EFFECT OF AG DOPED ON PHOTOCATALYTIC AND ANTIBACTERIAL ACTIVITY OF TIO_2 THIN FILMS

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ABSTRACT

In the present study, The Ag-doped TiO_2 thin films)0, 0.5 and 1 mol% of Ag (coated on glass slide prepared by microwave-assisted sol-gel route .The microstructures of the fabricated thin films were characterized by SEM, XRD, EDS and AFM techniques, and the results showed that all samples were anatase and rutile phase .The photocatalytic activities of the Ag-doped TiO_2 thin films were also tested via the degradation of MB solution under UV irradiation and the results were compared with pure TiO_2 .The antibacterial activity of Ag-doped TiO_2 thin films was assessed by spread plate method against *E.coli* as test bacteria under UV irradiation and the results were compared with pure TiO_2 .The results show that Ag-doped TiO_2 thin films exhibits greater photocatalytic and antibacterial activity than those of pure TiO_2 .It was found that the bacterial inactivation of the prepared Ag-doped TiO_2 thin films correlates closely to photocatalytic activity preformed by degradation of MB solution .In addition, 1%Ag-doped TiO_2 thin films showed photocatalytic and antibacterial activities at 81.43 and 91.02%, respectively.

KEYWORDS: Ag-doped TiO_2 thin films, Microwave-assisted sol-gel method, Photocatalytic activity, Antibacterial activity

1. Introduction

Titanium dioxide (TiO_2) is a semiconductor photocatalyst and exists in three main phases including anatase, rutile, and brookite [1-2] (Figure 1). Nowadays, TiO_2 is used in wide application in photocatalyst such as self-cleaning surfaces, antibacterial, solar cells, air and water purification, gas sensing, and optical coating [2-3] because of its high activity, chemical stability, low toxicity no-twain pollution, and low cost [1, 4-5]. TiO_2 processes of photocatalytic degradation and antibacterial properties due to its strong oxidation activity in the presence of light and the generation of reactive oxygen species such as hydroxyl radicals (OH), hydrogen peroxide (H_2O_2), and superoxide ions (O_2·-) from photocatalytic reaction [1]. The photocatalytic and antibacterial activity of TiO_2 nanoparticles depends not only on the properties of the TiO_2 material itself, but also on the modification of TiO_2 with metal or metal oxide. Previous studies reported that the addition of Ag in TiO_2 enhances its photocatalytic and antibacterial efficiency [6].

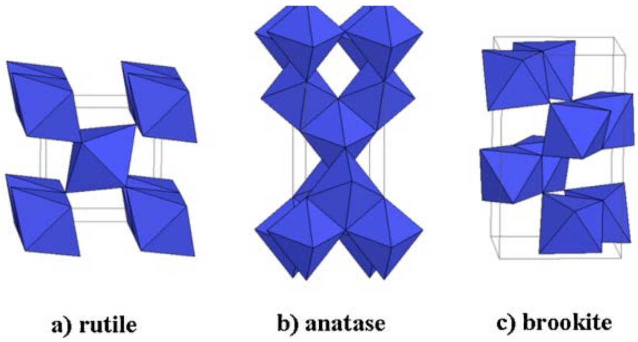

Figure 1 The crystal of TiO_2 a) rutile, b) anatase and c) brookite [7].

TiO_2 thin films have been synthesized by a variety of techniques. The sol-gel method has emerged as one of the most promising process as it is particularly efficient in producing thin, transparent, homogenous, multi component oxide layers of many compositions on various substrates at low cost and it allows the choice of refractive index and thickness of the layer by changing preparation conditions [8]. In the last few years, microwave irradiation has been reported to effectively enhance the efficiency of sol-gel method on the preparation of inorganic materials. The microwave-assisted sol-gel method has unique advantages of uniform and rapid heating in comparison with the conventional one. In addition, this method can significantly reduce the processing time and simplify the preparation procedures as well as improve the nanometer size fraction of particles. In addition, the method saves energy and appears today as a new technology for green chemistry development by means of solvent-free and/or less reactant needed. Recently, the microwave-assisted method has been used to synthesize different morphologies of TiO_2 product [9].

