



Nano structured TiO₂ thin films in the efficient removal of β-estradiol from aqueous solution: physico-chemical studies

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ABSTRACT

A template synthesis was performed to obtain the Nanostructured TiO₂ thin films by the polyethylene glycol (PEG) as template medium. The X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) methods were utilized to characterize these materials. Similarly, the scanning electron microscopic (SEM) images were obtained to demonstrate the surface morphology of thin films. Brunauer–Emmett–Teller (BET) specific surface area along with pore sizes was obtained by the N₂ adsorption/desorption method. The thin film samples were intended to employ for photocatalytic removal of an emerging micro-pollutant β-estradiol from aqueous solutions. The physico-chemical parametric studies were conducted to deduce the mechanism involved in degradation process. The presence of several cations and anions was assessed in photocatalytic degradation of β-estradiol. Radical scavengers were employed to obtain possible pathway of catalytic degradation of β-estradiol. An apparent mineralization of β-estradiol was obtained. Multiple cycles of operation were conducted using the thin film to ensure the repeated applicability of photo-catalyst for successive operations. The modification of TiO₂ with PEG showed greater hydrophilic behavior and hence; enhances the catalytic degradation of β-estradiol.

Keywords: Nanostructured TiO₂; Template synthesis; Thin films; β-estradiol; Mineralization; Mechanism

1. Introduction

Twenty first century is facing serious issues relating to the contamination of aquatic environment. Variety of emerging micro-pollutants which are indiscriminately discarded and discharged into the aquatic environment and found to be a key issue to be addressed adequately [1]. Among the micro-pollutants the endocrine disrupting chemicals (EDCs) pose serious environmental threat. EDCs, even at trace level affecting adversely the endocrine system that eventually, interferes the hormonal and homeostatic functions [2,3]. This damages the human reproductive system or even causes

cancers [4]. In fact, the estrogens are known to be female sex hormones that take important role in reproductive and non-reproductive systems [5]. EDCs are readily accumulated in water bodies and sewage effluents which greatly influence the habitat sanctuaries or drinking water. Among the natural or synthetic estrogens the β-estradiol is one of the most abundant and potentially aggressive estrogens and shows several diverse estrogenic effects [6]. It shows adverse effects in rat reproduction due to reduced testosterone concentration and sperm quality [7]. It is reported that β-estradiol may hinder greatly the endocrine system at even very low level i.e., ng/L [8]. It is further pointed that β-estradiol induces

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several biological disorders in animals [9]. Pregnant woman excretes β -estradiol even up to 5 mg/day and the estrogen concentrations of the influent of a conventional wastewater treatment plants often increased to level of several mg/L [10]. The formal wastewater treatment plants are reported to eliminate partly the EDCs from aqueous solutions, which results the increase in estrogen concentrations in the effluent of treated waters. Therefore, it requires an advanced treatment for complete removal of EDCs from aqueous solutions. In order to eliminate efficiently the micro-pollutants from water-bodies; an advanced treatment process is to be introduced which may enable to remove effectively the low level load of EDCs from wastewater treatment plants. The heterogeneous semiconductor photocatalyst TiO_2 has received greater attention during recent past due to its wide range of applications in environmental remediation, H_2 production, water splitting, and CO_2 reduction. Moreover, TiO_2 showed considerable interest due to its selective UV light-response, low toxicity, low cost, and stability in varied environmental conditions. It is reported that the photo-generated electron-hole (e^-/h^+) pairs lead to the formation of superoxide radical ($\text{O}_2^{\cdot-}$) or hydroxyl ($\cdot\text{OH}$) radicals on the heterogeneous catalyst surface and this enables it for efficient degradation of organic pollutants from aqueous medium [11,12]. Literature survey shows that the photo-Fenton like method using the peroxy-monosulphate is an efficient way of low level degradation of β -estradiol from aqueous solutions [13]. It is found that the UV-Vis/ H_2O_2 /Fe(II) method is significantly faster than the UV/ TiO_2 photocatalytic process at least in the degradation of β -estradiol. A newer Fenton-like approach is proposed for the faster degradation of bisphenol and 17 α -ethynyl estradiol using the silver nano-particles. A fully dispersed PVP-AgNPs (polyvinylpyrrolidone-capped silver nanoparticles) are introduced in presence of H_2O_2 and have shown relatively efficient degradation kinetics of EE2 and 17 α -ethynyl estradiol. The oxidation kinetics follows pseudo-first order, a retarded first order and Behnajady-Modirshahla-Ghanbery kinetic models [2]. Biodegradation of 17 β -estradiol is conducted using the bacteria collected from deep sea sediments having aerobic and anaerobic conditions [5]. Similarly, photo electrochemical method is proposed in the degradation of β -estradiol. The working glassy carbon electrode is modified with the ruthenium oxide nanoparticles supported on reduced graphene oxide and the efficient degradation of β -estradiol is obtained at an applied potential of 1.0 V (vs. Ag/AgCl reference electrode) using simultaneous white light illumination [1]. Another study shows the performance of Degussa P25 photocatalyst in the oxidative removal of several estrogens *viz.*, estrone (E1), 17 β -estradiol (E2), 17 α -ethynyl estradiol (EE2) and estriol (E3) in a multicomponent system using the UV-A and UV-C radiations. The quantum yields are varied from 2.1×10^{-3} to 3.9×10^{-3} under the UVC- TiO_2 whereas under UVA- TiO_2 photocatalysis it is varied from 1.2×10^{-3} to 1.8×10^{-3} [14]. Similarly, a photo-oxidation ($\lambda > 290$ nm), using the TiO_2 heterogeneous photocatalyst, of 17 β -estradiol (E2) and 17 α -ethynyl estradiol (EE2) is conducted and some of the degradation products are indeed identified [15]. Simultaneous treatment of hexavalent chromium (Cr(VI)) and EDCs *viz.*, bisphenol A (BPA), 17 α -ethynyl estradiol (EE2) and 17 β -estradiol (E2) is conducted employing solar radiations and TiO_2 nanotubes [16]. Similarly, the application of TiO_2 nano-pillar

thin film photocatalysts which was synthesized by the *in situ* modification of TiO_2 using the polyethylene glycol and the catalyst was utilized in the efficient removal of diclofenac sodium and tetracycline [17] or Alizarin Yellow [18]. The TiO_2 thin films were modified with the polyethylene glycol (PEG) to obtain the cracks free TiO_2 Nanostructure. The materials have shown reasonably a good removal capacity for methyl orange [19]. Similarly, the TiO_2 thin film was synthesized using the PEG as filler media, the film was obtained by the facile spray pyrolysis method. The PEG modified thin film was used as photoanode and found efficient in the splitting of water [20]. The PEG (2,000) modified TiO_2 was employed in the UV-Ultrasonication degradation of Rhodamine B from aqueous solutions. The PEG modified TiO_2 showed a good porous material and found excellent in photocatalytic activity [21]. The other study indicated the use of modifiers *viz.*, oleylamine and polyethylene glycol as hydrophobic and hydrophilic properties. However, the titania capped with the oleylamine and polyethylene glycol resulted with the amphiphilic titania which was employed with cement for efficient De-Nox process from the atmosphere [22].

