IN-SITU ORIENTAL GROWTH OF {001} FACET TiO_2 FILMS: FABRICATION, CHARACTERIZATION AND ITS APPLICATION FOR PHOTOCATALYTIC DEGRADATION OF BEZAFIBRATE IN WATER

*Murtaza Sayed, M. Ismail, Sanaullah Khan & Hasan M. Khan**

ABSTRACT

In this study, highly stable novel Titanium Dioxide (TiO_2) photocatalyst with exposed {001} facets was synthesized on Ti-sheet which was acting as supporting material. The synthesized material was characterized by FE-SEM, HR-TEM, XRD and XPS analyses. TEM analysis confirmed single crystalline nature of the as-synthesized photocatalyst. The XRD analysis showed that 80 % of the synthesized TiO_2/Ti film with exposed {001} facets was anatase in character. The fluoride ions (F^-) on the surface of TiO_2/Ti film was successfully removed by calcination treatment at 600°C. The photocatalytic activity of TiO_2/Ti film with exposed {001} facets was nearly 2.6 times higher than the ordinary, commercially available P25 catalyst and also showed long-term stability towards photocatalytic degradation of bezafibrate, a toxic pharmaceutical contaminant in wastewater.

Keywords: *{001} facets exposed TiO_2/Ti film, anatase, bezafibrate, calcination, degradation, photocatalytic stability, water contamination.*

1. INTRODUCTION

Titanium dioxide (TiO_2) is most widely used semiconductor for the photocatalytic applications due to its high photo reactivity, low cost, non-toxic nature, chemically and biologically inertness and high photostability (Friedmann, Mendive & Bahnemann, 2010). Currently, the efforts are being focused to modify the morphology of TiO_2 and to expose the {001} facets that are highly reactive sites due to the relative high density of unsaturated 5-fold Ti and the unique electronic structure. These facets are found to possess higher photocatalytic activity over thermodynamic stable {101} (Han, et al., 2009; Liu, et al., 2009; Liu, et al., 2010; Wu, et al., 2008; Yang, et al., 2009; Yang, et al., 2008; Liu, et al., 2010; Alivov, & Fan, 2009; Liu, Yu & Jaroniec, 2010). Yang and his co-workers for the first time synthesized single-crystalline anatase with 47% {001} facets through hydrothermally heating a mixed aqueous solution of TiF_4 and HF, where the selective absorption of F^- stabilizes the high-energy {001} facets (Yang, et al., 2008). This was later improved to 64% and the achieved anatase crystals were reported to generate more actively hydroxyl radicals (OH) upon UV irradiation when compared to the commercial Degussa P25 titania nanoparticles (Yang, et al., 2009). A number of publications in the recent years have been published on the increased exposure of {001} facets (Han, et al., 2009; Liu, et al., 2009; Liu, et al., 2010; Yu, Fan & Lv, 2010; Yu, et al., 2009; Dai, et al., 2009; Ariga, et al., 2009; Zhang, et al., 2009; Xiang, Lv & Yu, 2010; Sayed, et al., 2014).

Wang and his co-workers for the first time fabricated the TiO_2-film with exposed {001} facets by hydrothermal treatment of Ti-foil (Wang, et al., 2010). Zhang and co-workers synthesized {001} facets TiO_2 crystals on titanium substrate foil by hydrothermal treatment of titanium foil in a 60 mL of 0.5 % (v/v) HF solution at 180°C for 3 hrs (Zhang, et al., 2011). Wu and Tang synthesized exposed {001} facets TiO_2 film hydrothermally by immersing Ti-plate in a Teflon-lined autoclave for 1 to 24 hrs at 180°C (Wu & Tang, 2011). Till now, most of the work reported used exposed {001} facets in powder form for wastewater treatment. However, to avoid the subsequent catalyst recovery procedure, it is highly desirable to use immobilized catalysts. In the present study, we have hydrothermally synthesized {001} facets exposed TiO_2 film immobilized on Ti substrates for long-term photocatalytic applications.

Bezafibrate (BZF, p-[4-chlorobenzoyl-amino-ethyl]-phenoxy}-b-methylproponic acid) is a lipid regulator agent and is a widely used drug throughout the world and consequently has been frequently detected in the environment (Daughton & Ternes, 1999; Ternes, 1998). In sewage treatment plants in Germany, this drug has been found at the concentration of about 4.6 µg L^{-1} (Daughton & Ternes, 1999; Ternes, 1998). In rivers and water streams of Germany its concentration was nearly 0.35 µg L^{-1} (Ternes, 1998). In surface waters this drug has been detected at median concentrations of about 3.1 µg L^{-1} (Daughton & Ternes, 1999). There are numerous reports on the removal of BZF using different advance oxidation processes (AOPs) like photo-Fenton (Trov'a, Melo & Nogueira, 2008), photo-degradation using solar-simulated irradiation (Cermola, et al., 2005), ozonation and UV/H_2O_2 (Yuan, Zhang & Zhou, 2012). However no literature is available for the photocatalytic removal of BZF using {001} facets TiO_2 film. In the present study, hydrothermally synthesized {001} facets TiO_2 film has been investigated for removal of BZF from water.

