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Synthesis And Characterization of Copper Oxide Nanopowders And Their Nanofluids

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ABSTRACT

Two copper oxide nanopowders were synthesized by chemical reduction method in which sodium hydroxide solution was used as a reducing agent. The copper nitrate trihydrate and copper acetate monohydrate precursors were used for the synthesis of CuO nanopowders. Solid state characterizations of synthesized nanopowders were carried out by infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques. Nanofluids of synthesized nanopowders were prepared in water as well as in ethylene glycol: water (40:60) media. Thermal conductivity measurements of prepared nanofluids were studied at 25^0*C in which maximum thermal conductivity enhancement was observed in NF-4 nanofluid. The electrochemical behavior of synthesized CuO nanopowders were also carried out in acidic aqueous medium.*

Keywords: CuO nanopowders and nanofluids, FTIR, X-ray diffraction, Thermal conductivity and Electrochemistry.

INTRODUCTION

Nanofluids are a new class of fluids engineered by dispersing nanometer sized materials (nanoparticles, nanofibers, nanotubes, etc.) in base fluid[**1**]. They are two phase systems first phase is solid phase and another second phase is liquid phase. Nanofluid have been found to posses enhance thermo physical properties such as thermal conductivity, thermal diffusivity, viscosity and conductive heat transfer coefficients compare to those of base fluids like oil and water. Surfactants used in nanofluids are also called dispersant. Adding dispersants in two phase systems is an easy and economic method to enhance the stability of nanofluids. Copper nanofluids are stable due to the protective role of polyvinyl pyrrolidone (PVP), as it reacts the growth and agglomerations of nanoparticles by steric effect. The properties of nanofluids are different from the properties of conventional heat transfer fluids. The nanoparticles offer large total surface area as a result of which higher thermal conductivities are expected in nanofluids. The thermal conductivity property is a surface phenomenon. The increase in the thermal conductivity of nanofluids can also be attributed to the large surface area of CuO nanoparticles. There are many applications of nanofluids such as in heat transfer [**2, 3**], electronics [**4**], transportation [**5**], industrial cooling, nuclear system cooling [**6**], space and defense [**7**], mass transfer enhancement [**8**], energy storage [**9**], friction reduction [**10**], magnetic sealing [**11**], antibacterial activity [**12**] and in nano-drug delivery [**13**].

Nanofluids are solid-liquid composite materials consisting of solid nanoparticles or nanofibers with sizes typically of 1-100 nm suspended in liquid. Even a small amount (<1% volume fraction) of Cu nanoparticles or carbon nanotubes dispersed in ethylene glycol or oil is reported to increase the inherently the thermal conductivity of the liquid by 40% and 150%, respectively. Thermal conductivity of nanofluids depends on many factors such as particle volume fraction, particle material, particle size, particle shape, base fluid material, and temperature. There are some researchers who have studied the electrochemical behavior of Copper oxide in acidic and basic conditions [**14-16**].

Here, we report the synthesis of copper oxide nanopowders by chemical reduction method involving sodium hydroxide as a reducing agent and preparation of nanofluids by using synthesized CuO nano powders. The solid states characterizations by FTIR spectroscopy and X-ray diffraction studies. The liquid state characterizations by thermal conductivity and cyclic voltammetric studies.

MATERIALS AND METHODS

Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) , sodium laurel sulfate(SLS), ethylene glycol (EG) and sodium hydroxide (NaOH) were purchased from SDFCL ltd. Copper acetate monohydrate $(CH_3COO)_2Cu.H_2O$ was procure from Merck specialties (Pvt.) ltd. and poly vinyl pyrrolidone (PVP) was purchase from Central drug house ltd. All the chemicals were used without further purification. HPLC grade water was used in all experiment.

The infrared spectra of synthesized CuO nanopowders were recorded as KBr pellets using 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 Bruker Diffractometer (Model D8 ADVANCE) in range $10< 2\theta< 60$ with 1.5405Å Cu Kα radiation. The average particle size(d) was calculated from the line broading in XRD patterns using Debye- Scherrer formula: $D = 0.9\lambda/\beta \cos \theta$, where λ is wave length of X-ray (0.1541nm), β is FWHM (full width at half maximum) , θ is diffraction angle and D is particle diameter size.

