

Characterization of Copper Nanoparticles Prepared by Pulse Laser Ablation PLA

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ABSTRACT--- *Copper nanoparticles (Cu NPs) were prepared by used Nd:YAG pulsed laser ablation PLA in distilled water (DW) with diameter size (19:84 nm) . The synthesized nanomaterial is characterized with the optical properties UV-Vis spectroscopy, Nanoparticles diameter size studies by Scanning Electron Microscopy (SEM), the direct allowed transition with 2.32 eV optical band gap have been measured by photoluminescence spectroscopic techniques (PL), the result shown the intensity of surface Plasmon resonance (SPR) reduced and shifted to the red region after aged time .*

1. INTRODUCTION

Many efforts at the last few years have been directed to preparation and investigation of nanostructured materials. widely Known, nanostructured materials are solids composed of structural elements (mostly crystallites) which characteristic size falls in the range of (1 – 100) nm^[1]. They include nanocomposites, aggregated and cluster-assembled nanoparticles materials, nanocrystalline thin films, metal colloids as well as semiconductor nanostructures such as quantum dots, wires and wells depending on the size range, shape and chemical composition of nanoparticles different techniques have been used for producing such as chemical processes, physical methods and combined techniques^[2-4]. The conclusive goal for every technique is a fabrication of monodisperse particles with Specified by size and shape. In most cases -employed technique to synthesize nanoparticles in liquid is the chemical reduction of metal ions ,but there is an alternative method, laser ablation of a metal target in liquid has proven to be a powerful tool to prepare nanoparticles in liquid.^[5]

Intensive investigations on metal nanoparticles suspended in solutions have been undertaken because of their unique size-dependent electronic, optical, magnetic and chemical properties.^[6-9]

In recent, attention has been focused on Cu nanoparticles due to unique properties like catalytic and electrocatalytic.^[10,11] Since copper nanoparticles are highly unstable for oxidation compared with Au and Ag, Cu nanoparticles rapidly deposited after the Cu NPs exposure into the air, and an inert gas environment is required to stabilize copper colloids solution.^[12,13] According to Neddersen et al.,^[14] since copper metal is highly reactive, it is difficult to prepare stable colloids in the water and a solution with olive-green color was obtained by irradiating copper plate in an aerobic environment, indicating oxidation from copper to copper oxide.

The application of metal oxides nanoparticles are used as base for gas sensors, whereas the addition of metallic core inside this oxide improves sensitivity and selectivity of the sensor^[15]. The surface potential barrier is a lower value for Copper oxide nanomaterials comparable with the metals ,which affects their electron field emission properties, and therefore are highly applicable as electron sources in cathode ray tube and flat panel display^[16]. Copper oxide and copper@ copper oxide (core@shell) are considered as efficient catalytic agents^[17] and good gas-sensing^[18] and biosensing^[19] materials and also play an important role in the optoelectronics^[20] and solar cell applications^[21].

2. EXPERIMENTAL

As shown in Fig .1 set up of PLA (pulse laser ablation) ,Cu nanoparticles were produced by laser ablation of a Cu target (diameter = 14 mm, thickness = 0.47 mm, 99.99%) placed on the bottom of a glass vessel filled with 5 mL of distilled water (DW). The Cu target was irradiated vertically by a Q-switched Nd- YAG laser (DIAMOND-288 pattern EPLS), with wavelength ($\lambda = 1064$ nm) operating at 6 Hz. The laser beam was focused by a focal length (5 cm) plus 12cm) on the surface of a copper plate placed at the bottom of glass vessel containing 5 ml of the liquid. The spot diameter of the focused laser beam was 4 mm . The optical properties of the emerging nanoparticles solution was examined at room temperature by a UV-Vis absorption spectrophotometer (Metertech SP-8001). The photoluminescence (PL) measured by (SL174 SPECTROFLUOROMETER ELICO) with (Tungsten lamp source at range ($\lambda = 290-800$

nm) as an excitation light source. The irradiation time and laser power were varied to investigate the influence on the optical ,PL properties, SEM (S- 4160 -HITACHI) and AFM (AA3000 –USA) to clarify average diameters of the nonoparticales .

