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Structural and Fluorescence Properties of TiO_2/Ag Nanoparticles Bilayers

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Abstract

The optical properties of the TiO2 / Ag hybrid nanoparticles were improved as the particles were prepared with a pulsed liquid laser ablation (PLAL) technology. The effect of number of pulses (450) on the structural and optical properties of nanoparticles prepared in distilled water (DW) as growth media was examined using a Q-Switched Nd-YAG laser with wavelength (1064 nm), ablation energy (530 mJ) and repetition rate (1Hz). The distance between the target and the lens (10 cm). Several were used for the diagnosis such as X-ray diffraction analysis, fourier infrared transformations, TEM assays and fluorescence of the prepared samples. The results of X-ray diffraction analysis of the silver nanoparticles deposited on a glass slide showed that the crystal system is cubic and polycrystalline, with the direction being dominated by [111] at the level of the crystals. The results of X-ray diffraction analysis of a solution of titanium dioxide nanoparticles deposited on a glass slide revealed the presence of a quadrangular crystal system, indicating the presence of titanium dioxide particles in (rutile), and that the prevailing trend for crystalline levels is [110]. The functional groups of (TiO_2 / Ag) were determined in the liquid medium by the (FTIR) technique. Also, TEM images showed the presence of nanoparticles and microparticles in an almost spherical shape. The fluorescence measurement of (TiO_2 / Ag) hybrid particles showed that through the graph the peak values of (284.1) and (418.3) nm. This is roughly identical to the absorption spectrum results of a hybrid silver and titanium dioxide nanoparticle solution.

Keywords: Pulsed laser ablation in liquid (PLAL), Nanoparticles, microparticles, fluorescence.

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الخصائص التركيبية والفلورة للجسيمات النانوية ثنائية الطبقات للمركب Tio_2 / Ag

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الخلاصة

تم تحسين الخواص الضوئية للجسيمات النانوية الهجينة TiO_2 / Ag وتم تحضير الجسيمات باستخدام تقنية الاستئصال بالليزر النبضي باستخدام التكنولوجيا السائلة .(PLAL) تم فحص تأثير عدد النبضات (450) على الخواص التركيبية والبصرية للجسيمات النانوية المحضرة في الماء المقطر (DW) كوسائط نمو باستخدام ليزر Q-Switched Nd-YAG بطول موجة (1064 نانومتر) ، طاقة الاجتثاث (530 مللي جول))) ومعدل التكرار (1 هرتز). المسافة بين الهدف والعدسة (10 سم). تم استخدام العديد منها للتشخيص مثل تحليل حيود الأشعة السينية ، وتحولات فورييه للأشعة تحت الحمراء، وفحوصات TEM وفلورة العينات المحضرة. أظهرت نتائج تحليل حيود الأشعة السينية لجسيمات الفضة النانوية المودعة على شريحة زجاجية أن النظام البلوري مكعب ومتعدد البلورات، مع سيطرة الاتجاه [111] على مستوى البلورات. كشفت نتائج تحليل حيود الأشعة السينية لمحلول جزيئات ثاني أكسيد التيتانيوم النانوية المترسبة على شريحة زجاجية عن وجود نظام بلوري رباعي الزوايا، مما يشير إلى وجود جزيئات ثاني أكسيد التيتانيوم في (الروتيل)، وأن الاتجاه السائد للمستويات البلورية هو [110]. تم تحديد المجموعات الوظيفية لـ (TiO_2 / Ag) في الوسط السائل بتقنية (FTIR). أيضًا أظهرت صور TEM وجود الجسيمات النانوية والجسيمات الدقيقة في شكل كروي تقريبًا. أظهر قياس الفلورة للجسيمات الهجينة (TiO_2 / Ag) أنه من خلال الرسم البياني قيم الذروة البالغة (284.1) و (418.3) نانومتر. هذا مطابق تقريبًا لنتائج طيف الامتصاص لمحلول الجسيمات النانوية الهجين من الفضة وثاني أكسيد التيتانيوم.

الكلمات المفتاحية: الاستئصال بالليزر النبضي في السوائل، الجسيمات النانوية ، الجسيمات الميكروية و الفلورة.

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Introduction

The Nanoscience's have emerged as a noteworthy research course in our modern society, as a result of ongoing efforts to make something in a nanometer size using various tools and processes, especially in nanoparticle synthesis [1]. Because of their unusual magnetic, electrical, and optical properties, colloidal metal nanoparticles are of great interest to researchers from a broad variety of disciplines, including materials science, physics, engineering, and chemistry [2–3]. The noble metal nanoparticles such as Ag NPs have been the source of much interest due to their new electrical, optical, physical, chemical and magnetic properties [4]. It was very attractive for biophysical, biochemical, and biotechnology applications due to its unusual physical properties, especially due to its sharp absorption peak in the visible region. Silver nanoparticles are chemically stable. The resonance frequencies are strongly dependent on the shape and size of the particle as well as on the optical properties of the material within the near field of the particle [5]. Silver, for example, has been used for thousands of years as an antiseptic. On the other hand, one cannot ignore its catalyst value [6].

