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Studies on PMMA-co-PBA-TiO_2 Nanocomposite Films

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ABSTRACT

The polymer based nanocomposites were obtained by merging inorganic Titanium Dioxide (TiO_2) in the polymer system focusing on raising the optical transparency and to study the photo catalytic activity. The precursor chosen here is titanium (IV) isopropoxide which is the starting material for sol-gel synthesis to form a TiO_2 sol-gel solution. The choices of the polymers are acrylates namely methyl metha acrylate and butyl acrylate monomers which are copolymerized using benzoyl peroxide as initiator for enhanced copolymerization. This study involves synthesis of TiO_2 sol-gel solution and developing TiO_2 thin films coated over glass slides by spin coating technique to improvise the transmittance efficiency characteristic of glass. The deposited thin films were characterized for their structural, morphological, optical properties besides the elemental composition and photo catalytic activity. The prepared films were highly transparent were hydrophobic. The PMMA-co-PBA-TiO_2 nanocomposite films exhibited good photo catalytic activity.

Key words: TiO_2 nanocomposite films, sol-gel, photocatalytic activity, hydrophobicity, self cleaning

INTRODUCTION

TiO_2 is acclaimed for its renowned photocatalytic activity (Fujishima and Honda, 1972), superhydrophilicity, self cleaning, antifogging effects, etc. In general, TiO_2 can have prominent polymorphic forms namely anatase, rutile and brookite. Out of these three phases, brookite is neglected and focused phase is anatase because it exhibits appreciable photocatalytic activity. The peculiarity of TiO_2 was raised by Wang *et al.* (1998a) the discoverer of photo induced superhydrophilicity of TiO_2 thin films which paved the way for many researches since 1997. Further, the TiO_2 coated substrate on UV exposure will have remarkably good affinity towards water as the contact angle gradually reduces to zero. This notable superhydrophilic property provides self cleaning aspects and this had already been applied for some construction purposes (Hata *et al.*, 2000). Over the recent period of time, coating technology have gained its attention in automobile glasses and building windows. To attain various features such as antiabrasive, self cleaning, defogging, antireflective nature, several class of coatings have been applied over glasses. In particular, several studies have their focus on developing self cleaning, hydrophilic property of thin films by sheeting of water for removal of organic dirt and to make the surface clean. For quality based assurance this coating is focused on increasing the longevity over the glass without cracking and imparing its visibility.

Various synthesis routes are adopted for generation of TiO_2 Thin films via Techniques namely, spin coating, dip coating (Yu *et al.*, 2001), spray coating (Gao *et al.*, 1992) and sputter deposition (Sheng *et al.*, 1997; Wang *et al.*, 1998b; Rodriguez *et al.*, 2000). The New strategy is based on Sol-gel (Lokhande *et al.*, 2004, 2005; Kale *et al.*, 2006; Yuan *et al.*, 2006) preparation of TiO_2 solution and copolymerization of methyl metha acrylate and butyl acrylate monomers solution and subsequent coatings over glass substrate. Amongst the existing coating techniques spin coating is most preferred due to its feasibility with low cost devoid of expensive equipments (Vives and Meunier, 2010). Thickness and density of deposited layers are the parameters that govern the properties of sol-gel TiO_2 thin films.

In the present study PMMA-co-PBA-TiO_2 nanocomposite films were deposited over thoroughly cleaned glass substrates using spin coating and their structural, morphological, optical and photo catalytic properties were investigated.

MATERIALS AND METHODS

TiO_2 sol-gel synthesis approach: The precursor chosen for sol gel synthesis of TiO_2 was titanium (IV) isopropoxide solution (97% purity) (Sigma Aldrich, USA) and starting materials were isopropanol, acetic acid, methanol. Initially, 1.6 mL of the precursor solution was taken and added drop wise to 4.65 mL of isopropanol. This resulting solution should be stirred for 10 min at 60°C by using magnetic stirrer. Here the point to be noted is that the solution is concentration based, i.e., for obtaining clear solution exact amount as mentioned above should be added and water should be avoided or else it may leave the solution with milky precipitate which is undesirable characteristic for the coatings application. Flowingly acetic acid (5.13 mL) was added and stirred well under closed condition for 10 min at 60°C. Then, methanol of 12 mL was finally added to this solution and stirred for 2 h at 60°C. The obtained solution is called TiO_2 sol. From the prepared solution, a significant part of it was separated and utilized for gelation whereby the solution is heated at 80°C for 4-6 h and calcinated in muffle furnace at 500 °C to obtain TiO_2 nano-powder.

