Synthesis And Study The Concentration Effect On The Photocatalytic Activity of Titania Nanoparticles As Anti-Bactria Using Reactive Magnetron Sputtering Technique

Firas J. Al-Maliki (✉ dr.firas1990@yahoo.com)

University of Baghdad

Maryam A. Al-Rubaiy

University of Baghdad

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Abstract

In this work, the dc reactive magnetron sputtering technique was used to prepare and deposit nanostructured titanium dioxide (TiO_2) thin films on glass substrates. Titanium dioxide thin films of mixed phase (anatase + rutile) and single phase (anatase) were prepared using different gas mixing ratios, and for both of the two phases, they were diagnosed via x-ray diffraction (XRD). It was found that the contents of rutile in mixed phase dependent on the deposition time increased from the ratio of 40% to 46% and 50% as the deposition time increased from 3 hours to 3.30 and 4 hours. The photocatalytic activity of the mixed and single phase TiO_2 was measured by kill the bacteria *Escherichia coli* (E.Coli) under exposure to UV-radiation. It was proven that the photocatalytic activity in the mixed phase (TiO_2) gave better results weight fraction is 40% as an antibacterial activity. Based on the obtained results antibacterial activity of dioxide titanium nanoparticles was dependent on the concentration and phase of TiO_2 and weight fraction of mixed-phase.

1. Introduction

The research interest in nanostructured titanium dioxide (TiO_2) thin films is rapidly rising due to its numerous and potential applications, such as photocatalysis, photonics, optoelectronics, electrochemistry, and photoelectrochemistry [1]. These applications are used for the optical, electrical, chemical, and mechanical characteristics of TiO_2 thin films and nanoparticles [2]. Because of its outstanding properties, such as nontoxicity, high photocatalytic activity, chemical stability, ability to be coated as a thin film on a substrate, and Friendly to the environment, TiO_2 is being hailed as a potential photocatalyst among all semiconductor photocatalysts. [3]. the average nanocrystalline size, crystallinity, specific surface area, and phases involved are all known to affect the photocatalytic activity of pure- TiO_2 [4, 5]. TiO_2 exists as three different polymorphs: anatase, rutile, and brookite. The main source and the most stable form of TiO_2 is rutile, In terms of photocatalytic activity, anatase TiO_2 is more active than rutile TiO_2 . [6].

The mixed TiO_2 phase anatase/rutile, which is more popular than the single anatase or rutile phase, has greater photocatalytic activity than the single anatase or rutile phase, which is attributed to a synergistic effect between the two phases. [7]. The co-presence of anatase and rutile crystallites induces a high level of photocatalytic activity; the transfer of photoexcited electrons and positive holes between interconnecting anatase and rutile particles may enhance charge separation and hence improve the efficiency of utilization of electron-hole pairs [8]. Additional characterizations confirmed electron transport between the two phases, suggesting that phase composition is a fundamentally important factor in high photocatalytic activity [9].

The function of the Titania photocatalyst can be divided into these major categories: Purifying water, Preventing contamination, Deodorizing, Purifying the air self-cleaning, and Anti-bacteria [10]. Titania nanoparticles have a broad spectrum of activity against microorganisms, including Gram-negative and

positive bacteria, as well as fungus, which is especially important for drug-resistant strains. Furthermore, prior research has shown that TiO_2 may not only kill a complex cellular congregation with major implications in pathogenicity (fungal) as concentration increases, but it can also prevent fungus development at lower concentrations [11–13].

Synthesizing TiO_2 can be done in a variety of ways. TiO_2 films may be made using a variety of physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes and techniques, including sol-gel, pulsed-laser deposition, ion beam, and dc magnetron sputtering [14–16]. The dc closed-field unbalanced reactive magnetron sputtering technique offers several advantages over other techniques, particularly when it comes to producing very pure and homogenous thin films on vast areas of substrates at low processing temperatures. Changes in operating parameters such as total gas pressure, working gas pressures, inter-electrode distance, gas mixing ratio, electrical discharge power, substrate temperature, cooling rate, and sputtering time can alter the characteristics of sputtered TiO_2 films [17–19].

In the present work, the anti-bacterial effect of TiO_2 nanoparticles was investigated as a function of concentration under light irradiation.

2. Experimental Part

In the present work, Titanium Dioxide nanostructures were synthesized as thin films using reactive magnetron plasma sputtering deposition method. To produce TiO_2 thin coatings on glass substrates, the electric power for glow discharge which in turn generating plasma in the system was provided by a dc power supply, connected to the electrodes. The highest electrical power was 150W, with a discharge voltage of 3 kV with a discharge current of 50 mA, and a selected distance of 4 cm between the target and the substrate. More information about the system's working conditions and parameters tuning may be obtained elsewhere [20-21].

