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Archives of Applied Science Research, 2010, 2 (4): 288-295

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ISSN 0975-508X
CODEN (USA) AASRC9

ECR plasma assisted deposition of nano-TiO_2 for repeated applications of photocatalytic degradation

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ABSTRACT

ECR plasma assisted thin film of nano-TiO_2 has been deposited on glass substrate. Chemical sputtering is encorporated to immobilize TiO_2 nanoparticles. Efforts have been taken to overcome the difficulty of recovery and reuse of the TiO_2 nanoparticles for water purification. It is found to be successful to immobilize TiO_2 nanoparticles on glass substrate, which shows strong adhesion consequently easy for repeated use for photo catalytic degradation. SEM and AFM images were studied to understand the morphology of the deposited film. XRD and XPS reveal the crystal structure and present species of TiO_2 in thin film.

Key words: ECR Plasma, Photodegradation TiO_2 thin film, Chemical sputtering.

INTRODUCTION

Water pollution added to the scarcity of water has become an acute problem in recent times. Purifying and reusing the waste water is being thought as a solution. For the treatment of waste water, traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process are used. But these methods cannot be successfully employed in the complete destruction of dye pollutants [1], and have the further disadvantage of potential secondary pollution [2]. Heterogeneous photocatalysts have been found to be effective in degrading heavy organic compounds to CO_2, H_2O and small molecules [3-5]. Hence, heterogeneous photocatalysts have attracted growing attention in which TiO_2 is the most preferable material. Due to its stable and non-toxic nature, insolubility in water, high photocatalytic activity and abundance; TiO_2 is extensively used for advanced water treatment and water purification process.

However the commercially available TiO_2 has particulate nature, due to which it is difficult to recover it from suspension after photocatalytic reaction [6–10]. An alternative solution to overcome this problem can be found by using thin films of TiO_2. Which can be prepared by numerous techniques such as chemical vapor deposition [11], electron beam evaporation [12], ion assisted deposition [13], sol–gel processes [14], and sputtering [15]. We have deposited isolated nanoparticles of TiO_2 over substrates providing larger surface area for the photocatalytic process. The Electron Cyclotron Resonance (ECR) plasma assisted chemical sputtering has been employed for the deposition of titanium particles which are subsequently oxidized to yield nano-TiO_2. This method provides additional advantages in controlling the microstructure of the deposition. Considerably large roughness of the deposited film observed by AFM scan ensured a large surface area which plays an important role in photocatalysis. In addition strong adhesion of the deposited film rules out any chances for the TiO_2 particles to leach out. This was studied by observing the degradation rate of the same film repeatedly and was found to be consistent. Cyclic use of the film for the catalytic reactions thus makes the process much user friendly for the water treatment.

MATERIALS AND METHODS

Nanoparticles of TiO_2 were deposited using microwave assisted Electron Cyclotron Resonance (ECR) plasma. The ECR plasma was operated at 2.45 GHz microwave power launched in TE_{11} mode and magnetic field of 875 gauss at pressure of 10^{-2} mbar. The detail of the system is described in our earlier communication [16, 17]. There is an arrangement for holding the samples which is movable along the vertical axis of the chamber so as to change the distance of the sample from the ECR zone. A hollow cylinder of Ti metal, which served as the sputtering target, was mounted horizontally inside the processing chamber at a distance of 15 cm from the ECR zone. Hydrogen plasma was used to deposit the nanotitanium with the help of chemical sputtering. This was possible with a hollow cylinder of titanium, which served the purpose of sputtering target and was mounted horizontally inside the processing chamber at a distance of 15 cm from the ECR zone. Its axis was kept transverse to the plasma reactor axis.

