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Influence of SiO_2 Concentration on TiO_2 Thin Films as Protective Layer to Chlorophyll in Medicinal Plants against UV Radiation

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Abstract:SiO_2 doped TiO_2 (SiO_2 - TiO_2) nano structure thin films were prepared by dip coating method on glass substrates by varying the concentration of SiO_2 and annealed at 400°C for 3 hours in a muffle furnace. The films were characterized by X-Ray diffraction (XRD), UV- visible spectroscopy and Scanning Electron Microscopy (SEM) with elemental (EDAX) studies techniques. UV light impairs photosynthesis and reduces size, productivity and quality in many of the crop plants. Increased exposure of UV light reduces total chlorophyll content in plants. Development of nano science and technology provides new ways for better treatment of UV resistant films and fabrics using Titanium dioxide (TiO_2). TiO_2 has good Ultra Violet (UV) blocking power and is very effective in applications because of advantages such as non-toxicity, chemical stability at high temperature and permanent stability under UV exposure. The main objective of this study was to analyze the performance of SiO_2 doped TiO_2 thin films as a protective layer to the chlorophyll contents present in medicinal plants *Solanum nigrum* (Manathakkali) and *Solanum trilobatum* (Thuthuvalai) from UV radiation. The study revealed that crystallite size and transmittance of films decrease with increase in SiO_2 concentration. The thickness of the film increases with increase in SiO_2 concentration. However, the chlorophyll content increases in accordance with increase in SiO_2 concentration. This study showed that SiO_2 doped TiO_2 thin films are good absorber of UV light and protect the total chlorophyll content in medicinal plants.

Keywords: Chlorophyll, SiO_2 doped TiO_2 thin films, *Solanum nigrum*, *Solanum trilobatum*, UV radiation, XRD

1 Introduction

Frequent reports of skin cancer have made people increasingly aware of the danger of prolonged exposure to UltraViolet (UV) rays, which account for about 6 % of the terrestrial sunlight and under excessive doses is proved to cause erythema, certain skin cancers, keratitis and cataracts. There are organic and inorganic UV blockers. The organic blockers are called UV absorbers because they mainly absorb UV rays. Inorganic UV blockers are usually certain semiconductor oxides such as TiO_2, ZnO, Al_2O_3 etc., Compared with the existing organic UV absorbers, inorganic UV agents are preferred because of their unique features including non - toxicity and chemical stability under high temperature and UV ray exposure [1]. In the past decades, Titanium dioxide (TiO_2) has been investigated by many researchers due to its electric, optic, catalytic, chemical stability and non-toxicity properties [2, 3]. Another importance of TiO_2 in the recent years is its implementation in self - sterilizing surfaces in hospitals owing to its reliability and stability under radiation [4]. Some investigators observe that TiO_2 provides good UV protection by reflecting or scattering most of the UV-rays through its high refractive index and also it absorbs UV radiation because of its semi conductive properties [5, 6]. The phase structure and semi conducting properties of TiO_2 thin films can be strongly modified by doping with metals like Ag, Fe, Cu, Zn, SiO_2 [7] etc., Addition of dopant could increase the adhesion and mechanical stability of thin films on substrates which play a key role in device stability [8,9]. UV light has specific effects on various life forms and it is one of the most important environmental factors affecting the growth and development of plants. Its lethal effect can alter the composition of materials and conditions needed for the plants to grow. Increased exposure of UV light reduces total chlorophyll content in medicinal plants [10]. Recent research shows that chlorophyll has medicinal properties. Chlorophyll is beneficial to human body in numerous ways. It is known to be the green element that helps to clean the body from harmful toxins. It is also an active agent that the body uses to fight infection. A regular and recommended intake of chlorophyll keeps the circulatory and digestive systems healthier. The chlorophyll content in the plants portrays how chlorophyll plays an important role in their medicinal properties. *S.nigrum* plant has several medicinal

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benefits. The plants are used as an emollient and analgesic to treat itch, burns and neuralgic pains and are considered to be an expectorant and laxative. The leaves are said to have sedative and healing properties and are applied to heal cuts, ulcers, wounds, inflammations and skin diseases. An extract of the leaves and stem is used for treating dropsy, heart diseases, piles, gonorrhoea, fevers, eye diseases and chronic enlargement of liver and spleen. The plant *S.trilobatum* has been called as *kayakalpa* in Indian traditional method of medicine called Siddha. The whole plant (i.e. leaves, stem, flower and fruit) is used as medicine. The leaves are considered good for asthma and tuberculosis. In Siddha, the leaves are said to improve blood count and prevent the thickening of the blood, which leads to many diseases.

