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RESEARCH PAPER

Synthesis and Characterization of Cu Doped TiO_2 Thin Films to Protect Agriculturally Beneficial Rhizobium and Phosphobacteria from UV Light

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ABSTRACT

By using sol-gel dip coating technique, it was observed that Cu doped TiO_2 thin films with different thickness were deposited on the microscopic glass substrates. The influence of prepared Cu-TiO_2 thin films' thickness (5, 7, and 9 dip coatings) on the structural, morphological and optical properties was analyzed by various characterization techniques. The results proved that the thicker the prepared samples, the more will be crystalline improvisation, UV absorbance enhancement and band gap reduction. It was observed that average grain size would increase from 55.26nm to 66.16nm if the thickness of the film increased from 1.06μm to 1.70μm. The optical band gap energy decreased as 3.2 eV, 3.0 eV and 2.8 eV respectively for 5, 7 and 9 layered thin films. Also the intensity of PL spectra of Cu doped TiO_2 thin films increased due to its distinctive high photon absorption. The present work ascertains the performance of multilayer coated Cu-TiO_2 thin films on protecting soil beneficial microorganisms from UV light radiation. UV screening feature of Cu-TiO_2 thin films efficiently safeguards bacterial colonies against UV light. Further, the raised thickness (9 dip) of Cu-TiO_2 thin film shows the high survival rate of bacterial colonies since they absorb much incident UV irradiation. Hence the environment friendly Cu doped TiO_2 thin films can be used as a low cost UV filter to protect microorganisms.

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INTRODUCTION

Transparent conducting oxide (TCO) materials such as ZnO, CdO, SnO_2 and TiO_2 are of great interest due to their distinctive physical, chemical, optical and optoelectronic properties. Among these materials, TiO_2 plays the most promising role in several areas of research owing to its efficiency in photo catalytic, and bacterial activity, high refractive index, resistance to photo corrosion, chemical stability, low cost, and non-toxicity [1]. Thin film finds its application in the field of optoelectronic, electronic and photonics, as the layer of materials exhibits evidently more improved structural and optical characteristics than the bulk materials. The characteristics of thin films are very much dependent on their thickness as the thickness of the film

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resolves the performance of prepared thin films [2]. The structural and optical properties of TiO_2 films (wide band gap =3.2eV) can be strongly modified by doping with impurities like Ag, Fe, Zn and Cu [3]. Specially, Cu metal is found to be one of the most considerable elements which reduces the band gap energy of pure TiO_2 and makes it a visible light active material. Numerous works on the applications of Cu doped TiO_2 have been reported in the areas of solar energy [4], environmental remediation for chemical contaminants removal [5], and microbial treatment [6, 7]. So far, less number of papers discussed the ability of doped TiO_2 thin films on protection of micro organisms against ultraviolet radiation of sunlight, though ultraviolet light has specific effect on human health, crop yield, terrestrial ecosystem, etc [8, 9]. The prolonged exposure to UV light limits the growth of microorganisms by inhibiting conjugation and affecting the metabolic pathways in it. The agriculturally beneficial microorganisms such as Rhizobium, Azotobacter, Azospirillium, Phosphobacteria and blue green algae play vital role in enhancing soil productivity. The various tasks of soil organisms are fixing atmospheric nitrogen, releasing nutrients, increasing phosphorous availability, controlling pathogens, degrading pesticides and improving soil structure. More importantly the microorganisms need to function ages in the presence of sunlight for improving soil fertility. Similar soil bacteria should be sheltered from ultraviolet radiations. It necessitates the development of strong UV absorbers which can safeguard such bacteria. TiO_2 films have UV resistant/blocking property which efficiently transforms the destructive UV light energy into heat. This salient feature assists to protect the microorganism from UV light [10, 11].

In the present work, the Cu doped TiO_2 thin films (5, 7 and 9 layers) were coated on glass substrate with the varying number of dip coating cycles. The effect of the deposited films' thickness towards their structural, surface morphological and optical properties was studied. The UV absorbance/resistant nature of Cu-TiO_2 thin films on agriculturally beneficial microorganisms (Rhizobium and Phosphobacteria) has been investigated and reported.