* Radiation and Environment Chemistry Laboratory, National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan. Email: hmkhan3@gmail.com

2. MATERIALS AND METHODS

2.1 Chemicals

All the chemicals applied in the present study were of analytical grade and were used without further purification. Milli-Q water was used during all the experiments. Iso-propanol and Hydrogen peroxide (40 % V/V) were purchased from Beijing Chemical Reagent Company. 0.5 M NaOH and 0.5 M HCl were used for pH adjustment. Bezafibrate was purchased from Sigma-Aldrich.

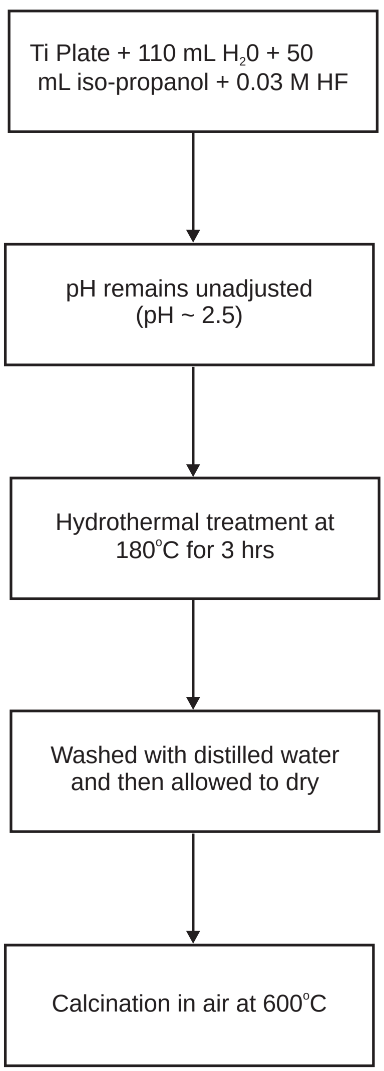

Figure-1: Synthesis steps of {001} Facets TiO_2 Film

2.2 Synthesis of {001} Facets TiO_2 Film

The synthesizing steps of {001} facets exposed TiO_2 / Ti thin-films are summarized in Scheme-1. In a typical experiment, pre-treated Ti foil was hydrothermally treated at 180°C in 0.03 M aqueous HF solution, and 110 mL H_2O in a Teflon-lined autoclave along with 50 mL iso-propanol with a total capacity of 160 mL. After hydrothermal treatment of 3 hours, the obtained Ti-sheets with exposed {001} facets was washed with milli-Q water, dried and then calcinated at 600°C for 90 minutes in air to remove the adsorbed surface fluoride ions. The process is illustrated in Figure-1.

2.3 Characterization

The field-emission scanning electron microscope (FE-SEM) images of synthesized {001} facets TiO_2 film were observed using an ultra-high-resolution field-emission scanning electron microscope (FE-SEM, S-5500, Hitachi, second electron resolution: 0.4 nm/30 kV) performed at an accelerating voltage of 5.0 kV. The high-resolution transmission electron microscopy (HR-TEM) analysis was conducted using a JEM-2011F electron microscope (JEOL, Japan). For the preparation of HR-TEM samples, Ti-sheet having grown {001} facets was first ultrasonically treated in absolute ethanol for 40 minutes and then a small drop from the upper layer of the suspension was placed on carbon film supported on copper grid and dried in air before being analysed for HR-TEM. X-ray diffraction (XRD) analysis of {001} facets exposed TiO_2 film supported on Ti-substrate was carried out with a Rigaku D/max-RB using Cu Kα radiation (λ= 0.15418 nm), operated at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) was carried out by using X-ray photoelectron spectroscope (XPS, PHI-5300, ESCA) at a pass energy of 50 eV, using Al Kα as

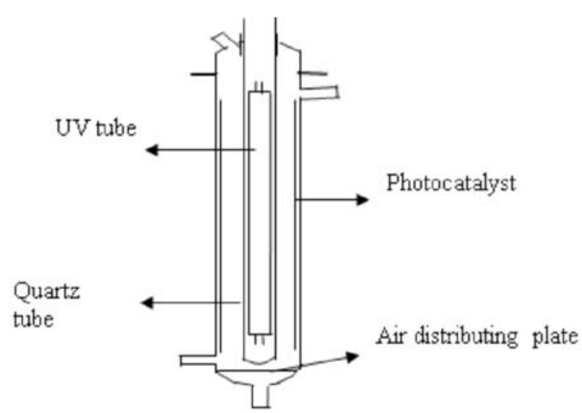

Figure-2: Experimental Setup for Evaluating the Photocatalytic Activity

an exciting X-ray source to investigate the chemical states of the surface elements.

