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Visible Photocatalytic Activity Of Vanadium Doped With Titanium Dioxide For Biomedical Applications

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Abstract: Infections are a common post-operative complication associated with high mortality rates after surgical procedures. Coating surgical instruments or implants with antibacterial or antifungal substances may reduce the occurrence rate of infections acquired during surgical operations. The high incidence rate of post-operative infections, caused for example by the implantation of biomedical devices and/or the general hospital environment, has a severe impact on patients' health. However, no studies have been reported on the prevalence of active species of fungal and bacteria. The present study systematically examines the antibacterial properties (against Staphylococcus, Bacillus, Serratia and Pseudomonas) of nanostructured thin films based on pure TiO_2 and TiO_2 with Vanadium as an additive, created using a simple and cost effective sol-gel process. The thin films were deposited on glass and Si substrates and their structural and morphological properties were investigated by standard spectroscopic techniques such as X-Ray Diffraction, Scanning Electron Microscopy and Atomic Force Microscopy. The drop test method was used to test for antifungal and antibacterial properties. Our results indicate that increased V concentrations are associated with increased antimicrobial activity in thin films based on TiO_2:V.

Keywords: post operative infection, anti microbial activity, coating instruments.

Introduction

Titanium dioxide (TiO_2) is an important compound, whose electronic structure continues to attract considerable attention for potential modern technological applications[1]. TiO_2 can be used for the decomposition of undesired compounds in air, waste water, solar energy conversion and the production of clean energy resources through the water splitting reaction[2]. However, the application of TiO_2 as a photo catalyst for visible light-induced chemical reactions has been hampered due to its large band-gap energy (3.2eV for anatase TiO_2), which requires ultraviolet (UV) light to activate and which in turn leads to the low efficiency[3].

Widening the absorption edge of TiO_2 from the UV to the visible spectral range could provide the groundwork to develop TiO_2 catalysts with visible light activity.

Many studies had been attributed to the doping of transition metals into TiO_2 to develop visible photo catalysts such as V, Cr, Mo, & Fe[4]. Among the transition metal ions, vanadium ion is attractive because vanadium doping can increase carrier lifetime and also extend the absorption range of TiO_2. Different methods had been chosen to prepare V-doped TiO_2 catalysts, such as the sol-gel method, metal ion-implantation method, co-precipitation method and hydrothermal method. Synthesis of V doped TiO_2 powders using sol-gel technique is promising due to its low cost and facile synthesis[5]. The performance of a TiO_2 photo catalyst is strongly dependent on a number of structural factors, such as crystal phase, grain forms and the degree of crystallinity[6] .

The metal doping in nanosize TiO_2 has no effect on the photocatalytic activity of Titanium and the visible light photocatalytic activity of doped vanadium is lower than that of undoped titania. The doped TiO_2 anatase nanocrystals have the highest visible light activity while undoped TiO_2 has photocatalytic activity only under UV-radiation excitation[7]. This property is exploited for anti microbial coating on surgical implants.

Experimental Procedure

Preparation of nano structured thin film

Pure TiO_2 thin film

4ml of titanium Isopropoxide was taken in a beaker and 80ml of 2-methoxy ethanol was added and stirred gently for 1 hour using magnetic stirrer to get a homogeneous solution.To the above mixture, 3ml of acetyl acetone was added as a stabilizing agent and stirred for 1 hour. Then 2 ml of polyethylene glycol (PEG) was added and stirred for 1 hour.Then 0.5N HCL was added and stirred for 1 hour.The solution was left for 4-5 hour stirring to get homogenous mixture. The contents were filtered using a whattman's filter paper and stored for further use. After ageing for 1 day, the stock solution was ready to be coated by dip coating technique.

Vanadium doped TiO_2 thin film

Different concentrations 0.50g (0.15 wt %), 1.0g (0.30 wt %), 1.5g (0.45 wt %) of ammonium metavandate was weighed and transferred to beaker. To this, 20ml of 2-methoxy ethanol solvent was added and stirred for 30 minutes. Then 1 ml of 0.1N Hcl was added to the above contents to make a clear solution. This mixture was the added to pure TiO_2 solution drop-wise and stirred for 4 to 5 hours. After ageing for 1 day, the solution was ready to be coated by dip coating technique.

Annealing

The coated substrates were annealed in hot air oven at 50^o C to evaporate the solvent. Then high temperature annealing was done at 200˚C, 400˚C and 600˚C respectively in Muffle furnace.

Anti Microbial Activity Testing – Drop Test Method

Nutrient agar medium was prepared using peptone (5.0 g), beef extract (3.0 g), and sodium chloride (NaCl) (5.0 g) in 1000 ml distilled water and the pH were adjusted to 7.0 and agar (15.0 g) was added to the solution. The agar medium was sterilized in aquilots of 15ml at a pressure of 15 lbs for 15 min. This nutrient agar medium was transferred into sterilized Petri dish in a laminar air flow chamber and allowed to solidify. Then 100 µl of bacterial suspension was grown in nutrient broth for 24 hours and standardized (0.5 McFarland standard). This was then added on each TiO_2 and C coated plates and kept in visible light and UV chamber for 3 hours. The plates were incubated at 37˚C for 24 h and colony forming units (CFU) were counted with a digital colony counter. For comparison purpose, a control was also prepared.

