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Preparation of Non-Agglomerated Spherical Copper Nanoparticles Using Nanosecond Pulsed Laser Ablation Technique in an Ambient Nitrogen Gas

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ABSTRACT

The method of preparing of spherical shape copper nanoparticles (Cu-NPs) with smooth surfaces using laser ablation of a copper target while surrounded by nitrogen gas is presented. A flow of nitrogen gas is injected to the ablation cell and the stream ablated copper nanoparticles which constitute with the plasma plume above the sample surface is directed towards the deposit material holder. The formed spherical shape non - agglomerated copper nanoparticles have the advantage of not losing energy during the demagnetization process which can be used in preparation of ferromagnetic material applications. Also these copper nanoparticles support drug stability and could improve therapeutic index in biomedical fields. The formed copper nanoparticles were obtained at pulsed excimer laser parameters 193 nm, 6 ns, and 8 mJ Cu-NPs were formed. A scanning electron microscope (SEM) is used to analyze the morphology of the generated NPs. Using the laser ablation method we could: - Directly generate spherical Cu-NPs from copper target without any preparation. - Form non agglomerated Cu-NPs as shown by SEM. - Produce Cu-NPs with a high distribution density and smooth surfaces shape.

Examination of Cu-NPs by using Energy Dispersive X-ray spectrometer (EDX) confirmed that the formed nanoparticles were high pure copper.

INTRODUCTION

Copper nanoparticles become a subject of great interest. They have been used in many applications such as medicine [1], heat transfer systems based on metal nanofluid which use copper nanoparticles with fluid [2,3], treatment of radioactive waste [4], gas separation [5], antimicrobial, antibacterial materials [6,7], dentistry as antibacterial and low toxicity dental materials [8-14], catalytic applications [15]. and ferromagnetism materials [16]. Spherical nanoparticles in ferromagnetic materials application do not release more energy compared to cubic nanoparticles, which require more energy during the demagnetization process. These spherical particles have an important advantage in some applications of ferromagnetic materials because the spherical nanoparticles shape and size can influence their magnetic anisotropy. The preferential alignment of the magnetic moments in a specific direction is referred to as this fundamental magnetic property. The anisotropy in spherical nanoparticles is caused by form anisotropy, which is the outcome of the energy difference involved in aligning the magnetic moment perpendicular or parallel to the nanoparticle surface [17].

The formed copper nanoparticles of uniform, symmetrical shape and non-agglomerate play a significant role for these applications. Copper nanoparticles can be formed by a variety of methods, such as precipitation from an aqueous solution, electrolysis technique, vapor deposition on a substrate or sputtering from a metal wire or plate.

The majority of techniques for treating nanoparticles are chemical methods but the disadvantage of chemical methods is that nanometer particles aggregate and stick together, with the problem that the spherical particles are poorly distributed [18,19]. On the other hand, laser ablation technology is simple, fast and can yield nanoparticles of high purity and ready for use immediately [20].

The current study examines the production of copper nanoparticles when a Cu target is ablated in the presence of N_2 gas environment and laser irradiance between (10^8-10^{10} W/cm^2). Using the Scanning Electron Microscope (SEM) attached with Digital Imaging Processing (SEM-DIP) technology, the shape of the produced nanoparticles is investigated [21]. To ascertain

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the particle size of the generated copper nanoparticles, the Particle Counting Method (PCM) is used to obtain the particle size distribution of the formed Cu-NPs [22]. The technique of energy dispersive x-ray (EDX) analysis is used to examine the produced nanoparticles.

EXPERIMENTAL PROCEDURES

The experimental setup is built for the ablation of a copper target and the deposition of ablated nanoparticles as shown in Fig. (1).

Nanosecond Excimer laser with 6ns pulse width, 193nm wavelength and pulse energy 9mJ is focused onto commercial copper target with a fused silica plano-convex lens (f=20cm). The laser is pulsed at 200 Hz. The lens is mounted on translation stage for precise and reproducible positioning. Laser irradiance 1.3×10^9 W/cm^2 is used and different quantity of pulses is selected. Copper target is used as a target sample in the center of the ablation cell. A flow of N_2 is injected to the ablation cell with the flow rate 13 l/min and the stream ablated nanoparticles material which constitute with the plasma plume above the sample surface with approximately 1 mm is directed towards the deposit material holder. The holder is placed in normal direction from the ablation cell output tube.

