High-resolution low-voltage scanning electron microscope study of nanostructured materials

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INTRODUCTION
Scanning electron microscopy (SEM) is one of the most powerful techniques for studying surface fine structured[1]. New instrumental developments, such as an improved objective lens with lower aberrations coupled with an aberration corrector have been reported to improve the resolution of SEM images in a general sense [2]. Furthermore, a low-voltage high-resolution (LVHR)-SEM has been developed for observation of surface fine structures through the introduction of an electron-beam deceleration method.

The length of the electron mean free path of 100 eV electrons beneath the surface of a solid sample needs to be below 1 nm in order to produce the necessary images required [3]. Therefore it should be possible to clearly observe surface morphology. However, the low impact energy required to produce such a situation significantly increases the diameter of probe because of the increased effect of chromatic aberration (C_a) at low accelerating voltages.

The diameter of an electron probe d_c can be expressed as: \(d_c = C_a \frac{\Delta E}{E_{acc}}\), where \(\Delta E\) is the energy spread with respect to the primary electron beam and \(\Delta E\) is the convergence angle of the beam [4]. Therefore, at lower voltages it is necessary to minimize both the energy spread and \(\Delta E\) in order to obtain the minimum probe diameter for high spatial resolution imaging. In this article we describe a new observation technique for high-resolution imaging at low landing energy SEM on nanostructured materials.

Nanoporous materials such as zeolites and mesoporous crystals have attracted a lot of attention in recent years. These types of materials have been widely used in the field of catalysis [5, 6], and are gaining prominence for researchers' ability to alter their properties via incorporation of various metal nanoparticles and organic molecules within the pore network. In order to precisely control this new functionality of nanoporous materials it is crucial to understand their structure, growth mechanisms and composition. Traditionally, nanoporous materials have been examined either in TEM for structure determination via diffraction and HRTEM or in SEM at relatively low magnification for overall particle morphology. The recent advances in low voltage SEM technology have been instrumental in the ability to observe the fine surface structure of these pore networks (see for example [7]), twinning and growth features in zeolites [8], especially since the majority of these materials are insulating. Moreover, the ability to filter collected signals and high-resolution low voltage backscatter imaging allow observation of compositional differences as well as precise location of nanoparticles within the individual pores.

MATERIALS AND METHODS
NEW OBJECTIVE LENS AND DETECTION SYSTEM FOR LVHR–SEM
We have developed a new objective lens called the super hybrid lens (SHL) a compound lens consisting of both magnetic and electrostatic lenses [4]. The SHL is capable of producing a small probe size even at low accelerating voltages (for example 1.2 nm at 1 kV and 3.0 nm at 0.1 kV) and moreover allows imaging down to 10 V.

A schematic drawing of the SHL installed in a JSM-7800F field-emission SEM (FE-SEM) is shown in Figure 1. Microscopes fitted with SHL are also capable of electron energy-selected imaging when combined with a new detection system consisting of two differently placed detectors: an upper electron detector (UED) and an upper secondary electron detector (USD), together with a filter located between SHL and UED, as shown in Figure 1.

This detection system is designed to act as a kind of simple spectrometer; that is, when a negative bias voltage, say -100 V, is applied to the filter, electrons with a kinetic energy larger than 100 eV can pass through the filter to be detected by the USD, whereas those with a kinetic energy lower than 100 eV are deflected by it to be detected by the USD. The results are nearly genuine secondary electron (SE) and backscattered electron (BSE) images at high magnification.

SAMPLE PREPARATION FOR LVHR–SEM
Contamination of the sample surface has a negative effect on imaging quality, and is particularly detrimental in low-voltage imaging where only the top few nanometers of the structure are probed with the electron beam. The main sources of contamination are from the specimen itself (physically adsorbed gaseous species), the specimen holder and the microscope chamber.

Therefore, we selected a highly conductive carbon

Figure 1
Schematic of the super hybrid lens in a scanning electron microscope.

Key: ACL: aperture angle control lens
LED: lower electron detector
OL: objective lens
SHL: super hybrid lens
SRBED: solid-state retractable backscatter detector
UED: upper electron detector
USD: upper secondary detector
stubs for our HR-SEM experiments. This stub was first polished with a sandpaper (#1200) and then with a filter paper to make the surface smooth. It was then cleaned by ultrasonication in alcohol and heated in vacuum. The samples described in this paper were prepared by one of two methods. With the first method, nanoparticles were dispersed in solution and then a drop was placed on the carbon stub. The stub was then heated in a vacuum oven for 10 min at 200°C and subsequently cooled to room temperature. The second preparation method was employed for dried particles, which were picked with a cotton ball and scattered on a carbon stub that was polished with filter paper and dried on a hot plate at 250°C. Samples were analyzed using a FE-SEM using the low-voltage condition.

