A short literature survey on iron and cobalt ion doped TiO_2 thin films and photocatalytic activity of these films against fungi

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ABSTRACT

In this study, a short recent literature survey which concentrated on the usage of Fe^{3+} or Co^{2+} ion doped TiO_2 thin films and suspensions were summarized. Additionally, a sol–gel method was used for preparation of the 2% Co or Fe doped TiO_2 thin films. The surface of the prepared materials was characterised using scanning-electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis and band gap of the films were calculated from the transmission measurements that were taken over the range of 190 and 1100 nm. The E_g value was 3.40 eV for the pure TiO_2, 3.00 eV for the Fe-doped TiO_2 film and 3.25 eV for Co-TiO_2 thin film. Iron or cobalt doping at lower concentration produce more uniformed particles and doping greatly affected the size and shape of the TiO_2 nanoparticles. Photocatalytic killing effect of the 2% Co doped TiO_2 thin film on *Candida albicans* was significantly higher than Fe doped TiO_2 thin film for short and long exposure periods. Doped thin films were more effective on *Aspergillus niger* for short exposure periods.

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1. Introduction

In general, photocatalytic action of a semiconductor catalyst such as TiO_2, ZnO, CdS largely depend on the hydroxyl radical ($HO^\bullet$) producing capacity. But it is well known that not only hydroxyl radicals but photogenerated electrons also play an important role for the reduction of several compounds. Photocatalytic action of a catalyst depends on two important parameters, one is the number of photogenerated hydroxyl radicals directly related to band gap and wavelength of light source and second is the ratio of e^-/h^+ recombination. Band gap reducing methods are largely applied by loading transition metal ions directly on semiconductor, which also shift the absorption wavelength to visible region. If the catalyst works in visible region this will allow the usage of the material under sun light which is more economical and involve the consumption of sustainable and renewable energy sources. There are numerous publications about doping the ions particularly on TiO_2 [1–3]. While some metal or nonmetal loadings produce extremely good catalyst [1,3–8] some others such as Cr^{3+}, Co^{2+} or Fe^{3+} were reported to be deleterious [9,10]. For example, silver loaded TiO_2 was superior for the oxidation of various organic contaminants and microorganisms [11–13]. On the other hand, bulk doping has also been reported as detrimental effects on the photocatalytic activities except for a slight improvement happening at trace doping amounts [14]. A short recent literature survey concentrated on the usage of Fe^{3+} or Co^{2+} ion doped TiO_2 thin films were discussed in following section.

Mechanistic studies reveal that increased hydroxyl radical production is the main effect for this enhanced properties as much as shifting the wavelength of the light source to visible region [3,15]. Among those ions iron (Fe^{3+}) are particularly interesting since its unique half-filled electronic configuration. Loading can reduce the band gap energy via formation of new intermediate energy levels. However, its activity depends on doped iron concentration (particularly % iron content). While it works very well at lower iron concentrations higher Fe^{3+} contents result in an increase of electron (e^-)–positive hole (h^+) recombination which leads to a decrease at hydroxyl radical production [16]. When Fe^{3+} doping is over a certain point, the loaded Fe^{3+} ions become a recombination center the trapped free carrier pairs easily recombine since quantum tunneling effect [17]. Additionally, higher ion loading might increase the transformation of anatase to rutile which leads to decreasing photoactivity [10].

The Fe^{3+} loaded TiO_2 particles were used for removal/degradation of variety of materials both in UV or visible region have

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Table 1
Published studies related to photocatalytic degradation with Fe^{3+} doped TiO_2 suspensions.