Synthesis of copper oxide nanopowders: Copper oxide nanopowders were synthesized by chemical reduction method in which sodium hydroxide (NaOH) was used as a reducing agent. There are some researchers who have used NaOH as a reducing agent for the synthesis of CuO nanoparticles. The details of synthesis process are given below.

Synthesis of V-1 nanopowder: 0.5M copper nitrate trihydrate was dissolve in 25mL water and 0.5M sodium hydroxide was also dissolve in 25 mL water by stirring. Sodium hydroxide solution drop by drop added to copper nitrate solution. The black colour precipitate was obtained after complete reduction of copper nitrate to copper oxide. 1% poly vinyl pyrrolidone (PVP=100mg) and 0.5M ascorbic acid were added to the resulting solution with continuous stirring. Precipitate was filtered and washed twice with water and twice with acetone and dried in vacuum. Black colour CuO nanopowder was collected.

Synthesis of V-2 nano-powder: Aqueous solution of 0.5M copper acetate monohydrate was reduced with 0.5M aqueous solution of sodium hydroxide and stirred for 3 h at 55^0C greenish color precipitate was obtained, filtered it, wash with water and drying at 80^0C in oven after that expose at 750^0C for 2 h in furnace. Crush the sample to find it as a powder form. Black color CuO nanopowder was collected.

Preparation of copper oxide nanofluids: There were four types of CuO nanofluids such as NF-1, NF-2, NF-3 and NF-4 were prepared by using two types of copper oxide nanopowders V-1 and V-2. The preparation methods are given below.

Preparation of NF-1: For the preparation of NF-1 CuO nanofluids, 50 mg V-1 copper oxide nano powder was mixed with 50 mL of water (base fluid) and stirring for 2 h. In the resulting solution 0.1% Poly vinyl pyrrolidone (PVP) (50mg) and 1.0% sodium laurel sulfate (SLS) (500mg) were mixed with continuous stirring for 3 h. In order to ensure a stable, uniform, continuous suspension and proper dispersion the resulting solutions were kept on sonicator for 2 h.

Preparation of NF-2: For the preparation of NF-2 CuO nanofluids, 50 mg V-1 copper oxide nano powder was mixed with 50 mL of ethylene glycol/water base fluid (40:60 v/v) and stirring for 2 h. In the resulting solution 0.1% poly vinyl pyrrolidone (PVP) (50mg) and 1.0% sodium laurel sulfate (SLS) (500mg) were mixed with continuous stirring for 3 h. For proper dispersion the resulting solutions were kept on sonicator for 2 h.

Preparation of NF-3: NF-3 was prepared by similar procedure used as in NF-1 but different nanopowder V-2 was taken.

Preparation of NF-4: V-2 nanopowder was used for the preparation of NF-4. Methodology and base fluid was same as NF-2.

RESULTS AND DISCUSSION

FTIR Spectra: The FTIR spectral studies of synthesized copper (II) oxide nanopowders were carried out between the range of 4000-400 cm^{-1} and these spectra are shown in figure1. The IR spectra of V-1 and V-2 CuO nanopowder are different because the synthetic route of both CuO nanopowder are different. In V-2 CuO nanopowder peaks at 520 cm^{-1} and 590 cm^{-1} are the characteristic bands of Cu(II)O nanopowder. For V-1 CuO nanopowder bands presents at 511cm^{-1} and 1383 cm^{-1}can be attributed to the vibration of Cu-O and stretching of Cu-O respectively. The IR bands at 677 cm^{-1}, 781cm^{-1} and 875 cm^{-1} due to the Cu-OH deformation. The IR peak displayed at 1047 cm^{-1}, 1349 cm^{-1} and 1422 cm^{-1} in the figure 1 are stretching bands of ONO_2. Band at 1649cm^{-1} was representing the H-O-H bending in V-2 CuO nanopowder. The IR peaks at 3444 cm^{-1} and 3546cm^{-1} were OH stretching bands of H_2O. There are some researchers **[17-21]** who have already studied about the infrared spectra of CuO nanopowder.