These studies indicated the potential use of heterogeneous photocatalyst TiO_2 in its pure or composite forms however; the practical application of photocatalyst is restricted due to difficulties in the effective separation of catalyst once the unit operation is completed. Moreover, it shows shadowing effect that eventually restricts the efficiency of catalyst [23]. Additionally, the phototoxicity of nanoparticles TiO_2 toward *Oryzias latipes* embryos and sac-fry under different irradiation conditions was studied [24]. However, the immobilized thin films of TiO_2 nanoparticles showed greater applicability due to its stability, repeated operation and easy phase separation. Moreover, the *in situ* modification of TiO_2 with PEG in the sol gel process greatly enhances the hydrophilicity. Additionally, the thin films are formed with no cracks and TiO_2 grains are distributed evenly on the substrate. Therefore, the present communication intends to utilize the thin films of TiO_2 nanoparticles in the degradation of one of potential estrogen β -estradiol. The detailed physico-chemical studies could enable to propose a plausible degradation mechanism of pollutant. Moreover, the repeated applications of thin films in reactor operations show the stability of catalyst and hence; its suitability in industrial applications.

2. Materials and methods

2.1. Materials

Polyethylene glycol, titanium(IV) isopropoxide, β -estradiol ($\text{C}_{18}\text{H}_{24}\text{O}_2$) (assay $\geq 98\%$) (Fig. 1), were obtained from the Sigma Aldrich. Co., USA. Acetylacetone, ethanol anhydrous, hydrochloric acid, sodium hydroxide, sodium chloride, oxalic acid, zinc chloride, cadmium nitrate tetrahydrate, copper(II) sulphate pentahydrate, sodium azide, glycine, 2-propanol, sodium hydrogen carbonate was obtained from the Merck India Ltd., India. Sodium nitrite was obtained from HiMedia, India Ltd., India and sodium nitrate extra pure was obtained from the LOBA Chemie, India Ltd., India.

UV-Vis Spectrophotometer Thermo Scientific (Model: UV – Evolution 220) was used for β -estradiol concentration measurements at the λ_{max} of 276 nm. Some of the

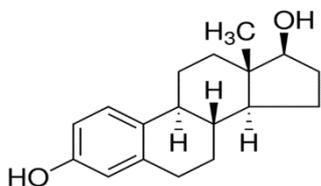


Fig. 1. Structure of β -estradiol

measurements were performed using the high performance liquid chromatograph (HPLC) (Model: Waters 515 HPLC pump, Detector: Waters 2,489 UV/Visible Detector, Column: Symmetry® C18 5 μ m (4.6 x 250 mm column)). The quantitative determination of β -estradiol was performed using the mobile phase of acetonitrile (65%) + water (35%) by v/v. The absorbance was obtained at 276 nm. The NPOC (Non-purgeable Organic Carbon) was recorded for the treated along with untreated samples using the TOC Analyzer (Shimadzu, Japan; Model: TOC-VCPH/CPN).

2.2. Methodology

2.2.1. Preparation of thin films

The immobilized TiO_2 Nano-particles onto the borosilicate glass were conducted by two different ways i.e., with and without polyethylene glycol (PEG). The PEG was used as filler media. A sol-gel preparation method was fully exploited using the titanium isopropoxide as a precursor material. A full description was given elsewhere [17,18]. However, a brief description is given herewith. The molar ratio of various chemicals used is: titanium isopropoxide: acetylacetone: ethanol: acetic acid: distilled water was taken at the (w/w) ratio: 2.8 : 1.3 : 18.4 : 0.58 : 2.25 g, respectively. The precursor titanium isopropoxide is taken along with acetic acid. The solution mixture was shaken for 2 h followed by sonication for 30 min. A sol (T1(S)) was obtained. This was safely kept for 1 d. Similarly, the sol (T2(S)) was obtained using the filler media i.e., 2.0 g of PEG (average molecular weight 8,000).

The two thin films F1 and F2 were obtained using the sols T1(S) and T2(S), respectively. Borosilicate circular glass disks (2.3 cm diameter and 0.5 mm thickness) were dipped separately (in vertical position) into the sol solutions T1(S) and T2(S) for 1 h. It was removed slowly and kept in open atmosphere for 12 h. The TiO_2 was immobilized on the glass surface. The disk was dried carefully at 100°C for 1 h, subsequently was annealed at 500°C for 3 h in an electric furnace (Nabertherm; Model No. LT/15/12/P330, Germany). The coating was conducted at least for three times in order to obtain smooth films. The TiO_2 Nanoparticle thin films were then stored in a closed and dry container under dark condition. On the other hand, the sol solutions T1(S) and T2(S) were dried at 120°C and then annealed at 500°C for 3 h to obtain the TiO_2 Nanoparticles powder. The samples T1(P) and T2(P) were then subjected for the Brunner-Emmett-Teller (BET) surface area analysis.

2.3. Materials characterization

The thin film catalysts i.e., F1 and F2 were subjected for the X-ray diffraction (XRD) analysis (PANalytical,

Netherland (Model X'Pert PRO MPD)). The XRD data was recorded at a scan rate of 0.034 of 2θ illumination utilizing the $\text{Cu K}\alpha$ radiation at a wavelength of 1.5418 Å. Surface structure of F1 and F2 were obtained by the scanning electron microscopic (SEM) (FE-SEM SU-70, Hitachi, Japan). X-ray Photoelectron Spectroscopic (XPS) analysis was performed using a Theta probe AR-XPS system (Thermo Fisher Scientific East Grinstead, UK). An $\text{AlK}\alpha$ monochromatic radiation ($h\nu = 1486.6$ eV) at a power of 150W with a spot size of 400 μ m. Further, aliphatic carbon peak was obtained at binding energy 284.6 eV and used as a reference. The BET specific area was obtained for these photocatalyst powder samples (T1(P) and T2(P)) using the Protech, BET surface area Analyzer (Model ASAP 2020).