Since SiO_2 doped TiO_2 thin films efficiently transform destructive UV energy into heat, they can be used to protect the chlorophyll content in *S.nigrum* and *S.trilobatum* medicinal plants from UV radiation. In this work, the properties of TiO_2 and SiO_2 doped TiO_2 thin films prepared by sol-gel dip coating method were studied and the effect of prepared thin films on medicinal plants against UV radiation was reported.

2 Experimental Methods

2.1 Materials

All chemicals are of analytical reagent grade and were used without any further purification. The TiO_2 and SiO_2 precursors were titanium tetra iso propoxide (TTIP) and tetra ethyl ortho silicate (TEOS) respectively. Ethanol and acetic acid were selected as solvent and stabilizer of TTIP.

2.2 Thin film preparation and coating process

Nano structure SiO_2 doped TiO_2 thin films were prepared by the following method. 4 ml of TTIP was mixed with 30 ml of ethanol. Then 1ml of acetic acid was added to stabilize the solution and stirred for half an hour. Finally, TEOS was added to the solution in various concentrations (1, 2 and 3 mol %). To get a transparent and clear solution, it was continuously stirred for an hour. The solution obtained was deposited on microscopic glass slides by dip coating technique with a dipping rate of 50 mm for 30 sec. Pre heating is necessary for evaporation of the organic elements present in the films. Hence, deposited films were pre heated at 100°C for 10 min. After cooling the substrate at room temperature, the next coating was done. Multiple coating was done during the film preparation process. Finally, the 6 times coated films were post annealed at 400°C for 3 hours. The pure TiO_2 film was prepared by the same method without adding TEOS. Figure 1 shows the flow chart for the preparation of thin films.

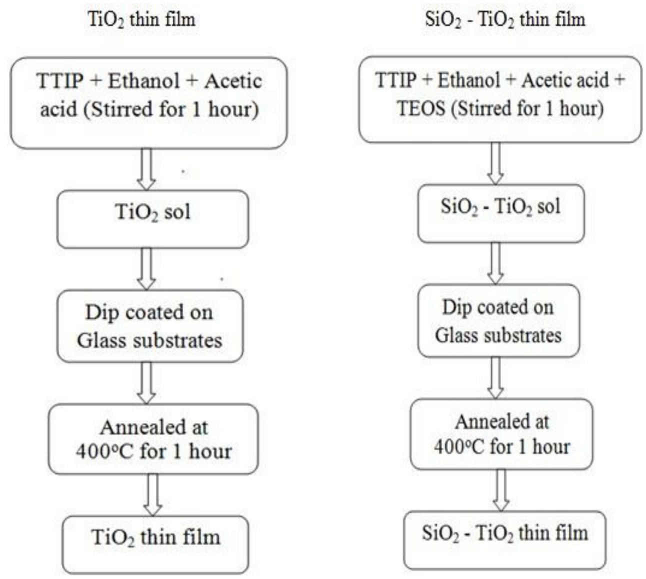

Figure 1: Flow chart for the preparation of TiO_2 and SiO_2 -TiO_2 thin films

The annealed films were characterized by X-Ray Diffraction (XRD), UV – visible spectroscopy, Scanning Electron Microscopy (SEM) and EDAX studies. The thickness of the films was measured by stylus profilometer.

2.3 Estimation of chlorophyll

UV light of wavelength 260 nm at a distance of 40 cm was used in this experiment to determine the effects of UV exposure on *S.nigrum* and *S.trilobatum* leaves. 1g of finely cut healthy fresh green leaves of *S.nigrum* was taken in six different 100 ml conical flasks. The control flask containing *S.nigrum* leaves was completely unexposed to UV light. i.e. maintained under room condition. One flask was completely exposed to UV light and the other four flasks were covered with prepared thin film samples with different concentration of SiO_2 with TiO_2 and pure TiO_2. Then they were exposed for 10 minutes to UV light.