In this paper, Ag-doped TiO_2 thin films coated on glass slide prepared by microwave-assisted sol-gel method. The physical properties of the prepared thin films are characterized by SEM, XRD, EDS and AFM techniques. The influence of the irradiated photo catalyst Ag-doped TiO_2 thin films on degradation of methylene blue (MB, $C_{16}H_{18}N_3S$) in aqueous system is studied. Finally, different amount of Ag doping in TiO_2 were used to observe their antibacterial activities of *E.coli* which will determine their performance as antibacterial material.

2. Experimental procedure

2.1 Materials and Reagent used

Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP, Sigma-Aldrich, reagent grade) was used as titanium precursor and silver nitrate ($AgNO_3$, Chem-supply, reagent grade) was taken as Ag precursor. TTIP was taken as titanium precursor because of its lower reactivity with atmosphere compared to other titanium source precursor. Ethanol (C_2H_5OH, RCL labscan limited), Nitric acid (HNO_3, J.T. Baker) and water were used as reagents in the present study.

2.2 Synthesis of Ag-doped TiO_2 thin films

Based on our previous studies [9], Ag-doped TiO_2 thin films were prepared via microwave-assisted sol-gel method. Firstly, $AgNO_3$ were varied as follows: 0, 0.5 and 1 mol%, respectively and TTIP, C_2H_2OH with fixed at 10 and 150 ml and with were mixed into 250 ml of water, and the mixture was vigorously stirred (1,000 rpm) at room temperature for 15 min. The solution was acidified to pH = 3 by adding few droplets of 3 M HNO_3 into the solution and stirred for 45 min. Finally, the treated solution was refluxed at 180 W for 3 h using a domestic microwave oven (Samsung, ME82V) to produce a milky solution. The thin films deposition onto glass slide substrate was performed by dip-coater using a withdrawal speed adjusted at 1.25 mm/s. Before coating, glass slide was ultrasonically cleaned in acetone (C_3H_{60}) and then dipped in absolute ethanol for 5 min, after which a thorough wash was carried out. The coated thin films were dried at 180 W for 1 h using a domestic microwave oven. Ag-doped TiO_2 thin films were designated as TP, T0.5Ag and T1Ag of various mol ratios of Ag to TiO_2 were 0, 0.5 and 1 mol%, respectively.

2.3 Characterization technique

The crystal structure was analysed by X-ray diffraction (XRD) on DMAX-2400 (X'Pert MPD, PHILPS, Netherlands, Cu Kα = 0.15406 nm) radiation at 56 kV and 182 mA with a secondary graphite crystal monochromator. The average crystallite size of the samples was determined using Scherrer's equation [10]. The morphologies were observed by a scanning electron microscopy (SEM, Quanta 400, FEL, Czech Republic). Energy dispersive spectroscopy (EDS) device coupled with SEM was used to determine the purity and composition of the prepared materials. Finally, the microstructure and roughness for Ag-doped TiO_2 thin films ware observed by atomic force microscopy (AFM, SPA400, SEIKO).

2.4 Evaluation of photocatalytic activity

The prepared Ag-doped TiO_2 thin films were used to decolorized the MB solution under UV irradiation (eleven 50 W of black light lamps). The photocatalytic course and setup were the same as previously described [1]. The Ag-doped TiO_2 thin films (size of 25x25 cm) were mixed in 10 ml and concentration was $1x10^{-5}$ M of MB solution. The suspension was stirred in dark conditions for 60 min to equilibrium system. After that the suspension were illuminated under UV irradiation for 3 h. 2 ml of the solution was kept every 30 min after UV illumination to determine the degradation performance of TiO_2 photocatalyst using a UV-Vis spectrophotometer (GENESYS™ 10S). The final efficiency was calculated by the following equation: E_t (%) = $(1-C_t/C_0)$ x 100, where C_0 and C_t stand for the concentration of reactants at initial and at a certain irradiation time, respectively.