Catalyst	Doping method	Target compound(s)	Degradation	Light source and type	Ref.
Fe-TiO$_2$	Co-precipitation Fe^{3+} + $TiCl_4$	Herbicides Mecoprop-MCCP, MCPA (2.7 mmol/L) Clopyralid (1 mmol/L)	MCCP: 50% with 0.13% Fe-TiO$_2$ (18 h) MCPA: 25% with 1.27% Fe/TiO$_2$ (18 h) CP: 25% with 1.27% Fe-TiO$_2$ (10 h)	50 W Halojen lamp ($\lambda > 400$ nm)	[18]
Fe-TiO$_2$	Sol–gel	2,4,6-TCP	98% with 0.5% Fe-TiO$_2$	8 × 8 W low pressure Hg lamp	[19]
C,S,N,Fe-TiO$_2$	Sol–gel	Rhodamine B (1×10^{-5} M)	64% with C,S,N-0.3% Fe-TiO$_2$ (150 min)	100 W Hg arc lamp ($\lambda = 420$ nm)	[20]
Fe-TiO$_2$	Co-precipitation	Phenol (1×10^{-4} M)	20% with 1.2% Fe-TiO$_2$ (180 min)	Metal halide lamp and 6 × 6 W fluorescent lamp ($\lambda = 365$ nm)	[21]
Fe-TiO$_2$ on activated carbon	Chemical vapour deposition	Methyl orange	31% with Fe-TiO$_2$ (approx. 3 h)	300 W high pressure Hg lamp ($\lambda > 400$)	[22]
Fe-TiO$_2$	Hydrothermal precipitation	Rhodamine B (20 ppm)	90% with 0.5% Fe-TiO$_2$ (4 h)	300 W high pressure Hg lamp ($\lambda = 365$ nm) 100 W high pressure Hg lamp ($\lambda < 420$ nm)	[23]
Fe-TiO$_2$	Plasma oxidative pyrolysis	Methyl orange (20 μM)	UV irradiation: 50% with 1% Fe-TiO$_2$ 100% with TiO$_2$ Visible light irradiation: 80% with 1% Fe-TiO$_2$ 55% with TiO$_2$	200 W high pressure Hg lamp ($\lambda = 365$–436 nm)	[24]
Fe-TiO$_2$	Sol–gel	Methanol (100 mM)	15.3% with 0.5 Fe-TiO$_2$	Xe lamp ($\lambda = 340$ nm)	[25]
Fe-TiO$_2$	Wet chemical	Chloroform (1×10^{-2} M)	[Cl$^-$]$_0$: 0.30 mM [Cl$^-$]: 0.79 mM with 0.2% Fe-TiO$_2$ (6 nm) [Cl$^-$]: 0.80 mM with 0.05% Fe-TiO$_2$ (11 nm)	1000 W Xe lamp ($\lambda = 310$–330 nm)	[17]

been summarized below. Suspension studies were summarized in Table 1 and thin film studies were in Table 2.

Since the first discovery of antibacterial effect of TiO_2 photocatalyst [32] photocatalytic removal of microorganisms employing TiO_2 thin films coated on various materials have been popular research area [6,8,33]. As seen from Table 1 Fe^{3+} doped TiO_2 suspensions have not been used for photocatalytic killing of specific microorganisms. However, antimicrobial activities of Fe^{3+}/TiO_2 thin films have been investigated by a few groups of investigators [26,27,29].

Doping of cobalt ions on TiO_2, especially in anatase form, were subject to many studies. Those studies present in current literature were summarized in Table 3.

Most of the basic research and publications related to preparation and photocatalytic behaviour of Co-TiO_2 with visible light response was discussed by Amadelli et al. in details giving all previous literature reports. As it was emphasized the influence of cobalt are contradictory: some authors report its deposition detrimental for photocatalytic action, while, in some cases, cobalt seems to improve photodegradation slightly or selectively for some organic compounds (see Amadelli et al. for the references). Two new papers were recently published and both studies indicates that photocatalytic activity of Co doped TiO_2 is lower than neat TiO_2 under UV light exposure [34,35]. But presence of 0.5% Co dopant in TiO_2 had resulted in a catalyst with the highest activity under visible irradiation. Additionally, Co doped TiO_2 thin films have been reported to exhibit ferromagnetism at room temperature conditions and suited for spintronic applications [38]. Although antimicrobial action of Fe doped TiO_2 thin films were previously investigated by a few

Table 2
Published studies related to photocatalytic degradation with Fe^{3+} doped TiO_2 thin films.

Catalyst	Doping method	Target compound(s)	Degradation	Light source and type	Ref.
Fe-TiO$_2$ thin film	Coated on soda lime silica glass by sol–gel	*Escheria coli* K-12 (10^3 CFU/mL)	92.5% with 0.5% Fe-TiO$_2$ (120 min)	2 × 10 W fluorescent lamp ($\lambda = 425$ nm)	[26]
Fe-TiO$_2$ thin film	Sol–gel spin coating and Fe plasma ion implantation	*Erwinia carotovora subsp. Carotovora* ZL1 bacteria (10^5–10^6 CFU/mL)	90% degradation (60 min)	($\lambda > 450$ nm and $\lambda = 350$–400 nm UVA)	[27]
Fe-TiO$_2$ thin film	Sol–gel	Basic blue 41 (10^{-5} M)	UV light: 55% with 0.05% Fe-TiO$_2$ Visible light: 10% with 0.05% Fe-TiO$_2$	450 W Xe lamp	[10]
Fe-TiO$_2$ thin film	RF magnetron co-sputtering	*Escheria coli* (ATCC 25922) (10^6 CFU/mL)	100% degradation with 2.5% Fe-TiO$_2$ (120 min)	65 W Hg lamp	[28]
Fe-TiO$_2$ thin film	Spin coating	*Escheria coli* (10^7 CFU/mL)	90% degradation with 0.1% Fe-TiO$_2$ (3 V potential, 15 min)	2 × 8 W ($\lambda = 370$ nm)	[29]
Fe-TiO$_2$ thin film	Sol–gel Dip-coating	Methyl orange (100 ppm)	50% degradation with 4% Fe-TiO$_2$ (5 h) 95% degradation with PEG + 4% Fe-TiO$_2$ (3 h)	Sun light	[30]
Fe-TiO$_2$ thin film	Sol–gel	*Escheria coli* (10^6 CFU/mL)	100% degradation with 0.5–1% Fe-TiO$_2$ (2 h)	125 W Hg lamp	[31]
Fe-TiO$_2$ thin film	Sol–gel Dip-coating	Ethanol in gas phase (590 ppm)	100% degradation with Fe-TiO$_2$ (150 min)	4 × 4 W fluorescent light	[9]

