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The Photocatalytic and Antibacterial Activity of Cu-Doped TiO_2 Thin Films

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Abstract

Thin films of TiO_2 and TiO_2 doped with Cu were prepared by sol-gel method. The prepared films were calcined at the temperature of 400 °C for 2 h with the heating rate of 10 °C/min. Physical properties as well as crystal compositions of the fabricated films were characterized by XRD, EDX SEM and AFM techniques. The results show that all samples have thickness range from 0.25 to 1.0 um. The film surfaces are typically uniform and dense with TiO_2 nanoparticles. The photocatalytic activities of the thin films were also tested via the degradation of methylene blue (MB) solution under UV irradiation. Finally, antibacterial activity efficiency was evaluated by the inactivation of *E.coli*. It was observed that higher Cu concentration gives better photocatalytic activity. With the highest dopant concentration investigated in this experiment (TiO_2-1.0Cu condition) the films show photocatalytic of 70 % and antibacterial activity of 100 %.

Keywords: TiO_2, thin films, photocatalytic activity, antibacterial activity, Cu dope

Introduction

In daily life, human beings are often infected by microorganisms like bacteria, mold, viruses, and so on. To impart sterility (e.g. hospital trays) and avoid infection (e.g. wound dressing), the use of antimicrobial agents is important [1]. Research has been intensively carried out in antibacterial materials containing various natural and inorganic substrates [2]. At present, a novel antibacterial technique of photocatalytic activity of Titanium dioxide (TiO_2) has attracted considerable attention since it has low cost, high photocatalytic activity, chemical stability and harmless side effect [3]. There are three types of TiO_2 crystal structure: anatase, rutile and brookite. The anatase crystalline TiO_2 has been found to be the most active photocatalyst due to the slow recombination rate of exited electron and hole compared to that of rutile and brookite. The photocatalytic activity of TiO_2 greatly depends upon its microstructure and physical properties due to different preparation conditions and methods. In general, TiO_2 is often used in two forms, i.e. powder or thin film. TiO_2 thin film can be prepared by several methods such as sol-gel [4-5], electrochemical deposition [6] and chemical vapor deposition (CVD) [7]. The sol-gel method has recently been developed as a general and powerful approach for preparing inorganic materials such as ceramics and glasses. In this method, a soluble precursor molecule is hydrolyzed to form a colloidal dispersion (the sol). Further reaction causes bonds to form among the sol particles, resulting in an infinite network of particles (the gel). The gel is typically heated to yield the desired material. The sol-gel method has advantages over conventional methods of synthesis. For example, high-purity materials can

be synthesized at low temperatures [8-9]. In addition, homogeneous multi-component systems can be obtained by mixing precursor solutions, which allows easy control of chemical doping for the prepared materials.

In the recent years, many studies have been devoted to further improve the photocatalytic and antibacterial properties of TiO_2 thin films, and the investigations suggest that those properties can be enhanced by doping with transition metal such as Ag [10], Fe^{3+} [11], N [12] and Cu [13-14], which has also been investigated widely aiming at extending photocatalytic activity and antibacterial into the UV region. In this work, thin films of Cu-doped TiO_2 coated on glass slides were prepared by sol-gel and followed by dip coating process. Based on our previous studies, the amount of Cu in the range of 0 to 1 mol% of TiO_2 is carried on. The effect of the Cu doping into TiO_2 thin films on the microstructure photocatalytic activity and antibacterial behavior were investigated.

Materials and methods

Raw materials

Titanium (IV) isoproxide (TTIP, 99.95 %, Fluka Sigma-Aldrich), and copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) were used as raw materials. Ethanol (C_2H_5OH, 99.9 %, Merck Germany) was used as a solvent.

