Electronic Supplementary Information

Facile synthesis of CuO Nanorods with Abundant Adsorbed Oxygen Concomitant with High Surface Oxidation States for CO Oxidation

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Proof of the Occurrence of Electrochemical Corrosion.

The corrosion should proceed mainly via an electrochemical corrosion rather than a general chemical reaction. We proved that point by a contrast experiment, that is, the state of the polished surface was sustained when a polished Cu foil was wholly immersed in an electrolyte of 1 M KOH even for a rather long time like 5 h. However, for the case in the preparation of CuO NRs, black species could be found in several minutes in the outer part of the foil (above the water-line). The Cu foil wholly covered by a liquid membrane presented the similar phenomenon. The above information indicates that oxygen plays an important role in corrosion reaction. Therefore, the corrosion of copper should proceed via an oxygen consumption type of corrosion. Such type of corrosion is similar to the case for ZnO reported previously by our group.[1]

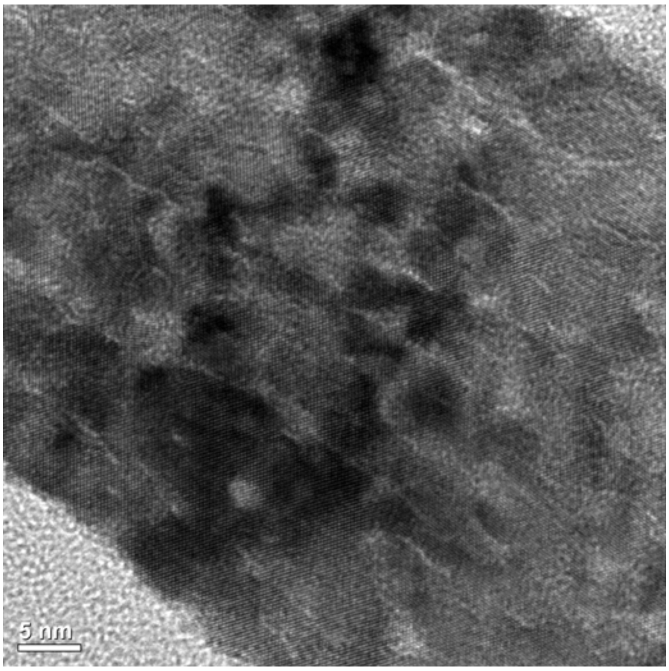

Figure S1. HRTEM image of the CuO NRs without annealing, which clearly shows that many grain boundaries are formed in the structures.

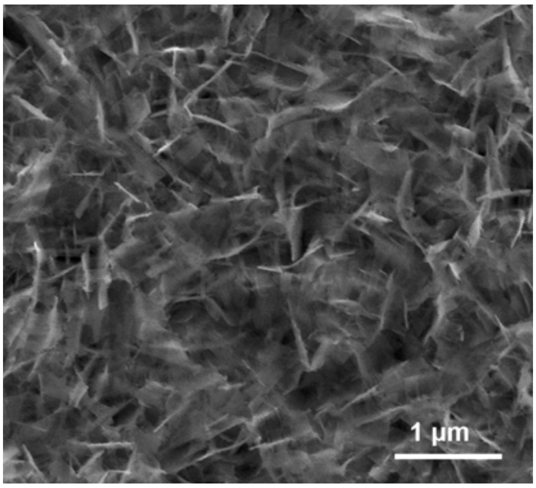

Figure S2. SEM image of a sample obtained via the corrosion of a Cu foil in a liquid membrane (wholly covering the substrate) of 1 M KOH for 5 days, demonstrating the formation of a floc-like structure.