PMMA-co-PBA copolymerization: The copolymerization procedure was carried out using the starting solutions such as methyl metha acrylate and butyl acrylate monomer solution. Molar proportion of the monomers is taken into consideration as follows: 0.05 M of methyl metha acrylate was mixed with 0.05 M of butyl acrylate. To facilitate the polymerization benzoyl peroxide (0.005 g) was used as initiator. The resulting solution was introduced to 25 mL of Toluene and refluxed for 6 h at 80°C. Now the copolymer obtained will be in toluene solution which can later be poured in methanol for coating purpose.

Spin coating approach: Before coating the prepared solutions, the glass slides were cleaned well by following procedure. The glass slides were immersed in solution containing 5 drops of Triton and 10 mL of distilled water. Then, the slides were ultrasonicated for 10 min. These slides were thoroughly washed in forced water flow until the triton gets fully washed off. Ultrasonication of glass slides for 10 min was done in presence of distilled water. These slides were transferred in acetone and ultrasonicated for 10 min. The solution was replaced with isopropanol and ultrasonicated for 10 min. Again solution was replaced by Acetone and ultrasonicated for 10 min. These cleaned glass slides were spread evenly and allowed to dry under mild heat. After that the slides were spin coated with TiO_2 sol, copolymer solution and heat treated at 150°C. The synthesized films were characterized using Fourier transform inrfared spectroscopy (FT-IR), Field emission

scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and UV-Visible spectroscopy. The contact angle analysis and photoinduced superhydrophilicity of the TiO_2-copoly-TiO_2 substrates were studied using Goniometery analysis.

RESULTS AND DISCUSSION

FT-IR spectra: Figure 1 and 2 shows the FT-IR Spectra obtained for TiO_2 sol-gel process and Acrylate copolymer which confirms the adsorption bands contributed by stretching vibration of Ti-O-Ti Network and polymer C-H bonds. The adsorption band was observed from range of about 400-1250 cm^{-1} is due to the stretching vibrations of Ti-O-Ti and Ti-O bonds and C-H bonds are due to the residual alkoxides.