2.4. Photo-catalytic degradation studies

Photo-catalytic degradation of β -estradiol was conducted using a self-made reactor having a black box (dimension: 60 x 45 x 45 cm) encompassed with a UV-C lamp ($\lambda_{\text{max}} = 253.7$ nm) (Model: Phillips TUV 11W, 4 P.SE; Poland). 50 mL of β -estradiol solution was taken in the reactor cell which was then placed inside the reactor. The thin film (prepared without PEG (F1)) or (prepared with PEG (F2)) was carefully placed at the bottom of the reactor. An UV lamp was placed over the beaker (i.e., 10 cm above the solution). The UV-radiation reaches the catalyst thin film through the β -estradiol solution, enabling the photocatalytic oxidation of β -estradiol onto the catalyst surface. The temperature inside the reactor was maintained at 25°C \pm 1°C using the self-assembled water-bath. Air was bubbled in the reactor vessel using a small aquarium air pump. The β -estradiol concentration was measured as a function of time using the UV-Vis spectrophotometer and the final β -estradiol concentration after 2 h irradiation was also measured by the HPLC. Always a blank experiment was performed taking bare borosilicate glass disk under identical UV irradiation for making a viable comparison.

Stock solution of β -estradiol (5.0 mg/L) was prepared in purified water. Further, the required experimental β -estradiol concentration was obtained by the successive dilution of stock solution. The pH of these solutions was maintained by adding drop-wise conc. HCl/NaOH solutions. The data for concentration dependence were obtained by varying the β -estradiol concentrations from 0.1 to 2.0 mg/L. The degradation efficiency of β -estradiol was obtained using the Eq. (1):

$$\text{Removal efficiency} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the concentrations of β -estradiol before and after the photocatalytic treatment.

3. Results and discussion

3.1. Characterization of thin films

XRD pattern of the photocatalysts F1 and F2 thin films are obtained and illustrated in Fig. S(1), (Supplementary). Fig. S(1) clearly revealed that both films show characteristic

peaks at the 2θ values of 25.38, 37.85, 48.16, 53.48, and 54.60 which are assigned to the TiO_2 anatase phase. Further, the particle size of the aggregated TiO_2 particles onto the borosilicate glass was obtained using the Scherer's equation and is found to be 25.3 and 21.8 nm respectively for the F1 and F2 thin films. The F2 thin film showed slightly smaller grain sizes of TiO_2 compared with the F1 thin film which eventually caused for even distribution of TiO_2 on to the borosilicate glass surface.

The surface morphology of immobilized TiO_2 particles are obtained by taking the SEM images of these two thin films, as illustrated in Fig. S(2) (Supplementary). It is observed that the F1 thin film is having heterogeneous surface structure with evenly distributed TiO_2 Nano-sized particles. The particles size of the TiO_2 is estimated to be less than 15 nm. However, the surface of F2 thin film is more disordered having some small cracks on it. However, the particle size of the TiO_2 have decreased on the solid surface. This shows that PEG templated immobilization of TiO_2 provides more structured aggregation of TiO_2 onto the surface. Therefore, the PEG modification caused for an morphological changes of TiO_2 that aggregated on the borosilicate glass.

A comparative X-ray photoelectron spectra for the thin film samples F1 and F2 along with a blank disk is illustrated in Fig. 2. It is evident from the spectra for a blank disk

contains with the characteristic photo peaks of C1s, O1s, and Si2p elements. However, the thin films F1 and F2 show with characteristic photopeaks of the Ti2p, C1s, and O1s at the binding energies mentioned in Table 1. It is interesting to note that the Si2p peaks for the F1 and F2 thin films are almost disappeared shows that the thin films of TiO_2 screened the Si. Moreover, the F1 and F2 samples showed additional peak of Ti2p, reaffirming the presence of Ti on the disk surface. Further, the Ti(2p) and O(1s) peaks are closely presented in Fig. 2 (insets). It is seen that Ti2p peaks are well splitted representing the $\text{Ti}^{4+}(2p_{3/2})$ and $\text{Ti}^{4+}(2p_{1/2})$ energy levels. The binding energy values further indicated that Ti is present in the fully oxidised form of Ti^{4+} [20]. On the other hand, the O(1s) peak which appears at 532.2 eV with the blank disk is shifted to the 538.5 eV. This chemical shift is due to the surface-adsorbed oxygen, such as O_2^- or O⁻ from the defect oxide or hydroxyl-like group or even bound with the titanium [25]. This, therefore, affirms that titanium is present with its particulate form and bound with oxygen atoms at the surface. Further, it is evident from the Table 1 that the percentage of carbon in the F1 and F2 thin films possessed with almost similar values that indicate that PEG is almost mineralized in F2 sample hence, causing the morphological modifications of the TiO_2 that aggregated on the solid surface.