Results and Discussion

Scanning Electron Microscopy

Morphological studies on the treated films of pure TiO_2 and TiO_2 with different concentrations of V as additive have been carried out by employing high resolution scanning electron microscopy (SEM).

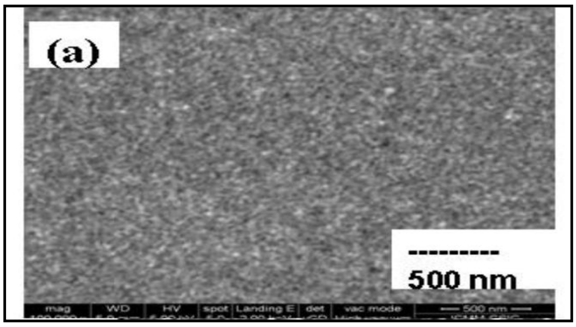
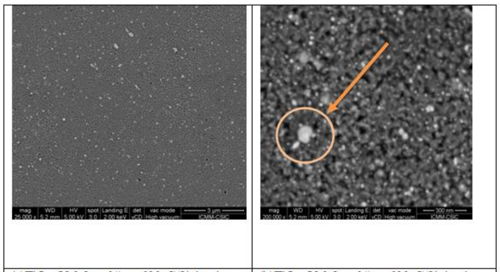


Figure.1 (a) Scanning Electron Micrographs of nanostructured thin films of pure TiO_2 annealed at 400°C for 3h in air ambient

The deposited and annealed films were uniform, homogeneous, crack free, and highly dense.



(a)TiO_2: V:0.3 wt%) at 600°C/3h in air
Low magnification

(b)TiO_2: V:0.3 wt%) at 600°C/3h in air
High magnification

Figure.2 SEM images of TiO_2:V loaded thin films annealed at 600˚ C at low and high magnification.

As can be seen in the low magnification SEM image film has several protruding particles on the surface.which is evident in the high magnification SEM image (shown in the circle).

Atomic Force Microscope

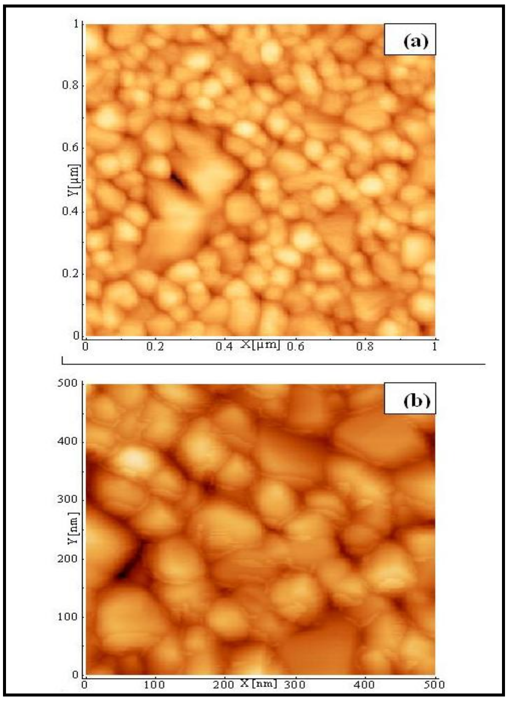


Figure.3 AFM image of the TiO_2: V loaded (0.3 wt %) film annealed at 400°C.(a &b)

The surface topography of the TiO_2: V loaded (0.3 wt %) annealed at 400°C for 3 hours was seen in this image. It was observed that the deposited and annealed film was nanostructured, with small pores distributed unevenly.

Drop Test Results – Antimicrobial Activity

The four species of bacteria were investigated for the antimicrobial testing are Staphylococcus, Bacillus, Serratia and Pseudomonas. All the species showed consistent susceptibility to TiO_2: V thin films. Different series of drop test experiments were conducted by varying different parameters.

- Different concentration of vanadium doping (0.15 wt%, 0.30 wt%, 0.45 wt %)
- Different number of dip coatings (1 dip, 3 dip, 6 dip)
- Different annealing temperatures (200˚C, 400˚C, 600˚C)

Effect of annealing temperature on microbial growth.