2.4 Photocatalytic Experiments

Photocatalytic activity was measured by taking 10 mg/L of BZF solution in a 120 mL cylindrical vessel, into which TiO_2/Ti sheet with dominant {001} facets was inserted. The design of photocatalytic reactor used in this study is shown in Figure-2. For irradiation purposes, a 10 W low-pressure mercury lamp (λ_{max} =254 nm) was used. An oxygen flow was supplied to the reactor at a flow rate of 30 mL min^{-1} from the bottom of the reactor. The reaction was allowed to reach the adsorption equilibrium in dark for 30 minutes, after adsorption equilibrium was attained, the UV lamp was turned on to carry out photocatalytic reactions. Five mL of sample was taken out after every 15 minutes and the concentration of BZF was determined using high-performance liquid chromatography (HPLC, Shimadzu, LC-10AD) with a UV detector (SPD-10AV) at 230 nm and a Kromasil C18 column (250 mm 4.6 mm) for separation. The mobile phase consisted of a mixture of methanol and water (70:30, v/v) at a flow rate of 1 mL min^{-1}. TiO_2 (Degussa P25) was coated on Ti-substrate by dipping 15-times the Ti-substrate in suspension prepared by dissolving 1 g of P25 in 100 mL of water and then calcination at 400°C for 90 minutes. P25 coated on Ti-substrate was used as the reference with which the photocatalytic activity of the synthesized photocatalyst was compared under the same experimental conditions. The photocatalytic degradation of BZF follows pseudo first-order reaction and its kinetics may be expressed as: ln (C_0/C) = kt, where k is the apparent reaction rate constant, and C_0 and C are the initial concentration and the reaction concentration of BZF, respectively.

