IRAQI JOURNAL OF APPLIED PHYSICS
Vol. 17, No. 4, October-December 2021, pp. 9-14

Photocatalytic Performance of Mixed and Single Phases of Titanium Dioxide Nanoparticles on Growth of Fusarium Oxysporum Fungal

Maryam A. Nima
Firas J. Kadhim

*Department of Physics,
College of Science,
University of Baghdad,
Baghdad, IRAQ*

In this work, the photocatalytic activity was considered to inactivate Fusarium oxysporum fungal under UV radiation exposure using highly-pure TiO_2 nanoparticles. These nanoparticles were extracted from thin film samples prepared by dc reactive magnetron sputtering system. The mixed-phase (anatase+rutile) films were prepared using two different gas mixing ratios and different deposition times (3, 3.30 and 4 hours). Accordingly, the weight fractions of rutile in mixed-phase were 40, 46 and 50%, respectively. The single phase (anatase) was produced without any heat treatment using specific mixing ratio of 50:50. The structural and spectroscopic characteristics of the prepared nanoparticles were determined and analyzed. At weight fraction of 40% of mixed-phase TiO_2, the best antifungal activity was achieved.

Keywords: Titanium dioxide; Photocatalytic activity; Nanoparticles; Antifungal
Received: 15 September 2021; **Revised:** 05 October 2021; **Accepted:** 12 October 2021

1. Introduction

Nanostructured materials have garnered considerable interest as catalysts and in another applications, due to their distinctive structural characteristics. The essential metal oxides such as titanium dioxide (TiO_2) have received a lot of attention, due to its alchemical stability, optical, physical, and electrical characteristics. The photocatalytic characteristics be applied to the removal of contaminants from both water and air in a variety of environmental applications including water purification [1,2]. Titanium dioxide is exists as anatase, rutile, and brookite. Although rutile is the most widespread and stable form of titanium dioxide, anatase is preferred for its high photocatalytic activity [3]. The mixed-phase (anatase/rutile) is widely used much more than the anatase or rutile phase have higher photocatalytic effectiveness than the single phase (anatase) or mixed phase (rutile) that is due to a synergistic impact between the two phases [4,5].

Titanium dioxide have a wide spectrum of antifungal activities microorganisms of fungal. Additionally, recent research has demonstrated that titanium dioxide cannot only destroy a complex cellular assembly with significant consequences for pathogenicity (fungal) as concentration rise, but it also has the ability to prevent the formation of fungus at decrease concentrations [6-8].

The direct current (DC) reactive magnetron sputtering method has that rely on momentum exchange to release atoms from a solid or liquid source. For decades, sputter deposition has been used to deposit thin films as a flexible, reliable, and successful approach. Operating factors such as total gas pressure, distance between electrodes, gas mixing ratio, electrical discharge power, substrate temperature, and sputtering time can all affect the properties of titanium dioxide films [9-12].

The anti-fungal activity of two structural phases of TiO_2 nanopowder is studied and compared in this work depending on the growth of fungal (Fusarium oxysporum) as a function of TiO_2 concentration.

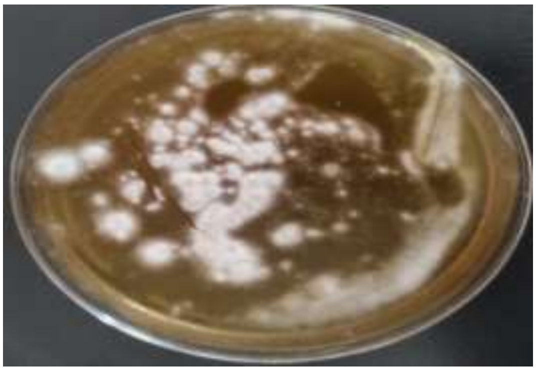
2. Experimental Part

Titanium dioxide thin films were deposited on glass substrates using a direct current, closed-field unbalanced reactive magnetron sputtering system. Highly-pure Ti (99.99%) target was sputtered in the presence of oxygen gas as a reactive gas and argon gas as a discharge gas with a constant inter-electrode distance of 4 cm. Three various deposition times (3, 3:5, and 4 hours) and three various mixing ratios of $Ar:O_2$ gases (50:50, 67:33, and 80:20) were used to prepare the film samples. The conditions of preparation in detail can be found elsewhere [13,14]. Nanopowders were extracted from thin film samples (Fig. 1) using conjunctional freezing-assisted ultrasonic extraction method [15,16].

