Photocatalytic and antibacterial properties of TiO_2 powder doped with Fe

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Abstract **- The Fe doped TiO_2 powders was synthesized by titanium (IV) isopropoxide, iron (III) nitrate nonahydrate, nitric acid and ethanol using sol-gel method. Follow by annealing at 500°C for 2 h in ambient with a heating rate of 10°C/min. The physical and chemical properties of synthesized powders were examined using XRD, SEM and BET. The photocatalytic performance was evaluated using means of degradation of methylene blue (MB) solution and antibacterial activity was investigated by the inactivation of Escherichia coli (E. coli) bacteria. The synthesized powders were anatase in phase with 10 to 100 µm of grain size according to the SEM images. The results from photocatalytic and antibacterial tests suggested that the performance TiO2 powder doped Fe was greater than pure TiO_2. Furthemore, the 5 mol% Fe doping exhibited the highest photocatalytic on MB (59.3%) and antibacterial activity (94.2%) under UV irradiation.**

Keyword - Fe doped TiO_2, Sol-gel, Photocatalytic activity, Antibacterial activity

1. Introduction

Titanium dioxide (TiO_2) is one the most popular commercially available nano-size materials that has found application in a variety of fields to date since its novel properties where published in the early 1970s [1]. Nano materials have shown that they process different chemical, mechanical, optical and electrical properties compared to their bulk counterparts due to its electron transfer properties [2] and they react faster and efficiently [3].

Photocatalysis of TiO_2 was first discovered in 1972 in an experiment done by Fujishima and Honda [4]. This discovery marked the beginning of series of research studies and investigations on TiO_2 and its properties as a photocatalyst in a variety of fields such as energy conversion and environmental remediation [5]. The application of TiO_2 photocatalysis has been report for over the past two decades as a promising solution to water and air contamination [6]. The photocatalyst has been found to have properties of an antibacterial agent. It has on many occasions been reported to kill both of Gram negative and Gram positive bacterial as well as a variety of viruses [7, 8]. The antimicrobial property of TiO_2 was first realized by Matsunaga *et al*., in 1985 [9]. The photocatalyst was used to inactivate microorganisms under UV irradiation of various microorganisms such as bacterial, cancer cell as well as algae [6, 10].

Recently, it was demonstrated that doping TiO_2 with various transition metals, including iron (Fe) greatly improved photocatalytic and antibacterial activity [11-14]. This present paper deals with the preparation of Fe doped TiO_2 powders by sol-gel method. Also the amount of Fe (0, 1, 3 and 5 mol%) doped TiO_2 on the microstructure, photocatalytic activity and inactivation of *E. coli* bacteria was investigated.

2. Experimental

2.1 Raw materials

Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP, Aldaich chemistry, 97%), iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, Fluka Sigma-Aldrich, 97%), nitric acid (HNO_3, Fluka Sigma-Aldrich, 97%) were used as starting materials and ethanol (CH_3CH_2OH, Merck, 36.5-38.0%) was used as solvent.

2.2 Synthesis of Fe doped TiO_2 powders

The Fe doped TiO_2 powders were prepared by sol-gel method. Firstly, $Fe(NO_3)_3.9H_2O$ was introduced to maintain the mole ratio of Fe in the TiO_2 at 0, 1, 3 and 5 mol% of TiO_2 and TTIP with fixed volume at 10 ml were mixed into 150 ml of CH_3CH_2OH 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 HNO_3 [15]. Finally, it was vigorously stirred at room temperature for 45 min, dried at 100°C for 24 h and calcined at 500°C for 2 h in ambient with a heating rate of 10°C/min [16]. For this work the Fe doped TiO_2 powders containing 0, 1, 3 and 5 mol% were designated as TP, T1Fe, T3Fe and T5Fe, respectively.

2.3 Characterization

The morphology and particle size of the Fe doped TiO_2 powders were characterized by scanning electron microscope (SEM) (Quanta 400). The specific surface area of synthesized powders was analyzed using quanta chrome BET surface analyzer. 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) [17- 20].

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

Where D is the average crystallite size, k is equal to 0.9, a shape factor for spherical particles, λ is the X-ray wavelength (λ = 0.154 nm), θ is the Bragg angle and $\beta = B - b$, the line broadening. B is the full width of the diffraction line at half of the maximum intensity and b = 0.042 is the instrumental broadening [20].

