



Preparation and Study Physical Properties of Metallic Ag, Au, and Zn Nano Composite Colloidal Nanoparticles via PLAL method

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ABSTRACT

In this work, silver, gold and zinc nanoparticles were prepared and then mixed to obtain silver, gold and zinc nanocomposite easily and simply using Nd: YAG laser, were prepared using the pulsed laser ablation in liquid (PLAL) method to investigate the effects of different solutions on the properties and size of nanoparticles at constant energy (520 mJ) and the number of pulses (2000) for Ag, Au and (4000) for zinc using the laser's with wavelength 1064, frequency 1 Hz and. The results were analyzed The results were analyzed using XRD, single crystalline phase cubic for AgO nanoparticles, cubic crystalline system for AuNP, and crystalline phase with a cubic structure for ZnO nanoparticles, while determining UV-visible peak SPR the nanoparticles at 399 nm for AgO nanoparticles, at 524 nm Au nanoparticles, and at 301 nm ZnO nanoparticles and the energy gap of the nanoparticles was determined, studying and preparing these nanoparticles is very useful in medical and industrial applications.

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1. INTRODUCTION

Particles in the condensed phase with diameters ranging from 1 to 100 nm are referred to as "nanoparticles" (NPs). Nanoparticles (NPs) have a large surface area in comparison to their size. They were initially presented to the field of nanotechnology in 1974. There are three main ways to synthesize nanoparticles (NPs): chemical, biological, and physical processes. Pulsed laser ablation is a well-known physical process that produces particles with great purity [1,2]. Because it requires specific experimental conditions, this method is considered simple, affordable, and ecologically friendly. Highly crystalline nanostructures can be easily formed in a single step using water and a target substance, ensuring superior purity [3]. Gold nanoparticles have been widely developed for use as drug delivery systems and contrast agents.[4] This is because gold nanoparticles have exceptional properties, including chemical stability, facile bioconjugation with various compounds, and high biocompatibility with human cells [5]-[6]. Despite the variety of methods used to synthesize gold nanoparticles, each approach has its own pros and cons. The use of environmentally friendly techniques in synthesizing gold nanoparticles has recently gained popularity due to increased awareness of environmental issues [7]-[8]. For thousands of years, people have utilized silver and its compounds for therapeutic and antibacterial purposes [9]-[10]. Silverware was used by the ancient greeks and Romans to preserve food, wine, and water from spoiling [11]. Hippocrates promoted wound healing and treated ulcers with silver preparations [12]-[13]. Additionally, silver nitrate was applied to wounds and used to disinfect instruments [14]. Spelter, another name for zinc, is a trace mineral [15]. It is a bluish white, diamagnetic, fairly active transition metal with an atomic number of 30, an oxidation state of +2. It is brittle, complex, and a strong electrical conductor. It dissolves in acids and alkalis and has low melting and boiling temperatures [16]-[17].

Zinc has a crucial functional role in cellular metabolism through its involvement in DNA and protein synthesis, cell division, the immune response, wound healing, and the catalytic activity of more than 200 enzymes [18]-[19]. Not to mention the hundreds of proteins that carry and circulate zinc, zinc has possible bonds with about 10% of human proteins. Moreover, it is an essential component for taste and scent perception [20]-[21], promoting proper development and growth during childhood, adolescence, and pregnancy [22].

2. METHOD

The target materials were sheets of gold, silver, and zinc with a high purity of about 99% and dimensions (1 cm, 1 cm, 2 mm). The target was cleaned and washed with ethanol, then in an ultrasonic acetone bath for 10 min to remove impurities, and then washed with distilled water. Before ablation, the target was placed in a glass container containing 5 mL of deionized water. The target was then exposed to a vertical laser beam, which produced a plasma plume on the target's surface and a cavitation bubble due to intense pressure and fluid entrapment. The distance from the laser focusing lens to the surface of the target material was set to 10 cm, taking into account light refraction using energy parameters. The ablation was performed using an Nd: YAG laser with an energy of 520 mJ, a frequency of 1 Hz, a wavelength of 532 nm, and several pulses for the gold and silver (2000 pulses/second, respectively, and for the zinc (4000 pulses/second). Then the nano-hybrid was prepared from these materials by bombarding 3 ml of gold and 3 ml of silver with several pulses (2000) pulses/second, then mixing the resulting solution of the two materials and drying it until it became 3 ml of gold and silver water, then bombarding it with a zinc strip with some pulses (4000) pulses/sec. In the production of the prepared film material, the drip-casting technique was used for its importance and simplicity in producing thin films. The solutions are carefully deposited onto horizontally positioned glass substrates using a pipette after thorough cleaning to ensure cleanliness.

