Enabling Lab-in-Gap Transmission Electron Microscopy at Atomic Resolution

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Abstract: Hitachi Lab-in-Gap transmission electron microscopy (TEM) technologies are introduced. The term Lab-in-Gap refers to a special function that allows *in situ* and *in operando* TEM studies of materials in gas or liquid environments while stimulations, such as thermal or electrical fields, are applied to the specimen sitting in the pole piece gap in a TEM system. Physical or chemical process can be activated and imaged in real time using TEM or other imaging modes. The new generation environmental TEM platform with large pole piece gap and advanced aberration correctors opens wide possibilities for integrating multiple stimuli sources as well as large-area, sub-Å resolution live imaging for dynamic structural changes.

Introduction

In February 2014, the Basic Energy Sciences Division of Department of Energy held a workshop on Future of Electron Scattering and Diffraction [1]. The goal of the workshop was to identify the frontiers in electron scattering and diffraction that address the grand challenges in chemistry, material science, physics, and biology. The workshop participants concluded there were four key areas where the next generation instrumentation would have major impacts. One of them was the Lab-In-Gap type of microscope. The name of Lab-In-Gap is for a special type of microscope that allows *in situ* and *in operando* microscopy study of materials in gas or liquid environments while other stimulation fields such as thermal or electrical fields are applied to specimen. In particular, Lab-In-Gap refers to enabling physical or chemical lab work in the pole-piece gap of the electron microscope; the microscope serves as a real-time observation tool to reveal the ongoing dynamic processes such as chemical reactions on an unprecedented atomic-spatial-resolution level if modern techniques are employed.

For a transmission electron microscopy (TEM) system, an electromagnetic objective lens focuses an electron beam of say 60 to 300 kV. An important design for the electromagnetic objective lens is the upper and lower pole pieces with a gap between them. The pole piece gap allows one to insert a TEM specimen and objective aperture into the symmetrical magnetic field (Figure 1). The key concept for the Lab-In-Gap microscope is to take full advantage of the pole piece gap, namely building miniaturized devices or reaction cells in the pole piece gap. In order to do so, modification of existing TEM products is required in many aspects. For example, on one hand, the pole piece gap is usually made very narrow, typically less than 5 mm, to guarantee a high imaging resolution, which is a core value of the TEM. On the other hand, sufficient room is needed in the gap to add functional devices or measurement mechanisms around the TEM specimen to mimic what can be done in a physical or chemical lab. Another challenge is the sample environment. When a stimulus is applied to specimen in a TEM column, the dynamic response of the specimen structure can be observed in real time using TEM; this is called *in situ* TEM observation. *In situ* TEM technology has a long history [2]. Many *in situ* TEM datasets reflect some process that is happening in high vacuum, and these data may or may not directly correlate to what would happen in the real world. The environment in the real world consists of gas and liquid. Ideally, when doing an *in situ* TEM study, a gas or liquid environment should also be available in the TEM specimen area. It is clear that the Lab-In-Gap electron microscope should provide a gas or liquid environment, a large space in the pole piece gap, mechanisms for stimulation of the specimen, and sensors for measuring the effects. Even with all these modifications, the microscope should still be able to deliver high-resolution images. For today's materials research, atomic resolution is a minimum requirement, and sub-Å resolution is highly desired.

Current Hitachi Lab-In-Gap TEM Technologies and Examples

Hitachi has been developing and manufacturing *in situ* and environmental TEM technologies and platforms for two decades. The two famous early stage Lab-in-Gap types of Hitachi TEM systems are the 300 kV model H-9000; one was installed at Argonne National Laboratory, Illinois, and another at the IBM Thomas J. Watson Research Center at Yorktown Heights, New York. The one at Argonne National Laboratory has a special design in which an ion beam is introduced from