MATERIALS AND METHODS

Preparation of Cu doped TiO_2 thin films

Cu doped TiO_2 thin films were prepared by using sol-gel method. Titanium tetra isopropoxide (Ti $(OC_3H_7)_4$) was added as precursor and absolute ethanol (C_2H_6O) as solvent. The acetic acid (CH_3COOH) was added to initiate hydrolysis by an esterification reaction with ethanol. Initially TiO_2 sol was prepared by adding 4.5 ml of Titanium Tetra IsoPropoxide (TTIP) with 30 ml ethanol and 0.9 ml of acetic acid. This composition was stirred for 30 min using a magnetic stirrer. During the sol-gel synthesis copper II nitrate trihydrate (Cu $(NO_3)_2.3H_2O$) of 0.02 mol% was added to the solution as a copper precursor and stirred for 1 hour. The film was deposited on ultra-cleaned glass substrates by dip coating process at room temperature with the drawing speed of 45 mm for 30 sec. The coated glass substrates were dried at 100°C for 15 minutes. The process was repeated for 5, 7 and 9 times to get three different thin films of various thicknesses and named as C54, C74 and C94 respectively. The prepared films were amorphous in nature, as well as tensile stress might have been developed at the interface, due to substrate constraint. However increase in deposition temperature can reduce tensile stress reasonably [12]. To improve crystallinity the prepared samples were annealed at 400°C for 3 hours in muffle furnace.

The structural characterization of Cu doped TiO_2 film was carried out by X-ray diffraction (XRD) using X'PERT PRO X-ray diffractometer which was operated at 40 KV and 30 mA with $CuK\alpha_1$ radiation of wavelength 1.5407 Å and the scanning range was 10–60 degrees. The surface morphology and elemental composition were studied using Scanning Electron Microscope (SEM) EVO18 Carkzeiss and S– Flash 6130 with Bruker EDX. The surface topology was studied using Atomic Force microscope (AFM) Nano surf Easy scan 2. The thickness of the film was measured using Mitutoyo Surfest SJ-301stylus profilometer. UV-Visible spectra were recorded in the range of 200-800 nm using Schimadzu 1800 UV-VIS-NIR spectrophotometer. The photoluminescence (PL) spectra of the sample were recorded employing Schimadzu RF – 5301 luminescence spectrophotometer with xenon lamp as the source at room temperature exited at 410 nm wavelength.

Isolation and preparation of Rhizobium and Phosphobacteria strain

Isolation of rhizobium was done by using Yeast Extract Mannitol Agar (YEMA) as described by Rajendran *et al*. [13]. The healthy nodules collected from groundnut plant roots were washed under tap water to remove adhering mud and soil particles, after that they were treated carefully with 5% hydrogen peroxide for surface sterilization. The nodules were repeatedly washed in sterile water for 3- 4mins and then treated with 70% ethyl alcohol for about one minute and 0.1% $HgCl_2$ for two minutes. The nodules were crushed in sterile water. About 0.1 ml of this solution was spread plated in YEMA medium and incubated at 37°C for seven days. After seven days incubation, Rhizobium was observed as white watery colonies in YEMA medium. These colonies were inoculated in nutrient broth and incubated at 37°C for 24 hour. This broth culture of Rhizobium was used for further experiment.

For isolation of Phosphobacteria, 1g Rhizosphere soil was suspended in 100ml of distilled water. This soil solution was spread plated in Pikovskaya's medium and the plate was incubated at 30°C for five days [14]. After five days incubation, white colonies showing phosphate solubilizing zone around them were isolated. These colonies were inoculated in nutrient broth and incubated at 37°C for 24 hour. Then the broth culture of Phosphobacteria was used for further experiment.

The 5 ml culture of both Rhizobium and Phosphobacteria were centrifuged at 3000 rpm for 10 minutes. The supernatant was discarded and the pellet was washed with 5 ml sterile water and again centrifuged. The process was repeated for three times, and then the pellet was washed with 5 ml sterile water.

UV screening effect of Cu doped TiO_2 thin films on agriculturally beneficial bacteria

The Rhizobium pellet culture suspended in 5ml sterile water was equally taken in 5 different conical flasks. Three conical flasks were covered with Cu doped TiO_2 thin films of different thickness (C54, C74 and C94) and exposed to UV rays of 260 nm for 5 minutes at a distance of 30 cm and one conical flask was used as a control and that was used to compare the survival rate of bacteria in the flask with the same in other flasks. Fourth conical flask was directly exposed to UV rays. The experimental arrangement was shown in Fig. 1. All the cultures were inoculated in nutrient agar plates by spread plate technique in laminar air flow chamber and incubated at 37°C for 24 hr. The experiment was repeated with phosphobacteria microorganism.

