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Study of the Structural and Optical Properties of the TiO_2:Au Nanocomposite Mixture Prepared by Laser Ablation Method

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ABSTRACT

In this study, TiO_2, Au, and a mixture of TiO_2: Au nanoparticles (NPs) were produced using a Nd: YAG pulsed laser. X-Ray diffraction (XRD), Transmission electron microscopy, and Ultraviolet–visible spectroscopy (UV) was used to characterize the produced nanoparticles. The XRD patterns of TiO_2 NP showed that the diffraction peaks values were corresponded to the ICDD card number (21-1272) for the anatase form of TiO_2 NPs. The XRD patterns of Au NPs values were corresponded to the ICDD card number (00-004-0784) of Au NPs. The XRD patterns the mixture TiO_2: Au nanoparticle with mixing ratios (4:1, 3:2 and 2.5:2.5), it was found that the diffraction peaks were (2θ~ 38.138° and 64.687°) of TiO_2 nano-particles, and the diffraction peaks were (2θ~ 44.341° and 77.577°) Au NPs. The average crystalline size of the prepared nanoparticles was determined by Scherer's technique, it was found that the average crystalline size (TiO_2 NPs) is (23.36 nm), whereas mixing titanium oxide with gold nanoparticles (TiO_2: Au) increased the average crystallite size to (34.18, 34.15, and 34.20 nm) for the mixing ratios (4:1, 3:2, and 2.5:2.5), respectively. The TEM images showed that the TiO_2 NPs are light grey in the combination of (TiO_2: Au) NPs, while for the ratio (4-1), the Au NPs are dark, spherical spheres. However, when the ratio of Au particles is increased to (2:3), the TiO_2 particles remain light grey but are smaller in size. The absorption spectra of pure TiO_2 NPs is in the UV spectrum, whereas the absorption spectrum of the (TiO_2: Au) mixture shifts towards the wavelengths of visible light in the range (520-540 nm), according to the optical characteristics of TiO_2 NPs and a mixture of (TiO_2:Au) NPs. The optical energy gap of pure TiO_2 NPs is 3.22eV, and it decreases as the proportion of gold nanoparticles in the mixture increases.

Keywords: *TiO_2 NPs, Nd: YAG pulsed laser, structural properties, XRD, TEM.*

1. INTRODUCTION

Due to their extensive range of applications, TiO_2 nanoparticles are generating a lot of attention, consequently; titanium dioxide is a crucial study issue. Examples include photocatalysis, the photovoltaic conversion process in solar cells, antimicrobial coatings, and gas sensors [1,2]. Many of the aforementioned applications are dependent on the crystal structure and form of nanoparticles because the surface characteristics of nanoparticles have a significant influence in altering the volumetric physical properties at the nanoscale level [3, 4]. TiO_2 is a frequently used photocatalyst because of its resistance to water and ultraviolet (UV) radiation. However, the requirement for an UV excitation source limits their technological relevance to a small number of applications [5.6]. Doping TiO_2 with Au NPs increased the visible photocatalyst response, and the catalytic properties of Au depended on the support and method of Au preparation [7]. Since the surface properties of nanoparticles significantly affect how a material behaves when it is on the nanoscale, many of the applications listed above depend on the structure of the crystals and shape of the nanoparticles [8-10].

Laser ablation is a unique technique of fundamental importance for the fabrication of TiO_2 nanoparticles in the liquid phase, and it is also a promising technology to deal with the incorporeal production by reactive rapid cooling of the excised species at the plasma-liquid interface [11]. Many previous studies have been conducted regarding the preparation of pure titanium dioxide particles doped with other nanomaterials. Sonawane et al. 2006 [12] produced thin Au/TiO_2 films using the sol-gel dip coating method. Due to the presence of gold nanoparticles in the titania structure, UV-vis spectroscopy revealed a shift in optical absorption wavelength to the visible region. Ghorbani et al. (2016) [13] employed a Nd:YAG pulsed laser to synthesize a composite material consisting of gold (Au) and titanium dioxide (TiO_2) nanoparticles. The findings of their research revealed that the nanocomposite exhibited an absorption spectrum characterised by a surface plasmonic absorption peak centered at around 530 nm, which coincided with the absorption spectra of TiO_2. Yasmin et al. 2022 [14], synthesized TiO_2 NP_s powder by anodization process, and (Au/TiO_2**)** NPs catalyst by photodeposition method the XRD patterns showed that the