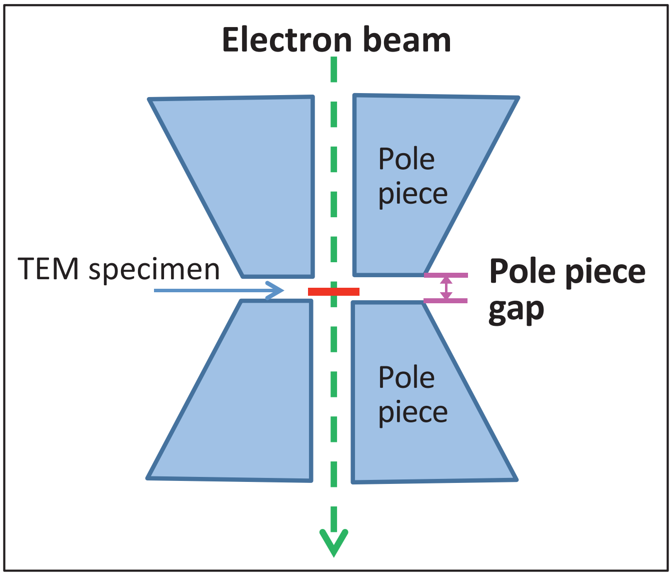

Figure 1: Schematic illustration of objective lens structure used for a TEM system (not to scale). The lens is composed of upper and lower pole pieces. The TEM specimen is loaded in the pole piece gap.

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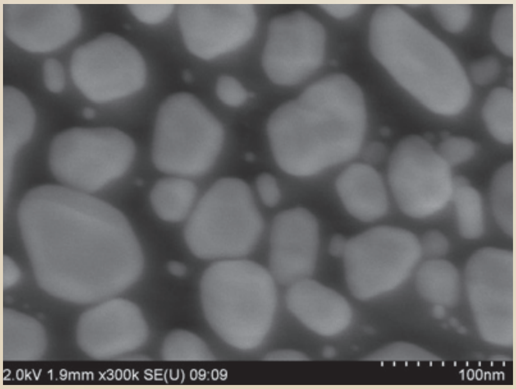
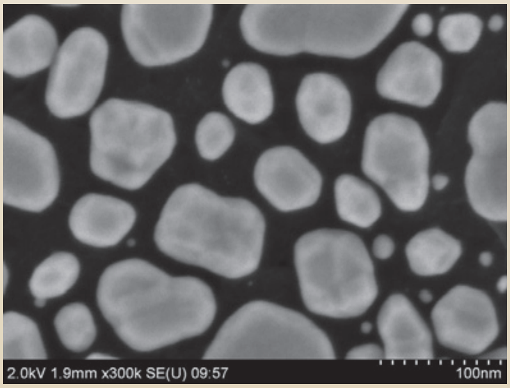


Mesoporous TiO2 Before UV Cleaning



Mesoporous TiO2 After 5 minutes of UV Cleaning

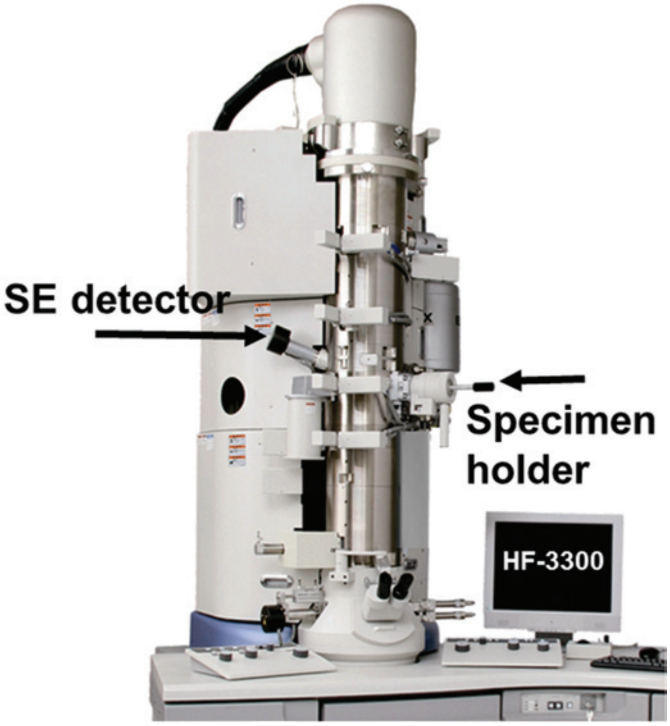


Figure 2: Photo of the Hitachi 300 kV CFEG HF-3300 gas environmental TEM/STEM/SEM. The arrow indicates the secondary electron (SE) detector above the specimen position. SE and STEM images can be acquired simultaneously.

a high elevation angle to the specimen chamber located in the pole piece gap. The accelerated ion beam irradiates the specimen, resulting in structural change and/or byproducts, which are imaged and recorded by a TEM camera. At IBM, the specially designed H-9000 allows the pressure in the specimen chamber to vary from 2×10^{-10} to 5×10^{-5} Torr. Since the time it started to generate data from 1993, numerous papers have been pulished, and this IBM TEM group has become one of the pioneers and leaders in the field of *in situ* gas and liquid environmental TEM.