The ablated Cu-NPs shape and size are investigated using a JSM-5600-LV type scanning electron microscope (SEM). The formed Cu-NPs are analyzed using an energy dispersive X-ray (EDX) spectrometer. EDX is a technique used for elemental analysis of materials [23]. Both the target material and the generated nanoparticles will be analyzed using it. The formed SEM images were mathematically analyzed by using digital image processing technique (DIP) [22] . This technique is able to show different kind of information about the image such as its gray level histogram, horizontal and vertical line profiles, etc. It also includes some advanced image analysis functions such as Fourier analysis and correlation analysis; it can enhance the analysis of low resolution and distorted images. Particle counting method (PCM) is a statistical method that can be used with DIP technique to obtain statistical analysis of the nanoparticles formed.

A flat commercial copper sample without any chemical preparation was used as a target. The excimer laser is set to drill mode, capable of producing 10,000, 20,000, and 30,000 pulses. To investigate the impact of varying the number of laser shots on the creation of copper nanoparticles, all laser parameters remain constant.

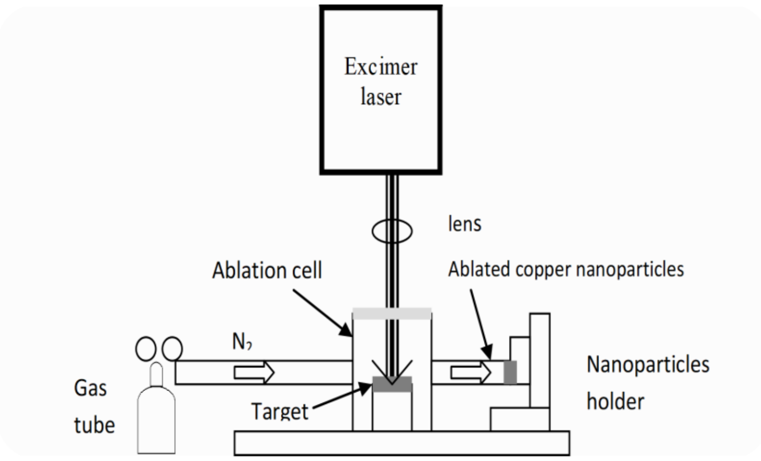

Fig. (1): The experimental setup

RESULTS AND DISCUSSION

Ablated Copper Nanoparticles Cu-NPs

Figure (2) shows the copper sample's surface prior to laser irradiation. It is evident that even at high magnification, the flat surface is free from any laser irradiation effects.

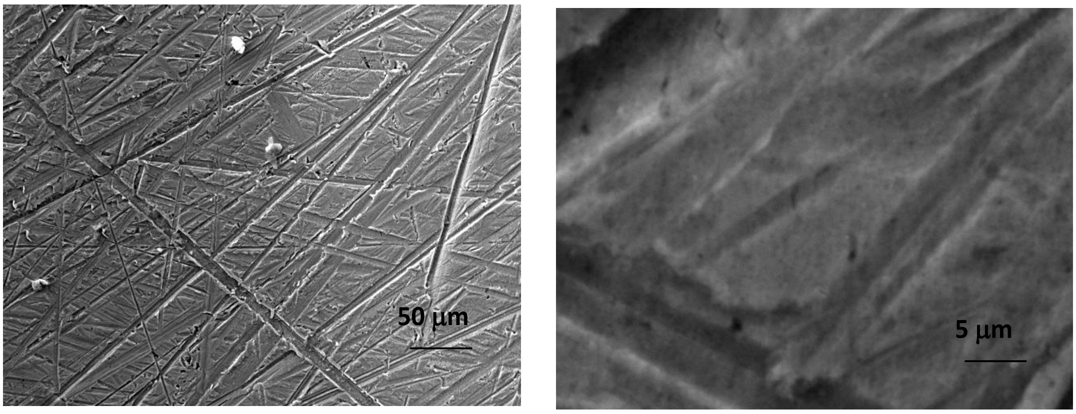

Fig. (2): SEM photomicrograph of the copper sample's surface taken prior to laser irradiation

As seen in Fig. (3), the effect of the laser after irradiation deforms the surface with areas coated in nanoparticles. Everywhere on the irradiated regions are the produced nanoparticels.