2.5 Evaluation of antibacterial performance

The antibacterial effect of Ag-doped TiO_2 thin films was prepared the same as previously described [1, 11]. The antibacterial activity of Ag-doped TiO_2 thin films against the bacteria *Escherichia coli (E.coli)* were prepared by used 1 ml of 10^3 CFU/ml concentration of *E.coli* dropped on thin films (size of 2.5x2.5 cm) that placed in Petri dish plate and then exposed to either UV irradiation (eleven 50 W of black light lamps) for 0 to 60 min. Then, 0.1 ml of mixture suspension was sampled and spread on nutrient agar (NA) plate and incubated at 37°C for 24 h. After incubation, the number of viable colonies of *E.coli* on each NA plate was observed and disinfection efficiency of each test was calculated in comparison to that of the initial or control as following equation: M_t (%) = (1-N_t/N_0) x 100, where N_0 and N_t are the average of live bacterial cells at initial and at a certain irradiation time, respectively.

3. Result and Discussion

3.1 Characterization

Figure 2 shows the XRD spectra of pure TiO_2 (TP) and as-synthesized Ag-doped TiO_2 samples with different amount of Ag (T0.5Ag and T1Ag), respectively. For both TiO_2 and Ag-doped TiO_2, a series of characteristic peak at 25.2° (1 0 1), 37.9° (0 0 4), 47.9° (2 0 0) and 62.6° (2 0 4) are observed that are index to anatase TiO_2 (JCPDS file No. 21-1272) and the peak 56.6° (2 2 0) belong to rutile TiO_2 (JCPDS file No. 21-1276) [12]. However, no peaks of Ag could be observed for Ag-doped TiO_2 sample, probably due to the low content of silver in this composites photocatalyst which is below the detection limit of XRD technique. The average crystallite sizes of the Ag-doped TiO_2 samples determined from FWHM by using Scherrer's formula were estimated to be 20.7 nm, 16.8 nm and 13.8 nm for TP, T0.5Ag and T1Ag, respectively. It was apparent that Ag added in TiO_2 has significant effect on crystallite size. The crystallite size of anatase phase decreased with an increased Ag doping. The smallest crystallite size was observed from 1%Ag-doped TiO_2 thin films.

The EDS spectrum image taken from the T1Ag sample is presented in Figure 3, where the presence of Ag, Ti and O atoms derived from Ag-doped TiO_2 thin films is shown. The surface and cross-section morphology of the Ag-doped TiO_2 thin films was studied using SEM as showed in Figure 4. Based on the existing scale, the average thickness of all thin films is about 0.1-0.5 μm compared with glass slide. Figure 5 show the surfaces roughness of Ag-doped TiO_2 thin films are 2.715, 3.521 and 4.467 nm for 0, 0.5, and 1 mol% of Ag doping, respectively. It was found that the surfaces roughness increases when doping Ag in TiO_2 thin films and surfaces roughness increases with an increase in Ag doping due to the contribution of Ag effect. It was found that the highest surfaces roughness was observed from 1%Ag-doped TiO_2 thin films.

