

Synthesis of Colloidal Copper Oxide Nano particles using Pulsed Nd: YAG Laser Ablation in Liquid

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ABSTRACT

This work reports the attempts to carry out pulsed laser ablation in liquid (PLAL) for synthesizing colloidal copper oxide nanoparticles (NPs). Copper oxide NPs was synthesized by 7ns Nd:YAG laser ablation of high purity copper target immersed in different solutions; ethanol, acetone, and water. The optical and morphological properties of copper oxide NPs were investigated. It was found that the optical absorbance, energy gap, size, and distribution of copper oxide nanoparticles are dependent on liquid type. Plasmon peak was observed at 550nm for Cu NPs ablated in acetone and methanol liquids, while it was disappeared for those ablated in water. Atomic Force Microscopy (AFM) analysis showed that the average grain size of copper oxide particles ablated in acetone, ethanol, and water were 276 nm, 300, and 360nm, respectively. Fourier Transform Infrared (FTIR) was used to study the vibrational frequencies between the bonds of atoms for a synthesized copper oxide NPs at different liquids. All these results confirm the complete oxidation of ablated copper.

Keywords: Laser ablation, copper oxide, nanoparticles, liquids, AFM, FTIR .

تحضير المحلول الغروي للجسيمات النانوية لأكسيد النحاس باستخدام
طريقة الاستئصال بالليزر النبضي بالسائل

الخلاصة

يهدف هذا البحث الى تحضير محلول الجسيمات النانوية لأكسيد النحاس باستخدام طريقة الاستئصال بالليزر النبضي . تم تحضير الجسيمات النانوية لأكسيد النحاس بزم من 7 نانو ثانية بواسطة الليزر نوع (Nd-YAG) لهدف من النحاس عالي النقاوة مغطس بمحاليل مختلفة مثل الايثانول والاسيتون والماء . تم البحث عن الخواص البصرية وطبيعة السطح لجسيمات الاوكسيد النانوي. وجد ان

الامتصاص البصري وفجوة الطاقة وحجم وتوزيع جسيمات اوكسيد النحاس جميعها يعتمد على نوع المحلول. شوهدت ذروة البلازمون عند 550 نانومتر لجسيمات النحاس النانوية المستتصلة بالاسيتون والكحول , بينما تختفي الذروة بالنسبة للجسيمات المستتصلة بالماء . بينت تحاليل مجهر القوى الذرية (AFM) ان معدل الحجم الحبيبي لجسيمات النحاس المستتصلة بالاسيتون والكحول والماء هي 276 نانومتر و300 نانومتر و360 نانومتر على التوالي . استخدم مطيافية تحويلية فورير للاشعة تحت الحمراء (FTIR) لدراسة الترددات الاهتزازية بين اواصر الذرات للجسيمات النانوية لاوكسيد النحاس المحضرة عند سوائل مختلفة . تؤكد جميع هذه النتائج حصول اكسدة تامة للنحاس المستتصل .

INTRODUCTION

Metal nanoparticles have been intensively studied within the past decade. Nanosized material have been an important subject in basic and applied sciences sparked their application in a broad ranges of different fields, including; chemistry, physics, biology, materials science, medicine, catalysis and so on [1,2]. Metal NPs have been prepared in many methods by using laser ablation technique [3], Chemical reduction method [4], Photo-reduction [5], Microorganisms [6], Arc-Discharge method [7] and Bio surfactant [8]. Laser ablation technique has attracted much growing interest since it is extensively employed for synthesis of new novel materials especially for drilling microvias in the high density printed circuit board in the micro electronic packaging [9]. Laser ablation plasma is formed above the surface of the solid target when an intense laser beam strikes the target. Laser ablation provides a simple and contaminant-free method which can be used for large number of materials [10]. Copper oxide is an excellent nanoparticles system for investigating the size induced structured transformations and phase stability [11]. Copper oxide has two phases; i.e. cuprous oxide (Cu_2O) and cupric oxide (CuO) [12]. Among all the metal oxides; cuprous oxide is mostly p-type, direct energy gap with band gap of ~ 2 eV and cupric oxide has a monoclinic crystal structure and presents p-type semiconductor behavior with an indirect energy gap of (1.21-1.51) eV. Copper oxide nanomaterials may have the advantage of a lower surface potential barrier than that of the metals, which affects electron field emission properties. Copper-oxide is considered as a potential field emitter, an efficient catalytic agent, as well as a good gas sensing material. It also plays an important role in the optoelectronics and solar cell [13, 14]. Lasers have open new doors in the processing of nanomaterials and their characterization. Pulsed laser ablation process has several advantages over other conventional routs including large number of available ablation parameters for controlling the size and shape inherent stoichiometry as their mother targets therefore, capability to produce nanomaterials of desired chemical composition and ability of producing nanomaterials having surfaces free from chemical contamination [15]. Laser ablation technique is used to synthesize colloidal nanoparticles of different metals and semiconductors [16, 17].

