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Morphology and photoluminescence of nanostructured oxides grown by copper passivation in aqueous potassium hydroxide solution

Wojciech J. Stepniowski^{a,b,c*}, Stevan Stojadinović^d, Rastko Vasilić^d, Nenad Tadić^d, Krzysztof Karczewski^a, Shoshan T. Abrahami^b, Josephus G. Buijnsters^c, Johannes M.C. Mol^b

^a *Department of Advanced Materials and Technologies, Faculty of Advanced Technology and Chemistry, Military University of Technology, Kaliskiego 2 Str., 00-908 Warszawa, Poland*

^b *Delft University of Technology, Department of Materials Science and Engineering, Faculty 3mE, Mekelweg 2, 2628 CD Delft, The Netherlands*

^c *Delft University of Technology, Department of Precision and Microsystems Engineering, Faculty 3mE, Mekelweg 2, 2628 CD Delft, The Netherlands*

^d *University of Belgrade, Faculty of Physics, Studentski trg 12-16, Belgrade, Serbia*

Keywords: cuprous oxide; copper oxide; passivation; nanowires; photoluminescence

*Corresponding Author

W.J. Stepniowski

wojciech.stepniowski@wat.edu.pl

W.J.Stepniowski-2@tudelft.nl

phone: +48 261 83 94 46

Abstract

Copper foil was anodized in 1 M KOH at potentials ranging from -400 to -100 mV vs. Ag|AgCl electrode. Cyclic voltammetry showed a distinct peak with a maximum at around -150 mV. For anodizing at -100 and -200 mV, nanowires with diameters of ca. 19 and 24 nm respectively were found to be grown. Moreover, photoluminescence and X-ray diffraction show that the dominant phase is the CuO phase. At lower potentials, cuboidal micron sized crystals were formed and Cu₂O was found to be the major phase.

1. Introduction

Nanostructures made of cuprous and cupric oxides are gaining increased research interest due to their electrical and optical properties and potential applications in renewable energy harvesting [1-2], sensing and morphologically tuned surface wetting [1,3]. One of the recently reported and facile approaches of copper and cupric oxide fabrication is self-organized anodization of copper substrates which allows to form nanowires made of copper compounds like Cu_2O , CuO and $\text{Cu}(\text{OH})_2$ [2-6]. According to the Pourbaix diagram for copper, passivation is typically conducted in base solutions of NaOH [2-3, 5] and KOH [4, 6]. Despite some preliminary research on nanostructuring of copper surfaces, there are still many fundamental aspects to be explored like: investigation of the chemical composition, microstructure and morphology of the grown nanostructures. So far, no systemic study on the influence of passivation potential on the morphology, including quantitative image analyses, has not been reported yet. Moreover, passivation of copper, with cuprous oxide formation, allows to receive highly developed surface, which would allow to increase efficiency of Cu_2O -based solar cells [7] or photocatalytic water splitting [2].

The main goal of this letter is to investigate the morphology and chemical composition of copper oxide nanostructures by voltammetric, microscopic, X-ray diffraction and photoluminescence experiments.

2. Experimental

A 99.99% purity copper foil was obtained from industry (KGHM Polska Miedź S.A.). Prior to the passivation process, the foil was electropolished in 10 M H_3PO_4 at 5.0 V at 27 °C for 30 s using Pt grid as a cathode [8]. In order to get rid of traces of oxides, the samples were put into 0.2 M HCl for 30 min at room temperature. Then, the samples were rinsed thrice with DI water.

Passivation and cyclic voltammetry experiments were performed using ATLAS-SOLLICH 0531 potentiostat with the copper samples (surface area of copper was limited by an O-ring to 1 cm²) as working electrodes, Ag|AgCl reference electrode (RE) and Pt counter electrode (CE). All potential values reported are vs. Ag|AgCl electrode unless indicated otherwise explicitly. All the experiments were performed in 1 M KOH aqueous solution at room temperature.

Cyclic voltammetry was performed at a rate of 1 mV/s. Prior to cyclic voltammetry, the open circuit potential (OCP) was recorded for 2 hours and the voltammetric scan was started 100 mV below the final OCP value.