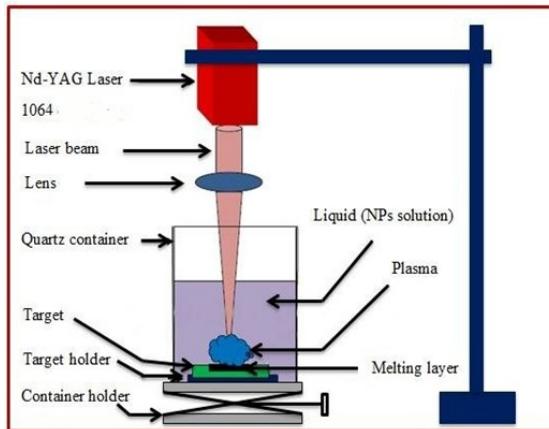


Figure 1. Illustration of the pulsed laser ablation method.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

XRD was performed to know the phase distribution and crystallinity of nanoparticles and to determine the X-ray diffraction patterns of silver, gold, zinc nanoparticles and silver-gold-zinc hybrid nanoparticles prepared by pulsed laser ablation technique at a wavelength (1064 nm) and energy (520 mJ.) and different number of pulses, and the X-ray diffraction examination was performed for gold, silver and zinc at the highest number of pulses, where the examination was performed for gold and silver at the highest pulse (2000) pulses and for zinc slice at (4000) pulses. Still, for the prepared silver-gold-zinc hybrid, the examination was performed at several pulses (1000-2000-3000-4000) for the prepared nanohybrid.

1-A- X-ray diffraction of AgNP results

It was shown from the results of the X-ray diffraction examination of the silver nanoparticles in figure (2), which have a single crystalline phase cubic Ag and of the facet-centered type (FCC). It was found that the peaks for the prepared silver oxide sample were at an angle of (20) at (32.56, 40.57). The crystalline levels appeared at those values, respectively ((111)(211)). It was found that the peaks were for the sample Silver prepared at an angle of (20) has two peaks at (38.47, 44.80) and has crystal levels ((111)(200)), where we notice good agreement between the results obtained experimentally with the international standards (JCPDS) with the following no. (1038-43, 0921-03, 1098-02), and these results are close to the results reached by the researcher, The crystal sizes of nanoparticles (cs) are known theoretically through the Debye-Scherer equation formula, and Figure (1) shows the structural characteristics of each of the silver nanoparticles[14]-[23].

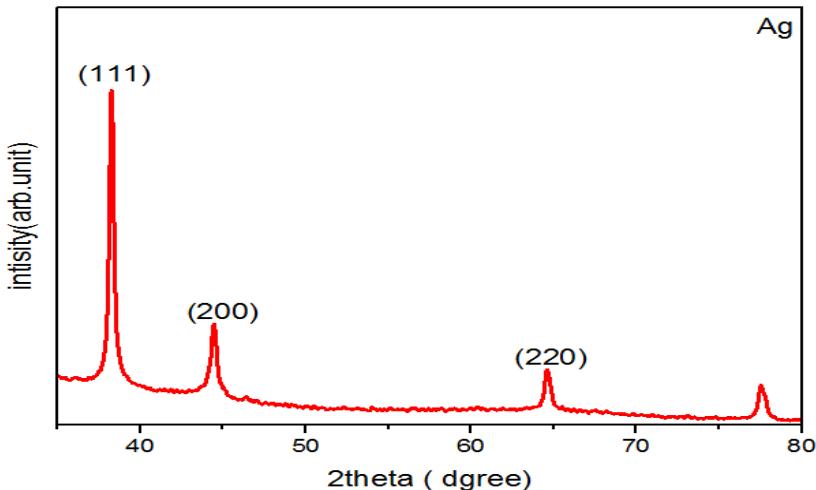


Figure 2. X-ray diffraction pattern of Ag nanoparticles prepared by laser ablation technique.