In this work, we have performed laser ablation of copper target in three types of solutions to synthesize copper oxide nanoparticles. Furthermore, the optical properties and morphological investigation of copper NPs were studied and analyzed.

EXPERIMENT

Copper oxide NPs were produced by laser ablation of high purity copper target immersed in three types of liquids; acetone, ethanol, and double distilled water (DDW) at room temperature. Figure (1) displays the schematic diagram of experimental set-up of PLAL system. The copper target is placed in the bottom of quartz vessel filled with 20ml of liquid. The copper target was irradiated with Q-switched Nd:YAG laser operated at wavelength of 1064nm, 7ns pulse duration, and repetition frequency of 6Hz. The laser energy used to ablate copper target was 40mJ/pulse, the ablation time was 6min. The laser beam was focused on copper target using focusing lens of 100mm focal length.

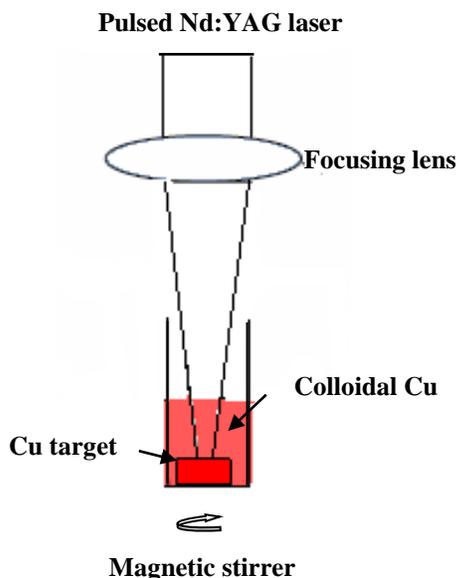


Figure (1). Schematic diagram of PLAL system.

The optical absorption of colloidal copper oxide was measured using spectrophotometer type SP8001 Meteric.Inc, Taiwan). Ablated Cu NPs were analyzed by atomic force microscopy (AFM) model (SPM AA 3000 Angstrom Advanced Inc. USA).

RESULTS AND DISCUSSIONS

After laser ablation of copper target, the color of suspension is changed from colorless to red (for acetone suspension), dark yellow (ethanol suspension), and transparent green (DDW suspension) as depicted in Figure (2), indicating the production of copper oxide colloidal nanoparticles [18]. Figure (3) shows the UV-VIS spectra of the colloidal dispersion containing particles synthesized by laser ablation of Cu target. These spectra were measured directly after ablation process. As obvious from Figure (3) there are significant absorption peaks at 560nm for acetone and ethanol containing copper oxide NPs, which are related to Surface Plasmon Resonance (SPR) of Cu. These is well agreed with other data reported by other workers [19].