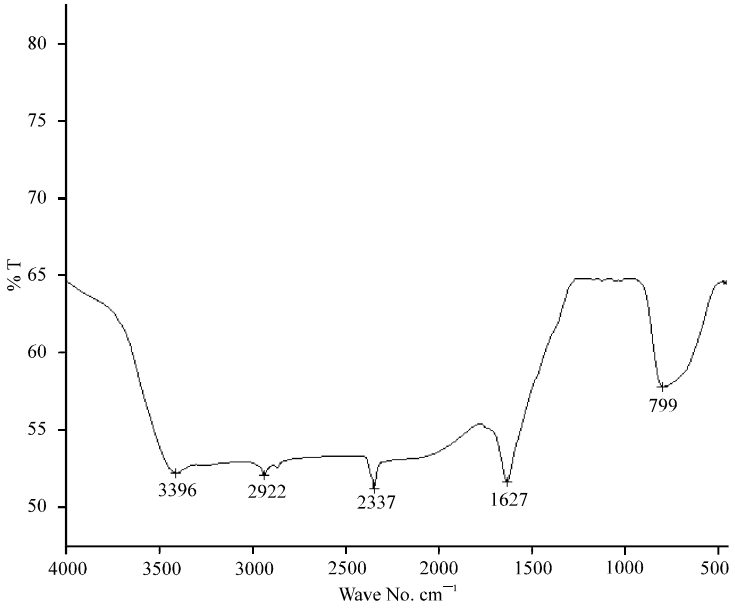

Fig. 1: FT-IR spectra of TiO_2 prepared by sol-gel process

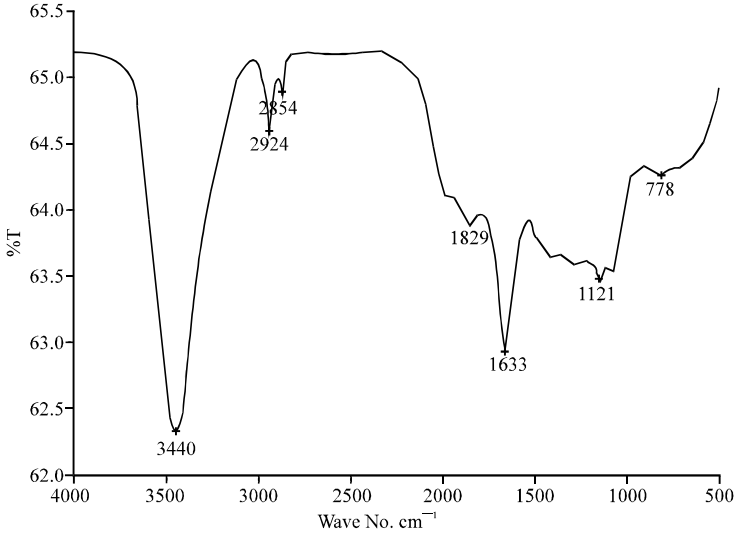

Fig. 2: FT-IR spectra of acrylate polymer

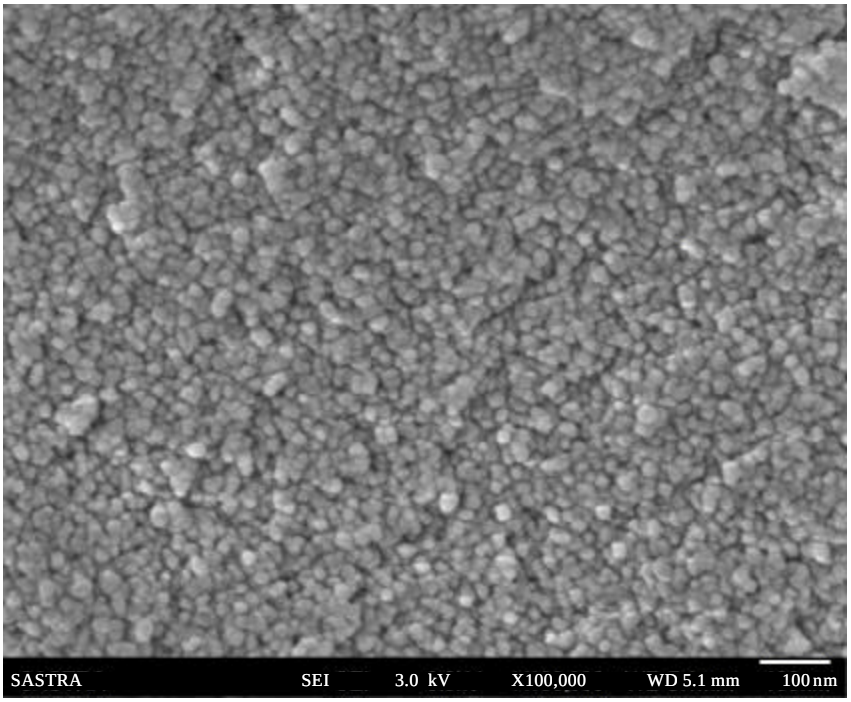

Fig. 3: FE-SEM micrograph of TiO_2 powder prepared by sol-gel process and calcined at 500°C