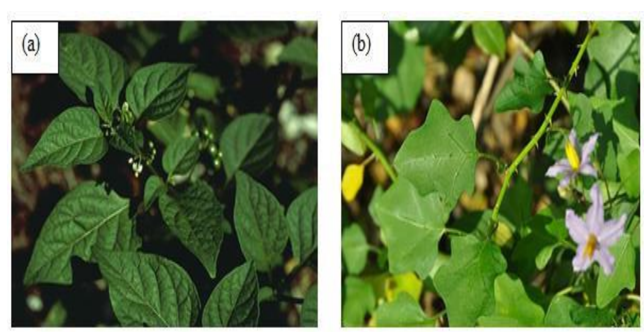

Figure 2: (a) *Solanum nigrum* and (b) *Solanum trilobatum*

The chlorophyll content was estimated using the method described by Arnon (1949) [11] on the UV exposed and unexposed leaves. 1g of finely cut fresh leaves was grounded to a fine pulp with the addition of 20 ml of 80%

acetone in a mortar and pestle. This solution was then centrifuged for 5 minutes at 5000 rpm. The supernatant was transferred to a 50 ml volumetric flask. The pellet was suspended in 20 ml of 80 % acetone, centrifuged for 5 min at 5000 rpm and then the supernatant was again transferred to the flask. This process was repeated until the pellet became almost colorless. The solution in the flask was made up to 100 ml with 80 % acetone. This procedure was repeated for all the samples. The standard (Systronics) UV spectrophotometer was used to record the absorbance of the solutions at 663 nm and 645 nm. The experiment was repeated thrice. The statistical software SPSS version 17.0 was used for analysis.

The amount of chlorophyll-a, chlorophyll-b and total chlorophyll were calculated in terms of mg chlorophyll/g of fresh leaves.

$$\text{mg chlorophyll a/g tissue} = [12.7(A_{663}) - 2.69(A_{645})] \times V/(1000 \times W)$$

$$\text{mg chlorophyll b/g tissue} = [22.9(A_{645}) - 4.68(A_{663})] \times V/(1000 \times W)$$

$$\text{mg total chlorophyll /g tissue} = [20.2(A_{645}) + 8.02(A_{663})] \times V/(1000 \times W)$$

Where,

A = absorbance at specific wavelengths,

V = final volume of chlorophyll extract in 80 % acetone which in this case is100 ml and W = fresh weight of tissue extracted which is 1g.

The same procedure was repeated for *S.trilobatum* leaves.

3 Results and Discussion

3.1 Structural analysis

XRD patterns of the pure TiO_2 and SiO_2 doped TiO_2 thin films for various concentration of SiO_2 are displayed in Figure 3.

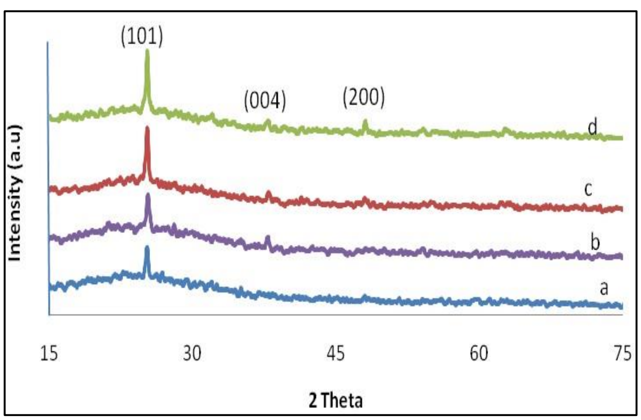

Figure 3: XRD pattern of (a) TiO_2 (b) 1 mol % SiO_2 - TiO_2 (c) 2 mol % SiO_2- TiO_2 (d) 3 mol % SiO_2- TiO_2 thin films

The deposited films show nano crystalline nature with high intense peak in (1 0 1) orientation having anatase phase with tetragonal BCC structure. They also show that the intensity and full width half-maximum (FWHM) increased with increase in SiO_2 concentration. The diffraction peak found in the XRD pattern is in good agreement with the JCPDS card no 89 - 4203. The crystallite size was determined using the Debye-Scherer's formula,

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta} (\mathrm{nm})$$

The crystallite size was found to be 67.9 nm for pure TiO_2 thin film. In various concentration of SiO_2 (1, 2 and 3 mol %) with TiO_2 the crystallite size was found to be 53.9 nm, 40.5 nm and 33.2 nm respectively. Addition of SiO_2 decreases crystal size and crystallinity in films by inhibiting the growth of particles in the crystalline network [12].

