Tailoring of optical, biological and magnetic properties of nanocrystalline Fe doped TiO₂ thin films

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Abstract

Fe doped TiO₂ films were synthesized by sol–gel dip coating method. The concentration of Fe³⁺ was varied as 1%–5% (w/w) in TiO₂. X-ray diffraction showed dominating rutile phase of TiO₂ along with brookite phase and hematite Fe₂O₃ phase. The content of the rutile phase varies depending on the Fe doping percentage. The high iron doping reduced the band gap and restrained the growth of TiO₂ crystallite. All films are ferromagnetic (FM) but the films with low Fe doping percentage have a good crystallinity and a strong ferro-magnetism. Although the Fe doping has not changed the crystal structure of TiO₂, but had affected its photo-catalytic and antibacterial properties. The bacteria E. coli were more vulnerable to Iron doped TiO₂ when compared to the bacteria Pseudomonas. 3% Fe doped TiO₂ had the best photo-catalytic activity. Fe doped TiO₂ can act as a remarkable antibacterial entity against microorganisms to save from bacterial infections.

1. Introduction

TiO₂ is highly optically transparent in the visible and near infrared region with high charge carrier mobility. So mostly used in solar cells. TiO₂ has been widely studied as a main material for substantial environmental applications; self-cleaning, self-sterilizing and de-polluting surfaces, due to its powerful photo-catalytic activity [1, 2]. Researches have shown that the structural properties, optical parameters and magnetic properties can be easily controlled, when TiO₂ is doped with some metal ions [3–7]. Metal doped TiO₂ thin films are now-a-days in use to enhance solar cell efficiency [3]. Among all transition metals, Fe element is taken as an appropriate dopant of TiO₂ being inexpensive and easy to handle. At the same time the ionic radius of Fe³⁺ is close to Ti⁴⁺ ion radius. TiO₂ is intrinsically n-type semiconductor when it is doped with iron it becomes p-type semiconductor. The electron transport layer is a beneficial component of solar cells and Fe doped TiO₂ can act as a transport layer due to the electron move and hole blockage [3].

Photo-catalytic activity of TiO₂ under ultraviolet (UV) irradiation is being broadly used to resolve a number of environmental pollution issues, decay of contamination from polluted water, dangerous bacteria [8] and cancer therapy [9].

The photocatalytic TiO₂, being chemical stable, broad-spectrum antibiosis and optical competent, is used for eradication of bacteria, fungi and viruses [10–12]. Although, the requirements for a UV source restrict its advantages. To overcome such problems, a general way is to tailor TiO₂ by doping with a metal ion which decrease band gap energy; hence, photo-excitation takes place in visible light. The most favoured dopants in this regard are Ag, Fe, Cu, Au and V [13–17].

Fe doped TiO₂ finds application in biosensors, biodiagnostics, antimicrobial and photocatalyst. Fe ions attack proteins in bacterial cell walls and decelerate bacterial growth [18–20].

E. coli produces many infections and resist the broad spectrum antibiotics. The launch of the new antibacterial agents can control the infectious diseases. TiO₂ could control the antibiotic resistant strain of E. coli [21]. In hospital, antibiotic resistant strains can cause infection in wounds and burnt patients, So it is a suitable disinfectant in hospitals. In the textile industry, cotton fabrics use TiO₂ with antibacterial effect, therefore, it is
better to manufacture the wound bands by such cotton fabrics to reduce infection in wounds [22]. Fe doping in TiO$_2$ has high antimicrobial characteristics in visible light and their properties persist after switching of light [23].

Fe doped TiO$_2$ thin films were coated by spin coating [3], spray coating [24], liquid phase deposition [25]. Anyhow, the reported techniques generally demand special equipment or a complex route, e.g. heat treatment to obtain the crystalline Fe-doped TiO$_2$ films, which would reduce their mass production and creates environmental issues. The sol-gel route is comparatively low temperature, inexpensive and reliable. Moreover dip-coating is best among sol-gel to deposit thin films because with lightweight and less equipment method to deposit thin films on a variety of materials.

In current work, Fe doped TiO$_2$ thin films were synthesized by sol–gel dip coating method using different contents of Fe(III) nitrate (Fe(NO$_3$)$_3$·9H$_2$O) as dopant. Role of Fe on the characteristics of TiO$_2$ films were explored.