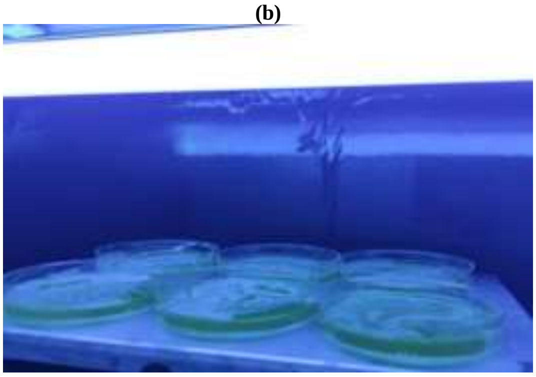
The fungal Fusarium oxysporum was chosen and prepared for the experiments of photocatalytic activity. To create the medium for fungal growth, 39 g of potato dextrose agar (PDA) was dissolved in 1 liter of distilled water. After 10 minutes of heating to fully melt, the medium was sanitized by autoclaving at 15 lbs., pressure (121°C), cool to 47°C, mix well then the medium was dispensed into sterile Petri dishes and stored in the fridge overnight. A small amount of the Fusarium oxysporum fungal was applied equally on the surface of the PDA.

Fig. (1) Photograph of TiO_2 nanopowder extracted from the thin film samples prepared in this work

An ultrasonic bath was used to dissolve TiO_2 nanopowders in deionized water, which was then homogenized using a vortex mixer. A small amount of TiO_2 nanoparticles was spread equally over the surface of PDA with deionized water as a control and the dishes were then exposed to UV radiation (200-400nm) for 60 minutes. The UV light source was placed at 10 cm away from the Petri dish. Finally, the cells were cultured at 37°C for 24 hours and then inspected for the creation of outgrowth inhibitory zones. Figure (2) shows the fungal (Fusarium oxysporum) before performing the experiments of photocatalytic activity.



(b)



(b)

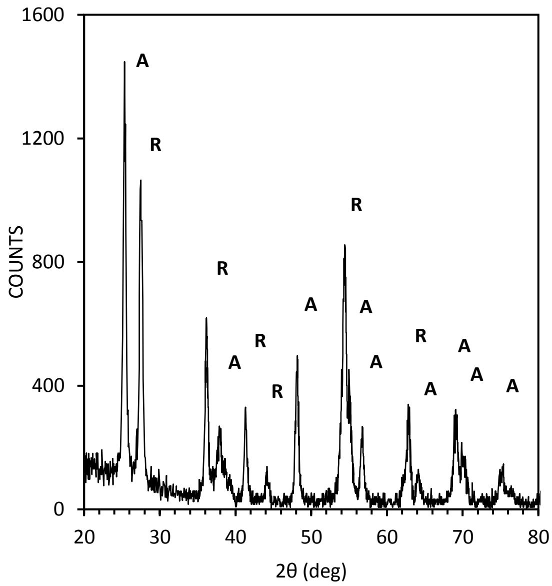
Fig. (2) Photographs of growth fungal (Fusarium oxysporum) (a) and the arrangement of photocatalytic activity measurement (b)

3. Results, and Discussion

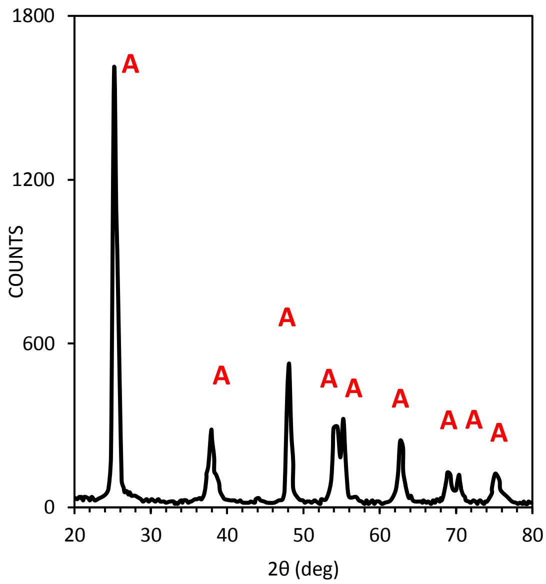
The x-ray diffraction patterns of TiO_2 (mixed- and single-phase) thin films prepared in this work are shown in Fig. (3). Both phases are identified (rutile; R and anatase; A) [17]. The weight fraction (f) of rutile phase in the prepared sample can be determined by following equation [18]:

$$f = \frac{1}{1+0.88\frac{I_A}{I_R}} \qquad (1)$$

where f is the weight fraction of rutile (R) in mixed-phase (A+R) and I_A/I_R is the ratio of anatase to rutile phase intensity as determined by x-ray intensities



(a)



(b)

Fig. (3) XRD patterns of mixed-phase TiO_2 sample (a) and single-phase TiO_2 sample (b) prepared using gas mixing ratio of 50:50 and deposition time 3 hours

For samples produced after deposition times of 3, 3:30, and 4 hours, the percentage quantities of rutile in mixed-phase (anatase-rutile) samples were 40, 46 and 50%, respectively. The XRD pattern of the TiO_2 sample of anatase phase only is shown in Fig. (3b), where no peaks belonging to the rutile phase were observed.

The Fourier-transform infrared (FTIR) spectrum of prepared titanium dioxide nanopowder in the range 400-4000 cm^{-1} is shown in Fig. (4). This spectrum was recorded using Shimadzu 8400S FTIR instrument. The IR bands at 3464 and 1639 cm^{-1} are allocated to the stretching and bending vibrations of the OH group in water molecules [19,20]. At roughly 486 and 622 cm^{-1}, the band associated with Ti-O stretching vibrations was found, whereas the peak at 420 cm^{-1} is attributed to Ti-O-Ti bonds in the TiO_2 molecule [21]. As a result, the samples may be classified as highly-pure with no peaks ascribed to contaminations.

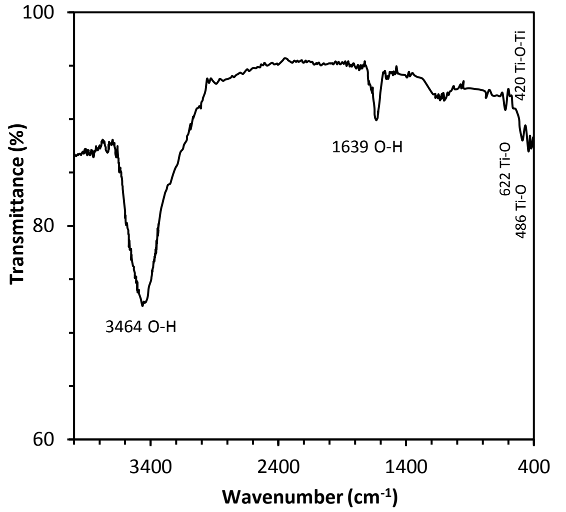
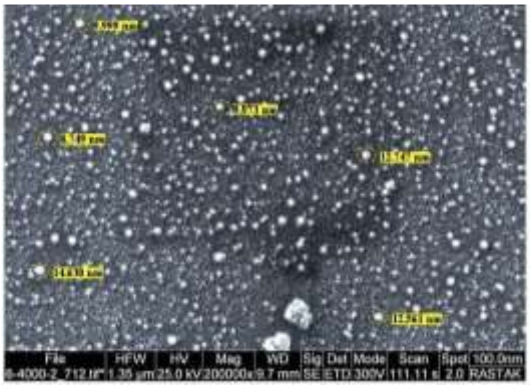
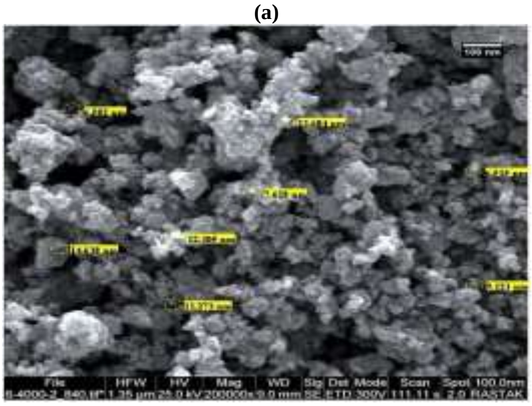