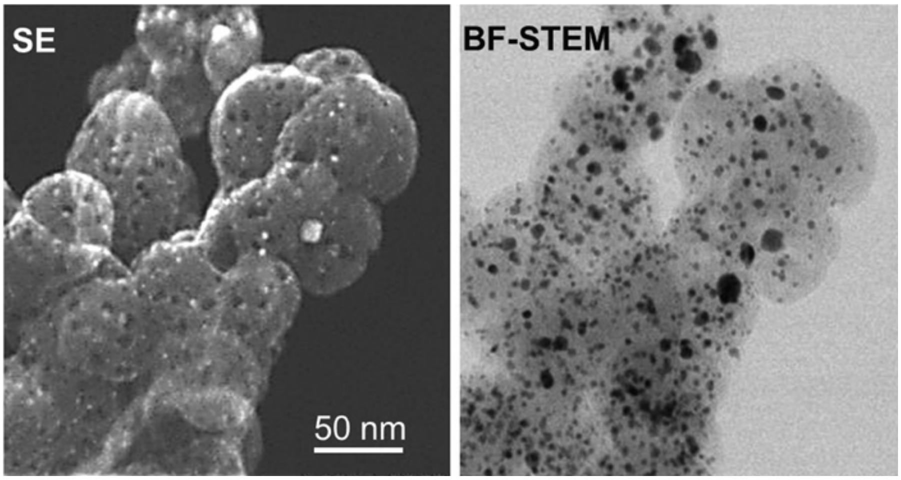


Figure 3: Simultaneously recorded SE and BF-STEM images at 300 kV accelerating voltage in the Hitachi HF-3300 ETEM. The catalysis sample under study contains Pt nanoparticles on a carbon support. The SE image reveals a pore formation on carbon surface during heating at 200°C in a 4 Pa air environment, whereas the BF-STEM image does not show such a structural change on sample surface.

Differential pumping. The accommodation of gas in the TEM specimen chamber is not possible for conventional TEM systems. Differential vacuum pumping is needed to decrease the gas pressure stage by stage along the TEM column [3]. This way, the crucial high vacuum can be maintained, especially in the electron gun area, while the specimen chamber is filled with gas. The current-generation Hitachi 300 kV LaB_6 emission H-9500 gas environmental TEM (ETEM) system is designed based on this technology. While the H-9500 serves as an atomic-resolution and affordable gas ETEM platform, there is a demand for a gas ETEM system with multiple imaging modes, a large pole piece gap, and strong capability for spectroscopy analysis. Hitachi therefore designed the cold field emission gun (CFEG) HF-3300 gas ETEM platform, which combines TEM, scanning transmission electron microscopy (STEM), and secondary electron (SE) imaging modes on one column. Three- or four-stage differential pumping between the specimen chamber and electron gun maintains a sufficient vacuum in the gun area when the specimen chamber is filled with gas. A picture of this microscope is shown in Figure 2.

SE/STEM imaging. In Figure 2 an arrow indicates the SE detector located above the specimen position. This high-efficiency SE detector can catch SE signals emitted from the upper surface of the specimen, allowing the simultaneous collection of STEM and SE images or movies [4]. Displayed side by side, the STEM image reveals the bulk structure of the specimen while the SE image shows the surface morphology.

Pt nanoparticles. Figure 3 shows the side-by-side SE and bright-field (BF)-STEM images for Pt nanocatalysts dispersed on a carbon support. Pt particles are in white contrast in the SE image and dark contrast in the BF-STEM image. When the sample was heated to 200°C in the presence of air, pores were formed on the carbon surface as shown in the SE image, whereas the pores cannot be seen in the STEM image [4]. Such simultaneous and live SE/STEM imaging at elevated temperature with a gas environment can be beneficial to the study of heterogeneous structures, especially when the surface structure and/or surface/object interface plays an important role like in heterogeneous catalysis systems.