1-B- X-ray diffraction of Au NP results

The results of the X-ray diffraction examination of gold particles revealed the appearance of a cubic crystalline system in Figure (3). has a crystalline phase. The cubic structure (cubic Au), where it was found that the peaks of the prepared gold sample were at angles (2θ) at (38.25, 44.40, 64.65, 77.44) and the crystal planes appeared at those values, respectively ((111)(002)(022)(113)) where We note good agreement between the experimentally obtained results with the following international standards no. (3723-016-98), and that the orientation of the crystal plane in the (111) direction is dominant, and these results are consistent[15].

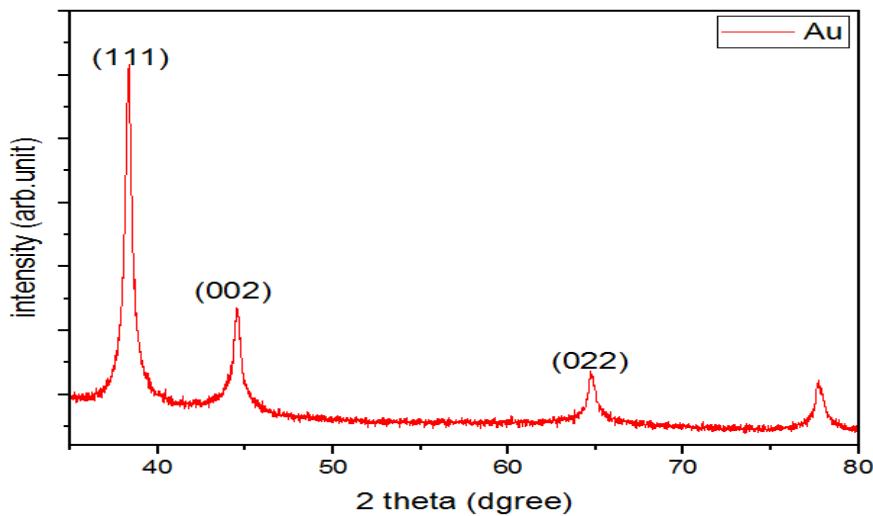


Figure 3. X-ray diffraction pattern of Au nanoparticles prepared by laser ablation technique.

1-C- X-ray diffraction of ZnONP results

The results of the X-ray diffraction examination of zinc particles showed the appearance of a crystalline system with a cubic structure in Figure (4). These prepared samples have a group of peaks representing the structure of nano-zinc oxide, which has a crystalline phase with a cubic structure. It was found that The peaks for the prepared zinc sample and at angles (2θ) at (32.43, 35.06, 36.94) for the international card no. (010749943) of zinc oxide and at an angle of (33.90) according to the international card no. (000211486) of zinc oxide, the crystalline levels appeared at those values and respectively ((100) (002)(101)), where we notice good agreement between the results obtained experimentally with international crystal standards, and that the direction of the crystal plane in the direction (101) is dominant, and these results are consistent with the results of the researcher [16]. The crystalline sizes of nanoparticles (cs) are known theoretically through the Debye-Scherer equation formula, and table (1) shows the agreement between the experimental measurements, with a small shift in the distances to the atomic levels (d) due to the twisting of the lattice due to defects that affect the process of preparing nanomaterials.