average crystallite size of Au nanoparticles was about 26.8 nm and that the prepared (Au/TiO_2) NPs were crystallites and nanosized. Israa et al. 2022 [15] used laser ablation to create TiO_2 NPs that were then analysed by UV-VIS, XRD, and SEM. They found a lower UV transmittance and a higher visible transmittance, with an estimated optical band gap of 3.89 eV, 3.8 eV, and 3.70 mJ at laser energies of 80, 120, and 160 mJ, respectively. Aliev et al. 2018 [16], synthesized TiO_2 films using a new method (modifier type), and the study's results have been compared with the results from films produced by the sol-gel method. The results showed that when the gold granules were introduced with titanium dioxide, there was an increase in the absorption over the entire spectral range, and a distinct peak was observed at the wavelength of 600 nm. The aim of this work is to prepare a mixture of titanium dioxide and nanoscale gold in different proportions by the laser ablation method, as well as to investigate the structural and optical characteristics of the produced samples.

2. MATERIALS AND METHOD

2.1 Materials

To prepare the colloidal solution of nanoparticles (TiO_2 and Au), a titanium target and a gold target were used, both with a purity of 99.99%. A (Nd:YAG) laser was used in the pulsed laser ablation system, which included the (Q-Switched Nd:YAG) laser manufactured by the Chinese company (HVAFEI).

2.2 Materials

The Au target was positioned at the bottom of one glass vessel, while the Ti target was positioned at the base of another glass container. Each vessel contained 5 ml of distilled water. Table 1 shows the parameters of the pulsed Nd: YAG laser. After the colloidal solutions of titanium nanoparticles and pure gold were prepared, the solutions were mixed with ratios of TiO_2: Au (4-1), TiO_2: Au (3-2) and TiO_2: Au (2.5-2.5). The colloidal solution of the mixture in an amount of (5 ml) and bombarding the colloidal solution of the mixture with a laser again at a rate of 3000 pulses with continuous stirring using an ultrasound device. The purpose of bombarding the mixture of nanoparticles prepared with a laser again is to reduce the size of the nanoparticles. After that, the solutions are placed in glass containers for the purpose of conducting XRD, TEM, and UV visible analyses.

Table 1 Parameters used in the laser beam to prepare TiO_2 NPs, Au NPs and the mixture TiO_2: Au nanoparticle

Parameters	Value
Wavelength (λ)	1046 nm
Repetition rate	1 Hz
Laser pulse energy	660 mJ
No. of pulses	800 pulse

3. RESULT AND DISCUSSION

3.1. The XRD analysis

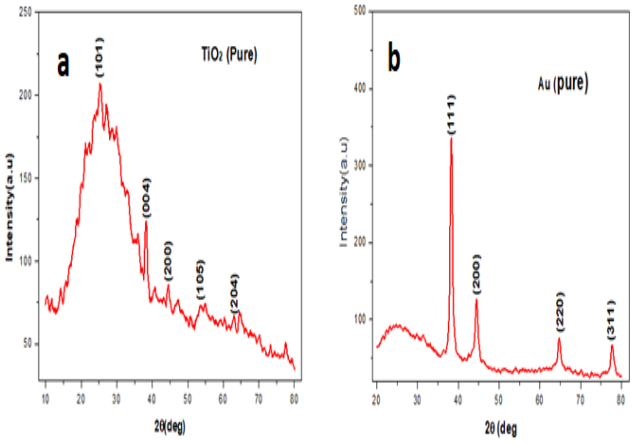
Figure 1 shows the XRD patterns of TiO_2 NPs, Au NPs, and the mixture of TiO_2 and Au nanoparticles prepared by the Nd:Yapulsed laser. The diffraction peaks were (25.382°, 38.199°, 44.589°, and 53.816), which corresponded to (101), (004), (220), and (105) favorite directions, respectively. According to Figure 1 (a), which depicts the XRD patterns of TiO_2 NPs, these values are a perfect match for the anatase form of TiO_2 nanoparticles' ICDD card number (21-1272), these results are consistent with [14]. The XRD patterns of Au NPs are shown in Figure 1(b), and it was discovered that the diffraction peaks were (2θ~38.3305°, 44.621°, 64.687°, and 77.707°), which corresponded to (111), (200), (220), and (105) favourite directions, respectively.