According to the obtained voltammetric results, passivations at -100, -200, -300 and -400 mV were performed for 1 hour to investigate the morphology of the formed oxides.

The morphology of the obtained nanostructures was investigated using Field emission scanning electron microscopy (FE-SEM, Quanta 3D FE-SEM). Quantitative image analyses were performed with NIS-Elements software (Nikon). At least 50 direct measurements were performed for each surface feature (diameter of nanowire, bundle or cuboid). The results are presented as an average value $\pm$ standard deviation.

Photoluminescence (PL) spectral measurements were taken on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer at room temperature, with a Xe lamp as the excitation light source. The obtained spectra were corrected for the spectral response of the measuring system.

3. Results and Discussion

Figure 1 shows a typical cyclic voltammogram of Cu recorded in 1.0 M KOH. Three peaks are noticeable at: -452, -152 and 610 mV. According to Ambrose et al. [9] the peaks

can be attributed to the oxidation of copper. At -452 mV, oxidation of Cu to Cu₂O (cuprous oxide) occurs (1) [9]:



However, also soluble species can be formed according to the following equation (2) [5]:



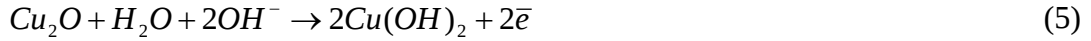
Further oxidation to Cu(II) occurs at higher (i.e., more positive) potentials, according to the voltammogram peak at -152 mV (Fig. 1). The oxidation occurs according to the following equations (3) [9]:



and (4) [5]:



Cuprous oxide may be oxidized as well according to the reaction (5) [9]:



With formation of soluble species (6-7) [9]:



At the beginning of the oxygen evolution peak, one can notice a small sub-peak at ca. 610 mV that according to the literature [9] can be attributed to the formation of Cu(III) (8-9):



According to the reactions, the use of different potentials may provide different chemical compositions of copper based nanostructures.

FE-SEM imaging reveals significant differences in surface morphologies after samples were passivated at or over -200 mV and at lower potentials. At -400 and -300 mV, the

formation of only cuprous oxide should be expected and at these potentials one can notice only cuboid structures with diagonals of $1.69 \pm 0.36 \mu\text{m}$ and $0.68 \pm 0.26 \mu\text{m}$, respectively (Fig. 2A-B, Table SI1). According to Fig. 1, at -200 mV oxidation to Cu^{2+} starts to take place. Top-view FE-SEM imaging of the Cu surface after passivation at -200 mV shows formation of nanowires (Fig. 2C). Thus, according to reactions (3-7), it can be expected that these nanowires are composed already of cupric oxide. Furthermore, accomplished oxidation to CuO may occur rather at potentials above -152 mV (Fig. 1) and well-formed nanowires are obtained at -100 mV (Fig. 2D). Worth noting is that the nanowires grow in bundles (Fig. 2C-D). Each bundle consists of few individual nanowires. For example, at -100 mV nanowires with average diameter of $19 \pm 7 \text{ nm}$ were formed, growing in bundles with a diameter of $90 \pm 23 \text{ nm}$.

Photoluminescence excitation and corresponding emission spectra of the oxide structures formed at -100 mV are shown in Fig. 3a. The excitation PL peaks are positioned at about 290 nm and 370 nm suggesting that the optimum excitation range is 350-390 nm. Wide emission PL bands are present in the visible region. Fig. 3b shows PL emission spectra of oxide structures formed at different passivation potentials excited at 360 nm. The passivation potential does not have an influence on the shape of the PL emission spectra. At least three shoulder peaks at about 416 nm, 440 nm, and 460 nm can be observed. These peaks can be attributed to defect related centers (oxygen vacancies, intrinsic defects, etc.) present in CuO [6]. Surface sensitive, experimental results suggest that CuO is the dominant phase on the top surface of obtained oxide structures [11]. The highest PL intensity is observed for oxide structure formed at -100 mV, indicating that the highest number of surface defects and/or impurities in CuO crystallites appears for this passivation potential. It also means that above -152 mV the CuO is the major phase formed via passivation. Additionally taken XRD patterns (see supporting information) show that at -400 mV only Cu_2O is formed, whereas for higher

potentials CuO appears and the most intensive CuO peaks are found for copper anodized at -100 mV. XRD indicates the formation of crystalline phases in the samples without post-treatment which is in contrast to typically formed anodic oxides, like anodic alumina [12] or titania [13] being amorphous.