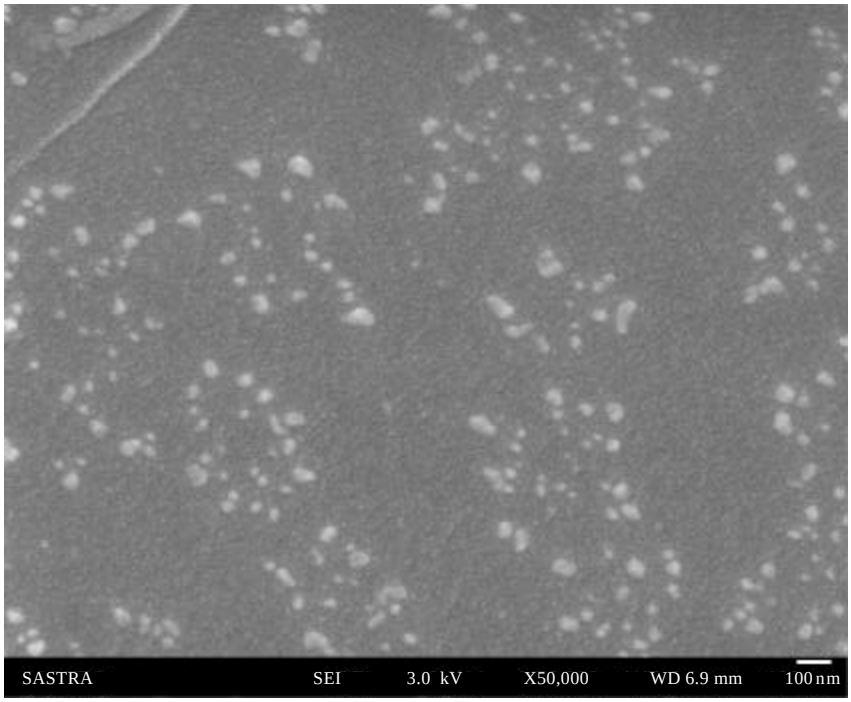

Fig. 4: FE-SEM micrograph of TiO_2 films annealed at 150°C

Surface morphology studies: Figure 3 shows the surface morphology of TiO_2 nano powder calcinated at 500°C. While, Fig. 4 shows the FESEM micrograph of TiO_2 films deposited over glass

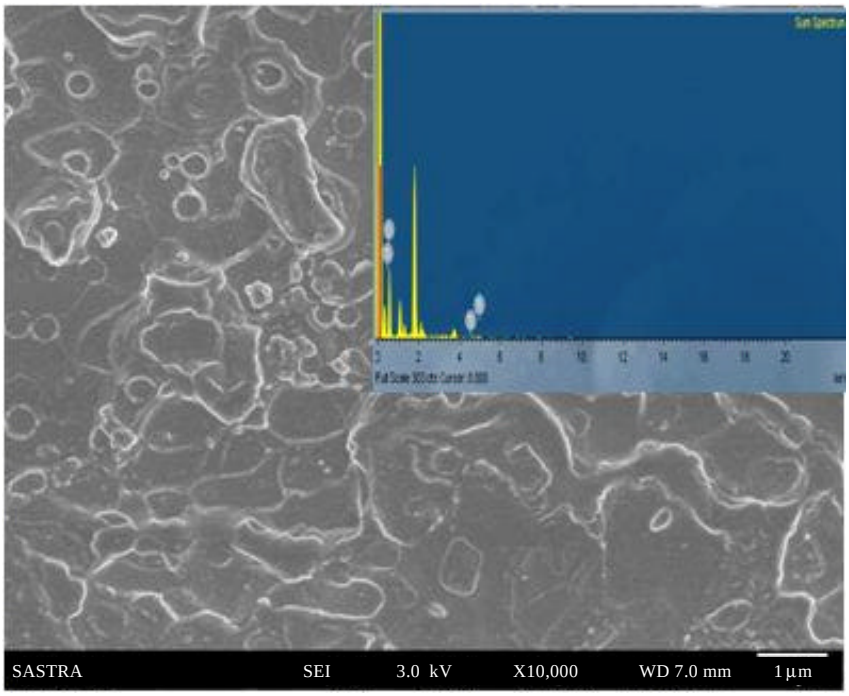

Fig. 5: FE-SEM micrograph of polymer coated over TiO_2 thin film and inset shows EDAX spectrum

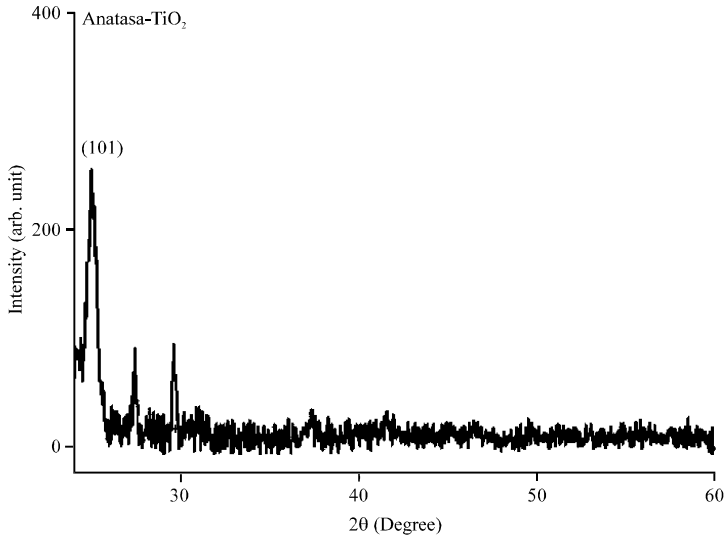

Fig. 6: XRD pattern of TiO_2 films annealed at 150°C

substrate at 150°C. As observed from the FESEM micrographs, the films were crack free and the surface was uniform. In addition, Fig. 5 shows the polymer over coat in TiO_2 thin film coated glass substrate along with EDAX studies that confirms the Ti-O-Ti network peak.

