**Eng. &Tech.Journal, Vol.34,Part (A), No.13,2016**

# Synthesis of Ag –$TiO_2$ Thin Films by Spin Coating process

**Sinan Salman Hamdi**
Production and Metallurgy Engineering Department, University of Technology/Baghdad.
Email: sinan_s_alhakeem@yahoo.com

**Received on: 8/5/2016 & Accepted on:29/9/2016**

## ABSTRACT:

In this research, Sol-gel technique prepared Ag–$TiO_2$ nano-composite thin films, which were deposited onto a glass substrate by the spin coating process. The microstructures and chemical ingredients of the obtained thin films were characterized by UV-visible spectroscopy (UV), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FT-IR). It was discovered that the silver nano-particles completely joined to the $TiO_2$ matrix, where those nanoparticles distributed uniformly. In this way, the molar percent of the silver nitrate watery solution dominated the morphology of the thin film. Ag-$TiO_2$ Nano composite is very useful for expanding antibacterial of nanomaterials purpose.

**Keywords:** Nano $TiO_2$-Silver; Spin Coater; Thin Films.

## INTRODUCTION

Researchers have demonstrated fixed interest in evolving antimicrobial substances including various organic chemical antibiotics and inorganic materials. The functional materials have a highly distinctive characteristics and ability of biological purpose, fore that the nanosized particles of organic and inorganic materials have attracted in order to raise attention in medical applications, especially when they became among those fine materials [1, 2]. Because of non-toxicity, it's high and fixed oxidizing power, long-range of the physical and chemical steadiness, of the most efficacious photocatalysis of which used these days is Titanium dioxide ($TiO_2$). The main features of inorganic antibacterial agents improved safely and firmness, comparing with organic antimicrobial materials [3, 4].

$TiO_2$ shows strong bactericidal activity, especially when exposed to irradiation close to UV light [5]. It has to be a reaction among the photo generated pits and electrons by way of aqua and oxygen consecutively, such as hydroxyl radicals (-OH) singlet oxygen ($O^{-2}$), and hydrogen peroxide ($H_2O_2$). Bacteria and the degradation of the toxic compounds which resulted from the bacteria itself could be finished off by $TiO_2$ and its deposits [6, 7].

It is worth to mention that, absolute oxidation can be accomplished for an entire cells and organic compounds of carbon dioxide [8], but still its defects like, its actual uses are obstructed by low quantity yields and the deficiency of visibility-light usage [9, 10]. For the purpose of finding solutions to overcome these obstacles, the use of silver by adding it to nanoparticles, exceedingly promoted the photocatalytic efficiency of $TiO_2$, where at Schottky barrier at each one of Ag–$TiO_2$ of get in contact with the region, it is noticed that its ability enabled it to confine electrons, and that decreases the assembly of light at the $TiO_2$ face. [11, 12]. Thus more electrons would be transferred due to the enhancement of charge separation. A sliver metal and its solutions considered as anantibacterial materials and have a low toxicity against cells, that feature made it as an effective antimicrobial factor for centuries [13].

Generally, silver ions react in the company of proteins leading to the inactivation of the proteins via responding by way of the SH bands of which existent in bacteria is the first of two effects of silver on bacterial cells, and the second, that silver ions can interact in the midst of DNA of bacteria, stopping a cell proliferation. Both the effects produce to kill the bacterial cells. All of

https://doi.org/10.30684/etj.34.13A.7
2412-0758/University of Technology-Iraq, Baghdad, Iraq

what mentioned in respect with, were reported by several studies to explain that damping impact of silver on bacteria [14, 15].