3.2 Morphological analysis

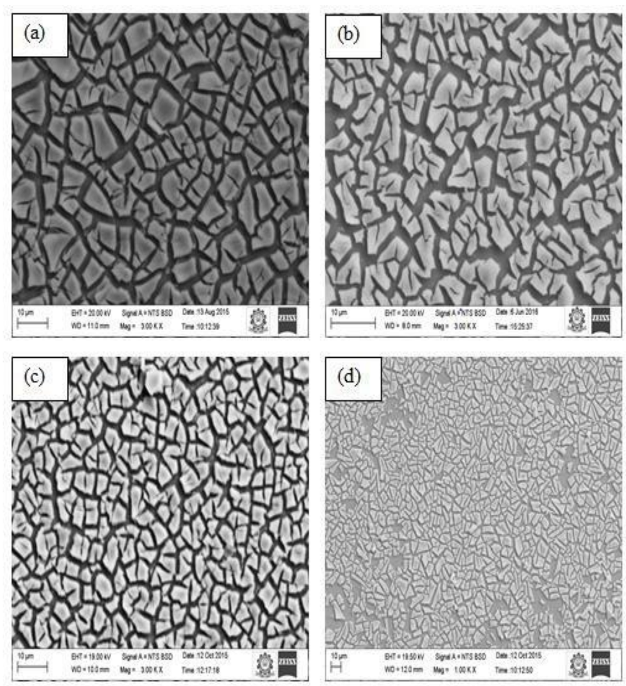

Figure 4: SEM micrograph for (a) TiO_2 and (b) 1 mol % SiO_2- TiO_2 thin films (c) 2 mol % SiO_2 - TiO_2 thin films (d) 3 mol % SiO_2 - TiO_2 thin films

SEM and EDAX spectra of TiO_2 and SiO_2 - TiO_2 thin films annealed at 400°C are shown in Figure 4 and 5. SEM micrographs indicate fractured morphology. The morphology of the films strongly depends on the concentration of dopant. At higher doping concentration, the growth of the grains suppressed and segregated due to the presence of compressive stress in the film [13].

The composition of the films was studied by EDAX analysis. For the TiO_2 spectrum, characteristic peaks of Ti and O were observed but for SiO_2 doped TiO_2 spectrum, characteristic peak of Si was observed along with peaks of

Ti and O. The atomic wt % of SiO_2 increases as the concentration of SiO_2 increases.

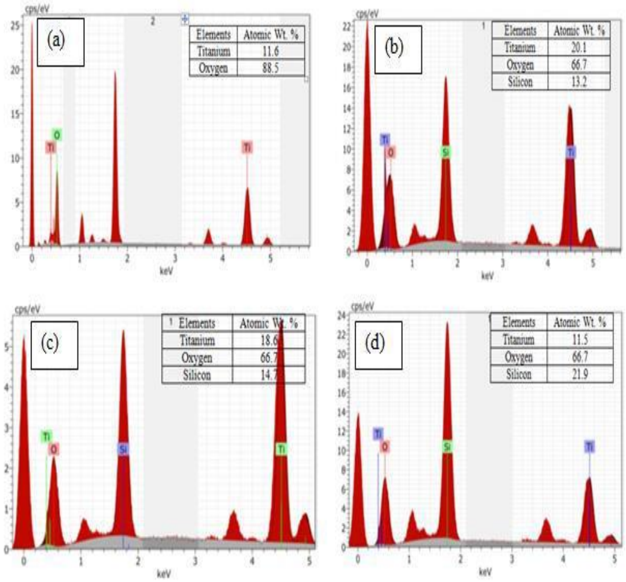

Figure 5: EDAX spectra for (a) TiO2 (b) 1 mol % SiO_2-TiO_2 (c) 2 mol % SiO_2 - TiO_2 (d) 3mol % SiO2 - TiO_2 thin films