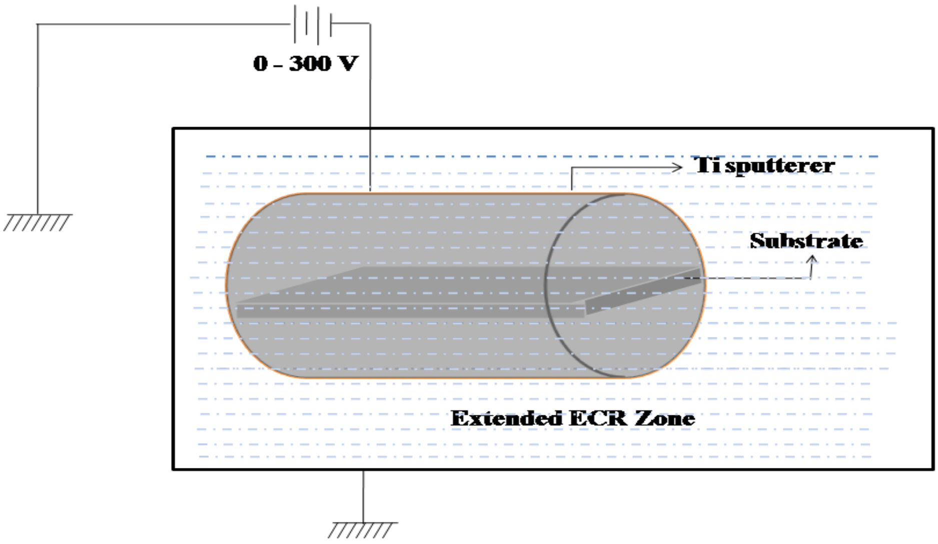

Fig 1: Schematic of Cathode and Substrate Assembly

Rectangular glass pieces of dimension 25×10 mm^2, were placed inside the cylinder as substrates for deposition as shown in Fig 1. These nanoparticles were transformed to their oxides by natural oxidation process at room temperature after exposure to atmosphere. The crystal structure of the deposited oxide was in turn, found by studying X-Ray diffraction pattern and the extent of oxidation was confirmed by X-ray photoelectron spectroscopy. This nanocrystalline film of TiO_2 was then used to study the photocatalytic degradation of methylene blue (MB) in aqueous solution. For this the film was placed in a 50 ml of 10^{-6} M solution of MB, and exposed to UV radiations obtained from Kr-85, 400W source for 30 min. Photocatalytic degradation was investigated by optical absorption measurements.

RESULT AND DISCUSSION

The morphology of the as deposited film is shown in the SEM (JSM 6360A) image shown in Fig.2 The film is not seen to be continuous but consists of particulates with size ranging between 200 nm to 600 nm. Also there are smaller particles which are not clearly resolved in this micrograph. Better resolved images, recorded by AFM (JSPM 5200) (Fig.3) shows that smaller particles have average dimensions of approximately 25 nm.