2. Experimental procedure

2.1. Procedure for sol preparation

For the preparation of sol, 0.404 g of iron nitrate nonahydrate Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 5 ml of deionized water, magnetically stirred for 10 min 10 ml of isopropanol was added into it and magnetically stirred for 1 h. Separately 29.304 ml of titanium tetra isopropoxide Ti(OCH$_3$)$_4$ was dissolved in 10 ml of deionized water and magnetically stirred for 10 min followed by the addition of isopropanol and stirred for 1 h. After these two steps, the sol of iron and titanium was combined. Diethylamine was added drop wise as a stabilizer and magnetically stirred for 3 h. Finally, sol of Fe doped TiO$_2$ was obtained with a dopant concentration of 1%. Similarly, for 2%, 3%, 4% and 5% dopant concentration five sols were prepared. 

2.2. Procedure for deposition

Dip coating was used to synthesis thin films of Fe doped TiO$_2$. For this purpose, glass slides were dipped coated at the optimized withdrawal speed of 250 mms$^{-1}$. The glass slide automatically came out from the sol and a layer of the sol was deposited on the glass slide. In this way five films were deposited from sols with different doping percentage. Films were annealed in a furnace at 400 °C for 4 h for densification, phase formation and crystallization.

The structure of the Fe doped TiO$_2$ thin films was recorded by using XRD Philips Panaanalytical Xpert Pro PW 3020. Optical Transmission measurements were carried out in the range 300–900 nm by using (Hitachi 2800 U) UV–VIS spectrophotometer. The Fourier transform infrared (FTIR) spectroscopy were performed by FTIR Model M 2000 Midac USA spectrophotometer by varying wavenumber from 400 cm$^{-1}$ to 2500 cm$^{-1}$. Magnetic properties were studied by Lakeshore 7407 Vibrating sample magnetometer. Thin films were studied by thermo gravimetric analysis and differential scanning calorimetry (TGA/DSC) with the help of SDT Q600 to study thermal properties. The TGA/DSC curves were registered at a constant heating rate of 2 K min$^{-1}$. The surface morphology of Fe doped TiO$_2$ thin films was studied using scanning electron microscopy (SEM-JEOL JSM-6480).

3. Results and discussions

3.1. FTIR

The FTIR spectrum of the Fe doped TiO$_2$ is shown in figure 1, in which the broad absorption band around 2426 cm$^{-1}$ presents O–H stretching of water. The presence of this weak and narrow band suggested complete removal of the moisture from the sample. Absorption peaks observed between 2538 cm$^{-1}$ and 2274 cm$^{-1}$ were because of the absorbance of CO$_2$ molecule from the atmospheric air [26]. Likewise, absorption bands recorded at 1636 and 1381 cm$^{-1}$ corresponded to the asymmetric and symmetric stretching of the carboxyl group (C=O) and the presence of (C–O) [27]. Deformation bands of O–C–O also had been recorded around 1129 cm$^{-1}$. Increase in Fe doping percentage did not shift these absorption bands significantly. An absorption band between 600 [28, 29] and 814 [29] cm$^{-1}$ was assigned to different vibrational modes of rutile phase of TiO$_2$. The absorption band at 450 cm$^{-1}$ corresponds to iron oxygen vibrational modes [30]. With the enhancement in the Fe doping, the absorption bands of TiO$_2$ became narrow and fluctuations in material’s bands decreased.

3.2. Thermal analysis

The TGA and DSC curves of Fe doped TiO$_2$ were shown in figure 2. Figure 2 showed that all the weight losses were accompanied by their corresponding exothermic or endothermic peaks. From 20 °C to 450 °C there were
Figure 1. FTIR of Fe doped TiO$_2$ with varying Fe concentration between 1%–5% atom.

Figure 2. (a) TGA and (b) DSC of Fe doped TiO$_2$ for different percentages of Fe.
two major weight losses with corresponding endothermic at 99 °C and exothermic peak at about 326 °C. Figure 2(a) showed that the first weight loss took place between 20 °C–120 °C which were due to the loss of moisture and second weight loss was between 120 °C–450 °C due to transformation of hydroxides into oxides. Over 450 °C material didn’t suffer any weight loss. From figure 2(b) an exothermic peak can be seen at 465 °C which showed crystallization of the sample. Moreover, with the enhancement of Fe-percentage in TiO₂, there was an increase in the percentage of weight loss with the crystallization achieved at lower temperature and the corresponding exothermic peak shifted below 450 °C. From these results it can be inferred that increase in percentage of Fe-doping, increased absorption of moisture by TiO₂. Moreover, these results displayed that all the Fe-doped TiO₂ samples were thermally stable between 450 °C and 900 °C. That’s why films were annealed at 400 °C.

