Preparation and characterization of colloidal Au-ZnO Nanocomposite via laser ablation in deionized water and study their antioxidant activity

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Abstract: A synthesis is carried out with Au-ZnO nanoparticles (NPs), using fundamental laser Nd:YAG (1064 nm) of Au and ZnO colloidal solution, with the metal objectives in deionized water being extracted, accompanied by laser radiation a second harmonic Laser 532nm with the mixed colloidal solution. The UV-visible display the Au nanoparticle peak at 525nm, and the ZnO peak at 415nm. The Au-ZnO NPs show a shift of the ZnO absorption at 390nm, which is excited, and a change in the Au absorption at 530nm, as the Au NPs plasmon resonance is transmitted through an interface charge. The optical band gaps of the ZnO, Au and Au-ZnO NPs are increased with laser fluence up to 13.8 J/cm². The antioxidant activities of prepared nanoparticles were measured using DPPH assay. The results showed the ability to scavenging of free radicals. Taken together, the results of this study demonstrated that the Au-ZnO nanocomposite could be used in future for therapeutic purposes.

Keywords: Au-ZnO nanocomposite; Laser ablation in liquid, optical properties; TEM; DPPH.

1. Introduction
Nanotechnology is the most exciting field of scientific research. Nanoparticles less than < 100 nm has to be dealt with. Nanoscience and nanotechnology include different science disciplines including physics, chemistry, biology and engineering that can have enormous impacts on people's lives in the near future [1,2]. The common structural elements or composites of nanoparticles may be popular and they have a broad variety of functions compared to bulk materials. The physical and chemical properties of metallic nanoparticles are usually determined by the following parameters: size, shape and composition [2,3]. Because of its excellent material properties, such as low cost, non-toxicity, ease of use, good stability, with high optical clarity, high electron mobility, small band spacing ~3.37eV in bulk and strong exciton bonding strength ~60meV [4,5]. Based on its structure, strong electric and heat transport, and exceptional photocatalytic properties, it exhibited high antibacterial activity. In addition, ZnO NPs has an exceptional biological potential because of their antibacterial, antifungal and anti-cancer, acaridical antidiabetic, gene delivery, drug delivery, pediculicide activities and other factors[6,7,9,10]. The use of inorganic materials such as ZnO has many benefits as it contains mineral elements which are important to humans. These have strong antimicrobial inhibitory activity against human pathogens [8,12]. Additionally, Gold nanoparticles are important noble, highly stable, chemically inert, sensitive precious metals. Golden nanoparticles are important. It has greater biological compatibility, high surface reactivity, and has different colors, depending on the form, size and aggregation. In the present study, the scavenging of free radicals was measured. Overall, the antioxidant activity of prepared nanocomposite has been investigated.

2. Experimental work
2.1. Preparation of nanomaterials
Prepared the ZnO NPs were obtained from Zn pellet with purity 99.8 % by the pulsed laser ablation in liquid (PLAL) method in 3ml of deionized water. Irradiation with Nd:YAG laser (1064nm, 9ns, 200 pulses, and 1Hz) is focused on the surface of the target with fluence 13.8 J/cm². PLA in the liquid was performed at room temperature.

The dispersion prepared in water has a various color dependent on the various laser energies. Au nanoparticles was prepared with the same conditions of ZnO, after prepared, we mixing with same ratio, and irradiated with post laser ablation by second harmonic Nd:YAG laser 532nm with 10.41J/cm², 100 pulses, The laser beam was focused on the targets using convex lens of 100mm focal length to produce sufficient laser fluence for the ablation.

A spectrophotometer (model-Shimadzu, 1200) with double beam of UV-vis was used to investigate the absorption spectra of the ZnO and Au NPs solution at various conditions at spectral range 300-700nm. The solutions put in cell made from quartz (optical path equal 1cm). After that the optical feature of the ZnO and Au NPs colloids were obtained. A transmitted electron microscope has been investigated (TEM by Day Peronic company, Iran), the size and shape of NPs were observed.