Structural studies: In order to investigate the crystal structures of TiO_2 thin films coated over the glass substrate, crystallization degree was determined by X-Ray Diffraction. Figure 6 depicts the XRD patterns obtained from the TiO_2-copoly-TiO_2 mulitilayer coating, annealed at 150°C. The XRD

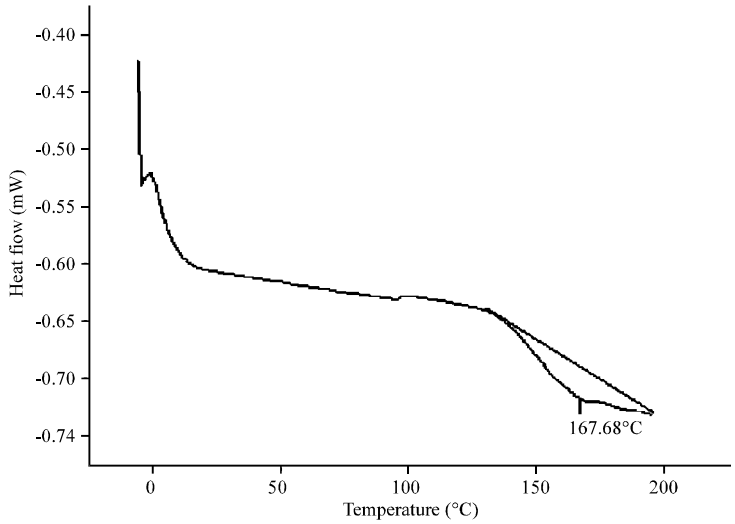

Fig. 7: DSC graph for acrylate polymer

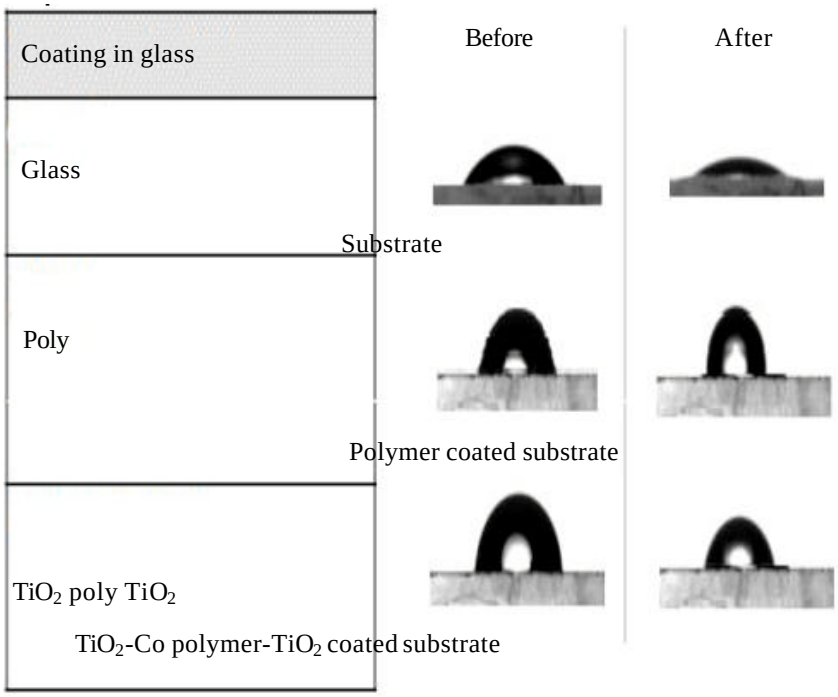

Fig. 8: Contact angle measurement in (a) glass, (b) polymer coated glass and (c) TiO_2-polymer-TiO_2 coated glass

result showed sharp peak of anatase phase which affirms the formation of crystallized state of thin films. This shows the possibility of obtaining the anatase phase for TiO_2 coated films which were annealed at significantly low temperature. The mathematical calculation for determining crystallite size was done by using Scherrer's formula. The average crystallite size for the TiO_2 thin films was around 15 nm.