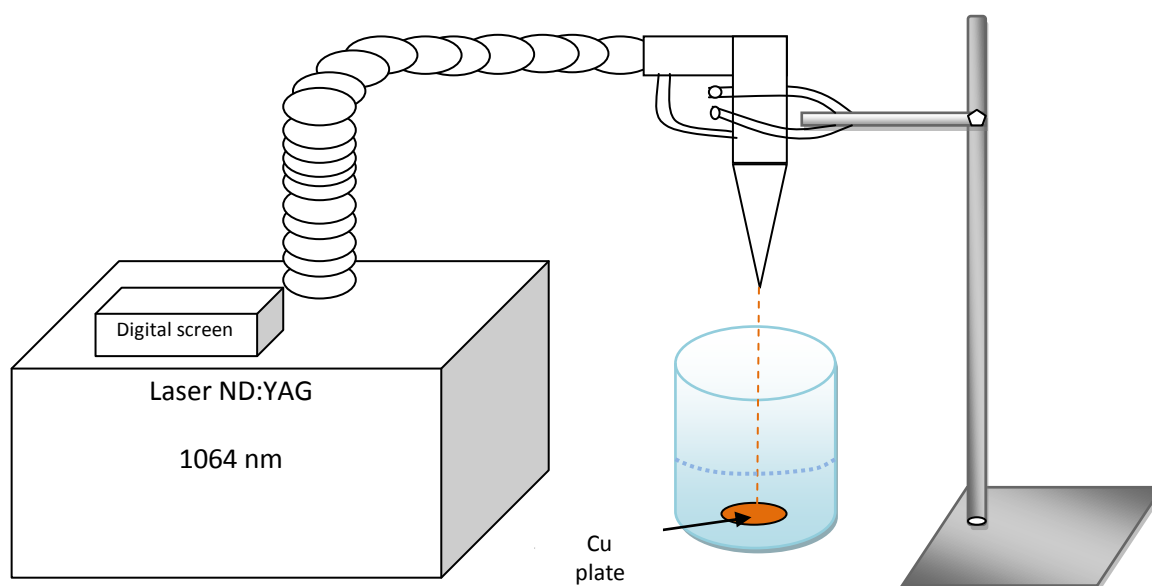


Fig -1 . Set up of PLA system

3. RESULTS AND DISCUSSION

3.1 UV-Visible absorption spectrum

The UV-Visible absorption spectrum of the as-synthesized solution of green color colloidal nanoparticles with the range (100–900) nm of the spectrum was observed. It exhibits an intense peak take a range ~ (193-218) nm and another peak with low intensity at ~ (624-630) nm as shown in Figure. 2 (a , c). The peak at a range ~ (193-218) nm is due to interband transition of copper electron from deep level of valence band while peak at ~ a range (624-630) nm is due to interband transition of copper electron from upper level of valence band, which is also known as surface plasmon resonance (SPR) peak and the intensity peak for the first range (193-218) nm and the intensity for SPR peak increased when the time increase . The SPR of colloidal copper nanoparticles reported previously^[22] with a peak at 590–640 nm is in agreement with the present result.

With the passage of time the intensity of surface plasmon resonance (SPR) peak decreases rapidly as shown in Figure. 2 (b , d) , which shows absorption spectra of colloidal solution of nanoparticles recorded on (2,4) days for lower power (200 mJ _ 1:25 mint) and (2,5,7,12) days for high power (600 mJ _ 1:25 mint) after the synthesis first day, which indicates oxidation and the SPR peak position shifted to the red region with the passage time of the produced nanoparticles taking place with time^[23] as shown in table 1 . It is possible that, due to aggregation and agglomeration ,partical size increases . From the Figure .2 (b,d) we can see at the lower power , the SPR peak finished at the 4 day comparable with the high power . The broadening of SPR peak is due to the agglomeration of the nanoparticles in the sample and high width of their particle size distribution. As no capping agent is used, agglomeration of nanoparticles is fully expected. The copper metal is the strongly oxidizing in nature, atoms on the surface of the nanoparticles get oxidized with the dissolved oxygen in the water, forming a thin layer of copper oxide on the surface of copper NPs with time. This explanation is strongly supported by UV-Visible absorption spectra, which shows decay and finally disappearance of the surface plasmon peak as time passes.

3.2 The optical bandgap

The optical bandgap of the as by synthesized nanoparticles with (200 mJ_1:25 mint) , is calculated using the Tauc relation^[24] $\alpha hv = (hv - Eg)^n$, where hv is the incident photon energy and n is the exponent that determines the type of electronic transition causing the absorption and can take the values 1/2, 2/3, 2 and 3/2. The best linear relationship is obtained by plotting $(\alpha hv)^{1/2}$ against hv , indicating that the optical bandgap of these nanoparticles is due to a direct allowed transition. Tauc plot for as synthesized colloidal nanoparticles is shown in Figure. 3. The bandgap of as synthesized colloidal nanoparticles is determined from the intercept of the straight line exponential region of at $\alpha = 0$, which is found to be 2.7 eV.