2.4 Photocatalytic activity test

The photo-degradation of organic compounds using Fe doped TiO_2 as catalysts occur when catalyst is illuminated with sunlight in presence of water containing dissolved oxygen and organic contaminants. The organic contaminants are decomposed to CO_2 and H_2O under these conditions, Eq. (2) - (6) [11, 13].

$$Fe\text{-}TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb}\ (Fe\text{-}TiO_2) \quad (2)$$
$$h^+_{vb} + OH^- \longrightarrow \bullet OH \quad (3)$$
$$h^+_{vb} + H_2O \longrightarrow \bullet OH + H^+ \quad (4)$$
$$e^-_{cb} + O_2 \longrightarrow O_2^{\bullet -}\ \text{(superoxide ion)} \quad (5)$$
$$IGOR + \bullet OH \longrightarrow CO_2 + H_2O + HNO_3 \quad (6)$$

Where, h^+ represents the hole with positive charge generated at the surface of catalyst. The methylene blue (MB) is attacked by hydroxyl radicals formed as given in the above equation and generates organic radicals or other intermediates. Finally the parent compounds and intermediates are oxidized into CO_2, SO_2^{2-}, NO_3^- and H_2O [13].

The photocatalytic activity was evaluated by the degradation of MB under UV irradiation using eleven 50 W of black light lamps. A 10 ml of MB with a concentration of 1×10^{-5} M was mixed with 0.0375 g of powders and kept in a dark chamber for 1 h, after that kept in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. After photo-treatment for a certain time, the concentration of treated solution was measured by UV-vis. The ratio of remained concentration to initial concentration of MB calculated by C/C_0 was plotted against irradiation time in order to observe the photocatalytic degradation and the percentage degradation of the MB molecules was calculated by Eq. (7) [15].

$$M = 100(C_0\text{-}C)/C_0 \quad (7)$$

Where M is the percentage degradation of the MB molecules, C_0 is the concentration of MB aqueous solution at the beginning (1×10^{-5} M) and C is the concentration of MB aqueous solution after exposure to a light source.

2.5 Antibacterial activity test

The antibacterial activity of powders against the bacteria *Escherichia coli* (*E. coli*) was studied. Aliquots of 10 ml *E. coli* conidial suspension (10^5 CFU/ml) were mixed with 0.05 g of powders. The mixture was then exposed to either UV irradiation (eleven 50 W of black light lamps) for 0, 20, 40 60 min. Then, 0.1 ml of mixture suspension was sampled and spread on Macconkey Agar plate and 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 initial or control (N/N_0) [14, 15]. Percentage bacterial reduction or *E. coli* kill percentage was calculated according to the following equation, Eq. (8) [21].

$$E = 100(N_0\text{-}N)/N_0 \quad (8)$$

Where E is the percentage bacterial reduction or *E. coli* kill percentage, N_0 and N are the average number of live bacterial cells per milliliter in the flask of the initial or control and powders finishing agent or treated fabrics, respectively.

3. Result and Discussion

3.1 Characterization

Figure 1 shows the XRD pattern of Fe doped-TiO_2 powders, heated at 500°C, 2 h in air. All samples have shown similar peaks with the highest peak at 25.26° which was indicated as 100% anatase phase. Fe-compound phase can not be verified in these XRD peaks due to a very small amount of Fe doping. The crystallite size of Fe doped TiO_2 with 0, 1, 3 and 5 mol% Fe were 20.7, 16.9, 16.6 and 13.8 nm, respectively. This result shows the Fe doping in range of 1-5 mol% exhibits nearly the same crystallite size of anatase phase.

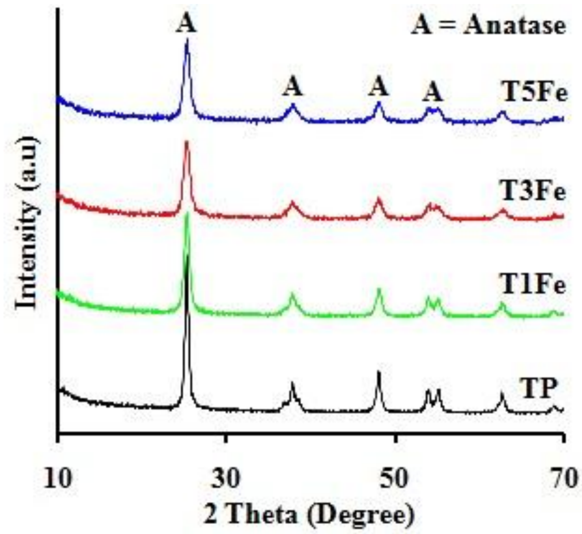

Figure 1 XRD pattern of Fe doped TiO_2 powders

The morphology of calcinated Fe doped TiO_2 powders at 500°C, 2 h in air observed by SEM is shown in Fig. 2. The Fe doped TiO_2 with 0, 1, 3 and 5 mol% Fe exhibited irregular morphology due to the agglomeration of primary particles and with an average diameter of ~ 10 to 100 µm.