These values exactly match the ICDD card number (00-004-0784) of Au NPs, and these findings are consistent with [17]. Figure 1 (c) shows the XRD patterns of the mixture TiO_2:Au nanoparticle with mixing ratios of 4:1, 3:2, and 2.5:2.5. It was found that the diffraction peaks were (2θ~ 38.138° and 64.687) of TiO_2 nanoparticles, and the diffraction peaks were (2θ~ 44.341° and 77.577°) of Au NPs. These results are consistent with (18-20).

The average crystallite size of the generated nanoparticles was determined by the Scherrer technique [21]:

$$D = k\lambda / \beta \cos\theta \qquad (1)$$

where D is the crystallite size, K is a constant (equal to 0.94), λ is the wavelength of the x-ray radiation, β is the full width at half maximum, and θ is the angle of diffraction. From the results, it was observed that the crystal size of TiO_2 NPs is 23.36 nm, while in the case of mixing titanium oxide with gold nanoparticles (TiO_2:Au), it led to an increase in the average crystallite size to 34.18, 34.15, and 34.20 nm for the mixing ratios (4:1, 3:2, and 2.5:2.5), respectively. The results showed that the average particle size changed slightly, as well as the absence of a change in the full width at half maximum and its stability with the change of mixing ratios, as shown in Table 2.



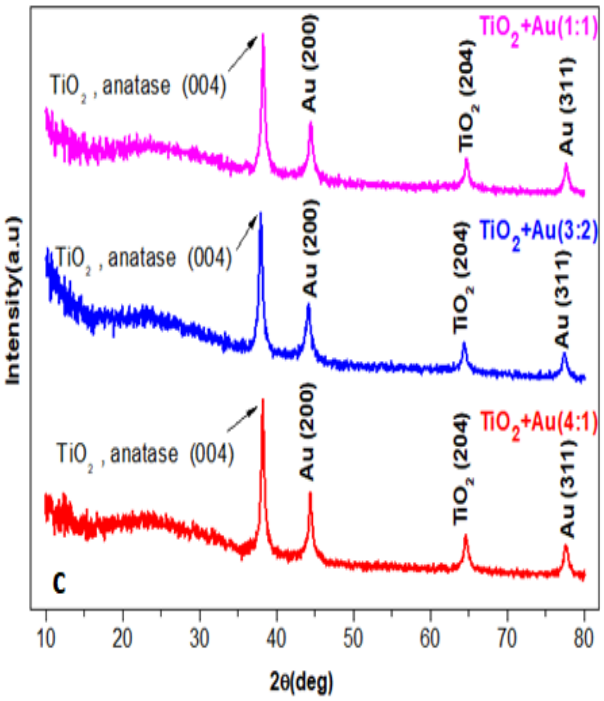


Figure 1 XRD patterns of (a) TiO_2 NPs, (b) Au NPs and (c) Mixture of TiO_2: Au NPs.

Table 2 Data for the X-ray diffraction of TiO_2 and Mixture of TiO_2: Au NPs.