3.3. Structural properties

The structural analysis of Fe doped TiO₂ thin films was performed by x-ray diffraction (XRD). The XRD spectra of Fe doped TiO₂ thin films with varying Fe percentages was recorded. Figure 3 that most of the diffraction peaks belong to rutile phase TiO₂, one peak to brookite phase of TiO₂ and one peak to Hematite Fe₂O₃ according to the JCPDS cards numbers 21–1276, 16–617 and 24–72 respectively. All thin films have shown the highest peak around 27.50° which was termed as 100% rutile phase. Furthermore, figure 3 shows that the intensity of diffraction peaks decreases with an increase in Fe percentage in the TiO₂ lattice. It means that increase in Fe impurities distorts the crystal structure of the rutile TiO₂. Fe²⁺ and Fe³⁺ are two Fe ions whose ionic radii are 0.78 Å and 0.68 Å respectively. The larger ionic radius of Fe²⁺ (0.78 Å) over the Ti⁴⁺ (0.68 Å) has produced the tensile strain in the film moving (110) peak is towards the lower 2θ values. Fe³⁺ in the films produce compressional strain in TiO₂ due to the smaller ionic radius (0.64 Å) of Fe³⁺ than Ti⁴⁺ (0.68 Å) and shifts (110) peak to higher 2θ values. Therefore, in this case, Fe ions mainly exist both in Fe³⁺ and Fe²⁺ ionic state due to which (110) peak shift its position due to increase in Fe doping. Hematite phase can be seen in figure 3 which predicted that Fe³⁺ ionic state is more probable. Fe³⁺ has ionic radius 0.64 Å close to Ti⁴⁺ ionic radius of 0.68 Å. So iron ion can penetrate into the crystal structure of TiO₂ and settle in a few of the lattice sites of TiO₂. This is the cause of the reduction of peak intensities with an increase in Fe doping indicating that the Fe has replaced Ti into the TiO₂ lattice. Fe doping in TiO₂ decreased the required annealing temperature to change the crystal phase from anatase to rutile. In the un-doped TiO₂, the annealing temperature of 500 °C was not adequate to form rutile phase; while Fe doping form rutile even at 400 °C of annealing temperature. Crystallite size and lattice strain of the thin films were evaluated using the Scherrer [31] and Williamson–Hall method [32] according to equations (1)–(3) respectively

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  
\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  
\[ \beta \cos \theta = k\lambda/D + 4\varepsilon \sin \theta \]
Table 1. Structural properties of Fe doped TiO₂ thin films.

| Dopant concentration | Crystallite size nm (Scherrer method) | Strain (William hall method) | Dislocation density (Pm⁻²) | Lattice constants (Å) |
|----------------------|--------------------------------------|------------------------------|-----------------------------|-----------------------|
|                      |                                      |                              | Scherrer method             | William hall method    |
| 1% Fe                | 31                                   | 21.4                         | 0.001165                    | 0.00587               |
| 2% Fe                | 36                                   | 17.47                        | 0.001                       | 0.0035               |
| 3% Fe                | 21                                   | 18.12                        | 0.001676                    | 0.00431              |
| 4% Fe                | 21.83                                | 19.83                        | 0.001666                    | 0.00126              |
| 5% Fe                | 21.73                                | 14.98                        | 0.001665                    | 0.00418              |

where D is crystallite size, θ is the diffraction angle, λ wavelength of the x-ray (Cu kα 1.54059 Å), ε is the lattice strain and the β be the full width at half maximum (FWHM).

Crystallite size was decreasing while the lattice strain was found to increase due to the appearance of the lattice defects and enhancement of straining force in rutile lattice owing to the structural distortion, which showed the existing Fe ions taking the place of Ti in the TiO₂ lattice. Table 1 shows the variation in crystallite size, strain evaluated by Scherrer formulas given in equations (1) and (2) while the dislocation density is evaluated by the relation

$$\delta = 1/D^2$$  \hspace{1cm} (4)

Scherrer equation has certain limitations in calculating the accurate crystallite size because it does not consider the strain that occurs in the lattice due to the imperfections or defects. Hence, Williamson–Hall plots are important to assess the crystallite size. The combination of the crystallite size and the strain effect on the line broadening of films was written in equation (3).

To evaluate structural properties by Williamson–Hall relation, equation (3) has been used. Thus, when $\beta \cos \theta$ was plotted against $\sin \theta$ (for each XRD pattern, a straight line is acquired with the intercept as crystallite size and the slope as lattice strain. Lattice constants were calculated by applying formulas

$$\sin^2 \theta = \lambda^2/4[(h^2 + k^2/a^2) + l^2/c^2]$$  \hspace{1cm} (5)

Table 1 compares structural properties results evaluated both by Scherrer and Williamson–Hall relation.