Fig. (4) FTIR spectrum of mixed-phase TiO_2 thin film prepared after deposition time of 3 hours

Scanning electron microscopy (SEM) was utilized to examine the surface profile and grain size of the prepared thin film samples, as illustrated in Fig. (5). Average particle size was 10.5 nm for the mixed-phase sample and 10.2 nm for the single-phase sample. The SEM image of the mixed-phase sample (Fig. 5a) reveals that the particles had nearly homogeneous distribution, which is one of the major advantages of the dc magnetron sputtering technique used for synthesis of nanostructures. On the other hand, the SEM image of the single-phase sample (Fig. 5b) clearly shows the aggregation and formation of large particles as only single phase is formed with a dominant crystal plane and some other planes.



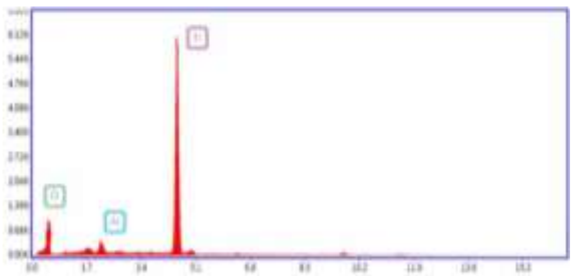
(a)



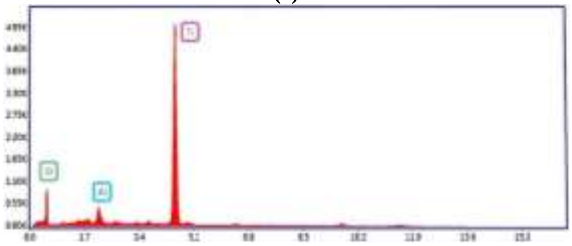
(b)

Fig. (5) SEM images of mixed-phase TiO_2 (a) and single-phase TiO_2 samples prepared after deposition time of 3 hours

Figure (6) shows the EDX spectra of the same TiO_2 samples. The presence of Ti and O is indicated by the weight ratio (Ti:O) of 37.73:61.25 for the mixed-phase sample and 60.37:37.59 for the single-phase sample. These results may highlight the structural purity of the prepared samples as no traces belonging to other elements than Ti and O were observed. The peak of Al in these spectra is originated from the material of sample holder.



(a)



(b)

Fig. (6) EDX spectra of mixed-phase TiO_2 (a) and single-phase TiO_2 samples prepared after deposition time of 3 hours

The UV-visible, spectroscopy was used to record and investigate the absorption spectra of both mixed-phase and single-phase TiO_2 film, samples in the spectral region,300-800 nm as shown in Fig. (7). The mixed-phase samples prepared after different deposition times showed identical behaviors as the absorbance is relatively high in the UV region (<380nm) and reasonably decreasing in the visible region. Obviously, the sample of higher thickness shows higher absorbance due to the higher optical density. The single-phase sample showed lower absorbance with respect to the mixed-phase samples in the same wavelength range (<380nm) as well as lower absorbance in the visible region. This is attributed to the contributions of both phases (rutile and anatase) in the mixed-phase sample while the only contribution in the single-phase sample is due to anatase phase.