Thin films preparation

TiO_2 and TiO_2 doped with Cu (TiO_2-Cu) thin films were prepared via sol-gel method. Firstly, $Cu(NO_3)_2.3H_2O$ to maintain the mole ratio of Cu in the TiO_2 at 0, 0.2, 0.6 and 1 mol% of TiO_2. TTIP with fixed volume at 10 ml were mixed into 150 ml of ethanol and the mixture was then vigorously stirred at room temperature for 15 min. The pH of the mixed solution was adjusted to about 3 - 4 by adding 3 ml of 2 M nitric acid (HNO_3). Finally, it was vigorously stirred at room temperature for 30 min until clear sol was formed. To fabricate TiO_2 and TiO_2-Cu thin films the sol were deposited on glass substrates by dip-coating process at room temperature with the drawing speed of dip-coater of about 1.25 mm/s. The coated specimens were then left to dry at room temperature for 24 h and calcined at the temperatures of 400 °C for 2 h with a heating rate of 10 °C/min.

Thin films characterization

The morphology and particle size of the fabricated thin films were characterized by Scanning Electron Microscope (SEM) (Quanta 400). Surface roughness of thin films was measured by atomic force microscope (AFM) for an area of 1×1 μm^2. The phase composition was characterized using an x-ray diffractometer (XRD) (Phillips X'pert MPD, Cu-K). The crystallite size was calculated by the Scherer equation, Eq. (1), [15].

$$D = 0.9\,\lambda / \beta \cos\theta_B \quad (1)$$

where D is the average crystallite size, λ is the wavelength of the Cu K_α line (0.15406), θ is the Bragg angle and β is the full-width at half-maximum (FWHM) in radians.

Photocatalytic activity test

The photocatalytic activity was evaluated by the degradation of MB molecules under the UV irradiation using eleven of 50W black lamps. Thin film with an area of 26 × 30 cm^2 was soaked in MB solution, 4 ml with 1×10^{-6} M/L concentration, and kept in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. After being centrifuged, the supernatant solutions were measured for the MB absorption at 665 nm using a UV-vis spectrophotometer (GENESYS™10S). The percentage degradation of the MB molecules was calculated by Eq. (2), [15].

$$\text{Percentage of degradation} = 100(C_0\text{-}C)/C_0 \quad (2)$$

where C_0 is the concentration of MB aqueous solution at the beginning (1×10^{-6} M) and C is the concentration of MB aqueous solution after exposure to a light source.

Antibacterial activity test

Antibacterial activity of TiO_2 and TiO_2-Cu thin films against the bacteria *Escherichia coli* (*E. coli*) were studied. Firstly, 1 ml of 10^3 CFU/ml concentration of *E. coli* was dropped on thin film placed in a Petri dish plate and then exposed to UV irradiation for 0, 1, 2, 3 and 4 h. Afterward, the Petri dish plate was filled with Macconkey Agar and gently rotated to distribute the agar evenly, allowing the agar to harden (about 10 min). Finally, it was incubated at 37°C for 24 h. After

incubation, the number of viable colonies of *E. coli* on each Macconkey agar plate was observed and disinfection efficiency of each test was calculated in comparison to that of the control. Percentage bacterial reduction was calculated according to the following equation, Eq. (3), [16].

$$\text{Percentage of bacterial reduction} = 100(N_0\text{-}N)/N_0 \quad (3)$$

where N_0 and N are the average number of live bacterial cells per milliliter in the flask of the control and thin films finishing agent or treated fabrics, respectively.

Results and discussion

Thin films characterization

Figure 1 shows the XRD patterns of TiO_2 and TiO_2-Cu thin films. Peaks marked as "A" correspond to anatase. It is found that thin films reveal only the anatase phase. Cu-compound phase cannot be verified in these XRD peaks due to a very small amount of Cu doping. Anatase phase fraction in TiO_2-Cu thin films seems to decrease with an increase in Cu doping. The crystallite sizes of anatase phases are 44.2, 27.6, 10.3 and 9.2 nm for 0, 0.2, 0.6 and 1.0 mol% of Cu doping, respectively. It is clearly seen that the crystallite size decreases with the increase of Cu dopant concentration.