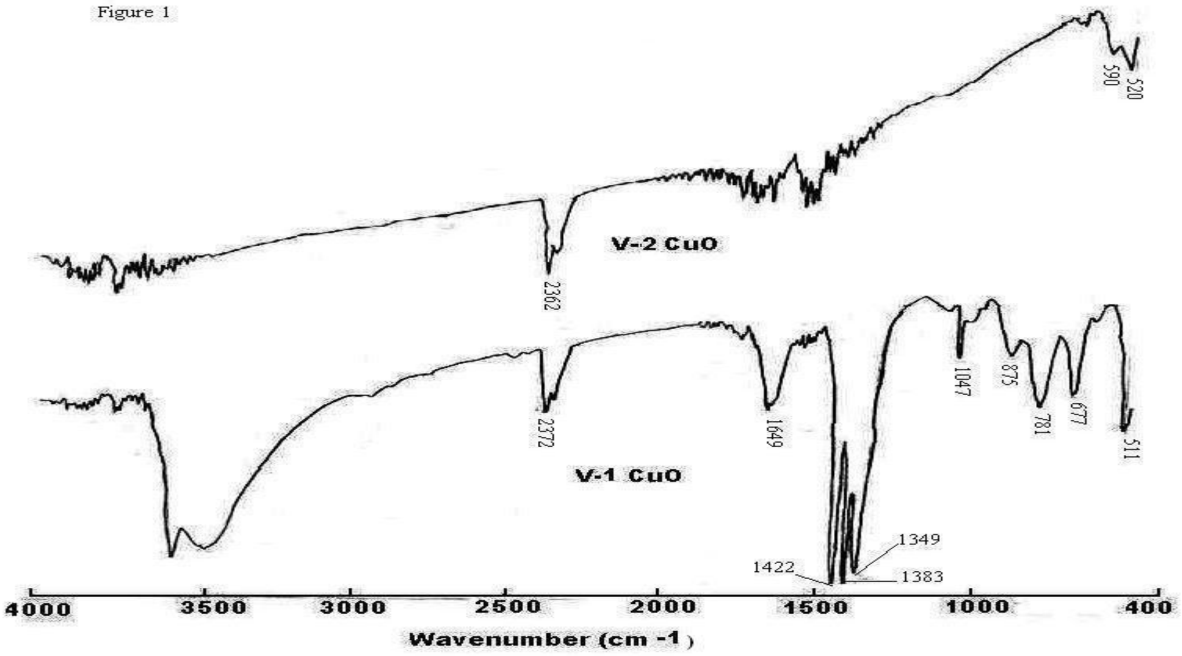

Figure 1: IR spectra of V-1 CuO and V-2 CuO nanopowders

X-Ray diffraction: X-Ray diffraction experiments were done between the range of 10< 2θ < 60. There are four peaks appear in the XRD of V-1 copper oxide nanopowders having2θ value 12.94, 35.73, 38.99 and 48.87 (Table1) in which value 12.94 match with copper nitrate JCPDS file 03-0068 and other three values match with CuO JCPDS file 05-661. The d-spacing values of V-1 CuO nanopowder are given in table 1. In the case of V-2 CuO nanopowder the 2θ peaks positions appeared at 32.67, 35.72, 38.88 and 48.94 in XRD having d-spacing values 0.2740, 0.2513, 0.2316 and 0.1860 nm respectively (**Table 1**). These values had compared with JCPDS, CuO file No. 5-661, is in good agreement. The particle sizes of V-1 and V-2 CuO nanopowders are in the ranges of 46 nm to 82 nm.