The surface states will play an important role in the nanoparticles, due to their large surface to volume ratio with a decrease in particle size. The specific surface area of Fe doped TiO_2 powders were based on the BET method using N_2 adsorption. It was found that Fe doped TiO_2 powders are decreased when the amount of Fe doping increased. The specific surface areas are 17.48, 15.76, 14.31 and 10.38 m^2/g for Fe doped TiO_2 with 0, 1, 3 and 5 mol% Fe, respectively.

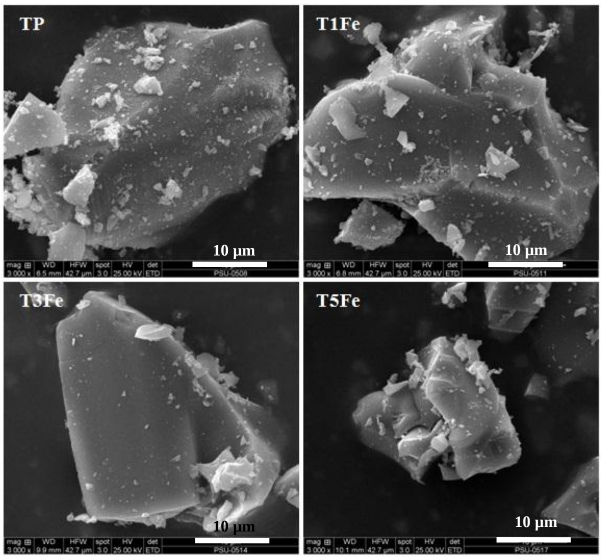

Figure 2 SEM image of Fe doped TiO_2 powders (magnification 3,000X)

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using Fe dope TiO_2 powders under UV irradiation are shown in Fig. 3. It was apparent that Fe added in TiO_2 has significantly effect on photocatalytic reaction under UV irradiation, with the photocatalytic activity increases with increasing Fe doping. This increase in photocatalytic activity with Fe doping is related to shift in optical absorption of the catalyst in visible region. TiO_2 absorbs only UV energy (below 400 nm) [11] whereas Fe doped catalyst absorbs UV and portion of visible energy hence there is increase in photo-catalytic activity. The presence of metal ions on the surface of the photo catalyst particles improves the rate of electron transfer to O_2 and consequently has a beneficial effect on the photo- oxidation rate of organic species. The more number of pores increases the hydroxyl content. In heterogeneous photo catalysis, the illumination of semiconductor produces electrons (e^-) and holes (h^+). The holes (h^+) are combining with OH^- ions and there is formation of hydroxyl radicals ($h^+_{vb} + OH^- \longrightarrow \bullet OH$). These surface hydroxyl radicals formed on the surface of the photo-catalyst are oxidizing species which ultimately affects the photo-catalytic activity. This suggests that the increase in hydroxyl content of the powder increases the photo-catalytic activity [13].

The MB degradation percentage of Fe doped TiO_2 powders under UV irradiation are shown in Fig. 4. It was found that MB degradation percentage of Fe doped TiO_2 powders under UV irradiation for 6 h are 31.24, 45.88, 52.89 and 59.34% for 0, 1, 3 and 5 mol% of Fe doping, respectively. It was found that 5 mol% Fe doped TiO_2 (T5Fe) powders show the best photocatalytic activity.

3.3 Antibacterial activity

The antibacterial activity of Fe dope TiO_2 powders were investigated against *E. coli* bacteria under UV irradiation, as presented in Fig. 5 and Fig. 6. For Fig. 6 displays the *E. coli* survival rate (N/N_0) after testing with UV illumination on Fe dope TiO_2 powders. The result shows that the *E. coli* survivals decrease with UV irradiation time. The *E. coli* survival rate of Fe dope TiO_2 powders under UV irradiation for 60 min are 0.89, 0.27, 0.19 and 0.06 for TiO_2 doped Fe with 0, 1, 3 and 5 mol% powders, respectively. It also indicates that the TiO_2 doped with 5% Fe (T5Fe) powders exhibit higher antibacterial activity compared to TiO_2 doped with 0, 1 and 3% Fe powders, respectively.