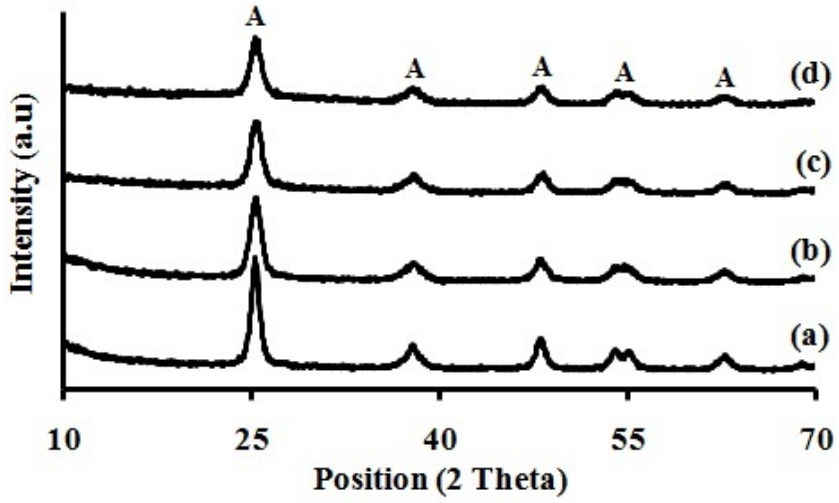

Figure 1 XRD patterns of (a) TiO_2, (b) TiO_2-0.2Cu, (c) TiO_2-0.6Cu and (d) TiO_2-1.0Cu thin films.

The presence of Cu and Ti in the TiO_2-Cu thin films was determined by EDX spectra and the result is shown in **Figure 2**, confirming the presence of the Ti and Cu composition in the films. The surface morphology was observed through SEM. **Figure 3** shows surface and cross-sectional morphologies of TiO_2 and TiO_2-Cu thin films. All TiO_2-Cu samples have the thickness in the range of 0.25 to 1.0 um.

AFM images taken from the thin films are displayed in **Figure 4**, revealing that the surfaces are uniform and dense with TiO_2-Cu nanocrystals. The surfaces roughness of TiO_2 and TiO_2-Cu thin films are 1.75, 1.61, 1.42 and 1.02 nm for 0, 0.2, 0.6 and 1.0 mol% of Cu doping, respectively. It is found that the surfaces roughness decreases with an increase in Cu doping due to the contribution of Cu effect.

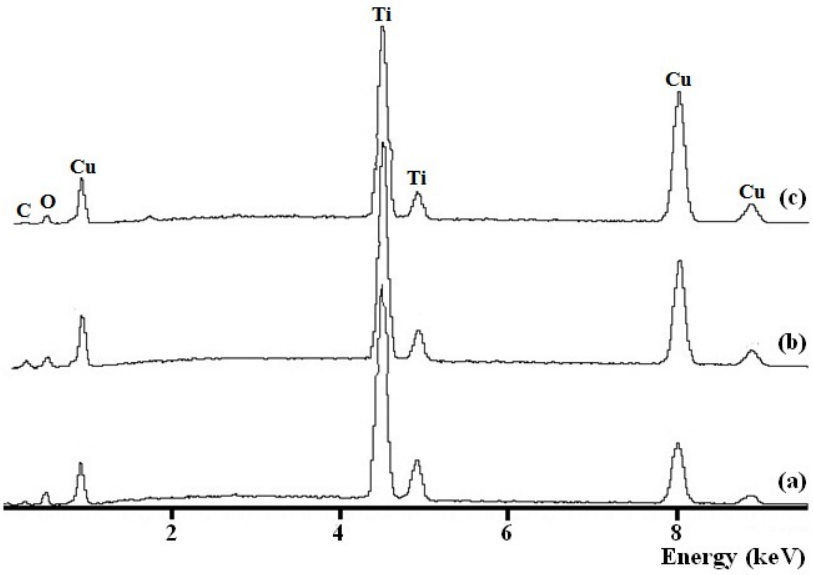

Figure 2 EDX spectra of (a) TiO_2-0.2Cu, (b), TiO_2-0.6Cu and (c) TiO_2-1.0Cu thin films.