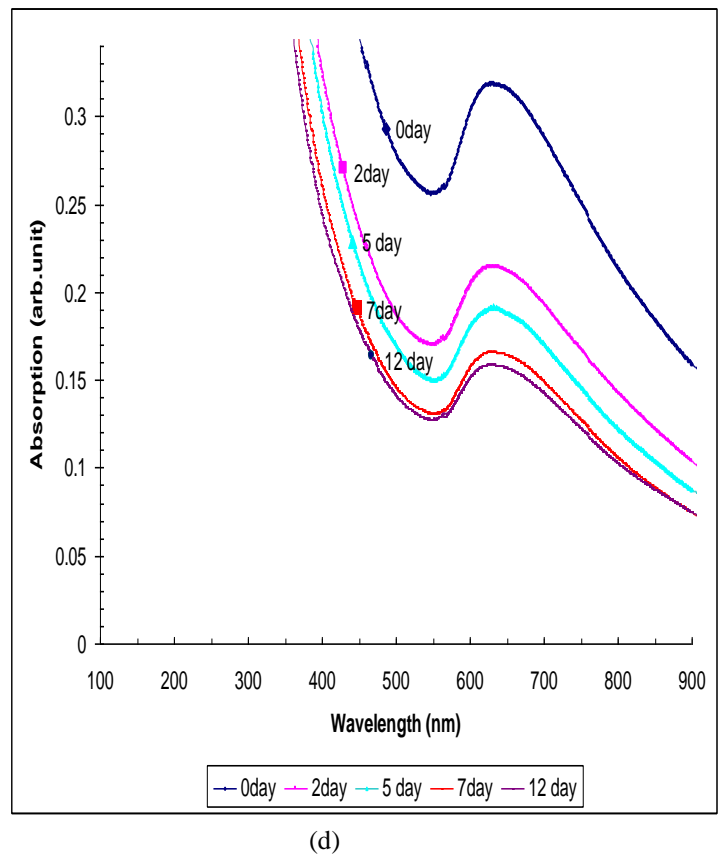
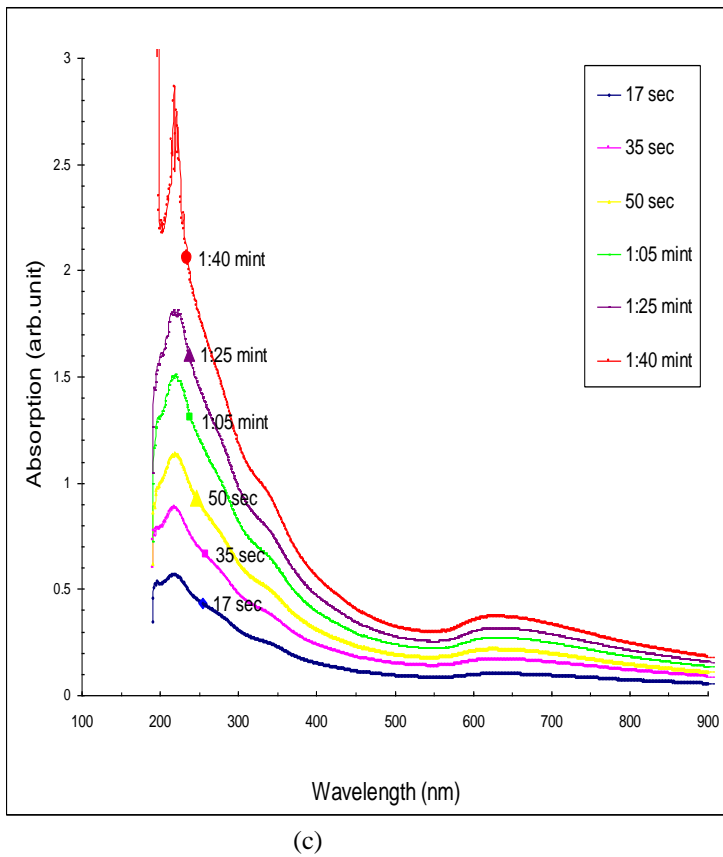
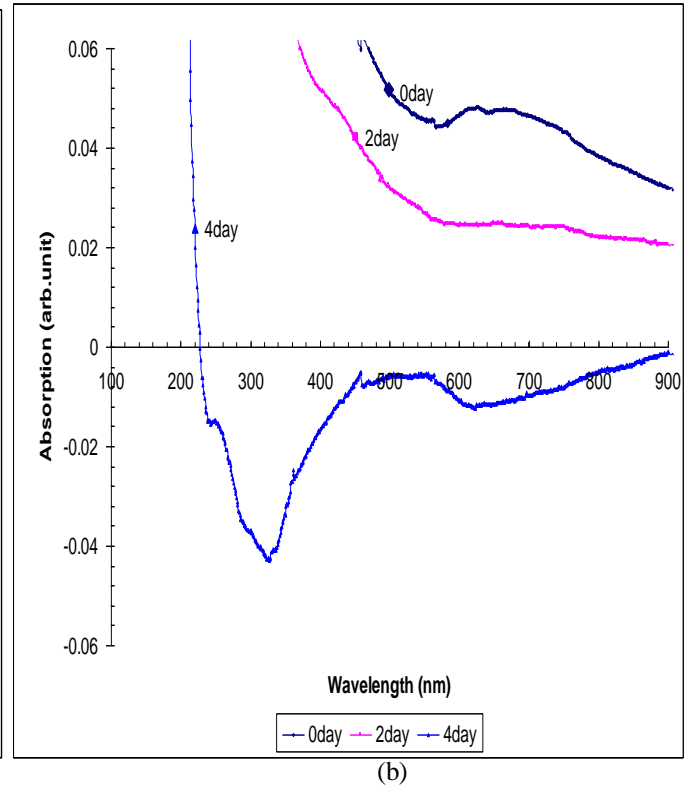
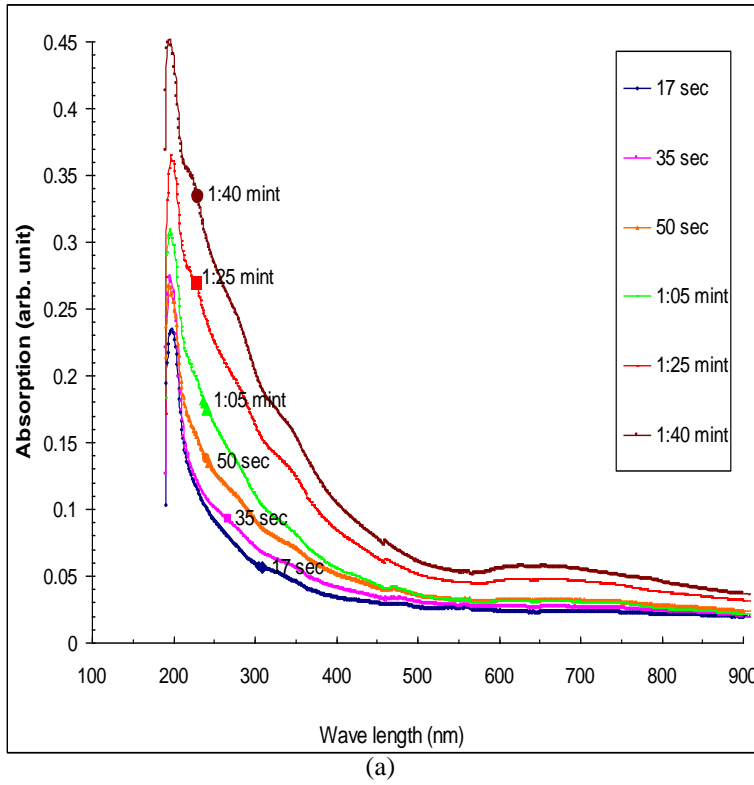


