Study of optical and morphological properties for Au-ZnO nanocomposite prepared by Laser ablation in liquid

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Abstract: The preparation of Au-ZnO nanocomposite involves the synthesis of Au and ZnO colloidal solutions by Nd:YAG laser (1064nm) ablation of metal targets in deionized water followed by laser irradiation of the mixed colloidal solution by a second harmonic Nd:YAG laser (532nm).

The UV-visible show the gold nanoparticle (NPs) peak at 525nm while the peak of the ZnO nanoparticle (NPs) at 375nm. The Au-ZnO nanocomposite showed a blue shift in the absorption of the ZnO excited, while due to the plasmon resonance and interfacial charge transfer of Au NPs lead to redshift in the absorption, also show the intensity absorption increases with the concentration of the metal nanoparticles. The morphological properties of nanoparticles have been characterized by Transmission Electron Microscopy (TEM).

Keywords: ZnO nanoparticles; gold nanoparticles; Laser ablation; Morphological properties, Optical properties.

1. Introduction

Nanotechnology is a relatively modern science, but since the beginning of life on Earth such nanometer structures have existed. The interest lies in a wide range of exhibits featured chemical and physical properties[1-3].

In the last few years, intense research was carried out into preparations of nanoparticles, Its structure consists of many nanocomponent composites, of which Raman surface-enhanced dispersal is very attractive nanocomposites with many applications. [4], photonic crystals [5], drug delivery applications [6], and heterogeneous catalysts [7]. But only a few studies for metal/semiconductor nanoparticles are available [8].

The storage properties of metals such as Ag and Au are required to facilitate charge separation in a nanocomposite metal-semiconductor [9]. These properties have been implemented in many areas, such as nanodevices [10], biomedicine [11], and photoluminescence [12]. Amongst all of the metal-semiconductors, the nanocomposites of Au-ZnO have received special attention because the gold nanoparticles have a wide range of highly absorbed lights, ranging from visible to IR, having unique electrical and optical properties according to their size and shape. [13]. The zinc oxide is an economical semiconductor compared with silicon and germanium. Zinc oxide has 3.37eV broad-band gap power, making it transparent in a visible area and the bulk of UV-blue activity [14-15].

There are many methods for preparing nanocomposites in a semiconductor-metal, but in pulsed laser ablation in liquid (PLAL) [16], As one of the better methods that used to make a composite nanostructure, the use of a variety of laser parameters and surrounding media around the target which affects the size/shape and structure of the resulting material is more attractive. [17-18]. The method is based on the use of high-intensity short pulses up to nanoseconds from high power laser sources to generate laser interactions to produce a small particle which has unique characteristics in the nanoscaled form [19].

In this work, the manufacturing of Au-ZnO nanocomposite by fundamental laser radiation were introduced. Also, investigation to the effects of second harmonic laser ablation on size particles after mixing Au-ZnO (core-shell) nanocomposite, the spectrum for optical absorption reveals an interesting production of two absorption peaks at 375nm and 525nm, respectively. This concept emerged from the fact that laser light contact with Au metal nanoparticles induces melting of these particles, but due to its high melting point ZnO nanoparticles can stand against laser light.
2. Experiential and details

As seen in the Figure 1, the gold target is placed in the form of a plate on the base of a glass cell and rotated to prevent a deep deposition of the metal. In a glass vial, placed 3ml of deionized water was collected from a laser Nd:YAG of 1Hz using 1064nm pulses with 9ns pulse length and a beam diameter of 2.4mm. The ablation was carried out for 200 pulse and different energy 400, 600, and 800mJ. the ablation of pure zinc target was done, with the same condition of prepare Au NPs. The colloidal solutions synthesized by Au and ZnO were combined in the same volume 1:1 ratio, and irradiated with the post-laser, 532nm and 600mJ, for 100 pulses.

![Figure 1: show the laser ablation experimental to produce materials nanoparticles.](image)

The optical property was calculated by using a (T80 + UV/VIP Spectrophotometer PG Instruments Ltd, Japan) quartz cell with 1cm path length within the 300-700nm wavelength range. And the transmitted electron microscope (TEM by DayPeronic company, Iran), the size and shape of NPs were observed.

3. Result and discussion

Figure (2a,b) shows the UV–visible absorption of the ZnO and Au nanoparticles. The absorption peaks of ZnO NPs around 375nm, and the peak of Au NPs at 525nm. The different absorption intensities depending on the different laser ablation energy as shown in Table (1) as reported in previous studies [2-20], when the electrons in the valance band absorb the energy from UV light, the electrons will be excited to the conduction band, that attributes the semiconductor behaviour of ZnO [22], but the absorption peaks of Au NPs originated from the Surface Plasmon Resonance of electrons inside the conduction band. Also, we can note that the absorption intensity for Au NPs decreases more than ZnO NPs with reduced laser energy, which indicates that the interaction of the nanosecond pulse laser with the metal nanoparticles causes the melting of the particles.