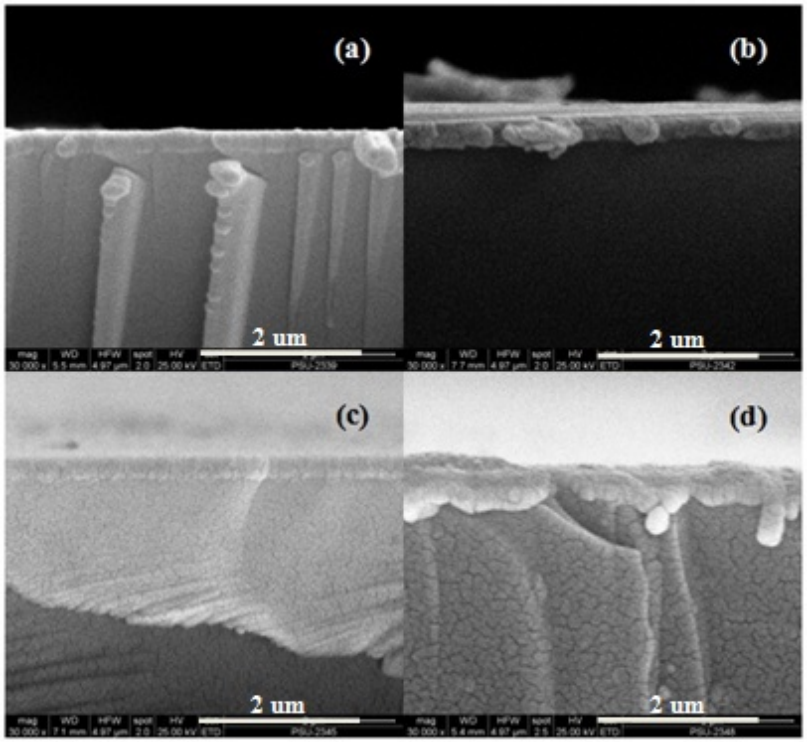

Figure 3 SEM surface and cross-sectional morphologies images of (a) TiO_2, (b) TiO_2-0.2Cu, (c) TiO_2-0.6Cu and (d) TiO_2-1.0Cu thin films (magnification 30,000×).

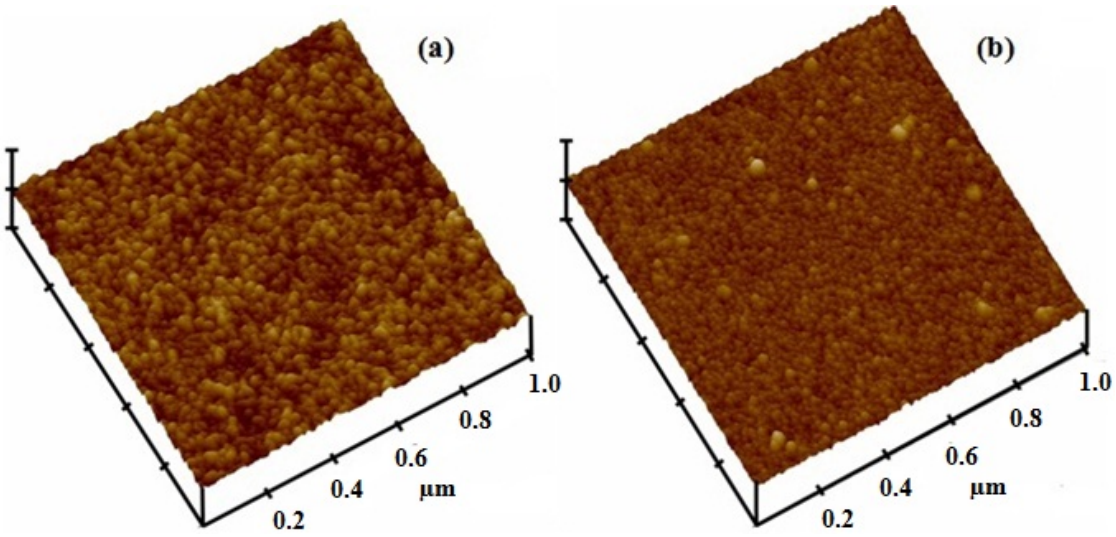

Figure 4 AFM images of (a) TiO_2 and (b) TiO_2 dope 1 % Cu thin films.