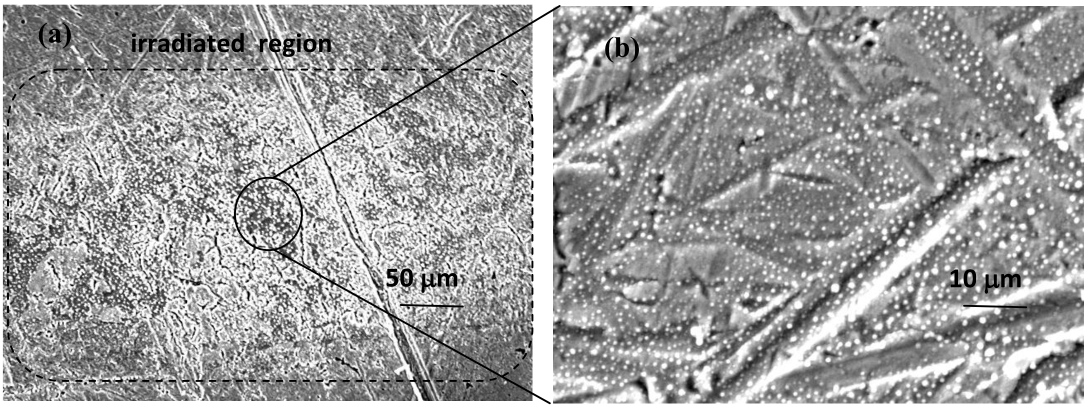

Fig. (3): SEM photomicrograph of copper sample following laser irradiation (a) magnification ×350 (b) magnification ×1900

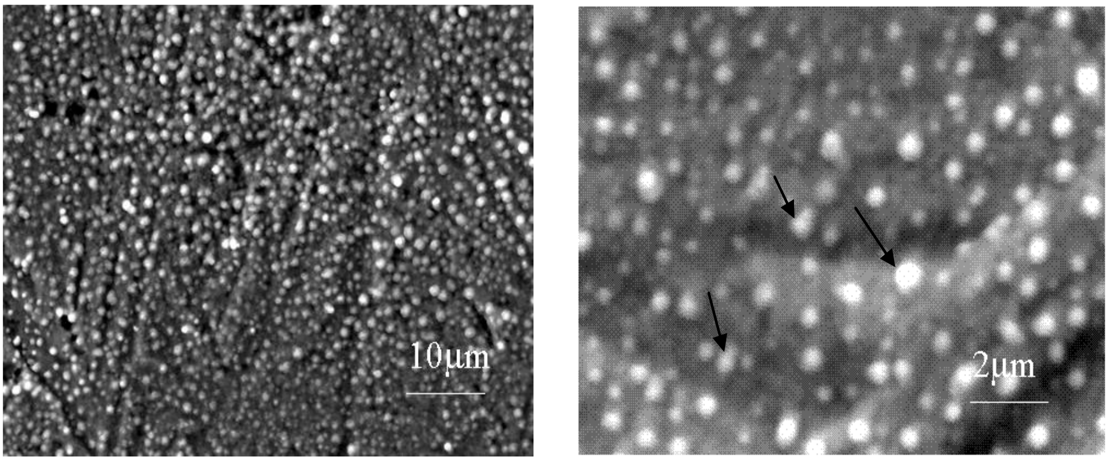

Fig. (4): SEM photomicrograph of the ablated Cu-NPs (10000 pulses 200Hz-RR and N_2 carrier gas).