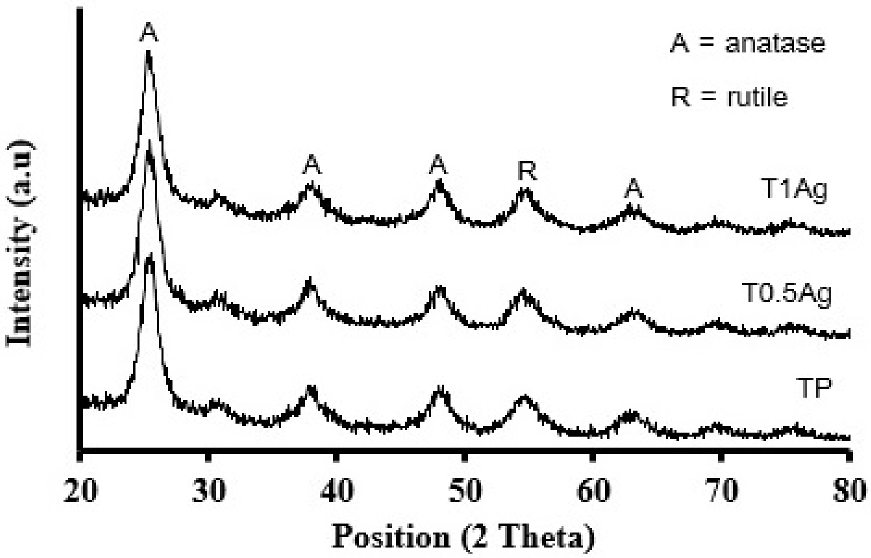

Figure 2 **XRD spectra of Ag-doped TiO_2 sample.**

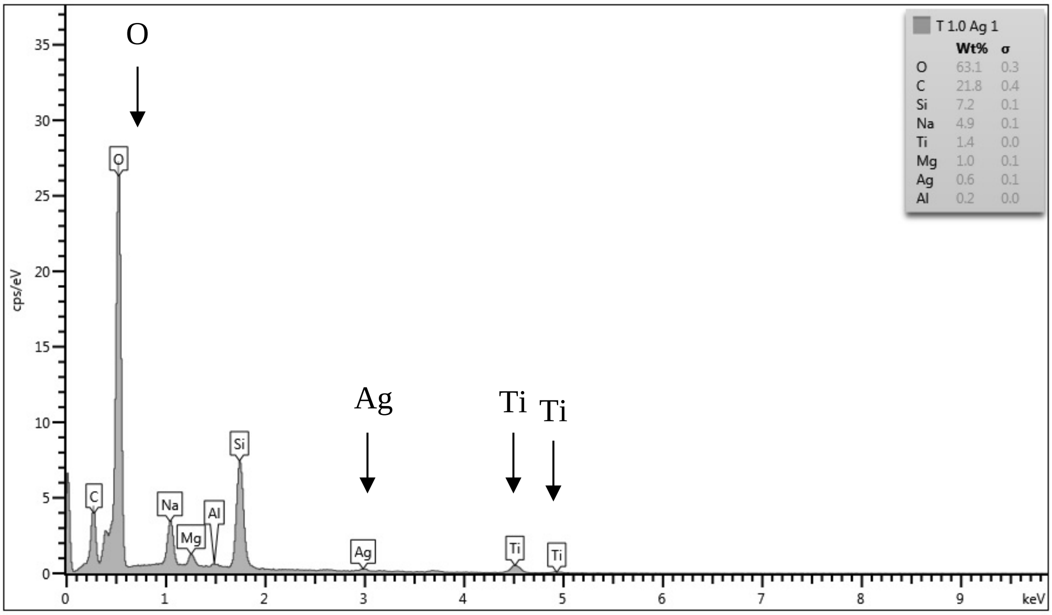

Figure 3 **EDS spectra image of 1%Ag-doped TiO_2 thin films.**

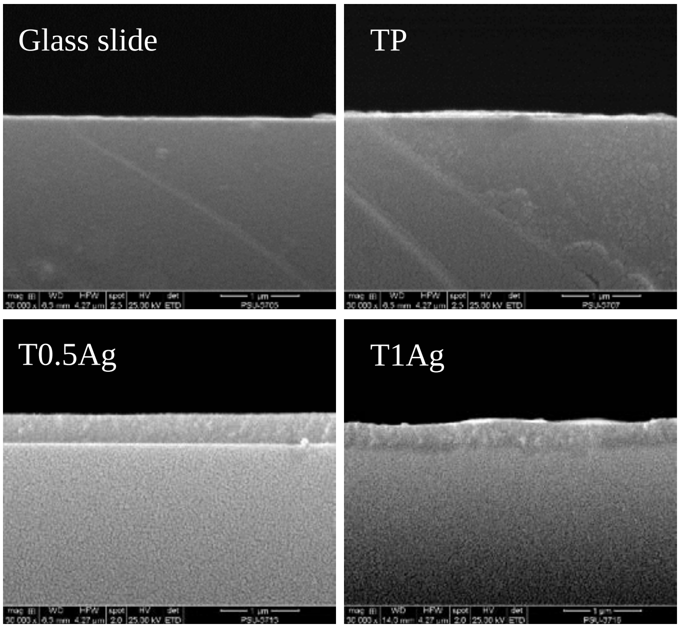

Figure 4 **The morphology of glass slide and Ag-doped TiO_2 thin films.**

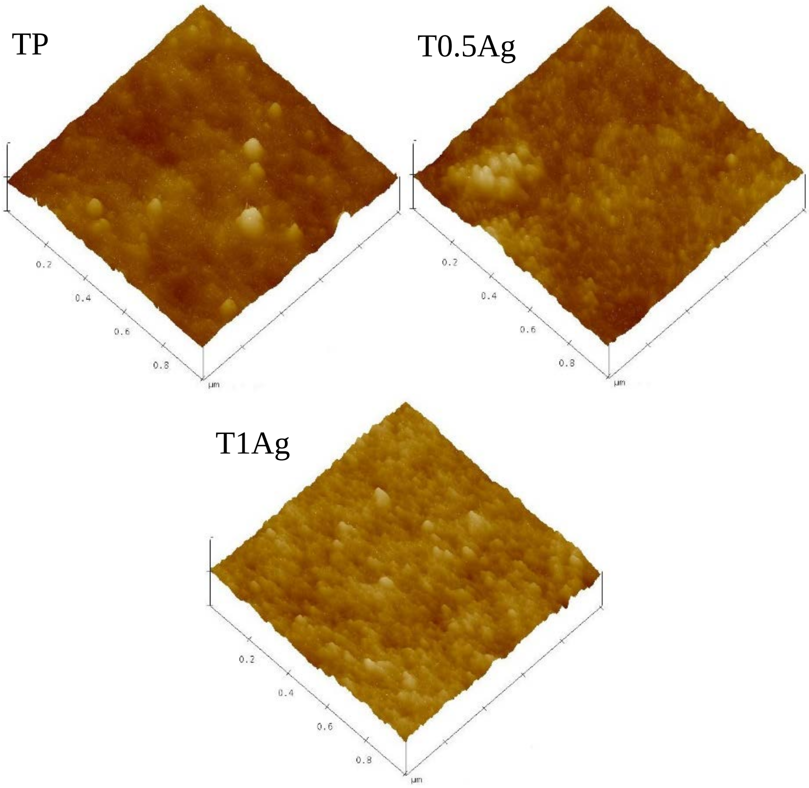

Figure 5 **AFM image of Ag-doped TiO_2 thin films.**

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using Ag-doped TiO_2 thin films under UV irradiation is show in Figure 6. It was apparent that Ag added in TiO_2 has significantly effect on photocatalytic reaction under UV irradiation compared with undoped Ag (pure TiO_2, TP). For Ag-doped TiO_2 thin films, it was found that the photocatalytic