3.3 Optical analysis

Figure 6 shows the UV visible transmittance spectra for TiO_2 and SiO_2 - TiO_2 thin films. The decrease in transmittance of the films is because of enhanced absorption because of the increase in film thickness. The transmission values at 500 nm were 78 % for pure TiO_2, 55 % for1 mol % SiO_2 – TiO_2, 48 % for 2 mol % SiO_2 – TiO_2 and 40 % for 3 mol % SiO_2 – TiO_2 thin films respectively. The thickness value increases as the SiO_2 concentration increases and the values are 1 µm, 1.5 µm, 2 µm and 2.5 µm for pure TiO_2, 1 mol % SiO_2 – TiO_2, 2 mol % SiO_2 – TiO_2, 3 mol % SiO_2 – TiO_2 thin films respectively.

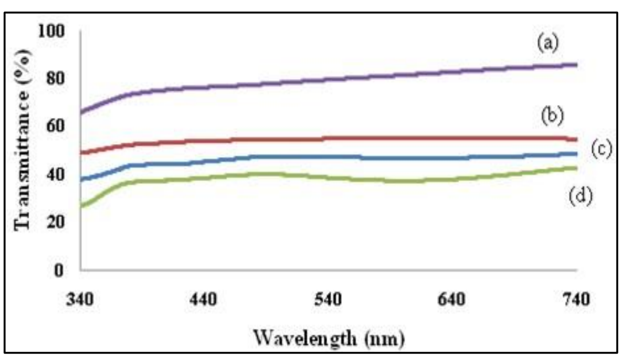

Figure 6: Transmittance spectra of (a) TiO_2 (b) 1 mol % SiO_2- TiO_2 (c) 2 mol % SiO_2- TiO_2 (d) 3 mol % SiO_2 - TiO_2 thin films

3.4 Chlorophyll analysis

Figure 7 shows the variations in the chlorophyll content for different concentrations of SiO_2 with TiO_2 and pure TiO_2 thin films for *S.nigrum* and *S.trilobatum* plants. From Figure 7, it was observed that total chlorophyll content is high (100 ± 6.4 %) in fresh *S.nigrum* leaves when it was unexposed to UV radiation. Total chlorophyll content gradually increases in such leaves even after the UV treatment while using pure TiO_2 and SiO_2 – TiO_2 thin films of various thicknesses as protective layer. In the UV completely exposed treatment, chlorophyll content is very low and the values are 43.8 ± 3.5 % and 62.8 ± 4.2 % for *S.nigrum* and *S.trilobatum* leaves respectively.

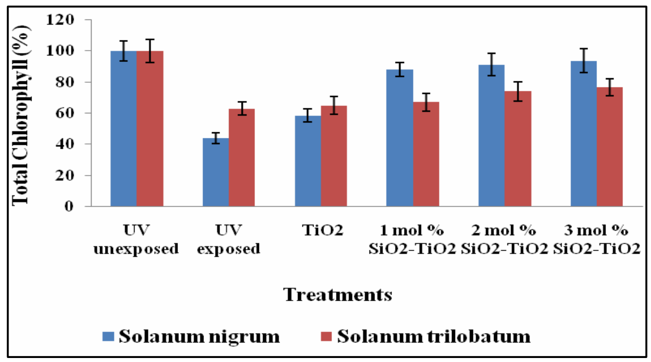

Figure 7: Comparison of total chlorophyll content (%) of *S.nigrum* and *S.trilobatum* for Pure TiO_2 and SiO_2 - TiO_2 thin films

It was also observed that total chlorophyll content of *S.nigrum* leaves is equal to 93.6 ± 7.3% for 3 mol % of SiO_2 - TiO_2 thin films. This value corresponds to total chlorophyll content of *S.nigrum* leaves in control treatment. Films of highest dopant concentration absorb maximum UV light since increased thickness protects the leaves from UV damage thereby increasing chlorophyll content. Similarly for *S.trilobatum* leaves, films with highest dopant concentration absorb maximum UV light and the chlorophyll content is about 76.7 ± 5.5 %.