3.4. Optical studies

Optical transmission of Fe doped TiO₂ thin films with Fe varying between 1–5 at% in the spectral range of 300–900 nm, are shown in figure 4. The sharp fall of the transmission of ~450 nm was consistent with the absorption of TiO₂ due to the interband transition. Sharp absorbance edge suggested that Fe doped TiO₂ thin films can be applied in transparent window material for antireflection coatings and optoelectronic devices. This portion of curve was used to evaluate the optical band gap energy.

The TiO₂ can have both direct and indirect transition [33]. In this project direct inter band transition was achieved and the band gap of thin films was calculated by Tuac’s relation [34]

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$  \hspace{1cm} (6)

where A is a constant and hν is the energy of photon.

The optical absorption coefficient (α) was interpreted from the transmittance data by taking into account transmission and reflection losses,

$$\alpha = 1/t^* \ln[2R^2T/ - (1 - R)^2 + \{(1 - R)^4 + 4R^2T^2\}^{1/2}]$$  \hspace{1cm} (7)

where t is the thickness of the film. The band gap energy (Eg) was assessed by from $(\alpha h\nu)^2$—$h\nu$ curves as displayed in figure 5. Recorded band gaps of thin films deposited with Fe % of 1, 2, 3, 4 and 5 % at were 3.07, 3.02, 3.08, 3.17 and 3.03 eV, respectively. When the doping percentage was increased, the value of Eg decreased slightly to 3.02 eV and then it increased. The decrement in the band gap energy with the increase in Fe % was due to the increasing density of donors. This decrease was also reported by other researchers [35]. Donor produce energy levels in the band gap close to the conduction band, and acceptor produce energy levels close to the valence band. With enhancement in the doping percentage, the density of states of dopants enhances and constitutes continuous energy states similar to the bands and decreases the band gap. Fe³⁺ produces shallow trapping sites, which decreased the band gap [36]. All band gap energies were lower than the pure bulk TiO₂ (3.30 eV). Since 3 and 4 at of Fe doping increased band gap to 3.08 and 3.17 eV respectively. This increase of the gap with the introduction of donor impurities was produced by the Burstein-Moss effect [37, 38], which was...
linked to the reality that the enhanced charge carriers already filled the lowest energy states (Burstein-Moss effect) and afterwards transitions could take place only in the higher energy states. The absorption edge of TiO2 exists in the ultraviolet range and may move to a shorter wavelength with enhancement in the carrier density. Filling of the energy states near the bottom of the conduction band produces this shift in the absorption edge. For 5% doping, band gap again decreased to 3.03 eV due to introduction of defects due to excessive doping [39]. The decrement in the band gap signifies that films can absorb most visible light which showed enhancement in photo-catalytic activity.

The extinction coefficient (k) is a key tool to find scattering and adsorption of light. The extinction coefficient can be evaluated by relation [40]:

$$k = \alpha \lambda / 4\pi$$  (8)

where \( \lambda \) is wavelength and \( \alpha \) is the absorption coefficient.

The extinction coefficients of thin films as a function of wavelength are shown in figure 6(a). Figure 6(a) and table 2 showed that \( k \) was increased with increasing doping percentage. The high value of \( k \) for thin films shows surface roughness. The films became less smooth with an increase in doping percentages which lead to increase in extinction co-efficient.

In the low photon energy range, the absorption coefficient curve contains exponential part known as Urbach tail. It appeared the localized states are stretched in the band gap and comes forward in the disordered and low crystalline material [41]. Urbach energy was calculated from the relation [42]:

$$\alpha = \alpha_0 e^{h\nu / E_u}$$  (9)

$$\ln \alpha = \ln \alpha_0 + \left( h\nu / E_u \right)$$  (10)

where \( \alpha_0 \) is a constant and \( E_u \) is Urbach energy and it is dependent on the structural disorder.

The values of \( E_u \) are shown in table 2. It is noted that Urbach energy changed by increasing Fe doping percentage owing to the variation in film thickness due to alleviation/decrement of defects in the structural bonding. This supported the XRD results which showed the crystalline phases of Fe doped TiO2.