Table 1: Particle size of V-1 and V-2 CuO nanopowders calculated by X-ray diffraction

CuO nanopowders	2θ 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
V-1 CuO nanopowder	12.96 35.73 38.96 48.93	06.48 12.86 19.48 24.46	0.00192 0.00795 0.00293 0.00358	72.23 17.89 50.21 42.57	0.6830 0.2512 0.2311 0.1861
V-2 CuO nanopowder	32.67 35.72 38.88 48.94	16.33 17.86 19.44 24.47	0.00178 0.00214 0.00315 0.00245	81.20 81.87 46.70 62.19	0.2740 0.2513 0.2316 0.1860

Thermal conductivity: Thermal conductivity of base fluids was recorded first before recording the thermal conductivity of CuO nanofluids at 25^0C. The values of thermal conductivity of water base fluid and ethylene glycol/ water base fluids were 0.6108 W mK^{-1} and 0.4943 W mK^{-1} respectively. The thermal conductivity of NF-1 and NF-3 nanofluids was 0.8303 W mK^{-1} and 0.8684 W mK^{-1} which showed 36% and 42% enhancements of thermal conductivities respectively over their base fluid (Table 2). In case of NF-2 and NF-4 nanofluids, the thermal conductivity values were 0.7823 W mK^{-1} and 0.7880 W mK^{-1} respectively. These thermal conductivity values were compared with their base fluid and more enhancement in thermal conductivity were observed such as 58% and 59% for NF-2 and NF-4 CuO nanofluids respectively (Table 2). The thermal conductivity enhancements in NF-1 and NF-3 nanofluids were comparatively low, may be due to some agglomeration or precursors effects or nature of base fluids. The thermal conductivity value of EG/ Water medium was greater than the water medium. Furthermore it was also clear that all nanofluids were showing more thermal conductivity enhancement over their base fluids (Table 2). NF-4 CuO nanofluid showed highest thermal conductivity enhancement in compare to other nanofluids.

Table 2: Thermal conductivity of NF-1, NF-2, NF-3 and NF-4 nanofluids

Sample	Thermal conductivity (W/mK)	Thermal diffusivity (mm^2/s)	Specific heat (MJ/m^3K)	Enhancement in Thermal Conductivity (%)
HPLC H_2O	0.6108	0.1540	3.135	-
NF-1	0.8303	0.6426	1.292	36
NF-3	0.8684	0.3652	2.378	42
40:60 Ethylene Glycol: Water	0.4943	0.1765	0.3595	-
NF-2	0.7823	0.5744	1.368	58.0
NF-4	0.7880	0.5689	1.386	59.4

Electrochemistry: The electrochemical behaviors of synthesized CuO nanopowders V-1 and V-2 were carried out by means of cyclic voltametry. Both copper (II) oxide nanopowders have properly dissolved in 1M H_2SO_4 solution before to initiate the cyclic voltammetric experiments. The pH values of all CuO solutions were less than 3.0. The experiments were performed at Gamry potentiostat instrument having three electrodes system where working electrode was platinum disc electrode, reference electrode was Ag/AgCl and platinum wire was used as a counter electrode.

The cyclic voltammetric (CV) experiment of V-1 CuO acidic solution was carried out in the potential range from 100 mV to -300 mV and the voltamograms are shown in figure 2a. In forward scan from 100 mV to -300 mV there was one cathodic peak Epc= -175 mV at 100 mV/s scan rate which showed the reduction of Cu^{2+} to Cu^{+} and during reverse scan from -300 mV to 100 mV there was one anodic peak Epa = -28 mV at 100 mV/s scan rate indicated towards the oxidation of Cu^{+} to Cu^{2+}. The value of peak potential separation ΔEp was -147 mV (Table 3) due to irreversible nature of the redox couple.

In case of V-2 CuO acidic solution, the CV experiment was preformed between the potential range from 100 mV to -400 mV and the voltammograms are shown in figure 2b. In forward scan from 100 mV to -400 mV one cathodic peak Epc was observed at -95 mV with scan rate 100mV/s due to the $Cu^{2+} \rightarrow Cu^{+}$ electrode reaction. In reverse scan from -400 mV to 100 mV one anodic peak Epa was obtained at +22 mV with 100 mV/s scan rate indicated $Cu^{+} \rightarrow Cu^{2+}$ electrochemical reaction. The ΔEp value was -117 mV (Table 3) showed the quasi reversible nature of redox couple. On the basis of anodic and cathodic peak potential of V-1 and V-2 solutions it could be clear that V-2 solution have easier oxidation and reduction than V-1 solution.