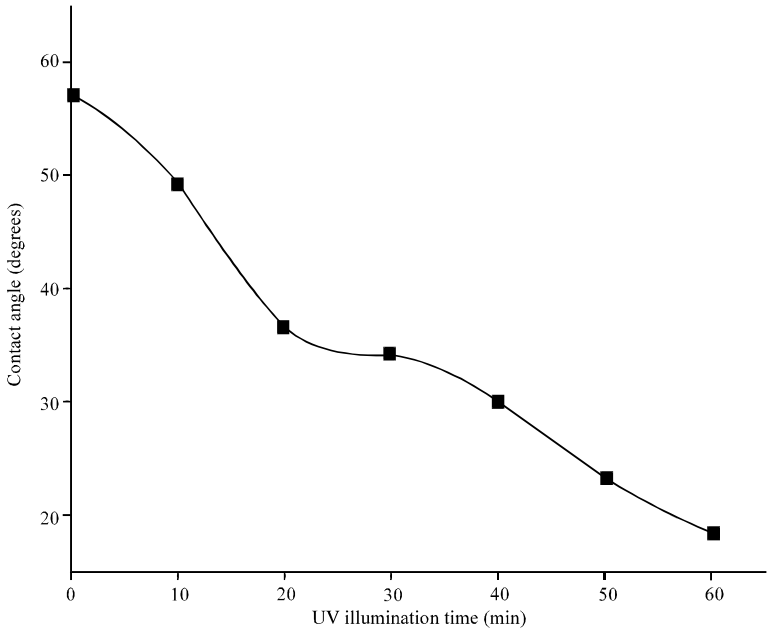

Fig. 9: Photoinduced super hydrophilicity of TiO_2-Copoly-TiO_2 coated substrate

DSC analysis: Figure 7 represents the DSC curve for the monomers which are combined to form copolymer by copolymerization reaction. DSC is devised for polymers to check their composition, melting point (T_m) and glass transition temperature (T_g). Standard compilations are available for most of polymers and this technique can show possible polymer degradation by the lowering the expected melting point, T_m. As an instance, T_m value is based on the molecular weight of the polymer, therefore lower grades will have lower melting point. The crystallinity percentage for a polymer can be found from the crystallization peak of the DSC graph as the heat of fusion can be evaluated from the area under an absorption peak. DSC studies the thermal degradation of polymers. The degradation for the copolymer was found to be attained at 167.68°C.

Contact angle measurement: The contact angle of the water droplet first reached 85° and gradually dropped to 56° which marks the hydrophilicity of the TiO_2 thin films which would further get reduced upon UV illumination. Whereas the Contact angle of TiO_2- poly- TiO_2 coat reached 80° which is due to the influence of the polymer. Plain glass (reference), Co-polymer coat, TiO_2-poly- TiO_2 coatings were taken and respective contact angle readings were obtained and graph was plotted. Figure 8 shows the comparison of the photographic results taken before and after contact angle measurement which confirms the hydrophilic nature of coated TiO_2 thin films. The superhydrophilicity is graphically depicted in Fig. 9. After UV illumination over TiO_2 coated substrate which will lead to gradual decrease of contact angle nearing to zero.

UV-visible spectroscopy: TiO_2 is an in-direct bandgap semiconductor confirmed by UV spectrophotometry analysis showing band gap at 3.7 eV according to Planck's equation:

$$\lambda = \frac{hc}{Eg}$$

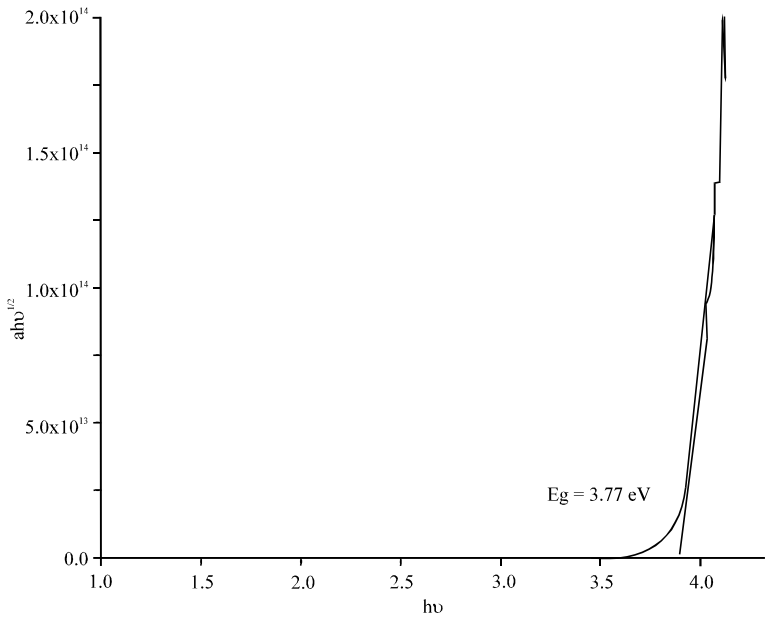

Fig. 10: Tauc's plot of TiO_2 thin film annealed at 150°C

where, h, c and Eg are the Planck's constant, speed of light and the semiconductor bandgap energy, respectively. When titanium oxide is irradiated with UV light, the electrons and holes are produced in conduction band and valence band, respectively. Reaction below describes the mentioned phenomenon:

$$TiO + h\nu \rightarrow TiO_2\ (e^-_{CB} + h^+_{VB})$$

In following, Ti^{+4} on the TiO_2 crystal surface is reduced by a surface trapped electron:

$$Ti^{+4} + e^- \rightarrow Ti^{+3}$$

Holes so generated, oxidize the O^{-2} anions. In the process, oxygen atoms are ejected and oxygen vacancies are created according to this reaction:

$$O^{-2} + 2h^+ \frac{1}{2} O_2$$

The water molecules can occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. Super hydrophilicity gets enhanced by hydroxyl groups existing in films arising from chemically adsorbed water molecules and some water molecules which are physically absorbed in TiO_2 surface. This could be better understood by reaction between TiO_2 and absorbed water molecules thereby forming Ti-OH groups. Hydrogen bonds and Van der Waals forces of interaction increases proportional to chemical absorption of OH on surfaces of TiO_2 films. This is defined as hydrophilicity of TiO_2 coated substrates discovered by Fujishima and Honda (1972). Figure 10 shows good transmittance which was achieved to ~90% which is appreciable for windows and automobile glasses.

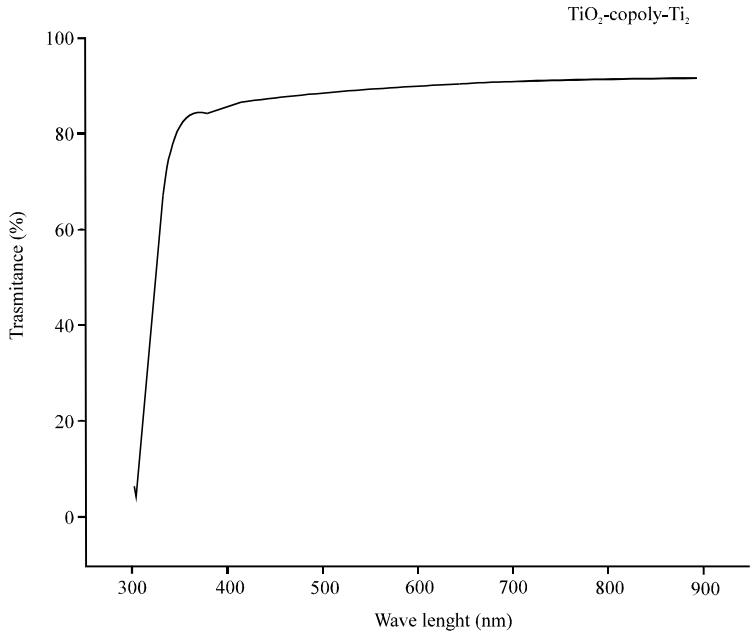

Fig. 11: Transmittance efficiency of TiO_2-copoly-TiO_2 thin film coating

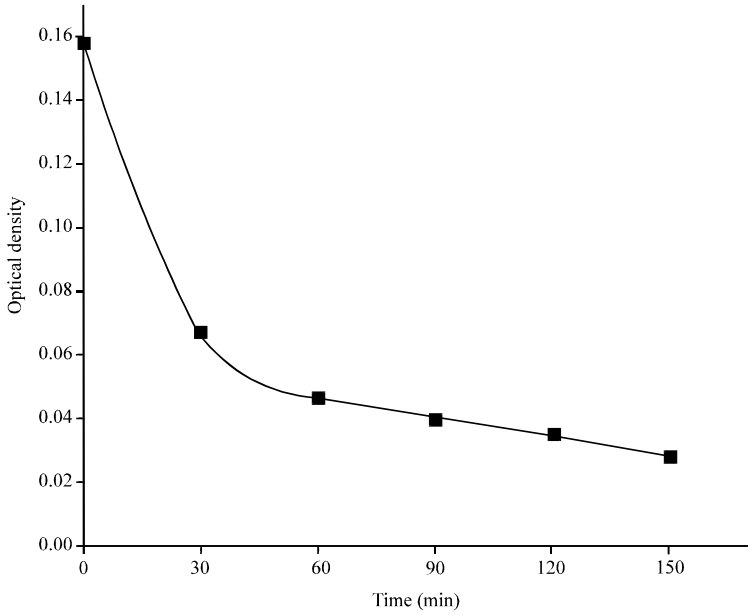

Fig. 12: Photocatalytic activity of TiO_2 by decolourisation of rhodamine dye solution

