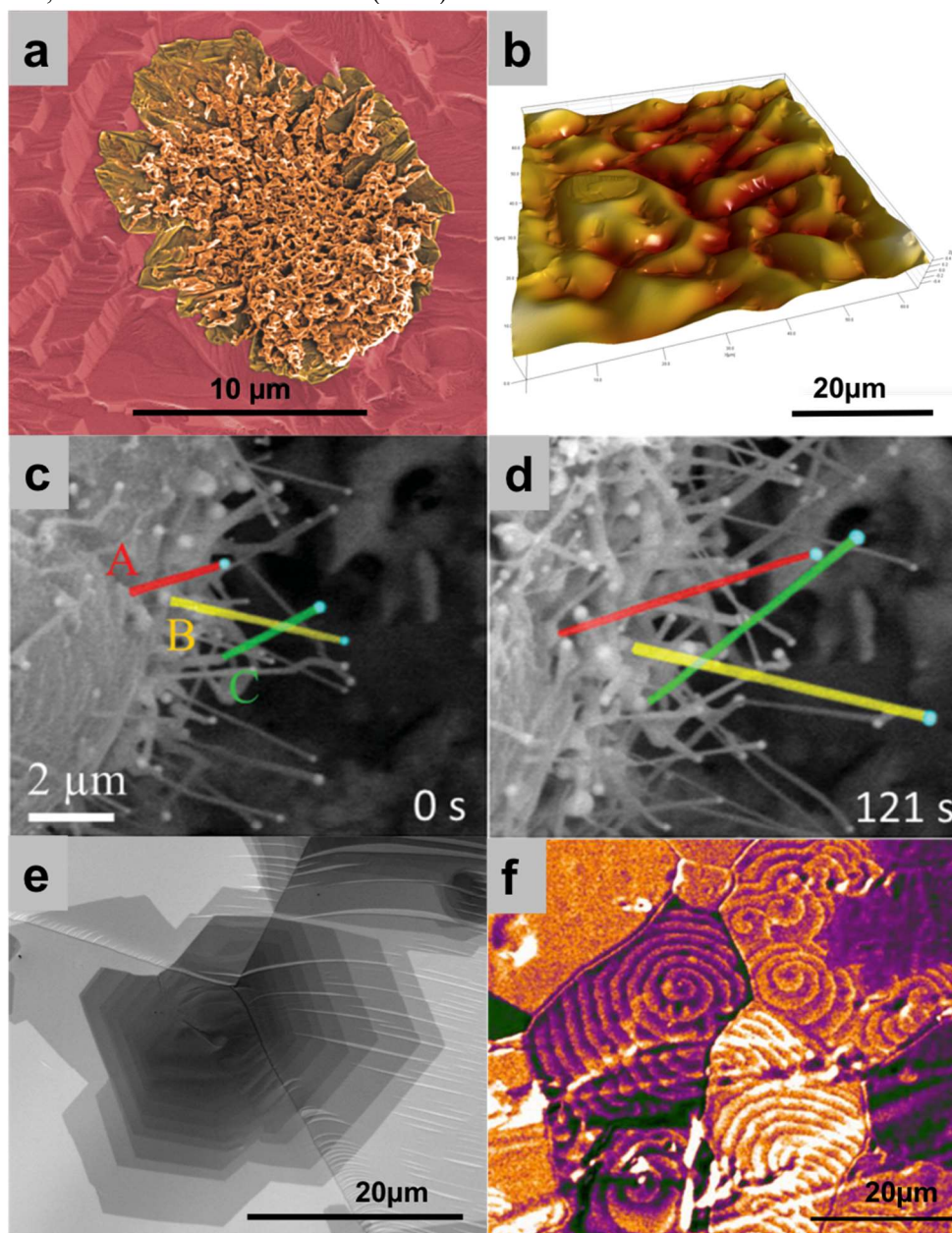


Figure 1. (a): oxidation of Cu₂O to CuO. (b): topography of a Cu catalyst during hydrogen oxidation. (c)-(d): vapor-liquid-solid growth of ZnS nanowires from CdS and ZnS with Ag catalyst particles. (e): few-layer graphene growing on a Pt substrate at 1000 °C during chemical vapor deposition growth. (f): spiral waves formed by the propagation of reaction-diffusion fronts in the hydrogenation of NO₂ on a polycrystalline Pt foil. Contrast in the colorized image is due to different absorbed molecular species.