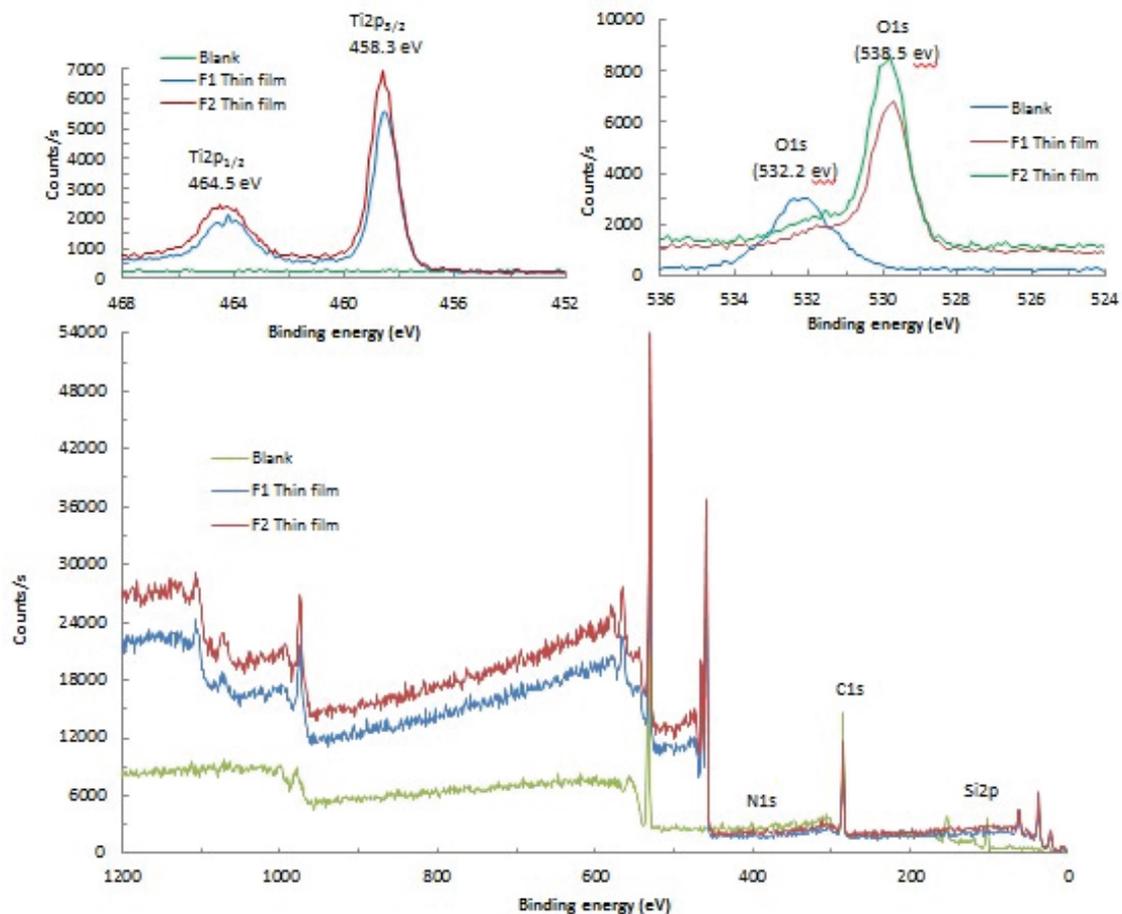


Fig. 2. X-ray photoelectron spectra of F1 and F2 thin films along with the blank disk. The characteristic peaks of (a) Ti2p and (b) O1s are shown in Inset.

Table 1
X-ray photoelectron data for the F1 and F2 thin films along with the blank disk

Samples	Peak binding energies assigned for various photoelectrons (eV)					
	C1s	N1s	O1s	Si2p	Al2p	Ti2p
Blank Disk	284.6 (48.94%)	399.6 (2.42%)	532.22 (31.04%)	102.3 (14.59%)	73.93 (3.01%)	–
F1 thin film	284.6 (37.6%)	399.63 (2.35%)	529.79 (41.83%)	101.06 (1.72%)	–	458.3 (7.91%)
F2 thin film	284.6 (32.64%)	399.6 (0.94%)	529.87 (46.31%)	101.69 (2.54%)	–	458.3 (17.56%)

% of respective element given in parentheses.

The BET specific surface area and pore sizes of two samples i.e., T1(P) and T2(P) are obtained. The specific surface area of T1(P) and T2(P) is found to be 5.21 and 1.42 m²/g, respectively. On the other hand the pore size is found to be 7.79 and 4.18 nm respectively for the T1(P) and T2(P) powders. This indicates that the meso-pore size of T2(P) is decreased significantly compared with the T1(P) sample whereas the BET specific surface area of T2(P) is found comparatively less than the T1(P) powder. Therefore, relatively smaller pore size with T2(P) solid could enhance the possibility of trapping efficiently the β -estradiol within the available pores and hence, could enhance the catalytic activity onto the solid surface.

3.2. Photocatalytic degradation of β -estradiol

3.2.1. Effect of pH in the degradation of β -estradiol

The pH dependence photocatalytic degradation of β -estradiol is an important quantity enabling to deduce a plausible mechanism involved at the photocatalyst surface. It was observed that the catalytic action greatly affected with the sorption behaviour of β -estradiol on to the catalyst surface. Moreover, the sorption of β -estradiol is likely to be dependent on the pH conditions maintained. This is possibly due to the surface properties of catalyst and also the speciation of β -estradiol. In view of this, the degradation of β -estradiol is studied at wide range of pH i.e., pH 4.0 to 10.0 and at constant β -estradiol initial concentration (1.0 mg/L). The percentage degradation of β -estradiol is obtained as a function of solution pH and illustrated in Fig. 3. Fig. 3 clearly shows that the percentage degradation of β -estradiol was slightly increased with the increase in pH from 4.0 to 8.0. However, at pH 10.0, a slight decrease in percentage removal of β -estradiol was observed. The percentage degradation of β -estradiol by the F1 and F2 thin film photocatalysts could be explained based on the surface properties of catalysts as well the speciation studies of β -estradiol in aqueous solutions. The point of zero charge for the TiO₂ powder (i.e., T1(P) and T2(P) solids) was obtained separately adopting the acid-base titration method and found to be 6.8. This indicates that the surface of F1 or F2 photocatalysts possessed a net positive charge below pH 6.8 however; it possessed a net negative charge at pH > 6.8. On the other hand, the β -estradiol molecule was mostly present in its molecular form at pH < 10.4 since the pK_a value of β -estradiol was reported to be

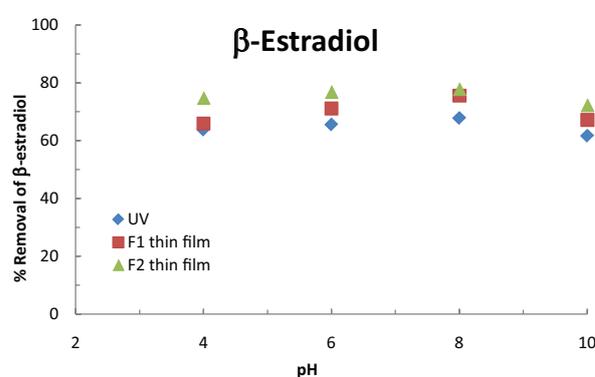
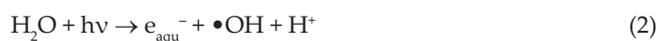


Fig. 3. pH dependence photocatalytic degradation of β -estradiol using the UV, F1, and F2 thin films from aqueous solution [Initial concentration of β -estradiol: 1.0 mg/L].