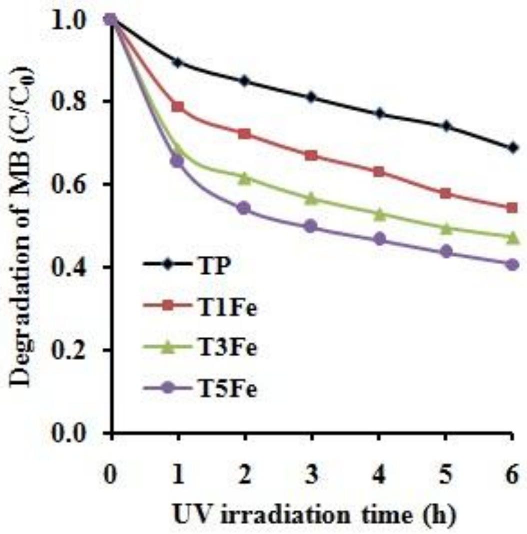

Figure 3 The photocatalytic activity of Fe doped TiO_2 powders under UV irradiation

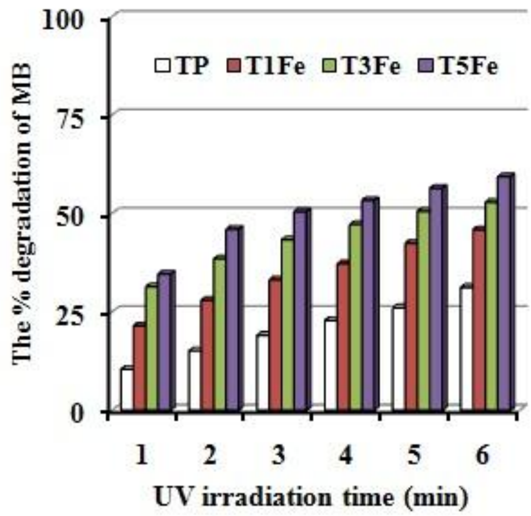

Figure 4 The MB degradation percentage of Fe doped TiO_2 powders under UV irradiation

The *E. coli* kill percentage of Fe dope TiO_2 powders under UV irradiation is shown in Fig. 6. It is seen that the percentage bacterial reduction or *E. coli* kill percentage increased at the presence of Fe doped TiO_2 powders. The pure TiO_2 (un-dope Fe, TP) powders showed a weak *E. coli* kill percentage under UV irradiation while introducing Fe to TiO_2 matrix led to increase in *E. coli* kill percentage. By increasing the Fe concentration in TiO_2 matrix antibacterial activity enhances remarkably. The *E. coli* kill percentage of Fe dope TiO_2 powders under UV irradiation for 60 min are 10.8, 73.3, 81.3 and 94.2% for TiO_2 doped Fe with 0, 1, 3 and 5 mol% powders, respectively. It was found that 5 mol% Fe doped TiO_2 (T5Fe) powders show the best antibacterial activity.

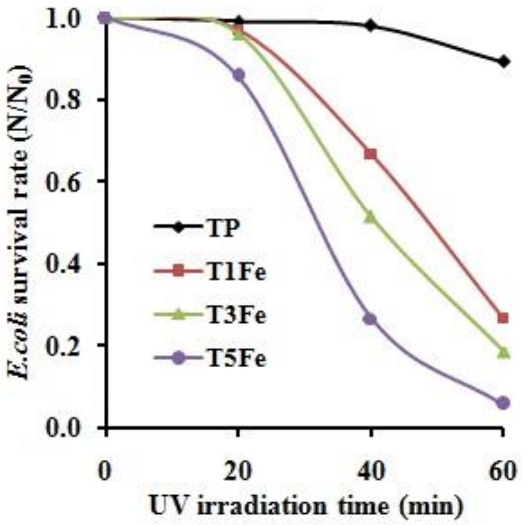

Figure 5 The antibacterial activity of Fe doped TiO_2 powders under UV irradiation

The antibacterial activity of Fe compound and Fe ions have been historically recognized and applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment. To date, the mechanisms have been proposed for the antibacterial activity of Fe particle is it penetrating inside bacterial cell, resulting in cell wall damage [21]. The photo of viable bacterial colonies (red spots) on fabricated Fe dope TiO_2 powders treated with UV for 0, 20, 40 and 60 min are illustrated in Fig. 7.