The optical conductivity (\( \sigma \)) can be evaluated by using the relation [43]

$$\sigma_{opt} = \alpha n c / 4\pi$$  (11)

The change of optical conductivity with different Fe doping percentage is shown in figure 6(b). The \( \sigma \) was changed with increase in doping percentage which was due to change in absorption. An enhancement in the optical conductivity of high photon energy was due large absorbance of Fe doped TiO2 thin films leading to increase in electron density in the conduction band [44].

The amplitude of the electromagnetic wave was decreased after moving through certain thickness is called the skin depth. The skin depth is determined by [45]

$$\chi = 1 / \alpha$$  (12)

The skin depth increases with an increase in the doping percentage because the absorption increased with enhancement in thickness of films (figure 6(c)).
3.5. Magnetic studies

Figure 7 shows M-H curves of TiO$_2$ thin films deposited under Fe doping, clearly indicating a ferromagnetic behavior. Table 3 showed that magnetization were decreasing with an increase in the Fe doping percentage both for the in-plane and out of plane magnetic field except for 2% and 5% Fe doping while coercivity, retentivity and squareness ratio were increasing except for 1% of Fe doping. As the Fe percentage increased the carrier density and the mobility decreased, which enhanced oxygen deficiency leading to ion scatterings [46]. The room temperature ferro-magnetism recorded for all samples does not rely on iron doping. Fe$^{3+}$ ions are not ferromagnetic at room temperature, but induced ferro-magnetism was due to bound magnetic polaron (BMP). Higher iron percentage enhanced the concentration of oxygen vacancies and the ferromagnetic magnetization. Magnetic properties of Fe doped TiO$_2$ thin films were due to the large number of oxygen vacancy centers. The interaction of Fe$^{3+}$ ions with the nearby oxygen vacancies creates bound magnetic polarons (BMPs). The magnetic moment of the BMPs created ferro-magnetism in Fe doped TiO$_2$ thin films. For these films, Fe ions are bound with the Ti defect sites and oxygen orbitals. However, Fe ions form oxides in TiO$_2$ lattice which is evident from the XRD pattern of figure 3 which showed the existence of hematite phase, hence mixing of Fe-3d and Ti-
3d state are forbidden. Coey and co-workers [47] put forward BMP model and proposed that defect coupled magnetic entity is the main cause of recorded magnetization in Fe doped TiO₂ thin films. Although, this model doesn’t consider the exchange interaction between the host Ti cation and Fe dopant. As saturation magnetization initially enhanced with enhancement in Fe doping concentration to 2%, but again decreased to 4%. Further increase in doping to 5% increase magnetization. This proposed that Fe ions are not only cause of the recorded magnetism and the interaction among Fe³⁺ and Ti⁴⁺ ions emerging due to overlapping of Fe-3d and Ti-3d orbitals must be taken into account. The nature and intensity of such magnetic interaction would decide the magnetic properties of thin films. The ferro-magnetism recorded in these thin films is not affected by the presence of a secondary phase hematite which is anti-ferromagnetic [48].
Table 2. Optical Properties of Fe doped TiO$_2$ thin films.

| Dopant concentration | Thickness ($\mu$m) | Refractive index | Directband Gap (eV) | Extinction coefficient K | Optical conductivity $\times 10^{12}$ | Skin depth | Urbach energy (meV) |
|----------------------|-------------------|------------------|---------------------|--------------------------|--------------------------------------|------------|-------------------|
| 1% Fe                | 2.57              | 1.67             | 3.07                | 0.0192                   | 2.50                                 | 0.00027    | 0.099             |
| 2% Fe                | 2.93              | 1.67             | 3.02                | 0.0257                   | 3.87                                 | 0.00019    | 0.105             |
| 3% Fe                | 2.73              | 1.66             | 3.08                | 0.0175                   | 1.97                                 | 0.00028    | 0.064             |
| 4% Fe                | 2.05              | 1.7              | 3.17                | 0.0294                   | 5.87                                 | 0.00016    | 0.075             |
| 5% Fe                | 1.07              | 1.80             | 3.03                | 0.0600                   | 26.5                                 | 0.00064    | 0.059             |

Figure 7. Hysteresis curves for Fe doped TiO$_2$ thin films (a) in-plane and (b) out of plane applied magnetic field for different percentages of Fe.