10.4 [26]. The sorption of β -estradiol is slightly affected due to the positively charged surface at low pH values as also observed previously that the sorption capacity of β -estradiol by the few-layered graphene oxide nano sheets from aqueous solutions is decreased at lower pH values. Therefore, this possibly restricted the effective catalytic degradation of β -estradiol. Moreover, it is also mentioned that at higher concentration of H⁺ ions (i.e., at pH 4.0) the \bullet OH radicals are greatly suppressed Eq. (2) or H⁺ ions scavenged the \bullet OH radicals which eventually decreases the catalytic activity of TiO₂ in aqueous medium [27,28]:



Further increase in pH i.e., pH 6.0 to 8.0 favored greatly the percentage degradation of β -estradiol. This is due to the reasons that the β -estradiol shows an enhanced affinity toward the solid surface and the reactivity of \bullet OH radical is pronounced at neutral to alkaline pH conditions [28]. However, a slight decrease in percentage degradation of β -estradiol is observed at pH 10.0. This is due to the fact that the β -estradiol molecule starts dissociating (i.e. the conjugated base) in aqueous solutions around pH 10.0 ($pK_a = 10.4$) [20]. Hence, the solid surface of catalyst and β -estradiol molecule possess net negative charge which ultimately, electrostatically, repels each other and therefore, causes in decrease of β -estradiol degradation at this pH. Previously, it was observed that there was no marked change

in the degradation of β -estradiol by ultrasonication (20 kHz) within a pH region 4.0 to 9.0 [8].

It is further interesting to note that a marked increase in percentage degradation of β -estradiol is observed using the thin films F1 or F2 compared with the bare disk. This evidenced the useful photocatalytic activity of thin films in the degradation of β -estradiol from aqueous solutions. Moreover, F2 thin film shows relatively enhanced catalytic behaviour than F1 thin film. This is due to the structural distribution of grains/and pore size of F2 thin film as studied by the BET measurements. F2 showed much reduced mesopores which efficiently traps the β -estradiol molecule and hence, enhances the catalytic action.

3.2.2. Concentration dependence degradation of β -estradiol

Effect of β -estradiol concentration in the photocatalytic degradation of β -estradiol is conducted varying the concentration of β -estradiol from 0.1 to 2.0 mg/L at pH 6.0. The final concentration of β -estradiol is measured at the end of 2 h UV illumination. Using the initial and final concentration of β -estradiol the percentage degradation of β -estradiol is calculated and results are illustrated in Fig. 4. It is noted that increasing the initial concentration of β -estradiol from 0.1 to 2.0 mg/L the respective decrease in percentage removal of β -estradiol is from 100.0% to 32.2% (by UV only); from 100.0% to 38.9% (by F1 thin film) and from 100.0% to 49.5% (by F2 thin film). An apparent decrease in percentage degradation of β -estradiol at higher initial concentrations is due to the fact that at higher β -estradiol concentration the effective penetration of UV light is restricted by an inner filter effect. Hence, the solution itself becomes somewhat impermeable for UV-radiations; this causes limited generation of active hydroxyl radicals and hinders the photocatalytic activity of catalyst [29]. Otherwise, increasing the concentration of pollutants may saturate the catalyst surface which reduces photonic activity of catalyst [30].

On the other hand the results further pointed that the thin films F1 and F2 showed significantly higher photocatalytic activity, at least in the oxidation of β -estradiol, compared with the blank disk UV treatment. Moreover, the PEG templated thin film F2 shows much enhanced photocatalytic activity than the F1 thin film. This again favors the assumption that β -estradiol molecules are effectively trapped

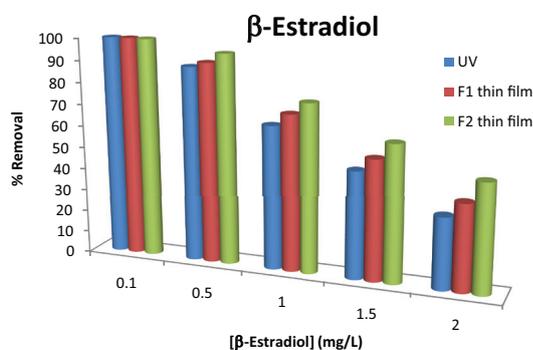


Fig. 4. Concentration dependence photocatalytic degradation of β -estradiol using thin films from aqueous solutions [pH of β -estradiol solution: 6.0].

within the meso-pores at the catalyst surface and therefore, the active species degraded efficiently the β -estradiol from aqueous solutions. Similar results were obtained using the TiO_2 thin films in the degradation of EE2 estrogen from aqueous solutions [31].

3.2.3. Kinetic studies

Time dependence photo-catalytic degradation of β -estradiol is utilized to deduce the kinetics of degradation process. The time dependence change in concentration of β -estradiol is obtained. Initial 90 min time dependence degradation data is utilized to discuss the kinetics of degradation. In general the degradation kinetic of the β -estradiol is presented with usual pseudo-first order rate equation:

$$r = -\frac{d[\beta\text{-estradiol}]}{dt} = [k_{\text{photolysis}} + k_{\text{photocatalysis}}][\beta\text{-estradiol}] = k_{\text{app}}[\beta\text{-estradiol}] \quad (3)$$

where β -estradiol represents the concentration of β -estradiol and k_{app} is the pseudo-first-order rate constant. It is obvious that the k_{app} depends on the concentration of β -estradiol.

Integration of Eq. (3) for the extreme conditions i.e., at $t = 0$ the $[\beta\text{-estradiol}] = C_0$ and time ' t ' the concentration of β -estradiol is C_t . Eq. (3) reduced to Eq. (4):

$$\ln\left(\frac{C_0}{C_t}\right) = k_{\text{app}} \cdot t \quad (4)$$

The straight lines are obtained between the $\ln(C_0/C_t)$ against time ' t '. The results are illustrated in Fig. 5 (e.g., pH 6.0 and at β -estradiol initial concentration 1.0 mg/L) in the photocatalytic degradation. The pseudo-first-order rate constants (k_{app}) and R^2 values are obtained for the F1 and F2 thin film photocatalysts along with the blank disk UV treatment at different pH values and the whole result is given in Table 2. The results clearly indicated that the degradation of β -estradiol is followed with the pseudo-first order rate kinetics since

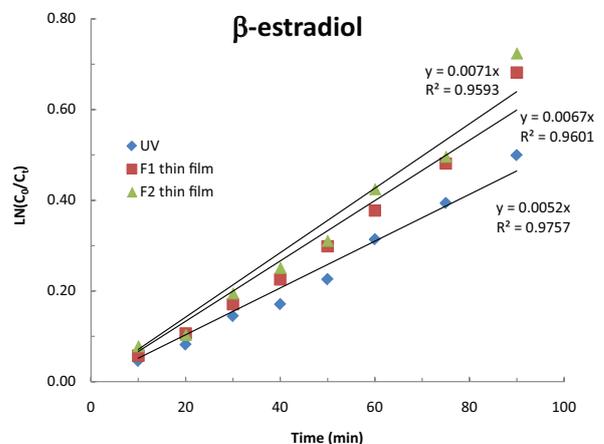


Fig. 5. Kinetics of photocatalytic degradation of β -estradiol using thin films F1 and F2 along with blank disk-UV.

the value of R^2 is reasonably high. Further, it is noted that the pseudo-first order rate constant values are not significantly changed with the variation of pH from pH 4.0 to 10.0 using the thin film photocatalysts F1 or F2. These results are in accordance to the pH dependence degradation studies. Moreover, it is again reaffirmed that an apparent pseudo-first order rate constant is significantly high for the thin films F1 and F2 compared with the blank disk-UV treatment. Similarly, F2 thin film showed relatively higher rate constant values compared with the F1 thin film. This again indicated the applicability of F2 thin film in its photocatalytic implication. Similar, pseudo-first order rate kinetics was obtained for the degradation of several estrogens including (E1, E2, E3, EE2, BPA etc.) and showed that the rate kinetics was independent of estrogen initial concentrations [27]. Peroxymonosulphate used Fenton like process (UV-Vis/PMS/Fe(II)) showed significantly high first-order rate constant value compared with the UV/TiO₂ process for the degradation of 17 β -estradiol [13].