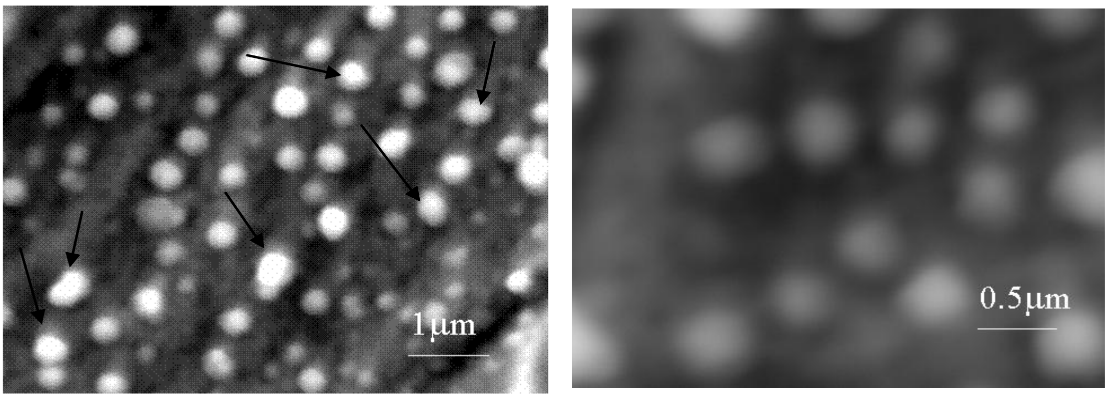

Fig. (5): SEM photomicrograph of the ablated Cu-NPs (20000 pulses 200Hz-RR and N_2 carrier gas).

The generated copper nanoparticles that are ablated with 10,000 excimer laser pulses at a constant gas flow rate and laser settings are displayed in Fig. (4). In the presence of ambient N_2, homogenous copper nanoparticles are produced using 10,000 laser pulses. The nanoparticles that are produced are non-agglomerated and spherical in shape. All experimental parameters are fixed and the numbers of pulses were changed to study its effect on the formation of nanoparticles. With the number of pulses of 10,000, the formation of the spherical shape of the particles became better compared to 20,000 pulses as shown by arrows in Figs. 4 and 5.

Copper nanoparticles produced by the excimer laser ablation technique are depicted in Fig. (5), where the number of laser pulses is increased to 20000 shots. The particles take on the same form. The nanoparticles on the holder's surface are dispersed throughout.

By changing several variables for the present experimental setup, such as the gas flow rate and the number of pulses, obtaining spherical particle shapes did not produce any satisfactory results. The experimental parameters previously mentioned and displayed in Figures 4 and 5 produced the best results. Calculating the size of produced nanoparticles is done by applying SEM particle counting method in conjunction with Digital Image Processing (DIP).

Size distribution of copper nanoparticles is depicted in Fig. (6). The statistical calculations presented in the figure indicate that the presence of 126–306 nano-sized particles of the total formed nanoparticles, 16.9% have a size of 180 nm, indicate that they are in the nano-structure scale. The remaining portion is separated into two groups: the first group comprises 15.5% of nano-sizing around 199 nm and 238 nm, while the other percentage is roughly 10% with nano-sizing around 126 nm, 222 nm, and 258 nm. The formed nanoparticles have nearly spherical shapes and are not agglomerated on the surface of the holder.

Every nanoparticle in the earlier SEM images appeared to be spherical. Special DIP- software is utilized to display the morphology of the generated nanoparticles and a selected area containing nanoparticles is used to clarify this in order to validate that the particles have a spherical shape. The morphology in Figure (7) confirms that the nanoparticles are spherical, smooth and uniform because the majority of the studied nanoparticles have roughly the same full width at half maximum (FWHM) distance, demonstrating the uniformity and smoothness of the generated nanoparticles' geometrical shape.