The sputtered target was a titanium sheet with a purity of 99.99 %. A two-stage rotary pump (Edward 8 m^3/h) was run at a base pressure of around 3×10^{-2} mbar to prevent contamination of the chamber during the deposition process. To produce the discharge plasma, a glass substrate was exposed to pure argon gas at the start of the thin-film preparation process. All samples were reactively sputtered in a combination of Argon gas (99.99%) as precursor gas and Oxygen gas (99.99%) as reactive gas. The film samples were prepared as a function of different deposition time (3, 3.30, and 4 hours) and three different mixing ratios of $\text{Ar}:\text{O}_2$ gases (50:50, 67:33, and 80:20). Before pumping the gas mixture to the deposition chamber, a stainless steel mixer was employed to control the mixing ratios. Conjunctional freezing-assisted ultrasonic extraction was used to extract nanopowder from thin-film samples [22]. Figure (1) shows a photo of TiO_2 sample, synthesized in the present work, as thin film and as extracted powder.

The bacteria *Escherichia coli* (*E. coli*) samples have been selected and prepared for testing in the application of photocatalytic activity. For 24 hours, *Escherichia coli* have been cultured in nutrient broth at 37°C. Before overnight growth, a small swab of the *E. coli* sample by using a sterile swab has been taken and distributed evenly on the surface of nutrient agar. TiO₂ nanopowder (extracted from the prepared films) of different concentrations 0.25, 0.5, and 1 g have been dissolved in sterilized deionized water by using an ultrasonic bath, homogenized by a vortex mixer, added to the plates, and then the dishes have been exposed to UV irradiation (200-400 nm) for 90 minutes. The UV source is placed at a distance of 10 cm from the Petri dish. Finally, incubated at 37°C for 24 hour and then the formation of growth inhibitory zones have been examined, as shown in the figure (2).

3. Results And Discussion

The crystalline structure of the samples synthesized under various processing parameters was investigated using X-ray Shimadzu diffractometer with Cu K α radiation ($\lambda=1.54060\text{\AA}$) at 40.0 kV and 30 mA, Figure (3) include x-ray diffraction patterns. The first one (A) represents the mixing phase structure (anatase /rutile) of one of the prepared TiO₂ samples, in which the diffraction peaks at 25.2°, 37.8°, 48°, 55.1°, 56.7°, 62.8°, 69.2°, 69.8°, and 75.4° are corresponding to (101), (004), (200), (105), (211), (118), (116), (220) and (125) crystal planes. According to JCPDS, card no. 21-1272, they confirm the formation of the anatase (A) phase. While the peaks at (27.5°, 36°, 41.3°, 44.1°, 54.5° and 64.3°) Correspond to the rutile phase (110), (101), (111), (210), (211) and (310) crystal planes according to the JCPDS card no. 00-021-1276 [23]. The second pattern (B) indicates the single phase structure (anatase only) of the samples which are prepared with making a heat sink under the substrate. The weight fraction (f) of the rutile phase in an anatase-rutile combination may be calculated using the equation [7]:

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

Here f is the weight fraction of rutile in mixed-phase (anatase + rutile) and I_A/I_R is the ratio of the intensity of anatase (I_A) phase to that of rutile (I_R) phase that is determined from the x-ray intensities. For samples prepared following deposition times of 3, 3:30, and 4 hours, the relative quantities of rutile in mixed-phase (anatase-rutile) samples were 40%, 46%, and 50%, respectively.

On the other side, the crystallite size of the particles was calculated from Deby-Scherrer's equation using the XRD line broadening [21].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

Here D is the crystallite size, θ is the diffraction angle, λ is the x-ray radiation wavelength (0.15406 nm) for CuK, K is a constant typically chosen as 0.89, and β is the full-width at half-maximum (FWHM) [24]. At

gas mixing ratios of Ar: O₂ equal to 0:50, 67:33, and 80:20, the average crystallite size determined to be 18.3, 19.9, and 17.5nm respectively for mixing phases (anatase + rutile).