Table 3

Published studies related to photocatalytic degradation with Co^{2+} doped TiO_2 suspension and thin films.

Catalyst	Doping method	Target compound(s)	Degradation	Light source and type	Ref.
Co-TiO$_2$	Sol–gel Suspension	Methyl orange (10 ppm, 1 g/L catalyst)	90% degradation with 0.5% Co-TiO$_2$	Visible	[34]
Co-TiO$_2$-TiO$_2$	Sol–gel	$Cr_2O_7^{2-}$ (3.89×10^{-4} M) Methyl orange (1.09×10^{-4} M) (2 g/L catalyst)	92.7% degradation with 0.5–2% Co-TiO$_2$	375 W medium pressure Hg lamp	[35]
Co-TiO$_2$-SiO$_2$	Suspension		UV irradiation:	60 W ($\lambda = 253.7$ nm) 500 W ($\lambda > 400$ nm)	[36]
Co-MCM-41 Co-MTiO2 TiO$_2$/Co-MCM-41		Gentian violet Methyl violet Methylene blue Fuchsin basic Safranine T Rhodamine B (50 ppm, 0.25 g/L catalyst)	63.1% 8% 62.2% 63.2% 25.9% 7.7% with Co-TiO$_2$-SiO$_2$ catalyst (60 min) Visible irradiation:		
		Gentian violet Methyl violet Methylene blue Fuchsin basic Safranine T Rhodamine B	60% 62.7% 29.9% 17.7% 20% 10% with Co-TiO$_2$-SiO$_2$ catalyst		
Co-TiO$_2$	Wetness impregnation method Thin film	4-Chlorophenol (1 mM) Bisphenol A (0.8 mM)	4-Chlorophenol: 5% with 0.5% Co-TiO$_2$ Bisphenol A: 75% with 0.5% Co-TiO$_2$ 45% with TiO$_2$ (8 h)	Q 400 Medium-pressure Hg lamp ($\lambda > 420$ nm; $\lambda > 450$ nm)	[37]
Co-TiO$_2$	Sol–gel spin coating Thin film	NT[a]	NT*	NT*	[38]
Co/TiO$_2$	Sol–gel Thin film	Basic blue 41 (10^{-5} M)	UV light: 75% with 0.07% Co-TiO$_2$ (90 min) Visible light: 2% with 0.07% Co-TiO$_2$	450 W Xe lamp	[10]

[a] Not tested.

researchers employing some specific microorganisms there is no report related to Co doped TiO_2 suspensions or thin films in current literature.

Candida albicans is a diploid fungus (a form of yeast) and a causal agent of opportunistic oral and genital infections in human. Fungi are much weaker than bacteria and yeast due to their structural differences in the complexity and thickness of the cell envelope. *Aspergillus niger* is a prime example of this; it can be found growing on damp walls, as a major component of mildew and some strains of *A. niger* have been reported to produce potent mycotoxins called ochratoxins [39]. Mold fungi *A. niger* have been almost universally detected in water damaged buildings and many different type of chemicals have been used for mold inhibition. Such biocides are only effective for short-term antifungal purposes, and can themselves be toxic in some cases. Although both microorganisms are not particularly dangerous for human health, the infections can become serious in patients with a compromised immune system, such as those with cancer or HIV.

Research into neat or metal loaded TiO_2 particles has shown recent promise as a route to obtain self cleaning materials. Antimicrobial action and the main killing effect of TiO_2 nanoparticles is considered to be the penetration of the nanoparticle into the cell via the cell wall causing irrepairable damage [40] as much as reactive oxygen species such as hydroxyl radicals, superoxide ions or hydrogen peroxide generated from the photo-excited TiO_2. This aspect has been addressed with regard to the photocatalytic degradation ability of Fe doped TiO_2 thin films with respect to *E. coli* but their efficacy towards *yeast or fungie* has yet to receive extensive consideration. It might be interesting to investigate the disinfection of *C. albicans* and *A. niger* rather than *E. coli* employing Fe or Co doped TiO_2 thin film coated on glass surface. There are two main targets of this study. The first one is the production of a photoactive surface which is more effective than TiO_2 itself and second one is to achieve a photocatalytic activity which work at near visible light region.