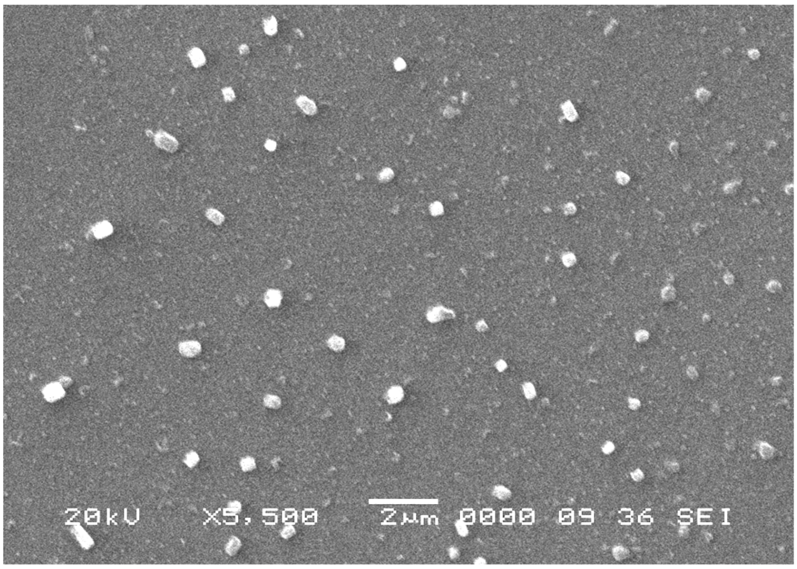

Fig 2:Scanning Electron Micrograph of nano-TiO_2

The grazing angle X-ray diffraction pattern (D8 Advance, Bruker axs) recorded for this film (Fig4), shows broad lines at 2θ = 25.3° and 2θ = 62.7°. These lines are characteristic of anatase phase of TiO_2 exhibiting (1 0 1) and (2 0 4) planes. From the FWHM for the two lines it seems that the crystalline sizes are much small and are equal to 1.5 nm when estimated from the Scherrer formula [18]. These crystallite sizes are much smaller than the particle sizes observed in AFM. It is possible that the particles are formed by the agglomeration of the crystallites during the growth process.

