Electronic Supplementary Information (ESI)

Revisiting Mg solubility in CuO nanorods : limit probed by neutron diffraction and effect on the particle toxicity towards bacteria in water

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S1. Crystallographic data of $Cu_{1-x}Mg_xO$ samples from X-Ray Powder Diffraction

Table S1. Results of Le Bail refinement for $Cu_{1-x}Mg_xO$ nanorods (monoclinic space group C 2/c (No.15)) from X-Ray Powder Diffraction (XRPD) Data. For each magnesium content x, the monoclinic cell parameters *a*, *b*, c and β are listed.

Magnesium content x	a (Å)	b (Å)	c (Å)	β (°)
0	4.6971(2)	3.4312(2)	5.1349(2)	99.486(3)
0.05	4.7110(3)	3.4110(2)	5.1314(3)	99.789(3)
0.10	4.7626(7)	3.3907(5)	5.1278(7)	100.134(4)
0.15	4.7639(9)	3.3939(9)	5.1275(9)	100.242(7)
0.20	4.7735(9)	3.3880(8)	5.115(1)	100.22(1)

S2. Le Bail fits of the neutron powder diffraction patterns of CuO (x = 0), $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) and $Cu_{0.8}Mg_{0.2}O$ (x = 0.2) samples

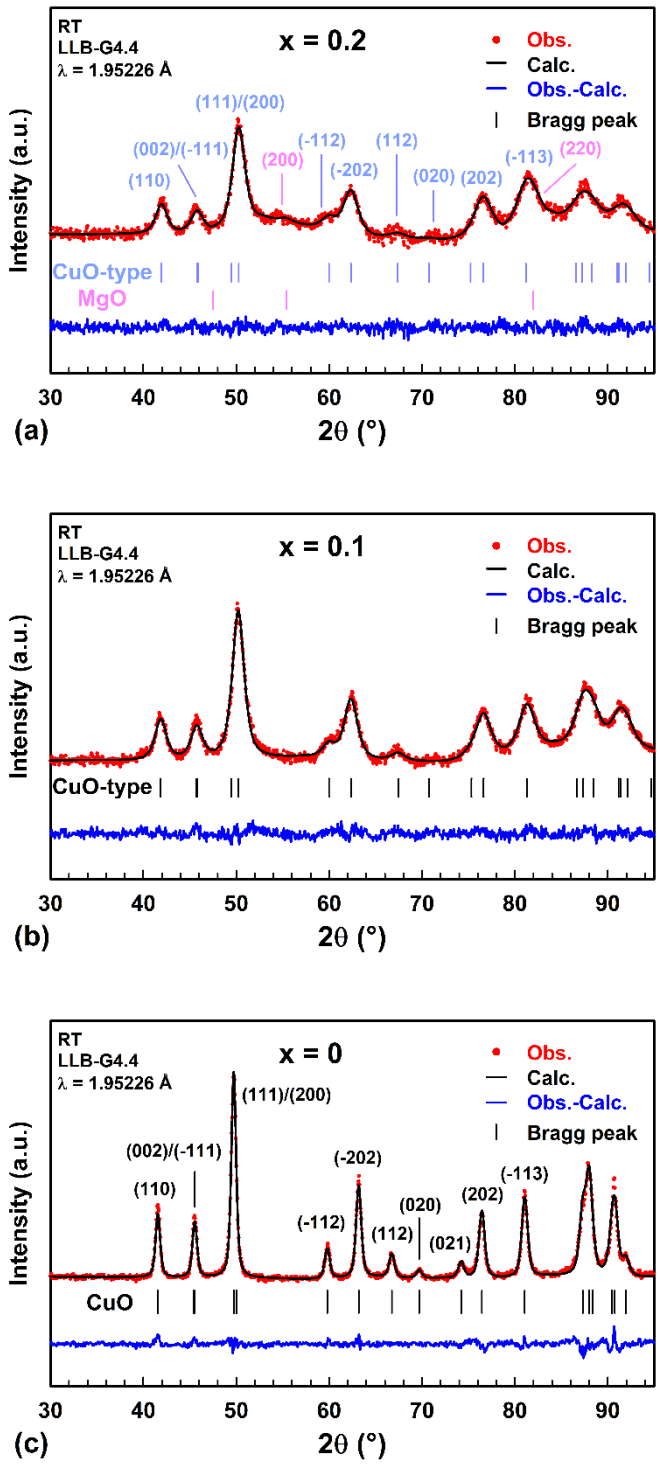

Fig. S1. Comparison of the observed NPD patterns (red dots) with the patterns calculated by the Le Bail method (black line) for raw powder samples of "$Cu_{0.8}Mg_{0.2}O$" (x = 0.2) (a), $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) (b) and CuO (x = 0) (c). The blue curve corresponds to the difference between observed and calculated patterns. Vertical markers give Bragg peak positions for MgO and the CuO-type phase (space groups F m-3m (No.225) and C2/c (No.15), respectively).

Table S2. Results of Le Bail refinement for $Cu_{1-x}Mg_xO$ nanorods (monoclinic space group C 2/c (No.15)) from Neutron Powder Diffraction (NPD) Data. For each magnesium content x, the monoclinic cell parameters *a*, *b*, c and β are listed.