Conclusions

Passivation of copper results in the formation of structures with varied morphology and chemical composition depending on the passivation potential:

- Passivation in KOH at -200 mV or greater potentials allows to form nanowires made mainly of cupric oxide, while anodizing at lower potentials results in the formation of cuboidal microstructures made of cuprous oxide.
- Obtained emission and excitation PL spectra reveal the presence of crystalline CuO on the top surface of obtained oxide nanostructures. The concentration of intrinsic and impurity related defects in such structures decreases with increasing passivation potential.
- Formed passive oxides were found to be crystalline.

4. Acknowledgements

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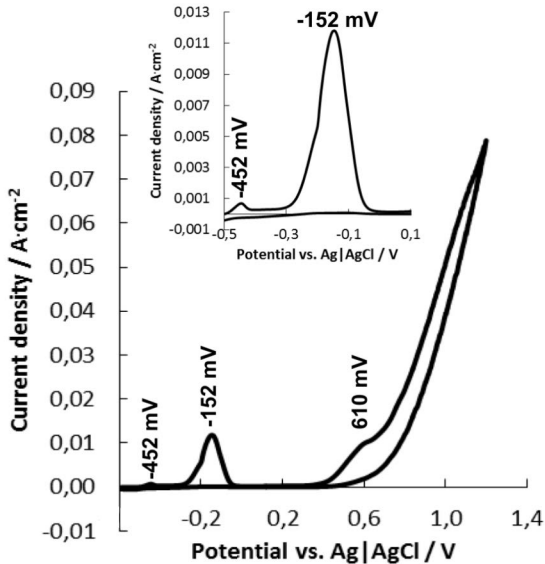
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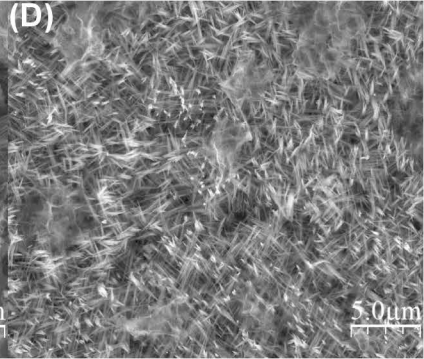
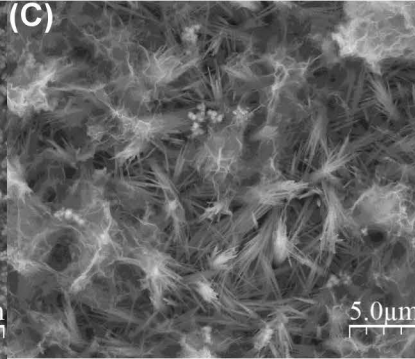
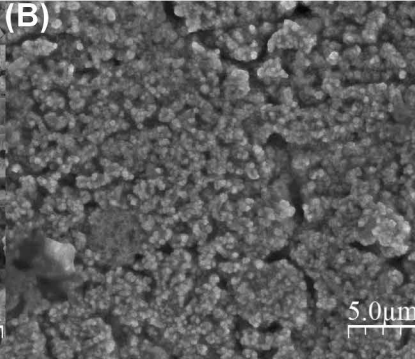
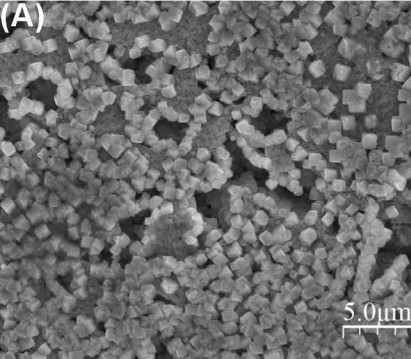
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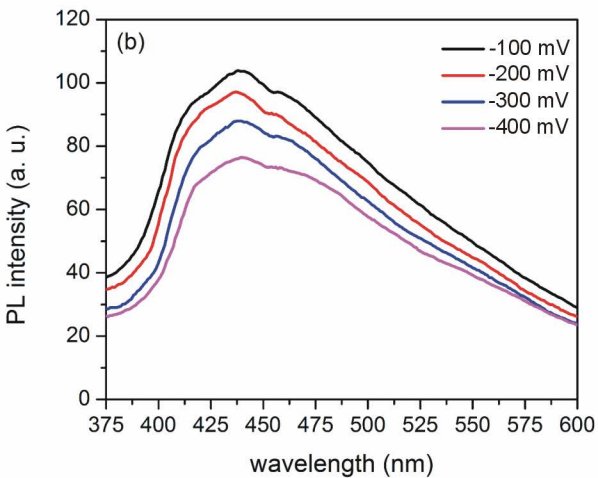
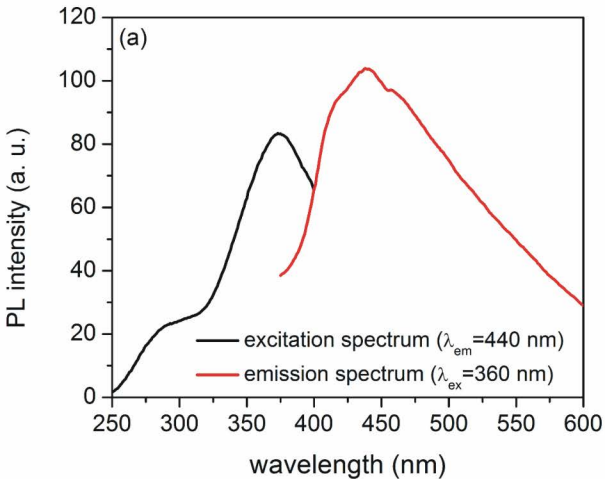
Fig. 1. Voltammogram of Cu in 1.0 M KOH at a scan rate of 1 mV/s. The enlarged range for the second oxidation peak at -152 mV is shown in the inset.