Titanium dioxide (TiO_2) is a metal oxide, it is a chemical compound containing an inorganic solid with a white color, thermally and chemically stable, cheap and non-flammable and not classified as hazardous. Titanium is the ninth most common element in the Earth's crust [7]. Nano titanium is the most promising nanomaterial as a semiconductor and that the diffusion of titanium nanoparticles in extremely fine sizes is suitable for most applications such as adsorbents, dyes and catalytic supports. Titanium dioxide exists in various sizes and shapes as spherical spheres. Nano rods, fibers, tubes and plates have attracted interest for their use in many fields [8]. Crystalline titanium dioxide is found in three different phases (rutile), (Anatase) and (Brookite). These phases are characterized by high refractive index, low absorption and propagation in the visible and near-infrared spectral regions, and high chemical and thermal stability [9].

Laser ablation of solids is a top-down process that has piqued interest since the ruby laser was invented in the 1960s [10,11]. The nucleation, growth, and assembly of clusters from laser-ablated species is typically a bottom-up process for the generation of micro/nanostructures by laser ablation. This study aims to prepare and study nanoparticles of the hybrid compound and to improve some of their structural and optical properties.

Silver Nanoparticles

Silver nanoparticles are of increasing interest for scientists due to their very good biological properties and limited side effects. Used since 1000 BC, silver proved its biocidal activity for a wide number of bacteria and recently it was also known to be active in the treatment of cancer [12,13]. As a consequence of silver multifunctionality (antiseptic [14], antitumoral, and IR-sensitizing agent [15]. Silver nanoparticles are widely used for their biological activity as colloidal suspension [16–17], or in association with other materials. Silver nanoparticles were associated with different components such as manganite [18]. carbon nanotubes, hydroxyapatite, and chitosan [19]. Mostly, silver nanoparticles play antibacterial [20].

Titanium Dioxide Nanoparticles

TiO_2 can also be practical in coatings, air purification, plastics, paper inks, pharmaceuticals, pharmaceuticals, food products, cosmetics, radiation protection, photo catalysis, sensor and toothpaste [19,21]. It is even used as a dye to color skim milk [22].

Currently, Nano-particles of Titanium dioxide properties are one amongst the most important fascinating analysis subjects because of extremely result accomplishment in biological, pharmacological submissions, environment substance decontamination, electronics arrangement, solar power cells, photo-catalysts, photo-electrodes in addition gases sensor of aboard American Food and Drug Administration (FDA) commendation of persecution in technology of nutrient besides medicines, ointments, paint pigments, cosmetics, also dentifrice [23].

Methods

Silver noble metals (Ag) and non-noble metals titanium were used to make Nanocrystalline colloidal solutions (TiO_2). The hybrid material was then formed. Laser ablation pulses were used to prepare the materials and instruments used to research the structural of nanoparticles.

The device contains a laser source (Q-Switched Nd: YAG) China originating from (HUAFEI) company in two wavelengths (1064and532) nm with maximum energy (1000) mJ per pulse, pulse time (10) ns, repetition rate (6) Hz, and effective beam diameter (2) mm for metallic targets with high purity 9.99 percent (silver and titanium) .To achieve high laser flux, the lens which used has a focal length of (20) cm. Metal goals were removed in the postgraduate laboratories of Diyala University's Department of Physics, Faculty of Science.

Preparation of Nanoparticles

Using laser pulse ablation (PLAL) technology in liquid and at room temperature, colloidal solutions were generated for metallic nanoparticles using high-purity targets (9.99%) of silver and titanium. As shown in the figure. 1, before and after each ablation stage, the metal targets were polished and cleaned by washing with ethanol and then water purification using an ultrasound system (ultrasound pathway), then the targets were cleaned to remove impurities. The target was then immersed in distilled water (DW) at the bottom of a glass bottle, with a volume of water used in all eradication operations (5) ml and the liquid height above the target surface (4) mm. The energy used for the laser is (530) mJ. The number of pulses is (450) striking the surface of metal targets. For all the targets used in this study, the distance between the target and the laser lens was (8) cm, and the diameter of the laser beam on the surface of the metal target was (2) mm. The targets were bombarded with a (Nd: YAG) laser with a wavelength (1064) nm, pulse time (10) nm and frequency (1) Hz, to produce colored colloidal solutions containing the nanoparticles of the metallic targets. Which was then extracted with the change in the color of the water after the ablation process. The absorbance was tested by the wave number using the FTIR instrument, the fluorescence, as well as the structural and surface properties, were measured using a beam diffraction (X-ray), and transmission electron microscopy (TEM) is a technique for examining objects with electrons (TEM).