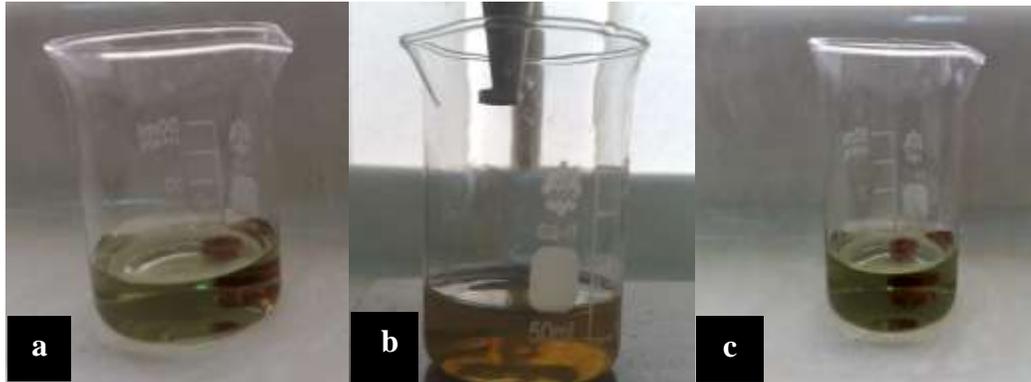


Figure (2). Freshly prepared colloidal copper oxide NPs in (a) DDW (Light green) (b) Acetone (yellow) and (c) ethanol (green).

Normally incident light produces oscillation in conduction electrons on the surface of Cu NPs and electromagnetic radiation is absorbed [20]. On the other hand, no remarkable peak was noticed in the case of DDW containing Cu NPs. This is due to the formation of copper contains only ionic species of Cu^+ [21].

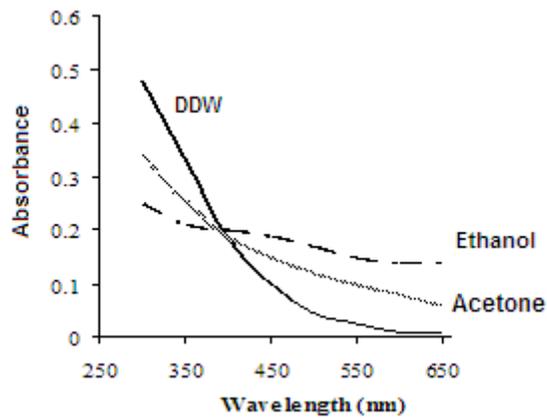


Figure (3). UV-VIS absorption spectra for Colloidal copper oxide NPs.

The absorption coefficient of copper oxide NPs was determined from absorption plot as function of photon energy $h\nu$. Optical energy gap for direct transition was deduced by linear part extrapolating of Figure (4) to $(\alpha h\nu)^2 = 0$. Table 1 lists the optical energy gap of ablated copper oxide NPs in different liquids.

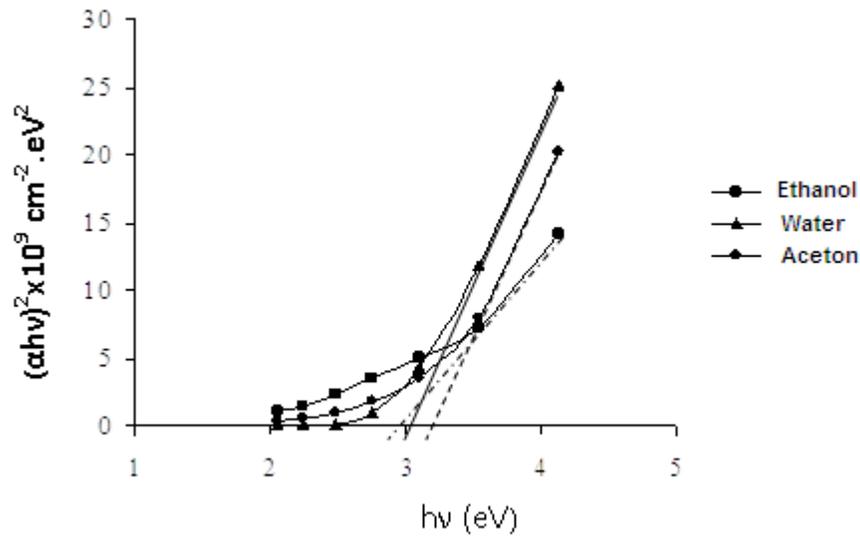


Figure (4). Plot of $(\alpha hv)^2$ versus (hv) .