On the other hand, regarding to the usage of silver ions, it is well known that Silver-doped another materials are chemically sturdy and liberate silver ions for a long period. Especially when silver crystal size is decreased, where the effect of silver nanoparticles became long term, steady and its release could be controlled. To carry out as a magnificent antibacterial coating inside the water disinfection, nourishment manufacturing as well as others in related these fields [16, 17]. The researchers sought to find manufacturing systems by combining the titanium and silver nanoparticles in order to use the $TiO_2$ on a larger scale in medical application, due to its significance in this field by expanding the nanometers antibacterial functions [18]. Synthesis of Ag/$TiO_2$ nanocomposites is accomplished by various synthetic methods. A solvothermal process in the literature review is usually utilized to acquire the nanoparticles. However for actual applications, exotic metal ions into $TiO_2$ particles and films is being presented by the sol–gel process, which considered as the most effective method, for instance, the films that containing $Ag^+$ under UV exposure the photoreduction occurs [19], also immediate calcination of the sol gel substance [20]. But, photo reduced silver not possible to be entirely scattered inside the deepness under the $TiO_2$ face, principally once the adhesion force is feeble for the outside top of coating [18, 21]. Positively, the use of the sonochemical method suppressed those defects. Mixtures of solution were exposed to intensive ultrasonic irradiation in sol gel processes, and that was reported since the early 1980s [22].

In this research, the sol gel technique is the appropriate way to make Ag/$TiO_2$ thin films were deposited onto glass substrate with several of the silver content. It could be controlled the morphological composite films by setting the molar ratio of $AgNO_3$ watery solution to $TiO_2$, when introduced the silver ion $Ag^+$. Forming multiphase nanocomposite thin films in the Ag/Anatase supported the interaction between the nanosized silver particles and the $TiO_2$ grains.

## Experimental Part:-

### Materials:-

The materials used in this work Titanium (IV) isopropoxide (Aldrich Chemicals Ltd., USA), Ethanol alcohol and Silver nitrate ($AgNO_3$). All materials were used without further purification; In addition to used deionized water in all the preparations.

### Preparation of Ag–$TiO_2$ Thin Film:

$TiO_2$ nanoparticles were doped with several % Ag prepared by sol-gel method. At first, 5gm of Titanium (IV) isopropoxide was dispersed in 100 ml of deionized water and ethanol alcohol at 25 °C. To this solution, Silver nitrate was diluted in water and added drop wise (the molar ratio of Ag to $TiO_2$ was ranged from 5: 1 to 25:1) and mixed by the magnetic stirrer for 1 h and the stirring was continued for 3 h at 70 °C. The solution was kept in dark for 24 h for gelation process. Dropts of the prepared solution was deposited onto washed glass substrate ($20 \times 10$ $mm^2$) by spin-coating at 2000 rpm for 40 s. The obtained films were dried at 80 °C for 2 h and then annealed at 450 °C for 1 h.

### Physio-chemical characterization of Ag–$TiO_2$ Thin Film:

Surface plasmon resonances of the sample were analyzed with a UV-Vis Spectrophotometer (Cary 300 Conc spectrophotometer), the wavelength range from (200- 800nm) at room temperature. The morphology of the obtained thin films was characterized by using SEM microscope with EDAX type (VEGA3 TESCAN). The crystal structures of the thin films was examined by an X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 1.54060\ \mathring{A}$) operated at 30 kV and 20 mA. The information to the particle size was obtained from the Sherrer Formula [23]:

$$D = 0.89\,\lambda / \beta \cos\theta \qquad \ldots(1)$$

Where D is the average particle size, λ is the wavelength of X-ray, β is the full width at maximum half of diffraction peak and θ is angle of the diffraction.

The mean particle size of the Ag–$TiO_2$ nanoparticles was determined to be about 15 nm.

FTIR spectra of the Ag -$TiO_2$ nanocomposite was obtained (400 – 4000 $cm^{-1}$) from (IR Affinity-1 FTIR spectrometer). The essential IR groups, like (C-N), (O-H), (C-H), (C=C), (N-H), (C-O) and (C-H) their symmetric and lopsided stretching, and their extending frequencies were studied order to decide the existence of practical group in the ethyl acetate. (Ogunmwonyi et al., 2010).

## Results and Discussion:-

The Ag–$TiO_2$ thin film appeared to be vivid ruby little clear which clearly indicates the formation of Ag–$TiO_2$ nanoparticles. The UV-Vis Spectra of the Ag–$TiO_2$ nanoparticles are given in Figure 1. from which it is clear that the Ag–$TiO_2$ surface plasmon occurred at 350 nm [23].