RESULTS AND DISCUSSION Figures 2a and 2b show LVHR-SEM images of magnetite (Fe₃O₄) particles taken at 1 kV and shows the shape and diameter of the individual particles and fine detail of surface topography. Figure 2b clearly shows 10 nm size primary particles without any surface damage or imaging distortions resulting from charging up of the Magnetite sample by electrons.

LVHR-SEM images of mesoporous silica SBA-15 taken at 1 kV are presented in Figure 3 and show fine surface structure. The micropores are clearly observed without damage and charging effects are negligible. The images clearly show pore diameters below 2 nm.

Figure 4 shows energy filtered electron images of Au on TiO₂ at a magnification of 150,000 at 2 kV. Figures 4a and 4b were obtained simultaneously with FE-SEM, using USD and UED, respectively, with a filter bias voltage of ~500 V. Figure 4a corresponds to a genuine SE image and shows very fine structural details of the rattle spheres, whereas Figure 4b corresponds to a genuine BSE image and shows compositional contrast. In the latter image a few gold particles including the one at the center with a size of 10 nm could be observed as bright contrast (the Au particles are pointed out with arrows). Thus, the present detection system is confirmed to serve as an energy filter especially at low voltages.

In order to observe the internal structure of the mesoporous specimen, we have employed an argon beam-based specimen preparation device, Cross-section Polisher (CP, JEOL Ltd)[9]. It has been demonstrated that LVHR-SEM combined with CP is a powerful technique to investigate both external and internal fine structures of nanostructured materials[7, 9]. Figure 5 shows a LVHR-SEM image of cross-sectioned SBA-15. The image clearly shows not only the arrangement of mesopores but also fluctuations of the pore size and shape without damage or contamination during cross-sectioning.

Specimen charging is one of the main contributors to the loss of information when observing nanoporous materials surfaces. The effect of charging manifests itself as either ‘flattening’ of the image due to the beam deflection close to the source of charging (in this case a nanoporous particle), or extremely high or low contrast and image distortion. Since charging is a result of a build-up of an inhomogeneous electric field generated when source electrons impact the specimen surface, it may be possible to balance the charge via precise control over the ratio of emitted to impact electrons using specimen bias.

The accelerating voltage which along with lens aberrations determines the minimum probe size and thus the resolution limit is retarded by a negatively charged stage bias to a lower landing energy. The landing voltage $E_{\text{landing}} = E_{\text{gun}} - E_{\text{bias}}$ and can be varied with a combination of gun voltage and specimen bias to achieve the necessary imaging performance and obtain high resolution ultra-low kV results, with typical values from 0–5 kV for specimen bias. This approach preserves the advantages of high kV imaging (gun brightness, small probe size) with added advantages of low landing voltage (reduced charging, specimen contamination, improved surface detail).

A practical advantage of this approach is that the influence of the stray magnetic fields on imaging is also significantly reduced, since the low energy primary electrons are only confined to a small area on the sample surface and the gun is operated at higher kV. An additional benefit is that specimen bias and the resulting electric field overcome the small electric fields that may exist at the sample surface under standard imaging conditions, and thus remove the streaking, localized charging and any other disruptions to the emitted electron trajectories.

The JSM-7800F has a beam deceleration mode allowing specimen imaging down to 10 V. This mode provides the ultimate surface sensitive imaging, without loss of resolution. Figure 6

![Figure 2](image) (a, b) LVHR-SEM images of magnetite (Fe₃O₄) particles. The images were taken at 1 kV with the UED detector. The images show the individual building blocks (5-10 nm) that make up the larger ~300-nm diameter particles.

![Figure 3](image) (a, b) LVHR-SEM images of mesoporous silica SBA-15. The images were taken at 1 kV with the UED detector. The images show the nanopore surface structure.

![Figure 4](image) Comparison of electron energy-selected images of Au nanoparticles on TiO₂. (a) USD SE image. (b) UED image with filter bias of ~500V highlighting the positions (arrows) of the Au nanoparticles (BSE compositional sensitivity) with respect to the TiO₂ support.
shows an image of SBA-15 taken at 10 V landing voltage, with nanopores clearly resolved. The image sensitivity to the surface confined information also highlights the various defects in the pore structure that get somewhat lost in the higher kV images.

CONCLUSIONS
The ability of the SEM to observe nanomaterials with ultra-high resolution and exceptional surface detail, in particular low-voltage SEM have been due in part to improvements in objective lens optics and the ability to deal with charging specimens via precise control of the landing energy of primary electrons and improvements in electron signal detection. Advances in instrumentation continue to push the boundaries of what is possible with electron microscopy and the resolution and analytical capabilities of SEM continue to improve in the low-voltage regime. An important consideration should also be given for sample preparation and mounting procedures, as those can substantially impact the imaging at low accelerating voltages. This paper demonstrates that the combination of SEM and improved sample preparation are key for observation or analysis of nanostructured materials.

REFERENCES

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