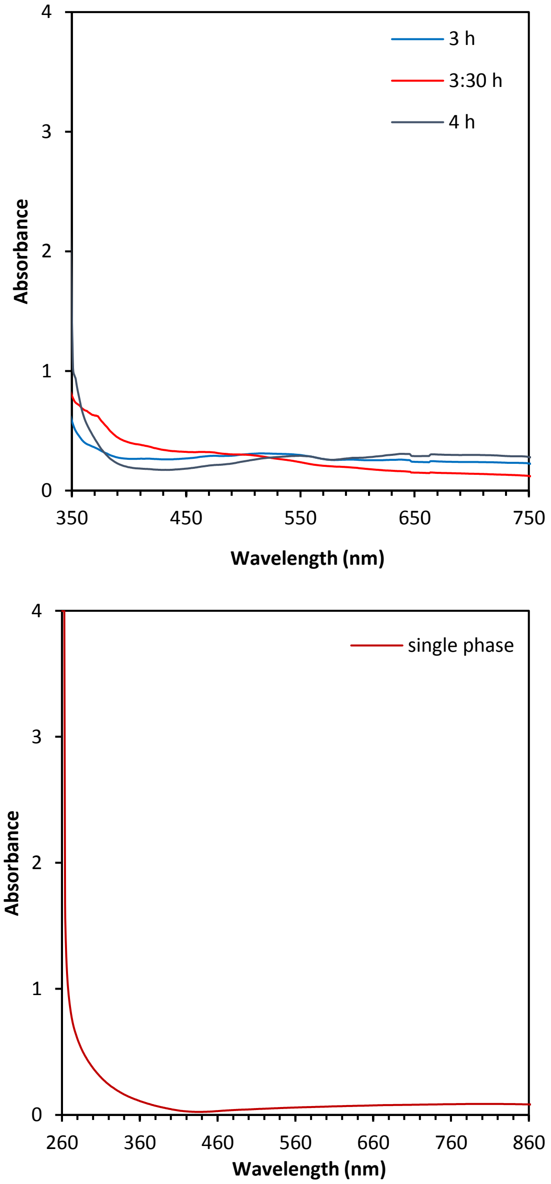


Fig. (7) Absorption spectra of mixed-phase sample (upper) and single-phase sample (lower)

The absorption characteristics of the TiO_2 nanopowders used for anti-fungal applications are very important as they determine how far the incident radiation (e.g., solar radiation) is invested to induce the photocatalytic activity of these nanopowders [22]. Therefore, the assessment of which samples are better can be based on the experimental test of the prepared samples to inactivate the fungal under test.

The energy band gap (E_g) can be calculated using Eq. (2) and extrapolation of the curve to intersect the photon energy ($h\nu$) axis, as shown in Fig. (8) to be 3.41eV for mixed-phase sample and 3.23 eV for single-phase sample [23,24] as

$$(\alpha h\nu)^r = A\,(h\nu - E_g) \qquad (2)$$

where α is coefficient of linear absorption, h is Planck's constant, ν is incident photon frequency, A is constant, and r is a constant determined by the type of optical transition. Here, r was chosen to be 0.5 to indicate that direct transitions are allowed [25]

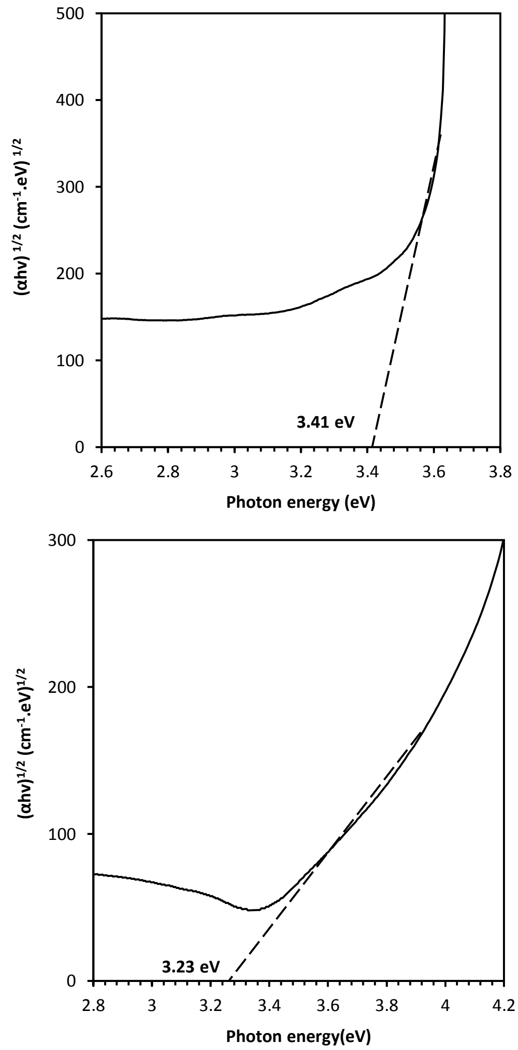


Fig. (8) Determination of energy band gap of mixed-phase sample (upper) and single-phase sample (lower)

The antifungal activity of TiO_2 nanoparticles at a concentration of (1g) against Fusarium oxysporum before, and after photocatalytic,treatment is depicted in Fig. (9). The activity of TiO_2 nanoparticles is associated with the light-induced free radical production which results in peroxidation when the radical contacts with the fungal cell membrane. The highly-active oxygen has the ability to oxidize organic molecules that results in inactivation and then decomposition of the fungal.