Figure 2.a and b, shows the SEM image of Ag–$TiO_2$ thin films samples at different the ratio of Ag to $TiO_2$ after drying and annealing at 450 °C for 1h. The images show all the particles at the nanometer scale. Figure2.A. show there are a bright particles surrounding the dark which indicated that individual silver particle dispersed with the $TiO_2$ as product of Ag–$TiO_2$ nanocomposite is more agglomerate, growth and regularly distributed than the Morphology which is appeared in Figure 2.B. The EDX spectra indicated to presence a small amount of silver within the $TiO_2$, that confirms individual silver ions interacted with the $TiO_2$ matrix as shown in Figure 3.

The evidence for the formation of elemental Ag–$TiO_2$ thin film is provided by X-Ray diffraction (XRD) analysis in Figure 4. The spectrum shows five major diffraction intensity peaks these showed that the entire of the eventual films display a pure anatase phase structure. The peaks of silver at $2\theta = 38.07°$ appeared at the same peak of the rutile $TiO_2$ and detected on $2\theta = 44.25°$ and 64.38° to the crystalline of metal silver [20, 24]. The eventual x-ray diffraction results of the films exhibit that four peaks (1 0 1), (1 1 1), (1 0 5) and (2 2 1) for $TiO_2$ crystal planes, respectively. The peaks were observed to originate from planes of the sample respectively (JCPDS no: 73-0370).

The FTIR Spectral analysis of metal ions as shown in Figure 5. The sample shows certain common absorption bands the hydroxyl (O-H) and the presence (N-H) vibration frequency which are exchangeable at 3450 $cm^{-1}$ [24, 25]. Mutual vibration peaks at 2325 $cm^{-1}$ are characteristic of a (C-H) symmetrical band and stretching of hydrocarbon (C=O) at 1785 $cm^{-1}$. The absorption peak at 1635 $cm^{-1}$ is attributed to the O-H bending vibration. Band below 1250 $cm^{-1}$ is due to Ti-O-Ti and Ti-O-Ag vibrations which are appearing unsymmetrical [22, 25].

## CONCLUSION:

The polycrystalline thin films of the Ag–$TiO_2$ were successfully synthesized on the glass substrate by the spin coating process. The morphology of the produced thin film might be controlled via different proportion of $AgNO_3$ in the direction of $TiO_2$ in the solution of which prepared previously. The liberation time of Ag+, increase the silver concentration in the samples lead to excellent raise in the cytotoxicity of the composite thin films will be extended by different Ag loadings with $TiO_2$. The regular distribution of the silver nanoparticles was discovered and entirely joint to the $TiO_2$ matrix. The synthesis process steps are not complex, suitable and inexpensive.

