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In-situ TEM Study of Optical and Mechanical Effects on Electrical Properties of CuO Nanowires

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Photoelectrochemical (PEC) cells have attracted great interest for mass production of hydrogen using unlimited solar energy [1]. To achieve high solar-to-hydrogen conversion efficiency, however, it requires the stable photo-electrodes with optimum band gaps for wide spectral coverage and effective charge separation. Metal oxides are shown promising properties besides its high abundance and relatively cost-effective, scalable fabrication [2]. However, most oxides are intrinsically n-type, suitable for photo-anodic water splitting. Copper oxide (CuO) is one of the most studied metal oxides as an intrinsically p-type photo-cathode with a band gap of 1.4eV, suitable for visible light spectrum [3].

Nanowire (NW) geometry is the promising alternative to the bulk system, since it offers enhanced light absorption, reduced carrier diffusion length, and increased surface reaction area – critical for effective solar-to-hydrogen conversion. In this study, the CuO NW arrays were synthesized on a copper foil using thermal oxidation method before annealed in air at 400 – 500^{o}C for 3-5 hours. The structure of CuO NWs was examined using aberration-corrected scanning transmission electron microscopy (STEM). Specimens for *in-situ* transmission electron microscopy (TEM) studies were prepared using a focused ion beam (FIB) system (FEI's Helios 650) by gently pulling out a single CuO NW and attaching it to a pre-loaded Cu grid with Pt. The Cu grid is loaded onto a scanning tunneling microscopy holder with miniature light-emitting diode setup that provides *in-situ* incoherent optical excitation. Optical and mechanical effects on electronic behaviors of NWs were examined *in-situ* in the TEM.

Single crystalline monoclinic CuO NWs, similar to one shown in Fig. 1, demonstrated symmetric Schottky diode behavior originated from back-to-back metal contacts during voltage biasing of -1 to 1V. These CuO NWs show a strong photo-electric response to light illumination due to reduction in Schottky barrier height and carrier depletion width. Under applied mechanical stress, considerable enhancement in conductance was observed in NWs with increased elastic bending (Fig. 2). Bending-induced distortion in crystal symmetry is likely to influence the energy band structure by either raising (under compressive stress) or lowering (under tensile stress) the band gap, in agreement with density functional theory (DFT) calculations. Furthermore, when higher voltage is applied, these NWs undergo sudden reduction from CuO to pure metalized Cu as demonstrated from selected area electron diffraction (SAED) and electron energy loss spectroscopy (EELS), as shown in Fig. 3.

In conclusion, our *in-situ* TEM studies have shown that a CuO NW exhibits a significant electrical response to visible light and mechanical stress. These findings contribute to understanding device physics of one of widely-known oxide semiconductors and provide key information not only to already existing nano-scale device technology, but also to the development of novel energy conversion materials.

References:
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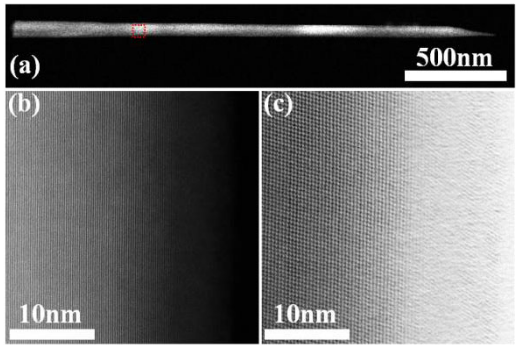

Figure 1. (a) Low magnification and (b, c) high-resolution dark-field and bright-field STEM micrographs of a single CuO NW.

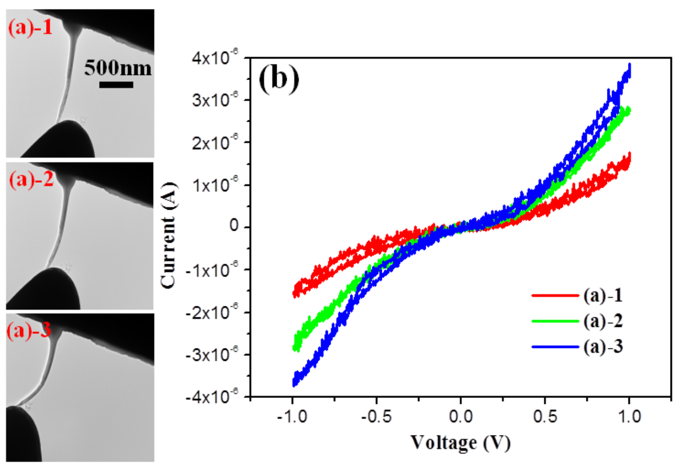

Figure 2. (a) TEM images of mechanical bending of a CuO NW in TEM and (b) I-V curves corresponding to each bending point.

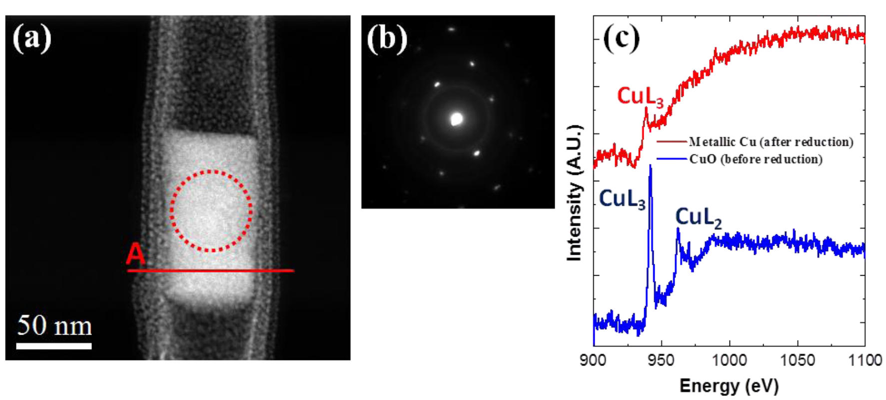

Figure 3. (a) STEM image of a CuO NW after reduction to Cu and (b) its diffraction pattern (from (a)-circle) and (c) EELS spectra of a CuO NW before and after (average from line-scan A) reduction.

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