In order to infer the structural properties of forming TiO₂ via sputtering method, Fourier-transform infrared (FTIR) spectroscopy in the range of 400– 4000 cm⁻¹ (using Shimadzu 8400S FTIR) has been employed as shown in the figure (4). The IR absorption bands appeared at around 3454, 1637 cm⁻¹ corresponds to the symmetric/asymmetric stretching and bending modes of vibration of a hydroxyl group (O–H bond) present in the structure, which indicate the presence of traces of water molecules due to humidity [25-26]. The peak at 420 cm⁻¹ is attributed to Ti–O–Ti bonds in the TiO₂ network, whereas the band assigned to Ti–O stretching vibration is at 444 and 653 cm⁻¹. As a result, the prepared samples, via sputtering method, may be described as extremely pure in which no peaks reflect the existence of any impurities.

AFM (Atomic force microscopy) was used to study the surface morphology. Figure (5) shows two-dimensional and three-dimensional AFM images of a TiO₂ sample prepared with an Ar: O₂ mixing ratio of 50:50 and a 3h deposition time with an average roughness of 3.47nm and a root mean square (R_{r.m.s.}) value of 4.33nm, a significantly homogeneous distribution of TiO₂ nanoparticles was generated. The large surface area to volume ratio of produced TiO₂ nanoparticles may provide an advantage for using such surfaces in photonic and optoelectronic devices that use TiO₂ nanostructures. Photocatalysts are another major application of TiO₂ nanostructures with a high surface area to volume ratio.

The UV-visible spectroscopy was studied in the spectral region of 300-800 nm by recording the absorption spectra of mixed-phase nanocrystalline TiO₂ film samples containing various quantities of rutile as illustrates in figure (6). For a sample with a 40 wt.% rutile phase, an absorption edge was found at around 339 nm, whereas this edge was shifted to approximately 351 and 437 nm for samples with 46 and 50 wt.% rutile phase, respectively.

The optical energy band gap (E_g) of nanocrystalline TiO₂ films can be calculated from their absorption spectra using the following equation [27-28]:

$$(\alpha h\nu)^r = A (h\nu - E_g) \quad (3)$$

where h is Planck's constant, ν is the frequency of incident photon., A is constant, α is the linear absorption coefficient, and r is a fixed value that depends on the type of the optical transition. The value of r is choose to be 0.5 indicates direct allowed transitions.

The band gap of mixed-phase nanocrystalline TiO₂ with rutile 40 wt.% was estimated to be 3.43eV, as shown in figure (7). While it becomes 3.39 and 3.35 eV, as the quantity of rutile is increased to 46 and 50 wt.%, respectively. This decrease in energy band gap is ascribed to the charge-separation mechanism (CSM) [29]

Figure (8) shows the absorption spectrum of single-phase (anatase) TiO_2 nanostructures after 3 hours time deposition with a heat sink under the substrate using a 50:50 gas-mixing ratio. Figure (9) depicts the energy of this directly allowed band gap, which was determined to be 3.21 eV in as-deposited Nanostructured TiO_2 thin films with an Ar: O_2 mixing ratio 50:50.

Figure (10) depicts the antibacterial effectiveness of TiO_2 nanoparticles at different concentrations (0.25, 0.5, and 1) g for (single and mixed) phase against *E. coli* before and after photocatalytic treatment. The TiO_2 nanoparticles' activity is associated with the light-induced generation of free radicals, which causes peroxidation when the radical reacts with the bacterial cell membrane. The extremely active oxygen species produced can oxidize organic compounds resulting in the disassembly and elimination of bacterial. The results showed that a concentration of 1g of mixing phases of dioxide titanium nanoparticles has good antibacterial effects more than other concentrations. Based on the attained results anti-bacterial activity of dioxide titanium nanoparticles was depended on the concentration, phase of TiO_2 , and weight fraction of mixed-phase.

4. Conclusion

In this study, it was shown that the weight fraction of the rutile phase in the mixing phase structure rutile /anatase depends on the deposition time. On the same path, the synthesis of anatase TiO_2 can be successfully achieved without any thermal treatment via this configuration of sputtering. On the other side, it was observed that the single phase and mixing phase of TiO_2 have anti-bacterial activity with slightly preference for anatase phase. Also the anti-bacterial activity of mixing phase TiO_2 change with the rutile content, where 40% rutile content shows more activity than other contents.