When a photon of energy higher or equal to the band gap value of the semiconductor is absorbed by a particle, an electron from valence band is promoted to conduction band with simultaneous generation of photo generated hole (h_{vb+}) in the valence band. The photo generated electron (e_{cb-}) in the conduction band is given by

$$\mathrm{TiO_2 + h\nu \rightarrow TiO_2 + e_{cb-} + h_{vb+}}$$

The e_{cb-} and h_{vb+} can recombine on the surface or in the bulk of the particle in a few nanoseconds and the energy is dissipated as heat or trapped in surface states and is given by

$$\mathrm{e_{cb-} + h_{vb+} + TiO_2 \rightarrow TiO_2 + heat(recombination)}$$

Fig. 1. Protection of bacterial culture from UV light using Cu doped TiO_2 thin films in Laminar air flow chamber

RESULTS AND DISCUSSION

Structural analysis

The XRD pattern of Cu-TiO$_2$ thin films, having different thickness annealed at 400°C for 3 hours is shown in Fig. 2. The XRD pattern demonstrates that all the three prepared (C54, C74 and C94) films have tetragonal (BCC) crystal structure with anatase phase which was confirmed by the prominent peak at (1 0 1) orientation. No peaks corresponding to rutile phase was detected in the recorded XRD pattern. In five layered Cu-TiO$_2$ thin film, three peaks corresponding to (1 0 1), (2 1 0) and (2 0 0) planes of TiO$_2$ anatase phase were observed (JCPDS: 89-4921). In case of seven layered Cu- TiO$_2$ thin film, pattern similar to five layers confirmed the formation of same phase. For the third sample with nine layered Cu-TiO$_2$ film, the formation of anatase phase was confirmed by matching five peaks corresponding to (1 0 1), (2 1 0), (2 0 0), (1 0 5) and (2 1 1) planes which match with data card (JCPDS: 89-4921, 78-2486). The calculated unit cell parameters were consistent with standard values. It was observed that the intensity of diffraction peaks increased while stacking more layers of atoms over the substrate. It indicates the improvement in crystallinity of C94 high thickness film and the peak intensity depends upon the crystallinity of the deposited films [15]. However no diffraction peaks belonging to Cu additives were perceived since Cu might be present in small amount as nano clusters [16]. The replacement of Ti^{4+} ions by Cu^{2+} is quite possible in the prepared Cu doped TiO$_2$ films since the ionic radius of Cu^{2+} is (0.87 Å) is close to ionic radius of Ti^{4+} (0.75 Å). It was reported that according to Hume-Rothery rules [17], if the ionic radius difference is less than 15%, then Cu^{2+}can dissolve into TiO$_2$ crystal lattice comfortably. The interplanar spacing (d$_{hkl}$) was calculated using the relation and listed in Table 1.

$$d_{hkl} = \frac{n\lambda}{2\sin\theta}\,(\text{Å}) \qquad (1)$$

The crystallite sizes of the films were determined by using Debye-Scherrer formula

$$D = \frac{K\lambda}{\beta\cos\theta}\ (\text{nm}) \qquad (2)$$

where, K = 0.94, λ = 1.5407 Å, β = Full Width Half Maximum (FWHM) and θ = diffraction angle. The Dislocation density ‘δ’ was calculated using relation

$$\delta = \frac{1}{D^2}\left(\frac{\text{lines}}{\text{m}^2}\right) \qquad (3)$$

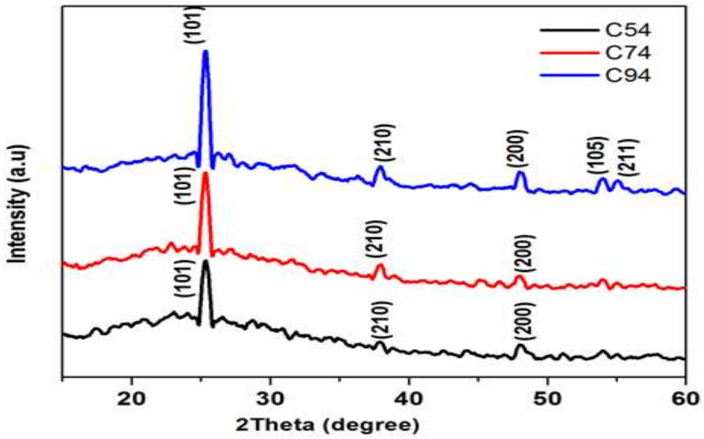

Fig. 2. XRD pattern of Cu doped TiO$_2$ thin films

Table 1. Micro structural parameters of Cu-TiO$_2$ films deposited at different dipping cycles