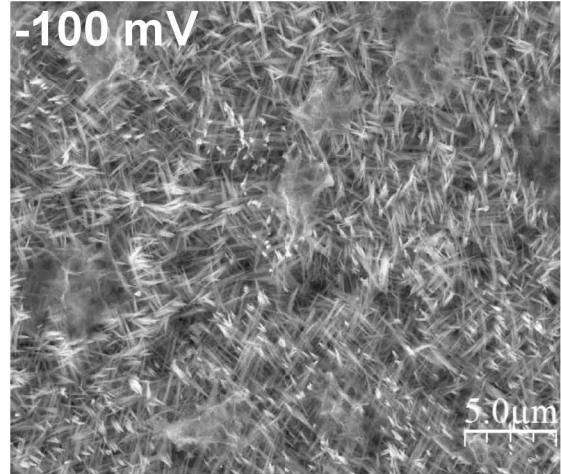
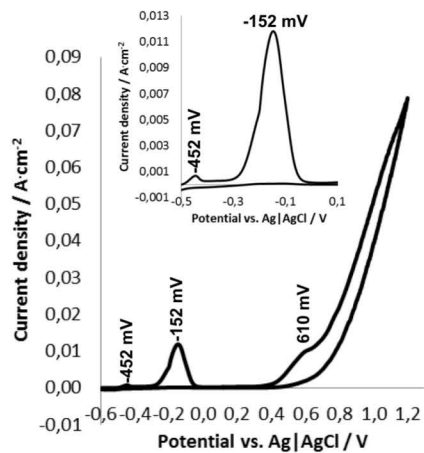
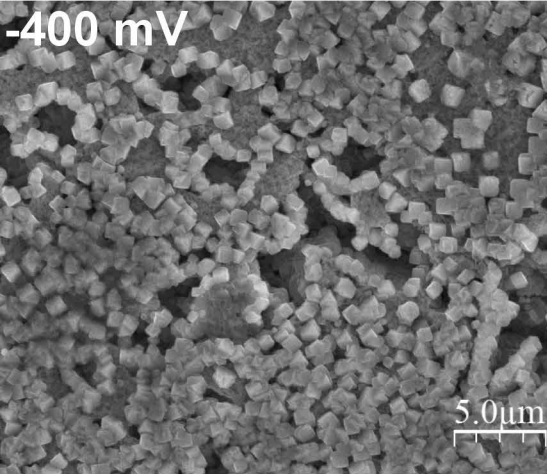
Fig. 2. Top-view FE-SEM images of the surface morphology of the oxides formed via copper passivation in 1.0 M KOH at -400 (A), -300 (B), -200 (C) and -100 mV (D).

