

Characterization of synthesized copper oxide nanopowders and their use in nanofluids for enhancement of thermal conductivity

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Three copper oxide nanopowders were synthesized by three different copper precursors, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $(\text{CH}_3\text{COO})\text{Cu} \cdot \text{H}_2\text{O}$ and characterized by FTIR, X-ray diffraction (XRD), thermal conductivity and cyclic voltammetry. These parameters were compared with the sample of CuO nano-powder procured from Sigma Aldrich. The positions of FTIR and XRD peaks are nearly similar for the synthesized CuO nanopowders as well as Sigma Aldrich CuO nanopowder. Substantial enhancement of thermal conductivity (60%) has been observed in nanofluid prepared from CuO nanopowder obtained from $(\text{CH}_3\text{COO})\text{Cu} \cdot \text{H}_2\text{O}$ precursor. The electrochemical behaviour of acidic solution of all CuO nanopowders indicates $\text{Cu}^{2+/0}$ and $\text{Cu}^{0/2+}$ electrode reaction and irreversible redox nature.

Keywords: CuO nanoparticle, Infrared spectroscopy, X-ray diffraction, Thermal conductivity

1 Introduction:

Efficient cooling is a technical challenge faced by hi-tech industries such as microelectronics, transportation, manufacturing and metrology. There is a strong need to develop heat transfer fluids with significantly higher thermal conductivity than pure fluids in these fields^{1,2}. It is well-known that crystalline solids have higher thermal conductivity by one to three orders of magnitude than traditional fluids like water, ethylene glycol, oil, etc. Therefore, fluids containing suspended solid particles are logically expected to have a higher thermal conductivity than pure fluids. Nanofluids containing metallic or non-metallic particles have attracted a great deal of research attention due to their higher heat transfer efficiency³. Nanofluids are suspensions^{4,5} of nanometer sized particles or metal particles in base fluids which act as heat transfer liquids⁶. Recent experiments on nanofluids have indicated that a significant increase in thermal conductivity could be achieved when they contain nanoparticles or larger particles⁷.

Copper nanoparticles, due to their unique properties and low cost of preparation have potential for applications in catalysis, cooling fluid or conductive inks⁸. It is well-known that the thermal conductivity of fluids, such as water or ethylene glycol, can be enhanced by addition of nanoparticles. These two-component systems have effective thermal

conductivities arising out of the thermal conductivities of the pure materials, the composition of the mixture, and the shape of the dispersed particles⁹.

The reaction and nucleation mechanism of copper electro-deposition from ammoniacal solutions were investigated by cyclic voltammetric techniques¹⁰. The process of adsorption / desorption of OH species onto Cu (111) and Cu (100) electrodes in 0.1M NaOH solution has been investigated by cyclic voltammetry¹¹. Although the anodic oxidation of copper in alkaline solution has been studied¹², the initial stage of the oxidation process has received little attention. A small anodic peak on the voltammogram, preceding the peak of Cu_2O formation was first observed by Ambrose *et al*¹³. after careful examination at high sensitivity and high sweep rates. This peak has been tentatively assigned to the formation of soluble $\text{Cu}(\text{OH})_2^-$ species. Cruickshank *et al*¹⁴. investigated the state of a Cu(100) surface in 0.1 M HClO_4 and in 0.1 M H_2SO_4 solutions as a function of the potential by the cyclic voltammetry techniques.

The present work involves synthesis of CuO nanopowder by chemical reduction, based on a method reported earlier²⁰ and subsequent characterization of the synthesized CuO nanopowder by FTIR spectroscopy, XRD, cyclic voltammetry and thermal conductivity enhancement studies.

Comparison between synthesized CuO nano-powders and CuO nanopowder procured from Sigma-aldrich done by FTIR, XRD and cyclic voltammetric analysis showed similar behaviour. The thermal conductivity of CuO nano fluids have been studied by preparing nanofluids in HPLC grade water and ethylene glycol/water (40:60) mixture for comparison.

2 Experimental Details

The preparation of nanofluids involves a two step reaction. In the first step, syntheses of copper oxide nano-powders have been carried out and in the second step, CuO nanofluids were prepared by using the synthesized copper oxide nanopowders. Copper oxide nanopowder procured from Sigma-Aldrich Ltd. was also used for preparation of nanofluids for the sake of comparison.

Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), copper nitrate trihydrate $\{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}\}$, sodium lauryl sulphate (SLS), ethylene glycol (EG) and sodium carbonate (Na_2CO_3) were purchased from SDFCL Ltd., copper acetate monohydrate $\{(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}\}$ was procured from Merck Specialties (Pvt.) Ltd. and polyvinylpyrrolidone (PVP) was purchased from Central Drug House Ltd. All the ingredients and solvents were used as such without any further purification. HPLC grade water was used in all the experiments.

The infrared spectra of synthesized and procured CuO nanopowders were recorded as KBr pellets using a Infrared Spectrophotometer (model FTLA 2000-100, ABB Inc. Analytical & Advance Solutions, Canada). Compact & Versatile Thermal Constant Analyzer (model TPS-500, Hot Disk AB, Sweden) was used for thermal conductivity measurements. Gamry Potentiostat/Galvanostat/ZRA instrument (model Reference 600) was used for cyclic voltammetric studies.

The X-ray diffractograms of CuO nanopowder samples were recorded using a Bruker Diffractometer (Model D8 ADVANCE) in the range $10 < 2\theta < 60$ with 1.5405 \AA Cu $K\alpha$ radiation. The average particle sizes (d) have been estimated by using Debye-Scherrer formula: $D = 0.9\lambda/\beta \cos\theta$, where λ is wavelength of X-ray (0.1541nm), β is FWHM (full width at half maximum), θ is diffraction angle and D is particle diameter.

2.1 Synthesis of Copper Nanopowders

Three copper oxide nanopowders designated as X, Y and Z were synthesized by chemical reduction

method by using sodium carbonate as a reducing agent. The methods of synthesis are described as follows:

Synthesis of the nanopowder X: 0.5 M aqueous solution of copper sulphate pentahydrate was mixed with 0.5 M aqueous solution of sodium carbonate and stirred for 3-5 h at 55°C . A greenish colour precipitate was obtained which was filtered, washed with water, dried at 80°C in an oven and then kept in a muffle furnace at 750°C for 2 h. Subsequently, the precipitate was crushed to obtain black coloured CuO nanopowder. The yield of CuO nanopowder was 30.7% based on amount of copper sulphate pentahydrate precursor.

Synthesis of the nanopowders Y and Z: The nanopowders Y and Z were synthesized using the same method as for X except that precursors used were copper nitrate trihydrate and copper acetate monohydrate, respectively for Y and Z. The yield of nanopowders, Y and Z were 31.5% and 40.3% based on amount of copper nitrate trihydrate and copper acetate monohydrate, respectively.

2.2 Preparation of Nanofluids

Two sets of nanofluids were prepared using HPLC water and ethylene glycol / HPLC water (40/60 v/v ratio) as dispersing mediums for each of the synthesized CuO nanopowders X, Y, Z. The three nanofluids prepared in HPLC water are henceforth denoted by X-1, Y-1 and Z-1 and those in ethylene glycol/ HPLC water are denoted by X-2, Y-2 and Z-2. Two additional nanofluids have been prepared using CuO nano powder procured from Sigma-Aldrich in HPLC water and EG/water, respectively for the comparison of properties. 50 mg each of CuO nanopowders was taken in 50 ml of water and 50 ml of (40:60) EG/water mixture in two separate sets of experiments, stirred for 2 h and then 50 mg of polyvinyl pyrrolidone (PVP) and 500 mg sodium lauryl sulphate were added in the respective solutions and stirred for 3 h at room temperature. The mixtures were subsequently sonicated for 2 h to get the well dispersed nanofluids.

3 Results and Discussion

3.1 FTIR Spectral Studies

Most of the researchers¹⁵⁻²¹, who prepared CuO nanoparticles, reported the characteristic peaks of the IR spectra of CuO in the range $400\text{-}650 \text{ cm}^{-1}$, but in some other cases^{22,23} an additional peak was observed

at about 1383 cm^{-1} which was explained to be due to $\text{Cu}^{2+}\text{-O}^{2-}$ stretching. This difference in spectral behaviour may be due to the different methods adopted for synthesizing the CuO nanoparticles.