Declarations

Authors declare that they do not have any conflict of interest related to this work

References

- [1] Jin, Y., Li, G., Zhang, Y., Zhang, Y., Zhang, L.: Photoluminescence of anatase TiO_2 Thin films are achieved by the addition of ZnFe_2O_4 . J. Phys. Condens. Matter. 13, L913–L918 (2001)
- [2] Karabay, I., Aydın Yüksel, S., Ongül, F., Öztürk, S., Asli, M.: Structural and optical characterization of TiO_2 thin films prepared by sol-gel process. Acta Phys. Pol. A 121(1), 265–267 (2012)
- [3] Wang, Y.W., Huang, Y., Ho, W.K., Zhang, L.Z., Zou, Z.G., Lee, S.C.: Biomolecule controlled hydrothermal synthesis of C-N-S-tridoped TiO_2 nanocrystalline photocatalysts for NO removal under simulated solar

light irradiation. J. Hazard. Mater. 169, 77-87. 2009.

[4] Baiju, K.V., Shukla, S., Sandhya, K.S., James, photocatalytic activity of Sol-Gel-Derived nanocrystalline Titania, j.Phys.Chem. C, 111(21), 7612-7622, 2007.

[5] MehranRiazian, Electrical properties, and enhancement of photocatalytic activity of TiO₂nanorods doped with SiO₂, S. Afr.j.chem.(Online), vol.70, 2017.

[6] Fasciani, C., Lanterna, A.E., Giorgi, J.B., Scaiano, J.C., Visible light production of hydrogen by ablated graphene: water splitting or carbon gasification, J.Am.Chem.soc. 139, 11024-11029, 2017.

[7] Firas J. Al-Maliki¹, Oday A. Hammadi, Esraa A. Al-Oubidy, Optimization of Rutile/Anatase Ratio in Titanium Dioxide Nanostructures prepared by DC Magnetron Sputtering Technique, Iraqi Journal of Science, Vol. 60, Special Issue, pp: 91-98, 2019.

[8] Hurum, D.C., Agrios, A.G., Gray, K.A., Rajh, T. and Thurnauer, C. "Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO₂ Using EPR", J. Phys. Chem. B, 107: 4545. 2003.

[9] Hurum, D C., Gray, K A., Rajh, T. and Thurnauer, M C. "Recombination pathways in the Degussa P25 formulation of TiO₂: Surface versus lattice mechanisms", J PhysChem B, 109: 977–980.2005

[10] M. Kaneko and I. Okura, In Photocatalysis: Science and Technology (Kodansha, 2002), p. 157.

[11] F. Haghighi¹, S. RoudbarMohammadi, P. Mohammadi, S. Hosseinkhani, R.Shidpour, Antifungal Activity of TiO₂ nanoparticles and EDTA on Candida albicansBiofilms, Infection Epidemiology & Medicine, Vol 1, No 1, Summer 2013.

[12] Berridge MV, Tan AS, Coy KDM, Wang R. TheBiochemical and Cellular Basis of Cell Proliferation Assays That Use Tetrazolium Salts.Biochemica; 4:14-19, 1996.

[13] Dunne WM. Bacterial adhesion: seen any goodbiofilms lately. ClinMicrobiol Rev; 15:155-166, 2002.

[14] M.H. Habibi, N. Talebian; The effect of annealing on photocatalytic properties of nanostructured titanium dioxide thin films, Dyes Pigments 73 (1) 103–110., 2007

[15] M. Stoller, M. Mescia, C. Valencia Peroni, A. Chianese; Production Of Nanoparticles Of Titanium Dioxide By Using A Spinning Disc Reactor, Chem. Eng. Trans. 11 (2007)71–76.

[16] R. Vijayalakshmi, V. Rajendran;Synthesis and characterization of nano-TiO₂ via different methods,Arch. Appl. Sci. Res. 4 (2) (2012) 1183–1190.

[17] A.A. Hussain, H.S. Wahab; Synthesis and spectroscopic characterization of anatase TiO₂ nanoparticles, Int. J. Nanotech. Nanosci. 2 (2014) 1–6.