Fig- 2. UV-Visible absorption spectrum of as synthesized colloidal solution of nanoparticles by laser ablation of copper in distilled water (a, b) at power 200mJ , (c, d) at power 600mJ

Table .1 The power ,passage time form the first synthesis day's for Cu NPs

Power mJ	Passage time After first day	SPR peak position nm	Power mJ	Passage time After first day	SPR peak position nm
200mJ -1:25 mint	0 day	625	600mJ- 1:25mint	0 day	626
	2 day	649		2 day	630
	4 day	-		5 day	632
				7 day	633
				12 day	634

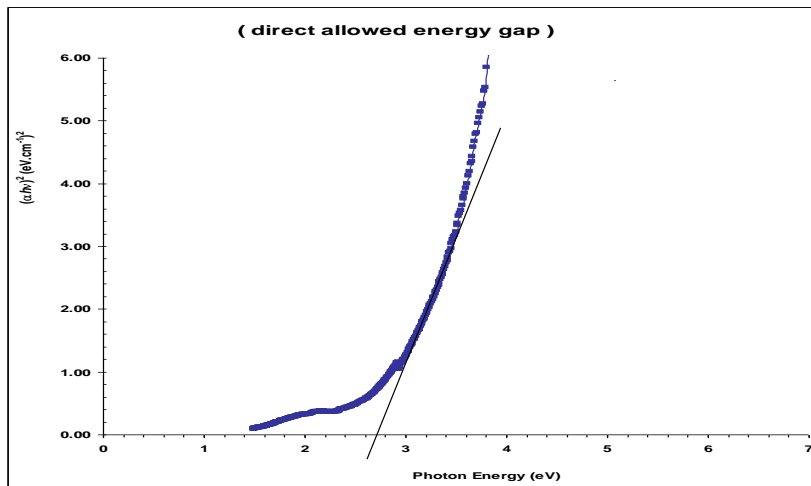


Fig- 3. Tauc plot of UV-Visible absorption of as synthesized colloidal nanoparticles for the calculation of band gap energy