Samples	2θ (deg.)	FWHM (deg.)	plane (hkl)	D (nm)
TiO_2 -Pure	38.199	0.36	(004)	23.36
TiO_2: Au (4-1)	38.138	0.246	(004)	34.18
TiO_2: Au (3-2)	37.876	0.246	(004)	34.15
TiO_2: Au (2.5-2.5)	38.194	0.246	(004)	34.20

3.2 Morphological analysis of the of Mixture of TiO_2: Au NPs.

Figure 2 shows the TEM images of the mixture of TiO_2 and Au nanoparticles prepared by the Nd:YAG pulsed laser. As we can see from Figure 2 (a) of the TEM images of the (4:1) mixing ratio of TiO_2: Au, the TiO_2 nanoparticles are light gray bulk, while the Au nanoparticles are dark spherical spheres. When the ratio of Au particles is increased to (2:3), we notice that the TiO_2 particles remain light gray but are small in size, as shown in Figure 2(b), but in Figure 2(C), we notice that the Au particles remain dark spherical and have a large size, with an agglomeration of TiO_2 and Au particles. These results are consistent with the findings of the researchers [13, 14, and 20]. As we can see from Figures (a and b), the resulting particles are nanostructured and their crystal size is less than 50 nm, and these results are consistent with the results of XR.

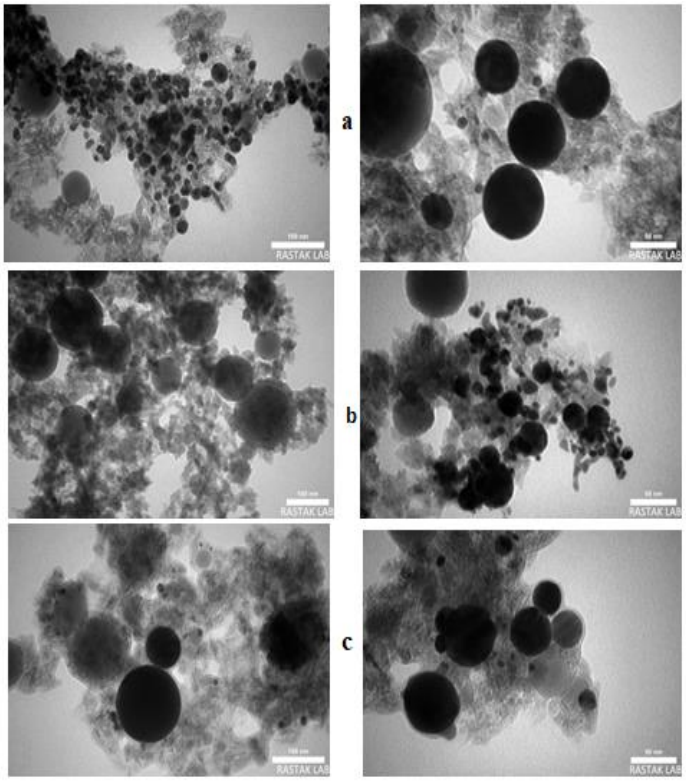


Figure 2 TEM images of the mixture TiO_2: Au nanoparticle at 20 nm and 50 nm, a (4:1), b (3.2) and c (2.5:2.5).

3.3 Optical properties

The optical characteristics of pure TiO_2 nanoparticles and a mixture of (TiO_2:Au) nanoparticles were studied in ratios (4:1, 3:2, 2.5:2.5). Figure 3 depicts the absorption spectra of the produced samples, and it reveals that the TiO_2 nanoparticles have a noticeable absorption peak in the UV spectrum. While we note that the absorption spectrum of the (TiO_2:Au) mixture shifts towards the wavelengths of visible light in the range (520–540 nm), this absorption is brought on by the gold nanoparticles' surface plasmon resonance (SPR) effect, which is brought on by the gold nanoparticles' collective oscillation in response to optical stimulation [15].

