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Environmental transmission electron microscopy for catalyst materials using a spherical aberration corrector

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ABSTRACT

Atomic resolution has been obtained using environmental transmission electron microscopy (ETEM) by installing a spherical aberration corrector (Cs-corrector) on the objective lens. Simultaneously, the technology for controlling the environment around a specimen in ETEM has advanced significantly in the past decade. Quantification methodology has recently been established for deriving relevant experimental data in catalyst materials from substantial and systematic ETEM observation at the atomic scale. With this background, this paper summarizes aspects of the evolutional microscopy technique: necessary conditions for atomic resolution in ETEM; reduction of the scattering of electrons by the medium surrounding a specimen; and an environmental cell for structural imaging of a crystalline specimen. The high spatial resolution of a Cs-corrected ETEM is demonstrated for different observation conditions. After statistical analysis combined with numerical image analysis of ETEM data is briefly described, the recent applications of the Cs-corrected ETEM to catalyst materials are reviewed. For gold nanoparticulate catalysts, the structural information on the reaction sites and adsorption sites are deduced. For Pt nanoparticulate catalysts, ETEM studies elucidate the correlation between the catalytic activity and the morphology of the nanoparticles. These studies also reveal oxidation and reduction on the topmost Pt surface layer at the atomic scale. Finally, current issues and the future perspectives of Cs-corrected ETEM are summarized, including the reproducibility of ETEM observation data, the control of environments, the critical evaluation of electron irradiation effects, the full implementation of transmission electron microscopy technology in ETEM, and the safety issues for an ETEM laboratory.

1. Introduction

The advancement of nanotechnology in the past two decades has brought about a great change in established experimental techniques to provide data with spatial resolution at the nanometer scale. It has also induced development of new methodologies to explore novel phenomena in nanometer space. Along with optical and X-ray microscopy techniques, transmission electron microscopy (TEM) has significantly advanced to meet the requirement in nanotechnology utilizing the wave nature of electrons. TEM has contributed to materials science since the invention by Ernst Ruska. Early in-situ studies of the dynamic nature of point defects and dislocations by diffraction contrast imaging elucidated the mechanism of radiation damage, plastic deformation and phase transformation in crystalline metals and alloys quantitatively within the accuracy available at the time of experiments. High-resolution TEM techniques also contributed to the semiconductor industry by providing structural data, especially on the artificial superlattices in semiconducting devices. The challenge of controlling the environment around a specimen in a TEM opened up a subsidiary field of TEM, which is environmental TEM (ETEM) [1–3]. It is vital to investigate the structures and properties of materials and devices in real environments and to analyze the synthesis processes of materials at the atomic scale using in-situ experimental techniques.

Because of the use of electromagnetic lenses with axial symmetry, TEMs had a practical limit in spatial resolution around 1990 that resulted from the spherical aberration (Cs) associated with any convex lens with the axial symmetry. Attempts were made to overcome this limit by varying the defocus of the objective lens, varying accelerating voltage and increasing accelerating voltage. As a result of the efforts of Rose et al., spherical aberration can now be corrected [4,5]. After 80 years, the TEM is reaching the final stage of development. More importantly, with the development of Cs corrector technology, the potential of the TEM at the atomic scale has been revealed in materials science and related fields [6–10]. Combined with evolutionary development in controlling the environments of a specimen in TEM [1–3,11–28], Cs-corrected

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ETEM is becoming one of the essential experimental techniques to investigate the structures and properties of materials and devices in real environments and analyze the synthesis process of materials in-situ at the atomic scale [19,29–32].

When using ETEM to study materials and devices, one attempts to correlate the properties of a specimen to atomic resolution images of a tiny part of the specimen. For catalyst materials, pioneering works have already attempted to correlate high-resolution TEM observations to the catalytic activity determined from catalysis chemical measurements [33]. The distribution of metal atoms and their clusters has been correlated with catalytic activity, using high-resolution STEM [34] and electron tomography [35]. ETEM provided initial results showing that the majority of metal catalysis particles change their morphology in specific gases [36]. Careful ETEM analysis led to the proposal of mechanisms of catalysis [37]. Given the atomic-scale accuracy of Cs-corrector technology, we need to develop further quantification methodologies in ETEM beyond analysis by human eyes. A quantification methodology is introduced to describe the structure of an object under ETEM observation numerically, thus allowing us to accumulate substantial numerical data by changing the partial pressure of constituent gases. It could be confirmed that the sampling area observed under atomic-resolution ETEM is a typical area responsible for the catalytic activity. Furthermore, electron irradiation effects need to be quantified to derive the intrinsic structure and properties of a catalyst specimen from ETEM observations by changing the electron current density, electron dose and the environments around the specimen systematically. In this communication, we focus on atomic-resolution ETEM imaging of catalytic materials and thus demonstrate the usefulness of the recently developed Cs-corrected ETEM, rather than reviewing thoroughly the history of the development of ETEM instrumentations and methodology. Readers can find other relevant reviews for the development of ETEM and its application, especially for catalyst materials [14,16,17]. The quantification methodology in ETEM analyses of catalyst materials, which was the firm basis for our atomic-resolution ETEM, is only briefly discussed, as it has previously been summarized elsewhere [19].

