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Imaging ZnO Nanobelts and Nanobelt-Supported Metal Nanocatalysts by Aberration-Corrected Scanning Transmission Electron Microscopy

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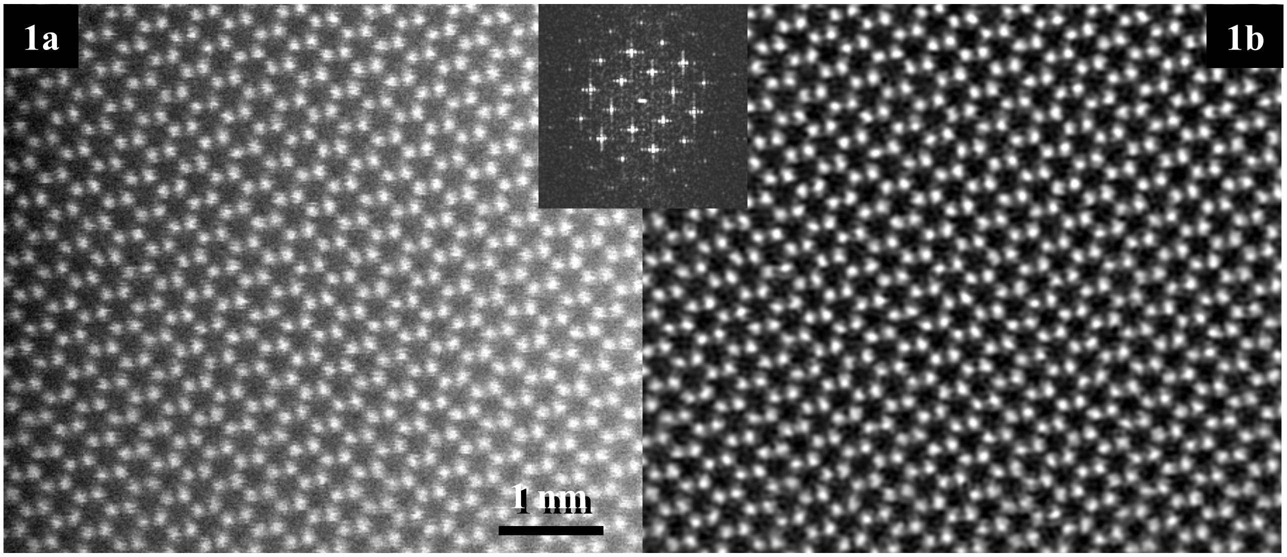
The development of aberration correctors and their routine applications in transmission and scanning transmission electron microscopy mode have enabled sub-Ångström imaging of practical nanoscale materials and nanocatalysts. To correctly interpret the observed image contrast of practical samples is, however, still challenging. For example, the contrast of the various features in a high-angle annular dark-field (HA-ADF) image can be affected by many parameters such as sample tilt [1], presence of amorphous materials [2], overlapping crystallites, electron-beam channeling, etc. The visibility and image contrast of individual monomers, dimers or small clusters supported on relatively thick crystalline substrates may be modulated by tilting the substrate crystal away from electron-beam channeling conditions or the major zone axes.

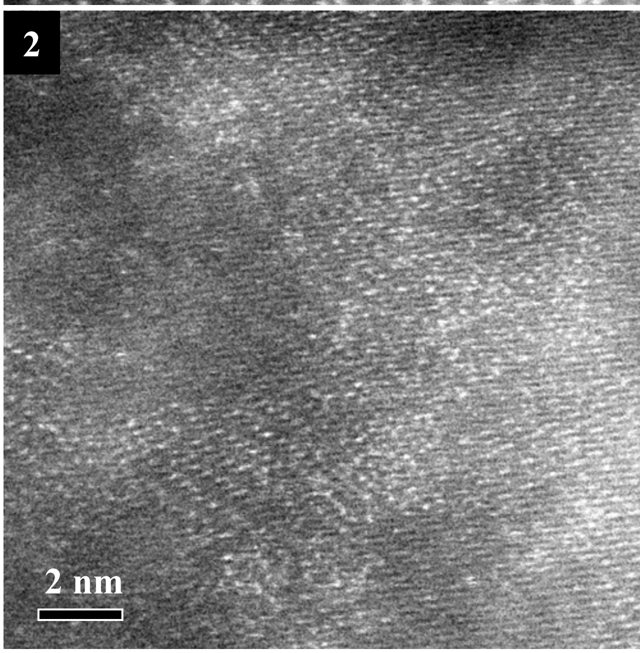
ZnO nanobelts or nanoribbons were fabricated by a thermal evaporation-condensation method in a high-temperature tube furnace. The deposition-precipitation of Pd was accomplished by dipping the ZnO nanobelts into an aqueous solution containing $Pd(NO_3)_2$ as precursor salts. Because ZnO nanobelts dissolve quickly in an acidic solution, the pH value of the aqueous solution was maintained, by adding NaOH, between 6 and 7. The precursor materials were then reduced in situ inside a JEOL 2200FS scanning transmission electron microscope (STEM) equipped with a CEOS Co. aberration corrector which provides a nominal imaging resolution of about 0.07 nm. A novel heater assembly, provided by Protochips Co. (Raleigh, NC), was used to heat up the precursor materials to desired temperatures.