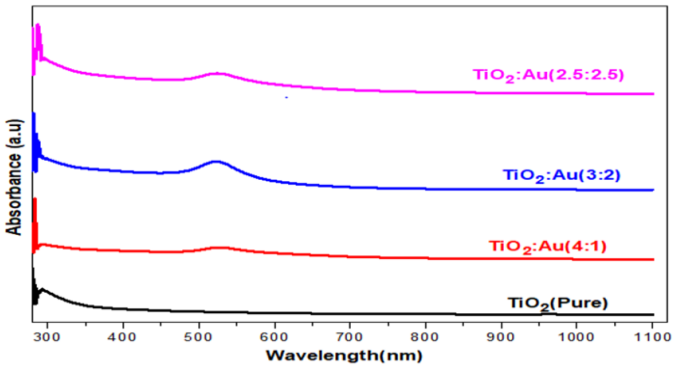


Figure 3 TiO_2 nanoparticles and a mixture of TiO_2 and gold nanoparticles' UV-visible absorption spectra.

The Tauc's method [22] was used to measure the energy gap of the nanoparticles prepared from the absorption spectra.

$$(\alpha h\upsilon)^n = B\,(h\upsilon - E_g) \qquad (2)$$

If it was:
B: Planck's constant, hυ: photon frequency, hν: photon energy, E_g: energy gap, n: exponent which can have values of either 2 or 1/2 for direct transmission and for indirect transmission respectively, and α: the absorption coefficient (cm^{-1}).

Figure 4 shows the energy band gap of pure TiO_2 nanoparticles and a mixture of (TiO_2:Au) nanoparticles were studied in ratios (4:1, 3:2 and 2.5:2.5). Where we notice that the value of the optical energy gap for pure TiO_2 nanoparticles is 3.5615 eV , and the energy gap decreases as the proportion of gold nanoparticles in the mixture increases, it reached (3.322, 3.302 and 3.112 eV) and the ratios were (4:1, 3:2 and 2.5:2.5), respectively.

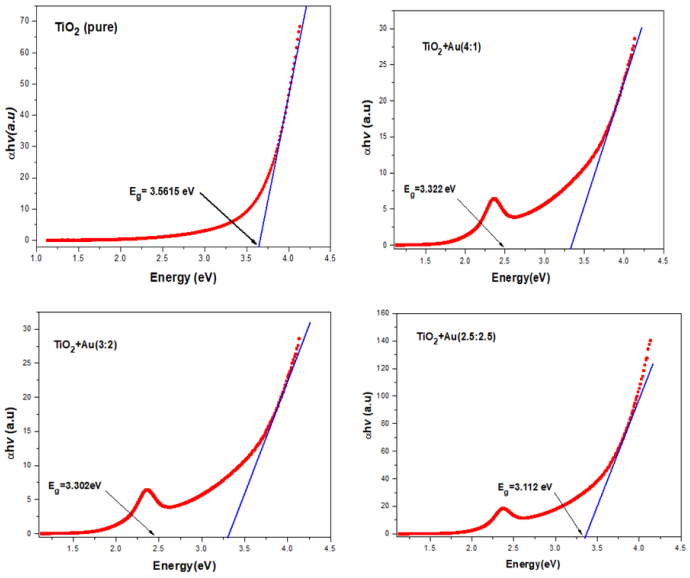


Figure 4. TiO_2 nanoparticles' optical band gap and the mixture of TiO_2 and Au nanoparticles.

4. Conclusions

TiO_2 NPs, Au NPs, and the mixture of TiO_2: Au nanoparticles prepared by Nd:YAG pulsed laser. XRD patterns showed that the TiO_2 nanoparticles in anatase form, and the crystal size of (TiO_2 NPs) is (23.36 nm), while in the case of mixing titanium oxide with gold nanoparticles (TiO_2: Au) , it led to an increase in the average crystallite size. The optical characteristics demonstrate that the region of the UV spectrum where the pure TiO_2 nanoparticles absorb light corresponds to the spectrum of UV light, while the absorption spectrum of the (TiO_2:Au) mixture shifts towards the wavelengths of visible light in the range. The optical energy gap for pure TiO_2 nanoparticles is 3.22eV, and the energy gap decreases as the proportion of gold nanoparticles in the mixture increases.

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