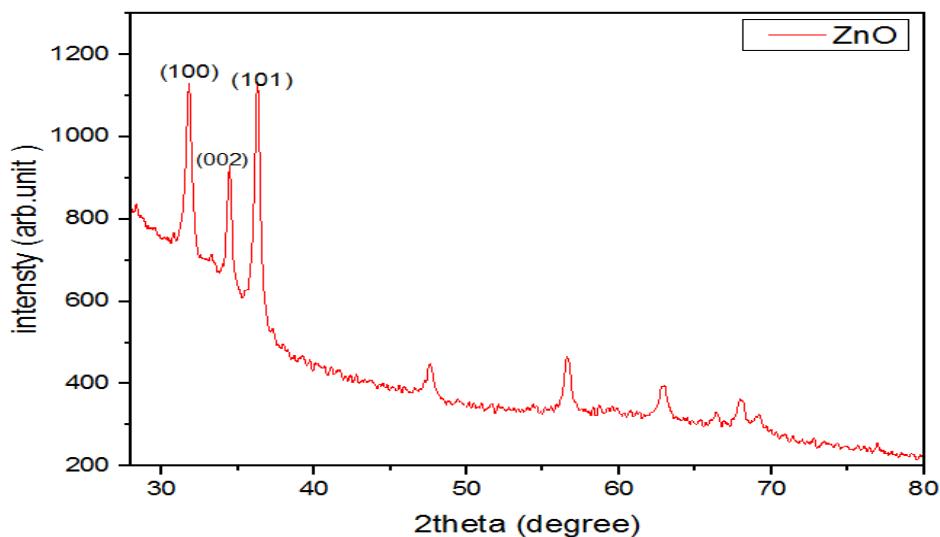


Figure 4. X-ray diffraction pattern of Zn nanoparticles prepared by laser ablation technique.

1-D- X-ray diffraction of Au/Ag/ZnO-NP results

To determine the X-ray diffraction patterns of a hybrid compound of silver, gold, and zinc nanoparticles, the medium was deionized water. The results of the X-ray diffraction examination of the hybrid of silver, gold and zinc showed that these prepared samples showed many results as a hybrid compound and had a group of peaks, including the structure of nano-silver and silver oxide, which have a crystalline phase. It was found that the peaks of the prepared sample were at an angle of (20) at (77.61) for silver oxide and an angle of (64.94) for nanosilver. The crystalline levels appeared at those values, respectively ((220)(023)) We notice good agreement between the results obtained experimentally with the standards of the two international cards (JCPDS) no. (0921-03) and card no. (1038-43), and it also contains clear peaks for zinc oxide and at the corner (44.74), which also showed good agreement, and the level appeared. The crystalline is (100), according to the international card no. (1486-021-00), and it also contains clear peaks of nano-gold at the corner (38.53) and the back of the crystal plane (111), according to the international card no. (3723-016-98), as shown in the figure. (5). The crystalline sizes of the nanoparticles (cs) are known theoretically through the Debye-Scherer equation, and Table 1 shows the structural properties of the compound for the hybrid of silver, zinc, and gold [24]-[25].

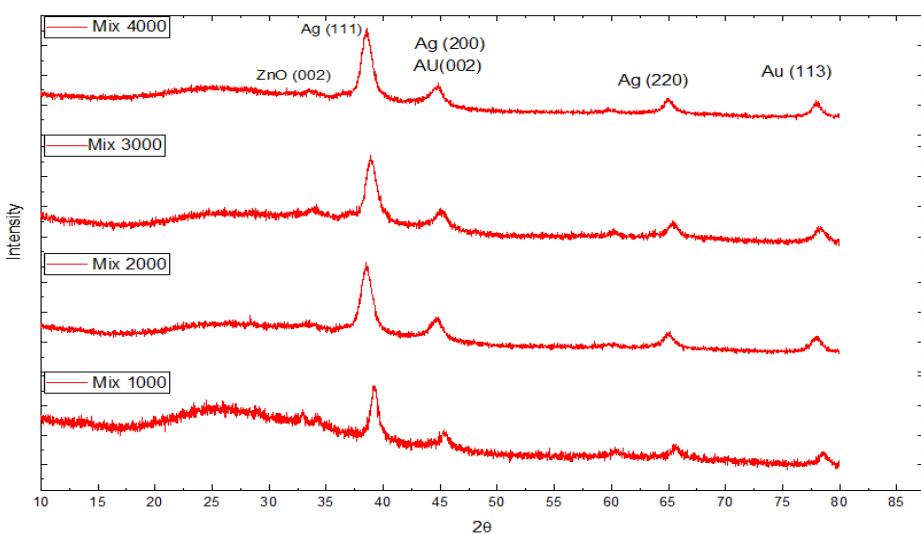


Figure 5. X-ray diffraction pattern of mix nanoparticles prepared by laser ablation technique.