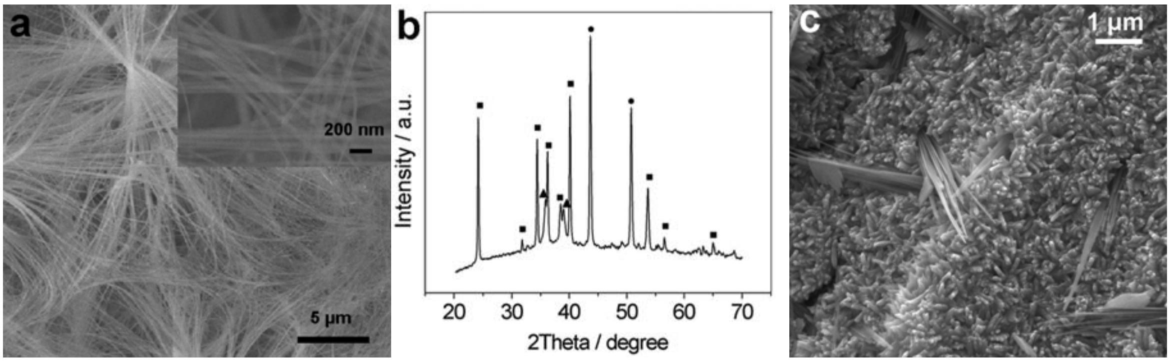

Figure S3. (a) SEM image of a sample grown via the corrosion of a Cu foil in a liquid membrane of 1 M KOH for 80 min. The Cu foil was partially immersed in 1 M KOH solution. Inset is an enlarged image. (b) The corresponding XRD pattern ("■", "▲", and "●" stand for $Cu(OH)_2$, CuO, and Cu substrate, respectively), which indicates $Cu(OH)_2$ takes a predominant proportion. The power X-ray diffraction (XRD) measurement was performed on a D8 ADVANCE (Bruck) X-ray Diffractometer using a Cu Kα radiation (1.5406 Å) of 40 kV and 20 mA. (c) SEM image showing the transition of a sample from $Cu(OH)_2$ nanowires to CuO NRs.

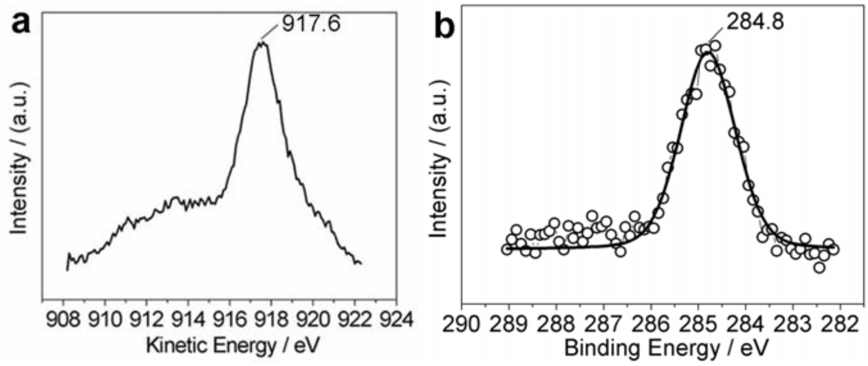

Figure S4. (a) Cu LMM Auger line and (b) C 1s XPS peak of the annealed NRs which mainly shows the hydrocarbon composition. The content of carbon species in this sample is determined to be only 5.9 at.%.

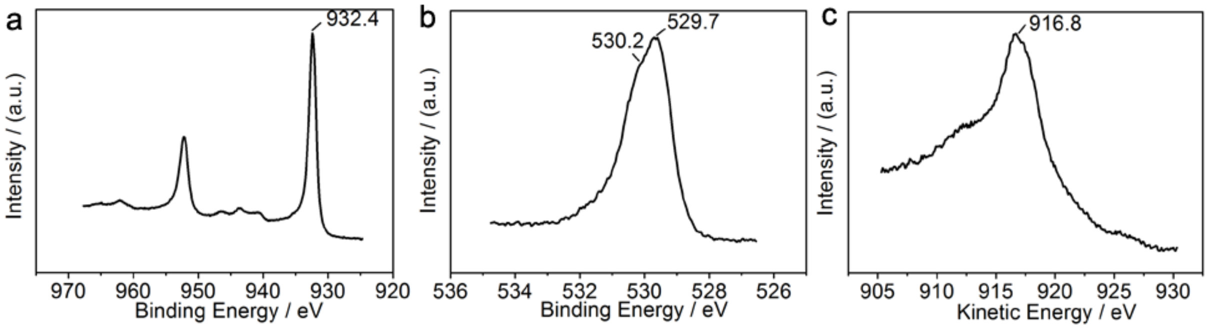

Figure S5. XPS of the CuO NRs with ion sputtering surface treatment. (a) Cu 2p photoelectron line. (b) O 1s photoelectron line. (c) Cu LMM Auger line. The content of the detected carbon species by XPS is 4.8 at.%. This sample presents a Cu 2p3 binding energy of 932.4 eV and an Auger kinetic energy of 916.8 eV, indicating the 1+ oxidation state of the Cu atom while the atom ratio of O/Cu is 0.94. This special phenomenon is mainly derived from the ion sputtering treatment which induces the reduction of the sample. The O 1s XPS shows a main peak at 529.7 eV which is derived from the O in CuO, while another peak at 530.2 eV is attributed to the O in Cu_2O. This also indicates the reduction of the surface CuO by ion sputtering treatment.