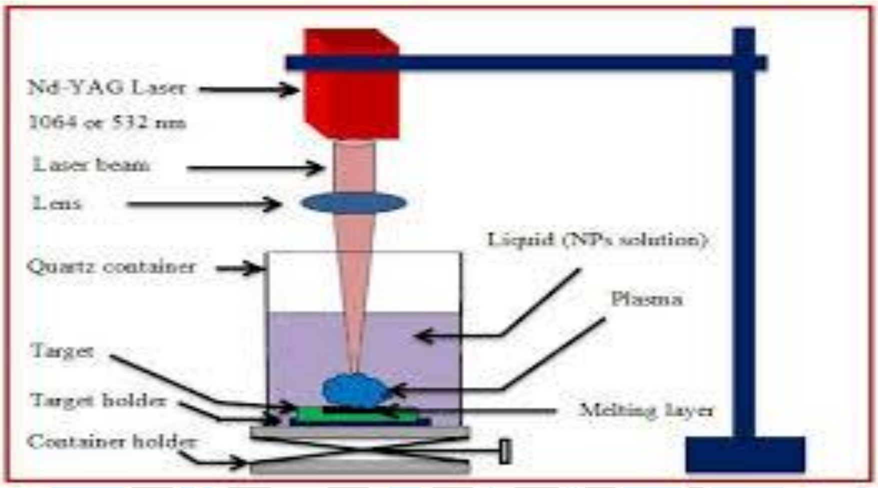

Figure 1: Pulsed laser ablation setup in liquid

Results and Discussions

X-ray diffraction of silver nanoparticles

The X-ray diffraction analysis of the silver nanoparticles deposited on the glass revealed that the crystal system is cubic in form and multi-crystalline, as shown in figure 2, with peaks at angles (38.40), (44.64), (64.84), and (77.88) that correspond to the levels [111], [200], [220], [311].
The obtained results also revealed that the distance between the atomic levels (d) and the diffraction angles (2) corresponding to the diffraction peaks of the prepared films corresponds to the results of the international numbered card (04-0783) for the silver content to a large extent, and that the crystal plane is dominant in the direction [111]. Figure 2 is also in line with the findings of the researcher (ISRAA Ali Hameed), [7], as well as the findings of the researcher (I.A.Abdul Hassan) [24].

The (X-ray) diffraction results of a solution of nanoparticles titanium dioxide particles deposited on a glass slide revealed the appearance of a quadrangular crystal framework, indicating that the titanium dioxide particles are in the (Rutile) phase. We can see that the levels [110], [101], [111] and [211]. correspond to angles (27.6), (36.2), (41.4), and (54.45) respectively.

These results are very similar to the results of the titanium dioxide values mentioned on the numbered card (21-1276). As shown in the figure, the direction of the crystal plane towards [110] is dominant as shown in figure 3.

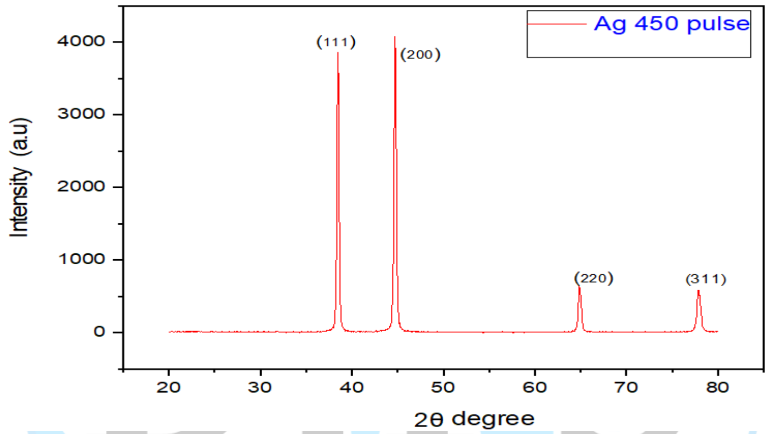

Figure 2: X-ray diffraction of silver Nanoparticles

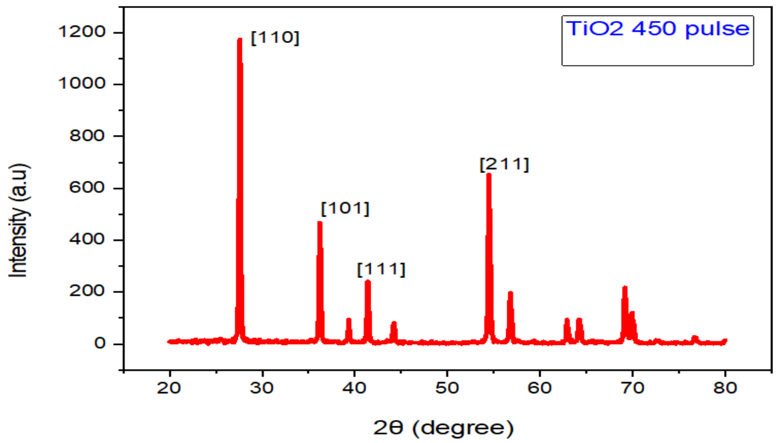

Figure 3: Shows the X-ray diffraction of titanium dioxide (rutile phase)