activity increases with increases Ag doping due to a small of crystallite size of anatase phase and high surfaces roughness. The photocatalytic reaction of Ag-doped TiO_2 thin films under UV irradiation for 3 h are 0.48, 0.32 and 0.19 for Ag doping with 0, 0.5 and 1 mol% thin films respectively. The MB degradation percentage of thin films under UV irradiation is shown in Figure 7. It was found that MB degradation percentage of thin films under UV irradiation for 3 h are 51.77, 68.30 and 81.43% for 0, 0.5 and 1 mol% of Ag doping, respectively. It was found that 1%Ag-doped TiO_2 thin films show the best photocatalytic activity under UV irradiation.

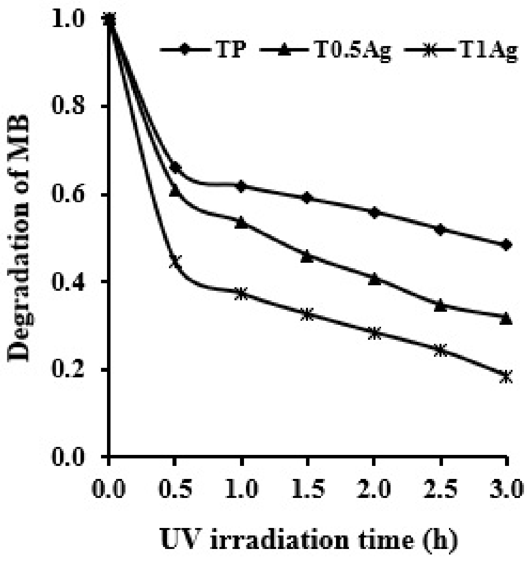

Figure 6 The photocatalytic activity of Ag-doped TiO_2 thin films.