The FTIR spectra of Sigma-Aldrich copper (II) oxide and synthesized copper (II) oxide nanopowders are shown in Fig. 1. In case of Sigma-Aldrich CuO nanopowder, there are two vibration bands at 482 cm^{-1} and 536 cm^{-1} and one stretching band at 1383 cm^{-1} which are the characteristic bands of Cu (II) O nanoparticles and one broad band at 1048 cm^{-1} which is due to the ONO_2 stretching. For Y and Z-CuO nanopowders, FTIR spectra exhibit only two peaks at 527 cm^{-1} and 590 cm^{-1} (Fig. 1), which can be attributed to the vibration of Cu-O, confirming the formation of pure CuO nanopowders. In case of X-CuO nanopowder, peaks at 527 cm^{-1} and 579 cm^{-1} (Fig. 1) are attributed to the vibration of Cu-O, and an additional peak at 1109 cm^{-1} is due to the SO_4

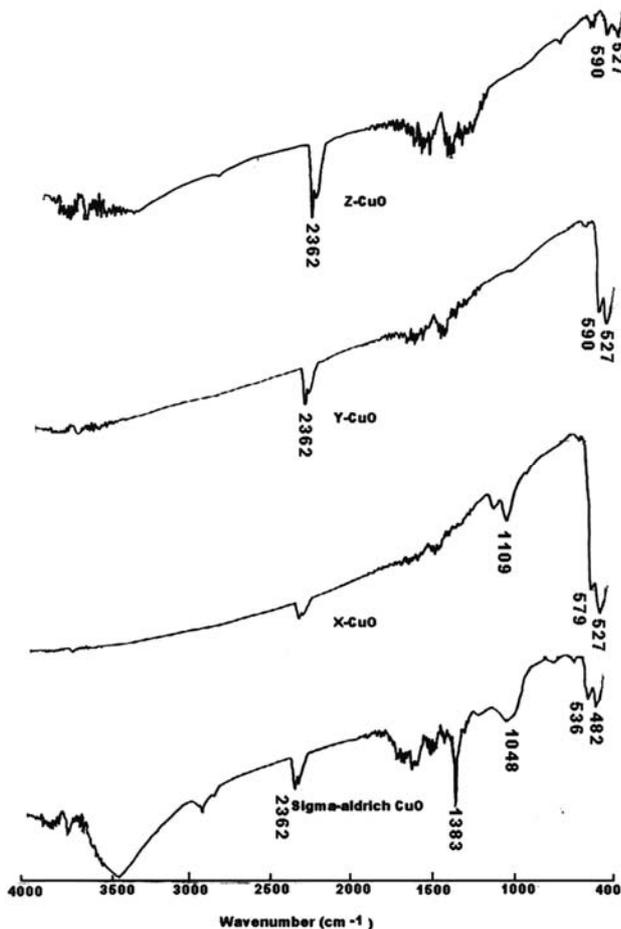


Fig. 1 — FTIR spectra of Sigma-Aldrich CuO, X-CuO, Y-CuO and Z-CuO nanopowders

stretching. A sharp peak at 2362 cm^{-1} in all CuO nanopowders is due to the presence of atmospheric CO_2 .

3.2 X-Ray Diffraction Studies

X-Ray diffraction is one of the most important characterization tools in solid state chemistry and nano material science to determine the size of compound. In this case, X-ray diffraction studies of synthesized copper oxide nano powders as well as sigma-Aldrich CuO nanopowder have been conducted for comparison of their particle sizes.

The comparative X-ray diffraction behaviour of Sigma-Aldrich CuO nanopowder and synthesized CuO nanopowders are shown in Fig. 2. There are three sharp and well developed peaks having 2θ values at about 35.6 , 38.8 and 48.8 deg with d spacing values at near about 0.25 , 0.23 and 0.18 nm, respectively are similar in all synthesized nanopowders and Sigma-aldrich CuO nanopowder. These values are in good agreement with those in JCPDS, CuO file No. 5-661. The sizes of the CuO particles are in the range $28\text{-}92$ nm (Table 1). The XRD results thus confirm the formation of copper oxide nanopowder of diameter less than 100 nanometer.

