

INFLUENCE OF PRESSURE AND TEMPERATURE ON X-RAY INDUCED  
PHOTOREDUCTION OF NANOCRYSTALLINE CuOA. Kuzmin<sup>1</sup>, A. Anspoks<sup>1</sup>, L. Nataf<sup>2</sup>, F. Baudelet<sup>2</sup>, T. Irifune<sup>3</sup>

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X-ray absorption spectroscopy at the Cu K-edge is used to study X-ray induced photoreduction of copper oxide to metallic copper. Although no photoreduction has been observed in microcrystalline copper oxide, we have found that the photoreduction kinetics of nanocrystalline CuO depends on the crystallite size, temperature and pressure. The rate of photoreduction increases for smaller nanoparticles but decreases at low temperature and higher pressure.

**Keywords:** *copper oxide, high-pressure, nanocrystalline, radiolysis, x-ray absorption spectroscopy*

## 1. INTRODUCTION

Nanocrystalline copper(II) oxide (CuO) attracts much attention due to a wide range of possible applications, including gas sensors, catalysis, batteries, supercapacitors, field emission displays, nanoenergetic materials, photodetectors and solar cells [1]. Better understanding and optimization of device operation requires monitoring of the oxide structure-functional property relationship under *in situ* and *in operando* conditions. Nowadays such studies widely involve experiments utilising high-intensity synchrotron X-ray radiation [2]–[5].

It is known that in some cases the intense incident X-ray beam may alter the conditions of the experiment and lead to changes in chemical structure and properties of a sample. In particular, a reduction of metal ions, including Cu<sup>2+</sup>, occurs in aqueous solutions due to radiolysis [6], [7]. Therefore, this effect finds an application for synthesis of metal nanoparticles [6]–[12]. The radiolysis process causes the production of reducing radicals such as hydrated electrons and hydrogen atoms under

X-ray or  $\gamma$ -ray irradiation of a solution [13], [14].

In this study, we use a polychromatic focused synchrotron X-ray radiation to follow kinetics of nanocrystalline CuO photoreduction as a function of crystallite size, temperature and pressure. Note that we deliberately neglected this effect in our recent study of copper oxide at high pressure due to a short time of the experiment [15].

## 2. EXPERIMENTAL STUDY

Nanocrystalline CuO was prepared by a decomposition of  $\text{Cu}(\text{OH})_2$  precipitate in air at the two temperatures of 130 °C and 150 °C [16]. The precipitate was produced by the reaction of aqueous solutions of copper nitrate and sodium hydroxide. Commercial polycrystalline CuO powder (Aldrich, 99+% purity) was used for comparison.

X-ray powder diffraction patterns (Fig. 1) of CuO samples were measured at room-temperature using the Bruker AXS D2 PHASER Bragg-Brentano  $\theta/\theta$  diffractometer equipped with the LynxEye detector and copper anode ( $\text{Cu K}\alpha$ ) tube. The samples were rotated during the measurements, and their patterns were collected in the angular range  $2\theta$  from 10° to 90° with the step of  $\Delta(2\theta)=0.04^\circ$ . The lattice parameters and crystallite sizes were evaluated from the analysis of diffraction patterns by the Rietveld method [17] using the Profex code [18].

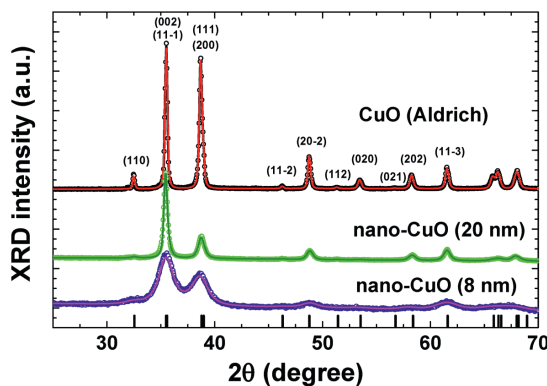


Fig. 1. Powder X-ray diffraction patterns of CuO: open circles – experiments, solid lines – Rietveld refinements. The vertical bars correspond to monoclinic CuO phase (space group  $C2/c$  (No. 15)) [19].

