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Influence of Temperature and Doping on Photo-Catalytic Activity of TiO_2 Films

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Abstract: Titanium dioxide (TiO_2) thin films were synthesized by the sol-gel method. The titanium (IV) iso-propoxide and ethanol were used as precursor of TiO_2 and solvent, respectively. The TiO_2 sol was spin coated on glass substrates and pre-heated at 50°C for 15 min. The films were annealed at different temperatures for two hours in ambient air to obtain TiO_2 films. The same methodology was followed with the doping of different wt. % of tin (Sn) in TiO_2 sol to prepare Sn-TiO_2 films. The crystal structure of the TiO_2 films was analyzed by x-ray diffraction (XRD) patterns and found to be anatase phase after annealing at 300°C and higher temperatures. The films were tested for photo-catalytic activity for the degradation of methyl orange dye in the presence of UV light. The photo-catalytic property of the TiO_2 films varied with the annealing temperature and the doping of Sn.
Key words: TiO_2; sol-gel; XRD; SEM; photo-catalyst.

Introduction and Experimental

TiO_2 attracted many researchers in the fields of science, industry and technology for potential applications [1], [2], [3]. TiO_2 films can be prepared by various methods including the sol-gel method [4]. The sol-gel method has an exceptional advantages including large area deposition of films on flat as well as curved surfaces at room temperature and cost effective. The treatment of colored waste water containing harmful dyes is one of the most important requirements for water purification and recycling in the present scenario. TiO_2 is a very good photo-catalyst which may be used for the splitting of water in to hydrogen and oxygen [5] and degradation of poisonous organic dyes [6] etc.

Present investigation highlights the crystal structure and morphology of TiO_2 films and dependence of photo-catalytic activity of TiO_2 film with annealing temperature and doping concentration of Sn.

Titanium tetraisopropoxide and absolute ethanol were mixed with the volume ratio of 1: 8 and 0.2 ml of concentrated HCl added as a catalyst to the mixture and stirred constantly for 1 hr using a magnetic stirrer. The

resultant sol was stored in an air tight beaker for 24 hrs for complete hydrolysis and condensation processes. Then a few drops of the sol were placed on the glass substrates and spin coated at a speed of 3000 rpm for 30 minutes. The TiO_2 films obtained were dried at 50^oC for 15 minutes and then annealed at different temperatures for 2 hrs in ambient air. The film thickness was measured by envelope technique [7]. The film thickness was in the range 120-250 nm.

The structural investigations were performed with Philips (model PW1710) x-ray diffractometer by using Cu Kα radiation and the surface morphology of TiO_2 films were analyzed by scanning electron microscopy (SEM). 20 ppm methyl orange (MO) solution of was prepared and taken in a 100 ml beaker and placed on the hot plate with stirrer in a wooden chamber containing UV lamp with cold water circulation system. TiO_2 films on glass substrates annealed at different temperatures were placed in the beaker separately and irradiated with UV light. The absorbance of the dye solution was measured after every 1 hr duration for 10 hrs using UV/VIS/NIR Spectrophotometer (Ocean Optics, USA). The maximum absorption was observed at a wavelength of 464 nm.

Results and discussions

Figure 1 shows the x-ray diffraction patterns of TiO_2 film deposited on glass substrates annealed at 200^oC, 300^oC and 400^oC for 2 hr in air. It has been observed that the film annealed at 300^oC and higher temperature showed crystalline (anatase) phase of TiO_2 and below which is amorphous. The crystallinity of the film improved with the increase of annealing temperature.

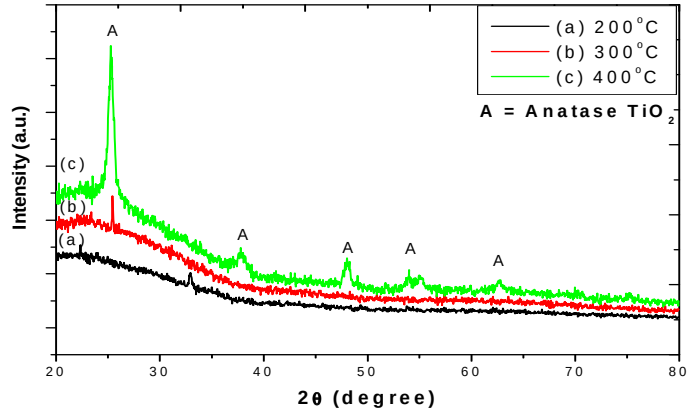

Fig.1 XRD patterns of TiO_2 film annealed at different temperatures in ambient air for 2 h.

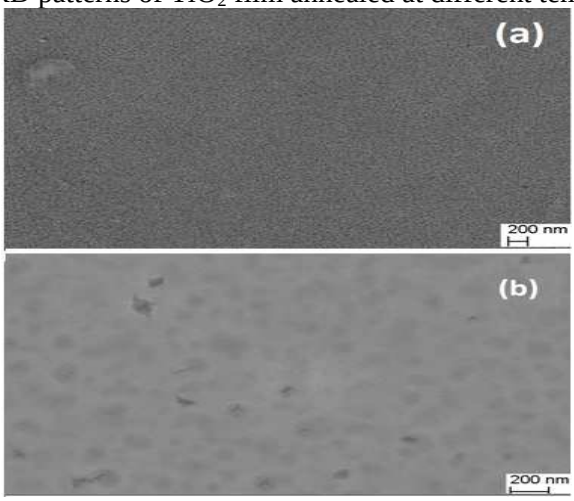

Fig. 2 SEM images of (a) TiO_2 film (b) 3 wt.% Sn-TiO_2 film annealed at 400^oC for 2 hr.