Dip coating cycles	Thickness (μm)	Crystallite sizeD (nm)	Inter-planar spacing d (Å)	Dislocation Density δ x 10^{14} (lines/m^2)	Micro Strain ε	Lattice Constant a (Å)	c (Å)	V(Å)^3
5	1.06	55.26	3.5135	3.24	0.0360	3.787	9.488	136.07
7	1.36	60.45	3.5168	2.74	0.0328	3.793	9.478	136.36
9	1.70	66.16	3.5171	2.28	0.0301	3.793	9.470	136.21

where 'D' is the crystallite size of Cu doped TiO$_2$ thin film. The micro strains (ε) was caused by crystalline defects and determined using the following relation

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (4)$$

It was found that 'δ' and *'ε'* decreased with the increasing number of dip coating cycles which implied that lattice imperfection and strain were reduced due to increase in crystallite size as well as the thickness of the film [Table 1]. In the multistep coating process the thickness and crystallite size increased about 38 % and 16% whereas dislocation density and microstrain decreased about 42% and 19% respectively. The variation of crystallite size, dislocation density, micro strain and thickness of the films with number of dipping cycles are shown in Fig. 3a and 3b.

Surface morphology and Elemental Analysis

The surface morphology of Cu doped TiO$_2$ thin films (C54 and C94) was examined by scanning electron microscopy technique. Fig. 4a and 4b show the SEM micrographs of C54 and C94 respectively. The 5 layered films (C54) show the sparsely cracked granular particles. Crack formation might be provoked by different factors such as lattice mismatch, evaporation of solvent molecules which are not bonded properly with the substrate and thermal expansion. In other words the relaxation of tensile stress would lead to crack formation [18]. The 9 layered (C94) film demonstrated densely packed cracking patterns with flake like morphology. More closely packed cracking was owing to the nucleation on the substrate further followed by stacking of more atoms in C94 thin films [19]. It was obvious that the crack formation increased with increased thickness because of reduced adhesion induced by annealing. To corroborate the chemical composition of prepared Cu-TiO$_2$ thin films, it was characterized using EDX. In the EDX spectra**,** the characteristic peaks of Ti, O and Cu were observed which revealed that the obtained thin films are composed of Ti (33 wt %), O (66 wt %) and Cu (0.75wt %).

Surface topography

Atomic force micrographs (2D and 3D) of 9 layered Cu-TiO$_2$ thin films deposited on glass substrate are shown in Fig. 5(a) and 5(b) respectively. AFM image exhibits the distribution of well-defined spherical grain of Cu-TiO$_2$ on the surface of the film and the bright grain emerged from the surface of the film indicate the attachment of Cu particles on the TiO$_2$ surface [20]. The average roughness and root mean square values of C94 thin films are about 1.86 nm and 2.77 nm respectively. The low roughness value characterizes the good homogeneity of the TiO$_2$ particles on the surface of the film [21].

Photoluminescence Analysis

The Photoluminescence spectrum of a material revealed the utility of trapping, migration and transfer of electron and holes in semiconducting materials. The PL spectra of prepared thin films recorded at room temperature with excitation wavelength of 410 nm are shown in Fig. 6. The