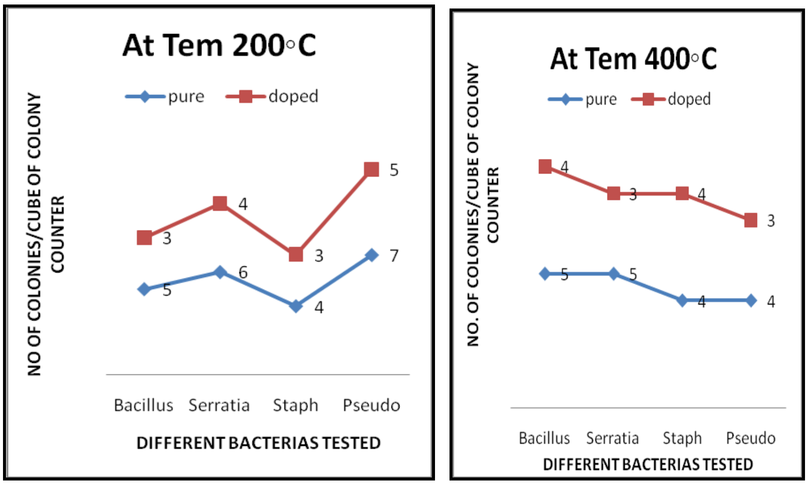


Figure 4. Colony forming units of different bacteria's on nanostructured thin films of pure TiO_2 and TiO_2 with .30%wt concentrations of V as additive annealed at 200°Cand 400°C for 3h in air ambient. The above graph shows that annealing temperature plays a key role in better film deposition and anti microbial activity. Action of 400°C doped films was more than 200˚C.As compared to staphylococcus, serratia growth was hindered at 200°C annealed 3 dip coated films.

Drop test images

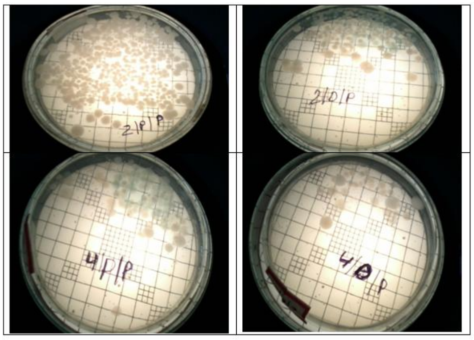


Figure 5. Photographs showing the activity of nano structured thin films (pure and doped) at different annealing temperature. (2/P- pure at 200°C, 2/D-doped at 400°C, 4/P-pure at 400°C, 4/D-doped at 400°C).

Above images of bacterial growth clearly indicates that doping with higher annealing was effective as compared to undoped thin films.

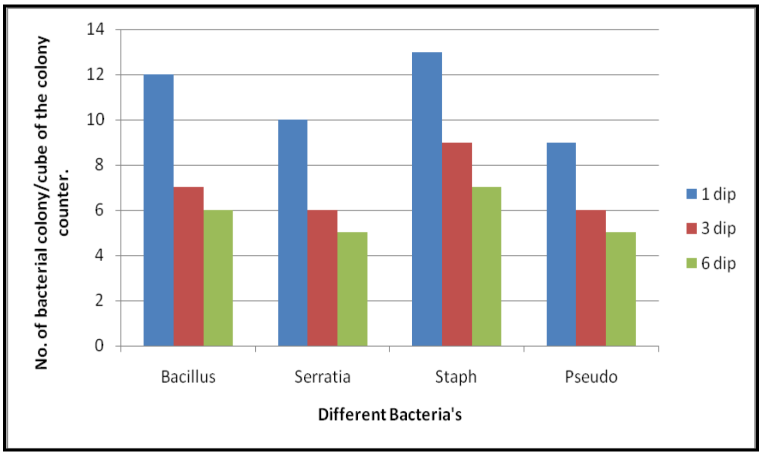


Figure 6. Graph showing the viability of different bacterial strains on the nanostructured thin films and the influence of the number of dips.

Comparing the growth of all the four bacterial species with the different dip coatings at .45% wt concentrations of V as additive annealed at 400^{o}C for 1h in air ambient. Thin TiO_2 was more effective against Serratia, and least effective for Staphylococcus.

Conclusion

Titanium dioxide and titanium dioxide doped with vanadium were prepared using cost effective sol-gel method. Thin films were coated on glass substrates using dip coating technique at a speed of 450 mm/min with wetting time of 1 min and drying time of 2 min. Film length was about 50-55mm.

Antibacterial and antifungal studies were done for four species – Staphylococcus, Bacillus, Serratia and Pseudomonas.The SEM images shows that at low temperature annealing, the particle grain size was large and at high temperature, fine grains were obtained. This was due to the phase transition from rutile to anatase phase. The results were confirmed with AFM images.

From the anti microbial test, it was observed that annealing temperature plays an important role in determining the anti microbial activity. As compared to Staphylococcus, Serratia growth was hindered in 200^{o}C annealed 3 dip coated film. It was also observed that the effect of doping with higher annealing temperature showed higher antimicrobial activity. The coatings showed maximum anti microbial effects against Serratia and least against Staphylococcus. The maximum decrease in microbial growth was found in 6 dip coatings for all the four species of bacteria.

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