3.3 Thermal Conductivity Studies

Initially, thermal conductivity of base fluids such as HPLC grade water, ethylene glycol/water (40:60) and subsequently that of CuO nanofluids X-1, Y-1, Z-1 and X-2, Y-2, Z-2 were recorded at 25°C . The thermal conductivity value observed for HPLC grade water was 0.6108 W/mK and that for ethylene glycol/water was 0.4943 W/mK . For X-1, Y-1 and Z-1 CuO nanofluids, the thermal conductivity values were 0.6529 , 0.6766 and 0.6841 W/mK , respectively (Table 2), which showed 7% , 11% and 12% increase in thermal conductivity over the respective base fluid. In case of X-2, Y-2 and Z-2 CuO nanofluids, the thermal conductivity values were 0.7751 , 0.7576 and 0.7918 W/mK , respectively (Table 2) which are much higher than the thermal conductivity value of their respective base fluid (0.4943 W/mK). For X-2, Y-2 and Z-2 CuO nanofluids, there were significant enhancements of thermal conductivity such as 56% , 53% and 60% , respectively (Table 2) over their base fluid. The nanofluids prepared using 40:60 ethylene glycol/water medium had more enhancements than those prepared in water medium. The thermal conductivity value of Sigma-Aldrich CuO nanofluid in HPLC

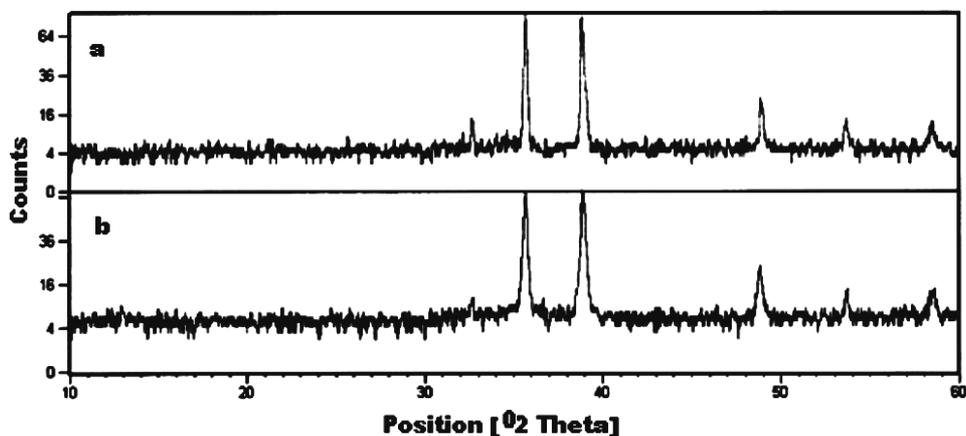


Fig. 2 — X-ray diffractogram of (a) synthesized and (b) Sigma-Aldrich CuO nanopowder

Table 1 — Estimation of particle size of copper oxide nanopowders on the basis of X-ray diffraction

Sample	2 θ of the intense peak (deg.)	θ of the intense peak (deg.)	FWHM of the intense peak (radians)	Size of the particle (D) nm	d-spacing nm
Sigma-Aldrich CuO nanopowder	35.668	17.834	0.00248	58.70	0.2517
	38.880	19.440	0.00313	46.99	0.2316
	48.835	24.417	0.00238	64.00	0.1865
X-CuO nanopowder	35.686	17.843	0.00275	52.99	0.2516
	38.858	19.429	0.00287	51.26	0.2317
	48.930	24.465	0.00530	28.70	0.1861
Y-CuO nanopowder	35.700	17.850	0.00206	70.47	0.2515
	38.820	19.410	0.00197	74.36	0.2319
	48.917	24.458	0.00169	90.17	0.1862
Z-CuO nanopowder	35.797	17.898	0.00157	92.58	0.2508
	39.029	19.514	0.00173	84.87	0.2307
	49.039	24.519	0.00237	64.32	0.1857

Table 2 — Thermal conductivity of CuO nanofluids in water (X-1,Y-1 and Z-1) and in 40:60 EG/ Water (X-2,Y-2 and Z-2)