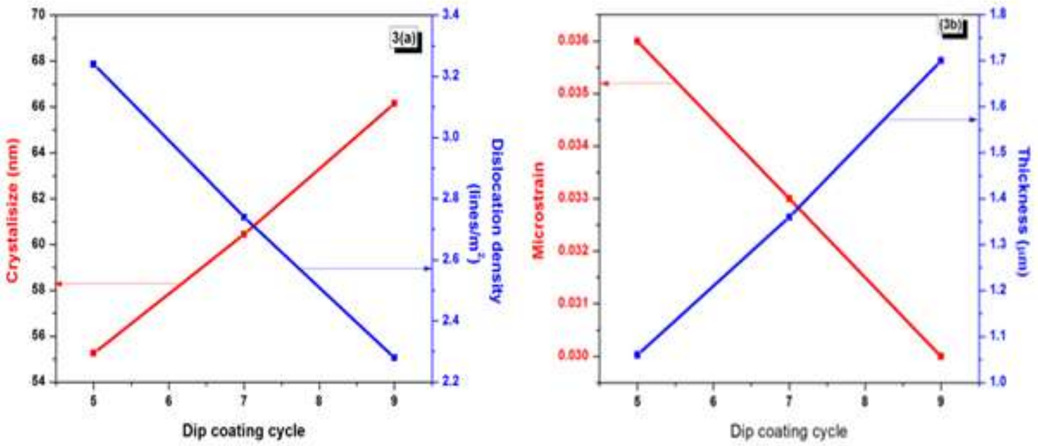

Fig. 3. (a) Variation of crystallite size and Dislocation density (b) Micro strain and thickness with number of dipping cycles

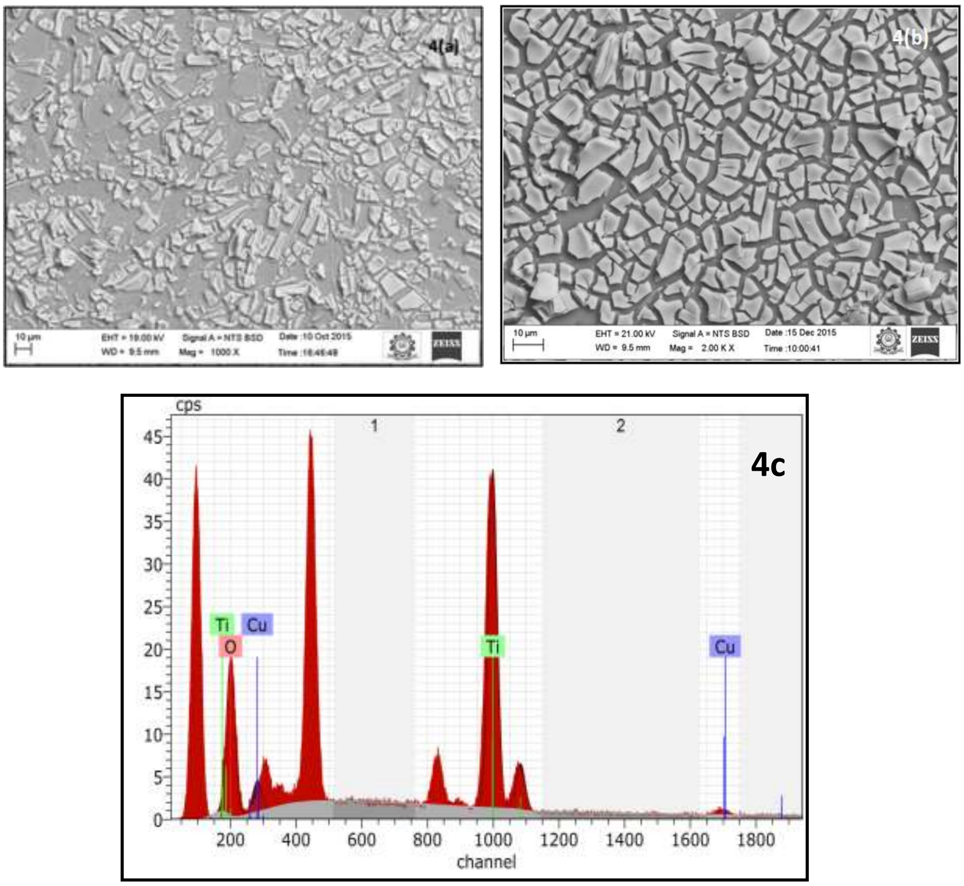

Fig. 4. SEM images of (a) C54 and (b) C94 and (c) EDX spectrum of Cu-TiO$_2$ thin films