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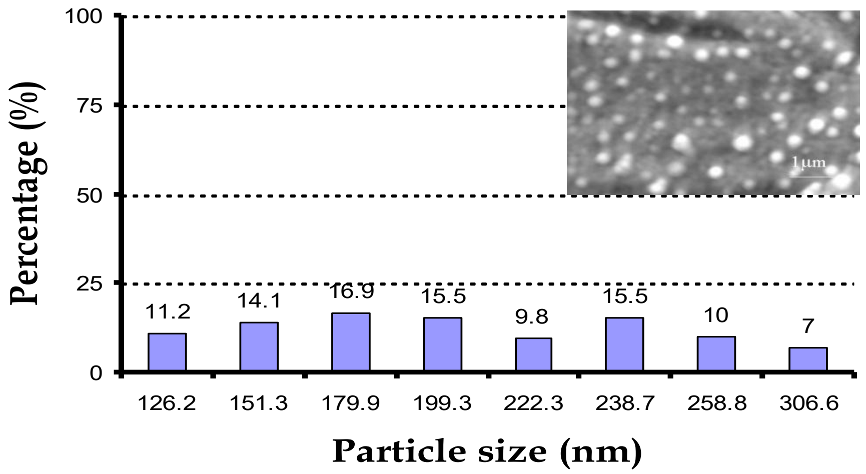


Fig. (6): Statistical analysis of the generated nanoparticles' size distribution

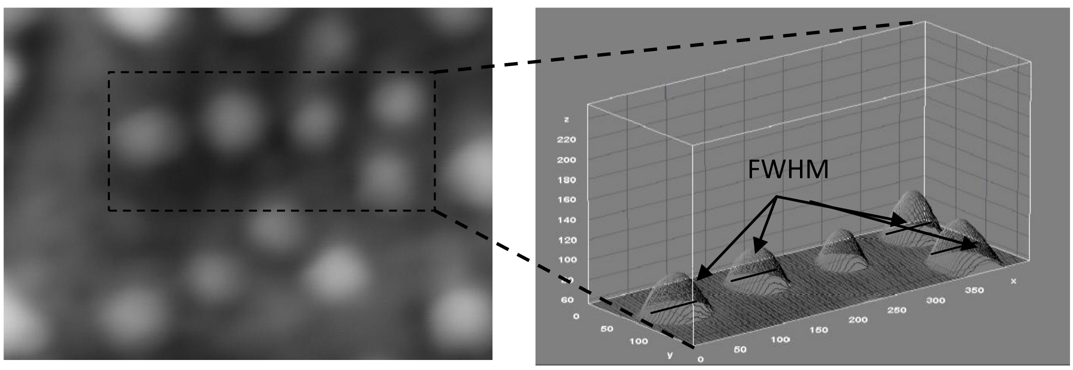
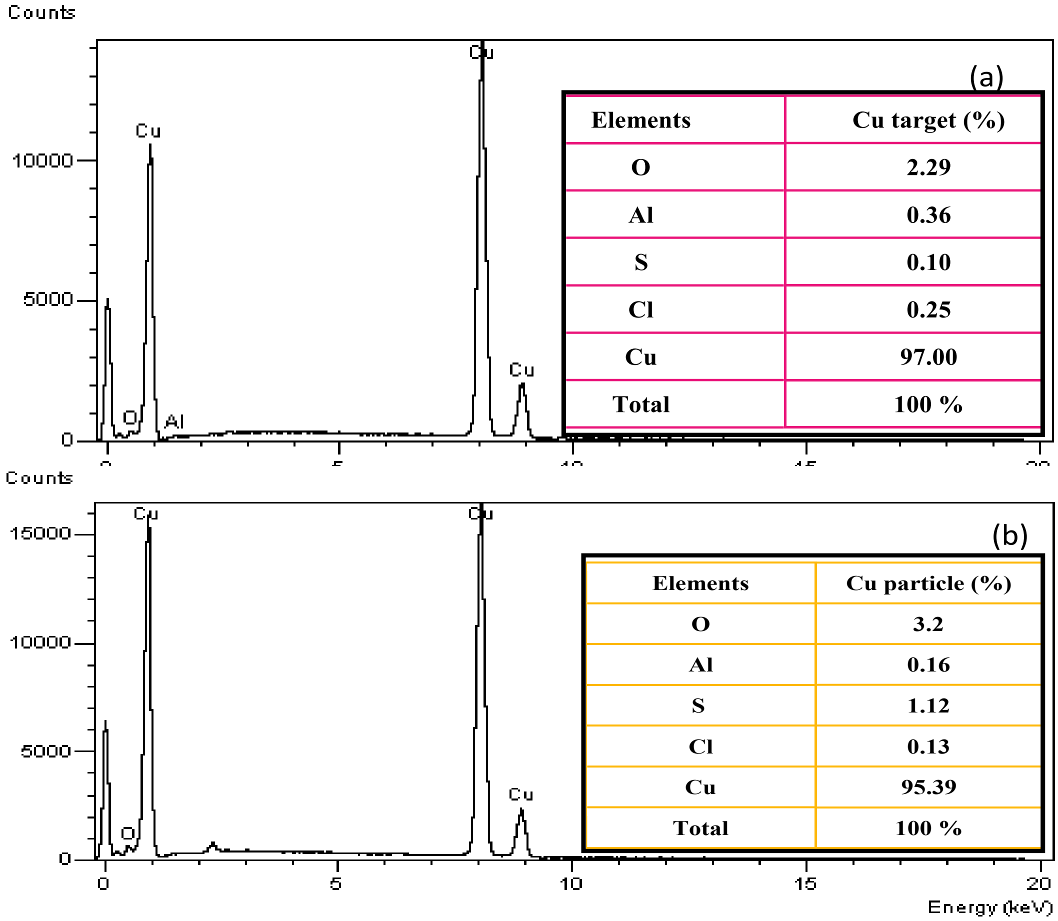


