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UV screening performance of TiO₂ thin films on agriculturally beneficial Rhizobium and Azotobacter

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Abstract: Rhizobium and Azotobacter are agriculturally beneficial living organisms present in biofertilizers which fix atmospheric nitrogen into Ammonia and increases soil fertility thereby promotes plant growth. UV radiations kill or inactivate microorganism thereby prevent the growth and development of the plants. Titanium dioxide (TiO₂) is a wide band gap semiconductor, an efficient light harvester and has strong UV light absorbing capability. Here, we reported that the UV screening effect of TiO₂ thin films as a protective layer in the enhancement of growth of Rhizobium and Azotobacter. TiO₂ nanostructure thin films of different thicknesses were prepared using sol-gel dip coating method on glass substrate by different coating cycles and annealed at 350°C for one hour. It is found that the crystallite size and roughness increases with increase in number of coating cycles. Energy gap and transmittance decreases with increase in film thickness. This study showed that TiO₂ thin films act as protective layer against UV radiation and enhance the survival rate of organisms.

Keywords- Beneficial organism; TiO₂ thin film; XRD; AFM; UV Screening effect.

Introduction and Experimental:

In recent years, Titanium dioxide (TiO₂) has been extensively used in numerous fields because of its excellent properties. TiO₂ belongs to the class of semiconductor with relatively wide band gap (3.2 eV for anatase and 3.0 eV for rutile structures). When exposed to the light of energy corresponds to its band gap, charge carriers such as electrons and holes are produced and oxidation and reduction reaction occurs on the TiO₂ surface. In comparison to the crystallite phase of TiO₂, anatase is most photoactive due to the difference in energy band structure [1] and the rutile protects the materials from ultraviolet radiations due to good scattering effect [2].

UV light impairs photosynthesis and reduces size, productivity, and quality in many of the crop plant species. Overexposure to UV radiations kills or inactivates the cells of living micro organisms. Rhizobium, Azotobacter, Azospirillum and blue green algae are living micro organisms advantageous in enriching soil fertility and fulfilling plant nutrient. TiO₂ thin films have UV resistant properties and efficiently transform destructive UV light energy into heat when exposed to UV radiations. This advantage enhances its ability to protect the micro organisms from ultraviolet light. Here, we studied the effect of film thickness of TiO₂ on the

enhancement of survival rate of agriculturally beneficial organisms rhizobium and azotobacter, as protective layer against UV radiation.

Materials and Methods:

The TiO₂ sol was prepared by adding 6.3 ml of TTIP-Titanium Tetra Isopropoxide (Ti (OC₃H₇)₄), to a mixture of 5 ml acetic acid and 50 ml ethanol and stirring the mixture for 15 minutes using magnetic stirrer. The film was coated on glass substrates at a constant rate of 25 mm/min using a dip coating machine. The dip coated glass substrates were dried by heating at 150°C for 5 minute and the process was repeated for 4, 6, 8 and 10 times to get four different thin films samples of various thicknesses. Finally all the samples were annealed at 350°C for 1 hour in muffle furnace.

Agriculturally beneficial microbes Rhizobium [3] and Azotobacter [4] were isolated from soil. UV screening performance of thin films was experimented by the following process. A laminar air flow chamber was used in this experiment to determine the effect of UV light exposure on organisms. The UV irradiated culture spread uniformly on 5 different nutrient agar plates and one more agar plate with culture unexposed to UV light were incubated at 37°C for 24 hours. After the incubation, the number of surviving microbes in each plate was counted by colony counter.

Results and Discussion:

Structural properties

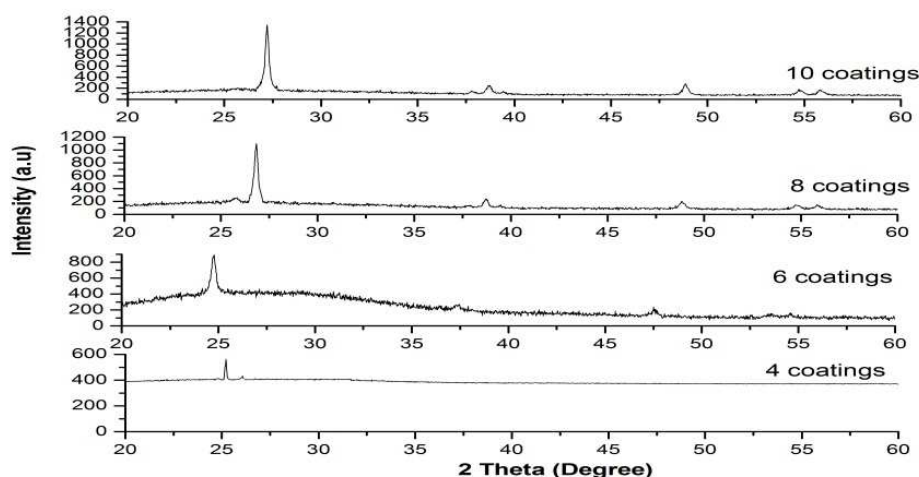


Figure 1 XRD patterns of TiO₂ thin films for different number of coatings

Table 1 Parameters of TiO₂ thin film for different coating cycles

No. of coatings	Thickness (μm)	Crystallite size D (nm)	Band gap (eV)	Transmittance at 500 nm (%)	Survial rate of Rhizobium (%)	Survial rate of Azotobacter (%)
4	0.5	14.9	4	90	62	66
6	0.85	23.4	3.8	69	64	76
8	1.55	29.4	3.7	62	76	82
10	1.82	56.9	3.6	51	82	87