Table (1) Optical band gap of copper oxide NPs Dispersed in of different solutions.

Colloidal copper oxide NPs	E_g (eV)
Ethanol	2.8
Water-DDW	3
Acetone	3.2

The optical energy gap of copper oxide NPs dispersed in acetone as stated in table (1) is 3.2eV which is much greater than that $E_g = 1.8\text{eV}$ for bulk CuO. This value of energy gap indicates that the Cu NPs is oxidized due to reaction with oxygen dissolved in acetone. Copper is an active chemical material and can react easily with the vapors of surrounding liquid. The chemical reaction could happened before or after laser ablation process due to contact with oxygen dissolved in colloidal solution [21]. When the light absorbed by Cu NPs produces electrons in conduction band and holes in valence band, these carriers will confined in potential well with small lateral dimension. The energy difference between the position of conduction and free electrons led to quantization of their energy levels when the size of particles is grow to be comparable to de Broglie wavelength of the carrier [22, 23]. The increase in energy gap of colloidal Cu NPs is ascribed to quantum size effects. The values of energy gap of copper oxide NPs dispersed

in DDW and ethanol is less than that for acetone solution, this probably due to the kinetic of oxidation process and/ or to Cu NPs size and distribution.

Figure(5) (a,b) demonstrate 2D and 3D AFM images of copper oxide NPs ablated in acetone with scanning area of $1\mu\text{m}\times 1\mu\text{m}$. The average grain size reaches 236nm in diameter and its height around 7nm. It can be noticed from AFM images that particles have different morphologies with nanoparticles sizes (see Figure 6). The sub-microparticles are agglomerated from many copper oxide nanoparticles, the nanoparticles combine and pack together to form sub-microparticles [24]. Figure (7) (a,b) shows AFM images of copper oxide NPs ablated in ethanol , the grain diameter and its height were 360nm and 45nm , respectively. While the grain size diameter and height for copper oxide NPs ablated in DDW found to be 260nm and 40nm, respectively. The dependence of copper oxide NPs grain size on solution type is probably due to thermal conductivity of solution which is in turns affect the cooling rate of ablated Cu particles.

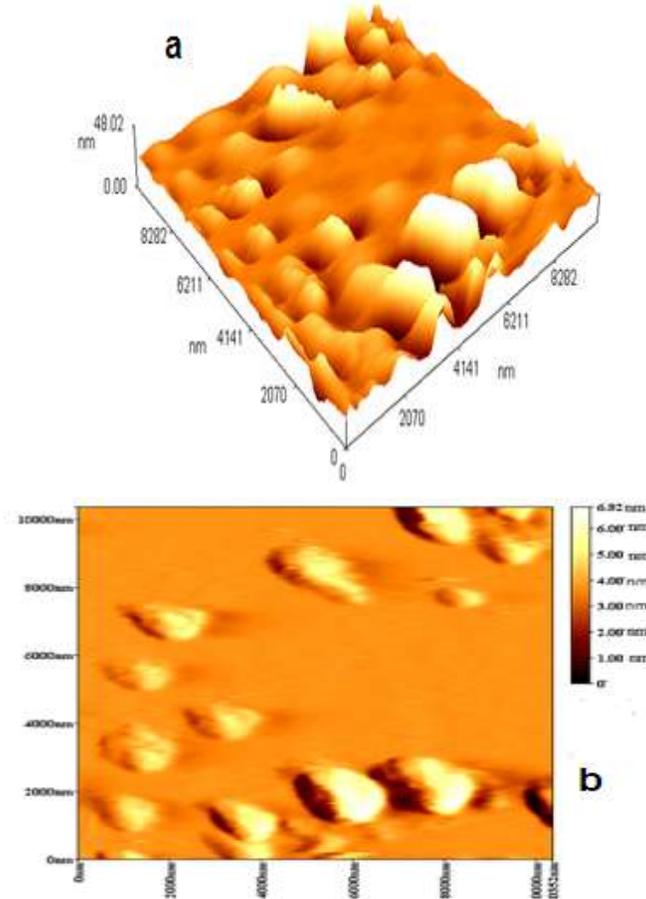


Figure (5). AFM images of copper oxide NPs ablated in acetone (a) 3D (b) 2D.