2. Experimental

2.1. Isolation and growth of C. albicans and A. niger

C. albicans (ATCC 60193) and *A. niger* (DSM, 1988) strain was obtained from the culture collection of Karadeniz Technical University, Department of Microbiology and Clinical Microbiology. *C. albicans* strain was prepared using sterile YEPD (1% yeast extract, 2% peptone, 2% dextrose) liquid growth solution containing 20% glycerol at 1 McFarland turbidity. The treated cells were then re-suspended and diluted to 2×10^6 colony forming units (CFU/mL) with sterilized water. Suspensions were portioned to 1 mL parts and stored at $-80\,^\circ$C until required.

Growth media was prepared as following: 65 g of sabouraud dextrose agar (Oxoid, ABD) was dissolved in 1 L of distilled water and autoclaved for 1.5 h. After cooling the solution was dispersed into Petri dishes. Solid media were stored overnight in a fridge before application.

A. niger which is prominent among indoor molds was used for photocatalytic tests. This specie can grow and colonize on solids easily under moisture and temperature conditions conducive to spore germination [41]. *A. niger* was grown on Eosine Methylene Blue (EMB) agar medium in the form of single colonies. Then colonies were incubated in Mueller-Hinton Broth (MHB) at $37\,^\circ$C until provide a 0.5 McFarland turbidity.

2.2. Preparation of TiO$_2$, Fe-TiO$_2$ and Co-TiO$_2$ thin films

A sol–gel method was used for preparation of the thin films. An aliquot of 8.4 mL of titanium isopropoxide (TiP) was dissolved in 20 mL absolute ethanol. Another portion of 130 mL absolute ethanol containing 0.22 mL concentrated HCl and 0.5 mL distilled water was slowly added to this solution and the resulting sol–gel solution was left stirring for 24 h. Iron and cobalt doped TiO_2 thin films were prepared in the similar manner. In this preparation 130 mL absolute ethanol containing 0.0549 g of $FeCl_3 \cdot 6H_2O$ or 0.135 g of $CoCl_2 \cdot 6H_2O$ (which is equal to 2% of TiO_2), 0.22 mL concentrated HCl and 0.5 mL distilled water was slowly added to TiP solution. Glass slides were cleaned in an ultrasonic bath prior to coating, dip coated and dried at $120\,^\circ$C for 20 min. Coated materials were calcinated at $450\,^\circ$C for a further 20 min [9].

2.3. Surface analysis

The surface morphology of the films was studied using a Philips NovaSEM scanning electron microscope. The optical transmission of the films was measured with a Unicam UV2-100 dual beam UV–vis spectrophotometer in air at room temperature. The thicknesses of undoped and doped TiO_2 thin films were measured using a PHE 102 Spectroscopic Ellipsometer.
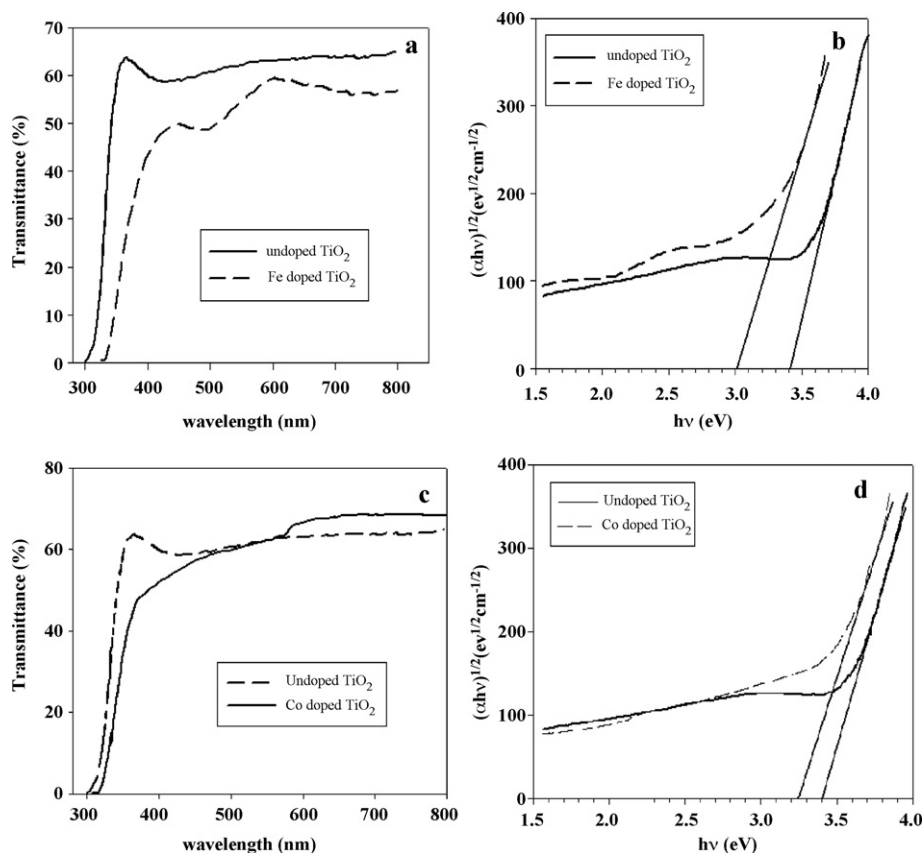
Fig. 1. UV–vis. Transmission spectrum (a and c) and the optical band gap energies (b and d) calculated from absorption spectra of TiO$_2$ and doped TiO$_2$ thin film coated glass using sol–gel method.