Photocatalytic activity

The photocatalytic degradation of MB by using TiO_2 and TiO_2-Cu thin films under UV irradiation is illustrated in **Figure 5**. The photocatalytic reaction rate (R) can be expressed as $R = 1.00e^{-kt}$ where k is the rate constant and t is the treatment time in hour [15]. This rate equation can also be applied for TiO_2-Cu thin films. It is apparent that Cu added in TiO_2 has significant effect on photocatalytic reaction under UV irradiation. Their photocatalytic efficiencies in terms of k values, shown in **Table 1**, decreased with increasing Cu dopant concentration. The TiO_2-1.0Cu thin film is found to give the highest photocatalytic efficiency among other conditions, due to the smallest crystallite size of anatase phase and high concentration of OH radicals on the TiO_2 surfaces [17]. The MB degradation percentage of TiO_2-1.0Cu under UV irradiation for 6 h is 70 % while that of TiO_2 is 53 % (**Figure 6**). It was also found that k values of TiO_2-Cu thin films are superior to that of TiO_2 due to photo-induced electron trapping effect of Cu, higher concentration of OH radicals on TiO_2-Cu surface and their smaller crystallite size [17].

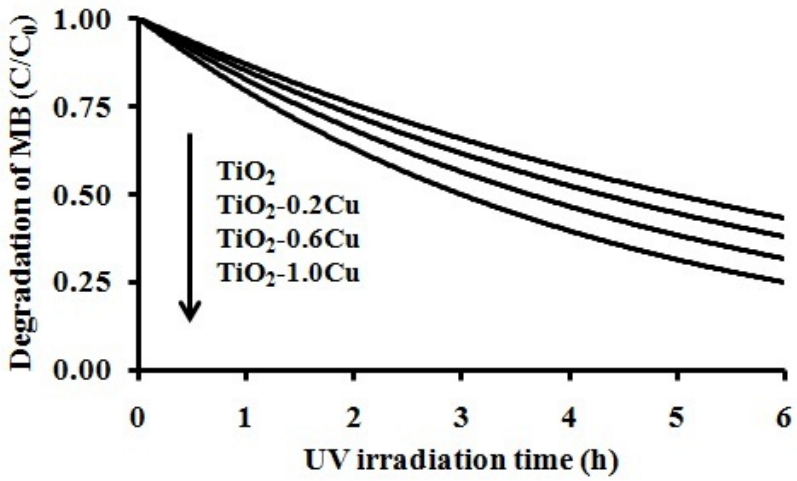

Figure 5 Photocatalytic activity of TiO_2 and TiO_2-Cu thin films under UV irradiation.

Table 1 Equations and rate constants of photocatalytic reactions of TiO_2 and TiO_2-Cu thin films under UV irradiation.

Sample	Rate Equation (*R*)	Rate constant (*k*)	R^2
TiO_2	1.00exp(-0.12t)	0.12	0.90
TiO_2-0.2Cu	1.00exp(-0.16t)	0.16	0.92
TiO_2-0.6Cu	1.00exp(-0.19t)	0.19	0.94
TiO_2-1.0Cu	1.00exp(-0.23t)	0.23	0.98

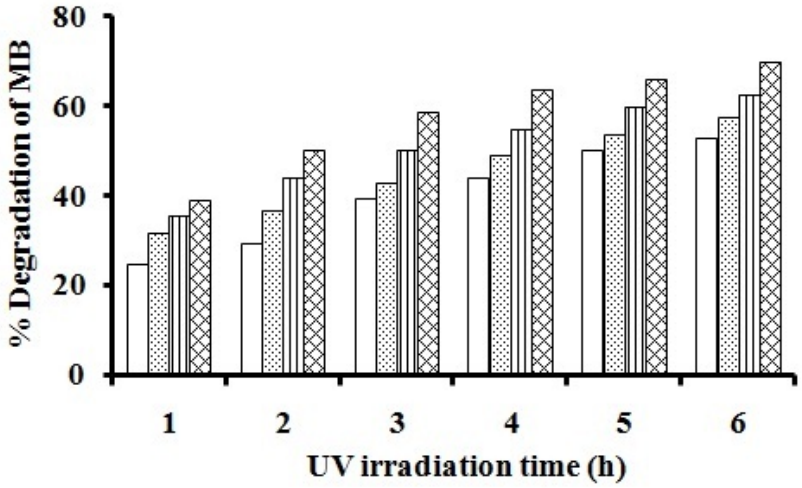

Figure 6 The degradation of MB of (□) TiO_2, (⊡) TiO_2-0.2Cu, (▥) TiO_2-0.6Cu and (▨) TiO_2-1.0Cu thin films.