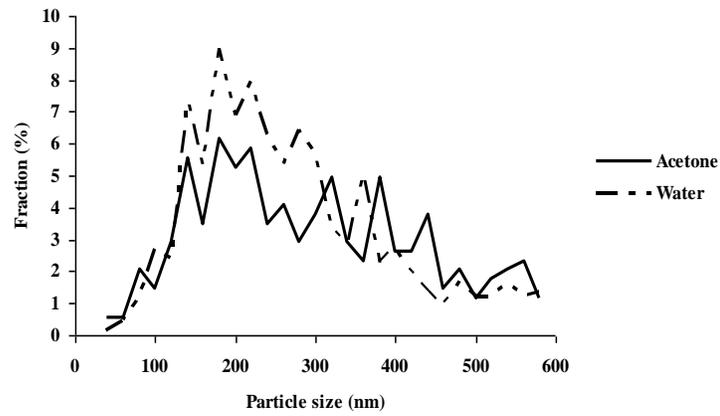


Figure (6). Particles size and their distribution for Copper oxide nanocolloidal.

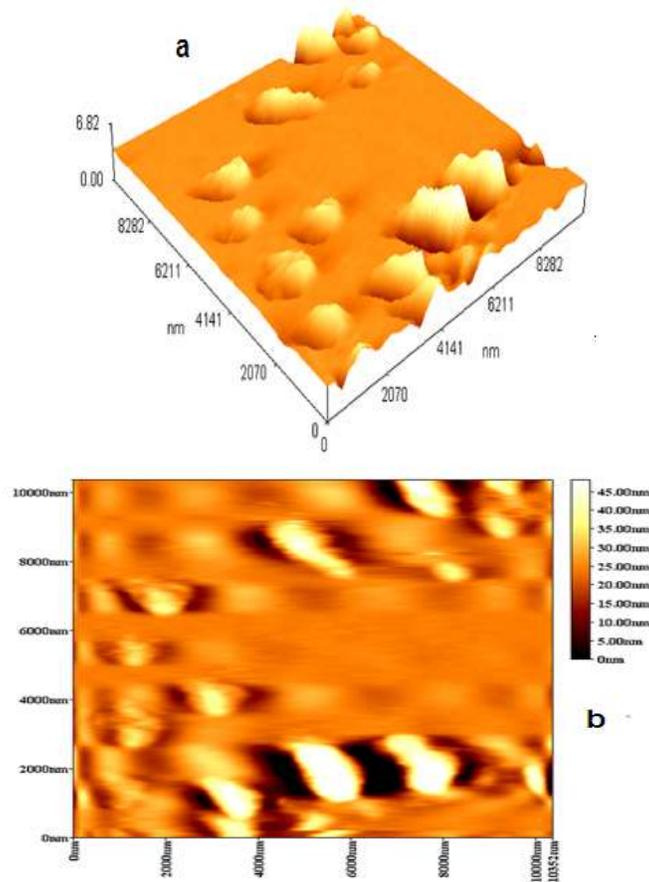


Figure (7). AFM images of copper oxide NPs ablated in ethanol (a) 3D (b) 2D.

Figure (8) shows FTIR for copper oxide NPs dispersed in acetone solution, an absorption peak observed at 630 cm^{-1} which can be assigned to the Cu (I)-O vibration. Three distinct absorption peaks related to CuO located at 540 cm^{-1} , 501 cm^{-1} and 439 cm^{-1} , which can be assigned to the vibrations of Cu (II)-O bonds. These results in good agreement with those of Cu_2O NPs reported previously [25, 26]. The vibration of the Cu-O bond in Cu_2O emerges in higher frequencies than those of CuO, the Cu^+ ion has a symmetrical d^{10} electronic configuration which leads to equivalent Cu-O bonds but this is not the case in CuO [27].