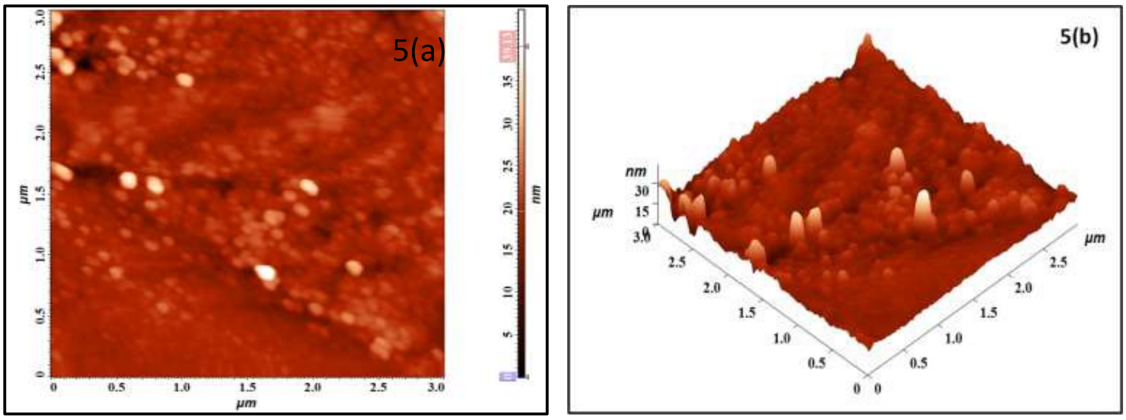

Fig. 5. AFM (a) 2D and 5 (b) 3D image of Cu-TiO$_2$ thin films (C94)

spectra show three distinct visible light emission peaks. The peaks at 457nm (2.7eV), 485nm (2.6eV), 545nm (2.3eV) and 560nm (2.2eV) are assigned to deep level emission of material in the visible region. As the number of layers increased from 5 to 9, transmittance of the films decreased indicating the creation of more oxygen vacancies [22]. The blue emission peak at 485nm (2.6eV) was likely due to crystal defects, most probably arising out of the oxygen vacancies in the lattice [23]. Another blue emission peak at 457nm and green emission peak at 537nm were due to the color centers associated with oxygen vacancies [24]. It was perceived that intensity of films raised since decreased tensile strain and improved grain size remarkably influenced the luminescent properties of doped TiO$_2$ films upon adding thickness [25- 26].

Optical Analysis

The recorded optical transmittance spectra of C54, C74 and C94 thin films are shown in Fig. 7. The transmittance of deposited thin films was found to be decreased when stacking of Cu-TiO$_2$ layers on the substrate changed from 5 to 9 layers. The increase in thickness of the film caused a change in band structure which led to a red shift in optical absorption edge [27]. The decline in transmittance was associated with shift in absorption edge and increased grain size of Cu-TiO$_2$ particles [28-29]. The spectra revealed that the transmittance was constant in the visible region and the transmittance decreased when it approached to zero in UV region. It suggested that the absorption property of prepared samples was dominant in the UV region and exhibited Cu-TiO$_2$ thin films an excellent UV screener/filter.

The band gap energy of Cu doped TiO$_2$ thin films can be determined from a plot of $(\alpha h\nu)^2$ versus energy ($h\nu$), as shown in Fig. 8.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (5)$$

Where A is a constant, E_g is the band gap value. The band gap value has been determined by extrapolating the straight line portion at $\alpha = 0$ as seen in Fig. 8. It was observed that the band gap of the material decreased from 3.2eV to 2.8eV with increase in thickness of the film. The decrease in band gap with increase in number of coating cycles might be influenced by the change in film density, grain size and dislocation density [30]. The band gap shrunk gradually since dislocation density decreased with the increase in thickness. Thus the improved long range translational periodicity of