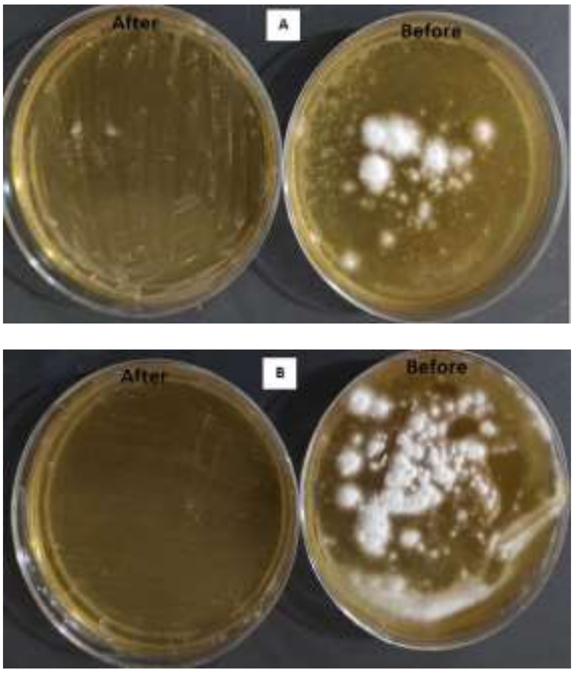


Fig. (9) Anti-fungal activity of TiO_2 nanoparticles (a) mixed-phase and (b) single-phase samples at concentration of 1g against F. oxysporum with 60 minutes of UV radiation exposure

4. Conclusion

In this study, high-quality mixed-phase nanostructured TiO_2 thin films were prepared using dc reactive magnetron sputtering technique. It was found that the weight fraction of the rutile phase in the mixed-phase samples depends on the deposition time, after which the sample was prepared. The sample with 40% rutile content exhibited the best photocatalytic activity. Synthesis of single-phase (anatase) TiO_2 samples was achieved without any heat treatment. It was also found that both types of TiO_2 samples (mixed- and single-phase) exhibit significant antifungal activity.

