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Synthesis of Gold and Copper Nanomaterials by Pulsed Laser Ablation Method

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Received: 31 May 2022 Accepted: 14 July 2022

DOI: https://dx.doi.org/10.24237/djps.1804.599B

<u>Abstract</u>

The study included the effect of laser parameters (wavelength, number of pulses, and laser energy) on the structural and optical properties of pure gold particles, gold alloys, and copper nanoparticles that were prepared using a nadium-type pulsed laserNd-YAG type for high purity noble elements (gold, copper, and gold alloys) in distilled water, as pure gold and gold and copper alloys were used to prepare the above colloidal nanoparticles the structural properties of the prepared models were shown. The X-ray diffraction patterns were examined. (XRD) and scanning field electron microscope, while the behavior of the ultraviolet and visible absorption spectra of the samples prepared using (UV-Vis) X-ray diffraction assays showed the prepared nanoparticles at energy 660.m J. The number of pulses is 1000. All the prepared particles were of the face-centered cubic type. The XRD results also indicated the best prevailing directionality for plane (111) for all samples prepared from pure gold and gold alloys as well as copperFESEM assays showed the prepared particles at 1000 pulses and an ablation energy of 660 diameters. Au(83.7nm,13.8,50.7,56.5,35.4nm) and Cu (60.1nm) NPs were spherical as highlighted. EDS results for Au and Cu samples showed that the purity of the Au material was 100%, and the Cu was 100%. The results of UV-Vis spectroscopy of Au and Cu NPs showed



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that the colloidal Au and Cu NPs have their surface plasmon resonance for Au pure Au at (519 and 523 nm) and (Au –Cu) alloys, at 530, 580, 577, and 541 nm, respectively. These results were at the wavelength (532nm) of 1000 pulses. The results of the Dynamic Light scattering (DLS) for Au alloy NPs of different weights showed that the Au alloy NPs are non-toxic with the presence of some agglomerates in the solution, as the zeta potential showed that the Au alloys and Cu solutions are Unstable substances.

Keywords: Au and Cu alloy NPs, Wave length 532nm, PLAL technique; Structure and optical properties.

تصنيع المعادن النانوية من الذهب والنحاس بطريقة الاستئصال بالليزر النبضى

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الخلاصة

تضمنت الدراسة تأثير معاملات الليزر (الطول الموجي، عدد النبضات، وطاقة الليزر) على الخصائص التركيبية والبصرية لجسيمات الذهب الذهب الذهب وجسيمات النحاس النقي النانوية التي تم تحضيرها باستخدام الليزر النبضي نوع نادميوم حياك لأهداف من العناصر النبيلة (الذهب، النحاس) العالية النقاوة في الماء المقطر اذ تم استخدام الذهب النقي وسبائك الذهب وجسيمات الناتوية الغروية اعلاه حيث بيئت الخواص التركيبية للنماذج المحضرة تم وسبائك الذهب وحسيمات الناتوية الغروية اعلاه حيث بيئت الخواص التركيبية للنماذج المحضرة تم فحص انماط طيف حيود الاشعة السينية (الذهب، النحاس) العالية النقاوة في الماء المقطر اذ تم استخدام الذهب النقي وسبائك الذهب والنحاس لتحضير الجسيمات الناتوية الغروية اعلاه حيث بيئت الخواص التركيبية للنماذج المحضرة تم فحص انماط طيف حيود الاشعة السينية (CRC) والمجهر الالكتروني الماسح للمجال (Mac) فيما تم در اسة سلوك الخوص المتصاص الاشعة الفوق البنفسجية والمرئية الخاصة بالعينات المحضرة باستخدام جهاز (Uv-Vis) فيما تم در اسة سلوك فحوصات حيود الاشعة الفوق البنفسجية والمرئية الخاصة بالعينات المحضرة باستخدام جهاز (1000 معاملات معرب الحيات المحضرة عند الطاقة للم وعدو الاشعة الفوق البنفسجية والمرئية الخاصة بالعينات المحضرة باستخدام جهاز (Uv-Vis) اظهرت فحوصات حيود الاشعة الفوق البنفسجية والمرئية الخاصة بالعينات المحضرة باستخدام جهاز (1000 من وع محصر فحوصات حيود الاشعة المينية للجسيمات المحضرة عند الطاقة للم وعد نبحات (Mac) الفهب والنحاس كما اظهرت فحوصات (FE-SEM) أن جميع الجسمات المحضرة عند الطاقة للمستوي (111) لجميع العينات المحضرة الذهب والنحاس كما اظهرت فحوصات (FE-SEM) أن جميع الجسيمات النانوية من الذهب وسبائك الذهب والنحاس (Sec المعرب ليوجوه وان افضل اتجاهية سائدة للمستوي (111) لجميع العينات المحضرة الذهب والنحات (عدوسات (عدوسات كالدهب والنحاس كما ظهرت فحوصات (FE-SEM) أن جميع الجسيمات النانوية من الذهب وسبائك الذهب والنحاس SNS (Sec المعرب ووية فحوصات (Sec المعرب المعرب الحمرة) عند الطول الموجي 532 ما محمرة (Sec المعرب قليورت نتائج مطيافية تشتت الطاقة Sec (60.11 الباديس (Sec المولا) والغيات ما نوع الخاس (Sec المول الموجي Sec المول الموجي Sac المول الموجي Sac المول الموجي Sec المول الموجي Sac الموي الموجي Sac المول الموي Sec الموالي ال



