Supporting Information

Acidic Ionic Liquid: An Alternative to HF for {001} Reactive Facet Controlled Synthesis of Anatase Titania

Sofia Sandhu, Satwant Kaur Shahi, Vasundhara Singh *
*Department of Applied Sciences (Chemistry), Punjab Engineering College (Deemed to be University), Chandigarh-160012, India Tel: +91-9888222214; E-mail: vasun7@yahoo.co.in

TiO_2 with exposed {001} facets has an octahedral structure, its equilibrium shape can be seen as in (Fig. 1a), top view (Fig. 1b) and its cross section along [001] direction can be illustrated as in Fig. 1c. According to Scherrer formula, the average length (*l*) related to (200) peak and thickness (*d*) related to (004) peak can be calculated from the formula:

$$D = 0.89\lambda / \beta \cos\alpha$$

where,

D is the length or width,

$\lambda = 0.15406$ nm is the wavelength of X-ray,

β is the full width half maximum (FWHM) of peaks, and

α is the diffraction angle.

The average length (*l*) can be obtained according to the values of FWHM and α of (200) peak, and thickness (*d*) to (004) peak.

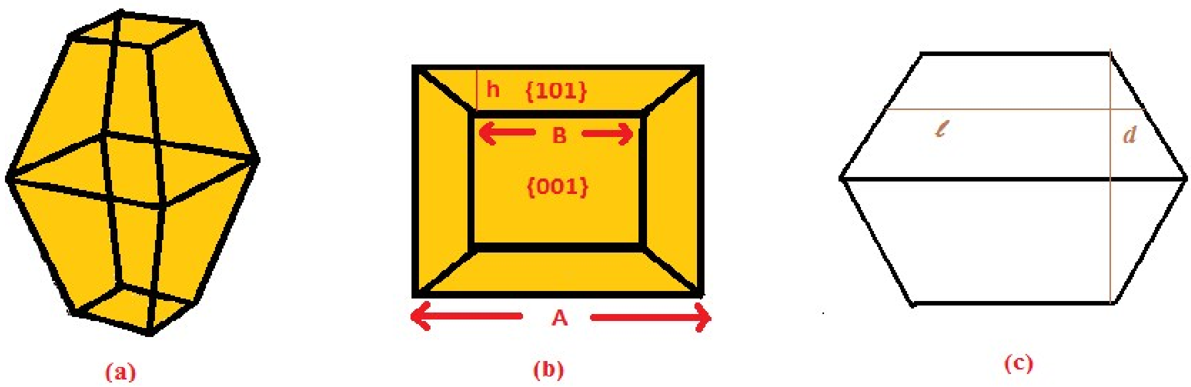


Figure 1 (a) Equilibrium shape of anatase TiO2 with exposed {001} facets (b) Top view of TiO_2 crystal with exposed {001} facets. (c) Cross section of [001] direction.

The calculation of the percentage of high reactive {001} facets is as follows:

$$B = l - \frac{d}{2} / \tan\theta$$

$$A = l + \frac{d}{2} / \tan\theta$$

$$h = \frac{d}{2} / \sin\theta$$

$$S_{(001)} = 2 \times B \times B = 2(l - \frac{d}{2} / \tan\theta)^2$$ (S_{001} is the area of all $\{001\}$ in a TiO_2 single crystal)

$$S_{(101)} = 8 \times h \frac{A+B}{2} = 8hl = 4dl / \sin\theta$$ (S_{101} is the area of $\{101\}$ facets)

$$P_{(001)} = \frac{S_{(001)}}{S_{(001)} + S_{(101)}}$$

Here, $\theta = 68.3°$ is the theoretical value for the angle between [001] and [101] axes of anatase TiO_2.