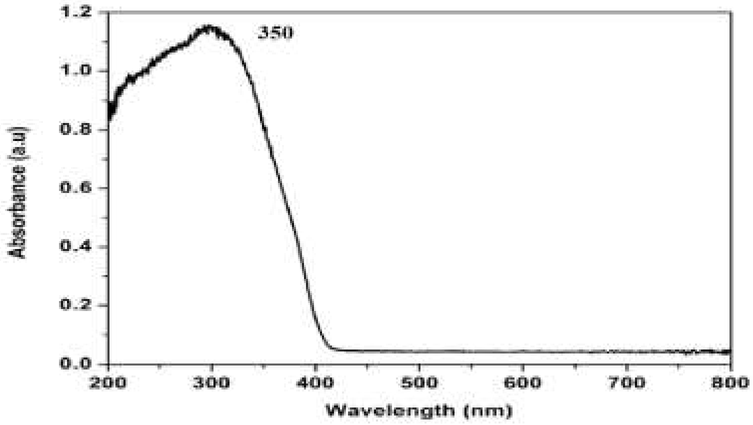

**Figure.1 UV–Vis spectrum of Ag–$TiO_2$ thin film for molar ratio 25:1.**

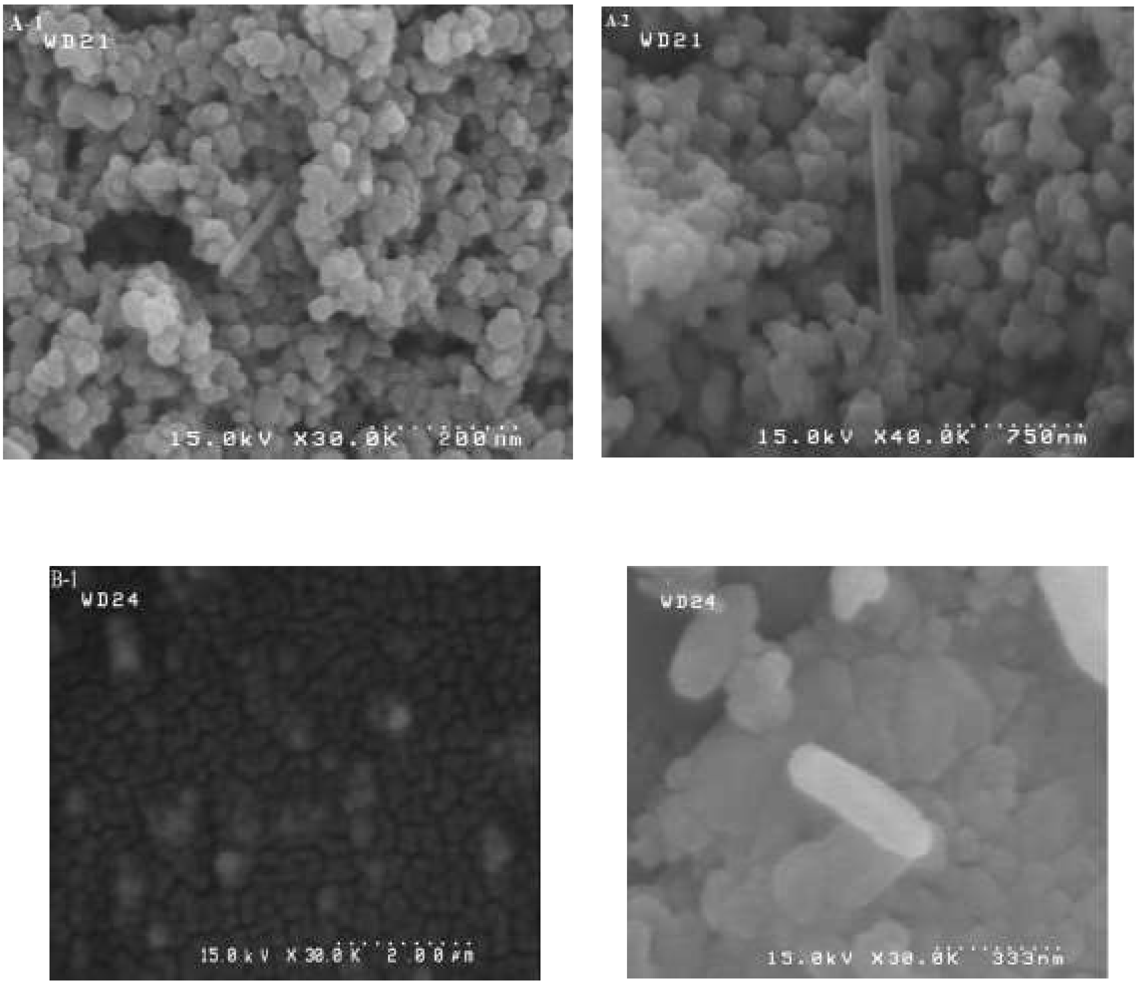

**Figure.2 SEM images of Ag–$TiO_2$ thin film at different molar ratio: A. 25:1 Ag/$TiO_2$, B. 5:1 Ag/$TiO_2$ thin films.**