Table 3. Magnetic properties of Fe doped TiO$_2$ thin films.

| Dopant concentration | Coercivity $H_c$ (Oe) | $M_s$ (emu cm$^{-3}$) In field | $M_s$ (emu cm$^{-3}$) Out field | $M_s$ (emu cm$^{-3}$) In field | $M_s$ (emu cm$^{-3}$) Out field | $M_s/M_s$ In field | $M_s/M_s$ Out field | Anisotropy In field $\times 10^6$ | Anisotropy Out field $\times 10^6$ |
|----------------------|------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------|---------------------|-------------------------------|-------------------------------|
| 1% Fe                | 176.74                 | 157.07                         | 0.00898                       | 0.000106                       | 0.0247                        | 0.0280              | 0.0276              | 0.0264                       | 1.62                          | 1.70                          |
| 2% Fe                | 144.59                 | 135.81                         | 0.00931                       | 0.00977                        | 0.0228                        | 0.0243              | 0.0245              | 0.0249                       | 1.37                          | 1.35                          |
| 3% Fe                | 169.82                 | 136.12                         | 0.00897                       | 0.01012                        | 0.0256                        | 0.0245              | 0.0285              | 0.241                        | 1.55                          | 0.141                         |
| 4% Fe                | 174.10                 | 150.68                         | 0.00012                       | 0.000136                       | 0.0357                        | 0.0354              | 0.0299              | 0.0261                       | 2.12                          | 2.08                          |
| 5% Fe                | 175.50                 | 157.7                          | 0.00023                       | 0.00257                        | 0.00693                       | 0.00690             | 0.0308              | 0.268                        | 4.03                          | 0.413                         |
3.6. Antibacterial activity

The antibacterial activity of Fe doped TiO2 thin films was tested against the Escherichia coli and Pseudomonas gram-negative bacteria using the well diffusion method. Petri plates were thoroughly washed and left inside an autoclave to sterile. After the procedure of sterilization, the nutrient agar medium was put in each sterile Petri plate and waited till it gets hardened in a laminar air flow chamber. After hardening, fresh bacterial culture with known population count was laid on the plate with a sterile cotton swab (spread plate technique). Three wells each of 5 mm in diameter were created in the agar plates by using a sterile cork borer and the wells were filled with 200 ml solution of the Fe doped TiO2 with different Fe contents. All the plates were placed in an incubator at 37 °C for one day. When incubation was complete, the plates were examined for the generation of clear inhibition zone encircling the well which is a sign of the antibacterial activity of the Fe doped TiO2. The zone of inhibition was assessed by evaluating the diameters of the inhibition zone around the well. The MBC for both E. coli and Pseudomonas was equal to 1 mg ml\(^{-1}\) as no usable cells were found after 48 h while for 4 at wt% Fe MBC was 8 mg ml\(^{-1}\) for Pseudomonas. 2 and 3 at wt% of Fe did not show any antibacterial activity against Pseudomonas. The antibacterial activity of the Fe doped TiO2 was compared with antibiotic disc Meropenem for the E. coli and Pseudomonas bacterial strains. The zone of inhibition for E. coli was 27 mm and for Pseudomonas was 39 mm. Figure 8 and table 4 showed the antibacterial activity of Escherichia coli E. coli and Pseudomonas gram-negative bacteria. It can be concluded from the results deduced by the antibacterial activity of Fe doped titanium dioxide that the highest concentration of Fe dopant showed higher antibacterial activity for E. coli and Pseudomonas bacteria. The bacteria (E. coli) were more vulnerable to Iron doped TiO2 when compared to the bacteria Pseudomonas and increasing the concentration of the Fe doped TiO2 increases the antibacterial activity. The Iron doped TiO2 inactivated the E. coli by the diffusion of the small particles ranging from 21 to 36 nm into E. coli membranes. Iron doped TiO2 do not destroy all cells, but due to the magnetic properties of Iron doped TiO2, these could destroy bacteria by interaction.

E. coli and Pseudomonas are bacteria which cause nosocomial infections. These infections are difficult to treat with antibiotics. Moreover, antibiotic resistance can complicate remedy. Introduction of the novel
Table 4. Antibacterial activity of Fe doped TiO2 against E. coli and Pseudomonas Aeruginosa.

| Concentration | 1% Fe | 2% Fe | 3% Fe | 4% Fe | 5% Fe |
|---------------|-------|-------|-------|-------|-------|
|               | E. coli | P. A | E. coli | P. A | E. coli | P. A | E. coli | P. A | E. coli | P. A |
| 1             | 29.5 mm | 24.0 mm | 20.5 mm | — | 23.66 mm | — | 12.5 mm | — | 22.33 mm | 25.0 mm |
| 2             | 28.5 mm | — | — | — | 18.0 mm | — | — | — | 19.0 mm | 26.0 mm |
| 4             | 10.0 mm | — | 18.0 mm | — | — | — | — | — | 15.3 mm | — |
| 8             | — | 26.6 mm | — | — | 15.0 mm | 22.5 mm | 17.0 mm | 25.2 mm | — | — |

Antibacterial entity can affect the mortality and morbidity rate of the infections. Nanoparticles have impeded a broad spectrum of bacterial strains. Metal oxides bear the positive charge and the microorganisms bear negative charges; these opposite charges induce electromagnetic attraction among metal oxide and microorganisms causing death of micro-organisms [49]. Nanoparticles damages enzymes and DNA by rupturing the cell walls of bacteria producing cell death [30].