Experimental data:

XRD Data of samples prepared by using AIL [Bmim]HSO_4:

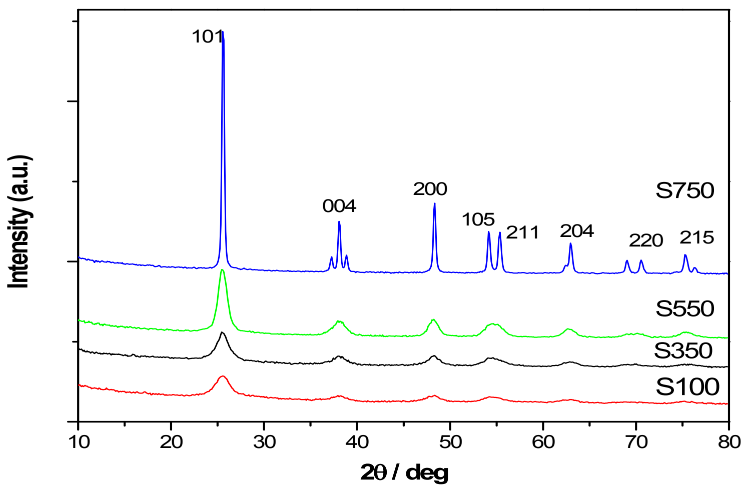


Figure 2 XRD patterns of calcined TiO_2 nanoparticles synthesizsed via sol-gel method using AIL Bmim HSO_4: (a) S100, (b) S350, (c) S550 and (d) S750

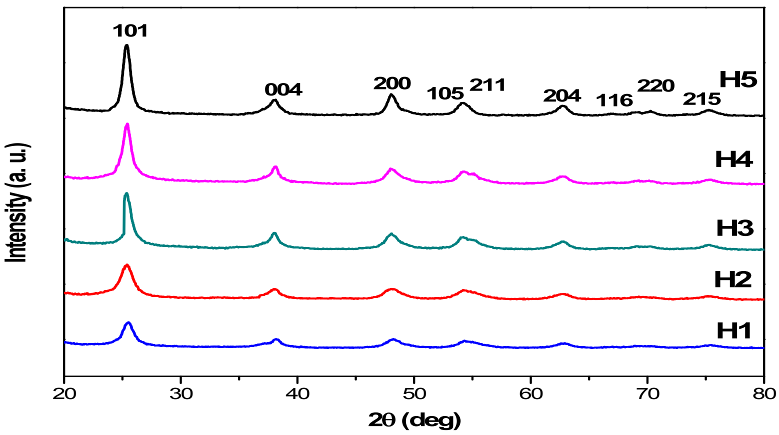
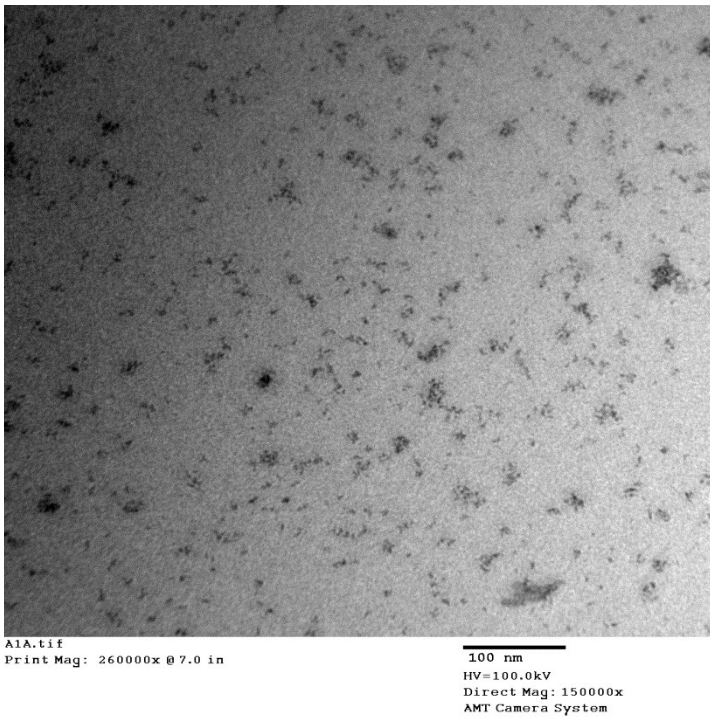
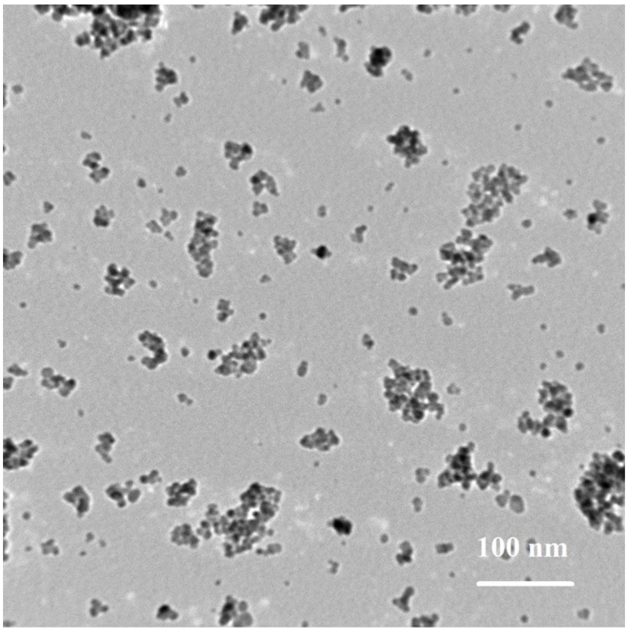


