Photocatalytic and antibacterial properties of TiO₂ powder doped with Fe

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Abstract - The Fe doped TiO₂ 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 TiO₂. Furthermore, the 5 mol% Fe doping exhibited the highest photocatalytic on MB (59.3%) and antibacterial activity (94.2%) under UV irradiation.

Keyword - Fe doped TiO₂, Sol-gel, Photocatalytic activity, Antibacterial activity

1. INTRODUCTION

Titanium dioxide (TiO₂) 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 TiO₂ 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 TiO₂ and its properties as a photocatalyst in a variety of fields such as energy conversion and environmental remediation [5]. The application of TiO₂ 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 TiO₂ was first realized by Matsumaga 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 TiO₂ 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 TiO₂ powders by sol-gel method. Also the amount of Fe (0, 1, 3 and 5 mol%) doped TiO₂ on the microstructure, photocatalytic activity and inactivation of E. coli bacteria was investigated.

2. EXPERIMENTAL

2.1 Raw materials

Titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄, TTIP, Aldaich chemistry, 97%), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Fluka Sigma-Aldrich, 97%), nitric acid (HNO₃, Fluka Sigma-Aldrich, 97%) were used as starting materials and ethanol (CH₃CH₂OH, Merck, 36.5-38.0%) was used as solvent.

2.2 Synthesis of Fe doped TiO₂ powders

The Fe doped TiO₂ powders were prepared by sol-gel method. Firstly, Fe(NO₃)₃·9H₂O was introduced to maintain the mole ratio of Fe in the TiO₂ at 0, 1, 3 and 5 mol% of TiO₂ and TTIP with fixed volume at 10 ml were mixed into 150 ml of CH₃CH₂OH 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 HNO₃ [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 TiO₂ 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 TiO₂ 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].

\[ D = \frac{k \lambda}{\beta \cos \theta} \] (1)
Where $D$ is the average crystallite size, $k$ is equal to 0.9, a shape factor for spherical particles, $\lambda$ is the X-ray wavelength ($\lambda = 0.154$ nm), $\theta$ 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$_2$O under these conditions, Eq. (2) - (6) [11, 13].

\[
\begin{align*}
\text{Fe-TiO}_2 + hv &\rightarrow \text{e}^- + h^+ (\text{Fe-TiO}_2) \quad (2) \\
h^+ + \text{OH}^{-} &\rightarrow \text{•OH} \quad (3) \\
h^+ + \text{H}_2\text{O} &\rightarrow \text{•OH} + \text{H}^+ \quad (4) \\
\text{e}^- + \text{O}_2 &\rightarrow \text{O}_2^- \quad \text{(superoxide ion)} \quad (5) \\
\text{IGOR} + \text{•OH} &\rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{HNO}_3 \quad (6)
\end{align*}
\]

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$_2^-$, NO$_3^-$ and H$_2$O [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 $1 \times 10^5$ 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].

\[
M = 100(C_0 - C)/C_0 \quad (7)
\]

Where $M$ is the percentage degradation of the MB molecules, $C_0$ is the concentration of MB aqueous solution at the beginning ($1 \times 10^5$ 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 ($10^7$ CFU/ml) were made 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].

\[
E = 100(N_p-N)/N_0 \quad (8)
\]

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](image)

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.
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$^+$ + OH $\rightarrow$ •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 dope TiO$_2$ powders under UV irradiation are shown in Fig. 4. It was found that MB degradation percentage of Fe dope 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.
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 5](image5.png) **Figure 5** The antibacterial activity of Fe doped TiO$_2$ powders under UV irradiation

![Figure 6](image6.png) **Figure 6** The E. coli kill percentage of Fe doped TiO$_2$ powders under UV irradiation

![Figure 7](image7.png) **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 doped exhibited the highest photocatalytic (59.3%) and antibacterial activity (94.2%) under UV irradiation.

5. ACKNOWLEDGEMENTS

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6. REFERENCE


