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In Situ Investigation of the Carbothermal Reduction of ZnO Nanowires

Jingyue (Jimmy) Liu[1] and Lawrence F. Allard[2]
[1.] Department of Physics, Arizona State University, P. O. Box 1504, Tempe, AZ, USA.
[2.] Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA.

Carbothermal reduction is among the oldest chemical processes, commonly used in the production of metals from the corresponding metal oxides or ores (e.g., iron from iron oxides). By using carbon as a reducing agent, decomposition of metal oxides at temperatures much lower than their typical decomposition temperatures can occur. However, a detailed fundamental understanding of such a reaction process, especially on an atomic scale, is still not available [1]. In view of the recent advances in utilizing the carbothermal reduction process to grow metal oxide nanostructures, especially ZnO nanostructures [2], and the interest in developing C/ZnO nanocomposites, we investigated the interaction of carbon with ZnO nanowires (NWs) at elevated temperatures by *in situ* aberration-corrected scanning transmission electron microscopy (STEM) techniques.

The ZnO NWs were fabricated by a thermal evaporation-condensation method in a high-temperature tube furnace [2]. The attachment of carbonaceous species to the synthesized ZnO NWs can be accomplished via ethanol steam reforming (a coking process), by soaking them with acetone, or by directly depositing them onto a carbon film support. The NWs were heated in the ~2 x 10^{-5} Pa vacuum of a JEOL 2200FS STEM/TEM instrument, using Protochips Inc. (Raleigh, NC) Aduro^{TM} E-chip MEMS-based heating technology, which allows precision heating/cooling at up to 10^6 °C/sec [3]. The microscope is equipped with a CEOS GmbH (Heidelberg, Ger.) aberration corrector for the probe-forming lenses, which provides a nominal imaging resolution of about 0.07 nm [3]. It was used to analyze the detailed structural information of the ZnO NWs and their interactions with carbon.

Figure 1a shows a composite image formed by combining a high-angle annular dark-field (HAADF) and a bright-field (BF) STEM image, clearly revealing the relatively flat {10-10} surfaces of the synthesized ZnO NW and the carbonaceous coating layer. Figure 1b shows a ZnO NW after being heated inside the microscope at 600 °C for 5 minutes. A new crystalline phase was seen to form on the outside layers of the ZnO NW. Figure 1c shows a different ZnO NW with Pt nanoparticles. It appears that the presence of the Pt nanoparticles prevented the direct contact between carbon and the ZnO surface, thus effectively reducing the rate of the carbothermal decomposition of the ZnO. When the heating temperature was increased to 800°C, significant ZnO decomposition and vaporization occurred. Figure 2 shows the morphology of the ZnO NWs after being heated *in situ* at 800°C for 30 minutes. *Ex situ* experiments on the heat treatment of carbon-coated ZnO NWs showed similar morphological changes. The presence of the newly formed polar surfaces ({10-11} and {0001} nanofacets) significantly modified the catalytic properties of the ZnO nanowires [4].

References

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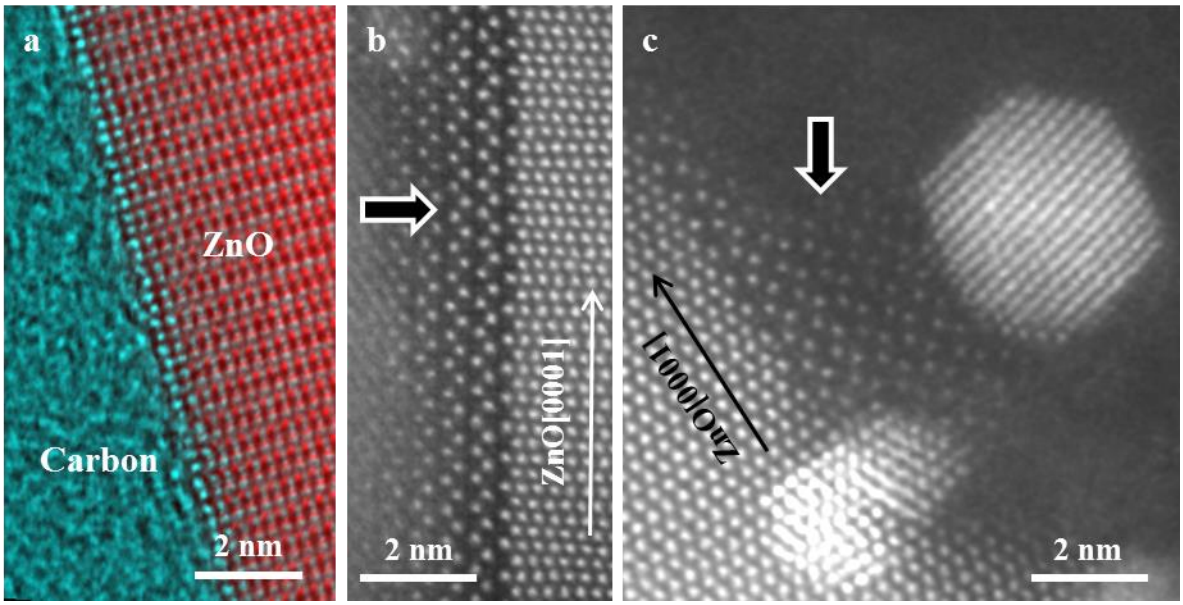