Functional devices. As aforementioned, the ideal Lab-In-Gap electron microscope not only needs a gas or liquid environment, but also miniaturized functional devices. The easiest way to add a functional device to the specimen area in a TEM system is to build such a device in the tip of the TEM specimen holder. The first Hitachi *in situ* heating TEM holder was reported in 1993 [5]. The built-in heating device can heat the specimen to as high as 1500°C, while sample drift is low enough to allow for atomic-resolution imaging at temperatures above 1000°C [5–7].

In 2006 a Lab-In-Gap type of Hitachi TEM holder with two built-in heaters and

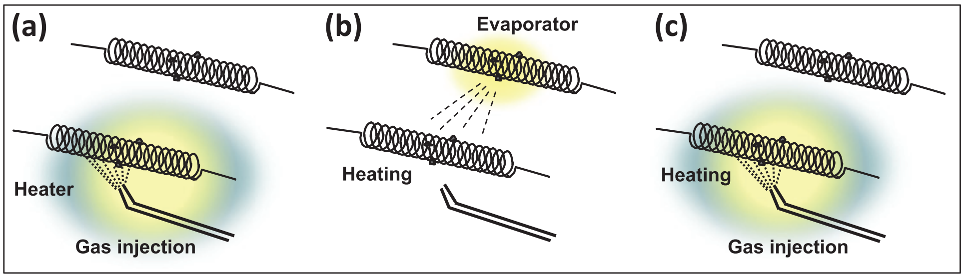


Figure 4: Schematic illustration for a type of Lab-In-Gap workflow employing a specially designed Hitachi double heater-gas injection *in situ* TEM holder. (a) Heater and gas injection are both on to prepare the oxide substrate. (b) The Evaporator is on to deposit materials on the substrate placed on the Heater. (c) After deposition, the sample assembly may be heated with or without gas.

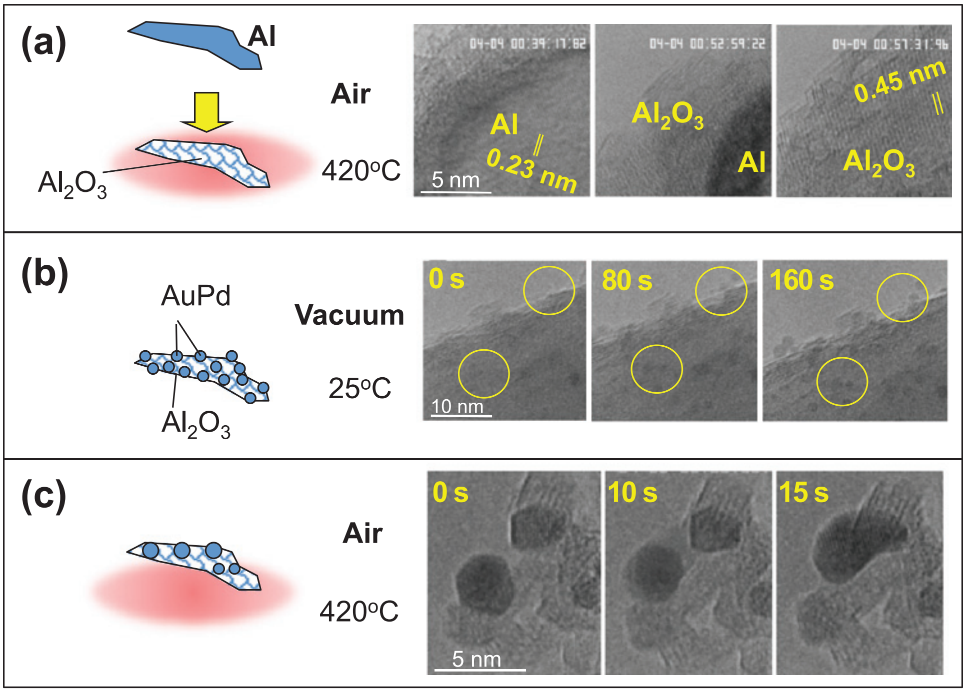


Figure 5: Workflow for synthesis of a catalysis system within the TEM pole piece gap and corresponding live TEM observations of structural changes. (a) Oxidation of Al to form Al_2O_3 support. (b) Evaporation deposition of AuPd nanoparticles on Al_2O_3 support. (c) Heating AuPd/Al_2O_3 system in an air environment and observation of motion and coalescence of two nanoparticles.

