

Supporting Information

High Crystal Quality and Purity Cu₂O by Consecutive In-Situ Annealing and Thermal Oxidation of Cu under H₂ and O₂ at Elevated Temperatures

Matthew Zervos ^a, Ioannis Paschos ^b, Pavlos Savvidis, ^b Nikoleta Florini ^c, Konstantinos Koutsokostas ^c, Philomela Komninou ^c, Nektarios N Lathiotakis ^d, P. M. Levendis ^e, Sarantos Marinakis ^e

^a, * Nanostructured Materials *and* Devices Laboratory, School *of* Engineering, University *of* Cyprus, PO Box 20537, Nicosia, 1678, Cyprus.

^b International Center for Polaritonics (ICP), Department *of* Physics, Westlake University, Zhejiang, Hangzhou, Xihu, 310024, China

^c Department *of* Condensed Matter and Materials Physics, School *of* Physics, Aristotle University *of* Thessaloniki, GR-54124, Thessaloniki, Greece.

^d Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou 48, GR-11635 Athens, Greece.

^e Department of Chemistry, University *of* Patras, University Campus, GR-26504 Rion, Achaia, Greece.

S1. Oxidation of Cu in Air

We tried to obtain Cu_2O via the thermal oxidation of Cu in air at 1040°C for 60 min without supplying any Ar and O_2 but the Cu was converted into CuO not Cu_2O . In this case the Cu was inserted in a 1200 mm long, 1" quartz tube at room temperature with both ends open to air. This was heated up in a 500 mm long single zone furnace. The temperature was ramped to 1040°C at $30^\circ\text{C}/\text{min}$ and maintained at this temperature for 60 min after which the tube was retracted during cool down. The complete oxidation of Cu from Cu^0 to Cu^{+2} is attributed to the reaction of Cu with excess O_2 during the temperature ramp at low and intermediate temperatures.

We also tried to obtain Cu_2O from Cu in a controlled fashion by using a constant flow of 150 ml/min Ar and 50 ml/min O_2 during the purge, ramp and thermal oxidation step at 1040°C for 60 min at 1 atm but the Cu was again completely oxidized into CuO due to the excess of O_2 at low and intermediate temperatures.

S2. Dry Oxidation of Cu

A $120\ \mu\text{m}$ thick Cu was loaded into a 600 mm long, 1" diameter, hot wall reactor which was purged at room temperature with a high flow of 1000 ml/min Ar and 50 ml/min H_2 for 10 min in order to eliminate air and moisture after which the temperature was increased to 1040°C at $30^\circ\text{C}/\text{min}$ using a flow of 100 ml/min Ar and 50 m/min H_2 in order to prevent the thermal oxidation of Cu during the temperature ramp. Once the temperature reached 1040°C , the same flow of 100 ml/min Ar and 50 m/min H_2 was maintained for a further 30 min to eliminate all oxides from the Cu and promote grain growth. At the end of this step, the H_2 was purged with 100 ml/min Ar for 15 min in order

to avoid a violent reaction upon admitting O₂. Subsequently, the thermal oxidation of Cu took place under 100 ml/min Ar and 25 ml/min O₂ at 1040°C for different times i.e. 10, 30 and 60 min. To suppress the reaction of Cu₂O with O₂ during cool down the tube was purged with a flow of 1000 ml/min Ar for 15 min at 1040°C. The same flow of Ar was maintained for 30 min upon cool down. When the temperature fell below 1000°C, the Cu₂O was moved rapidly in less than 10 s to the cold end of the reactor outside the heated zone on the upstream side using a rod under a flow of 1000 ml/min Ar to prevent air reaching the Cu₂O from the downstream end that was open to air during the transfer. The Cu₂O was removed from the heated zone between 800°C and 900°C and exposed to the air after cooling down to room temperature. The Cu was not completely converted into Cu₂O within 10 minutes. We find that the Cu is converted into Cu₂O after 30 or 60 min of thermal oxidation. The Cu₂O obtained in this way was covered with a layer that had a distinct silver-grey mirror-like surface but one could only see the ruby-like dark red Cu₂O crystal beneath under direct sunlight. Even though the thermal oxidation of Cu was carried out under Ar and O₂ at 1040°C one might argue that traces of H₂ left over from the temperature ramp might react with the O₂ leading to the formation of H₂O which may be responsible for the growth of Cu₂O. Consequently, we carried out the thermal oxidation of Cu by using O₂ at 1040°C and a low pressure of 1 mbar to eliminate all H₂O. In this case the 1" tube was purged with 100 ml/min Ar for 10 min after which the temperature was ramped to 1040°C at 30°C/min under 100 ml Ar/min. Upon reaching 1040°C, the flow of Ar was interrupted and a flow of 50 ml/min O₂ was initiated and maintained for 60 min after which cool down took place under 100 ml/min Ar at 0.1 mbar. It should be emphasized here that no H₂ was used in this process. In this case, we obtain dark red Cu₂O crystals via dry oxidation according to $4\text{Cu} + \text{O}_2 \rightleftharpoons 2\text{Cu}_2\text{O}$. However, the Cu₂O crystals

were not so transparent as those obtained after annealing the Cu under H₂ and have a higher content of black inclusions of CuO.

S3. Wet Oxidation of Cu

For completeness, we investigated the wet oxidation of Cu via the in-situ reaction of H₂ and O₂ at 1040°C. The room temperature purge, ramp and annealing steps using Ar and H₂ are identical to those described in S2. However, the oxidation took place under 100 ml/min Ar, 10 ml/min O₂ and 20 ml/min H₂ at 1040°C for different times i.e. 15, 30 and 60 min after which the cool down process etc. is again identical to that described in S2.

The reaction of 10 ml/min O₂ and 20 ml/min H₂ at 1040°C was not violent or an issue in this short reactor which had a length of 600 mm but was in the case of a 1200 mm long tube. We find that the Cu was converted into ruby-like, dark red Cu₂O under 10 ml/min O₂ and 20 ml/min H₂ at 1040°C for 30 min but shorter times i.e. 5 min were not sufficient for the complete conversion of the Cu into Cu₂O. We find that 10 ml/min O₂ and an excess of H₂ i.e. 30 ml/min H₂ resulted into the complete oxidation and growth of dark-grey, opaque CuO via the complete reaction of O₂ and H₂; an even larger excess of 40 ml/min H₂ prevented the complete oxidation via reduction leaving Cu beneath the opaque CuO. To avoid using H₂ and O₂ for the in-situ generation of H₂O we used a bubbler with de-ionized (DI) H₂O on a hot plate set at 100°C that was fed with Ar from a separate manifold and connected to the upstream side of the 1" tube via a valve used to isolate the bubbler from the reactor. The process was repeated in the same way except that thermal oxidation at 1040°C took place under 100 ml/min Ar and 25 ml/min O₂ for 30 min along with a flow of 1000ml/min Ar which was established through the heated bubbler containing H₂O. The Cu was converted into ruby-like, dark red Cu₂O due to the availability of O₂. We tried to obtain Cu₂O via

the wet oxidation of Cu at 1020°C for 30 min using 1000 ml/min Ar flowing through the bubbler with H₂O maintained at 100°C but without any O₂. This did not result in the growth of Cu₂O. In summary, Cu₂O is formed through dry oxidation, which requires O₂, rather than through wet oxidation using only H₂O.