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الذهب Au والنحاس Cu أن المادة نقية 100 %Au و النحاس100 %وأظهرت نتائج التحليل الطيفي المرئي للأشعة فوق البنفسجية لـ Au و Cu NPs أن الغروبين Au و Cu NPs لهما خصائصهما الخاصة. رنين البلاز مون السطحي لـ Au النقي عند (Cu NPs و 513) وسبائك الذهب حاصا عند (530 و 580 و 577 و 541) على التوالي. كانت هذه النتائج عند1000 نبضة. أظهرت نتائج تشتت الضوء الديناميكي (DLS) لسبائك الذهب النانوية Au NPs بأوزان مختلفة أن سبائك مي مواد غير سامة مع وجود بعض التكلات في المحلول، حيث أظهرت إمكانات زيتا أن سبائك مع ومحاليل النحاس هي مواد غير مستقرة.

الكلمات المفتاحية: سبانك الذهب والنحاس النانوية، تقنية الاستئصال بالليزر، للطول الموجي 532nm، در اسة الخصائص البصرية و الفيزيائية

Introduction

Materials in the nanoscale got the attention of many researchers, as they entered into wide applications as a result of fabricating stronger materials [1], high memory capacity, and smaller electronics [1,2]. Au NPs are being used in biomedical applications such as cancer therapy (as drug carriers), cellular imaging, molecular diagnosis, and targeted therapy, and as contrast agents, photothermal agents, and radio sensitizers. Their usefulness is because of their stability and unique optical, electronic, magnetic, oxidation resistance, and structural properties, in addition to their structure, composite, and shape [3]. Metal NPs such as Au NPs have been a source of great interest for their unusual physical properties, especially because of their sharp Plasmon absorption peak in the visible region [4]. The resonance frequencies depend on particle shape and size and they are stable for a long period of months also exhibited absorbance, which provided a powerful detection tool and shows promise in enhancing the effectiveness of different targeted cancer treatments. Therefore, it's a source of great interest and application because of its novel electrical, optical, and catalyst properties [5] Among the most important advantages of using the pulsed laser ablation method in liquids are: equipment licenses and the possibility of controlling the eradication process. You do not need a vacuum chamber using as little heat as possible on the target material and making it simple to obtain nanoparticles in a



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single step without heat treatments the size and aggregation of nanoparticles can be controlled by adding chemicals [14]. The materials produced in this way are free from pollution. Nanoparticles can be used in many vital applications depending on their physical properties, such as size.

Experimental procedure

Experimental procedure Firstly, for the preparation of Au-Cu alloys, pure Au (99.999%) and Cu (99.999%) were used as precursors. Five circular disc samples of pure Au, pure Cu, and Au-cu alloys with names (A1, A2, A3, A4, A5, and Cu) with different weight connections were paneled as shown in the table (1). Second, as highlighted were synthesized using ablation at a laser Nd: YAG, with laser energy (660mj) at laser wavelengths (532 nm) and the number of laser pulses (1000) at 1Hz frequency. and the distance between the laser lens and the target is 15 cm. The sample is washed thoroughly with distilled water and then placed in an ultrasonic device for 5 min. 2-Then it is returned to be washed with ethanol and placed in the ultrasonic device again for 10 minutes. 3). Then it is washed with distilled water and placed in acetone and also placed in the ultrasound machine for 10 minutes. 4: Just as a used glass beaker is cleaned in the same way as before for the purpose of its use, the sample is placed inside it and 3 mL of distilled water is added to it. It is placed on a rotating base and is bombarded with a laser. The fabrication of Au-Cu composite nanoparticles was discovered using XRD, TEM, FE-SEM, EDS, DLS, and Zeta iyala _ College Potential, UV analysis.