Photocatalytic activity of TiO_2-copoly-TiO_2 films: The photocatalytic activity of TiO_2 is performed by recording the degradation of Rhodamine B in aqueous solution under UV radiation. The photo catalytic reactor consists of UV tube which is in proximity with the reaction vessel containing the quartz tube and dye solution. Before reaction, the dye solution of 2 ppm is prepared by mixing RhB and water stirred by a magnetic stirrer for 45 min in dark condition to ensure the proper adsorption-desorption equilibrium of dye molecules on the TiO_2 coated surfaces to act as efficient photocatalysts. First, the standard plot was done for the dye and the peak was found to be 573 nm before the decolourisation. Figure 11 denotes Rhodamine B dye degradation

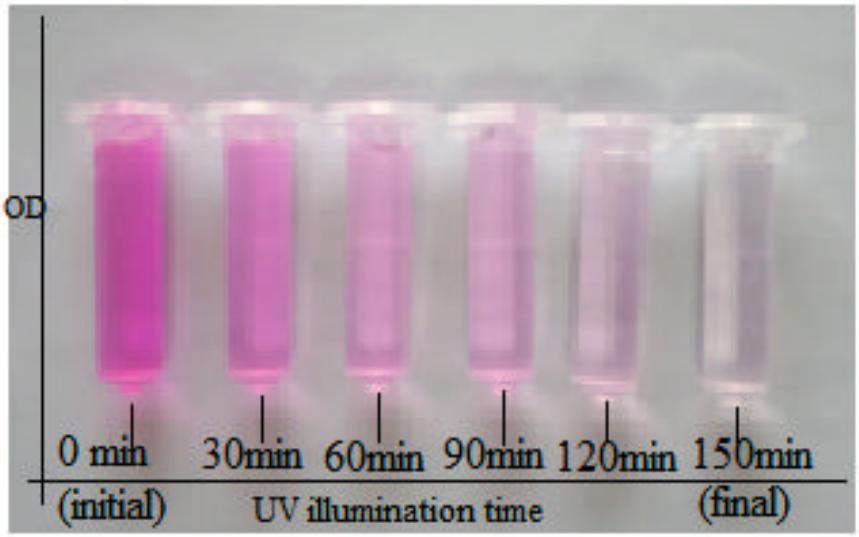

Fig. 13: Photocatalytic activity of TiO_2 by decolourisation of rhodamine B dye

experimentation which was done at variant times taken every 30 min to find the reduction in the dye concentration by taking photographs of the solution until the whole solution is converted from pink to colourless state to ensure complete degradation of the dye molecules. From Fig. 12 the dye concentration gradually diminishes as the illumination time proceeds and the minimum concentration was observed at 2.5 h. This indicates the photocatalytic activity of TiO_2 (Fig. 13). Also OD (Optical Density) values are taken and graphs are plotted for OD versus UV illumination time. UV-V is spectrophotometry measurements were done to determine concentration of the dye in the spectral range of 300-800 nm and was found with peak value of 573 nm. At last degradation of Rhodamine B solution is marked by decrease in concentration of the solution by UV-spectrophotometry analysis.

CONCLUSION

Blurry perception of view through the glasses installed in automobiles and building windows is an always recurring difficulty that causes inconvenience to the automobile drivers as well as for eye sight , as the water droplets creates hindrance via reflection and refraction of light during rainy season. The synthesis of TiO_2 sol-gel solution and development of TiO_2 thin films coated over glass slides by spin coating was done to improvise the transmittance efficiency characteristic of glass. FTIR spectra confirm the Ti-O-Ti network in sol-gel and C-H bonds in Copolymer system respectively. SEM characterization results confirms the uniform coating of thin films without cracks, uniform sized TiO_2 nanoparticles after calcination of TiO_2 sol to nanopowder at 500°C. UV-Vis spectroscopy reveals that the coating is transparent with good transmittance achieved up to ~90%. The contact angle measurement gives the information about the superhydrophilic surface nature of TiO_2-copoly-TiO_2 coating over glass substrate exhibiting good hydrophilicity. These coatings could be a better alternative for automobile industry and also for self cleaning windows application.

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