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Transmission Electron Microscopy (TEM)

TEM results showed that the metal particles were mostly spherical. Mineral colloidal solutions were prepared with distilled water with a wavelength (1064) nanometers from a laser (ND: YAG) and the number of (450) pulses and an energy of (530) mJ.

(TEM) images are shown in figure 4 taken at (50) nm scale, and the statistical distribution of the particle diameters of the colloidal solution of silver nanoparticles is clear from the drawing in which the nanoparticle diameters are concentrated approximately at (17.5) nm for the scale. It was observed that the nanoparticles were nearly spherical and that the distribution and appearance of some particles at a large size was due to the clustering phenomenon [7], as evidenced by the (TEM) images measured at different scales accompanying the statistical distribution drawn in the Origin pro 8.5, It is a program specialized in plotting, analyzing and processing various data.

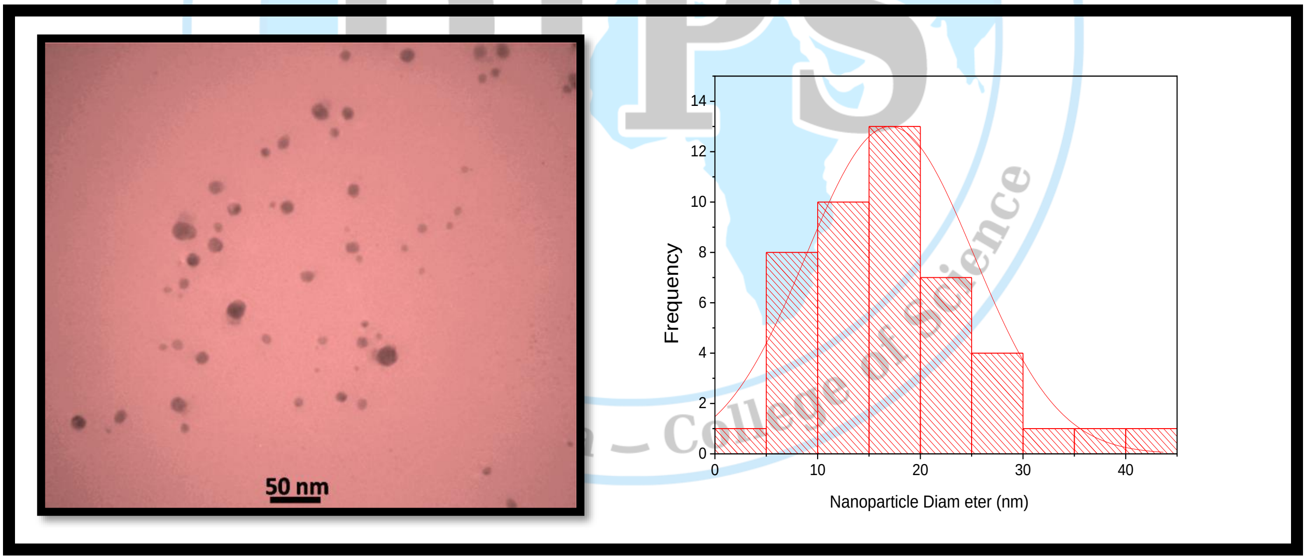

Figure 4: TEM images and the statistical distribution of the colloidal solution of the prepared silver nanoparticles with a power of (530) mJ and the number of (450) pulses on the scale (50) nm.

Figure 5 shows (TEM) images of the titanium dioxide nanoparticle solution and the distribution of these particles diameters at scale (50) nanometers. The graph shows approximately the center of the distribution of the diagonals at (59) nm for different scales, respectively.