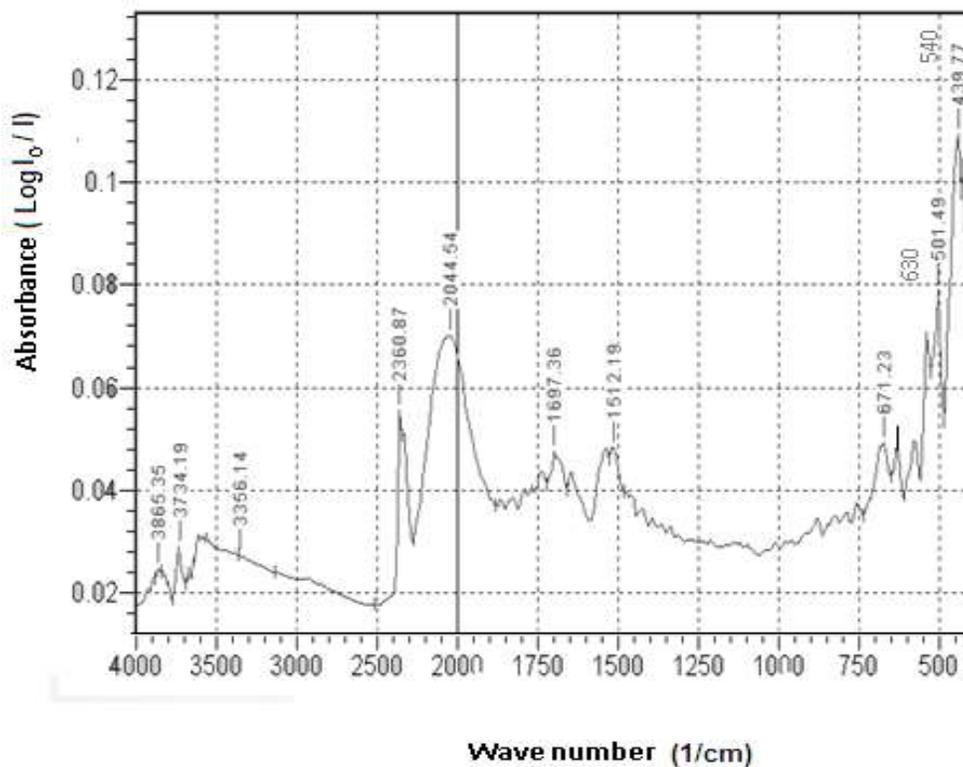


Figure (8). FTIR spectrum of colloidal copper oxide NPs dispersed in acetone solution.

Furthermore, another two absorption peaks located at 1690 cm^{-1} and 1760 cm^{-1} were observed, which assigned for CuO and Cu_2O [28]. For copper oxide NPs ablated in ethanol the FTIR spectrum (not shown here) has only bonds assigned for Cu(I)-O vibration, no bonds belong to Cu(II)-O vibration was noticed.

CONCLUSIONS

Colloidal Copper oxide nanoparticles have been prepared successfully by pulsed laser ablation of copper target in acetone, DDW, and ethanol. Formation of copper oxide nanoparticles was emphasizing by optical absorption measurements. The value of energy gap of CuO nanoparticles ablated in acetone at 300°K was 3.2eV due to blue shift arising from decreasing of ablated particle size (quantum size effect). Atomic force microscopy confirmed that synthesized CuO NPs have different grain size and morphology. FTIR measurements revealed that the absorption peak observed at 630cm⁻¹ is assigned to Cu(I)-O vibration, while the other three peaks observed at 540cm⁻¹, 501cm⁻¹ and 439 cm⁻¹ are assigned to Cu(II)-O bonds.

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