

## Toward Quantitative *In Situ* TEM of Materials and Devices in Gases and Liquids at the Atomic Scale

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Among the various observation methodologies, *in situ* transmission electron microscopy (TEM) has recently advanced with technological developments such as aberration correction of lenses, fast digital cameras, and miniaturized specimen containers with various functions. These advances have enabled observation of a variety of phenomena in materials and devices at higher spatial and temporal resolution, especially in gases and liquids. The first crucial era of *in situ* TEM started in the 1970s using a large specimen room, which was only available in high-voltage TEM apparatus at that time, for examining plastic deformation and the interaction of point defects in metals and alloys. Electron irradiation was used to intentionally generate point defects in a crystalline thin foil, and then the kinetics of point defects was analyzed using quantitative high-voltage TEM [1], even though point defects have not been identified by direct TEM imaging even now. Environmental TEM (ETEM) was also introduced in high-voltage TEM apparatus by Swann and Tighe to reveal chemical reactions and others properties *in situ* [2]. Given the recent advances in TEM technology, it is now possible to investigate the essential static and dynamic characteristics of materials and devices by quantitative *in situ* TEM at the atomic scale.

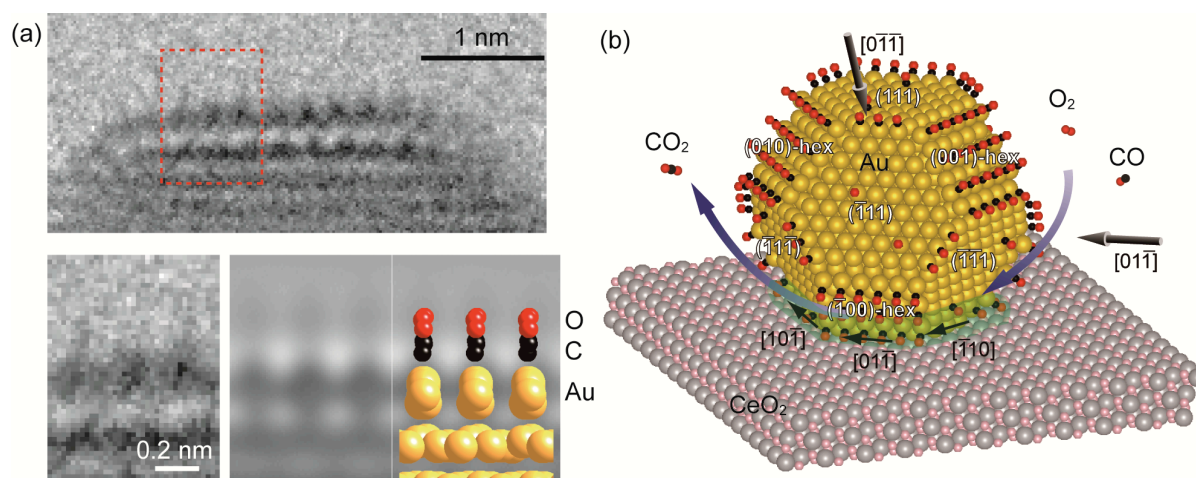
First, we briefly summarize our recent *in situ* ETEM studies of catalyst materials (Fig. 1) [3]. The conditions necessary for atomic-resolution ETEM using a Cs corrector of the objective lens have been described elsewhere [3]. We studied the gold nanoparticulate catalysts Au/CeO<sub>2</sub> and Au/TiO<sub>2</sub>. It is well-known that gold, the most stable metallic element, shows remarkable catalytic activity for CO oxidation even below room temperature. Haruta gold catalysts were prepared using the deposition precipitation method, and exhibited high catalytic activity at room temperature. Gold atoms on a crystalline gold surface are frequently displaced by electrons with energy higher than 400 keV. Therefore, ETEM observation was performed with electrons of 80, 200, and 300 keV to suppress the electron-irradiation effect. Systematic acquisition along with both numerical and statistical analyses of the ETEM imaging data led to the intrinsic catalyst structure in the reaction environments. The quantitative analyses further indicated that the activation sites of oxygen molecules at room temperature are most likely to be at the perimeter interface between gold nanoparticles and metal oxide supports. More importantly, the perimeter interface is not structurally rigid. Glimpse of gas molecules that interact with the surface of a gold nanoparticle is now possible with recently developed ETEM.