a gas spray nozzle was developed [8]. Figure 4 shows the design principle and operational workflow of this device. The tip of a TEM specimen holder contains two heating filaments made from spiral tungsten wires. The one at the bottom position is marked "Heater" and the upper one "Evaporator." The two heating filaments can be turned on and off independently. A gas nozzle is placed close to the Heater and can spray gas when needed. The purpose behind this holder design is to put the substrate material on Heater and precursor materials on Evaporator. When Evaporator is turned on, the precursors are evaporated and deposited onto the substrate. The substrate temperature can be controlled by the Heater during and after the evaporation deposition. Gas injection is controlled from outside the TEM column. Because the gas ETEM system can accommodate gas in the TEM specimen chamber, no Si_3N_4 membrane window, as is used in the window-type gas environmental cell holder [2], is needed. Therefore, high-resolution TEM imaging is readily achievable.

Results

Figure 5 shows results from a Lab-In-Gap type of *in situ* TEM experiment using the special function holder shown in Figure 4. The entire process, from the synthesis of the Al_2O_3 substrate and deposition of AuPd nanoparticles on the Al_2O_3 support to the observation of nanoparticle behavior on the support surface at elevated temperatures, was done totally *in situ* within the TEM pole piece gap. Image and movie recording were active from the beginning to the end [8]. As shown in Figure 5a, the process started with a small piece of metal aluminum setting on the Heater. It was heated to 420°C in the presence of air. The Al was oxidized to form Al_2O_3, which was used as the support material in the following steps. The Heater was then turned off, and air was pumped out of the specimen chamber. The Evaporator was turned on to make an evaporation deposition of AuPd nanoparticles onto the Al_2O_3 support. The formation of nanoparticles on the Al_2O_3 surface can be seen in the corresponding TEM images (Figure 5b). After evaporation the Evaporator was turned off, and the Heater and the gas nozzle were switched on again to heat the assembly to 420°C while the sample chamber was filled with air. TEM imaging reveals the behavior of the nanoparticles on the support. Figure 5c shows the movement and coalescence of two nanoparticles to form a single crystalline particle.

Discussion

Advanced Lab-In-Gap Electron Microscopy. Obviously, integrating miniaturized devices into the narrow TEM pole piece gap is nontrivial, especially when multiple stimuli or measurement mechanisms are desired. Increasing the pole piece gap would make more complicated Lab-In-Gap tasks possible. With this goal in mind, Hitachi developed a state-of-the-art ETEM platform with a significantly widened pole piece gap compared with that in the standard HF-3300 or H-9500. To compensate for the loss in resolution due to the increase in the pole-piece gap, a hexapole TEM imaging aberration corrector was installed onto the TEM column. It is a so-called B-COR corrector made by CEOS GmbH in Germany. This aplanatic aberration corrector not only corrects up to 5th-order spherical aberrations of the objective lens, but also the off-axis aberrations [9]. Atomic-level and even sub-Ångstrom imaging resolution is thus achievable with the aberration-corrected, wide pole piece gap ETEM platform. Furthermore, the correction of parasitic off-axis astigmatism and 3rd-order azimuthal off-axis coma fulfills the need for high-resolution imaging in a large field of view. Large-size digital cameras such as 4k × 4k or 8k × 8k pixels can be used for *in situ* TEM without a concern of losing image resolution at distances far from the center of the field of view.

New experiments possible. Lab-In-Gap electron microscopy will soon enter a regime of precise control of multiple stimuli sources, gas or liquid environments, quantitative onsite measurement, and large area sub-Å resolution live imaging and spectroscopy analysis for dynamic structural and chemical changes inside and on the surface of specimens.

Conclusion

Hitachi started the efforts for Lab-In-Gap electron microscopy in the early 1990s. The efforts included designing gas environmental TEM systems as well as special *in situ* TEM specimen holders with different functions. Various types of Hitachi gas ETEM platforms are briefly introduced in this article, and an example is given of Lab-In-Gap electron microscopy realized by applying a double heater-gas injection TEM holder on a gas ETEM system. The latest Hitachi wide-pole-piece-gap, aberration-corrected ETEM platform has paved the way toward integration of multi-functional devices in the TEM specimen area.

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