Figure (2c) shows the optical absorption spectra of the mix of Au-ZnO nanoparticle after irradiated with second harmonic of Nd-YAG laser at 532nm, its shows two absorption peaks at 530nm and 416nm for Au-ZnO NPs, the high temperature generated by post-laser radiation which affected comportment and caused the maximum Au NPs from 520nm shall be 525 as shown in Table (1), whereas the ZnO NPs are nearly constant, due to the wavelength of the ZnO NPs are far from the laser wavelength, therefore, result in a density increase for the ZnO shell around the AuNPs. This shows that the particle size of Au NPs is becoming smaller and surrounding of ZnO NPs that are not affected by laser energy as being within the range of UV-visible, so we can confirm that the core/shell nanoparticles of Au-ZnO have been formed within the solutions.
Figure 2: show the UV-visible absorption for (a) ZnO NPs, (b) Au NPs and (c) Au-ZnO NPs at different laser energy.

Figure (3) shows the bandgap for ZnO, Au and Au-ZnO, whereas the bandgap for ZnO NPs increase with the same laser energy behaviour for Au NPs, whereas Au-ZnO nanocomposites increase the bandgap more than Au NPs, which indicates the role of energy in transforming Au NPs to the smallest particles size.
Figure 3: Show the bandgap for (a) ZnO NPs, (b) Au NPs and (c) Au-ZnO NPs at different laser energy.

Table 1: Effect of different laser energy on UV-vis peak and energy gap at different laser energy.

|                | Au NPs |          |          |          |
|----------------|--------|----------|----------|----------|
| Absorption peak (nm) | 530    | 525      | 520      |
| Energy gap (eV)     | 3.02   | 3.08     | 3.12     |
| ZnO NPs             |        |          |          |          |
| Absorption peak (nm) | 370    | 375      | 395      |
| Energy gap (eV)     | 3.3    | 3.3      | 3.16     |
| Au-ZnO NPs          |        |          |          |          |
| Absorption peak (nm) | 420/535| 420/525  | 415/525  |
| Energy gap (eV)     | 3.15   | 3.08     | 3.4      |

Figure (4a,b) shows the TEM image for the pure ZnO and Au nanoparticles, ZnO NPs with an average size of 40nm and Au NPs were almost spherical with an average size of 35nm, The colloidal solution was slightly turbid after ablation. And ZnO NPs are formed because of the rapid reactive cooling immediately after ablation; During this process, Zn(OH)$_2$ quickly breaks up into ZnO clusters[24], which can be more clear by this reactions:

\[
\text{Zn}_{\text{clusters}} + 2\text{H}_2\text{O} = \text{Zn(OH)}_2 + \text{H}_2
\]  
\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}
\]  

Additionally, the melting point of Au and ZnO are 1064 and 420°C, respectively. Therefore, the melting point of metal nanoparticles decreases according to the following equation with particle size [25]:

\[
T_M(d) = T_{MB} \left(1 - \frac{4\sigma_{SL}}{H_f P_d d}\right)
\]
where, $T_{MB}$, $\sigma_{sl}$, $H_f$, $\rho_s$, and $d$ are bulk melting temperature, solid liquid interface energy, bulk heat of fusion, the density of solid, and particle diameter, respectively.

Whereas the semiconductor material follows a different dimension, based on the equation below.

\[ T_M(d) = T_{MB} \left( 1 - \frac{c}{d} \right)^2 \]  

Here, $T_{MB}$, $c$ and $d$ are in order bulk melting temperature, material constant, and particle diameter.

From eq. (4) The semiconductor melting point depending on the size of the quadratic particle can be noted. Thus, the depression at the melting point in semiconductor nanoparticles is also less pronounced and does not melt as metal nanoparticles during laser irradiation.

Figure (4c) shows both the nanocomposite of Au-ZnO and the nanoparticles of ZnO possess a diameter of around 45-50nm. While Au NPs are a uniform, spherical particulate matter of 30-35nm on average, there is a clear nearly 15nm thick shell covered in an average 40nm diameter. The shape of the core/shell nanostructures was similar to the Au NPs centers that were previously irradiated by laser ablation, but the overall sizes become larger.

![Figure 4](image)

**Figure 4:** Show the TEM images for a) pure ZnO, b) pure Au, and c) Au-ZnO nanocomposite, by leaser ablation using Nd:YAG laser wavelength 1064nm at laser energy 800mJ and post-laser by the second harmonic with wavelength 532nm for 600mJ.

**Conclusion**

In this present work, prepared Au, ZnO, and Au-ZnO (core-shell) nanocomposite by using Nd:YAG laser wavelength 1064nm with various laser energy 400, 600, and 800mJ. A decrease in the particle size of Au-ZnO performed through applying second harmonic laser ablation 532nm. It was found the absorption peak for ZnO NPs at 375nm and Au NPs at 525nm, while for Au-ZnO (core-shell) nanocomposite found after applying secound harmonic Nd:YAG laser led to a blue shift of...
absorption. Also, the bandgap of Au NPs increases with energy, opposite for ZnO NPs, while, the Au-ZnO (core-shell) nanocomposite has different behaviour. The UV-visible and TEM characteristics confirm formation and clearly show the core-shell nanostructure of Au-ZnO.

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