

Cu₃N Nanowires: Growth and Properties

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S1. Growth of CuO Nanowires on Cu Foils

Several attempts have been made in order to achieve a dense and uniform distribution of CuO nanowires (NWs). The CuO NWs were not obtained for shorter growth times or smaller gas flows of oxygen than those mentioned in the main paper. In particular, we did not obtain a uniform distribution of CuO NWs by using 75%Ar:25%O₂ for 60 min, similar to air, which resulted in the formation of isolated networks of CuO NWs on the Cu foil. The coverage and uniformity did not improve by using 75%Ar:25%O₂ and increasing the oxidation time from 60 to 120 min.

A uniform and dense network of CuO NWs on the Cu foil over areas up to 15 × 30 mm² was formed for 300 ml/min O₂ flow and an oxidation time of 2h. However, their integrity and adhesion to the underlying Cu was poor. More specifically, we found that the bulk CuO layer supporting the CuO NWs cracked, revealing the underlying red Cu₂O layer on top of the Cu foil. This occurred upon cooling down and even at room temperature without manipulating the Cu foil and is attributed to the lattice mismatch between the intermediate layer of CuO and Cu₂O which gives rise to interfacial stress leading to the breakup of the CuO layer supporting the CuO NWs. We tried to improve the integrity of the CuO NWs by pre-annealing the Cu foil at 600°C for 1 h under a flow of 450:50 Ar:H₂ but this had a negative impact on the uniformity and density of the CuO NWs attributed to an increase in the size of the crystal grains of the Cu foil. In addition, cold-roll-pressing of the Cu foils resulted in a better integrity but the growth of CuO NWs occurred mainly near the edges of the Cu foil, attributed again to an increase in the size of the grains. We also observed that a controlled rate of cooling did not always give a CuO NW network of solid integrity.

Finally, we tried to improve the integrity of the CuO NWs by in-situ etching of the Cu surface under 300:100 ml/min $\text{NH}_3:\text{O}_2$ at 600 °C for 30 min. The reaction of NH_3 with O_2 leads to the formation of H_2O that reacts with the Cu surface giving $\text{Cu}(\text{OH})_2$ which has a melting point of just 80°C. In this case we obtained a sparse network of CuO NWs. Evidently the preparation and structural properties of the Cu foil is critical for the realization of a stable network of CuO NWs that is suitable for the realization of energy storage and conversion devices.

In short , the growth of CuO NWs on Cu foils is straightforward but the CuO NWs are not firmly anchored to the underlying Cu foil due to the intermediate bulk layers of CuO and Cu_2O that have a significant degree of lattice mismatch. Before considering the conversion of the CuO into Cu_3N NWs under NH_3 and $\text{NH}_3:\text{H}_2$, it is useful to describe the reduction of the CuO into Cu NWs under Ar: H_2 flow.

S2. Reduction of CuO into Cu Nanowires

The reduction of the CuO into Cu NWs under Ar: H₂ is important as the reaction of Cu with NH₃: O₂ gives Cu₃N as shown by Matsuzaki *et al.*^{S1} and more recently by Zervos *et al.*^{S2}

The reduction of cupric oxide i.e. CuO by H₂ was investigated in detail as early as 1921 at Princeton by Pease and Taylor.^{S3} The same approach is still used today for the reduction of CuO nanostructures into Cu as shown by Khadga *et al.*^{S4} who used 240 ml/min of 4% H₂ in He at 285 °C for 60 min in order to reduce CuO nanoscale rods into Cu. The reaction pathway and change in the oxidation state of Cu, i.e. reduction from +2 to 0, occurs via the following intermediate steps i.e. $\text{CuO} \rightarrow \text{Cu}_3\text{O}_4 \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$ and can be described by the overall reaction $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$. Similarly, Kim *et al.*^{S5} described the reduction of CuO and Cu₂O into metallic Cu under He:H₂ flow and showed that the complete transformation to metallic Cu starts near 300° C while Rashid *et al.*^{S6} obtained Cu NWs with curly like shapes in just 3% H₂ in Ar at 300°C. It should be noted here that Cu NWs can also be obtained by electrodeposition^{S7} but this is more complicated than the reduction of CuO into Cu NWs as it requires the formation of a nanostructured template on a conductive substrate.

Initially we attempted to reduce the CuO to Cu NWs at low temperatures, i.e., 200°C for 30 min under 290:10 ml/min Ar:H₂. We found that the CuO NWs were partially reduced to CuO and Cu₂O as shown by the XRD in Fig S1 (a) and also observed that they remained straight while there was no reduction in the network density, as shown in Fig S1 (b). Increasing the temperature to 300 °C gave similar results. Consequently, we used a gas

flow of 100 ml/min pure H₂ and the CuO NWs were reduced to Cu and Cu₂O at 300°C for 15 min. We observed an increase in the Cu and Cu₂O peaks in Fig S1 (c) by extending the reduction time from 15 to 30 and 60 min. The Cu/Cu₂O NWs were very narrow and had a curly shape, as shown in Fig S1 (d) while a visible condensation of H₂O was also observed at the cool end of the reactor due to the reaction of the hydrogen with the oxygen. It is quite plausible that the H₂O formed by the reduction of CuO under H₂ will react in the process with Cu giving Cu(OH)₂ that has a low melting point of 80°C and consequently the CuO NWs will suffer a reduction in their size.