2. Necessary conditions for atomic-resolution ETEM

Acquiring atomic-resolution ETEM images requires the standard technology for atomic resolution TEM. It was claimed [14,16,17] that atomic resolution was achieved in the successive stages of the development of ETEM with the technology available at the time of development. The technology that is now available for atomic-resolution ETEM includes a Cs corrector and a device to reduce the blur in images that is caused by the coexistence of the chromatic aberration of the objective lens and the energy spread of electrons at the electron source. Instead of installing a corrector for the chromatic aberration (Cc Corrector), monochromators for the electron gun have been preferentially installed to reduce the energy spread. We identified five issues relevant to making ETEM a reliable tool for nanotechnology [19]:

1. Developing robust, easy-to-use ETEM for high spatial resolution in well-controlled environments.
2. Quantifying the effects of intense electron irradiation.
3. Understanding the significance of microstructural heterogeneity, especially that observed at atomic scale in real catalyst particles.
4. Imaging atoms and molecules during chemical reactions.
5. Bridging the temperature and pressure gaps between atmospheric and high vacuum conditions, which is an issue that has long been discussed.

The issues need to be addressed to establish a firm experimental foundation for quantitative atomic-resolution ETEM observations of materials and devices that are operating in gases.

In this section, we summarize the conditions required for atomic-resolution ETEM.

2.1. Reduction of the scattering of electrons by the medium surrounding a specimen

The effect of the gas or liquid surrounding the specimen needs to be considered in atomic-resolution ETEM [19,38–41]. The incident electron wave that passes through the medium layer (gas and/or liquid) above a specimen cannot be approximated as a planar wave. The electrons scattered by a specimen are subsequently scattered by the medium layer below the specimen. Elastic and inelastic scattering by the medium-layer degrade coherent ETEM images. The effect of gas on ETEM images was discussed only qualitatively until a theoretical analysis led us to simulate and evaluate the degrading of ETEM images by gas molecules quantitatively [39]. More recently, it was shown that ETEM images in gas are more degraded under electron irradiation with higher electron current density (higher dose rate) [40]. To reduce the scattering by the medium, the path of electrons in the medium layers should be shortened [19,39].

In tracing the technical development of ETEM, it is seen that two types of environmental cell (E-cell) were defined for introducing gas into a TEM in the early 1970s and intuitive drawings were made of the pole pieces of the objective lens [Ref. 3, [Fig. 1]]; the E-cells are the differentially pumped aperture type and window type. The purposes of application of E-cells at that time were to reduce contamination of the specimen, to study wet biological materials, and to study chemical reactions at elevated temperatures [3]. E-cells have been developed by several different research groups using TEMs made by different manufacturers, especially for exploring chemical reactions including catalytically chemical reactions [1–3,11–28]. In our view, the definitive pioneering work employing ETEM of differential pumping aperture type was published by Hashimoto et al. [2] in 1968 in collaboration with JEOL. They observed in situ the growth process of plate-shaped Cu crystal that formed via the reduction of CuI at elevated temperature in hydrogen gas and the growth process of ribbon-shaped molybdenum oxide crystals formed by the heating of ammonium molybdate in air. Several different designs have been proposed to introduce gas and liquid in a specimen chamber in a TEM, a few of which are commercially available.

In the differential pumping aperture E-cell for gas, the column of a TEM is heavily modified to install a differential pumping vacuum system [11–19]. In the differential pumping aperture type, sets of orifice plates are arranged along the path of electrons. The first set of orifice plates needs to be close to the specimen to keep the pressure of gas around a specimen higher than that in the other parts of the column, in particular the electron gun and the accelerating tube, which should be at pressures less than 10^{-5} Pa. Usually, the first set of plates is placed in the bores of a pair of pole pieces of the objective lens. A large chamber around a specimen provides a laboratory for specimen and materials syntheses measurements. Alternatively, it is possible to introduce gas of low pressure into a specimen chamber of conventional TEMs and ultra-high-vacuum TEMs without any modification of the columns of the TEMs, though the maximum pressure of gas during observation is limited to the order of 10^{-3} Pa [42–44].

A window-type E-cell for gas and a window-type E-cell for liquid (a liquid cell) are preferentially installed in a specimen holder of side entry type [20,22–28], and a pair of parallel thin foils acts as windows that are transparent to the electron beam to some extent. With the introduction of microelectromechanical system

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