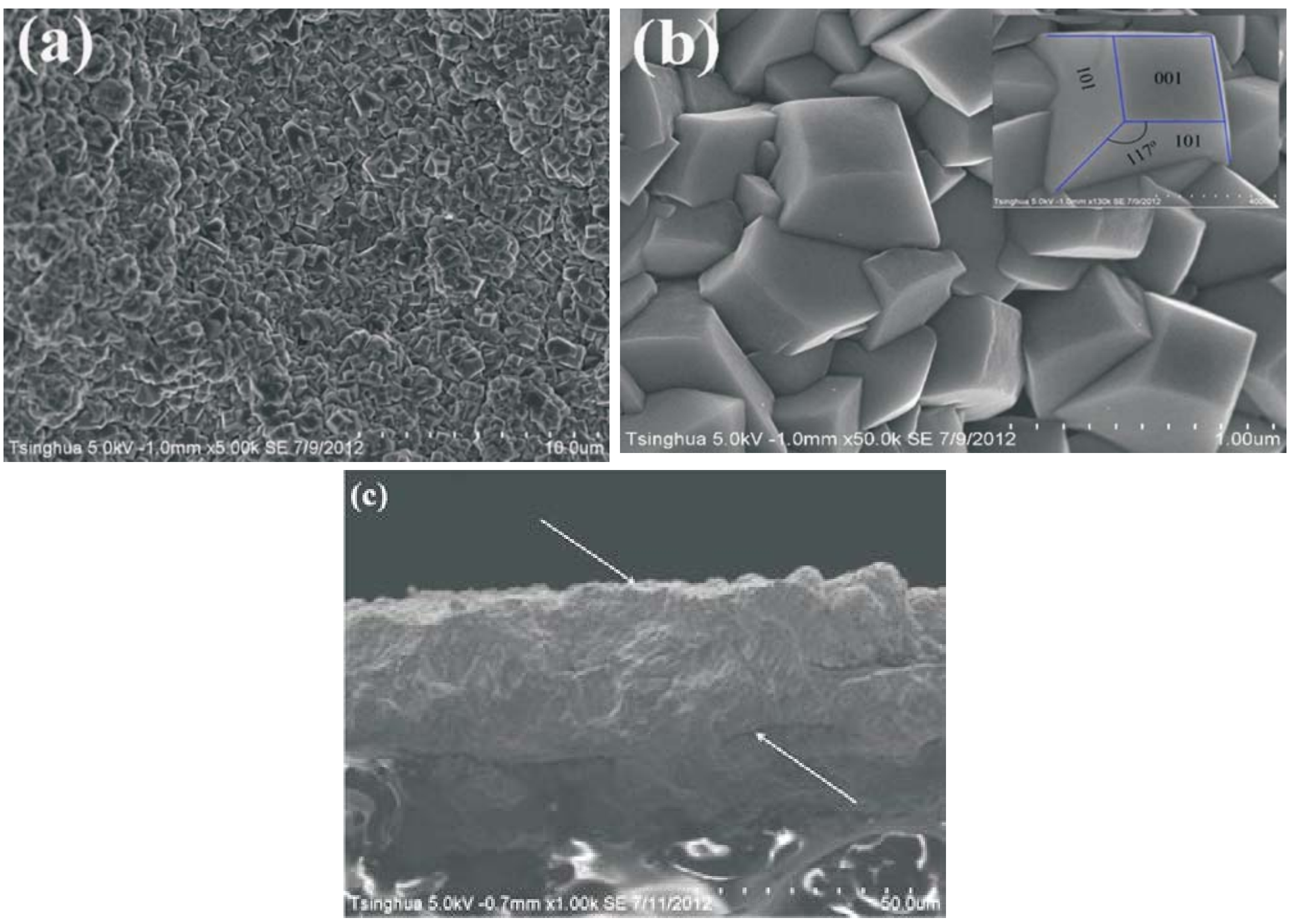

Figure-3: FE-SEM of {001} Facet TiO_2 Films Grown on Ti Substrate in the 120 mL Water + 50 mL Iso-propanol Solution at the pH of 2.5 (a and b) and Cross-Sectional View of the {001} Facet TiO_2 Film (c). Other Conditions: Hydrothermal Time of 3 hours, Hydrothermal Temperature of 180°C and the HF Concentration of 0.03 M.

3. RESULTS AND DISCUSSION

3.1 Morphology and Phase Structures

Figure-3 shows the FE-SEM images of {001} facet TiO_2 films grown on the Ti substrate in the 120 mL water + 50 mL iso-propanol mixed solution at natural pH of the hydrothermal system (pH ~ 2.5). Other synthesis conditions are hydrothermal time of 3 hours, hydrothermal temperature of 180°C and the HF concentration of 0.03 M. As shown in Figure-3 (a, b), the exposed surface of the film consists of truncated tetragonal pyramidal TiO_2 nanocrystals. According to the structural information of the anatase single crystal, the one square surface of the pyramidal can be ascribed to {001} and four isosceles trapezoidal surfaces are {101} facets of anatase TiO_2 single crystals (Figure-3(b)). The interfacial angles between the top and isosceles trapezoidal faces are about 111.7°. The average size of {001} facets is about 350 nm. The film thickness was estimated roughly to be 30 µm.

The addition of hydrofluoric acid during synthesis can play dual roles for growing TiO_2 films with oriented anatase {001} facets. One is to partially dissolve Ti foil into soluble titanium complex for the growth of TiO_2 crystals. The other is to act as morphology-controlling