Fig. 3. (a) PL excitation and emission spectra of oxide structure formed via copper passivation at -100 mV in 1.0 M KOH; (b) Influence of passivation potential on PL emission intensity (excitation wavelength 360 nm).









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Karczewski^a, Shoshan T. Abrahami^b, Josephus G. Buijnsters^c, Johannes M.C. Mol^b

^a *Department of Advanced Materials and Technologies, Faculty of Advanced Technology and
Chemistry, Military University of Technology, Kaliskiego 2 Str., 00-908 Warszawa, Poland*

^b *Delft University of Technology, Department of Materials Science and Engineering, Faculty
3mE, Mekelweg 2, 2628 CD Delft, The Netherlands*

^c *Delft University of Technology, Department of Precision and Microsystems Engineering,
Faculty 3mE, Mekelweg 2, 2628 CD Delft, The Netherlands*

^d *University of Belgrade, Faculty of Physics, Studentski trg 12-16, Belgrade, Serbia*

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*Corresponding Author

W.J. Stepniowski

wojciech.stepniowski@wat.edu.pl

W.J.Stepniowski-2@tudelft.nl

phone: +48 261 83 94 46

Table SI1. Morphological features of oxide structures formed by copper passivation.

Potential / mV	Diameter of individual nanowires / nm	Diameter of nanowire bundle / nm
-100	19 ± 7	90 ± 23
-200	24 ± 5	72 ± 14
	Diagonal of the cuboidal structures / μm	
-300	0.68 ± 0.26	
-400	1.69 ± 0.36	