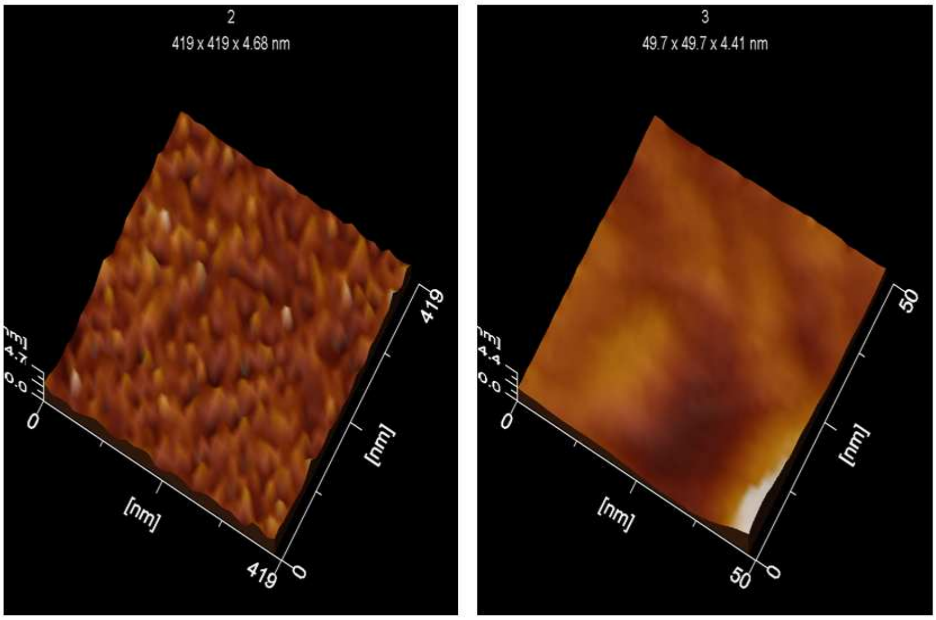

Fig 3: Atomic Force Microscopy images of nano-TiO_2

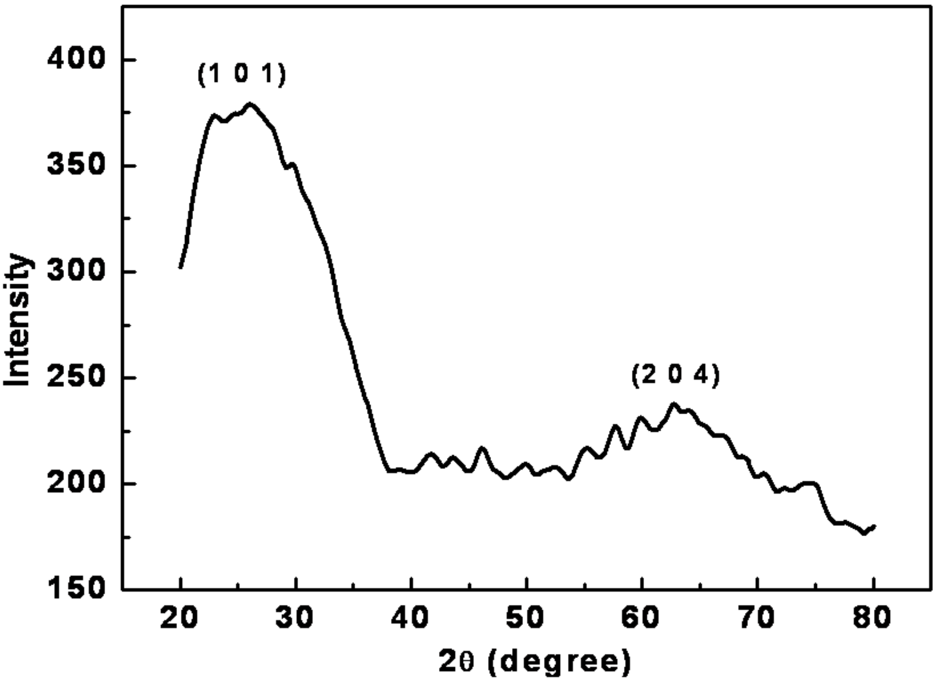

Fig 4: X-ray diffraction pattern of Nano-TiO_2

Such a growth of crystallites can be expected to arise from the plasma assisted sputtering process inside the confined plasma. Under the negative biased condition the cylindrical titanium electrode helps in confining of the plasma electrons inside the central zone. Consequently the ions get accelerated towards the cathode to chemically sputter out the titanium atoms to be deposited onto the substrate. Hydrogen ions are too light to effectively contribute in the physical sputtering process. However atomic hydrogen chemically reacts with Ti metal to form metal hydride (TiH). Ionization potential of Ti is 6.8 eV and the dissociation energy of TiH is 2.59 ±0.014 eV [19], since the electron temperature in the hydrogen rich ECR plasma is measured to around 15 eV, [20] at a given pressure in the present experiment it is quite possible that as a result of the interaction with the precursors, various other species of metal hydride like Ti-H or TiH^+, also are formed. In the present case, these hydride species are expected to act as the precursors for the growth of Ti nanoparticles onto the glass substrate. Subsequent motion of the negatively charged hydride precursors towards the glass substrate is then expected. The positively charged hydride precursor may capture an electron and release energy more than 2.6 eV which is dissociation energy of TiH, leading dissociation of TiH, into Ti and H atoms. Heterogeneous nucleation of titanium occurs on the substrate leading to the growth of its nanoparticles. On account of extremely high reactivity, these nanoparticles are oxidized when exposed the atmosphere and thus get converted into TiO_2. The oxidation of titanium particles was also confirmed by X-ray photoelectron spectroscopy (V. G. Microtech Unit ESCA 3000). Fig 5 shows the XPS spectrum exhibiting $Ti_{2p3/2}$ and $Ti_{2p1/2}$ lines, appearing at 457 eV and 463 eV respectively. These positions of binding energies correspond to the Ti^{+4} in TiO_2 [21], thus proving the complete oxidation of the nanoparticles.