The photocatalytic degradation of β -estradiol is modelled with the Langmuir-Hinshelwood (L-H) model to its linear form Eq. (6):

$$r_0 = \frac{k_r \cdot K \cdot C_0}{1 + K \cdot C_0} \quad (5)$$

or

$$\frac{1}{r_0} = \frac{1}{K \cdot k_r} \cdot \frac{1}{C_0} + \frac{1}{k_r} \quad (6)$$

where " $1/r_0$ " is the dependent variable, " $1/C_0$ " is the independent variable, $1/k_r$ is the linear coefficient and $(1/(k_r \cdot K))$ the slope of the straight line. Using the L-H equation, the adsorption constant and the rate constant are evaluated while plotting $1/r_0$ against $1/C_0$. The values of k_r (mg/L/min) and K (L/mg) are found to be 0.013 and 2.21 (R^2 : 0.966; for F1 thin film) and 0.010 and 2.71 (R^2 : 0.979; for F2 thin film), respectively for the degradation of β -estradiol at pH 6.0.

3.2.4. Mineralization of β -estradiol

The photo catalytically treated samples (max. 2 h irradiation) of β -estradiol were subjected to the total organic carbon (TOC) measurements in order to assess an apparent mineralization of β -estradiol. Using the initial and final TOC values, the percentage of mineralization was obtained and presented as a function of β -estradiol concentration

(0.1–2.0 mg/L) and solution pH (pH 4.0–10.0) (cf Fig. 6). Fig. 6(a) clearly indicates the percentage mineralization of β -estradiol was almost unaffected with the increase in initial β -estradiol concentration from 0.1 to 2.0 mg/L. Quantitatively, around 50% of the β -estradiol was mineralized by the F2 thin film for 2 h of UV illumination. These results further showed that a significant percentage of β -estradiol is mineralized using the F2 thin film. However, possibly, a prolonged illumination may entail a complete mineralization of β -estradiol from aqueous solutions. It was mentioned that the \bullet OH radical readily breaks the C-C, C=C, C \equiv C, or C=O and O-H bonds in aqueous solution of organic pollutants resulting the formation of CO₂ and other inorganic compounds [32,33].

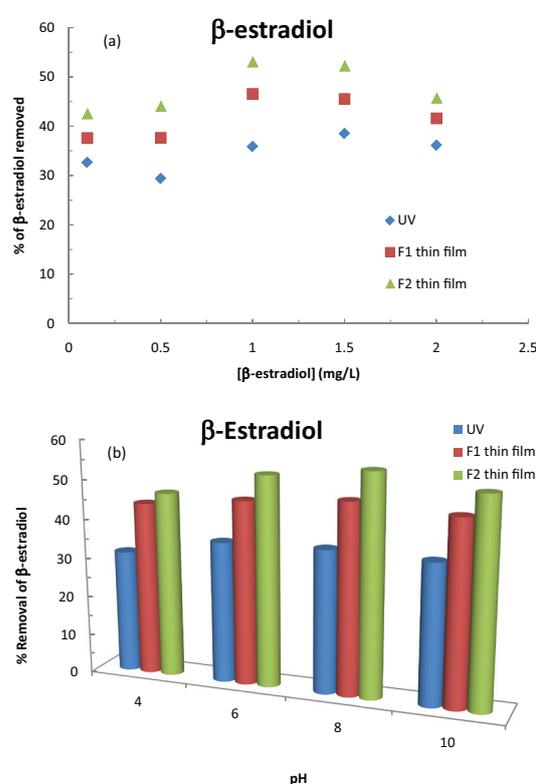


Fig. 6. Percentage of mineralization of β -estradiol as a function of: (a) β -estradiol initial concentration (solution pH: 6.0); (b) solution pH (Initial concentration of β -estradiol: 1.0 mg/L), in the photo-catalytic degradation of β -estradiol using thin films.

Table 2

Apparent rate constant values obtained for the photocatalytic degradation of β -estradiol using the F1 and F2 thin films along with blank disk photolysis at varied pH values [Initial concentration of β -estradiol: 1.0 mg/L]

Samples	Pseudo-first order rate constant (min ⁻¹)							
	pH							
	4.0		6.0		8.0		10.0	
	$k_{app} \times 10^{-3}$	R^2	$k_{app} \times 10^{-3}$	R^2	$k_{app} \times 10^{-3}$	R^2	$k_{app} \times 10^{-3}$	R^2
UV	3.9	0.949	5.2	0.976	4.5	0.996	4.3	0.992
F1 thin film	6.3	0.959	6.7	0.960	7.1	0.952	6.1	0.998
F2 thin film	8.5	0.981	7.1	0.959	8.0	0.956	6.4	0.993

The other study showed a significant TOC removal using the photoelectro-Fenton process in the degradation of tetracycline from aqueous solutions [30,34].

Similarly, the percentage TOC removal as a function of pH is presented in Fig. 6(b). It is evident from Fig. 6(b) that no significant change is observed within the pH region 6.0 to 10.0. However, slightly a less percentage of TOC is removed at pH 4.0. These results are in a line to the degradation studies conducted separately as a function of pH.