Sample	Thermal conductivity (W/mK)	Thermal diffusivity (mm ² /s)	Specific heat (MJ/m ³ K)	Enhancement in Thermal Conductivity (%)
HPLC water base fluid	0.6108	0.1540	3.135	-
X-1 CuO nanofluid	0.6529	0.1816	3.595	7.0
Y-1 CuO nanofluid	0.6766	0.2008	3.370	11.0
Z-1 CuO nanofluid	0.6841	0.2039	3.355	12.0
Sigma-aldrich CuO nanofluid	0.6852	0.2132	3.213	12.0
40:60 EG/water base fluid	0.4943	0.1765	0.3595	-
X-2 CuO nanofluid	0.7751	0.6278	1.235	56.0
Y-2 CuO nanofluid	0.7576	0.5822	1.302	53.0
Z-2 CuO nanofluid	0.7918	0.6095	1.300	60.0
Sigma-aldrich CuO nanofluid	0.6007	0.2519	2.385	21.0

water medium was 0.6852 W/mK and in ethylene glycol/water (40: 60) medium was 0.6007 W/mK. Furthermore, Sigma-aldrich CuO nanofluid in ethylene glycol/water (40:60) medium showed more thermal conductivity enhancement (21%) than the nanofluid of water medium (12%). On the basis of thermal conductivity studies of all nanofluids, it can

be seen that Z-2 CuO nanofluid showed the highest thermal conductivity enhancement (60%) (Table 2).

3.4 Cyclic Voltammetric Studies

All electrochemical experiments were conducted using a Gamry potentiostat instrument having three electrode systems. The reference electrode was

Ag/AgCl (1M KCl), counter electrode was a platinum wire and a platinum electrode was used as the working electrode. The electrolyte solution was 0.1 M KCl. All CuO nanopowders were dissolved in 0.1 M H₂SO₄ solution prior to their use in the cyclic voltammetric experiments. The pH of all the solutions was about 3.0.

Cyclic voltammetric study of Sigma-aldrich CuO solution was carried out in the potential range -400-600 mV. There were two oxidation peaks Epa1 and Epa2 at 36 mV and 230 mV, respectively and one reduction peak Epc1 at -113 mV as shown in voltammogram [Fig. 3(a)]. The sharp anodic peak Epa1 at 36 mV was due to deposition of copper on the surface of electrode (Cu^{0/2+}) and corresponding

cathodic peak Epc1 at -113 mV was due to Cu^{2+/0} electrode reaction. The peak Epa2 at 230 mV may be due to the oxidation of new species generated in the solution. The value of ΔE_{p1} at -149 mV, clearly indicates that redox reaction is irreversible. The cyclic voltammetric studies of X, Y and Z-CuO solutions were performed in similar potential region. For X-CuO solution, the value of anodic peak potential Epa1 at 132 mV was due to deposition of copper on the surface of electrode involving Cu^{0/2+} electrode reaction and the value of cathodic peak potential Epc1 at -74 mV was because of Cu^{2+/0} electrode reaction. The ΔE_{p1} value at -206 mV, indicates the irreversible nature of redox couple [Fig. 3(b)]. The voltammograms of Y and Z-CuO solutions showed