Figure 1a shows an atomic-resolution HA-ADF STEM image of a ZnO (0001) nanobelt. The corresponding diffractogram is shown in the inset. Figure 1b shows the band-filtered image of Fig. 1a to better reveal the atomic positions of the Zn/O columns. The diffractogram indicates that periodicities better than 0.09nm are clearly revealed in the HA-ADF image. Figure 2 shows a HA-ADF image of a Pd/ZnO nanobelt precursor material. The brighter dots represent individual Pd atoms located on top of Zn columns (grey dots). It is interesting to note that some of the Pd atoms are aligned together to adapt to the lattice spacing of the Zn layers of the ZnO single crystals. Figure 3 shows an atomic-resolution HA-ADF image of a PdZn alloy nanoparticle, obtained after in-situ heating of the precursor sample at 500°C for about 30 minutes, clearly revealing an epitactical relationship between the PdZn alloy nanoparticles and the ZnO nanobelts. The epitactical growth of PdZn on the ZnO support makes the catalyst more resistant to sintering. The contrast modulation of the PdZn alloy nanoparticle may be due to the disturbance of the electron beam channeling condition by the relaxation of the interface dislocation networks between the PdZn nanoparticle and the ZnO substrate. The contrast mechanisms of nanoparticles epitactically grown on ZnO and the visibility of individual atoms on ZnO nanobelts will be discussed [3].

References

[1] Z. Yua, D.A. Muller and J. Silcox, *Ultramicroscopy* 108 (2008) 494.
[2] K.A. Mkhoyan et al., *Ultramicroscopy* 108 (2008) 791.
[3] This research at the Oak Ridge National Laboratory's High Temperature Materials Laboratory was sponsored by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program, and by the University of Missouri.





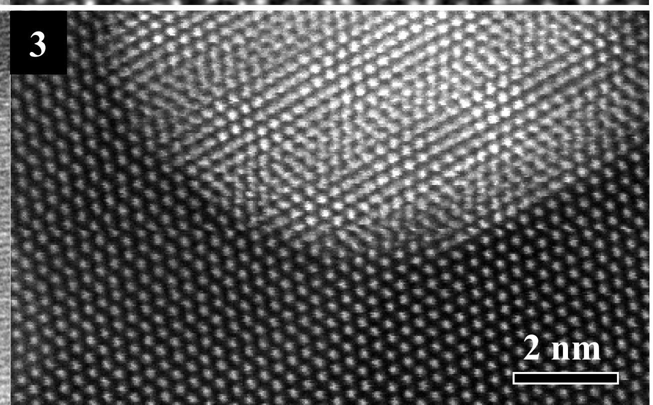


Fig. 1. Atomic-resolution HA-ADF image of a ZnO (0001) nanobelt: a) raw image and b) band-filtered image. The diffractogram is shown in the inset.

Fig. 2. Atomic-resolution HA-ADF image of a Pd/ZnO precursor material reveals the individual Pd atoms. The ZnO crystal was tilted away from strong channeling conditions in order to enhance the visibility of the Pd atoms.

Fig. 3. Atomic-resolution HA-ADF image of the Pd/ZnO precursor material after being heated inside the microscope at a nominal 500°C for 30 minutes. The patterned contrast of the PdZn alloy nanoparticle may be due to the relaxation of the dislocation networks at the nanoparticle-ZnO interface.

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