Fig. (7): SEM micrograph of formed nanoparticles with micrograph analysis of the nanoparticles that were produced using the DIP analysis approach, showing their 3-D morphology.



Elements	Cu target (%)
O	2.29
Al	0.36
S	0.10
Cl	0.25
Cu	97.00
Total	100 %

Elements	Cu particle (%)
O	3.2
Al	0.16
S	1.12
Cl	0.13
Cu	95.39
Total	100 %

Fig. (8): EDX analysis spectra (a) copper target and (b) copper nanoparticles.

Energy Dispersive X-Ray (EDX) Analysis

To ensure that the nanoparticles have the same elemental composition and that re-ablation of these particles will yield the same results, EDX analysis of the copper target was performed out for both the target surface and the deposit nanoparticles.

The surface spectrum analysis of the commercial copper target and the ablated Cu-NPs are shown in Fig. (8). The analysis reveals similar elemental composition spectra analysis for both cases, with the elements, O, Al, S, Cl, and Cu, Between 95% and 97%, the predominant element is copper. Based on the EDX results, it is evident that the NPs generated are form of highly pure copper ablated from the target material irradiated by laser.

CONCLUSION

High distribution, homogenous spherical shape and non agglomarted Cu-NPs were produced by using Nanosecond Excimer laser with 6ns pulse width, 193nm wavelength and pulse energy 9mJ in an ambient N_2 gas.

Cu-NPs with diameters ranging from 126 to 306 nm were covered the whole ablated area. 16.9% of a formed Cu-NPs have a size of 180 nm. The remaining portion is separated into two groups: the first group comprises 15.5% of nano-sizing around 199 nm and 238 nm, while the other percentage is roughly 10% with nano-sizing around 126 nm, 222 nm, and 258 nm. The spherical shape of the produced nanoparticles was confirmed by DIP.

Laser ablation technique in presence of N_2 gas succeeded in preparing spherical nanoparticles with smooth surfaces which have smaller magnetic field gradients compared to cubic nanoparticles which have edges and corners. In addition, Laser ablation technique is easy to prepare and apply compared with chemical methods, and it offers a workable way to create high-purity spherical nanoparticles from the target material.

The elemental composition of the ablated Cu-NPs were matched the original target material, as demonstrated by EDX technique. The analysis reveals similar elemental composition spectra analysis for both cases, with the elements, O, Al, S, Cl, and Cu, between 95% and 97%, the predominant element is copper.

All the produced nanoparticles that contain a very high percentage of copper can be used to enhance thermal conductivity of Nano-fluids [24].

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