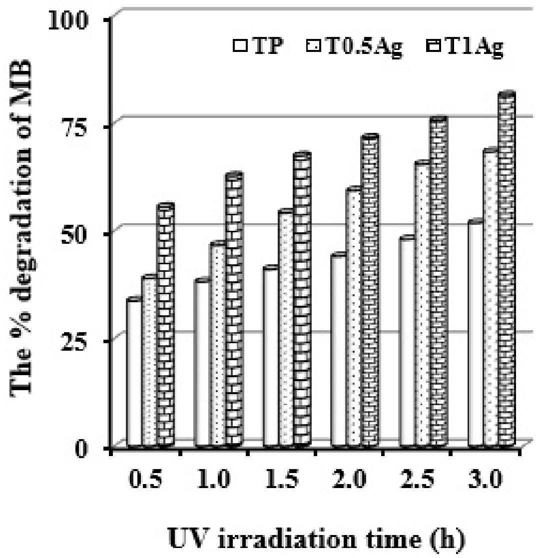

Figure 7 The MB degradation percentage of Ag-doped TiO_2 thin films.

3.3 Antibacterial activity

The antibacterial activity of Ag-doped TiO_2 thin films were investigated against *E.coli* bacteria under UV irradiation, as presented in Figure 8-9. For Figure 8 displays the *E.coli* survival rate after testing with UV irradiation on Ag doping on TiO_2 thin films. The result shows that the *E.coli* survivals decrease with UV irradiation time. The *E.coli* survival rate of Ag-doped TiO_2 thin films under UV irradiation for 60 min are 0.38, 0.20 and 0.09 for Ag doping with 0, 0.5 and 1 mol% thin films respectively. It also indicates that the TiO_2 doped Ag with 1 mol% thin films exhibit higher antibacterial activity compared to 0.5%Ag-doped TiO_2 and pure TiO_2 thin films, respectively (T1Ag>T0.5Ag>TP). The *E.coli* kill percentage of Ag-doped TiO_2 thin films under UV irradiation is shown in Figure 9. It is seen that the percentage bacterial reduction or *E.coli* kill percentage increased at the presence of Ag-doped TiO_2 thin films. The pure TiO_2 thin films showed a weak *E.coli* kill percentage under UV irradiation while introducing Ag to TiO_2 matrix led to increase in *E.coli* kill percentage. By increasing the Ag concentration in TiO_2 matrix antibacterial activity enhances remarkably. The *E.coli* kill percentage of Ag-doped TiO_2 thin films under UV irradiation for 60 min are 61.72, 80.05 and 91.02% for TiO_2 doped Ag with 0, 0.5 and 1 mol% thin films, respectively. It was found that 1%Ag-doped TiO_2 thin films show the best antibacterial activity under UV irradiation.

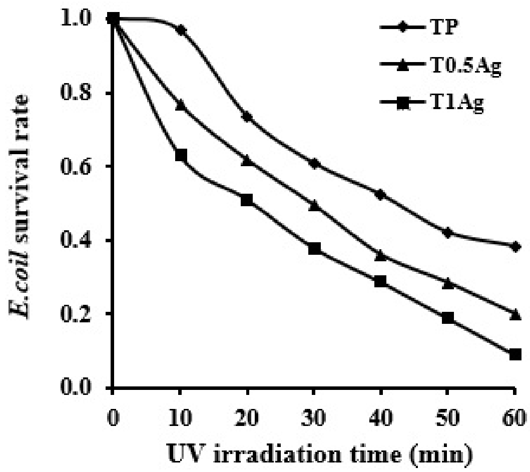

Figure 8 **The antibacterial activity of Ag-doped TiO_2 thin films.**

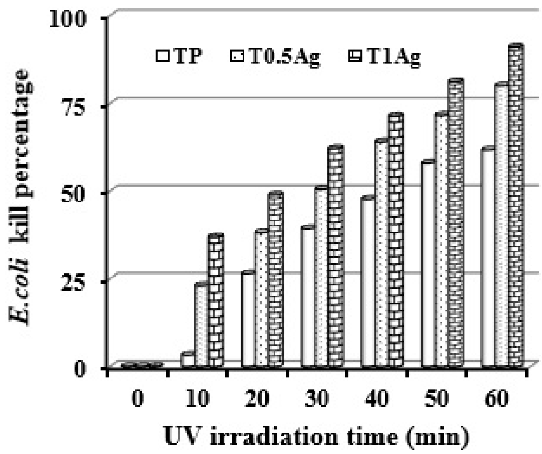

Figure 9 **The *E.coli* kill percentage of Ag-doped TiO_2 thin films.**

The photo of viable bacterial colonies on synthesized Ag-doped TiO_2 thin films treated with UV irradiation for 0, 20, 40 and 60 min are illustrated in Figure 10. It is very obvious that the cell walls and cell membranes were damaged when microbial cells came into contact with Ag-doped TiO_2 thin films being activated by UV irradiation. In this sense, the photo-generated hydroxyl (OH°) and super oxygen (O_2^-) radicals acted as powerful oxidizing agents which react with peptidoglycan (poly-*N*-acetylglucosamine and *N*-acetylmuramic acid) of bacterial cell wall [11].