2.4. Experimental details

C. albicans and *A. niger* (1×10^8 CFU/mL, suspended in normal saline) solution was used for thin film treatment. The edges of thin film coated materials were sealed with beeswax and the surface was divided into three equal portions before applying the antibacterial drop-test method. Briefly 180 μL of bacterial solution was added onto the each surface of the thin film coated material and the control (an uncoated substrate sealed with beeswax) then irradiated with the same lamp and illuminated from above with a 6 W 365 nm wavelength lamp (Type ENF-260C, Spectroline, at a light intensity of 350 μW/cm^2) located 10 cm from the reaction vessel. The system was covered with aluminum foil and the temperature of the reaction mixture was kept at room temperature.

After irradiation for the required period (certain intervals over 1 h) a 10 μL aliquot of the solution was withdrawn and directly cultivated on sabouraud dextrose agar for 24 h at 37 °C. The number of living colonies was counted to determine the number of viable cells expressed as the number of colony forming units. All experiments were carried out in triplicate; particular attention was paid to those experiments which involved thin film coated materials. Glass slides were cleaned before coating in a ultrasonic bath. All equipment (petri dishes, glassware, pipets and pipet tips) were sterilized with ethanol prior to use.

3. Results and discussion

3.1. Surface analysis

In order to obtain the band gap energies of prepared thin films, transmission measurements were taken over the range of 190 and 1100 nm. The wavelength dependence of the optical transmittance of the undoped and Fe or Co doped TiO$_2$ films, which were ca. 800 nm thick, (Figs. 1 and 2 respectively) showed that the optical band edge shifted to higher wavelength for both doped films.

As seen from Fig. 1, the optical band edge shifted to the higher wavelengths for Fe doped sample. The maximum transmission of the undoped TiO$_2$ films was ca. 65%, but was nearer 57% for the Fe doped TiO$_2$. The TiO$_2$ thin film absorbed UVA radiation, whereas the absorption of the Fe-TiO$_2$ thin film coating did not extend far into the visible region. Furthermore, the optical band gap energy E_g was calculated from the absorption spectra (190–1100 nm) using the dependence of the absorption coefficient (α) on the photon energy;

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

where E_g is the optical band gap of thin films and A is constant. Extrapolation of the linear portion of the plot of $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ for undoped and doped TiO$_2$ thin films onto the energy axis yielded the band gap E_g of the film. The value of E_g was 3.40 eV for the pure TiO$_2$ and 3.00 eV for the Fe-doped TiO$_2$ films. The decrease in the band gap of Fe-doped TiO$_2$ film is attributed to the influence of near band levels, resulting from the introduction of iron, and related with iron and iron-vacancy complexes. It has been suggested that a small fraction of the iron incorporated into the TiO$_2$ lattice can act as an acceptor and could give rise to localized levels near the valance band. The E_g values of undoped TiO$_2$ were higher than those reported for the anatase (3.2 eV) and rutile (3.0 eV) forms of TiO$_2$ and have been attributed to thermal stress effects produced in the film. Similarly, E_g value was 3.25 eV for Co-TiO$_2$ thin film which was still higher than Fe-TiO$_2$. Subramanian et al. [38] also reported that the calculated band gap values were not greatly decreased with lower Co deposition and almost equal to the band gap of bulk-like TiO$_2$.

The surface of the prepared materials was characterised using scanning-electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis (Fig. 2).