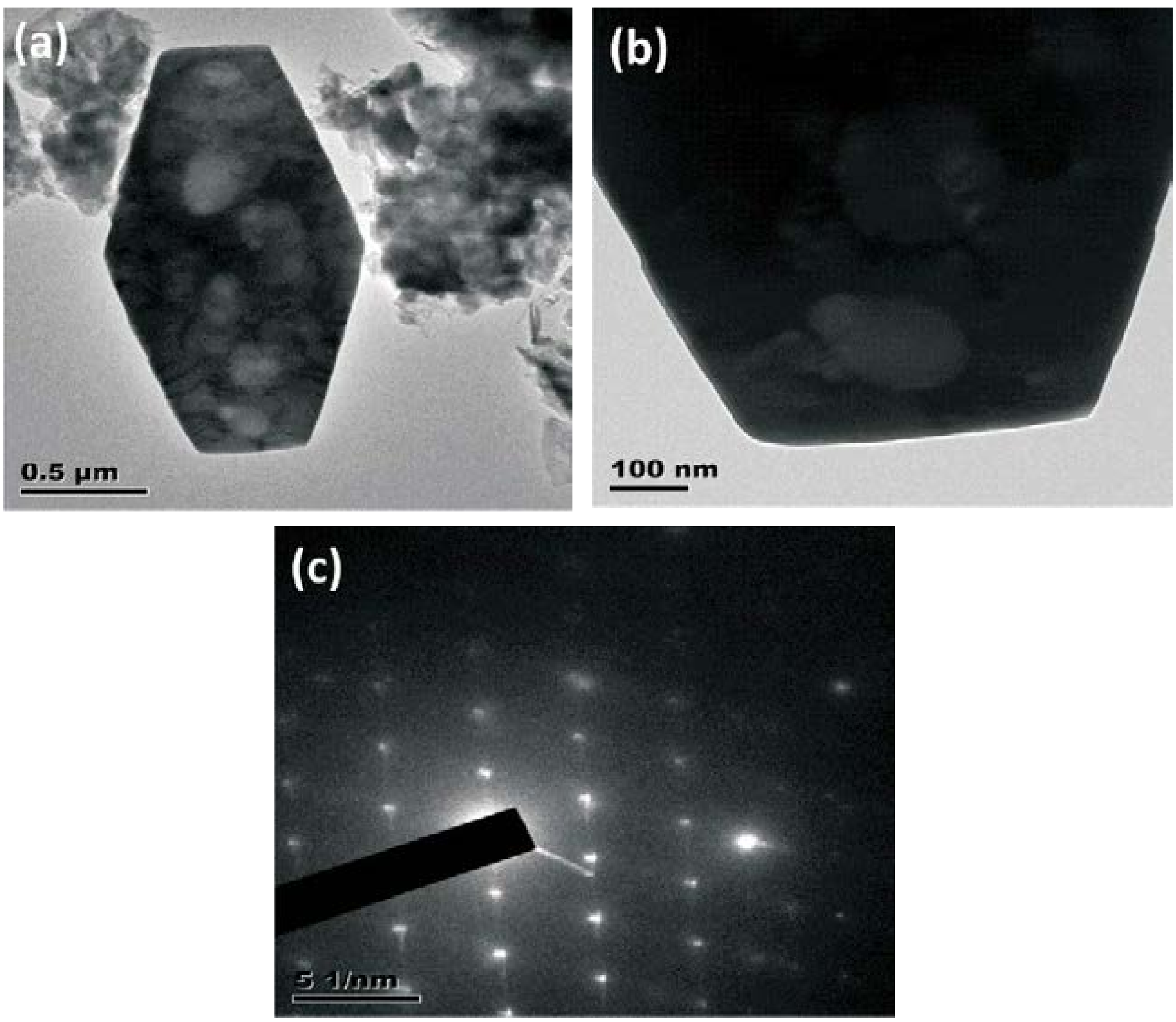

Figure-4: TEM Image of Single Crystal Anatase TiO_2 Scratched Off from Ti-substrate Prepared at Hydrothermal Condition of Mixed Water / Iso-Propanol Solvent (110 : 50 v/v) at 180°C for 3 hours (a) Exposed Side of {001} Facet (b), and (c) SAED Pattern

agent. The mechanism for synthesizing the single TiO_2 crystals in the hydrothermal process is shown as follows:

$$Ti + 6HF \rightarrow H_2TiF_6 + 2H_2 \quad (1)$$
$$H_2TiF_6 + 4H_2O \rightarrow Ti(OH)_4 + 6HF \quad (2)$$
$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (3)$$

Generally the surface of TiO_2 in aqueous media exists in one of the possible species that is $TiOH_2^+$, TiO_2^- or TiOH as illustrated earlier (Yang, et al., 2007). While using 0.03 M HF, when these fluoride ions are introduced to the system at pH = 2.3 nearly 94.8 % of previous dominated TiOH would be replaced by TiF through ligand exchange between surface hydroxyl (-OH) groups on TiO_2 and fluoride ions (F^-) in the aqueous solution, as illustrated by equation (4);

$$\equiv Ti\ \ OH + F \rightarrow \equiv Ti\ \ F + OH \quad (4)$$

Figure-4(a) shows the transmission electron microscopy (TEM) image of single crystal of TiO_2 particle on Ti-sheet. The top and bottom square surface area of the nanoparticle is the {001} crystal facet and the side isosceles trapezoidal surfaces corresponds to {101} crystal facet. Figure-4(b) shows the growth of TiO_2 particle along {001} axis. Selected area electron diffraction (SAED) pattern in Figure-4(c) confirms the single crystal nature of this TiO_2 particle. From XRD results shown in Figure-5, it is clear that the diffraction peaks at $2\theta = 25.22^\circ$, 36.82°, 37.67°, 38.54°, 47.94°, 53.79°, 55.02°, 62.64°, 68.72° and 70.51° can be attributed to (101), (103), (004), (112), (200), (105), (211), (213), (204) and (110) of the standard card JCPDS 21-1272 corresponding to anatase, suggesting a high phase purity for the achieved titania.

3.2 XPS Analysis

The as-synthesized {001} facets TiO_2 film was also investigated for the surface environment using XPS spectrum survey. Figure-6 shows that sharp photoelectron peaks appeared at 459.1 (Ti $2p_{3/2}$), 464.89 (Ti $2p_{1/2}$), 530.89 (O1s), 684.486 (F 1s), 284.72 (C 1s) eV. The XPS results clearly demonstrates that after calcination treatment at 600°C, there was no F^- on the surface of TiO_2/Ti film. The removal of F^- ions are necessary as it sometimes causes decrease in the photocatalytic performance of the catalyst (Han, et al., 2009).