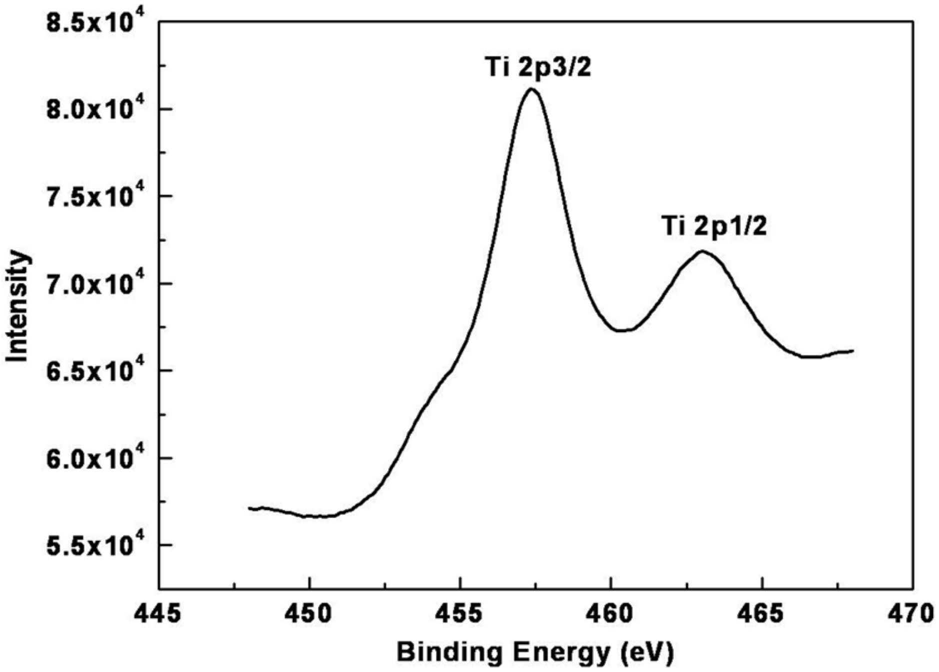

Fig 5: XPS Spectra of 2p peaks of TiO_2 particles

This nano-TiO_2 immobilized on glass substrate is further used as photocatalyst to study the degradation of aqueous solution of methylene blue aqueous solution. Photocatalysis by TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the TiO_2 producing electron-hole pairs as;

$$TiO_2 \xrightarrow{h\nu} e^- (TiO_2) + h^+ (TiO_2)$$

After exposure to UV-visible radiation the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding medium. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. Oxidation of water or OH^- by the hole produces the hydroxyl radical (•OH), an extremely powerful and indiscriminant oxidant. OH radicals rapidly attack pollutants at the surface, and possibly in solution as well, and are usually the most important radicals formed in TiO_2 photocatalysis. An important reaction of the conduction band electron is reduction of adsorbed O_2 to O_2^- [22].