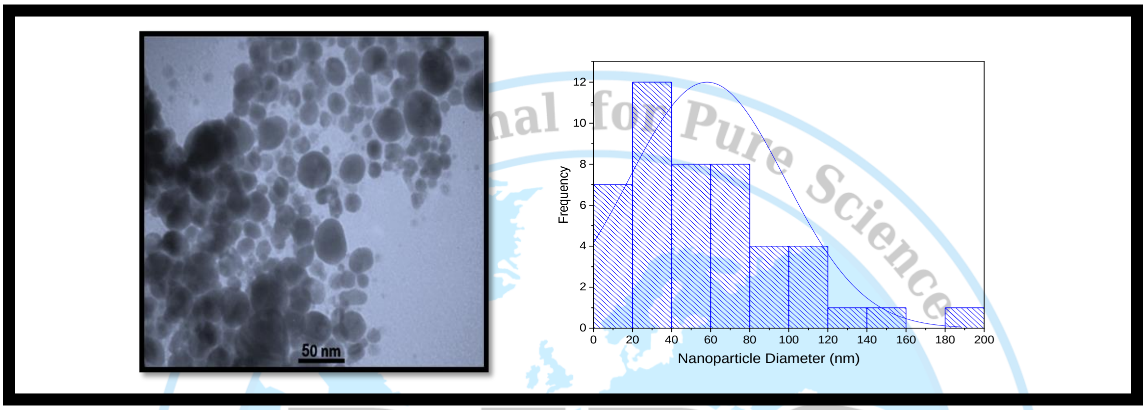

Figure 5: TEM images and the statistical distribution of colloidal solution of titanium dioxide nanoparticles prepared with a force of (530) mJ and some (450) pulses on a scale of (50) nm.

Figure 6 (TEM) shows images of a solution of hybrid silver and titanium dioxide nanoparticles and the distribution of these particles' diameters at a scale of (50) nm. The graph shows the centering of the diagonal distributions approximately at (62) nm.

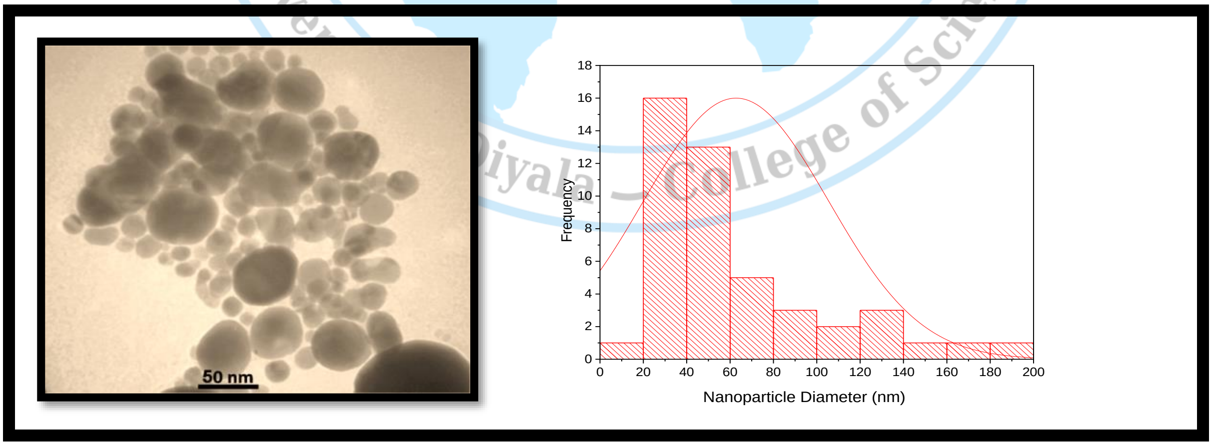

Figure 6: TEM images and the statistical distribution of the colloidal solution for hybrid silver and titanium dioxide nanoparticles prepared with a power of (530) and the number of (450) pulses on the scale of (50) nm.

Fourier Transform Infrared test results (FTIR)

The infrared spectroscopy examination is considered one of the important laboratory tests, and it is an important tool for obtaining information about the position of ions in the crystal structure through oscillations [25].

As a measurement was performed to identify the potential biomolecules responsible for identifying and reducing the factor of the nanoparticles that have been excised by the pulsed laser (PLAL) and the measurement of infrared spectroscopy (FTIR) is used in the determination of the active groups (chemical bonds) as the identity of the compound is determined based on how the absorption of chemical bonds in the range (400-4000) cm^{-1} as each compound has its own absorbance. As the results of the infrared spectroscopy of the solution of silver nanoparticles and titanium dioxide showed the presence of different packages, which indicates the multiplicity of active groups in these particles. Figure 7 shows the infrared spectroscopy (FTIR) sites and connections of chemical compounds and bond sites for (AgNps) prepared in distilled water medium with pulse numbers (450) pulses and a constant ablation energy (530 mJ) as they are composed of distinct functional groups in (AgNps) pure with the locations and intensity of the absorption beams of (AgNps).

It was note that the absorption beam appearing near the wave number (468.77 cm-1) is due to the vibration of the (Ag-O) coupling, and the absorption beam appearing near the wave number (1641 cm-1) is due to the vibration of the bundle (H-O) [26].

