Copper nanoparticles prepared by pulsed exploding wire
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Abstract
In this work copper nanopowder was created at different liquid medias like DDDW, ethylene glycol and Polyvinylpyrrolidone (PVP). Copper nanopowder prepared using explosion wire process and investigated the effects of the exploding energy, wire diameter, the type of liquid on the particle size, and the particles size distribution. The nanoparticles are characterized by x-ray diffraction, UV-visible absorption spectroscopy and transmission electron microscopy (TEM). The x-ray diffraction results reveal that the nanoparticles continue to routine lattice periodicity at reduced particle size. The UV-Visible absorption spectrum of liquid solution for copper nanoparticles shows sharp and single surface Plasmon resonance (SPR) peak centered at a wavelength of 590 nm in ethylene glycol media, but don’t have peak in PVP fluid. This peak indicated the production of pure and spherical copper nanoparticle.

Keywords
Cu nanofluids, exploding wire, Optical properties, XRD.

Introduction
Nanoscience and nanotechnology is a promising and fast developing field that broadly encompasses the fundamental understanding and resulting technological advances arising from the utilization of materials having the nanometer length scale[1]. Nanofluids, dispersed nanoparticles suspended in a base fluid, have gained wonderful interest from scientific and industrial communities because of their exclusive properties. They have been used in many industrial applications such as heat transfer, electronic, biomedical device manufacturing, and others [2]. Copper nanoparticles have been prepared using the methods such as thermal reduction, vacuum vapor deposition, microwave irradiation.
methods, chemical reduction, and laser ablation [3]. In this research the electrical explosion wire (EEW) was adopted because it is a very simple, effectiveness, and low-cost technique to fabricate different types of nanopowders. One can use this method for synthesis nanoparticle in liquid or air. Properties of nanoparticles obtained by EEW depend on several conditions include wire diameter, wire material, capacitor bank voltage, current pulse and properties of the ambient medium. In general, all of these properties could effect on the particles size and size distribution. The media surroundings of the explosion process effects on the size, shape size distribution and chemical reactions between wire materials and active medium. Ambient environment of EEW process in liquid showed a significant effect on the properties of synthesized materials [4, 5].

The electrical exploding wire experiment is performed by rapidly discharging an electrically stored source through a fine wire. The capacitor was charged using an applied voltage. The amount of stored energy can be evaluated by:

\[ E = \frac{1}{2} CV^2 \quad (1) \]

where C and V are the capacitance and charging voltage respectively. In this research, the method is the mixed between exploding wire technique and spark explosion method. When the first electrode (wire) touched the second electrode (plate) the wire vaporized and turned into plasma [5]. After that, wire evaporation, and convert to plasma. The plasma expands in the medium due to the enormous difference in the temperature and pressure between the plasma and the ambient liquid. The expanded plasma particles will gradually cool because of collisions with ambient liquid molecules. Finally, the plasma loses its expansive driving force. Hence, a low ambient pressure allows a large expansion volume. This leads to low number concentration of the substance during particle growth, resulting in small nano-particles. The vaporized particles condensed more efficiently in the liquid than in ambient air [6,7,8].

**Experimental work**

The schematic diagram of EEW apparatus for the preparation of metal nanoparticles in liquid media was shown in Fig.1. These apparatus consists of chamber for nanoparticles preparation and an electrical discharge circuit for generation of large pulse current. The electrical circuit consists of a capacitors bank 2500\(\mu\)F, 500V dc power supply, wire guides, wire supply unit, represents the first electrode, and the other electrode is a metal plate. When the wire is brought close to the plate as soon as contact is made the storage energy in 2500\(\mu\)F capacitors released through the two electrodes (wire and plate). The wire and the plate at the contact point were over heated, evaporated and converted to plasma state. Copper wires with three exploded in liquid to produce Cu nanoparticles. Three type of liquid were used as a medium represented by double distilled deionized water (DDDW), ethylene glycol, and Polyvinylpyrrolidone (PVP) of 5mM concentration. The typical experimental conditions are summarized in Table 1:

![Fig.1: Principle scheme of the experimental setup](image-url)
TEM and X-Ray were employed to confirm the nanoparticles shape, size and size distributions. The absorption spectrum of copper colloid was investigated by UV-visible from a double beam spectrophotometer in the wavelength range of 300-800 nm. TEM was used to determine the particle size and particles size distribution. To examine a stability of the prepared nanoparticles, the changes in the absorption spectrum with time were studied.