2.2. DPPH assay
The antioxidant activity of prepared nanoparticles was measured by using DPPH assay [13]. The colloidal Au-ZnO nanocomposite was evaluated for the DPPH scavenging activities. Each nanoparticle was mixed with DPPH solution and then absolute ethanol was added to reach a volume 0.5ml. The samples were kept in dark for 30min at 37°C. The Optical density of samples was measured at 517nm. The percentage of scavenging activity of the prepared nanoparticles was measured using the formula:

\[
\text{% Scavenging} = \frac{\text{OD Control} - \text{OD Sample}}{\text{OD Control}} \times 100\%
\]

2.3. Statistical analysis
The data of this study were analyzed using GraphPad Prism 6 [15].

3. Result and Discussion
The optical properties of the obtained ZnO, Au and Au-ZnO nanocomposites were measured UV-vis at fluence 13.8J/cm² shown in Figure (1). It is found that a distinct peak of about 415nm was found for pure ZnO-nanoparticles that’s attribute the semiconductor behavior [16]. The pure Au nanoparticles show a resonance absorption peak of 525nm on the Plasmon surface. Au-ZnO optical absorption spectra have an excitable absorption peak of around 390nm and a Plasmon-surface absorption peak of 530nm, respectively.

The Au particles are melted by radiation with a post-laser 532nm and smaller after irradiation, after depositing the ZnO on Au, to bind with Au nanoparticles, due to an increase in the refractive index of the surrounding medium. Also, a 25nm blue-shift is for ZnO nanoparticles.
Figure 1. UV-visible absorption for pure ZnO, Au, and Au-ZnO nanocomposite at influences 13.8J/cm².

Figure (2) Show the band gap for Au NPs found at 3.05eV and band gap for ZnO at 3.1eV these improvements related to laser fluence. While, the band gap of mixture Au-ZnO nanocomposites after ablation with post laser 532nm lead to rising of band gap to 3.2eV. That laser fluence actually means obtaining more energy, which implies ablating greater quantities of material. Also, it was found that the plasma plume produced by that laser fluence became more intense, and the nanoparticles of the samples could become denser.

![Graph](image1)

Figure 2: Band gap for pure ZnO, Au, and nanocomposite Au-ZnO at influences 13.8 J/cm².

In order to further study, the morphological properties of Au-ZnO nanocomposite, TEM analysis was performed. Figure (3), clarify low and high magnifications of TEM images and selected area of electron diffraction pattern from manufactured ZnO Adherent with a sputtered thickness of about 20nm on the surface of Au NPs. ZnO NPs with an average size of 40nm and Au NPs were almost spherical in form with an average size of 35nm, and the colloidal solution was slightly turbid after
ablation. The low magnification of the TEM image on the small area of the specimens showed a clear visualization of the spherical, irregularly shaped structures of Au NPs exhibiting a dark contrast, which is relatively well deposited on the surface of Au NPs.

**Figure 3.** TEM image for Au-ZnO at fluences 13.8 J/cm².

DPPH is stable free radicals, which are binding with replacement electrons [17]. DPPH can mix with a substrate that can give a hydrogen atom; this may give a rising reduced form with a color change from violet to yellow [18]. The DPPH radical scavenging (%) activity of Au nanoparticles, ZnO nanoparticles, and Au-ZnO nanocomposite is shown in Figures 4. The antioxidant activity of Au nanoparticles is 56.33 ± 5.487 for ZnO nanoparticles is 47.00 ± 2.887. While, for Au-ZnO nanocomposite was 79.67 ± 4.372. The result demonstrated that the Au-ZnO nanocomposite can give hydrogen atoms and remove the unstable electron from DPPH more than Au nanoparticles and ZnO nanoparticles alone.
Figure 4. Antioxidant activity for a) Au nanoparticles, b) ZnO nanoparticles, and c) Au-ZnO nanocomposite at influences 13.8 J/cm². Ascorbic acid used as a positive control at concentration 1mg/ml.

Conclusions
In this study, a basic laser simple method Nd:YAG PLAL was used to create pure nanocomposites like Au, ZnO and Au-ZnO, and the second harmonic laser of 532nm was also used to minimize the mixing size of particles as little as possible. We were able to understand the phase of Au-ZnO nanocomposite based on the interaction of the laser light with the colloidal solution. The UV-vis tests are characterized by the reported formation and clearly indicate Au-ZnO nanocomposite and demonstrate the interaction mechanism for ZnO on the Au surface. These nanoparticles have ability to scavenging free radicals.

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