XRD patterns of the films annealed at 350°C for different number of coatings is displayed in Figure 1. The prominent peaks detected at 24.78° and 25.12° can be attributed to the tetragonal (1 0 1) crystal structure with anatase phase for 4 and 6 coating films which is in agreement with standard JCPDS data (File No.21-1272). For 8 and 10 coating TiO₂ films the dominant peaks are observed at 26.89° and 27.22° and these films have tetragonal (1 1 0) crystal structure and rutile phase which are in agreement with standard JCPDS data (File No.21-1276). The phase change from anatase to rutile in the TiO₂ film growth may be due to film thickness and composition in the film. The crystallite size of the films determined using the well-known Debye-Scherrer's formula is shown in Table 1. The value3 of thickness of the film measured using Stylus profilometer is found to increase with number of coatings of the films [Table 1].

Surface morphology

AFM, SEM and EDAX spectra of 10 times coated TiO_2 thin film is shown in figure 2. The AFM image is covering an area of $3\mu\text{m} \times 3\mu\text{m}$ of TiO_2 thin films and the surface plot reveals that the film is quite rough with average roughness (S_a) of 13.4837 nm and Root mean square roughness (S_q) of 18.0748 nm. SEM micrograph of the nano crystalline TiO_2 thin film shows loosely agglomerated grains with inhomogeneous surface. In the EDAX spectrum, only characteristic peaks of Ti and O are observed which reveals that the obtained thin films are composed of Ti (39 wt %) and O (45%).

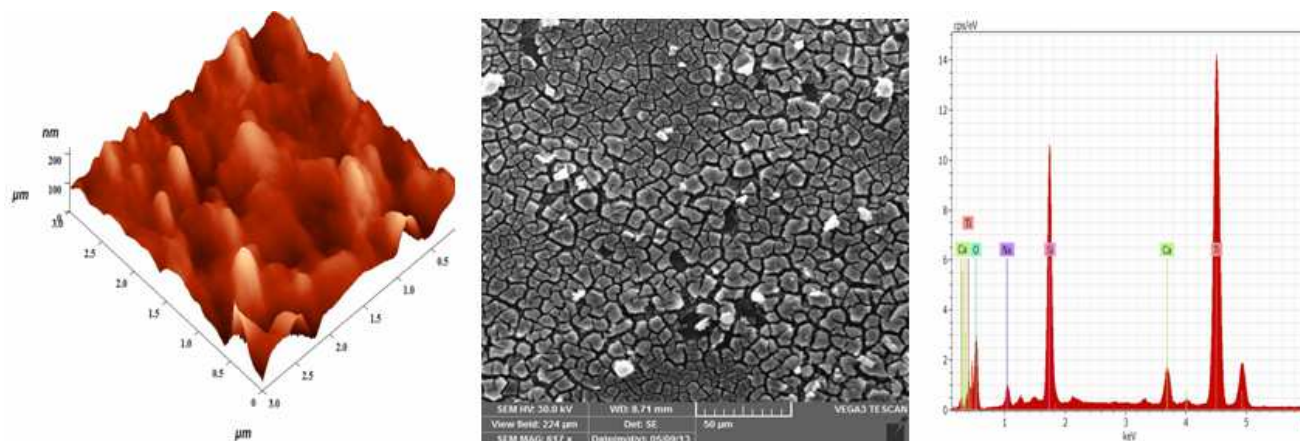


Figure 2 AFM, SEM and EDAX spectra of 10 times coated TiO_2 thin films

Optical properties

Figure 3 shows the UV–Visible transmittance spectra of TiO_2 thin films for different number of coating cycles in the wavelength range 200 – 800 nm. The decrease in transmittance of the films (Table 1) is because of enhanced absorption as a result of the increase in film thickness and the scattering effect originating from increased crystallite size.

The direct band gap values calculated using the Tauc's plot is found to decrease with increase in number of coating cycles (Table 1) which might be the result of the change in film density and increasing crystal size and it may be attributed to the quantum confinement limit of nano particles.

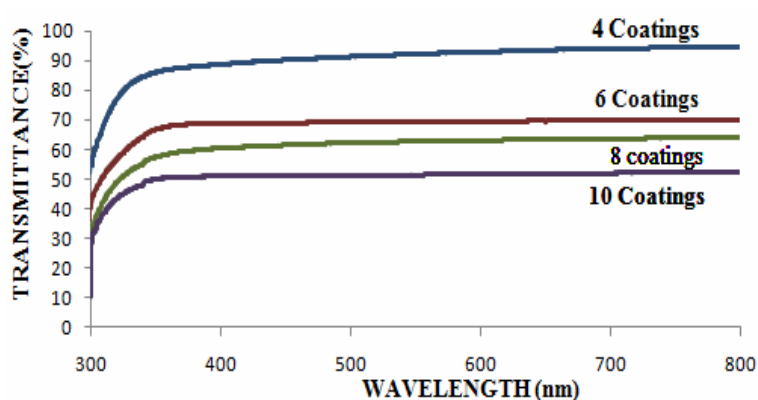


Figure 3 Transmittance spectra of TiO_2 thin films for different number of coatings

Results of UV screening effect of TiO_2 thinfilms

After incubation the organisms were counted using colony counter. The survival rate of microbes unexposed to UV is 100% whereas completely exposed to UV radiation is 29% and 41% for rhizobium and azotobacter respectively. The percentage of survival rate increases with increase in number of coatings for both organisms (Table. 1). The result showed that, the TiO_2 thin films protect the beneficial living microorganism by absorbing UV radiation.

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