Magnesium content x	a (Å)	b (Å)	c (Å)	β (°)
0	4.66(5)	3.41(5)	5.11(6)	99.5(5)
0.10	4.75(3)	3.37(3)	5.10(3)	100.3(3)
0.20	4.76(6)	3.39(6)	5.12(5)	100.3(3)

S3. EPR spectra of the aerated water suspensions of CuO (x = 0) and $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) nanorods in the presence of DMPO spin trapping agent

Low-intensity EPR signals were measured for both aerated water suspensions of CuO (x = 0) and $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) nanorods containing only DMPO spin trapping agent (Fig. S2). Each experimental EPR spectrum can be satisfactorily fitted with three superimposed signals: i) 4-line signal of •DMPO-OH spin adduct (a_N = 1.507±0.004 mT, a_H^β = 1.477±0.007 mT, g = 2.0057) [1, 2], ii) 6-line signal with parameters typical for DMPO-adduct with carbon-centered radical (a_N = 1.602±0.005 mT, a_H^β = 2.331±0.008 mT, g = 2.0055) and iii) 6-line signal compatible with •DMPO-C(O)R spin adduct (a_N = 1.493±0.004 mT, a_H^β = 1.843±0.004 mT, g = 2.0059) [3].

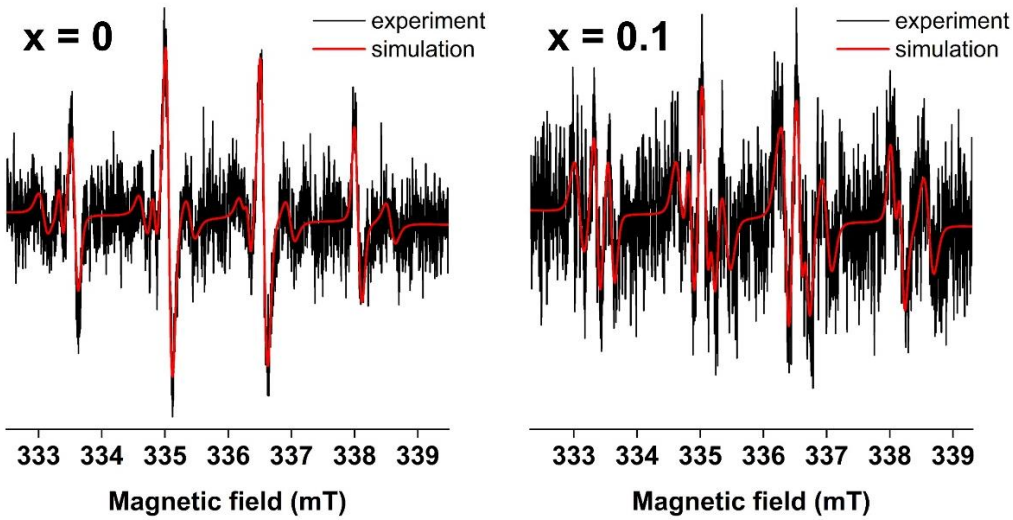

Fig. S2. Normalized experimental (black line) and simulated (red line) EPR spectra measured 22 min after the addition of DMPO spin trapping agent (c_0(DMPO) = 0.04 M) to the aerated water suspensions of CuO (x = 0) and $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) nanorods (loading 1 mg.mL^{-1}).

As shown in Fig. S3 (see the next section S4), few carbonate groups are mono-coordinated to terminal divalent cations (Mg and Cu) at the surface of nanorods. Carbonate $CO_3^{\bullet-}$ radicals (oxygen-centered radical anions) could be produced from the reaction of HCO_3^- anions with hydroxyl radicals HO• [4]. However, the rate constant for reaction of HO• with bicarbonate ions (8.5×10^6 M^{-1}s^{-1} [5]) is lower than the rate constant for the trapping of HO• by DMPO (3.4×10^9 M^{-1}s^{-1} [6]). Most hydroxyl radicals are thus rapidly trapped by DMPO. For $CO_3^{\bullet-}$ radicals that could still be produced, their detection in our experimental conditions is unlikely. Indeed, Zhang *et al.* [7] showed that $CO_3^{\bullet-}$ radicals promote the

oxidation of the spin trap DMPO to $DMPO^{\bullet+}$ cation radicals which in turn easily reacts with water molecules to form the $^{\bullet}$DMPO-OH spin adduct. Thereby, the production of low concentration of carbon-centered radicals (and its corresponding DMPO-adducts) may reflect a partial decomposition of DMPO in contact with Cu^{2+} ions.

S4. IR transmission spectra of CuO (x = 0) and $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) nanorods

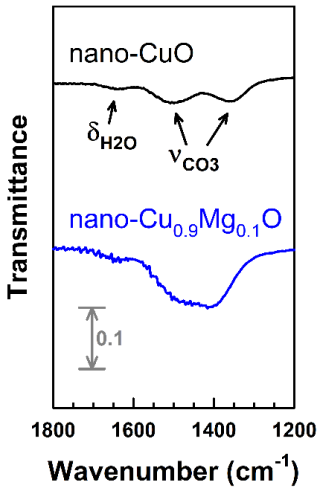

Fig. S3. Selected portion of IR transmission spectra of CuO (x = 0) and $Cu_{0.9}Mg_{0.1}O$ (x = 0.1) nanorods.

S5. References

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