Table 1. The structural properties of materials NPs

Materials		2θ (deg) Practical	2θ (deg) Standard	FWHM (deg)	crystalline size "D" (nm)	d _{hkl} (A°) Practical	(hkl)
Ag	32.96	32.01	2.8530	3.03	2.91538	(111)	
	38.94	39.38	0.4834	18.21	2.32793	(202)	
	40.71	40.91	0.0586	22.94	2.02283	(211)	
	44.80	44.6	0.8240	10.9	2.04813	(200)	
Au	38.25	38.32	0.9159	3.11	2.36564	(111)	
	44.40	44.54	0.8240	0.19	2.04813	(002)	
	64.65	64.71	2.6696	3.68	1.44346	(022)	
	77.44	77.74	0.4750	22.40	1.23136	(113)	
ZnO	32.43	32.39	4.3700	1.98	2.69086	(100)	
	33.90	33.69	0.3046	28.49	2.43536	(100)	
	35.06	35.14	3.1332	2.78	1.54528	(002)	
	36.94	36.92	4.6772	1.87	1.41645	(101)	
Mix	Au	38.53	38.26	0.2459	35.76	2.33646	(111)
	ZnO	44.74	44.59	0.2906	30.89	2.02585	(100)
	Ag	64.94	64.67	0.5560	17.70	1.43529	(220)
	Ag	77.61	77.24	0.2791	38.17	1.22535	(023)

3.2. FESEM Analyses

Figure (6) shows the results of FESEM measurement images of mix particles prepared at 500 pulses and combined as a hybrid composite with zinc oxide particles prepared at 1000 pulses. Where the particles were in the nanoscale range and the average diameters ranged from (35.84-99.6 nm) with an average of (61.33 nm) and the particles had spherical shapes.

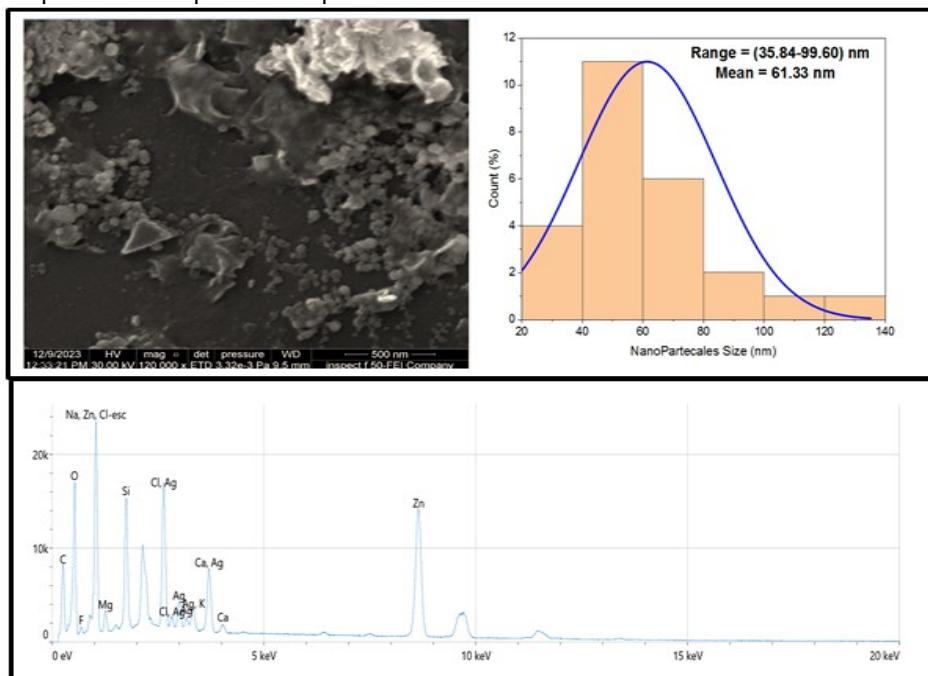


Figure 6. FESEM and Eds images of colloidal mix nanoparticles of 1064 nm PL1000.

Figure 7 shows the results of FESEM measurement images of mixed particles prepared at 500 pulses and combined as a hybrid composite with zinc oxide particles prepared at 2000 pulses. The particles were in the nanoscale range, and the average diameters ranged from (31.06-103.48nm) with an average of (47.82 nm), and the particles had spherical shapes.