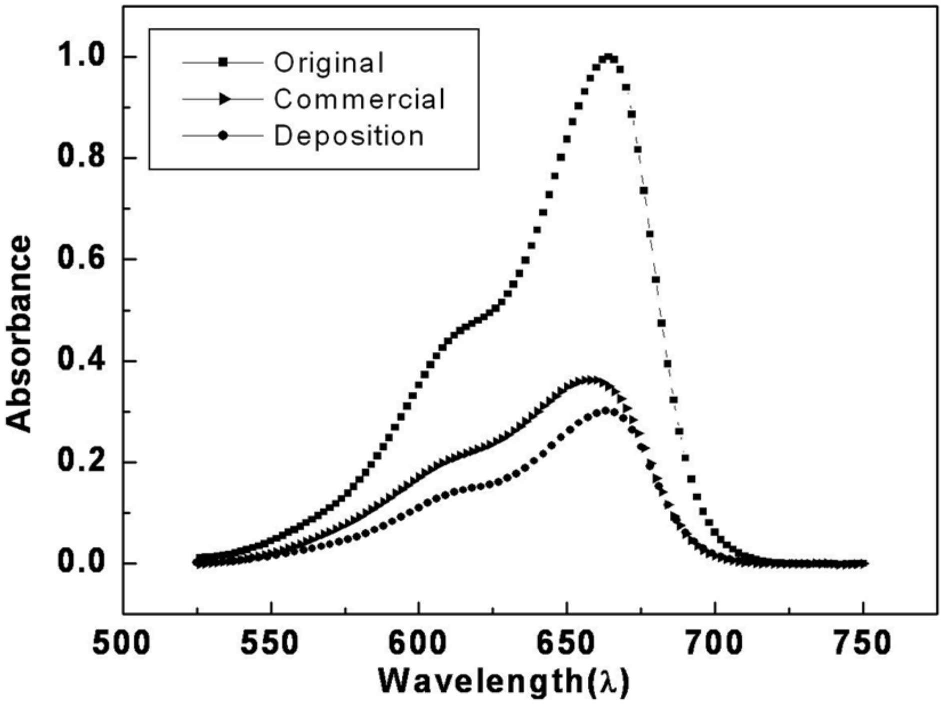

Fig 6: Photocatalytic activity of TiO_2 thin films

The photocatalytic degradation of MB, obtained using these films, is indicated by the absorption spectrum recorded from 500 nm to 800 nm in Fig.6. The concentration of MB is proportional to the intensity of the absorption peak observed at 664 nm. Here its relative concentration after degradation with respect to its original value was estimated by the intensity ratio C_t/C_o where C_t is the concentration of MB after degradation and C_o is the concentration of original MB before UV irradiation. Fanming Meng et. al. [23] have reported that the thin film of nano-TiO_2 deposited on glass by magnetron sputtering shows decrease in degradation after repeated use. After ultrasonic treatment for 10 min. in de-ionized water it shows the regeneration of degradation with small decrease (2.599 %) in rate.

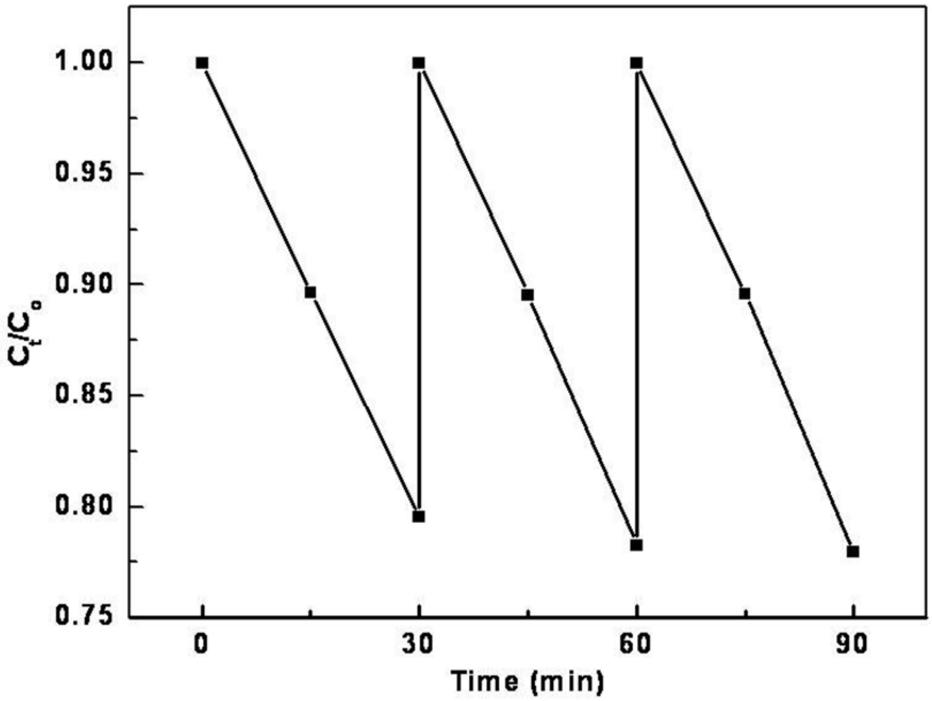

Fig 7: Cyclic Photodegradation of Methylene Blue (MB) using the same film thrice

Here the film was repeatedly used for degradation of MB by dipping it in its fresh solution and the variation in the ratio C_t/C_o after exposing to UV radiation for 30 min, is plotted for the four number of such trials. From Fig.7 it can be seen that the extent of degradation remains same even after repeated use. Thus the nanocrystalline film of TiO_2 seems to be well adherant to the substrate and thus can be effectively used continuously without the risk of its dissolution.

CONCLUSION

We have demonstrated the efficiency of nanocrystalline film of TiO_2 synthesized by ECR assisted deposition for photodegradation of the organic pollutant by taking MB as an example. The film of TiO_2 can be reused and thus is suitable for water purification. Hence the method of deposition is effective to overcome the difficulty of recovery and reuse of TiO_2 nanoparticles.

Acknowledgement

The authors acknowledge “Center for Nanomaterial and Quantum Systems” University of Pune, for financial support. SVB would like to thank CSIR, India for awarding her the ES project.

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