3.3 PL analysis

The PL spectrum of Copper nanoparticles consists in distill water with (200 mJ_1:25 mint) is recorded using (SL 174 SECTRO FLUOROMETER) has shown in Figure.4. Spectrum shows a wide intense green luminescence having one peak at 2.32 eV. The peak at 2.32 eV brith due to band to band transition of Cu nanoparticles and the peak 3.05 eV is due to the interband transition of copper electron from deep level of valence band . The valance band electrons absorb the light of (4.59 eV (270 nm)) as wavelength excitation and may excite to the conduction band. The transition of some electrons from the valance band to the conduction band emits green photons, corresponding to bandgap of the nanoparticles, while rest of the electrons transit to the defect levels by losing some of their energy by collisional relaxation. Transition of these electrons from defect levels close to the bottom of conduction band (donor level/electron trap level) to valance band or/and to the defect level (acceptor level/hole trap level), above the top of valance band, emits photons in the green regions. Jung and co-workers ^[25] have studied the PL spectrum of Cu₂O nanoparticles .

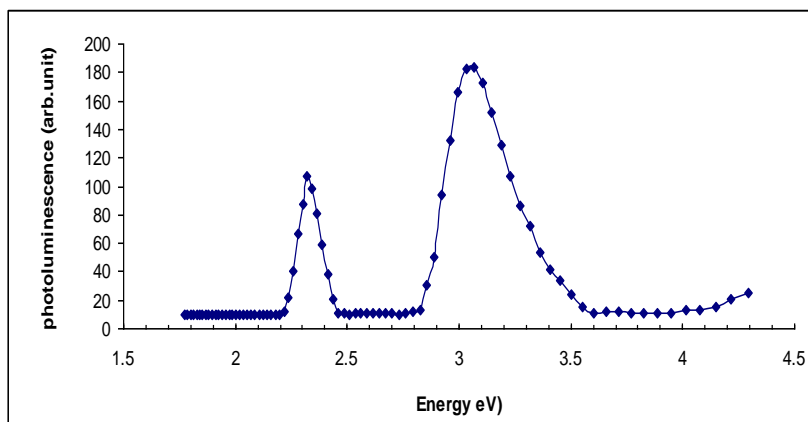


Fig- 4. Photoluminescence spectrum of colloidal solution of copper nanoparticles synthesized by laser ablation

3.4 (Scanning Electron Microscopy) SEM

The SEM (S-4160- HITACHI) supported the UV_Vis. Spectrum, Figure.5 shown the optimum condition for synthesis Cu NPs at power (200 mJ _1:05 mint) in distill water with SPR peak position at 625 nm ,the SEM image explained the diameter of Cu NPs equal to 19:84 nm .

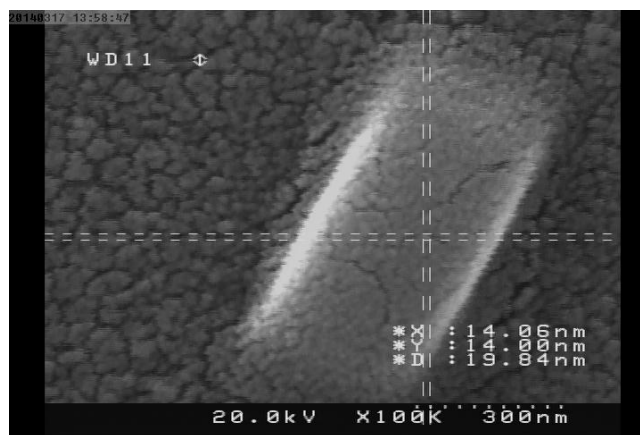


Figure -5

4. CONCLUSION

Copper nanoparticules prepared successfully by laser ablation with diameter size about (19:84 nm) and shown the effect of passage time on copper nanoparticules in distill water ,that found Cu NPs get oxidization and agglomeration of nanoparticles is fully expected with the passage time represented by reduced the intensity of SPR peak and shifted toward red region .

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