As shown in Fig. 2a, the formation of TiO$_2$ nanoparticles using the sol–gel approach was clearly proved and the diameter of the nano-particles ranged approximately 50–150 nm (Fig. 2a insert).
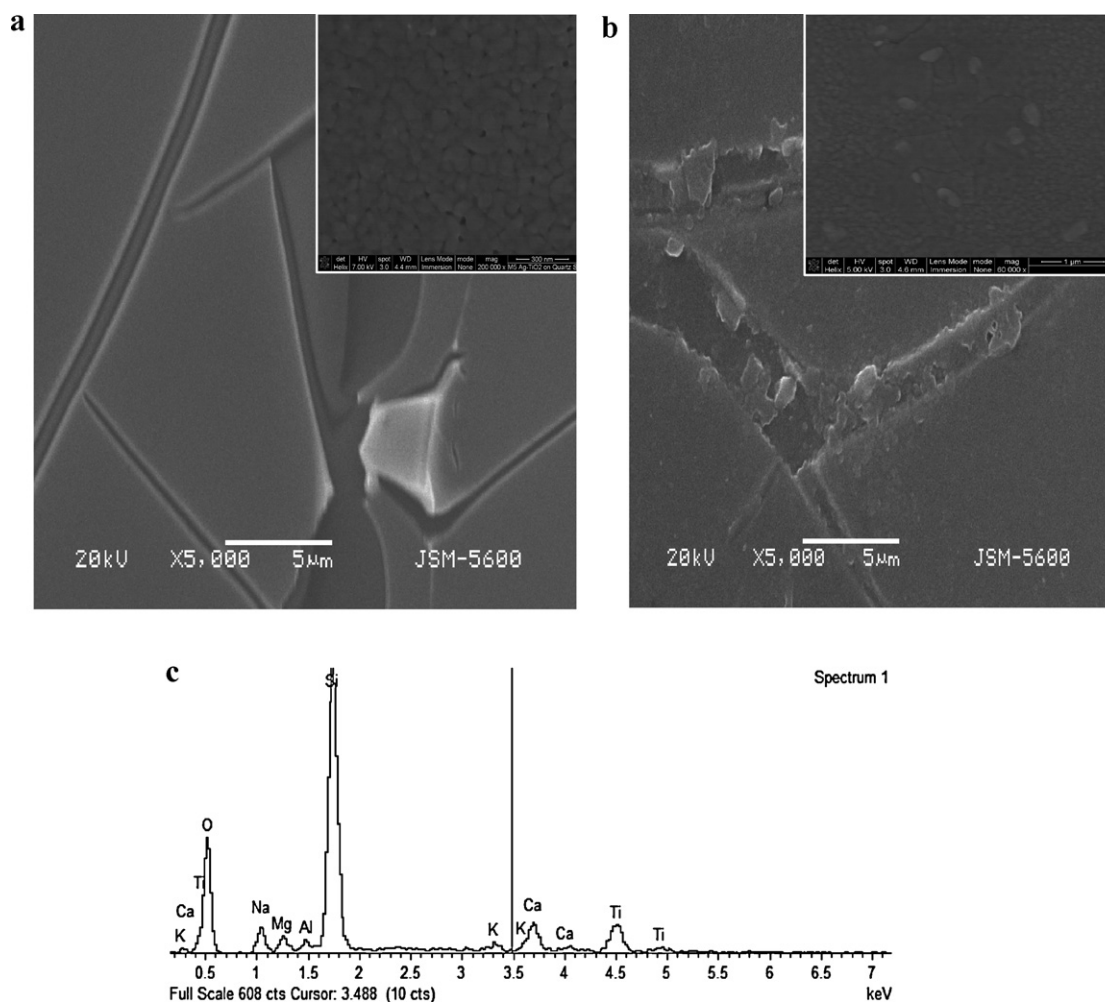
Fig. 2. SEM image of one layer of thin film coated on glass by sol–gel method: (a) TiO$_2$ thin film (inset at 300 nm scale), (b) Co-TiO$_2$ thin film (inset at 1 μm scale) and (c) EDX analysis of TiO$_2$ thin film.

Iron or cobalt doping at lower concentration produce more uniformed particles (Fig. 2b). SEM images that were taken in lower scale show that doping greatly affected the size and shape of the TiO$_2$ nanoparticles. Relatively smaller particles (10–100 nm) are present on the glass surface and larger particles are located randomly (Fig. 2b, insert). As shown by Subramanian et al. the density of the pores between TiO$_2$ nanoparticles decreased upon increasing the cobalt concentration and the grains were more equiaxed with continuous grain boundary which led an increased density of the film.

The EDX analysis was carried out to prove the presence of TiO$_2$ on the surface (Fig. 2c). The Fe or Co loaded TiO$_2$ films exhibit quite similar nano structures.