3.3 Photocatalytic Activity and Stability of {001} Facets Anatase TiO_2 Film

The photocatalytic activity of as-synthesized {001} facets was examined by decomposition of a model pharmaceutical compound, BZF. Figure-7 shows the comparison of rate constants of P25 and {001} facets TiO_2 sample prepared at hydrothermal condition of water/ iso-propanol 110:50, HF =0.03 M and pH = 2.5. It can be seen that as-synthesized photocatalyst prepared in the present study showed best

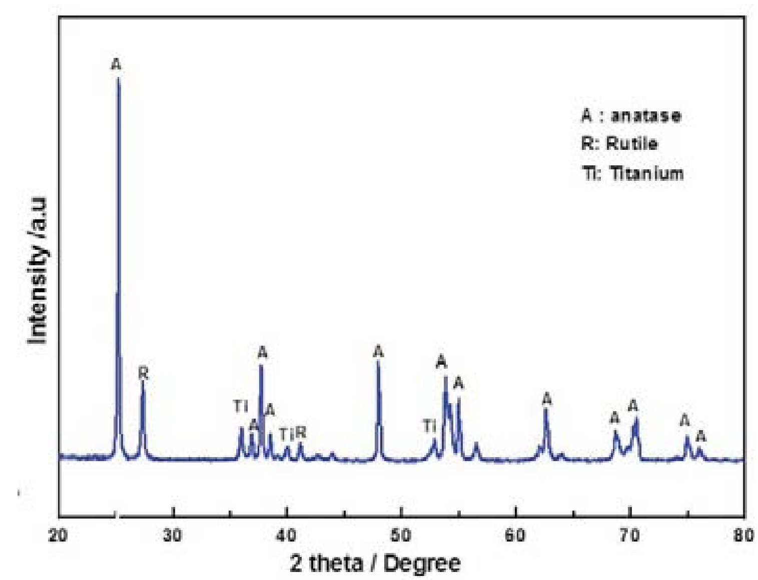

Figure-5: XRD Patterns of the {001} Facets TiO_2 Film Obtained by Hydrothermally Heating Ti Plates in HF= 0.03 M, 110 mL Milli-Q Water and 50 mL Iso-Propanol at 180°C

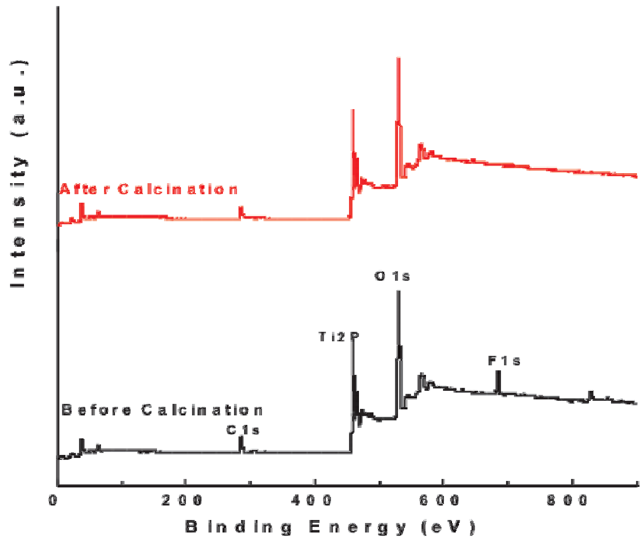

Figure-6: XPS Spectrum of TiO_2 Film with Oriented Anatase {001} Facets Before and After Calcination

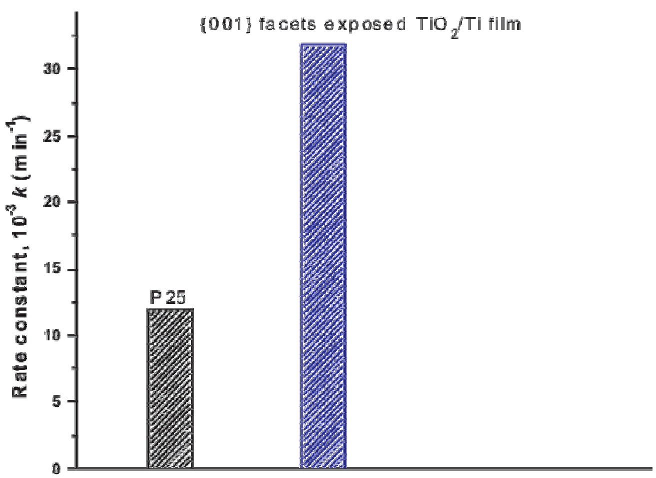

Figure-7: Comparison of Photocatalytic Activity of P25 with our as Synthesized {001} Facets TiO_2 Film Prepared in the Present Study

photocatalytic activity with a rate constant of 31.8×10^{-3} min^{-1}, which is nearly 2.6 times higher than that of conventional P25 coated on Ti-substrate. This may be due to the fact that in synthesized photocatalyst, the exposed percentage of {001} facets are higher as compared to ordinary TiO_2 particle.