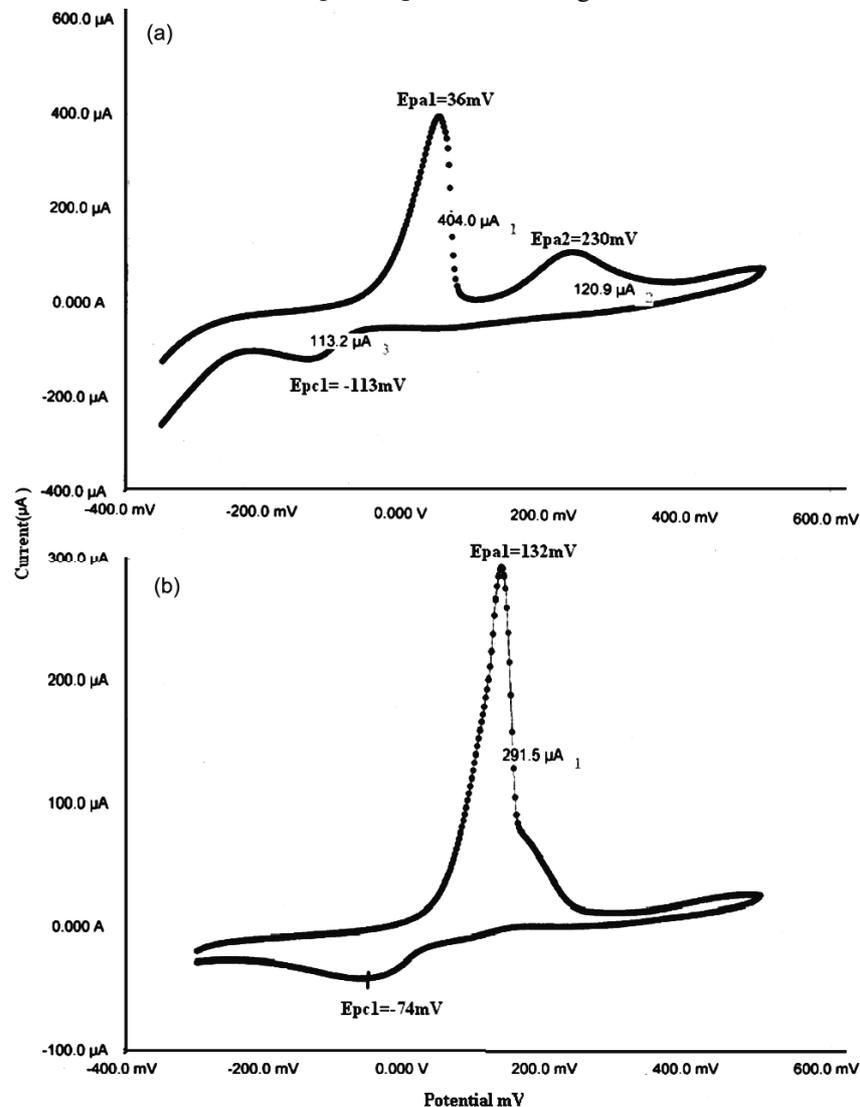


Fig. 3 — Cyclic voltammogram of (a) Sigma-Aldrich CuO and (b) X-CuO solution in 0.1 M H₂SO₄ at Pt/ Ag/AgCl/0.1 M KCl

Table 3 — Cyclic voltammetric data of X, Y, Z CuO solutions and Sigma-Aldrich CuO solution in 0.1 M H₂SO₄ at Pt/Ag/AgCl/0.1 M KCl

Sample	Epa1 (mV)	Epc1 (mV)	Ipa1 (μA)	Ipc1 (μA)	Ipc/Ipa	ΔEp1 (mV)	Epa2 (mV)	Ipa2 (μA)
X-CuO solution	132	-74	291.5	145.0	0.49	-206	NA	NA
Y-CuO solution	150	NA	617.4	NA	NA	NA	344	255.6
Z-CuO solution	146	NA	299.3	NA	NA	NA	252	138.8
Sigma-Aldrich CuO solution	36	-113	404.0	113.0	0.27	-149	230	133.0

NA= Not appeared

sharp oxidation peaks at 146 mV and 150 mV, respectively that may be due to strong deposition of copper on the surface of electrode.



Other oxidation peaks at 344 mV and 252 mV for Y and Z-CuO solutions, respectively may be due to oxidation of new species generated in the solution. No reduction peak was observed in reverse cycle. The Ipc/Ipa value for both X-CuO solution and Sigma-Aldrich CuO solution was <1.0 which indicates that the reactant might be adsorbed on the surface of electrode (Table 3).

4 Conclusions

All three synthesized CuO nano powders were showing similar behaviour as Sigma-aldrich CuO nanopowder as justified by FTIR and X-ray diffraction studies. FTIR spectra of all CuO nanopowders showed two bands in the range 450-600 cm⁻¹ which are the characteristic bands of CuO nanoparticles. The particle size of all CuO nanopowders was less than 100 nm. Substantial enhancement (60%) in thermal conductivity has been observed in Z-2 CuO nanofluid over the base fluid. The cyclic voltammogram of acidic solutions of all CuO nanopowder showed irreversible behaviour; the oxidation peak might be due to the deposition of copper on the surface of electrode involving Cu^{0/2+} electrode reaction and the reduction peak was due to Cu^{2+/0} electrode reaction.

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