3.2. Photocatalytic disinfection of C. albicans and A. niger

The efficacy of the thin film coated glass against both microorganisms was monitored for 60 min under light exposure (Figs. 3 and 4).

The percentage reduction in the number of living colonies (the killing effect) on coated and noncoated glass is shown in Fig. 4.

In the case of C. albicans, photocatalytic action of the Co-TiO$_2$ thin film coated glass was significantly higher than other coatings for short and long exposure periods. This result is also better than previous study carried out by Kühn et al. [42] for the degradation of C. albicans. They reported that 2 log reduction efficiency had been

achieved using a TiO$_2$ thin film coated UVA-transmittant Plexiglas® sheet for degradation of C. albicans at initial cell concentration 1.1×10^5 CFU/mL.

As seen from Fig. 4 around 60% of C. albicans died over the noncoated surface. This marked reduction was attributed to cell damage induced by light. This suggestion was verified using by another set of experiments in the absence of light and significance tests used to compare the results. The tests confirmed that the degradation percentages over uncoated and film coated materials were significantly different at the 95% confidence level ($t_{ex} > t_{crt}$ at $P = 0.05$). Moreover, there was a significant difference between photocatalytic abilities of TiO$_2$ and Co-TiO$_2$ thin film coated glass.

Degradation efficiencies of C. albicans on Co-TiO$_2$ thin film were significantly higher than Fe-TiO$_2$ (Fig. 4). Degradation percentages were 87%, 99% and 81% for TiO$_2$, Co-TiO$_2$ and Fe-TiO$_2$ coated glass after 60 min illumination, respectively. It should be noted that iron deposition decreases the degradation ratio at the beginning of exposure (only 17% reduction after a 20 min).

It is clear that A. niger seems to be much more resilient to the photocatalysis than C. albicans (Figs. 3 and 4). This result is quite surprising since the thickness of the cell envelope of the fungi is much weaker than yeast type and expected to be degraded easily. Mitoraj et al. [33] reports that visible light induced photocatalytic inactivation of A. niger was resistant to photocatalytic degradation as much as C. albicans. Carbon-doped titanium dioxide and TiO$_2$ modified with platinum (IV) chloride complexes were used
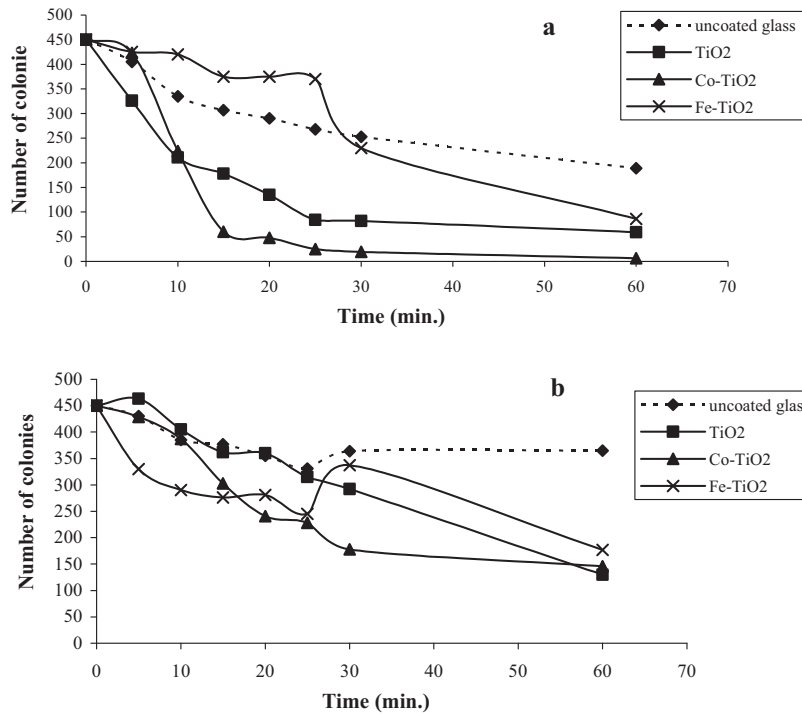
Fig. 3. Number of (a) *C. albicans* and (b) *A. niger* colonies during 60 min exposure with a UV lamp ($\lambda = 365$ nm).
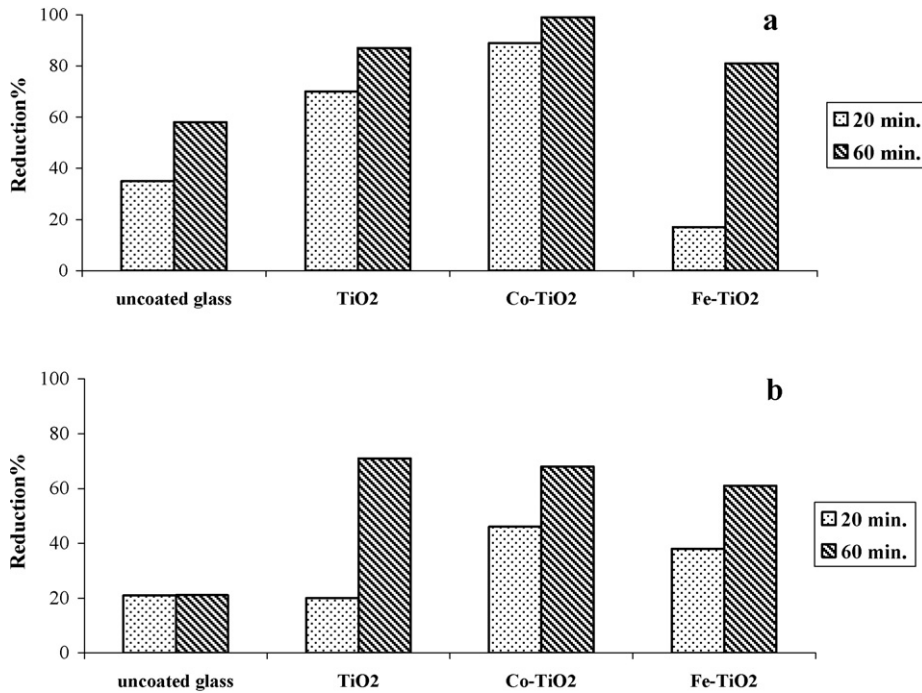