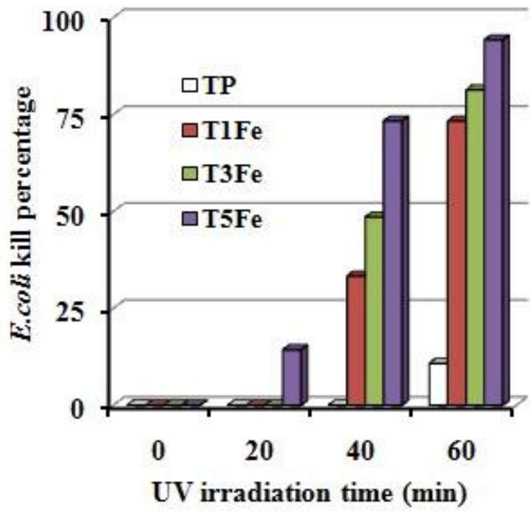

Figure 6 The *E. coli* kill percentage of Fe doped TiO_2 powders under UV irradiation

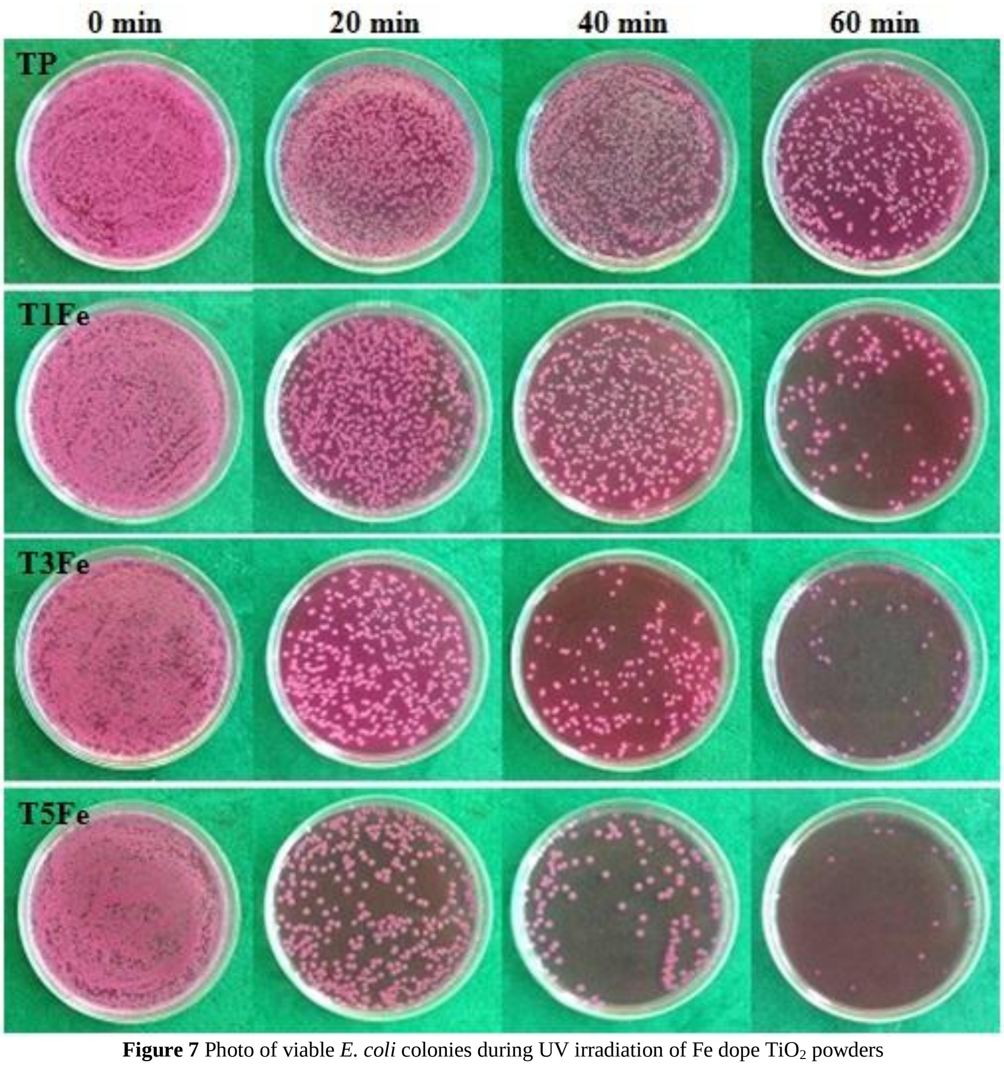

Figure 7 Photo of viable *E. coli* colonies during UV irradiation of Fe dope TiO_2 powders

4. CONCLUSION

In this work, Fe doped TiO_2 powders were prepared by sol-gel method and calcined at the temperature of 500°C for 2 h with a heating rate of 10°C/min. The results showed that all samples consisted of only anatase phase. It is found that the photocatalytic and antibacterial activity of Fe doped TiO_2 powders in proper concentration were greater than pure TiO_2 and 5 mol% Fe doping exhibited the highest photocatalytic (59.3%) and antibacterial activity (94.2%) under UV irradiation.

5. ACKNOWLEDGEMENTS

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