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Table 1: lists the objectives used in the research and their specifications.

COD SAMPLE	SAMPLE	SAMPLE SPECIFICATION
A1	Au12	50% Au-50% Cu
A2	Au15	65%Au-35%Cu
A3	Au18	75%Au-25%Cu
A4	Au21	87.5% Au-12.5% Cu
A5	Au24	100% Au
В	Cu	100% Cu

Result and discussion

XRD patterns of Au and CuO NPs by PLAL technique

XRD is a considerable technique that is commonly applied to discuss the structural properties to ascertain the crystalline nature and phase identification of pure Au and Cu nanocrystalline films; for this purpose, Fig 2 and table (2) also shows that the cubic structure of pure Au, Au-Cu alloys, at 532nm showed diffraction peaks at 20 (38.27, 40.18, 41.02. 41.44, 38.89,) corresponds to the crystal plane (111) equivalent to the standard card JCPDS file No (. 98-016-3723) of gold and and pure Cu [6]20 (36.52) corresponds to the crystal plane (111) equivalent to the standard card JCPDS file No (. 98-016-3723) of gold and and pure Cu [6]20 (36.52) corresponds to the crystal plane (111) equivalent to the standard card No (JCPDS 62-8621)



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Figure 2: X-ray diffraction pattern for gold alloys (A1, A2, A3, A4, A5, and B) for wavelength 532nm.

 Table 2: Summary of X-ray diffraction results for gold nanoparticles at 532 nm wavelength

SAMPLES	20 (DEG)	FWHM (DEG)	CRYSTALLINE SIZE (NM)	
Al	41.44	0.50	15.39	
A2	41.02	0.46	16.89	
A3	40.18	0.16	48.7	
A4	38.89	1.16	6.71	
	45.47	0.96	7.97	
A5	38.27	0.57 CO	13.56	
	44.42	0.87	8.74	
	64.74	0.76	9.14	
	77.67	0.61	10.59	
В	36.52	1.0856	7.26	

FE-SEM analysis an of Au and CuO NPs by PLA technique

The FE-SEM was used to examine pure gold, pure copper, and (Au-Cu) alloy nanoparticles in colloidal solutions synthesized by the PLAL technique using a different number of energy (660mj) and 1000 pulses were selected for each of the pure gold, pure copper, and (Au-cu) alloy



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samples. By observing the average diameters of nanoparticles for all gold alloys, it was found that the average size of nanoparticles at the wavelength (532nm) is (83.7, 13.8, 50.7, 56.5, 35.4nm) and copper nano particalesis (60.1nm) the results showed that the diameters of the gold nanoparticles were and as shown in Figure 3: Au shapes and particles are discussed in depth. 532nm wavelengths was spherical shape [7]. This indicates that the concentration of laser energy (660m J) is significant at the wavelength of 532nm, and when the number of pulses to 1000 pulses, it leads to a change in the shape of the nanoparticles, which leads to the occurrence of lumps. EDS was used to examine pure gold, pure copper, and (Au-Cu) alloy nanoparticles in colloidal solutions synthesized by the PLAL technique using energy (660mj). Also, 1000 pulses were selected for each pure gold, pure copper, and (Au-cu) alloys sample.