**Table 1: The experimental conditions were used for preparation copper nanoparticles.**

<table>
<thead>
<tr>
<th>Capacitance</th>
<th>2500 µF, 500V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameters of wire</td>
<td>(0.2, 0.3 ,0.4) mm</td>
</tr>
<tr>
<td>Liquid type</td>
<td>DDDW, Ethylene Glycol, PVP</td>
</tr>
<tr>
<td>Liquid content</td>
<td>100 ml</td>
</tr>
<tr>
<td>Number of explosion</td>
<td>10 times</td>
</tr>
<tr>
<td>Charging voltage for 0.25mm wire diameter</td>
<td>(200, 250, 275) Volt</td>
</tr>
<tr>
<td>Charging voltage for (0.3 and 0.4)mm wire diameters</td>
<td>(200, 250, 300) Volt</td>
</tr>
</tbody>
</table>

**Results and discussion**

The synthesis of the copper nanoparticles was immediately followed by UV-Visible analysis. UV-visible spectrum recorded in the absorbance mode in the range 300-800nm as shown in Fig.2 and Fig. 3 where Fig. 2 for Cu nanoparticles prepared in DDDW and Fig. 3 for Cu nanoparticles prepared in ethylene glycol. These figures show a single SPR peak for each curve, which indicates formation of copper nanoparticles. The SPR of NPs is mostly controlled by certain parameters, such as shape, morphology, size, composition and environment dielectric constant of the prepared nanoparticles. UV–Visible absorption spectrum of copper nanoparticles which were prepared in DDDW and ethylene glycol media showed surface Plasmon resonance (SPR) absorption peak centered around (600 nm) for all samples. The central peak position depends on the wire diameter, charging voltage and media type. The SPR has a maximum of absorption peak $\lambda_{\text{max}}$ for all diameters of wire, charging voltage, discharge energy and the types of fluid are shown in Table 2. It is clear that, the optical properties depend strongly on the liquid media. For the same wire diameter and the same charging voltage, the particles were prepared in DDDW were smaller than those prepared in ethylene glycol. The SPR absorption peak for copper nanoparticles prepared in DDDW is sharper than that of nanoparticles prepared in Ethylene Glycol. This means, that the nanoparticles prepared in DDDW have narrow particles size distribution and it has almost the same size.

The particle diameters estimated by SPR absorption peak position shows that the diameter of the particles decreases with decreasing of the metal wire diameter at fixed voltage. While the wire diameter increases, tend to shift the value of the $\lambda_{\text{max}}$ to long wavelength as shown in Table 2 that means the size of particles became larger. The maximum wavelength ($\lambda_{\text{max}}$) was shifted to the short wavelength, when the charging voltage increases for the same wire diameter. This means that the size of the particles became less.
Table 2: Plasmon absorption peaks at different diameters of wire and charging voltage for copper nanoparticles in three media.

<table>
<thead>
<tr>
<th>Dia. of wire (mm)</th>
<th>Charge voltage (volt)</th>
<th>Energy (Joule)</th>
<th>$\lambda_{\text{max}}$ with DDDW (nm)</th>
<th>$\lambda_{\text{max}}$ with Ethylene Glycol (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>200</td>
<td>43</td>
<td>589</td>
<td>592</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>58.6</td>
<td>587</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>76.2</td>
<td>581</td>
<td>586</td>
</tr>
<tr>
<td>0.3</td>
<td>200</td>
<td>49</td>
<td>591</td>
<td>601</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>68</td>
<td>589</td>
<td>593</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>101.5</td>
<td>586</td>
<td>590</td>
</tr>
<tr>
<td>0.4</td>
<td>200</td>
<td>49.08</td>
<td>600</td>
<td>608</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>76</td>
<td>595</td>
<td>606</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>107.8</td>
<td>593</td>
<td>600</td>
</tr>
</tbody>
</table>

Fig. 4 shows the UV-visible optical absorption spectra in the range 300-800 nm of the Cu nanoparticles which prepared in PVP (its concentration 5%). PVP media was found to be a very efficient stabilizer for the stabilization of copper nanoparticles. UV-visible optical absorption spectra of the colloid don’t have SPR copper peak because of high concentration of PVP. The copper nanoparticles prepared in PVP have large size compared with that prepared in ethylene glycol or DDDW, and these nanoparticles shows weak SPR peak, this means that the nanoparticles coated by PVP.