3.2.5. Effect of co-existing ions

The presence of co-existing ions *viz.*, sodium nitrite, sodium nitrate, sodium chloride, zinc chloride, copper sulphate, cadmium nitrate, glycine, oxalic acid, and EDTA in the photocatalytic degradation of β -estradiol is studied using the F2 thin film. The study is an attempt to simulate the real matrix water samples. The photocatalytic experiments are performed at pH 6.0 having initial concentration of β -estradiol 1.0 mg/L and co-existing ion concentration 5.0 mg/L. The solutions are illuminated for 2 h using the UV-light and subjected for the β -estradiol concentration measurements. The results are obtained as percentage of β -estradiol removed in presence of these co-existing ions and illustrated in Fig. 7. Fig. 7 clearly reveals that the presence of various ions affecting the percentage removal of β -estradiol at varied extent. It is interesting to observe that the presence of sodium nitrate and sodium nitrite could not affect the photocatalytic degradation of β -estradiol however; a marked decrease in presence of sodium chloride is recorded. This is possibly due to the fact that a competitive adsorption of chloride ions toward the active sites of thin films or due to the photogenerated hole is scavenged by the chloride ions with the formation of chlorine radical. It was reported previously that the photocatalytic degradation of dichloroacetic acid (DCA) using the layered TiO_2 Nanoparticle/Nanotube film is inhibited either due to the chloride ions forming chlorine radical with the hole at the catalyst surface or due to the competitive adsorption of chloride ions to the active sites of catalyst. The electron paramagnetic resonance (EPR) and adsorption studies of chloride ions onto catalyst surface enabled that competitive adsorption affected the degradation of DCA rather than the scavenging of hole by the chloride ions [34]. It was also mentioned previously that the presence of chloride or nitrate ions do not react with the photogenerated holes and not oxidized

to a radical state. Similarly, a slight decrease in the degradation of β -estradiol in presence of copper(II) sulphate and oxalic acid is possibly due to the competitive adsorption of copper(II) or oxalate onto the catalyst surface. Interesting to note that the presence of organic compounds *viz.*, glycine and EDTA could not affect the degradation percentage of β -estradiol. However, the other studies indicated that the removal efficiency of EE2 is dependent to the $\bullet\text{OH}$ and the presence organic compounds compete for the $\bullet\text{OH}$ and hence; causes a reduced photocatalytic activity for the EE2 [35]. The presence of Zn^{2+} , Cd^{2+} and glycine caused for some increase in percentage removal of β -estradiol from aqueous solutions. This is, perhaps, these ions are sorbed on the surface and effectively attracting the β -estradiol on the surface of catalyst and caused to enhance the photocatalytic degradation of β -estradiol.

3.2.6. Presence of scavengers

In order to pinpoint the involvement of active radicals in the photocatalytic degradation of β -estradiol, simulated experiments are conducted using variety of radical scavengers *viz.*, 2-propanol and HCO_3^- which scavenge the free $\bullet\text{OH}$ or $\bullet\text{OH}_{\text{bulk}}$ ($\bullet\text{OH}$ in aqueous medium) or the sodium azide which is used to assess the involvement of singlet oxygen occurred due to the interaction of superoxide radical and photogenerated holes (Eq. 7):



It is known that the singlet oxygen is one of reactive species which may oxidize the organics in aqueous medium [17]. Therefore, the 2-propanol, sodium azide, and sodium bicarbonate (1,000 mg/L) were taken in the photocatalytic degradation of β -estradiol using the F2 thin films and β -estradiol concentration 1.0 mg/L and at pH 6.0. The samples were treated for 2 h and then β -estradiol concentration was analyzed. The percentage degradation of β -estradiol is obtained in presence of these scavengers and illustrated in Fig. 8. Fig. 8 indicated that the presence of 2-propanol and HCO_3^- was affected significantly the removal of β -estradiol from aqueous solutions which inferred that the hydroxyl radicals predominantly, take part in the degradation process hence; the presence of both scavengers 2-propanol and

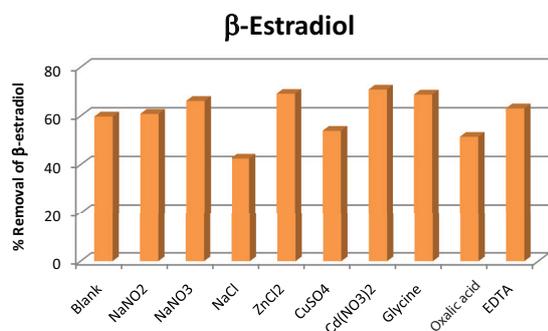


Fig. 7. Photocatalytic degradation of β -estradiol in presence of several co-existing ions using F2 thin film ([β -estradiol]: 1.0 mg/L; [Co-existing ions]: 5.0 mg/L; pH 6.0).

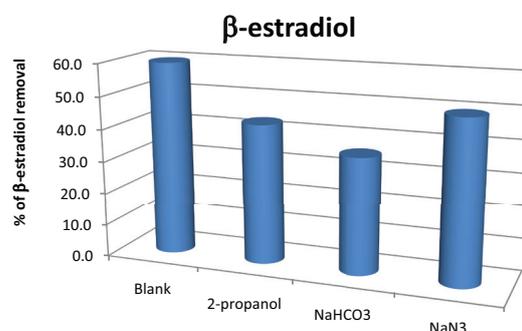


Fig. 8. Effect of radical scavengers in the degradation of β -estradiol using F2 thin film ([β -estradiol]: 1.0 mg/L; [Scavengers]: 1000.0 mg/L; pH 6.0).

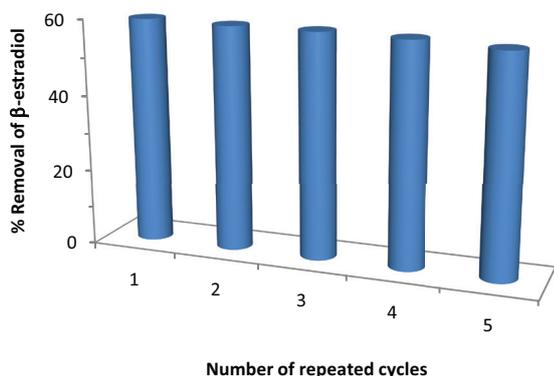


Fig. 9. Percentage degradation of β -estradiol by the thin film F2 for repeated operations ($[\beta$ -estradiol]: 1.0 mg/L; pH 6.0).

HCO_3^- suppressed significantly the degradation of β -estradiol from aqueous solutions. These results are in a line to other studies in which the photocatalytic degradation of diclofenac sodium and tetracycline hydrochloride was inhibited in presence of scavengers 2-propanol and HCO_3^- [36]. On the other hand, the presence of sodium azide insignificantly affected the oxidation of β -estradiol using the thin film F2. This indicated that in the oxidation process through the singlet oxygen is not involved predominantly.