Figure 1. a) HAADF and BF STEM composite image shows a ZnO NW coated with carbonaceous species; b) HAADF image showing a NW after being heated inside the microscope at 600 °C for about 5 min; and c) HAADF image of another ZnO NW with Pt nanoparticles. New crystal structures (indicated by the bold arrows in (b) and (c)) were formed after the heat treatment.

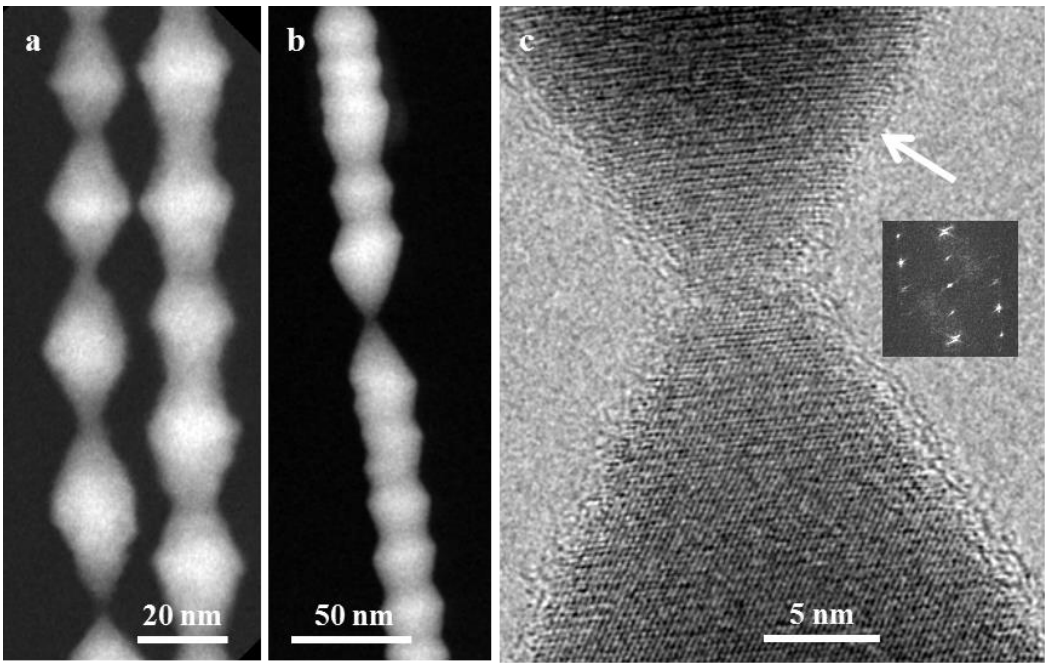

Figure 2. a,b) HAADF images showing the morphology of ZnO nanowires after *in situ* heat treatment at 800 °C for 30 min. The BF STEM image (c) and the digital diffractogram (inset) show the newly formed ZnO {10-11} surfaces (indicated by the white arrow). Traces of carbon material on the surfaces of the ZnO NWs were still discernible in the BF STEM image. The NW was oriented close to the ZnO [11-20] zone axis.

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