Figure 3 XRD of TiO_2 synthesized via Hydrothermal method-Bmim HSO_4

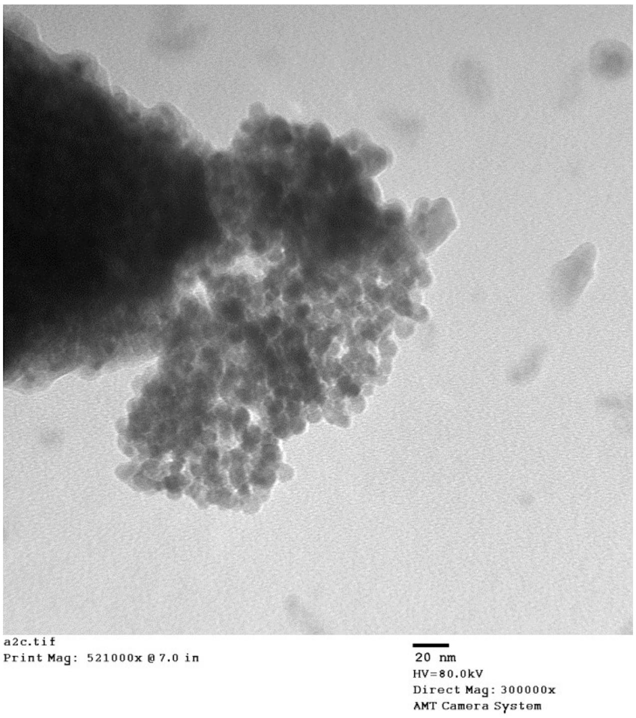
TEM Images of samples synthesized using Bmim HSO_4 AIL:



(a) S100


100 nm

(b) S350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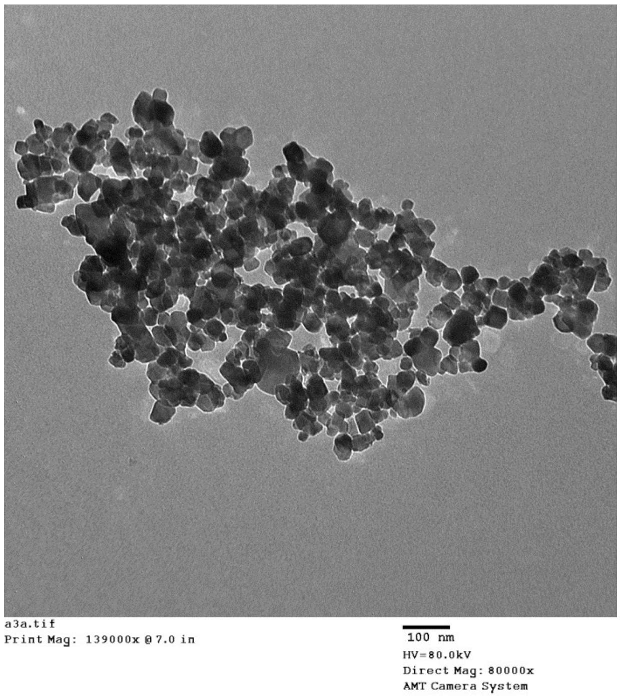
HV=80.0kV
Direct Mag: 300000x
AMT Camera System