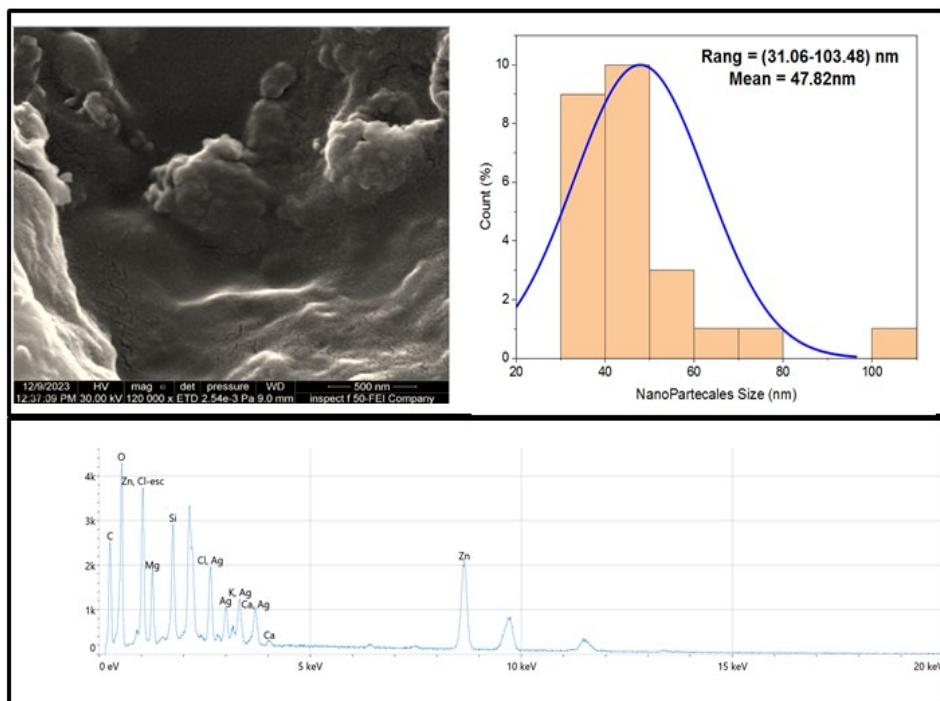


Figure 7. FESEM and Eds images of colloidal mix nanoparticles of 1064nm PL2000.

Figure 8 shows the FESEM images of mixed particles prepared at 500 pulses per second. and combined as a hybrid composite with zinc oxide particles prepared at 3000 pulses, where the particles were in the nanoscale range, and the average diameters ranged from (18.9 - 113 nm) with an average of (52.67 nm), and the particles had spherical shapes.

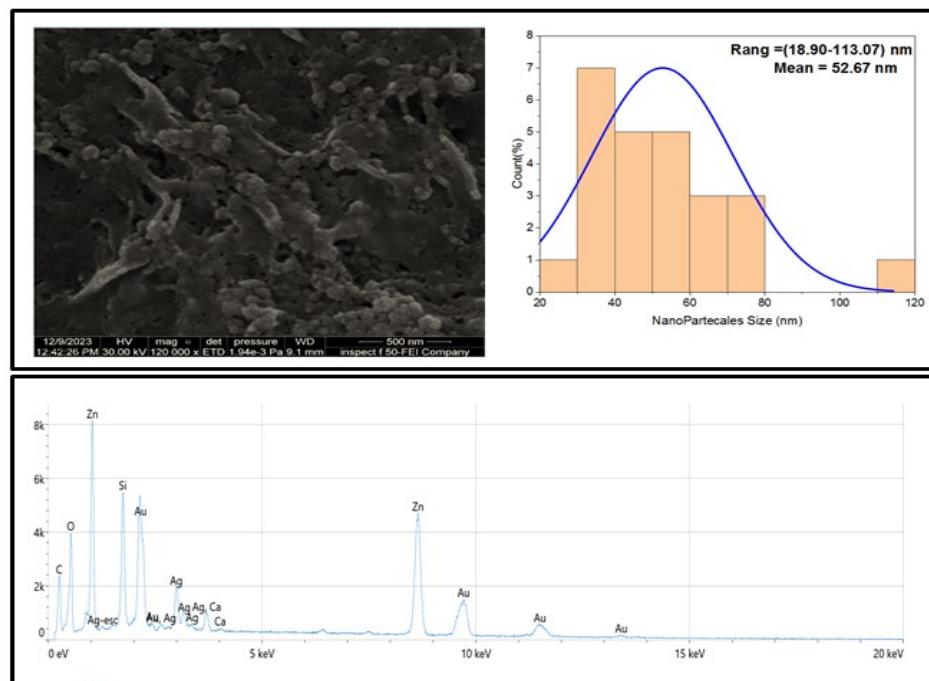


Figure 8. FESEM and Eds images of colloidal mix nanoparticles of 1064nm PL3000.