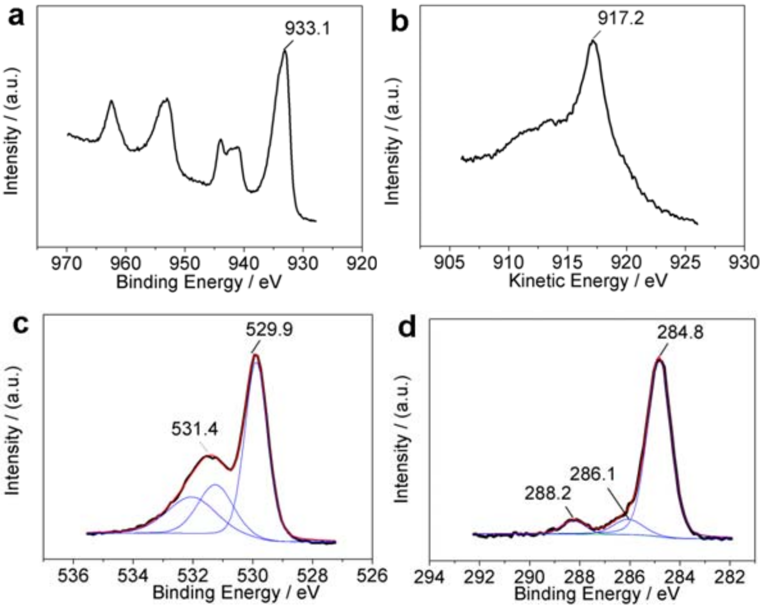

Figure S6. XPS of the new-prepared NRs without annealing. (a) Cu 2p photoelectron line. (b) Cu LMM Auger line. (c) O 1s photoelectron line. (d) C 1s photoelectron line. The content of the detected carbon species by XPS is 39.8 at.%.

The Cu 2p3 photoelectron line of the new-prepared NRs (Supplementary Figure 6a) shows a binding energy of 933.1 eV for the main peak with a clear shake-up peak, and the Auger parameter is 1850.3 eV, together indicating the 2+ oxidation state of the copper component. For the broad band of the O 1s XPS peak (Supplementary Figure 6c), it can be divided into two parts, the one at relatively high binding energy (~532 eV) (denoted as O_a), and the other above ~531 eV (denoted as O_b). The reason for the denotations is the complication of the C 1s photoelectron line as shown in Supplementary Figure 6d. The intensity ratios of O_a 1s and O_b 1s to that of Cu 2p3 are calculated to be 0.53 and 0.46, respectively. It is observed from the C 1s photoelectron line (Supplementary Figure 6d) that the new-prepared NRs mainly contain three types of carbon species: hydrocarbon (at 284.8 eV), C−O-like species (at 286.1 eV) (such as alkoxide), and C=O-like species (at 288.2 eV) (such as carbonate or carboxylate[2]). The intensity ratios of the C 1s peaks at 286.1 eV and 288.2 eV to Cu 2p3 peak are measured to be 0.23 and 0.16, respectively. In addition, the O 1s (main peak)/Cu 2p3 intensity ratio is determined to be 1.09, close to the stoichiometry of CuO. Therefore, for the oxygen-containing carbon species contributing to the O 1s broad band, C=O groups mainly devote to the O_a

1s peak, and C−O groups primarily support the O_b 1s peak. C=O-like species contains at least one O atom in its corresponding molecule. Thus, the OAC of this sample is calculated to be 0.53−0.23=0.30 at most.

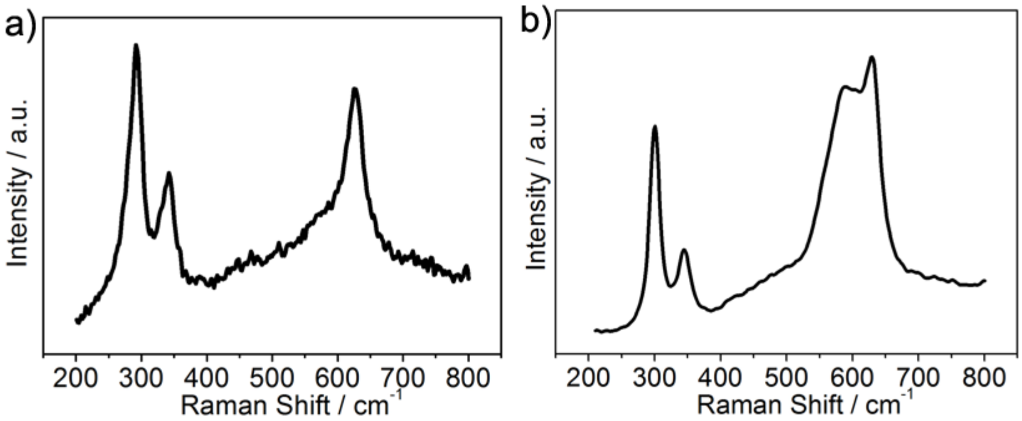

Figure S7. (a) Raman spectrum of the new-prepared CuO NRs, showing unobvious shoulder peak at 592 cm^{-1}. (b) Raman spectrum of the 5-day O_2 exposed CuO NRs.