(c) S550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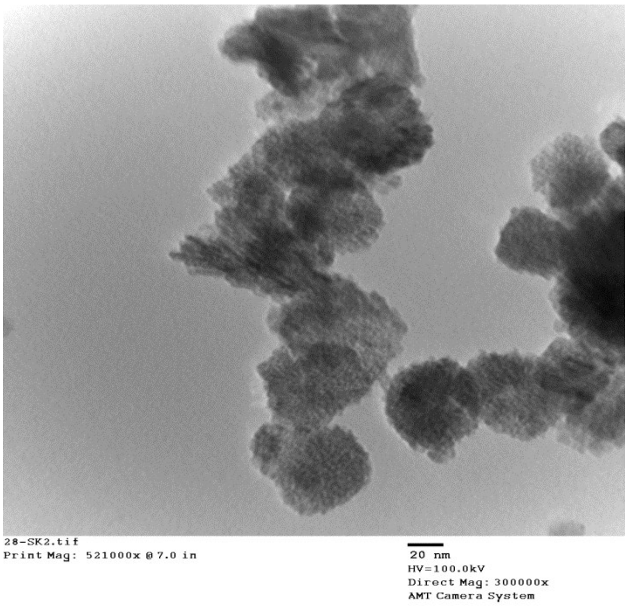
(d) S750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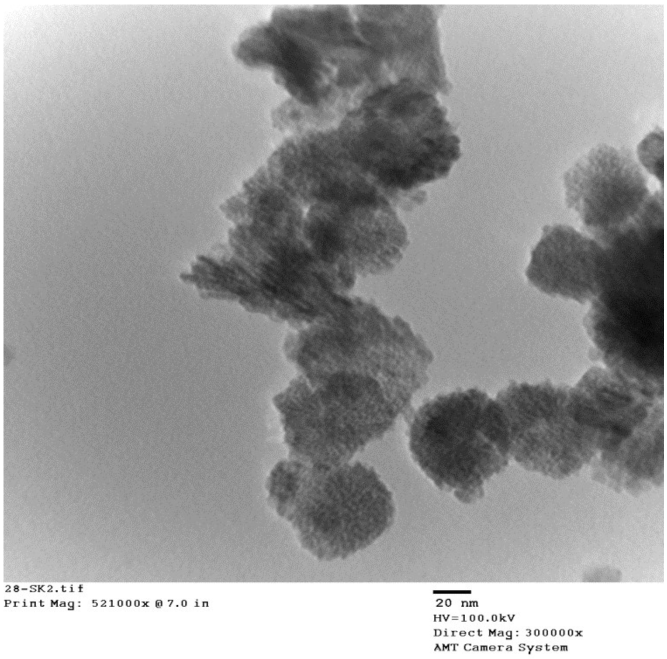
AMT Camera System

(e) H-1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HV=100.0kV
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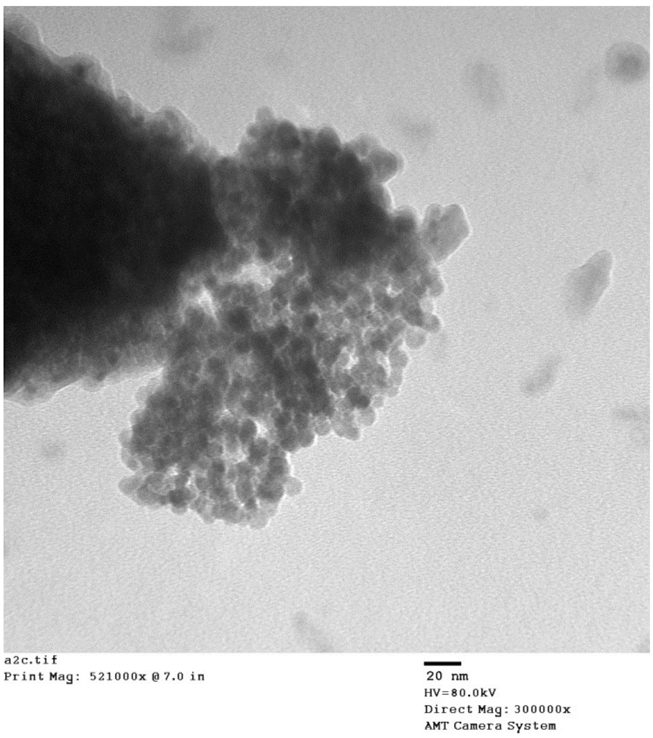
AMT Camera System