4 Conclusion

Pure TiO_2 and SiO_2 - TiO_2 thin films of various concentrations of SiO_2 were deposited on glass substrate by sol - gel dip coating technique resulting in highly efficient UV absorbing films. XRD study revealed that the thin films are in anatase phase with tetragonal structure having preferential orientation along (1 0 1) plane. The stoichiometric ratio of SiO_2 - TiO_2 thin films was confirmed with EDAX spectra. The study revealed that the crystallite size and transmittance of the SiO_2 - TiO_2 thin films decrease with the increase in dopant concentration. This study showed that SiO_2 - TiO_2 thin films are a good absorber of UV light that protects the chlorophyll content in *S.nigrum* and *S.trilobatum* leaves.

References

[1] Hongying Yang, Sukang Zhu, Ning Pan, Studying the mechanisms of titanium dioxide as Ultraviolet - blocking additive for films and fabrics by an improved scheme, Journal of Applied Polymer Science **92** (2004) 3201 – 3210.

[2] M.E.Yang Juan and J.M.F.Ferreira Hydrothed, Influence of tetra alkyl ammonium hydroxides on particle characteristics. Journal of The American Ceramic Society **84**(8) (2001) 1696-1706.

[3] Hang Ru-bin and Gao Lian, Effect of peptization on phase transformation of TiO_2 nanoparticles, Journal of Materials Research**36** (2001) 1957-1965.

[4] S.Dhanapandian, A.Arunachalam, C.Manoharan, Highly oriented and physical properties of sprayed anatase Sn doped TiO_2 thin films with an enhanced anti-bacterial activity, Applied Nanoscience, (2015).

[5] R.Mossotti, R.Innocenti, R.Dimechelis, P.D.Pozzo, Changes in the properties of wool fibres by using alternative materials, Proceedings of the 10^{th} International Wool Textile Research Conference, Aachen, Germany, Nov. 26–Dec. 1,**11**(2000) F1–P15 1–9.

[6] B.Bohringer, UV Protection by textiles, Proceedings of the 37th International man-made fibres congress, Dornbirn, Austria, **9** (1998) 1031–1044.

[7] T.Yuranova, R.Mosteo, J.Bandara, D.Laub, J.Kiwi, Self-cleaning cotton textiles surface modified by photoactive SiO_2 / TiO_2 coating, Journal of Molecular Catalysis A: Chem, **244** (2005) 160-167

[8] Leke Sikong, Jirapan Damchan, Kalayanee kooptarnond and Sutham Niyamwas, Effect of doped SiO_2 and calcination temperature on phase transformation of TiO_2 photo catalyst prepared by sol-gel method, Songklanakarin Journal of Science and Technology **30(3)** (2008) 385-391.

[9] Zhang Wenguang, Liu weimin, Wang chengtao, Tribological investigations of sol-gel ceramic films. Science in China B (2002) 84-90.

[10] P.Malliga, B.KarunaiSelvi, J.Pandiarajan, N.Prithivikumaran and K.Neyvasagam, Studies on the performance of TiO_2 thin films as protective layer to chlorophyll in Ocimum tenuiflorum L from UV radiation, AIP conference proceedings **1665** (2015) 080047.

[11] D.IArnon, Copper enzymes isolated chloroplasts, polyphenoloxidase in Beta vulgeries. plant physiology, **24** (1949) 1 – 15.

[12] Hamideh Samari Jahromi, Effects of Triton x 100 and Tetraethylorthosilicate on the Morphology and Photocatalyst Properties of TiO_2 Thin Film, International Journal of Thin Films Science and Technology **3**(2013) 1-16.

[13] Adrian Ohwofosirai, Mathew D.Fermi, Nwokike A.Ngozika, Toluchi O.Joseph, Osuji R.O., Ezekoye.B.A, A study of the optical conductivity extinction co-efficient and dielectric function of CdO by successive iconic layer adsorption and reaction (SILAR) techniques, American chemical science journal, **4**(6) (2014), 736-744.