Fig. 4. Degradation percentages of (a) *C. albicans* and (b) *A. niger* on glass base after 20 and 60 min exposure.

either in suspension or when immobilized at the surface of plastic plates. However our results given in Fig. 4a and b show that thin films behave in different way than suspension systems. In the case of thin films, the interaction between the cell and catalyst must be quite different because of the distance between the nanoparticle and the cell. Production of reactive oxygen species (HO$^\bullet$, H$_2$O$_2$ or O$_2^{-\bullet}$) in the presence of UVA light might be the main killing effect rather than nanoparticle penetration through

the cell wall as in suspension system. On the other hand light might be more effective since light penetration through suspension is inhibited by nanoparticles that randomly moved in aqueous suspension.

When photocatalytic degradation of *A. niger* is considered Co-TiO$_2$ and Fe-TiO$_2$ thin films are not more effective than TiO$_2$ thin film for long exposure periods. It can be said that there is not a significant difference between doped and un-doped thin films for

a long term exposure (60 min). Reduction percentages for shorter exposure (20 min) periods seem to be higher for Co-TiO_2 and can be ordered as follows:

Co-TiO_2 > Fe-TiO_2 > TiO_2
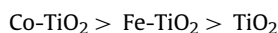
As indicated previously Co doping can reduce the band gap energy of TiO_2 via formation of new intermediate energy levels. It is known that Co is present as the divalent form which is located within the band gap of TiO_2 at interstitial position. So increased photocatalytic activity can be explained by the production of more active oxidant species. Cobalt seems to significantly improve the photodegradation of these microorganisms. But in the case of iron doping the doped Fe^{3+} ions become a recombination center the trapped free carrier pairs easily recombine since quantum tunneling effect [17]. Therefore photocatalytic activity of Fe-TiO_2 might be lower than expected value. It might worth to test Co and Fe doped TiO_2 thin films in visible light region for microorganisms employed in this study.

4. Summary

A short recent literature survey concentrated on the usage of Fe^{3+} or Co^{2+} ion doped TiO_2 thin films and suspensions were discussed and details of these studies were summarized in Tables 1 and 2. A sol–gel method was used for preparation of the 2% Co or Fe doped TiO_2 thin films. The surface of the prepared materials was characterised using scanning-electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis and band gap of the films were calculated from the transmission measurements that were taken over the range of 190 and 1100 nm. The value of E_g was 3.40 eV for the pure TiO_2 and 3.00 eV for the Fe-doped TiO_2 films. However, E_g value was 3.25 eV for Co-TiO_2 thin film which was higher than Fe-TiO_2.). Iron or cobalt doping at lower concentration produce more uniformed particles. According to SEM images doping greatly affected the size and shape of the TiO_2 nanoparticles. Photocatalytic killing effect of the 2% Co doped TiO_2 thin film on *C. albicans* was significantly higher than Fe doped TiO_2 thin film for short and long exposure periods. Doped thin films were more effective on *A. niger* for short exposure periods. These results support that produced materials can be used as self-cleaning material for many different purposes.

Acknowledgements

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