Photocatalytic stability over a long period of time is an important aspect of developing a suitable material for an industrial photocatalysis process. Figure-8 shows that more than 90% of BZF was degraded within 120 minutes by {001} facets TiO_2 film, when hydrothermal solution is added with mixed water iso-propanol solvent (110 : 50 v/v), which remained almost the same till the sixth photocatalytic run.

4 CONCLUSIONS

It can be concluded from this study that a highly stable and reactive anatase TiO_2 film with exposed {001} facets can be synthesized by a simple hydrothermal technique in the presence of an optimum dose of iso-propanol. The synthesized high energy {001} facets TiO_2 shows excellent photocatalytic activity, far exceeding that of commercially available P25, due to exposure of high percentage of {001} facets. The

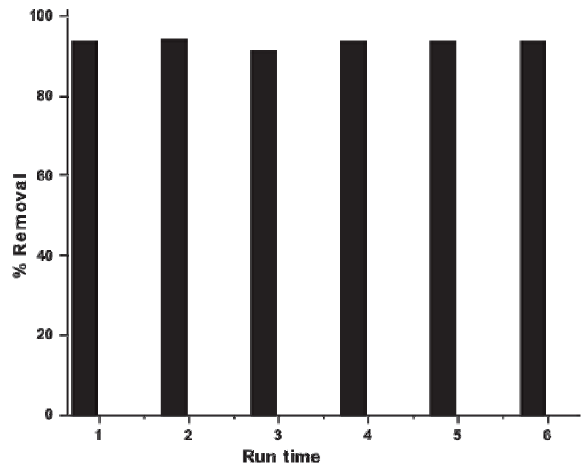

Figure-8: Cyclic Photocatalytic Performance of {001} Facets TiO_2 Film Towards Degradation of BZF Upto Sixth Photocatalytic Run

presence of optimum dose of iso-propanol in hydrothermal solution plays a crucial role in the enhance stability of {001} facets TiO_2 film.

ACKNOWLEDGEMENTS

One of the authors, Hassan M. Khan is thankful to Higher Education Commission (HEC) of Pakistan for funding this project. Murtaza Sayed is thankful to HEC for IRSIP award to carry out this work at Tsinghua University, Beijing, China, and Prof. Dr. P. Zhang of Tsinghua University, Beijing, for permission to use the research facilities.

REFERENCES

Alivov, Y., and Fan, Z.Y., 2009. A Method for Fabrication of Pyramid-Shaped TiO_2 Nanoparticles with a High {001} Facet Percentage, The Journal of Physical Chemistry C, 113, 12954-12957.

Ariga, H., Taniike, T., Morikawa, H., Tada, M., Min,B.K., Watanabe, K., Matsumoto, Y., Ikeda, S., Saiki, K., and Iwasawa, Y., 2009. Surface-mediated visible-light photo-oxidation on pure TiO_2 (001), Journal of the American Chemical Society, 131, 14670-14672.

Cermola, M., DellaGreca, M., Iesce, M.R., Previtera, L., Rubino, M., Temussi, F., and Brigante, M., 2005. Phototransformation of fibrate drugs in aqueous media, Environmental Chemistry Letters, 3, 43-47.

Dai, Y., Cobley, C.M., Zeng, J., Sun, Y., and Xia, Y., 2009. Synthesis of anatase TiO_2 nanocrystals with exposed {001} facets, Nano letters, 9, 2455-2459.

Daughton, C.G., and Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: Agents of subtle change?, Environmental Health Perspectives, 107, 907-938.

Friedmann, D., Mendive, C., and Bahnemann, D., 2010. TiO_2 for water treatment: Parameters affecting the kinetics and mechanisms of photocatalysis, Applied Catalysis B: Environmental, 99, 398-406.

Han, X., Kuang, Q., Jin, M., Xie, and Z., Zheng, L., 2009. Synthesis of titania nanosheets with a high percentage of exposed (001) facets and related photocatalytic properties, Journal of the American Chemical Society, 131, 3152-3153.

Liu, G., Yang, H.G., Wang, X., Cheng, L., Pan, J., Lu, G.Q., and Cheng, H.M., 2009. Visible Light Responsive Nitrogen Doped Anatase TiO_2 Sheets with Dominant {001} Facets derived from TiN, Journal of the American Chemical Society, 131, 12868-12869.