We tried repeatedly to convert the CuO NWs into pure Cu NWs between 200 and 300 °C under a flow of H₂ or a mixture of Ar:H₂ but residual Cu₂O was always detected. Moreover, we observed the complete loss of the CuO NWs above 400 °C. In order to prevent this, we deposited 240 nm of Cu on the surface of CuO NWs by sputtering and a typical SEM image is shown in Fig S1 (e). Subsequently the Cu/CuO NWs were annealed at higher temperatures of 400 °C and 500 °C under H₂. A typical SEM image of the reduced Cu/CuO NWs is shown in Fig S1 (f). The Cu/CuO NWs maintained their integrity but CuO as well as Cu₂O was still detected as indicated by the Raman spectra in Fig S1 (g).

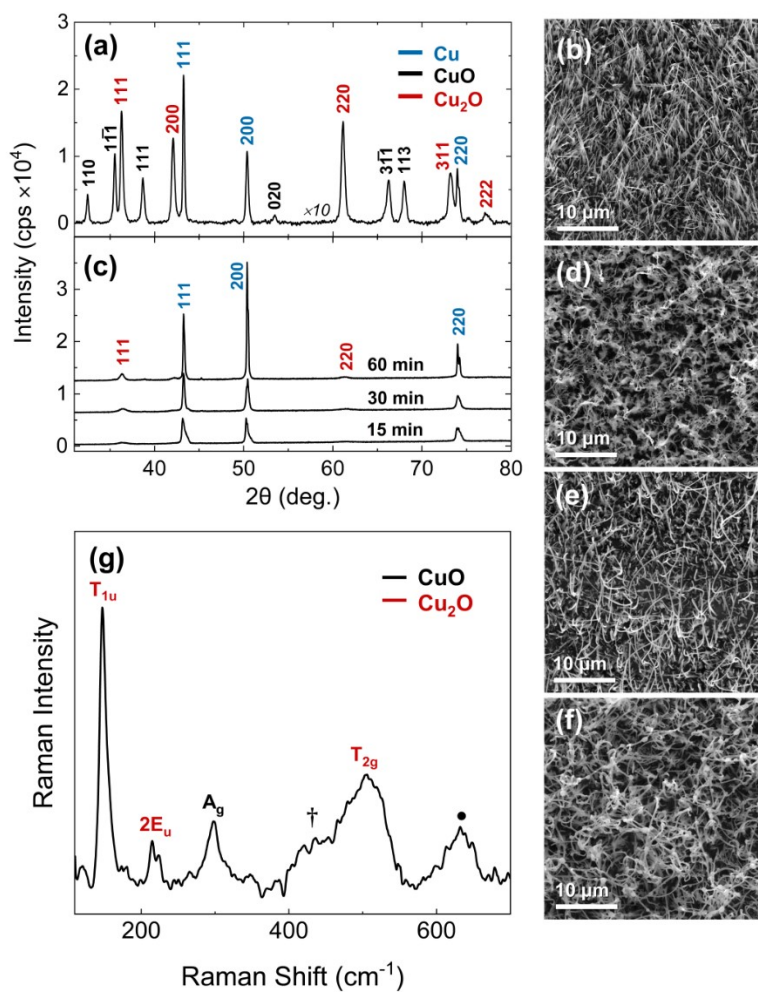


Fig. S1 (a) XRD pattern and (b) SEM image of the reduced CuO NWs under 290:10 ml/min Ar:H₂ at 200°C for 30 min. (c) XRD patterns of the CuO NWs under 100 ml/min H₂ at 300°C for 15, 30 and 60 min and (d) corresponding SEM image for 60 min. (e) SEM image of the CuO NWs coated with 240 nm Cu before and (f) after annealing under 100 ml/min H₂. (g) Raman spectra of the CuO NWs that were coated with 280 nm Cu and reduced under 100 ml/min H₂ at 400°C for 30 min. Both Cu₂O and CuO are present, the latter having a smaller contribution. The peaks indexed with † are attributed to Cu₂O and those with • to both CuO and Cu₂O.

S3. Nitridation of CuO into Cu₃N Nanowires

Initially, the CuO NWs were treated under a flow of NH₃ at 300, 350 and 400°C for 60 min. The CuO NWs maintained their integrity at 300°C and consisted mainly of CuO and Cu₂O. Higher temperatures of 350 °C and 400 °C resulted in the conversion of the CuO into Cu₃N NWs but an increased contribution of residual Cu₂O was still detected. In addition, we observed a small reduction in the network density of the CuO NWs. Similar results were obtained by treating the CuO NWs under a mixed flow of NH₃:H₂ but we observed a significant reduction in the density of the CuO NWs at 400°C consistent with our findings from the reduction of the CuO NWs under H₂ discussed above and also with Wang *et al.*^{S8} who found that the Cu₃N is less stable upon heating if it contains hydrogen, as well as Alexander *et al.*^{S9} who showed that the H₂ reacts strongly with 30% of the total lattice N in Cu₃N thereby leading to the formation of NH₃. This is expected to lead to Cu-rich Cu₃N with a higher conductivity according to Hayashi *et al.*^{S10} who observed that the resistivity of Cu₃N films decreased dramatically by hydrogen ion implantation. The conversion of CuO NWs into Cu and then Cu₃N NWs was also investigated. The CuO NWs were initially reduced under 100 ml/min H₂ flow at 400 °C for 30 min and then directly converted into Cu₃N under 300:10 ml/min NH₃: H₂ at 400 °C for 60 min. Intriguingly, this resulted in very short and sparse NWs; the phase of CuO was detected by XRD as well. It is interesting to mention that we tried to convert the CuO into Cu₃N NWs under NH₃: O₂ as well, which we used to get Cu₃N direct from Cu in our previous investigations^{S2, S11}, but we observed the complete loss of the CuO NWs despite the fact that the oxygen flow was very small. This surprisingly also occurred when we deposited an additional 240 nm of Cu over the CuO NWs.

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