Figure 2 (a) shows the SEM images of TiO_2 film annealed at 400^oC for 2hr in ambient air. The film exhibited porous morphology with granular structure. The agglomeration of grains was also observed in the figure. Figure 2 (b) shows the surface morphology of 3 wt. % Sn doped TiO_2 film annealed at 400^oC for 2 hr in air. The surface roughness increased with the doping of Sn in TiO_2 film. The ripple surface morphology was observed with the doping of Sn.

Figure 3 shows the photo-catalytic degradation of MO with time in presence of UV light using TiO_2 films annealed at different temperatures in ambient air for 2 hr. It is well-known that photo-catalytic degradation of organic dyes follows Langmuir–Hinshelwood kinetics [8]. This type of reaction may be represented as follows [9]:

$$\ln (C/Co) = - kt, \qquad (1)$$

where *C*o and *C* are the initial concentration of MO and the concentration at irradiation time *t* (h), respectively.

It has been observed that, the photo-catalytic activity is maximum at an annealing temperature of 400°C and above which the photo-catalytic activity decreases. It may be due to high degree of crystallization and porous surface morphology of the TiO_2 film.

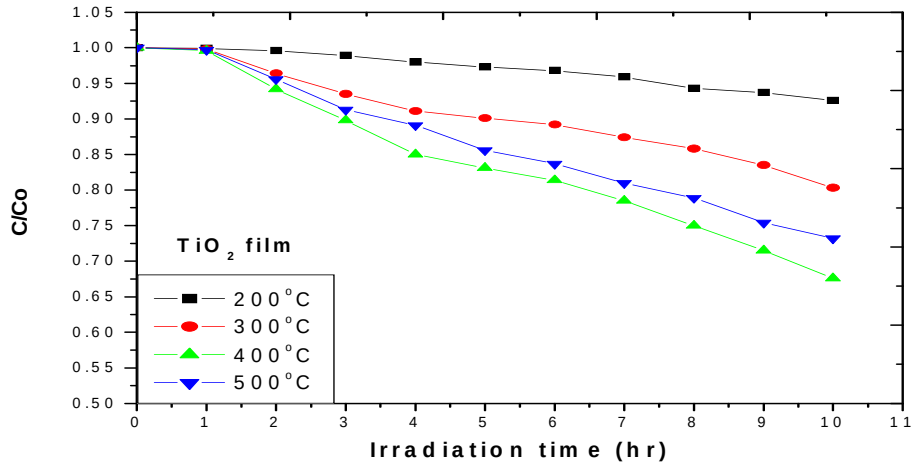

Fig. 3 Time effect on photo-catalytic degradation of methyl orange by TiO_2 films annealed at different temperatures for 2 hr.

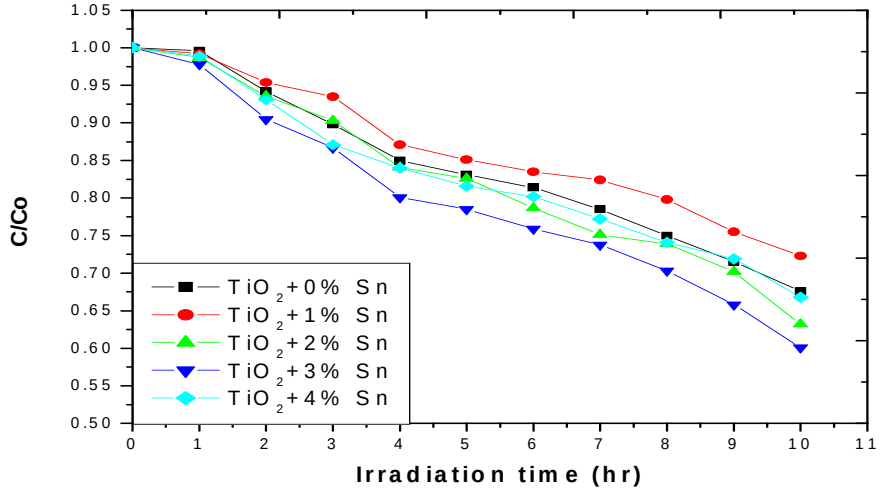

Fig. 4 Time effect on photo-catalytic degradation of methyl orange by different wt.% Sn doped TiO_2 films annealed at 400°C for 2 hr.

Figure 4 shows the photo-catalytic degradation of methyl orange dye in presence of UV light using TiO_2 films doped with different wt. % of Sn. The photo-catalytic activity of TiO_2 films varied with doping concentration. The degradation rate slightly decreased for 1 wt.% Sn and then increased from 2 to 4 wt. % Sn. The degradation rate is maximum for 3 wt. % Sn. This may be due to increased surface roughness of the films as observed in SEM images.

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