Figure 8 shows the infrared spectroscopy (FTIR) sites and connections of chemical compounds and bond sites for (TiO_2Nps) prepared in distilled water medium with pulse numbers (450) pulses and constant ablation energy (530 mJ) ,It was note that the absorption beam appearing near the wave number (478.3463 cm^{-1}) is due to the vibration of the (Ti-O) coupling, and the absorption beam appearing near the wave number (1660.71 cm^{-1}) This is due to the vibration of the beam (H-O), which is made up of the oxide present in titanium and from distilled water.

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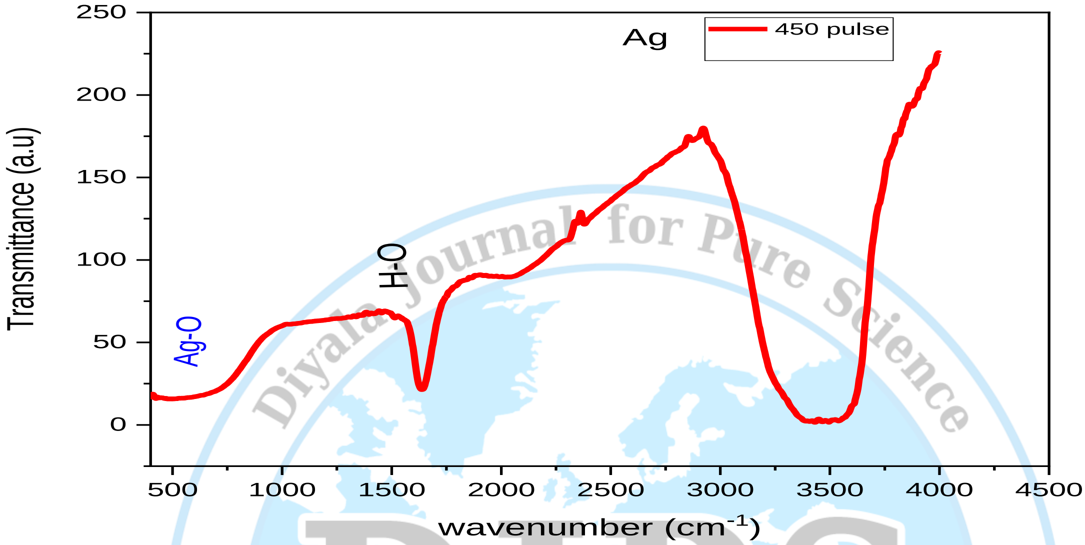

Figure 7: Diagram showing Fourier transforms of the infrared spectrum of a solution of silver nanoparticles.

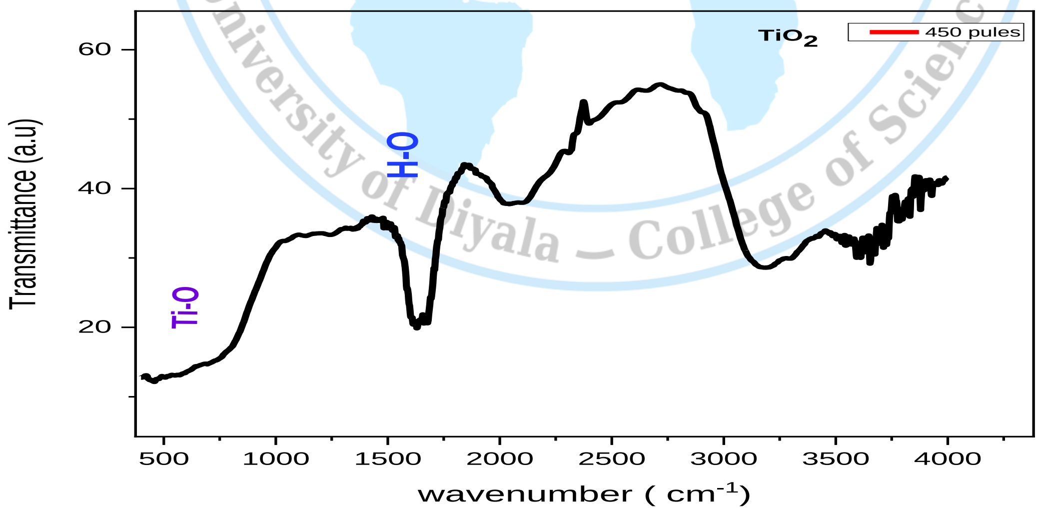

Figure 8: Diagram showing Fourier transforms of the infrared spectrum of a solution of Titanium Dioxide nanoparticles.

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Figure 9 shows FTIR sites, chemical compound connections, and bond sites for silver and titanium dioxide hybrid particles. Note that the absorption beam appearing near the wave numbers (443.77 and 484.13 cm^{-1}) is due to the (Ti-O) and (Ag-O) coupling vibration, and that the absorption beam appearing near the wave number (1635.635 cm^{-1}) is due to the vibration the package (H-O).