Pressure and temperature dependent Cu K-edge X-ray absorption spectroscopy studies of nanocrystalline and microcrystalline CuO samples were performed using the dispersive setup of the ODE beamline at SOLEIL synchrotron [20]. The SOLEIL synchrotron operated in the top-up mode with the energy  $E=2.75$  GeV and current  $I=450$  mA. The X-ray synchrotron radiation, produced by bending magnet, was dispersed and focused by a cooled single-crystal  $\text{Si}(111)$  monochromator bent in four points. The polychromatic photon flux on the sample was about 109 photons/s/eV in  $25 \times 35$   $\mu\text{m}$  FWHM. Two mirrors installed before and after the monochromator were used for a harmonic rejection. X-ray absorption spectra were recorded by

a Princeton Instruments PIXIS-400 CCD camera coupled with a scintillator. The sample pressure and temperature were controlled using a membrane-type nano-poly-crystalline diamond anvil cell (NDAC) [21], [22] and liquid helium cryostat. The silicon oil (Rhodorsil Oils 47V100) was used as pressure transmitting media. The pressure in the cell was monitored using the position of the R1-line of ruby fluorescence excited by a 473 nm DPSS laser.

### 3. RESULTS AND DISCUSSION

The results of the Rietveld refinement of the X-ray diffraction patterns (Table 1) suggest that the lattice parameters of nano-sized CuO are close to that of microcrystalline powder. Some evidence of the lattice expansion upon crystallite size reduction is observed; however, the effect is rather small. Note that the unit cell volume expansion was found previously in CuO powders with the average grain size of about 9.5–35.1 nm and explained by an influence of strain or oxygen depletion [23].

Table 1

Lattice Parameters Obtained by Rietveld Refinement

	CuO (Aldrich)	nano-CuO (20 nm)	nano-CuO (8 nm)
a (Å)	4.6861(2)	4.6823(8)	4.710(4)
b (Å)	3.4272(2)	3.4289(8)	3.448(4)
c (Å)	5.1335(2)	5.1390(5)	5.143(3)
b (°)	99.428(2)	99.419(8)	99.10(4)
y(O)	0.433(3)	0.390(5)	0.46(3)
V (Å <sup>3</sup> )	81.34	81.40	82.47
d (nm)	70(3)	20(2)	8(1)

The effect of temperature on the X-ray induced photoreduction of nano-CuO (8 nm) is shown in Fig. 2 for three temperatures (10, 190 and 260 K) at the pressure  $P = 1\text{--}2$  GPa. The appearance of metallic copper is well visible at  $T = 260$  K as a growing shoulder at 8983 eV and a reducing main peak at 9000 eV. However, the reduction process is not fully completed even after 70 min.

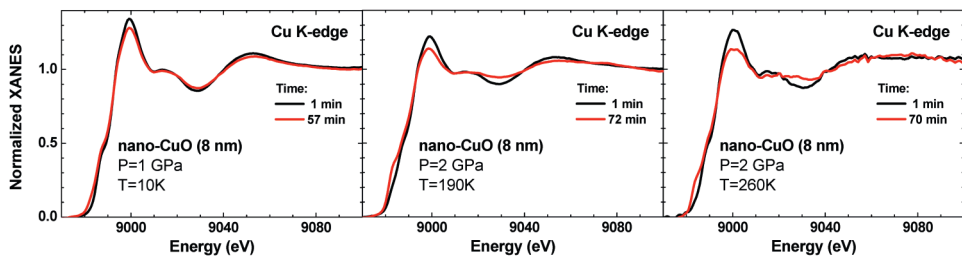


Fig. 2. Temperature-dependent Cu K-edge XANES of nano-CuO (8 nm) at  $P = 1\text{--}2$  GPa as a function of experimental time.