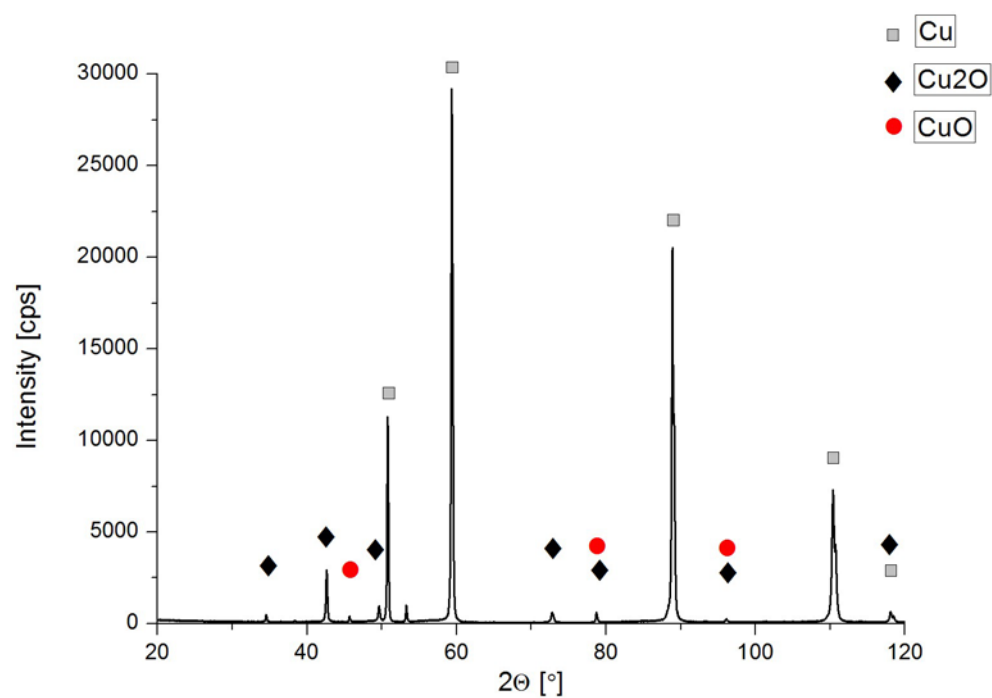


Fig. SI.1. XRD pattern of Cu after oxidizing at -400 mV in KOH solution for 1 hour.

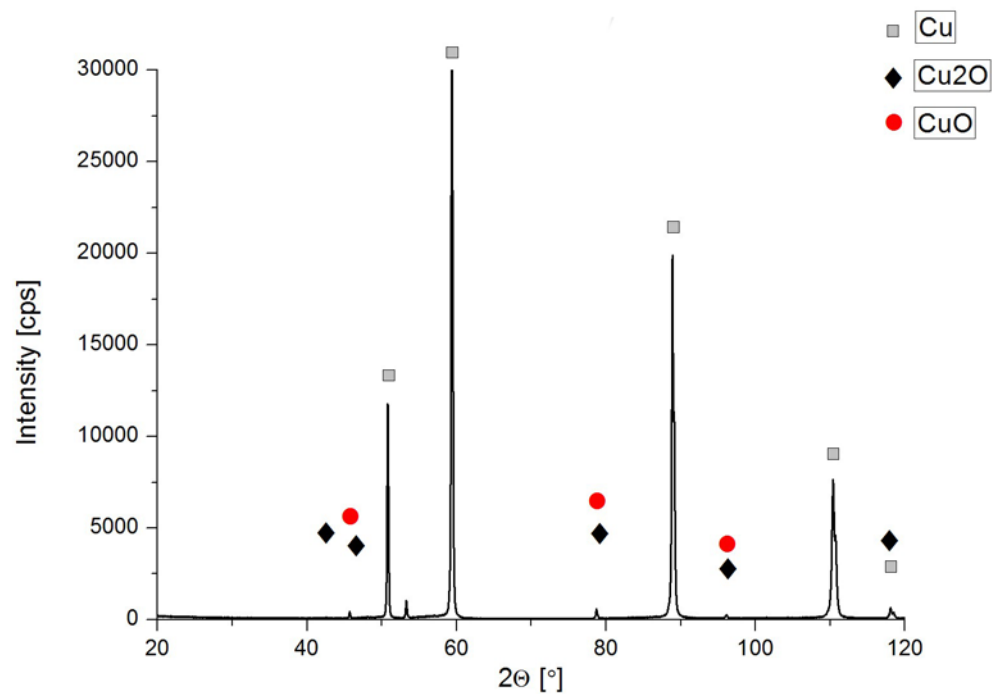


Fig. SI.2. XRD pattern of Cu after oxidizing at -300 mV in KOH solution for 1 hour.