Antibacterial activity

Figure 7 displays the *E. coli* survival rate (N/N_0) after testing with UV illumination on TiO_2 and TiO_2-Cu thin films. The result shows that the *E. coli* survivals decrease with UV irradiation time. It also indicates that the TiO_2 doped with 1.0 % Cu thin films exhibit higher antibacterial activity compared to TiO_2 and TiO_2 doped with 0.2 and 0.6 % Cu thin films, respectively. The *E. coli* kill rate percentages of TiO_2 and TiO_2-Cu thin films under UV irradiation are plotted in **Figure 8**. It is found that the *E.coli* kill rate percentage of TiO_2 and TiO_2-Cu thin films under UV irradiation for 4 h are 85, 95, 97 and 100 % for TiO_2 and TiO_2 doped with 0.2, 0.6 and 1.0 % Cu thin films, respectively. The photographs of viable bacterial colonies (red spots) on fabricated TiO_2, TiO_2-Cu thin films and the control treated with UV for 4 h. are shown in **Figure 9**.

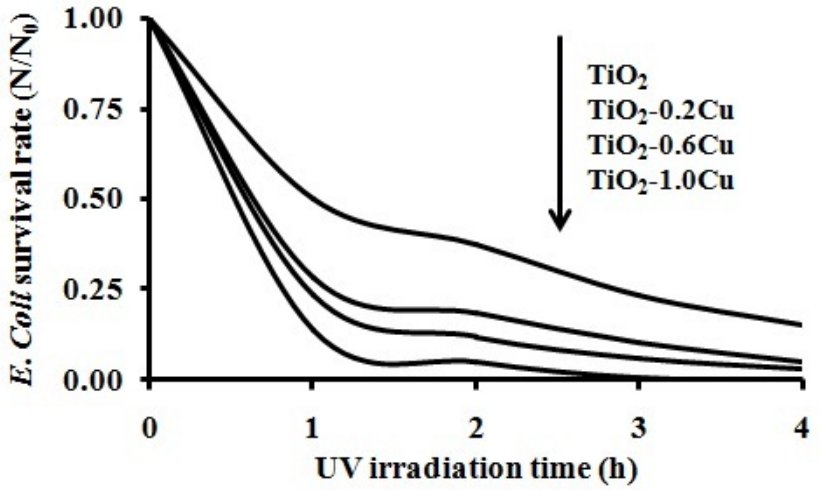

Figure 7 Antibacterial activity of TiO_2 and TiO_2-Cu thin films under UV irradiation.

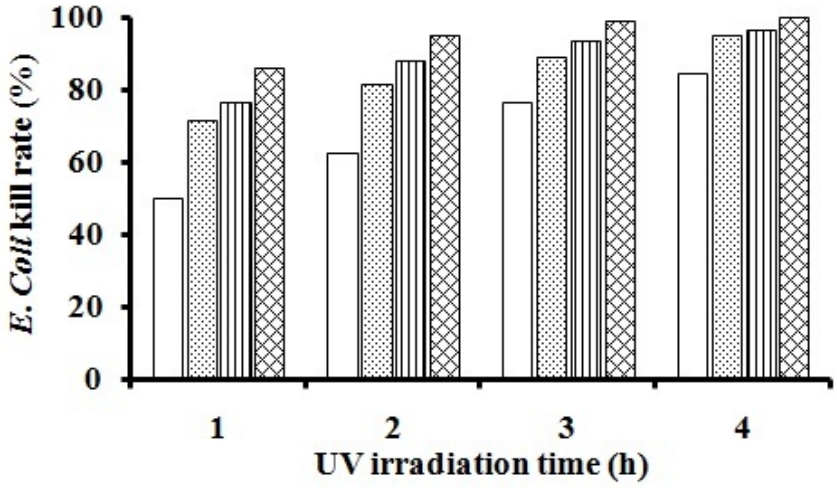

Figure 8 The % *E. coli* kill rate of (□) TiO_2, (⊡) TiO_2-0.2Cu, (▥) TiO_2-0.6Cu and (▨) TiO_2-1.0Cu thin films.