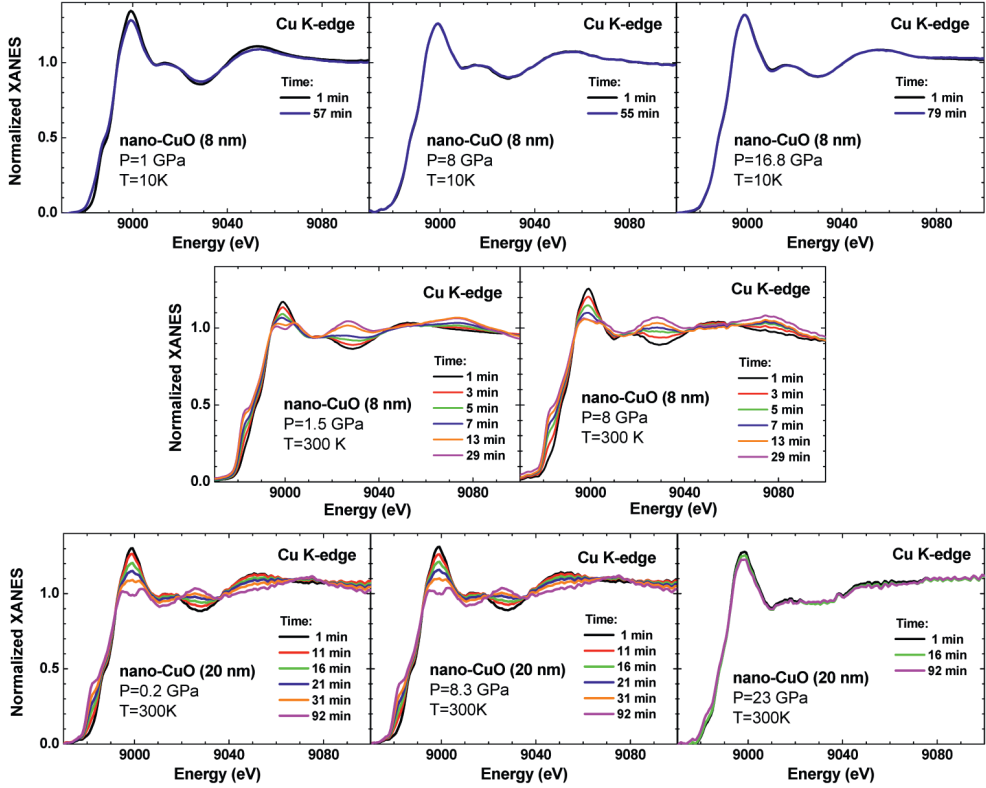


Fig. 3. Pressure-dependent Cu K-edge XANES of nano-CuO (8 and 20 nm) at T=10 and 300 K GPa as a function of experimental time.

A decrease of temperature down to 10 K significantly slows down the photoreduction of the oxide to metallic copper. At low temperature (10 K), the photoreduction of small (8 nm) CuO nanoparticles occurs only at low pressure ( $P=1$  GPa), whereas no effect is visible at 8 and 16.8 GPa (upper panels in Fig. 3). Thus, a retardation of the photoreduction effect due to radiolysis can be achieved by increasing pressure.

At the same time, a complete conversion of nano-CuO (8 nm) to metallic copper occurs for about 0.5 h at 300 K for the pressure below  $\sim 8$  GPa (middle panels in Fig. 3). Upon increasing crystallite size to 20 nm, the reduction process takes more time (about 1.5 h) at the pressure below  $\sim 8.3$  GPa (lower panels in Fig. 3). Further increase of pressure up to 23 GPa stabilizes the oxide phase in 20 nm CuO crystallites.

#### 4. CONCLUSIONS

X-ray induced photoreduction of copper oxide placed in a diamond anvil cell has been studied using synchrotron radiation X-ray absorption spectroscopy at the Cu K-edge as a function of crystallite size, temperature and pressure. We have not observed any photoreduction in the case of microcrystalline copper oxide, but it has clearly been detected from the change in X-ray absorption near edge structure of

nanocrystalline CuO. The rate of CuO photoreduction to metallic copper increases with a decrease in nanoparticle size, but slows down with a decrease in temperature or an increase in pressure. These findings are important for all studies dealing with high-flux X-ray beams, in particular, in the case of nanosized CuO catalysts.

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# SPIEDIENA UN TEMPERATŪRAS IETEKME UZ NANOKRISTĀLISKĀ CuO RENTGENSTIMULĒTO FOTOREDOCĒŠANU

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## K o p s a v i l k u m s

Rentgenabsorbcijas spektroskopija Cu K-malā tika izmantota, lai pētītu spiediena un temperatūras ietekmi uz vara oksīda (CuO) rentgenstimulēto fotoreducēšanu. Šajā procesā notiek vara oksīda transformācija par metālisko varu. Nanokristāliskā vara oksīda fotoreducēšanas kinētika ir atkarīga no kristālitu izmēriem, temperatūras un spiediena. Fotoreducēšanas ātrums palielinās mazās nanodaliņās, bet samazinās zemā temperatūrā un augstā spiedienā.

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