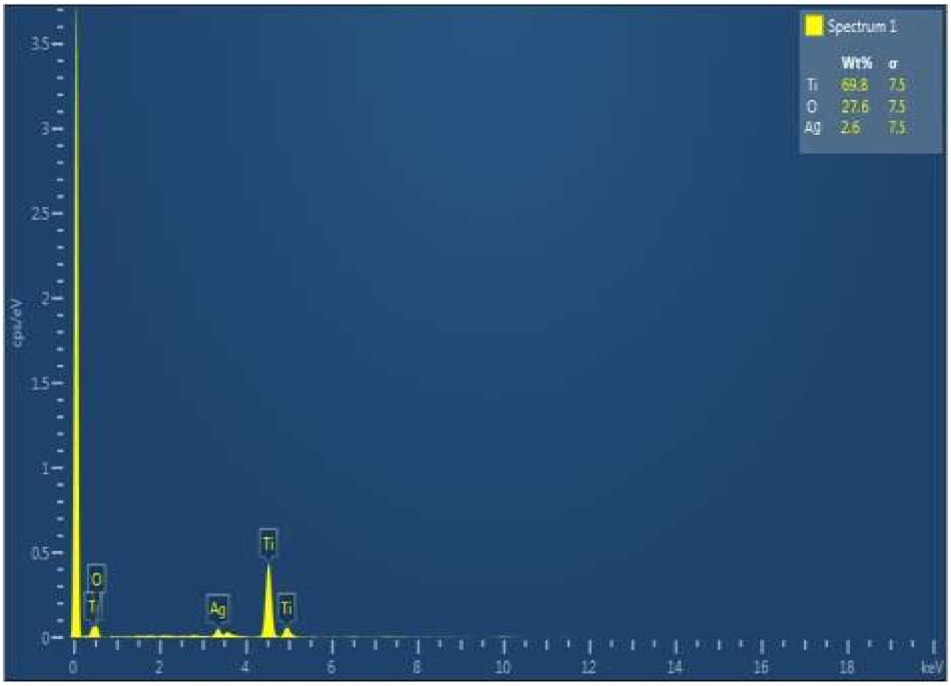

**Figure.3 Elemental analysis of Ag–$TiO_2$ thin film molar ratio 25:1.**

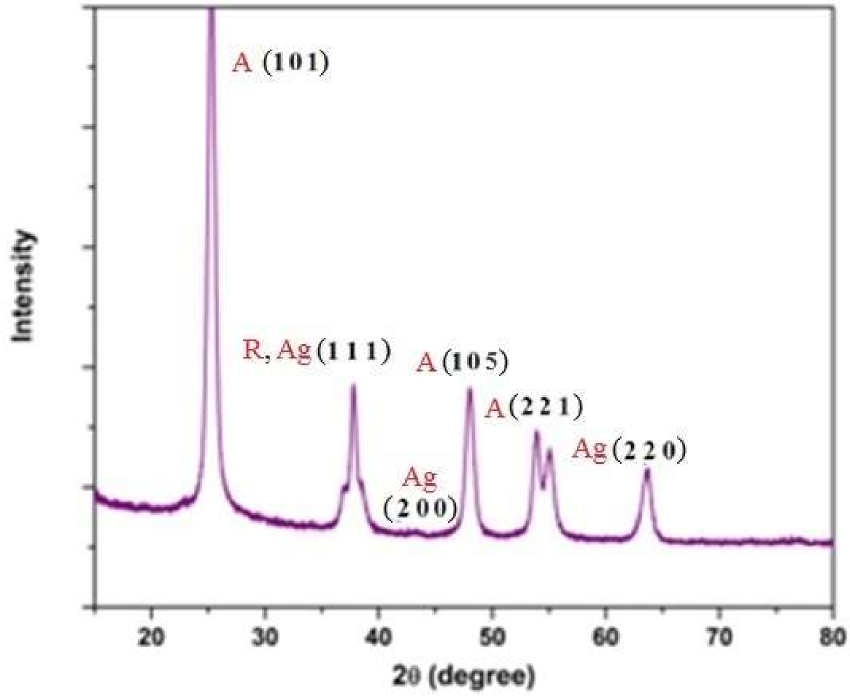

**Figure.4 The XRD analysis of Ag–$TiO_2$ thin film for molar ratio 25:1. A: anatase phase, R: rutile phase and Ag: metal silver.**

