Abstract #2289, 224th ECS Meeting, © 2013 The Electrochemical Society

Composition and structure control of copper oxide (Cu_2O and CuO) nanowires via thermal routes

Fei Wu, Parag Banerjee
Department of Mechanical Engineering and Materials Science, Washington University,
One Brookings Drive, St. Louis MO -63130, USA

Cupric oxide (CuO) and cuprous oxide (Cu_2O) are p-type metal oxides with a band gap of 1.3eV and 2.2eV, respectively making them attractive candidates for solar harvesting applications. Amongst a variety of synthesis methods available, none possesses the simplicity of Cu thermal oxidation. Here, high purity Cu foils are oxidized in atmospheric conditions to obtain 1) high density (10^{10} cm^{-2}), single crystal CuO nanowires (NWs) tens of microns long embedded in 2) a matrix of a thin CuO film (~ 1µm) with 3) a thicker Cu_2O sub-layer (6-8µm). **Figure 1A,B** show this structure. The causes for the high density NW formation has been attributed to outflux of Cu^{2+} ions from the Cu foil through the trilayered structure via short-circuited diffusion paths such as grain boundaries. Thus, while the structure possesses high surface area and high density 1-D nanostructures it does contain inhomogeneity in structure and composition which make practical applications hard to achieve.

In this work, we develop processes which induce controllable phase transformations that in turn produce nanowires and sub-layer structures ranging from pure CuO to pure Cu_2O, thus opening up avenues for their direct application in a variety of energy centric devices.

To obtain homogenous CuO NWs and pure CuO sublayer structure high purity Cu foils are cold-rolled to thicknesses of ~ 20µm. The resultant foil when oxidized consumes all the Cu and extensive oxidation past the consumption of all Cu atoms cause the conversion of the Cu_2O sublayer structure to CuO (**Figure 2A,B**).

For obtaining Cu_2O NWs and sublayer structure, reducing conditions are created using vacuum annealing inside closed carbon crucibles. Our results indicate that a complete conversion of the CuO to Cu_2O occurs at 400 ^oC for 3 hours (**Figure 2C,D**). Much of the NW structure is intact and no evidence of CuO phase is found.

Extensive structural characterization includes confocal Raman, XRD, SEM and TEM. Electronic properties are ascertained using current-voltage, photocurrent and conductivity vs. temperature measurements.

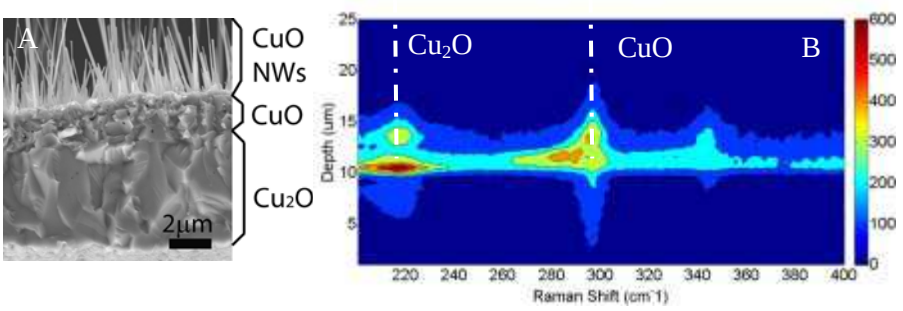

Figure 1: a) SEM cross-section of CuO nanowires (NWs) and underlying substructure which consists of 1µm CuO and 5-6µm Cu_2O layers b) confocal Raman showing Cu_2O and CuO signal confirming the presence of the tri-layered structure.

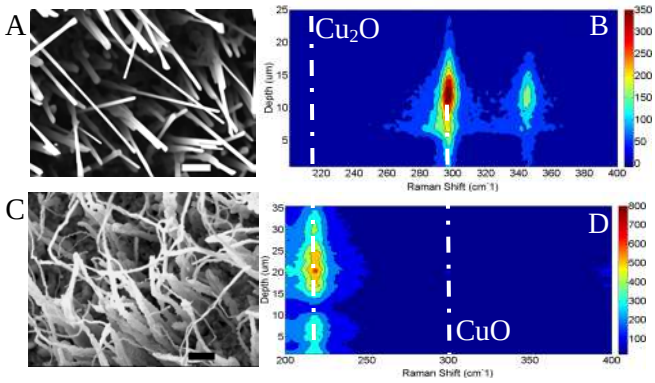

Figure 2: A) SEM of CuO NWs and B) confocal Raman showing complete conversion of substructure to CuO under Cu diffusion limited conditions C) CuO NWs are reduced to Cu_2O NWs under strongly reducing conditions and D) confocal Raman confirming the conversion process with no presence of CuO phase. The arrow bar is 2 µm.