In this research work, it was depicted that the different percentages of Fe doped TiO2 could impede the growth of antibiotic resistant strain of E. coli and Pseudomonas. In hospital, where resistant strains could be transferred easily and root cause of infection in surgical cuts and burnt patient; Fe doped TiO2 is best bactericide in hospitals.

In the textile field, cotton fabrics with antibacterial effect are manufactured [51], the suture or wound bands made from cotton fabrics tend to decrease the rate of infection in patients.

3.7. Photo-catalytic activity

The photo-catalytic activities of the catalyst Fe doped TiO2 thin films were studied by the degradation of organic dye methylene blue (MB) under sunlight irradiation. Consistently, 10 mg of catalyst Fe doped TiO2 was added to 200 μl of aqueous MB solutions. Before irradiation, the suspensions were stirred in the dark for half an hour to attain the absorption equilibrium of MB in colloidal solution. The photo-catalytic experiment was carried out under ambient conditions in a beaker equipped with a magnetic stirrer under sunlight. Afterwards a blank experiment was carried out to assure that no reaction took place in the absence of sunlight. Then, the solution was irradiated for 60 s at regular intervals of 15 s. The resulting solutions were examined using a UV–visible spectrophotometer. The effective percentage of dopants and catalyst Fe doped TiO2 dosage was also investigated by studying the absorption spectra with Fe dopant percentage of 1–5 at% and catalyst dosages of 0.01–1.0 g l\(^{-1}\).

Figure 9(a) showed changes of absorption edge with an increase in the Fe dopant and figure 9(b) displayed a move of absorption edge with change in irradiation time of solar light in the organic dye methylene blue. Figure 9 and table 5 showed that shift in the absorption edge to higher wavelength confirmed degradation of dye MB and occurrence of photo-catalytic activity.

Generally, photo-catalytic activity is governed by two processes that rely on each other, (1) the interaction of light with the photo-catalyst Fe doped TiO2 to generate electrons and holes and (2) the effect on the surface of Fe doped TiO2. The generated electron or hole will be captured and moved to the catalyst Fe doped TiO2 surfaces where it performed a redox reaction with the MB dye molecules, which overcome the electron and hole recombination and significantly enhance the photo-degradation efficiency [52–54]. The photo-catalytic activity is dependent on many parameters, for example the crystal size, band gap energy and certain surface area. In this project, the photo-catalytic activity enhanced with the increase in dopant concentrations. Fe ions doped in TiO2 has reduced the average crystal size and narrow the band gap. However, the optical gap was lowest for 2 at wt% of Fe doping and highest for 4 at% Fe doping while crystal size is lowest for 3% Fe doping and the highest for 2% Fe doping. Hence, it is assumed that the decrease in the average crystal size and the band gap might be required, but not key factors in the increase of photo-catalytic activity.

When sunlight is irradiated to the Fe doped TiO2 surface, a photo excited valence band electron is shifted to the conduction band leaving a hole in the valence band thus generating electron-hole pairs (EHP) and hole generated interact with the water molecules and electron interacted with oxygen at the surface of Fe doped TiO2 to generate reactive oxygen species (ROS) for example hydroxyl radicals (\(\cdot \text{OH}\)) and superoxide (\(\cdot \text{O}_2^-\)) respectively. The created ROS degraded organic species and showed photo-catalytic activity. The organic impurities, parental and intermediate compounds are disintegrated to CO\(_2\), HNO\(_3\) and H\(_2\)O. Reactions are expressed in following equations

\[
\text{Fe-TiO}_2 + h\nu \rightarrow e^- + h^+ (\text{Fe-TiO}_2) \\
\text{h}^+ + \cdot \text{H}_2\text{O} \rightarrow \text{OH}^- + \cdot \text{H}^+ \\
\text{e}^- + \cdot \text{O}_2 \rightarrow \text{O}_2^- (\text{superoxide ion})
\]
Where IGOR stands for interactive generation of organic reactions