3.3. Reusability of catalyst for multiple tests

The thin film F2 was intended to employ for repeated operations to ensure the stability of immobilized thin film of TiO_2 as well the practical applicability of photocatalyst in large scale operation. The β -estradiol (1.0 mg/L) is treated using the F2 thin film for 2 h at pH 6.0. This is termed as first cycle and at the end of each cycle, the thin film catalyst was washed with distilled water and dried at 110°C for 2 h and again employed for the next cycle keeping the other parameters identical as taken in the first cycle. The results of all five cycle experiments are illustrated in Fig. 9. Fig. 9 demonstrates that no significant decrease in percentage removal of β -estradiol was occurred even after the completion of five cycles of operations. Quantitatively, the percentage degradation of β -estradiol was decreased from 59.78% to 57.14% (i.e., 2.64%) for the cycle 1 to 5, respectively. These results inferred that the thin film is, chemically and mechanically, stable since the catalytic activity of catalyst was not hampered at least in the degradation of β -estradiol from aqueous solutions and could be employed for successive operations. Overall, the use of thin films eventually overcome the separation problem of catalyst from the reactor and perhaps found a 'cost effective' process. Therefore, this provides an enhanced applicability of catalyst in a large scale implementation of process.

4. Conclusion

TiO_2 nanoparticles were immobilized onto the surface of borosilicate glass substrate. The sol solutions of titania was prepared using the titanium isopropoxide precursor and polyethylene glycol as filler medium. The TiO_2 thin films were obtained without and with PEG and named as

F1 and F2 thin films. The XRD analysis of thin films showed that the TiO_2 was aggregated with its anatase phase. SEM images showed that small sized grains of TiO_2 were orderly aggregated onto the borosilicate glass and formed a thin layer of TiO_2 with F1 and F2 catalysts. Moreover, F2 thin film showed some micro-cracks onto the solid surface. XPS analysis indicated that Ti is present to its fully oxidized Ti^{4+} state and oxygen is bound with the Ti. However, the percentage of carbon present in thin films F1 and F2 is not changed significantly that inferred that the PEG predominantly modifying the morphological structure of thin films. The BET analysis inferred that the meso-pore size was significantly decreased with the PEG modified TiO_2 i.e., decreased from 7.79 (T1(P)) to 4.18 nm (T2(P)). The photocatalytic activity of these thin films F1 and F2 were assessed for the degradation of one of potent estrogen β -estradiol from aqueous solution and various physico-chemical parametric studies were conducted to propose the degradation mechanism. The pH dependence degradation of β -estradiol was almost independent within the pH region 4.0 to 8.0 however; a slight decrease in percentage degradation was occurred at pH 10.0 using both the catalysts F1 and F2 thin films. Increasing the concentration of β -estradiol from 0.1 to 2.0 mg/L caused a significant decrease in percentage degradation of β -estradiol. Further, the degradation was followed pseudo-first order rate kinetics and Langmuir-Hinshelwood model. An apparent mineralization studies indicated that within 2 h of treatment caused a significant decrease in percentage of TOC removal. Moreover, the percentage TOC removal was not affected significantly within the pH region 4.0 to 10.0 and concentration 0.1 to 2.0 mg/L. Presence of several interfering ions could not affect significantly the photocatalytic degradation of β -estradiol using F2 thin film however; chloride ions suppressed the degradation of β -estradiol due to competitive adsorption toward the active sites of catalyst. The scavenger studies showed that hydroxyl radicals are predominantly attributing the degradation of β -estradiol whereas the singlet $^1\text{O}_2$ is less involved in the degradation process. Moreover, the repeated use of catalyst shows no significant decrease in percentage degradation of β -estradiol which infers that the thin films are found, chemically and mechanically, stable. Therefore, the catalysts possess an enhanced applicability and, perhaps, could be a 'cost effective' treatment technology and it may further be employed for large scale implementation. Overall, the F2 thin film showed relatively higher photocatalytic action compared with the F1 thin film.

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Supplementary materials

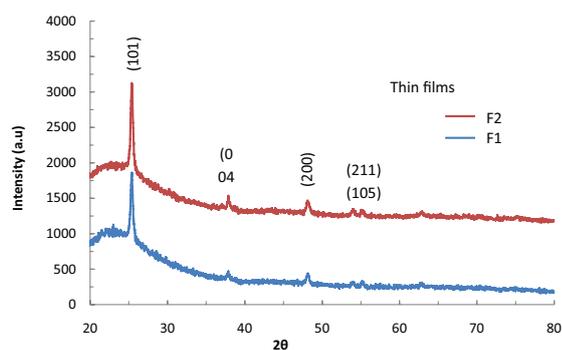


Fig. S1. X-ray diffraction pattern of F1 thin film and F2 thin film photocatalysts.

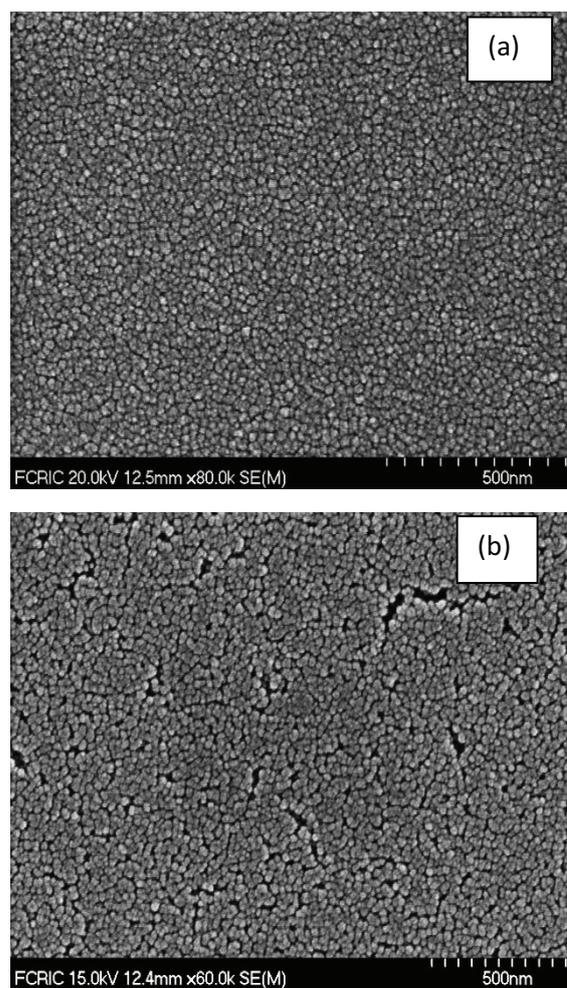


Fig. S2. Scanning electron microscopic (SEM) images of photocatalyst thin films (a) F1; and (b) F2.