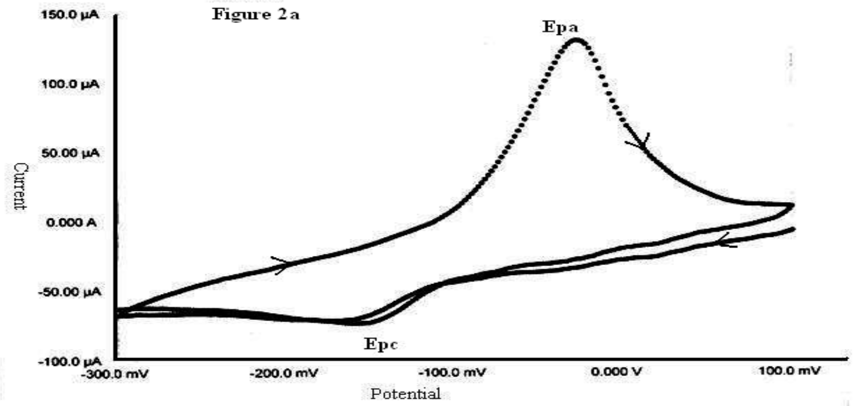

Figure 2a: Cyclic voltammogram of V-1 CuO solution in 1M H_2SO_4 at Pt /Ag/AgCl/0.1M KCl scan rate 100 mV/s

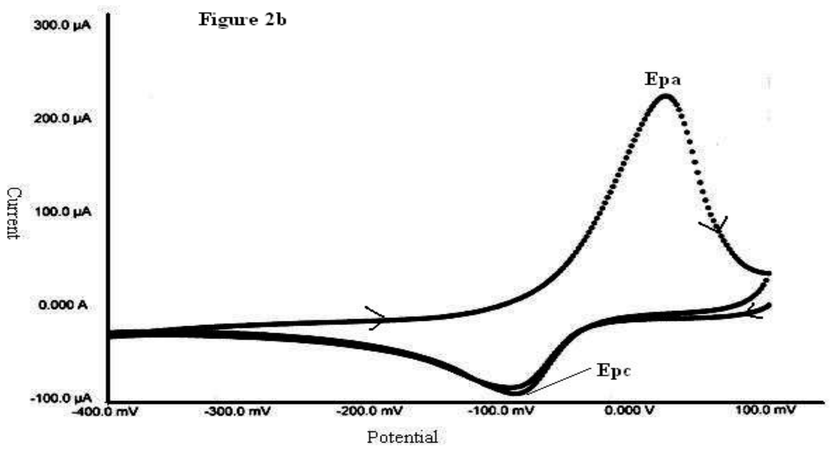

Figure 2b: Cyclic voltammogram of V-2 CuO solution in 1M H_2SO_4 at Pt Ag/AgCl/0.1M KCl scan rate 100 mV/s

Table3: Cyclic voltammetric data for V-1 and V-2 CuO solution in 1M H2SO4 at Pt /Ag/AgCl/0.1M KCl with 100 mV/s scan rate

Sample	Epc (mV)	Epa (mV)	Ipc (μA)	Ipa (μA)	Ipa/Ipc	ΔEp (mV)
V-1 CuO solution	-175	-28	-71.7	129.7	1.8	-147
V-2 CuO solution	-95	+22	-90.0	222.0	2.4	-117

APPLICATIONS

There are many applications of nanofluids such as in heat transfer , electronics, transportation, industrial cooling, nuclear system cooling, space and defense, mass transfer enhancement, energy storage, friction reduction, magnetic sealing, antibacterial activity and in nano-drug delivery.

CONCLUSIONS

FTIR and X-ray diffraction studies were confirming the formation of CuO nanopowder. The particle size of the V-1 and V-2 nanopowders were calculated and obtained bellow than 100 nanometer. It was a maximum enhancement 59.4% in thermal conductivity have been observed in NF-4 CuO nanofluid. In the electrochemical behavior of acidic solution of V-1 and V-2 CuO nanopowder it could be clear that V-2 CuO solution have easier oxidation and reduction than V-1 CuO solution.

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