Metal ions can easily accept electrons, so $\text{Fe}^{3+}$ ions doped in the TiO$_2$ capture electrons in the conduction band of TiO$_2$. Capturing of electrons by Fe reduced the recombination of EHP on the Fe doped TiO$_2$ thin films. This generated more OH$^-$ radical on the surface of Fe doped TiO$_2$ and boosts the photo-catalytic activity. Low % doping of Fe can’t capture electrons significantly due lower concentrations of reactive capturing centers, so the photo-catalytic activity is not as pronounced. A large percentage of Fe can play the role of recombination sites of electrons and holes. It will increase the recombination probability of electrons and holes in the material, generating defects in the material which scattered light and hindered the Sunlight to reach on the surface of the

\[
\text{IGOR} + \text{OH}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{HNO}_3
\]
Fe doped TiO$_2$. This process reduced the generation EHP and consequently OH$^-$ radical which led to decrease in photo-catalytic activity.

Table 6 showed a shift of absorption edge for different percentages of Fe dopant concentration and sunlight exposure for 60 s with the interval of 15 s. It is concluded that methylene blue degraded with respect to time.

| Dopant concentration | 0 min under sunlight | 15 min under sunlight | 30 min under sunlight | 45 min under sunlight | 60 min under sunlight |
|----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 1% Fe                | 531 nm               | 412 nm                | 526 nm                | 430 nm                | 532 nm                |
| 2% Fe                | 530 nm               | 527 nm                | 529 nm                | 399 nm                | 402 nm                |
| 3% Fe                | 536 nm               | 406 nm                | 401 nm                | 399 nm                | 411 nm                |
| 4% Fe                | 532 nm               | 408 nm                | 445 nm                | 355 nm                | 397 nm                |
| +5% Fe               | 515 nm               | 412 nm                | 527 nm                | 406 nm                | 390 nm                |

Figure 10. SEM micrographs show Fe doped TiO$_2$ thin films with Fe (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5 doping percentage.
under the exposure of sunlight, which showed photo-catalytic activity of Fe doped TiO2. Table 5 showed that increase in doping percentage of Fe increased photo-catalytic activity. The highest result of photo-catalytic activity was shown by the 3% doping of Fe in TiO2.

Fe doped TiO2 has powerful antimicrobial properties through reactive oxygen species produced during photo-catalytic process that destroys cell walls and kill viruses. Hence, Fe doped TiO2 can be used for the packing of fresh food. The Fe doped TiO2 might be applicable for the photo-catalytic degradation of organic pollutants present in wastewater.

3.8. SEM analysis

The surface morphology was assessed via scanning electron Microscopy (SEM) as shown in figure 10. Figures 10(a), (b) shows that granular morphology is becoming more prominent with Fe doping in the TiO2 at wt% and 2 at wt% doping percentage. However, granular morphology is reduced 3% at wt doping percentage (figure 10(c)) and the morphology convert to a more smooth film structure. Figure 10(d) shows that Film becomes smooth but certain cracks also appeared. The appearance of cracks on the surface of the film is interconnections of the pores that enhance in number and size with an increase in the Fe percentage.  Further increase in Fe doping to 5% at wt, surface morphology changed to many cracks and few agglomerated grains as shown in figure 10(e). Grain size increased with increase in Fe dopant percentage to 184, 330, 682, 1316 nm.

4. Conclusions

Fe-doped TiO2 films were synthesized by dip coating method using Fe (III) nitrate dopant source. The x-ray diffraction study showed that all the films have dominated rutile phase, and Fe doping facilitated the rutile phase formation of TiO2 films at a low annealing temperature of 400 °C. TiO2 films obtained from Fe (III) doping exhibited lower transmission. Band gap was quite lower than pure TiO2 thin films lying in the range 3.03–3.17 eV for varying Fe doping percentage. Hybridization of the Fe dopant with the oxygen vacancy has induced defect state in Fe doped TiO2 thin film thus modifying the electronic structure which is the origin of ferro-magnetism. Antibacterial activity was studied against bacteria E. coli and the bacteria Pseudomonas. An increase in the concentration of the Fe in TiO2 increased the antibacterial activity. Fe doped TiO2 will be the best bactericide in hospitals. Fe doped TiO2 can be used for the packing of fresh food. 3 atom.% Fe doped TiO2 showed the best photo-catalytic activity. However, increased percentage of Fe dopant decreased the photo-catalytic activity. The Fe doped TiO2 might be applicable for the photo-catalytic degradation of organic pollutants present in wastewater. It is concluded that researchers and industrialists can design devices that is dependent on Fe doped TiO2 thin films including solar cell and diodes.

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