Transmission electron microscopy of nano-scale materials in liquid and gas environments

DH Alsem[1], RR Unocic[2], GM Veith[2], KL More[2] and NJ Salmon[1]

1. Hummingbird Scientific, 8300 28th Ct NE, Lacey, WA 98516, USA
2. Materials Science and Technology Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

daan@hummingbirdscientific.com
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Transmission electron microscopy (TEM) has an unmatched ability to characterize the structure and chemistry of materials at varying length scales via a combination of imaging, diffraction, and spectroscopy methods. To establish critical structure-property relationships *in operandi*, the use of TEM has moved beyond traditional post-mortem characterization, to a more relevant mode where many different *in situ* experiments are performed within the TEM [1]. Conducting real-time observations of materials interactions at high spatial and temporal resolution in their native gas or liquid environment has attracted increasing attention across physical and biological science disciplines, with the promise of providing critical insight regarding the fundamental mechanisms that control the physiochemical properties of materials. A key challenge of this work has been the ability to contain a fluid (liquid or gas) in the high vacuum environment of the microscope, which has been accomplished via sealing the fluid inside a micro-fabricated cell with electron transparent membranes [2]. In order to expand the versatility of this characterization approach, Hummingbird Scientific has developed two specialized *in situ* environmental fluid cell TEM specimen flow holders, one for experiments conducted in liquid and one for experiments in gas. The basic principle is to use two micro-fabricated chips stacked together (with a spacer of designated thickness) that forms a flow channel (Figure 1a), which are integrated into the tip of the specialized TEM sample holders. Recently, electrical biasing capabilities have been integrated in the flow cell design, enabling a wide variety of electrochemical experiments, e.g., materials for electrical energy storage devices. This has also provided an opportunity to integrate a sample heater into the cells.

The liquid holder has been used to study nanoparticle growth, coalescence, and movement within a liquid layer, as shown in Figure 1b, where the self-assembly of Au nanoparticles in water is observed *in situ*. Additionally, *in situ* TEM studies have been used to monitor the structural evolution of deposited thin films or focused ion beam (FIB) lift-out samples held within the liquid cell, in order to study electrochemical processes.

The *in situ* atmospheric pressure gas specimen holder is being used to study gas catalysis reactions. Figure 2a is a high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image of Au nanoparticles supported on TiO_2, which was acquired during a CO oxidation experiment in a C_s-probe corrected FEI Titan operated at 300kV. When imaging at atmospheric pressure (Fig. 2b), we have been able to demonstrate ~2 Å resolution on Au nanoparticles (Fig. 2c) in an uncorrected FEI Titan operated at 300 kV.

The availability of these unique *in situ* holders has opened up new research directions that can be used to answer critical scientific questions regarding materials functionality for a broad range of materials [3-5]. The recent results presented here summarize current capabilities for *in situ* microscopy using membrane-type environmental fluid cells, the use of which will allow researchers to perform a variety of *in operandi* studies of nano-scale energy and catalytic materials. [6]

References

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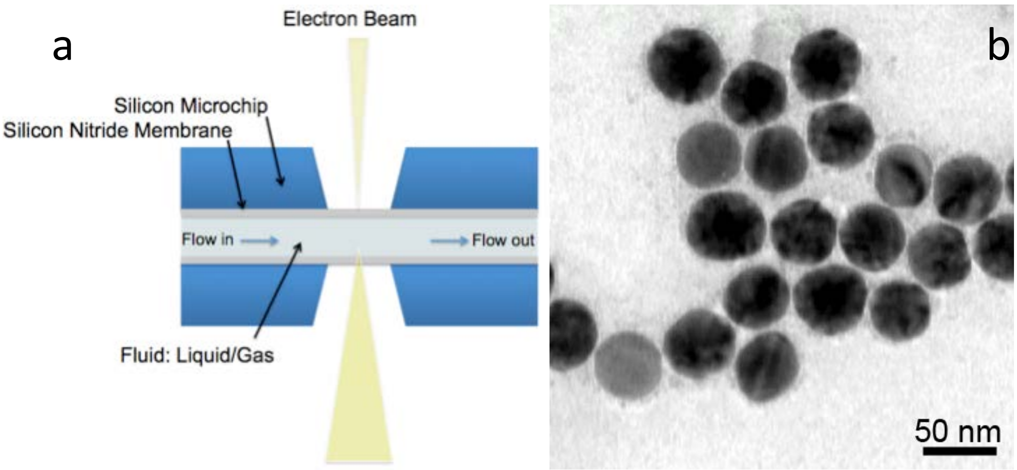

Figure 1: *(a) Basic cell stacking principle used to create environmental cells inside the TEM; (b) Bright-field (BF) TEM image showing the self-assembly of Au nanoparticles in water.*

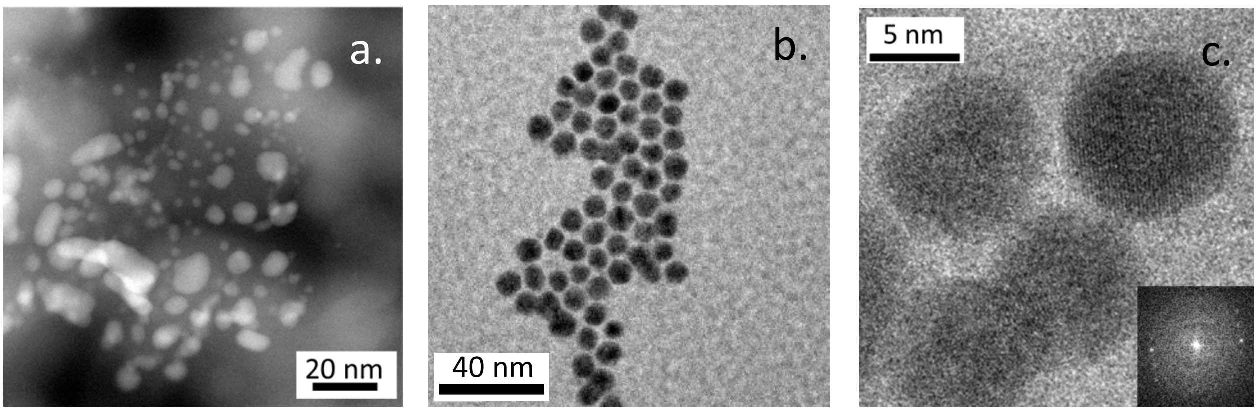

Figure 2: *(a) HAADF STEM image of Au catalyst nanoparticles on TiO_2 support imaged through CO gas mixture; (b) Gold nanoparticle self-assembly in ~1.1 atm nitrogen gas; (c) Atomic resolution of 10 nm gold nanoparticles in nitrogen at 1.1 atm pressure (BF TEM image at 300kV) – inset: FFT of the high resolution image shows ~2 Å planar spacing.*