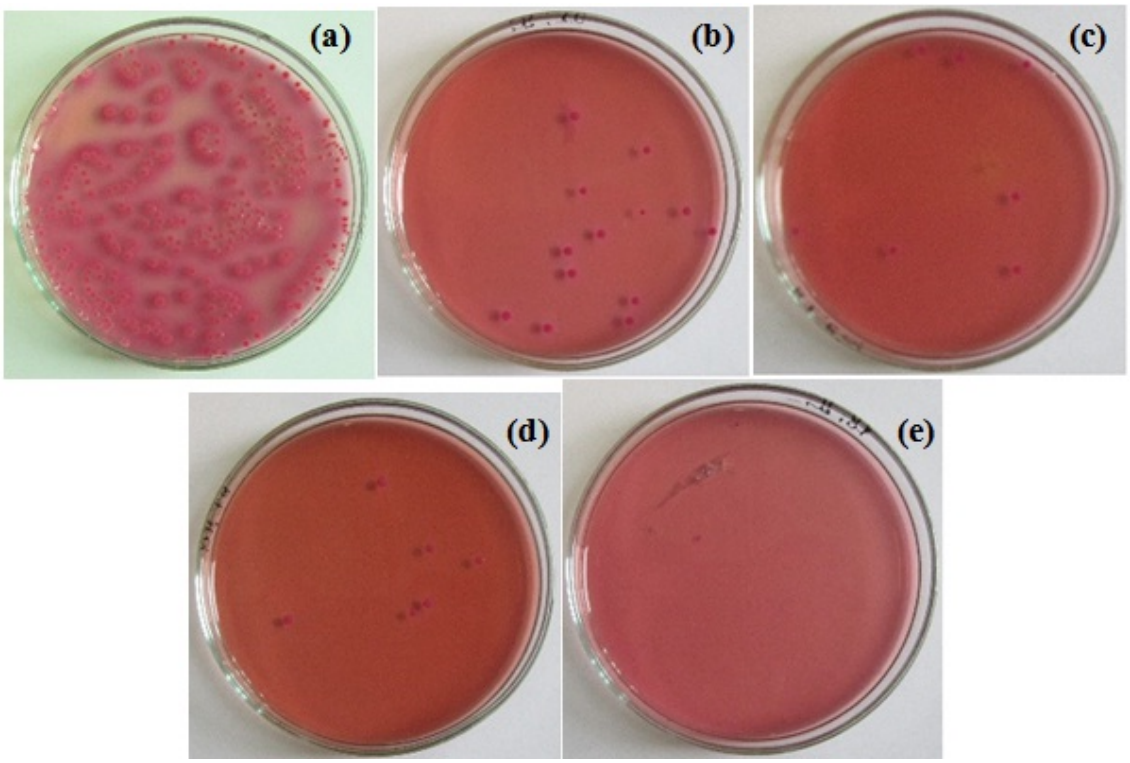

Figure 9 Photo of viable *E. coli* colonies during 4 h UV irradiation for (a) control, (b) TiO_2, (c) TiO_2-0.2Cu, (d) TiO_2-0.6Cu and (e) TiO_2-1.0Cu thin films.

Conclusion

In this work, TiO_2 and TiO_2 doped with Cu thin films were fabricated by sol-gel method. The effect of Cu doping into TiO_2 thin films on phase transformation, crystallite size, morphology, photocatalytic activity and antibacterial behavior were investigated and concluded as followings,

1. TiO_2 and TiO_2-Cu thin films reveal only the anatase phase. Anatase phase fraction in the TiO_2-Cu thin films tends to decrease with increasing Cu dopant. The crystallite sizes of anatase phases decreases with an increase in Cu dopant. All TiO_2 and TiO_2-Cu samples have the thickness in the range of 0.25 to 1.0 um. Their surfaces are dense and very smooth.

2. The photocatalytic and antibacterial activity of TiO_2-Cu thin films increases with Cu doping concentration.

3. It can be noted that TiO_2 doped with 1.0 % Cu thin films exhibits higher photocatalytic; and antibacterial activity under UV irradiation are 70 and 100 %, respectively.

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