References

[1] S. Pavasupree et al., "Hydrothermal synthesis, characterization, photocatalytic activity and dye-sensitized solar cell performance of mesoporous anatase TiO_2 nanopowders", Mat. Res. Bull., 43 (2008) 149-157.
[2] R.A.H. Hassan and F.T. Ibrahim, "Preparation and Characterization of Anatase Titanium Dioxide Nanostructures as Smart and Self-Cleaned Surfaces", Iraqi J. Appl. Phys., 16(4) (2020) 13-18.
[3] D.P. Macwan, P.N. Dave and S. Chaturvedi, "A review on nano-TiO_2 sol-gel type syntheses and its applications", J. Mater. Sci., 46(11) (2011) 3669-3686.
[4] F.J. Al-Maliki1, O.A. Hammadi and E.A. Al-Oubidy, "Optimization of Rutile/Anatase Ratio in Titanium Dioxide Nanostructures prepared by DC Magnetron Sputtering Technique", Iraqi J. Sci., 60(Special Issue) (2019) 91-98.
[5] F. Haghighi et al., "Antifungal Activity of TiO_2 nanoparticles and EDTA on Candida albicans Biofilms", Infec. Epidem. Med., 1(1) (2013).
[6] F.J. Al-Maliki, O.A. Hammadi, B.T. Chiad and E.A. Al-Oubidy, "Enhanced photocatalytic activity of Ag-doped TiO_2 nanoparticles synthesized by DC Reactive Magnetron Co-Sputtering Technique", Opt. Quantum Electron., 52 (2020) 188.
[7] M.V. Berridge et al., "The Biochemical and Cellular Basis of Cell Proliferation Assays That Use Tetrazolium Salts", Biochemica, 4 (1996) 14-19.
[8] W.M. Dunne, "Bacterial adhesion: seen any good biofilms lately", Clin. Microbiol. Rev., 15 (2002) 155-166.
[9] A.A. Hussain and H.S. Wahab, "Synthesis and spectroscopic characterization of anatase TiO_2 nanoparticles", Int. J. Nanotech. Nanosci., 2 (2014) 1-6.
[10] W.B. Mi, E.Y. Jiang and H.L. Bai, "Structure, magnetic and optical properties of poly-crystalline Co-doped TiO_2 films", J. Magn. Magn. Mater., 321(16) (2009) 2472-2476.
[11] S.H. Faisal and M.A. Hameed, "Heterojunction Solar Cell Based on Highly-Pure Nanopowders Prepared by DC Reactive Magnetron Sputtering", Iraqi J. Appl. Phys., 16(3) (2020) 27-32.
[12] E.A. Al-Oubidy and F.J. Al-Maliki, "Effect of Gas Mixing Ratio on Energy Band Gap of Mixed-Phase Titanium Dioxide Nanostructures Prepared by Reactive Magnetron Sputtering Technique", Iraqi J. Appl. Phys., 14(4) (2018) 19-23.
[13] F.J. Al-Maliki and E.A. Al-Oubidy, "Effect of gas mixing ratio on structural characteristics of titanium dioxide nanostructures synthesized by DC reactive magnetron sputtering", Physica B: Cond. Matter, 555 (2019) 18-20.
[14] O.A. Hammadi, M.K. Khalaf, F.J. Kadhim and B.T. Chiad, "Operation Characteristics of a Closed-Field Unbalanced Dual-Magnetrons Plasma Sputtering System", Bulg. J. Phys., 41(1) (2014) 24-33.
[15] O.A. Hammadi, "Production of Nanopowders from Physical Vapor Deposited Films on Nonmetallic Substrates by Conjunctional Freezing-Assisted Ultrasonic Extraction Method", Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys., 232(4) (2018) 135-140.
[16] O.A. Hammadi, "Effects of Extraction Parameters on Particle Size of Titanium Dioxide Nanopowders Prepared by Physical Vapor Deposition Technique", Plasmonics, 15(6) (2020) 1747-1754.

[17] M. Ladd and R. Palmer, **"Structure Determination by X-Ray Crystallography"**, 5th ed., Springer (NY, 2013), 568.
[18] S.F. Bertram, **"Handbook of X-rays"**, ed. E.F. Kaelbe, McGraw-Hill (NY, 1976), 817.
[19] F.J. Al-Maliki and N.H. Al-Lamey, "Synthesis of Tb-doped titanium dioxide nanostructures by sol–gel method for environmental photocatalysis applications", J. Sol-Gel Sci. Technol., 81(1) (2016) 276-283.
[20] J.G. Yu et al., "Effects of pH on the microstructures and photocatalytic activity of mesoporous nanocrystalline titania powders prepared via hydrothermal method", J. Mol. Catal. A: Chem., 258(1-2) (2006) 104-112.
[21] K. Balachandran, R. Venckatesh and R. Sivaraj, "Synthesis of nanoTiO_2-SiO_2 composite using sol-gel method: effect of size, surface morphology and thermal stability", Int. J. Eng. Sci. Technol., 2 (2010) 3695-3700.
[22] O.A. Hammadi, F.J. Kadhim and E.A. Al-Oubidy, "Photocatalytic Activity of Nitrogen-Doped Titanium Dioxide Nanostructures Synthesized by DC Reactive Magnetron Sputtering Technique", Nonl. Opt. Quantum Opt., 51(1-2) (2019) 67-78.
[23] A. Zachariah et al., "Synergistic Effect in Photocatalysis As Observed for Mixed-Phase Nanocrystalline Titania Processed via Sol-Gel Solvent Mixing and Calcination", J. Phys. Chem. C, 112 (2008) 11345-11356.
[24] Y. Zhao et al., "Synthesis and optical properties of TiO_2 nanoparticles", Mater. Lett., 61 (2007) 79-83.
[25] E.A. Al-Oubidy and F.J. Kadhim, "Photocatalytic activity of anatase titanium dioxide nanostructures prepared by reactive magnetron sputtering technique", Opt. Quant. Electron., 51(1) (2019) 23.