Figure 9 shows FESEM images of mixed particles prepared at 500 pulses and combined as a hybrid composite with zinc oxide particles prepared at 4000 pulses, where the particles were in the nanoscale range. The average diameters ranged from (15.61-64.63 nm) with an average of (52.67 nm), and the particles had spherical shapes.

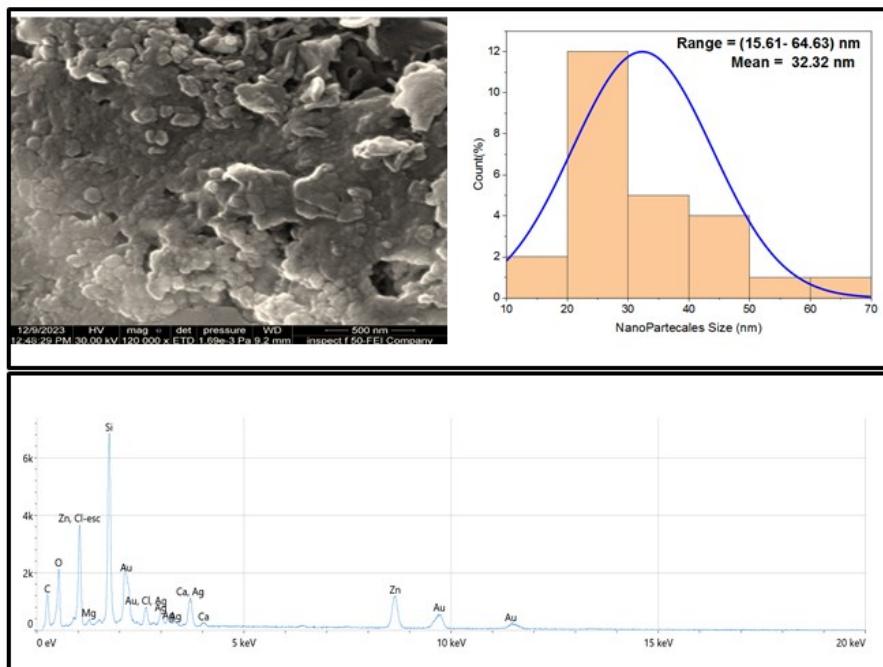


Figure 9. FESEM and Eds images of colloidal mix nanoparticles of 1064 nm PL4000.

3.2 Optical Properties Results

3.2.1 UV-Vis spectra

In wavelength (1064 nm), where figure (10-a) shows the location of the surface plasmon peak of the silver nanoparticles at about (399 nm) and the absorbance (2.06 a.u.), nanoparticles have been produced, which can be attributed to the absorption due to the interband transition in Au nanoparticles. Inter band absorption can occur at shorter wavelengths in noble metals due to an electron transition in the conduction band above the fermi level [19]-[20]. Figure (10-b) shows the absorption spectrum of the gold nanoparticles solution, where we observe of the surface plasmon peak around (524 nm) and this indicates that the prepared nanoparticles are almost spherical [26]. Figure (10-c) shows the surface plasmon resonance peaks (SPR) obtained for the colloidal solutions of Zinc nanoparticles as they were nearly constant from (301 nm). Table (2) shows the absorption and surface plasmon resonance values of metal nanoparticles.