**Fig. 2:** UV-VIS. spectra of Cu colloid prepared by EEW in DDDW at different diameter; (a) 0.2 mm (b) 0.3 mm (c) 0.4 mm.

**Fig. 3:** UV-VIS. spectra of Cu colloid prepared by EEW in ethylene glycol at different diameter; (a) 0.2 mm (b) 0.3 mm and (c) 0.4 mm.
In order to observe a stability of the prepared copper colloid by the changes in the absorption spectrum with time were studied for copper colloid synthesized by EEW using wire with diameter 0.3mm and with charging voltage 250 Volt. The changes in the absorption spectrum with time were shown in Fig.5. The spectral change indicates that the diameters of the nanoparticles are increased more under aging effect, which is interpreted to the metal nanoparticles are aggregated. The changed observed as red shift in SPR peaks position with time. The peak position was shifted to long wavelength and still has the same intensity for fresh nanoparticles, this means that the nanoparticles become larger, but the peak width fixed with time. This confirms that the particles size distribution remains steady. Fig.6 shows two images one for the fresh sample and the other after two months.
X-ray diffraction (XRD)

Fig.7 shows the crystal structure of the bulk copper used in this work. By comparing between the resulting copper spectra for d-spacing, intensity of the peaks, and Miller Indices values with (ICDD) card 96-410-5041 for copper, it is clear that the crystal structure of bulk copper was face center cubic (FCC), the major peak with the highest of crystallinity in the spectra of this figure is at d=1.0168Å and the reflected planes are 111, 200 and 202.

![X-ray diffraction pattern for bulk copper metal](image)

**Fig.7: X-ray diffraction pattern for bulk copper metal.**

a) XRD study for copper nanoparticles in DDDW media

Fig.8 shows the x-ray diffraction pattern in the range of 30°-70° for copper nanoparticles produced using explosion wire with diameter 0.4 mm charging voltage 300Volt in distilled and deionized water (DDDW) media.
From the figure it was observed three diffraction peaks at 35.66º, 38.73º and 43.36º, which can be assigned to diffraction from 002, 200 and 202 planes respectively. Table 3 shows the full width at half maximum d-spacing, Miller indices and crystallite size (C.S nm).

XRD diffraction patterns for the prepared nanoparticles shows x-ray diffraction belonged to the monoclinic structure. All diffraction peaks of sample correspond to the characteristic monoclinic structure of copper oxide. Average C.S of copper oxide nanoparticles calculated using Scherrer equation was 9.1 nm. The oxidation process may be taken off after preparation when the sample dry for x-ray diffraction study. Also from the table it appear that the particles it have very small practical size.

<table>
<thead>
<tr>
<th>20</th>
<th>FWHM</th>
<th>Int.(A.U)</th>
<th>hkl</th>
<th>C.S(nm)</th>
<th>AV.C.S(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.66</td>
<td>1.1242</td>
<td>199</td>
<td>002</td>
<td>7.4</td>
<td>9.1</td>
</tr>
<tr>
<td>38.73</td>
<td>1.0938</td>
<td>248</td>
<td>200</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>43.36</td>
<td>0.6871</td>
<td>73</td>
<td>202</td>
<td>12.4</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3: XRD peaks of Cu NPs that obtained from exploded Cu wires in DDDW media.**

**Fig. 8: X-ray diffraction pattern for copper oxide nanoparticles using exploded Cu wire in DDDW media.**

b) XRD study for copper nanoparticles in Ethylene glycol

Fig.9 shows the x-ray diffraction pattern in range of 40º- 80º for copper nanoparticles that dispersed in ethylene glycol. The x-ray diffraction declares no diffraction peaks which affirm amorphous structure. This indicates that the copper nanoparticles were fully encapsulated by ethylene glycol.
c) XRD study for copper nanoparticles in PVP media

The crystal structure of the Cu-nanoparticles dispersed in the PVP polymer was examined with x-Ray diffraction. Fig.10 shows the XRD pattern in range of 30°- 70° for the Cu nanoparticles dispersed in PVP. The X-ray diffraction shows no diffraction peak which confirms amorphous structure. This indicates that the copper nanoparticles were fully capped by PVP.