(f) H-3


a2c.tif
Print Mag: 521000x @ 7.0 in
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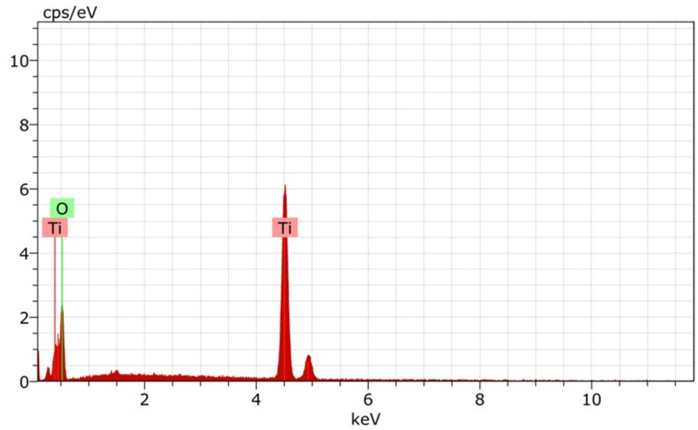
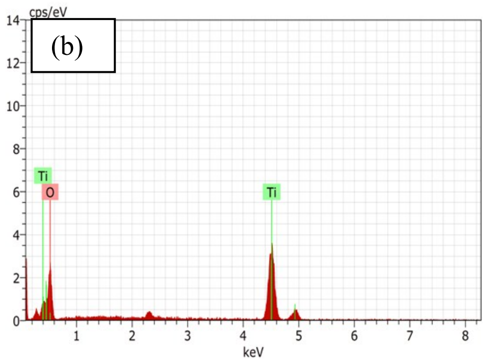
HV=80.0kV
Direct Mag: 300000x
AMT Camera System

(g) H-5

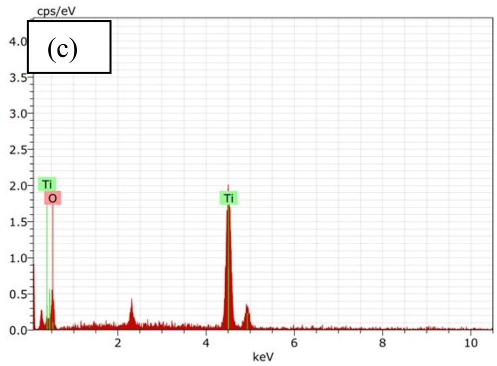
EDS Spectra of samples synthesized using Bmim HSO_4 AIL:



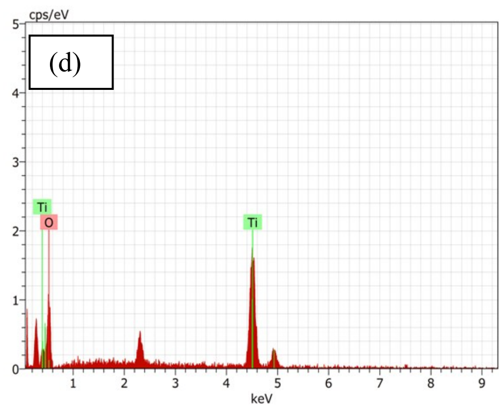
(a) S100



(b) H-1



(c) H-3



(d) H-5

Photocatalytic Degradation Curves:

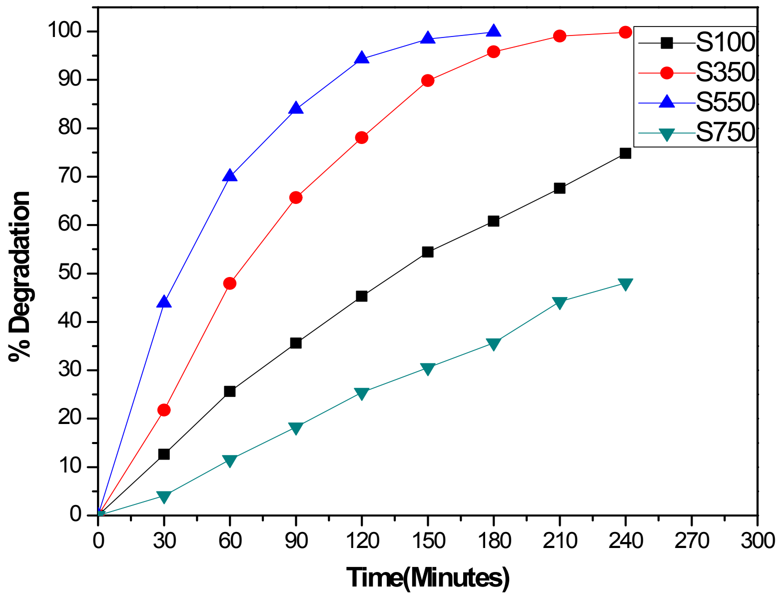


Figure 4 Photocatalytic degradation using sol-gel synthesized titania using AIL $[Bmim]HSO_4$

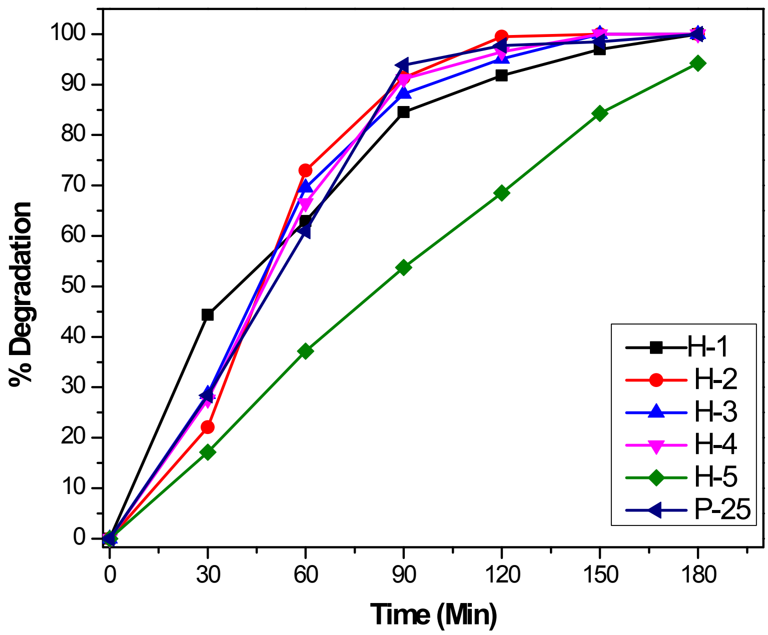


Figure 5 Photocatalytic degradation using hydrothermally synthesized titania using AIL $[Bmim]HSO_4$