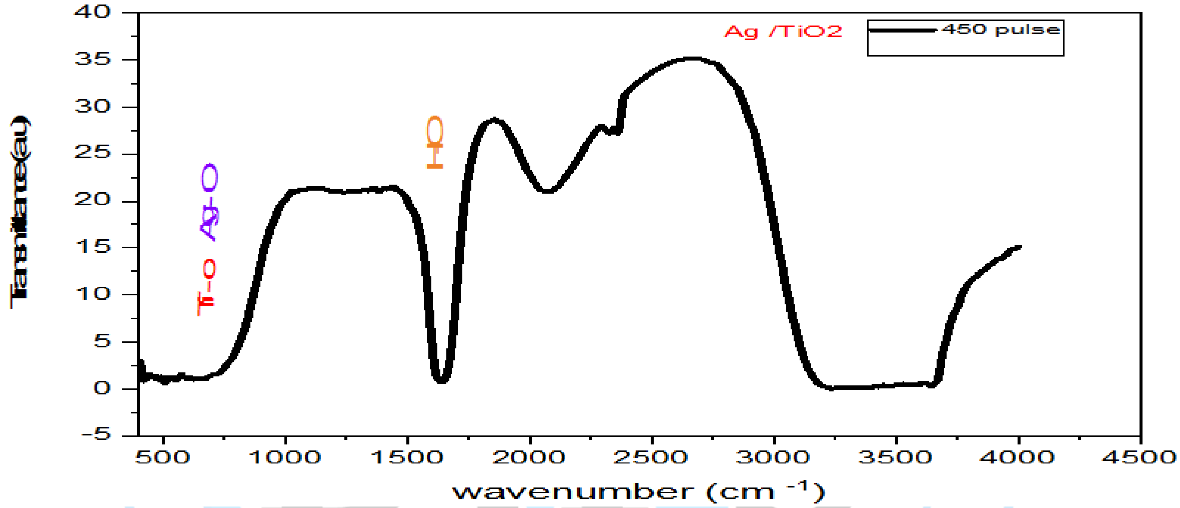

Figure 9: A graph showing the Fourier transforms of the infrared spectrum of a solution of silver particles and titanium dioxide nanoparticles hybrids

Fluorescence test results

Figure 10 shows the fluorescence measurement of silver nanoparticles for the number of pulses of (450) pulses and energy (530) mJ, and it was notice through the diagram that the peak value is at (406.3) nm.

Figure 11 shows the fluorescence measurement of titanium dioxide nanoparticles for the number of pulses of (450) pulses and energy (530) mJ, and it was note through the diagram that the peak value is at (296.4) nm, and this is almost identical to the results of the absorption spectrum of the particle solution. Nanoparticles of titanium dioxide.

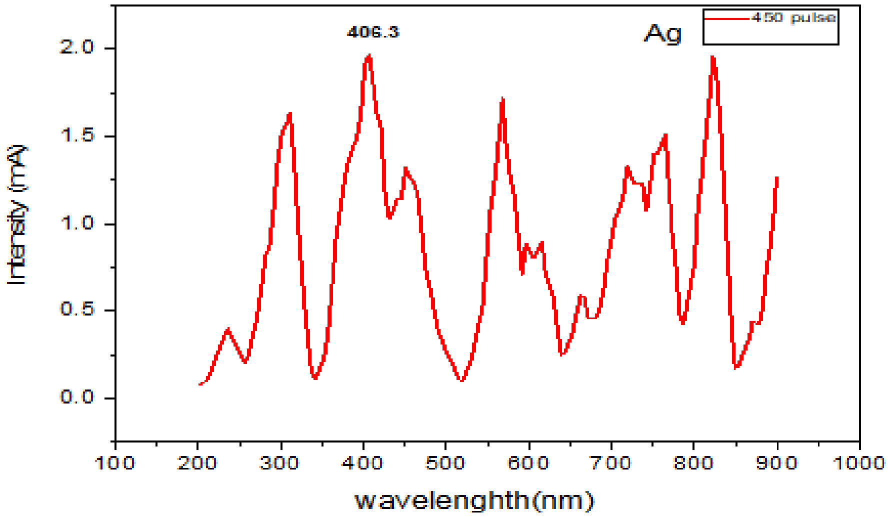

Figure 10: Illustrates the fluorescence measurement of silver nanoparticles for the number of pulses (450) and energy (530) mJ.