- [18] Y. Yang, Q. Zhang, B. Zhang, W.B. Mi, L. Chen, L. Li, C. Zhao, E.M. Diallo, X.X. Zhang; The influence of metal interlayers on the structural and optical properties of nanocrystalline TiO₂ films, *Appl. Surf. Sci.* 258 (10) (2012) 4532–4537.
- [19] W.B. Mi, E.Y. Jiang, H.L. Bai; Structure, magnetic and optical properties of poly-crystalline Co-doped TiO₂ films, *J. Magn. Magn. Mater.* 321 (16) (2009) 2472–2476.
- [20] O.A. Hammadi, M.K. Khalaf, F.J. Kadhimi and B.T. Chiad, Bulg; Operation Characteristics of a Closed-Field Unbalanced Dual-Magnetrons Plasma Sputtering System. *J. Phys.*, 41(1) (2014) 24-33.
- [21] Firas J. Kadhimi*, Esraa A. Al-Oubidy; Effect of Gas Mixing Ratio on Energy Band Gap of Mixed-Phase Titanium Dioxide Nanostructures Prepared by Reactive Magnetron Sputtering Technique. *J. Phys.*, Vol. (14), No. (4), 2018, 19-23.
- [22] O.A. Hammadi, "Production of Nanopowders from Physical Vapor Deposited Films on Nonmetallic Substrates by Conjunctive Freezing-Assisted Ultrasonic Extraction Method", *Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys.*, 232(4), 135-140 (2018).
- [23] A. Hu, X. Zhang, D. Luong, K. D. Oakes, M. R. Servos, R. Liang, S. Kurdi, P. Peng, Y. Zhou; Adsorption and Photocatalytic Degradation Kinetics of Pharmaceuticals by TiO₂ Nanowires During Water Treatment, *Waste Biomass Valoriz.*, 3 (2012) 443–449.
- [24] K. Balachandran, R. Venkatesh and R. Sivaraj; Synthesis of nano TiO₂-SiO₂ composite using sol-gel method: Effect on size, surface morphology and thermal stability, *Int. J. Eng. Sci. Technol.*, 2(8) (2010) 3695–3700.
- [25] J. Wei, L. Zhao, S. Peng, J. Shi, Z. Liu, W. Wen, Wettability of urea-doped TiO₂ nanoparticles and their high electrorheological effects, *J. Sol-gel Sci. Technol.* 47(2008) 311–315.
- [26] A. Kathiravan, R. Renganathan, Photosensitization of colloidal TiO₂ nanoparticles with phycocyanin pigment, *J. Colloid Interface Sci.* 335(2009) 196–202.
- [27] A. Zachariah, K. V. Baiju, S. Shukla, K. S. Deepa, J. James, K. G. K. Warriar, "Synergistic Effect in Photocatalysis As Observed for Mixed-Phase Nanocrystalline Titania Processed via Sol-Gel Solvent Mixing and Calcination" *J. Phys. Chem. C*, Vol. 112, pp. 11345–11356, 2008.
- [28] Zhao Y, Li C, Liu X, Gu F, Jiang H, Shao W, Zhang L, He Y, "Synthesis and optical properties of TiO₂ nanoparticles", *Mater Lett*, Vol. 61, pp. 79-83, 2007.
- [29] A. Zachariah, K.V. Baiju, S. Shukla, K.S. Deepa, J. James and K.G.K. Warriar, "Synergistic Effect in Photocatalysis As Observed for Mixed-Phase Nanocrystalline Titania Processed via Sol-Gel Solvent Mixing and Calcination", *J. Phys. Chem.*, Vol. C 112, pp. 11345-11356, 2008.

Figures

(A)

(B)

Figure 1

Photo of TiO_2 prepared using a gas-mixing ratio of 50:50 and inter-electrode distance 4 cm at deposition time 3:30 h as (A) thin film and (B) powder

Figure 2

Photo of bacteria (*E. coli*) before treatment

Figure 3

XRD patterns of TiO₂ nanostructures prepared using a gas mixing ratio of 50:50 and inter-electrode distance 4 cm (A) mixed-phase at deposition time 4 h and (B) single-phase at deposition time 3 h with heat sink

Figure 4

The FTIR spectrum of TiO_2 sample of mixed-phase prepared using Ar: O_2 mixing ratio of 50:50 and deposition time of 4 hour

Figure 5

AFM images of TiO_2 nanoparticles in two and three dimensions

Figure 6

Absorption spectra of the mixed-phase TiO₂ prepared using Gas mixing ratio of 50:50 at deposition time 3h (rutile content 40 wt.%), 3:30h (rutile content 46 wt.%), and 4h (rutile content 50wt.%)

Figure 7

Determination of Energy band gap of mixed-phase TiO₂ prepared using gas mixing ratio of 50:50 at deposition time 3h (rutile content 40 wt.%), 3:30h (rutile content 46 wt.%), and 4h (rutile content 50 wt.%)

Figure 8

Absorption spectrum of single-phase TiO₂ prepared using the gas-mixing ratio of 50:50 at deposition time 3h

Figure 9

Determination of Energy band gap of single-phase TiO₂ prepared using gas mixing ratio of 50:50 at deposition time 3h

Figure 10

Photos show the influence of TiO₂ nanoparticles (A) single phase (anatase) (B) mixing phase (rutile/anatase) as anti-bacteria at different concentration and with 1:30 hours uv. Irradiation