In electron-irradiation-sensitive materials and devices, intrinsic phenomena may be masked by electron irradiation. It is helpful to systematically acquire *in situ* TEM data as a function of electron current density  $\phi$ , electron dose  $D$ , and electron energy  $E$ . In several applications, the intrinsic phenomena and/or structures can be deduced at the atomic scale by extrapolating the systematically acquired *in situ* TEM data to both zero  $\phi$  and  $D$  [3]. It is now realized that another crucial era of *in situ* TEM has started [4]. For quantitative *in situ* TEM of time-dependent phenomena, for instance dynamic atomic motions in a chemical reaction, quantitative evaluation and removal of the electron-irradiation-induced phenomena that may appear in the background in *in situ* TEM data is required. The statistically random displacement of atoms by electron irradiation probably differs from the strongly correlated displacement

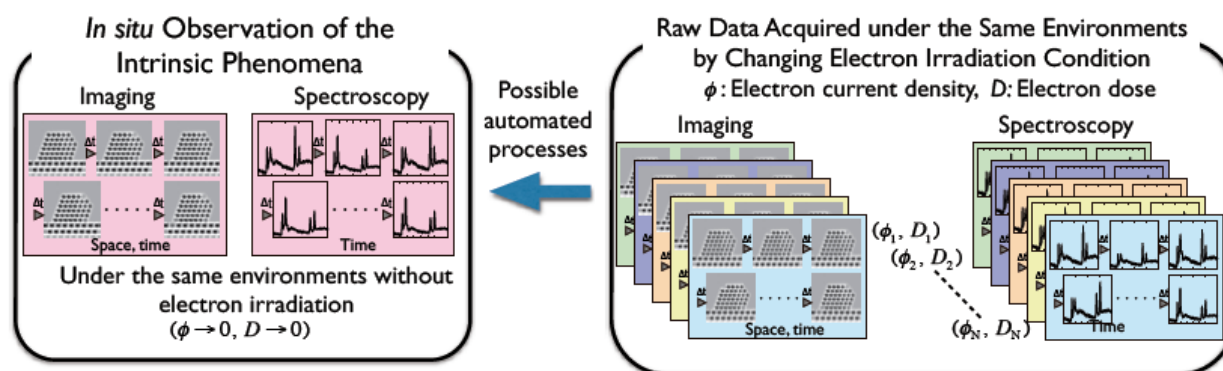
of atoms on the surface in various reaction environments. Technological development of a system for automated data acquisition and analysis of *in situ* TEM imaging combined with electron energy loss spectroscopy data, as is conceptually proposed in Fig. 2, is needed to further stimulate the ongoing *in situ* TEM of materials and devices.

#### References:

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 [2] H. M. Flower, N. J. Tighe and P. R. Swann in “High Voltage Electron Microscopy: Proceedings of the Third International Conference”, eds. P.W. Swann, C. J. Humphreys and M. J. Goringe, (Academic Press, London, 1974).  
 [3] S. Takeda *et al*, *Ultramicroscopy* (2015) doi:10.1016/j.ultramic.2014.11.017 and references therein.  
 [4] For instance, P. A. Crozier and T. W. Hansen, *MRS Bulletin* **40** (2015), 38.  
 [5] The authors acknowledge funding from Japan Society for the Promotion of Science Grant-in-Aid for Scientific Research (A) (No. 25246003) and Specially Promoted Research (No. 19001005).



**Figure 1.** (a) Gas molecules interacting with the catalytic gold surface. (b) Instantaneous structure of the gold catalyst under a reaction condition. Reproduced from [3] with permission from Elsevier.



**Figure 2.** Possible procedure for observing the intrinsic processes of materials and devices in real environments by *in situ* TEM. The procedure will be most useful in microscopy and diffraction methodologies using probes other than electrons.