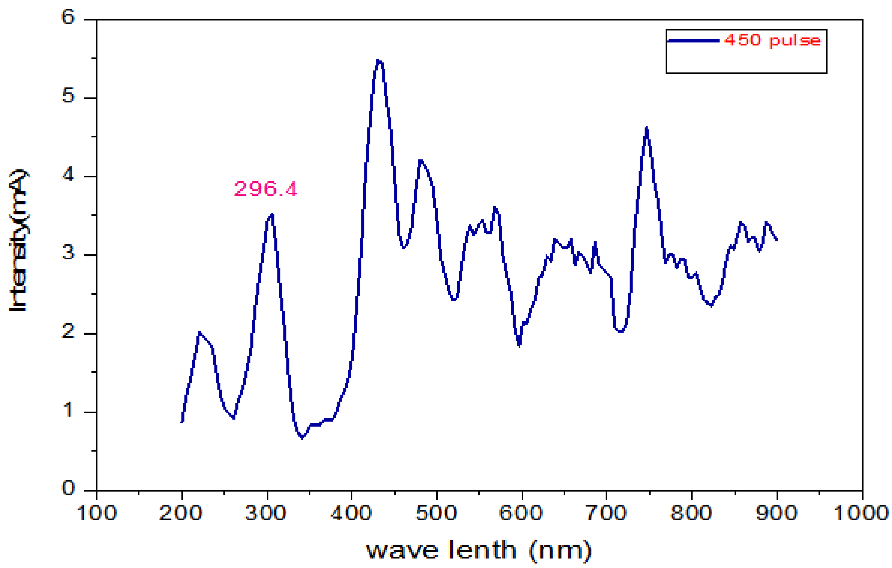

Figure 11: Shows the fluorescence measurement of titanium dioxide nanoparticles for the number of pulses (450) pulses and energy (530) mJ.

Figure 12 shows the fluorescence measurement of hybrid particles of silver and titanium dioxide nanoparticles for the number of pulses of (450) pulses and energy (530) mJ, and it was notice through the chart that the peak value is at (284.1) and (418.3) nm This is roughly identical to the results of the absorption spectrum of a solution of hybrid nanoparticles of silver and titanium dioxide.

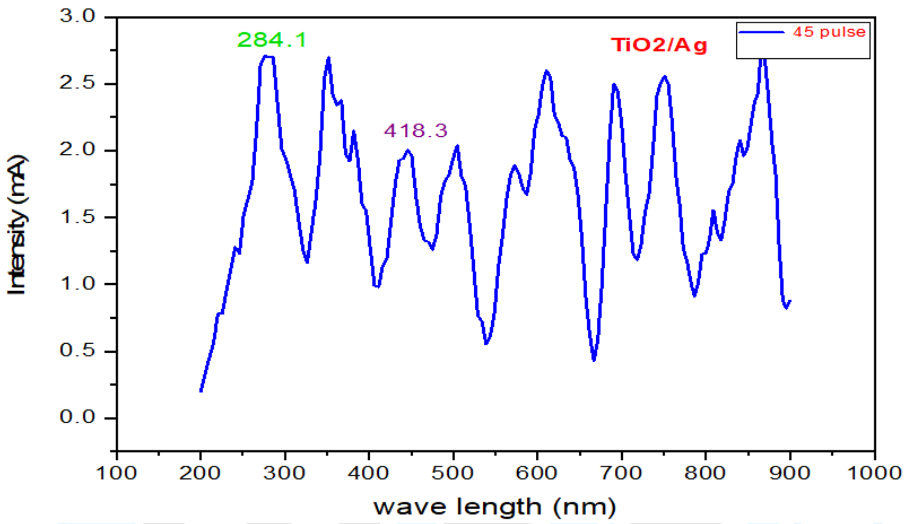

Figure 12: Shows the fluorescence measurement of hybrid particles of silver and titanium dioxide nanoparticles for the number of pulses (450) and energy (530) mJ.

Conclusions

In Conclusions, nanoparticles prepared by the method of pulsed laser ablation in liquids have many advantages compared to other methods of preparation, and it was can conclude that the success of the method of pulsed laser ablation in distilled water as a liquid medium for ablation such as the color shift of these solutions is an indication of the formation of colloidal solutions that contain metal particles of metals. Used, the particle size and the size of their distribution can be controlled through the parameters of the laser (number of pulses and energy) and through the surrounding medium (the fluid in which the ablation is performed). Through TEM, it showed that got almost spherical particles of silver, titanium dioxide, and hybrid particles. Through fluorescence testing, colloidal solutions of silver, titanium dioxide and hybrids were examined, and we note through the graph that the peak value is at (406.3) nanometers for silver nanoparticles and the peak value is at (296.4) nanometers for titanium dioxide nanoparticles and the peak value is at (284.1) nm and at

418.3 nm for the hybrid, which corresponds to the absorbance peak values in the infrared scan. In addition to the FTIR assay, we found bonds formed in (Ag-O), (Ti-o) and (H-O) compounds.

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