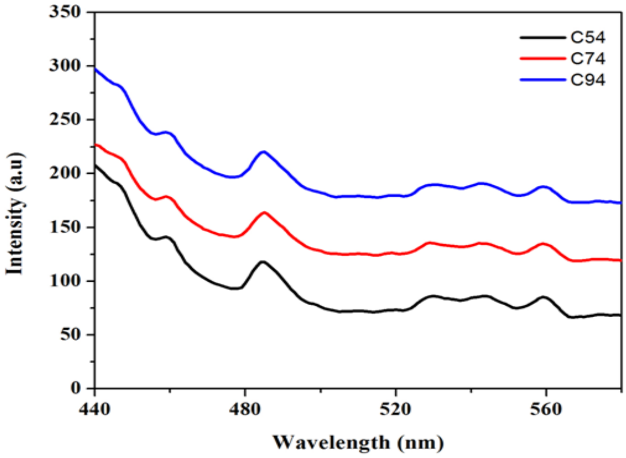

Fig. 6. Photoluminescence spectra of Cu doped TiO$_2$ thin films

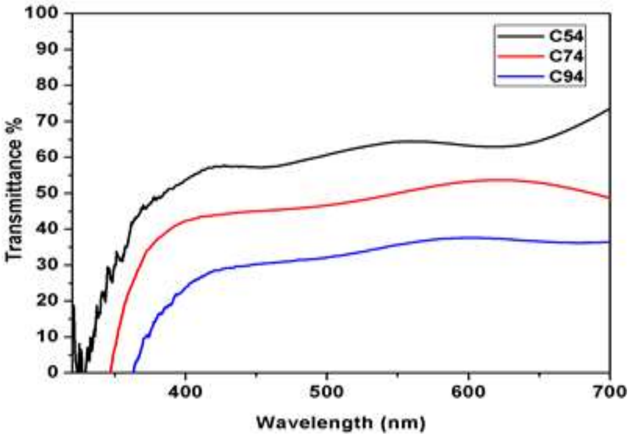

Fig. 7. Optical Transmission spectra of Cu doped TiO$_2$ thin films

higher thickness film C94 led to reduction in band gap with in energy levels.

Protection of Rhizobium and Phosphobacteria from UV light using Cu-TiO$_2$ thin films

After incubation, the bacterial colonies were counted using colony counter and the results are recorded in Table 2 and each value is the mean of two replicate experiments. Fig. 9 shows the response of Rhizobium and Phosphobacteria to UV filter effect of Cu-TiO$_2$ thin films of different thicknesses. Thin films prevented penetration of UV light by absorbing it completely or in other words it back scattered UV radiation. The back scattered radiation was dissipated into heat radiation. It was clearly seen that the conical flask exposed to UV light without any Cu-TiO$_2$ films on it displayed minimum percentage of survival rate of Rhizobium and Phosphobacteria as 18% and 12% respectively. The flasks covered with thin films and exposed to UV light showed better survival rate. In addition this percentage of survival rate increased with increasing thickness of the film. In both samples, the films with 9 layers (C94) defended more bacterial colonies and it acted as the best protective layer against UV light. Fig. 10 shows the photo of viable Rhizobium and Phosphobacteria colonies exposed to UV light rays. The result confirms that the Cu-TiO$_2$ thin films prevent the UV rays fairly and enhance the growth of soil beneficial organisms like Rhizobium and Phosphobacteria.