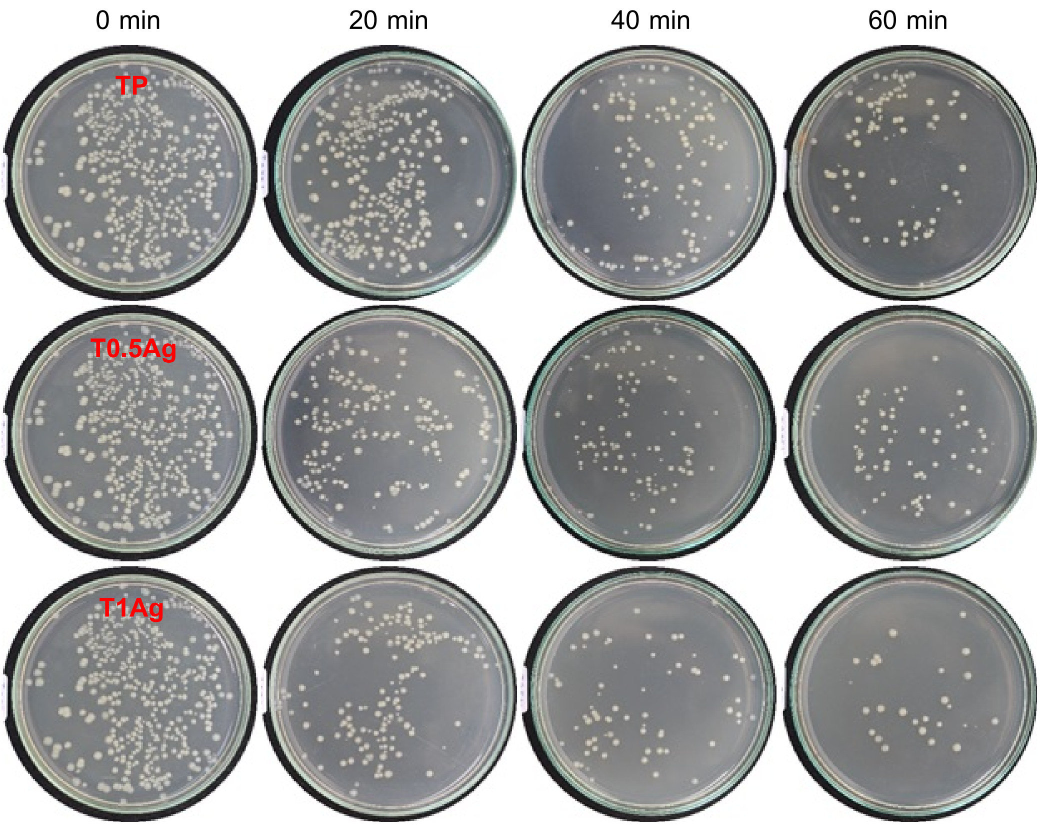

Figure 10 Photo of viable *E.coli* colonies on synthesized Ag-doped TiO_2 thin films.

4. Conclusions

In this work, Ag-doped TiO_2 thin films were prepared by microwave-assisted sol-gel method and dipped coating on glass slide. All thin films were characterized by XRD, SEM, EDS and AFM technique. The photocatalytic activity was determined by means of degradation of MB solution and antibacterial activity was evaluated by the inactivation of *E.coli* bacteria. It was found that Ag affects to phase, morphology, photocatalytic activity and antibacterial of *E.coli* activity on TiO_2 thin films. It can be note that 1%Ag-doped TiO_2 thin films have highest photocatalytic and antibacterial activity at 81.43 and 91.02%, for under UV irradiation 3 h and 60 min, respectively.

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