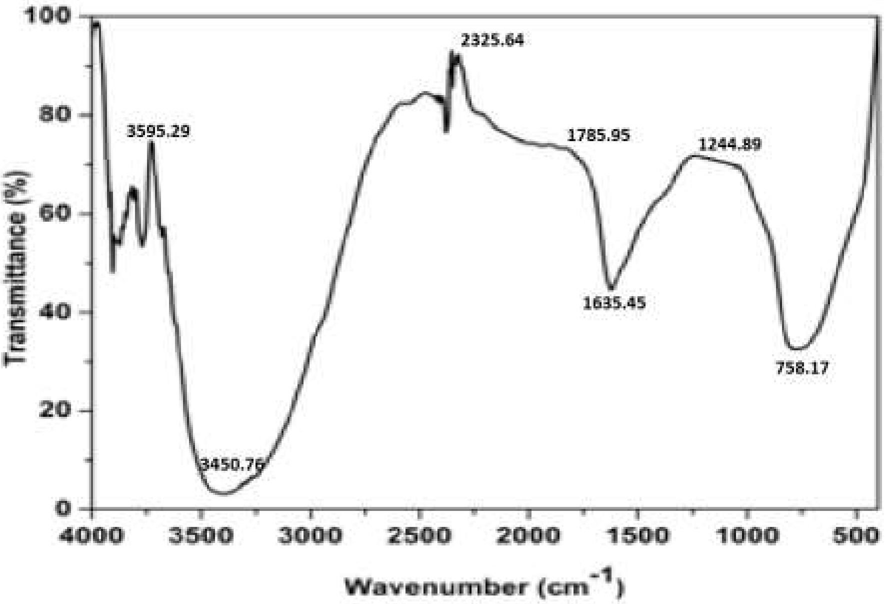

**Figure.5 FTIR spectrum of Ag–$TiO_2$ nanocomposite for molar ratio 25:1**

## REFERENCES

[1]. B. Yu. et a.l, "Synthesis of Ag–$TiO_2$ composite nano thin film for antimicrobial application", Nanotechnology, vol. 22, 115603, (9 pp.), 2011.

[2]. Siddhartha Shrivastava, Tanmay Bera, Arnab Roy, Gajendra Singh, P Ramachandrarao and Debabrata Dash, "Characterization of enhanced antibacterial effects of novel silver nanoparticles", Nanotechnology, 18225103, (9 pp.), 2007.

[3]. Bogdan et al., "Chances and limitations of nanosized titanium dioxide practical application in view of its physicochemical properties", Nanoscale Research Letters, Vol. 10, (10 pp.), 2015.

[4]. Alex Omo Ibhadon, and Paul Fitzpatrick, "Heterogeneous Photocatalysis: Recent Advances and Applications", Catalysts, 3, pp. 189-218, March 2013.

[5]. Thomas Verdier 1, Marie Coutand, Alexandra Bertron and Christine Roques, "Antibacterial Activity of $TiO_2$ Photocatalyst Alone or in Coatings on E. coli: The Influence of Methodological Aspects ", Coatings, Vol. 4, pp. 670-686, 2014.

[6]. Yoshio Nosaka and Atsuko Y. Nosaka, "Fundamentals: Active Species, Mechanisms, Reaction Pathways", 1st Edition. Germany. Wiley-VCH Verlag GmbH & Co. KGaA, 2013.

[7]. Anh Nguyen, Linda Zou, Craig Priest, "Evaluating the antifouling effects of silver nanoparticles regenerated by $TiO_2$ on forward osmosis membrane", Journal of Membrane Science, vol. 454, pp. 264–271, 2014.

[8]. Carlos A. Martinez-Huitle and Sergio Ferro, "Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes", Chem. Soc. Rev., Vol. 35, pp. 1324–1340, 2006.

[9]. Gang Liu, Lianzhou Wang, Hua Gui Yang, Hui-Ming Cheng and Gao Qing (Max) Lu, "Titania-based photocatalysts—crystalgrowth, doping and heterostructuring", J. Mater. Chem., Vol. 20, pp. 831–843, 2009.