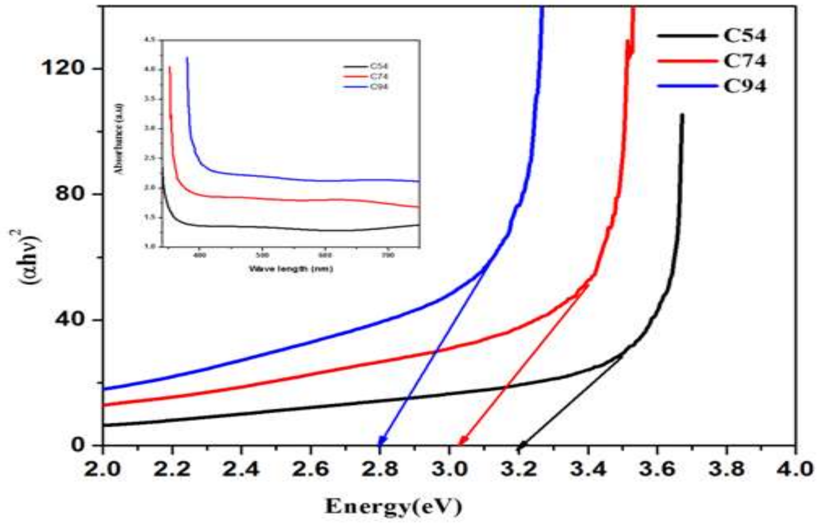

Fig. 8. Direct band gap of Cu doped TiO$_2$ thin films with insert of absorption

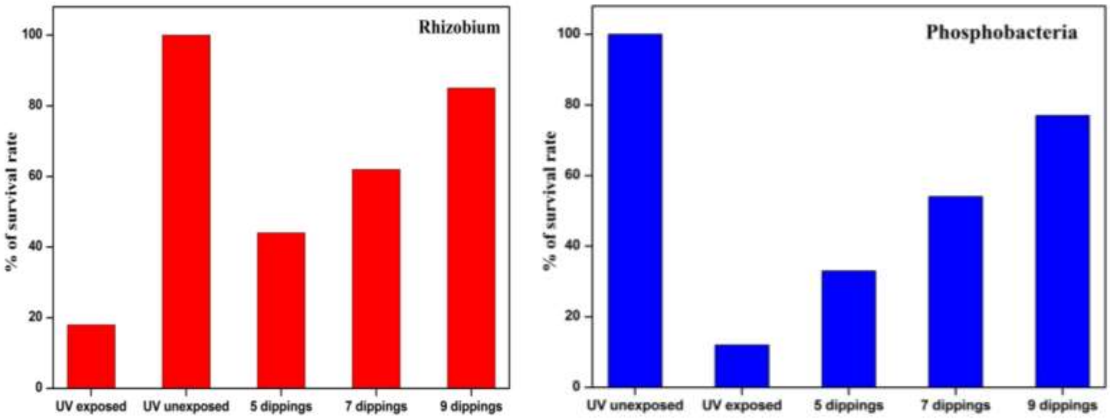

Fig. 9. Response of Rhizobium and Phosphobacteria with UV radiation on Cu-TiO$_2$ films

Table 2. Survival rate of *Rhizobium* and *phosphobacterium* of Cu doped TiO$_2$ thin films

Treatments	Survival rate of Rhizobium (%)	Survival rate of Phosphobacteria (%)
UV exposed	18	12
UV unexposed	100	100
5	44	33
7	62	54
9	85	77

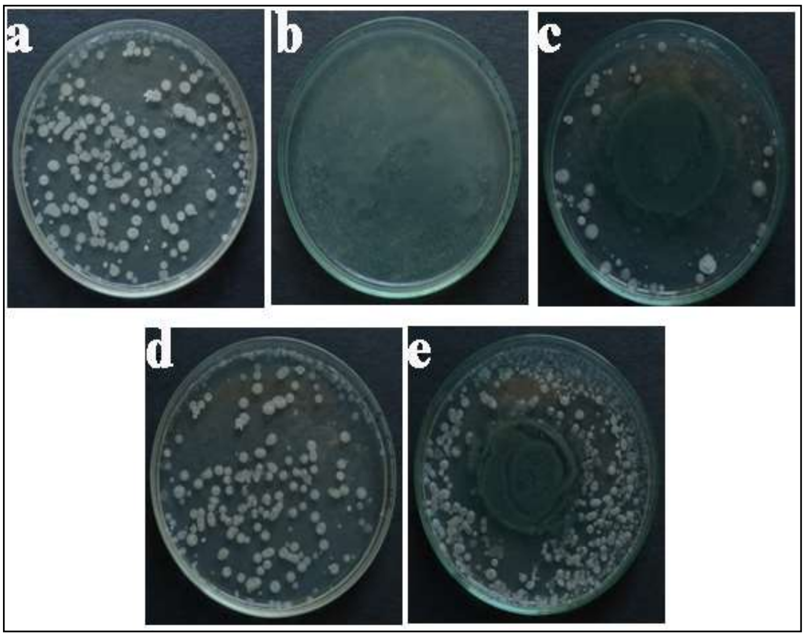

Fig. 10. Photo of bacterial colonies (a) unexposed to UV light (b) exposed to UV light (c) 5 dip (d) 7 dip (e) 9 dip exposed to UV light rays

CONCLUSION

The Cu doped TiO$_2$ thin films of various thicknesses have been deposited on glass substrate by sol-gel dip coating technique. The present study confirms that the properties of Cu doped TiO$_2$ thin films are considerably influenced by film thickness. The deposited Cu-TiO$_2$ films show increase in the nanometer sized spherical grains and improve the film structure with the increase in thickness. The larger grain size improves the optical properties of TiO$_2$ films. The increase in thickness minimizes the defect density in the band gap. The feasibility in the protection of soil beneficial microorganisms by exploiting high UV absorbance nature of Cu-TiO$_2$ thin film was discussed. Furthermore, anti UV effect of high thickness Cu-TiO$_2$ thin films shows high survival rate of microorganisms. This beneficial effect of Cu -TiO$_2$ thin films can be employed in protecting constructive microorganisms and human skin from harmful UV radiations.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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