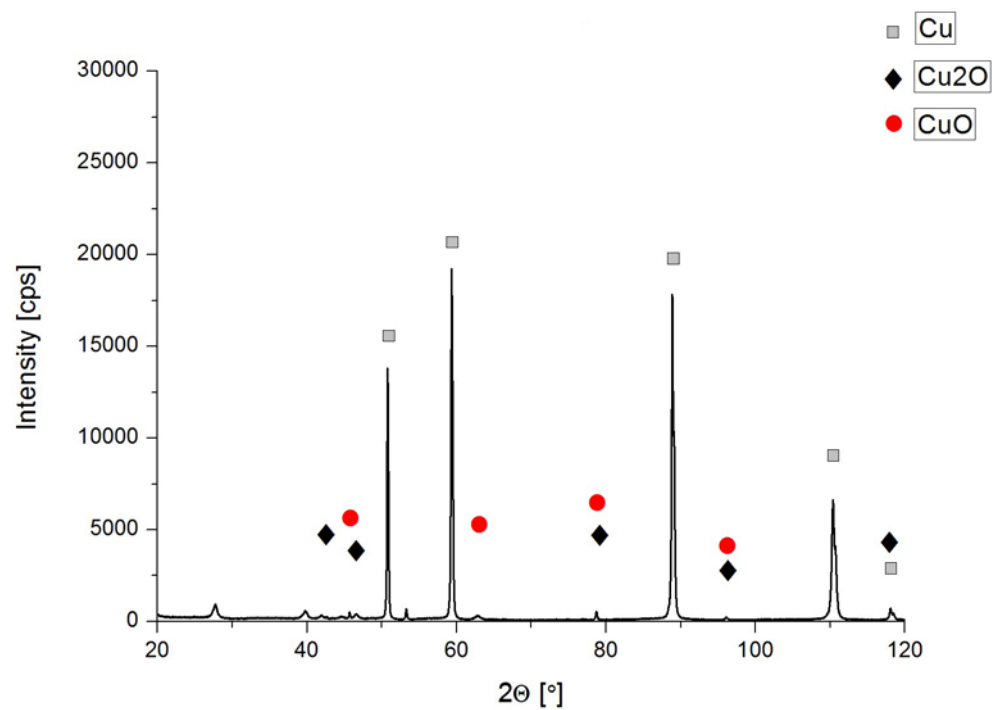


Fig. SI.3. XRD pattern of Cu after oxidizing at -200 mV in KOH solution for 1 hour.

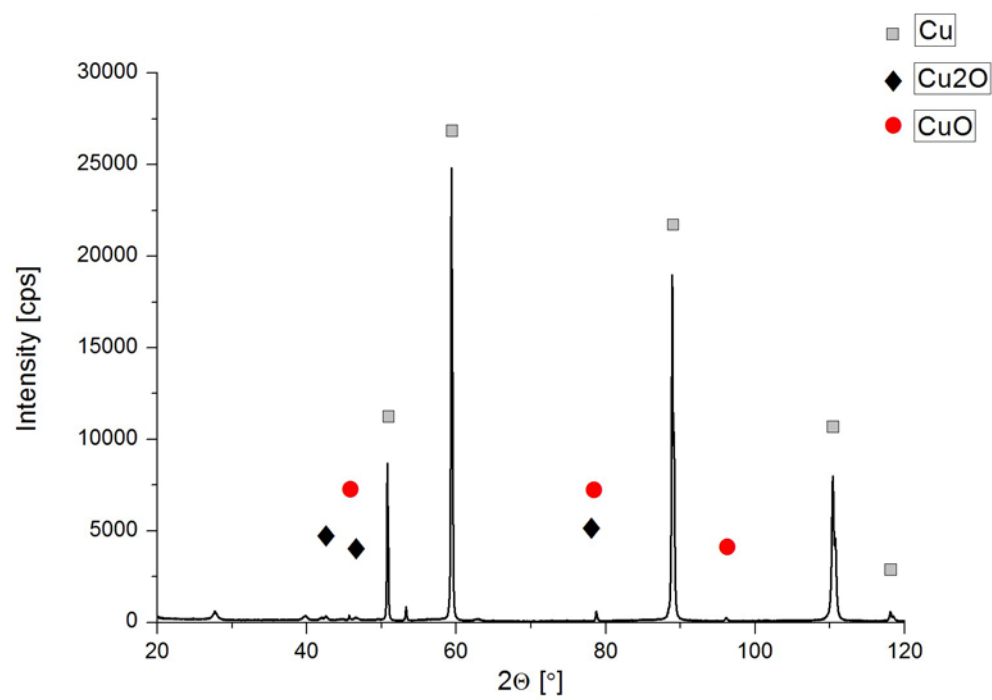


Fig. SI.4. XRD pattern of Cu after oxidizing at -100 mV in KOH solution for 1 hour.

X-ray diffraction patterns were taken using a Rigaku Ultima IV diffractometer with Co K α radiation ($\lambda=1.78897$ Å) and operating parameters of 40 mA and 40 kV with a scanning speed of 1°/min with resolution of 0.02° in the range of 20–120°.