[10]. Y. Liu, C.Y. Liu, J.H. Wei, R. Xiong, C.X. Pan, J. Shi, "Enhanced adsorption and visible-light-induced photocatalytic activity of hydroxyapatite modified Ag–$TiO_2$ powders", Applied Surface Science, Vol. 256 , pp.6390–6394, 2010.

[11]. Soumit S. Mandal and Aninda J. Bhattacharyya, "Electrochemical sensing and photocatalysis using Ag–$TiO_2$ microwires", J. Chem. Sci. Vol. 124, No. 5, pp. 969–978, 2012.

[12]. Sundaramurthy J., Li, N., Kumar P.S., Ramakrishna, S., "Perspective of electrospun nanofibers in energy and environment ", Biofuel Research Journal, vol. 2, pp. 44- 54, 2014.

[13]. Erik Unosson, "Antibacterial Strategies for Titanium Biomaterials", Ph.D. Dissertation, Department of Engineering Sciences, Applied Materials Sciences, Uppsala University, Sweden, 2015.

[14]. Thanaa I. Shalaby, Ola A. Mahmoud, Gihan A. El Batouti, Ebtihag E. Ibrahim, "Green Synthesis of Silver Nanoparticles: Synthesis, Characterization and Antibacterial Activity", Nanoscience and Nanotechnology, Vol. 5, No. 2, pp. 23-29, 2015.

[15]. Halah H. Rashed, "Silver Nanoparticles Prepared by Electrical Arc Discharge Method in DIW", Eng. & Tech. Journal, Vol.34, No.2, 2016.

[16]. Tamasa Panigrahi, "Synthesis and Characterization of Silver Nanoparticles using leaf extract of Azadirachta indica", M.Sc. Thesis, National Institute of Technology, India, 2013.

[17]. Mahendra Ra, Nelson Duran, "Book of Metal Nanoparticles in Microbiology". Berlin. Springer Heidelberg. 2011.

[18]. Bogumiła Reidy, Andrea Haase, Andreas Luch , Kenneth A. Dawson and Iseult Lynch, " Mechanisms of Silver Nanoparticle Release, Transformation and Toxicity: A Critical Review of Current Knowledge and Recommendations for Future Studies and Applications ", Materials, Vo. 6, No. 6, pp. 2295-2350, 2013.

[19]. V.K. Sharma et al., "Silver nanoparticles: Green synthesis and their antimicrobial activities", Advances in Colloid and Interface Science, 145, pp. 83–96, 2009.

[20]. Victor Elias Torres Heredia, "Silver Nanostructures: Chemical Synthesis of colloids and composites nanoparticles, plasmon resonance properties and silver nanoparticles monolayer films prepared by spin-coating", Ph.D. Thesis, Universidad Politécnica de Catalunya, Spain, 2011.

[21]. Y.Q. Liang et al., "Silver nanoparticles supported on $TiO_2$ nanotubes as active catalysts for ethanol oxidation", Journal of Catalysis, vol. 278, pp. 276–287, 2011.

[22]. Quan Chen, Chris Boothroyd, Andrew Mcintosh Soutar, Xian Ting Zeng, "Sol–gel nanocoating on commercial $TiO_2$ nanopowder using ultrasound", J Sol-Gel Sci Technol, Vol. 53, Issue 1, pp 115-120, 2009.

[23]. Qusay J.Rasheed, "Synthesis and Optimization of Nisin-Silver Nanoparticles at Different Conditions", Eng. & Tech. Journal, Vol.33, No.2, 2015.

[24]. Lopez Goerne et al., "Study of Bacterial Sensitivity to Ag-$TiO_2$ Nanoparticles", J Nanomed. Nanotechol. , 2012.

[25]. K. Mani Rahulan, N. Padmanathan, L. Devaraj Stephen and Charles Christopher Kanakam, "Structural features and existence of three photon absorption in Ag doped TiO2 nanoparticles, synthesized by sol-gel technique", Journal of Alloys and Compounds, Vol.554, pp.432-437, 2013.