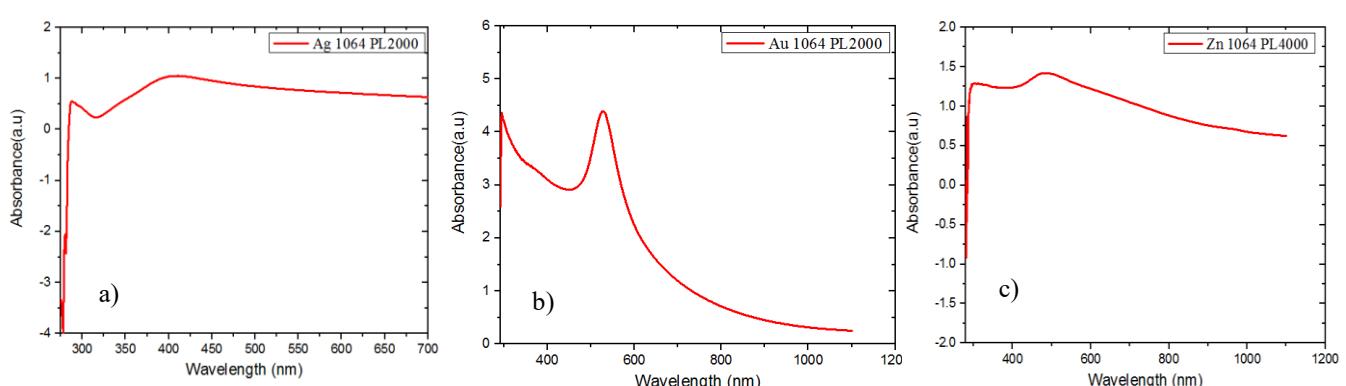


Figure 10. UV-Visible absorption spectra a- AgNP, b- AuNP, c- ZnNP at wavelength 1064nm.

Table 2. The absorption and surface Plasmon resonance values of metals nanoparticles

Parameters	Pulse/sec	Absorbance(a.u.)	SPR
Ag NPs	2000	0.555, 1.05	399 nm
Au NPs	2000	4.3	524 nm
Zinc NPs	4000	2.06	301 nm

3.2.2. Energy Gap (E_g)

In wavelength (1064 nm) Where we note that the value of (E_g) is (3.89 eV) for silver nanoparticles prepared, as the (E_g) value of the gold NPs particles generated reached (3.17 eV). Zinc particles exhibite considerable rise in the value of (E_g) as (3.98 eV). Figure (11) shows the optical energy gap of the prepared nanoparticles [27].

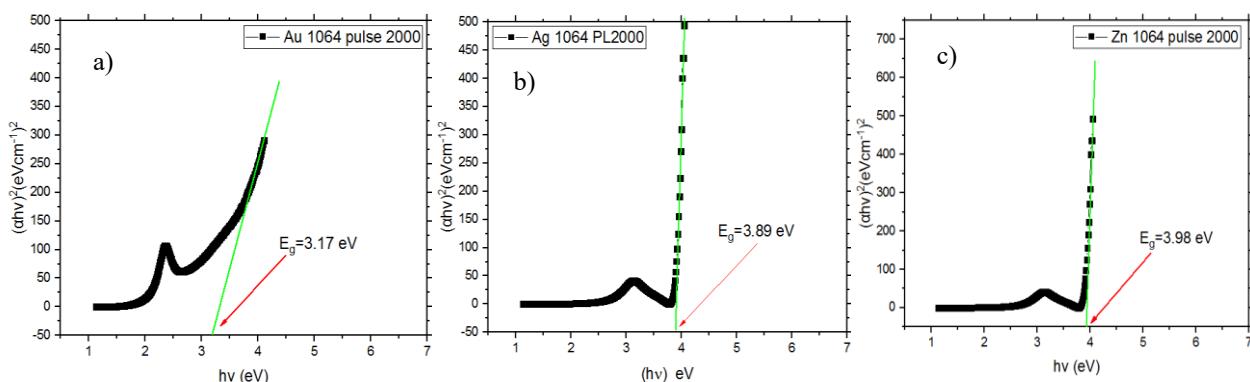


Figure 11. Direct band gap estimations of colloidal a- AgNP, b- AuNP, c- ZnNP at wavelength 1064 nm.

4. CONCLUSION

In this work, nanoparticles of metals were prepared in an easy and environmentally friendly way by using a Nd: YAG laser in a liquid medium, where an average size of diameters less than 50 nm was obtained, as well as a stable nano mix and no agglomeration was obtained for a time estimated at 5 months from silver, gold and zinc, and this indicates high stability and surface plasmon resonance determination of metals. The surface plasmon resonance of the metals was determined, and the results showed a peak (SPR) for silver at 399 nm and gold at 524 nm, while the zinc peak was at 301 nm. The absorption factor calculated the energy gap, and such particles are of great importance in many applications.

Conflict of Interest:

The authors declare no conflict of interest.

Source of Funding:

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Ethical Clearance:

Ethical approval was not required for this study.

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