An energy dispersive X-ray spectroscopy (EDX) spectrum of the energy versus relative counts of the detected X-rays is obtained and evaluated for qualitative and quantitative determinations of the elements [8] as shown in Fig. 3. The strong peaks observed in the spectrum are related to Au pure, Au alloys and Cu). The elemental constitution of Au-Cu nanoparticles with two major peaks was found to weigh The EDS examination of the samples also revealed that the percentage of the presence of Au Pureit was 100%, and the percentage of Au alloys in all its was (86%Au-14%Cu), (76.5%Au-23.5%Cu), (63.2%Au-36.8%Cu), (55.9%Au-44.1%Cu), and the percentage of copper at the wavelength (532.nm) as shown in the following table**3**

SAMPLE	ELEMENT	LINE TYPE	WT%	ATOMIC%
A1	Au	L series	48.6%	23.4%
	Cu	k-series	51.4%	76.6%
A2	Au	L series	63.2%	35.7%
	Cu	K-series	36.8%	64.3%
A3	Au	L series	76.5%	51.2%
	Cu	K-series	23.5%	48.8%
A4	Au	L series	86%	66.5%
	Cu	K-series	14%	33.5%
A5	Au	L series	100%	100%
В	Cu	K.Series	100%	100%

 Table 3: EDX results for wavelength 532nm and energy 660m j.



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Figure 3: FE-SEM examination and EDSresults for wavelength 532nm, energy 660m J, number of pulses of 1000 pulse (a) A1, (b) A2, (c) A3, (d) A4, (e) A5 (f) Cu.

The samples were also tested on a Dynamic Light Scattering (DLS) scale, where the solutions of pure gold and pure copper and (Au-Cu) alloy nanoparticles (Au Nps) were kept at 25 °C. The viscosity reached 0.89 mph.s, which meant that the average size of the NPs at wave length



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form (532 nm) there were (A1) Au NPs at a wavelength of 532 nm, and the Z-Average was 107 nm, as for the DLS analysis of the solutions of Au NPs and Cu NPs at a wavelength of 532 nm [9-10]. The results of the zeta voltage show that the colloidal solutions of gold and gold and copper alloys are unstable. at wavelengths of 532nm [11].



Figure 4: Size distribution analysis by dynamic light scattering (DLS) for goldalloyes at wavelength 532nm



Figure 5: Zeta potential analysis of nanoparticle solutions



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Optical Properties of Pure Au and Pure Cu and (Au-Cu) alloys nanoparticles

NPs of pure gold and pure copper, and (Au-Cu) alloys were made in distilled water at the wavelength (532nm) using a Q-switched Nd: YAG-pulsed laser. A color change occurred in gold colloidal solutions from faded to red, while the color became green with the copper solution. and displays the color of pure gold, pure copper, and (Au-Cu) alloys nanoparticles colloidal solutions synthesized by PLAL technique with increased energy (660mj) and (1000pulse). Gold and (Au-Cu) alloys and pure copper colloidal solutions showed SPR absorption bands at (525,517 nm) and (536,530,580,577nm) of pure gold Nps and (Au-Cu) alloys, respectively. With the increase of laser pulses, the absorbance of gold NPs (0.139–0.908 arb. units) and (Au-Cu) alloy NPs (0.612–2.212 arb. units) We note from the figure that the absorption spectrum decreases with increasing wavelength, as the transmittance increases at wavelengths greater than 400 nm. [12–13] increased as well



Figure 6a: The plasmon resonance absorption scheme of gold alloys particles of different weights with several 1000 pulses and a power of 660 m J



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Figure 6b: As for copper, it was found at the wavelength of 532nm.

Conclusions

There are many methods for preparing metallic nanoparticles (Au and Cu) NPs by the pulsed laser ablation of liquids (PLAL) technique, which has received much attention because it is a simple and inexpensive method. Its shape, optical properties, and Au NPs have found their way into many applications, including vital ones, and have succeeded in preparing alloys. XRD of Au was studied after being deposited on glass bases, where it was found that it has a cubic crystal structure for pure gold Au at a wavelength of (532) nm. FE-SEM analysis shows the surface morphology of NPs was studied, where the results showed that all the NPs were of spherical shapes and small diameters. It also showed that the diameters of the NPs for all weights of Au and Cu at the wavelength of 532 nm were smaller. EDS results for Au and Cu samples showed that the purity of the Au material was 100%, and the Cu was 100%. The results of UV-Visible spectroscopy of Au and Cu NPs showed that the colloidal Au and Cu NPs have their surface plasmon resonance at 532 nm for Au (518, 539, 534, 532, and 546nm). As for copper, it was (530 nm) as for the 1000 pulses. The results of the DLS for Au alloy NPs of different weights showed that the Au alloy NPs are non-toxic with the presence of some agglomerates in the solution, as the zeta potential showed that the solutions. Colloidal solution of gold particles, copper particles, and gold-copper alloy particles is unstable.



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