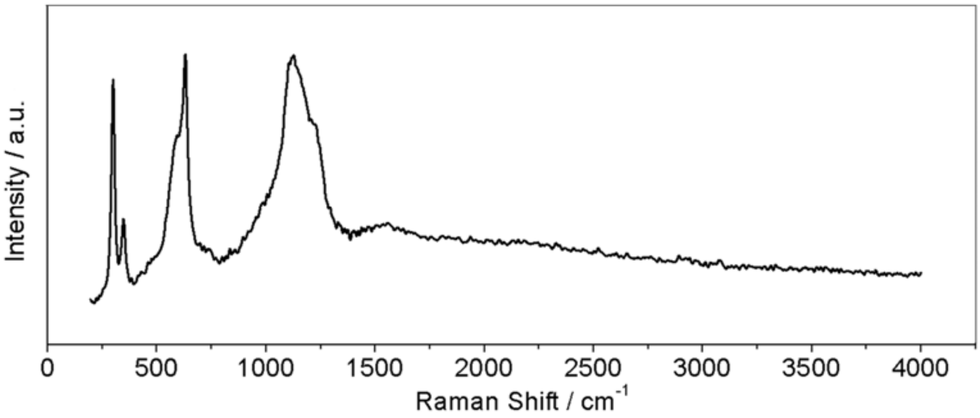

Figure S8. Full scan of Raman spectrum of the annealed CuO NRs, showing unobvious peak at 3600 cm^{-1} reflecting the characteristic of hydroxyl. The broad band above 1100 cm^{-1} should be derived from the contributions from two-phonon processes[3] and adsorbed oxygen.[4] Detailed discussion on the broad band is beyond the scope of this paper.

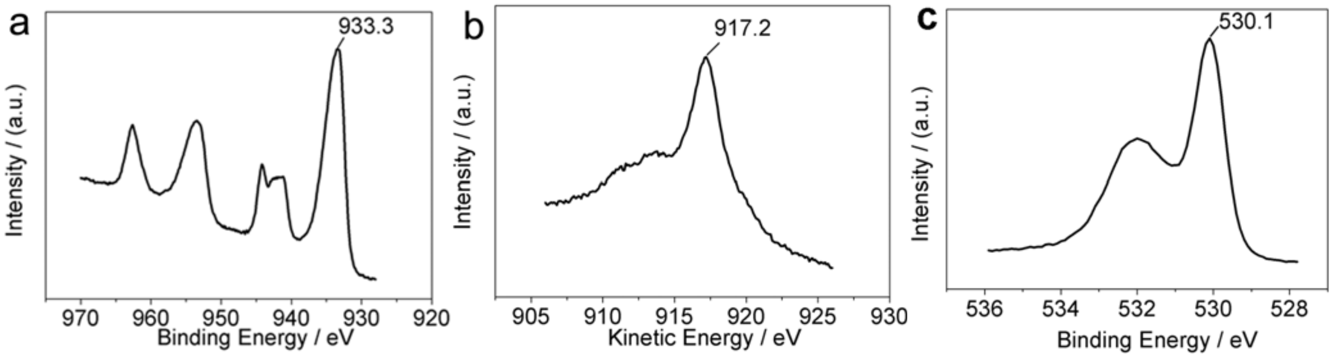

Figure S9. (a) Cu 2p photoelectron line, (b) Cu LMM Auger line, and (c) O 1s photoelectron line of the NRs after exposure to CO at 60 ºC for 5 days. The ratio of $O_{lattice}$ 1s/Cu 2p3 is measured to be 0.96, showing the CuO as the dominant composition of the surfaces of the NRs.

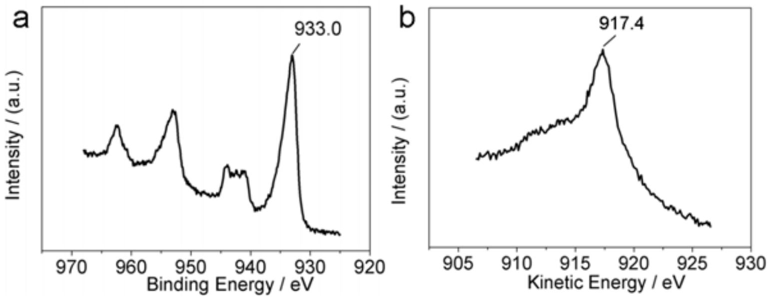

Figure S10. (a) Cu 2p photoelectron line and (b) Cu LMM Auger line of the octadecane-adsorbed CuO NRs after 5-days exposure to O_2 at room temperature.

References

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