Transmission electron microscope

TEM images of the suspended copper, which was synthesized by EEW method in different media and the corresponding particles size distribution, are shown in Fig.11. TEM image with histograms for particles size distribution of copper colloid 0.3mm wire diameter in DDW media was shown Fig.11-c. The images proved the formation of spherical shape Cu nanoparticles at different sizes in the matrix depending on the experiment conditions. The copper nanoparticles average diameter is 4.3nm with normal distribution. It's
clear that the nanoparticles are agglomerated. TEM image analysis with histograms for particles size distribution of a selected sample of Cu NPs, which were synthesized using 0.3 mm exploded wire in ethylene glycol media are shown in Fig.11-b. This image confirmed the synthesized Cu nanoparticles are spherical in shape and grown with well-defined morphology. The diameters of these nanoparticles were found to be in the range between 8-50 nm, with a mean value of about 18 nm. In some regions agglomeration of small nanoparticles was observed. TEM image with histograms for particles size distribution of copper colloid 0.3 mm wire diameter in PVP media was shown Fig.11-c. The image shows that the nanosized copper particles are well-formed and dispersed. The average particles size, where 17 nm in ethylene glycol and PVP media. From the image of TEM, varies size are observed with range of 5-46 nm and the particles have spherical shapes and little agglomerate. The prepared particles in PVP had higher sphericity than that prepared in Ethylene Glycol and DDDW, moreover, they have little agglomeration. The copper nanoparticles prepared in DDDW have the narrowest particles size distribution from that prepared in the other media, and it have the smallest average particle size. This agrees with the results obtained from the width of the SPR absorption peak.

**Fig.11:** TEM image and size distribution of copper nanoparticles produced by wire explosion process the wire diameter 0.3 mm and charging voltage was 300 Volt (a) in DDDW, (b) in ethylene Glycol. And (c), in PVP.
FT-IR Spectrum

A) FT-IR Spectroscopy for Cu nanoparticles in PVP media

Fig. 12 shows the FTIR spectrum for the copper nanoparticles obtained by exploded wire for 0.2 mm wire diameter in PVP media. Metals generally give absorption bands in the fingerprint region below 1000 cm\(^{-1}\) arising from inter-atomic vibrations. Absorption bands are observed in the figure at, 736.76, and 568.96 cm\(^{-1}\). Due to the Cu–O. PVP presents the peaks at 2960.53, 1649.02, 1492.8, 1290.29 cm\(^{-1}\) corresponding to the C–H, C=O, C–C and C–N, respectively.

![FTIR spectra of synthesized Cu NPs from 0.2 mm exploded wire in PVP media.](image)

B) FT-IR Spectroscopy for Cu nanoparticles in ethylene glycol media

FTIR spectrum of the Cu nanoparticles obtained by exploded wire for 0.2 mm wire diameter in ethylene glycol media shown in Fig. 13 which shows the following absorption bands at 1108.99 cm\(^{-1}\) for (C–O–C), 1072.35 cm\(^{-1}\) for (C–OH stretching), 1224.71 cm\(^{-1}\) assigned to (CH\(_2\) twisting), 1596.95 cm\(^{-1}\) to (CH\(_2\) asymmetric bending), 1583.45 cm\(^{-1}\) due to (C=O stretching), 2839.02 cm\(^{-1}\) for (CH symmetric stretching), 2914.53 cm\(^{-1}\) for (CH asymmetric stretching). The peaks of Cu nanoparticles positioned between 900 cm\(^{-1}\) and 400 cm\(^{-1}\). The characteristic peaks of Cu-O positioned at around 606 and 525 cm\(^{-1}\) these peak belong to Cu-O stretching (oxygen come from hydroxyl groups of ethylene glycol chain).

![FTIR spectra of Cu NPs obtained by exploded wire for 0.2 mm wire diameter in ethylene glycol media.](image)
Conclusions

The NPs diameters estimated from SPR absorption peak position shows that the diameters of the particles decreases with the decrease of the copper wire diameter, at fixed voltage. For the same wire diameter and the same charging voltage, the particles prepared in DDDW smaller than that prepared in PVP and Ethylene Glycol. The SPR absorption peak for copper nanoparticles prepared in DDDW it has a full width smaller than that for nanoparticles prepared in Ethylene and it have the smallest particles size and narrow particles size distribution. Also for the NPs prepared by the same condition the SPR peak position shifted to the longer wavelength with increase the wire diameter. The copper nanoparticles were prepared in PVP it appeared least effected by preparation condition within the experimental condition used in this work, and the copper nanoparticles capped by thick layer of PVP, this layer prevented the particles from more growth and more agglomeration.

References