Liu, M., Piao, L., Lu, W., Ju, S., Zhao, L., Zhou, C., Li, H., and Wang, W., 2010. Flower-like TiO_2 nanostructures with exposed {001} facets: Facile synthesis and enhanced photocatalysis, Nanoscale, 2, 1115-1117.

Liu, M., Piao, L., Lu, W., Ju, S., Zhao, L., Zhou, C., Li, H., and Wang, W., 2010. Flower-like TiO_2 nanostructures with exposed {001} facets: Facile synthesis and enhanced photocatalysis, Nanoscale, 2, 1115-1117.

Liu, S., Yu, J., and Jaroniec, M., 2010. Tunable Photocatalytic Selectivity of Hollow TiO_2 Microspheres Composed of Anatase Polyhedra with Exposed {001} Facets, Journal of the

American Chemical Society, 132, 11914-11916.

Sayed, M., Pingfeng, F., Khan, H.M., and Zhang, P., 2014. Effect of Isopropanol on Microstructure and Activity of TiO_2 Films with Dominant {001} Facets for Photocatalytic Degradation of Bezafibrate, International Journal of Photoenergy, 2014, 11.

Ternes, T.A., 1998. Occurrence of drugs in German sewage treatment plants and rivers, Water Research, 32, 3245-3260.

Trov'a, A.G., Melo, S.A.S., and Nogueira, R.F.P., 2008. Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process-Application to sewage treatment plant effluent, Journal of Photochemistry and Photobiology A: Chemistry, 198, 215-220.

Wang, X., Liu, G., Wang, L., Pan, J., Lu, G.Q.M. and Cheng, H.M., 2010. TiO_2 films with oriented anatase {001} facets and their photoelectrochemical behavior as CdS nanoparticle sensitized photoanodes, Journal of Materials Chemistry, 21, 869-873.

Wu, G., Wang, J., Thomas, D.F., and Chen, A., 2008. Synthesis of F-Doped Flower-like TiO_2 Nanostructures with High Photoelectrochemical Activity, Langmuir, 24, 3503-3509.

Wu, J.M., and Tang, M.L., 2011. Hydrothermal growth of nanometer-to micrometer-size anatase single crystals with exposed (001) facets and their ability to assist photodegradation of rhodamine B in water, Journal of Hazardous Materials, 190, 566-573.

Xiang, Q., Lv, K., and Yu, J., 2010. Pivotal role of fluorine in enhanced photocatalytic activity of anatase TiO_2 nanosheets with dominant (001) facets for the photocatalytic degradation of acetone in air, Applied Catalysis B: Environmental, 96, 557-564.

Yang, H.G., Liu, G., Qiao, S.Z., Sun, C.H., Jin, Y.G., Smith, S.C., Zou, J., Cheng, H.M., and Lu, G.Q., 2009. Solvothermal Synthesis and Photoreactivity of Anatase TiO_2 Nanosheets with Dominant {001} Facets, Journal of the American Chemical Society, 131, 4078-4083.

Yang, H.G., Sun, C.H., Qiao, S.Z., Zou, J., Liu, G., Smith, S.C., Cheng, H.M., and Lu, G.Q., 2008. Anatase TiO_2 single crystals with a large percentage of reactive facets, Nature, 453, 638-641.

Yang, S.y., Chen, Y.-y., Zheng, J.-g., and Cui,Y.-j., 2007. Enhanced photocatalytic activity of TiO_2 by surface fluorination in degradation of organic cationic compound, Journal of Environmental Sciences, 19, 86-89.

Yu, J., Fan, J., and Lv, K., 2010. Anatase TiO_2 nanosheets with exposed (001) facets: improved photoelectric conversion efficiency in dye-sensitized solar cells, Nanoscale, 2, 2144-2149.

Yu, J., Wang, W., Cheng, B., and Su, B.L., 2009. Enhancement of photocatalytic activity of mesporous TiO_2 powders by hydrothermal surface fluorination treatment, The Journal of Physical Chemistry C, 113, 6743-6750.

Yuan, H., Zhang, Y., and Zhou, X., 2012. Degradation of Bezafibrate with UV/H_2O_2 in Surface Water and Wastewater Treatment Plant Effluent, Clean - Soil, Air, Water, 40, 239-245.

Zhang, D., Li, G., Yang, X., and Jimmy, C.Y., 2009. A micrometer-size TiO_2 single-crystal photocatalyst with remarkable 80% level of reactive facets, Chemical Communications, 4381-4383.

Zhang, H., Wang, Y., Liu, P., Han, Y., Yao, X., Zou, J., Cheng, H., and Zhao, H., 2011. Anatase TiO_2 Crystal Facet Growth: Mechanistic Role of Hydrofluoric Acid and Photoelectrocatalytic Activity, ACS Applied Materials & Interfaces, 3, 2472-2478.