XRD Data of Titania samples prepared using AIL $[HO_3S(CH_2)_3MIM][CF_3SO_3]$

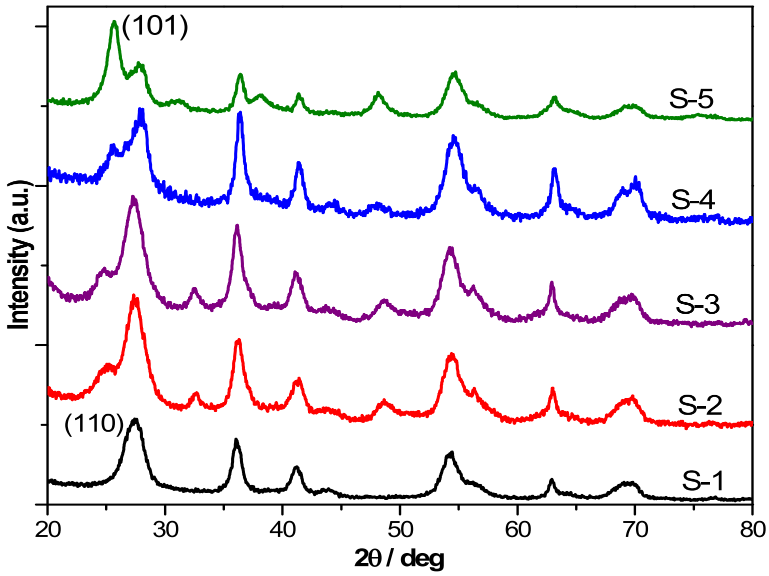


Figure 6 XRD patterns of synthesized TiO_2 via sol-gel method with different molar concentration of aqueous solution of AIL $[HO_3S(CH_2)_3MIM][CF_3SO_3]$: S-1 (2M), S-2 (1M), S-3 (0.5M), S-4 (0.1M), S-5 (0.01M).

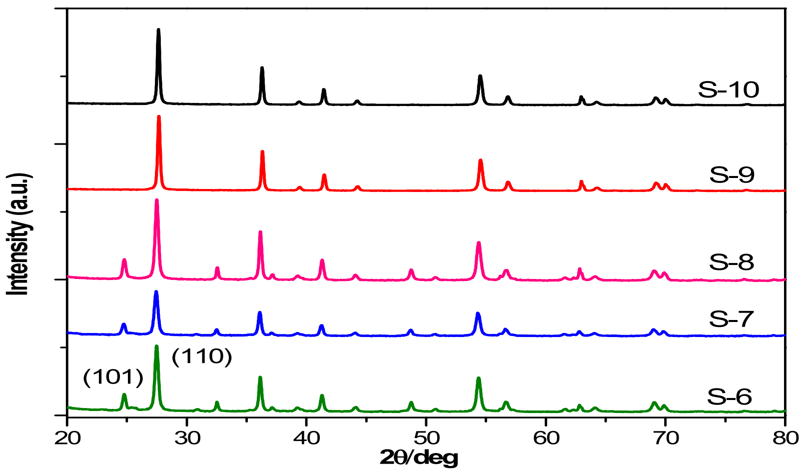
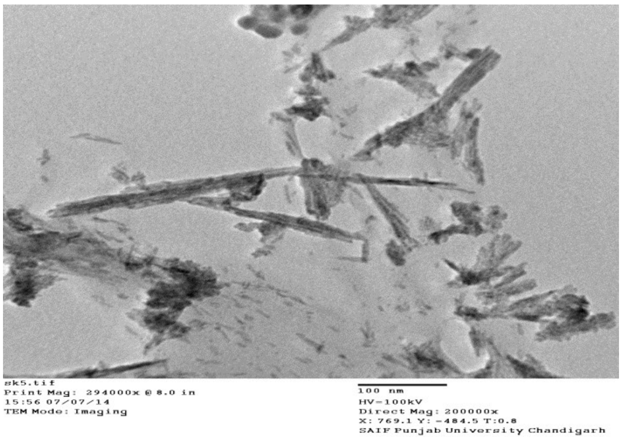


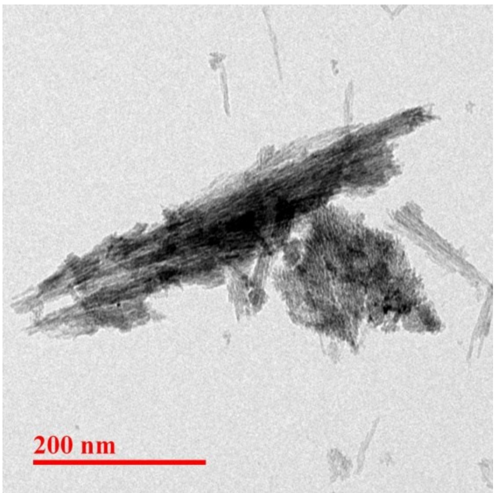
Figure 7 XRD patterns of synthesized TiO_2 via hydrothermal method with different molar concentration of aqueous solution of IL: S-6 (2M), S-7 (1M), S-8 (0.5M), S-9 (0.1M) and S-

10 (0.01M).

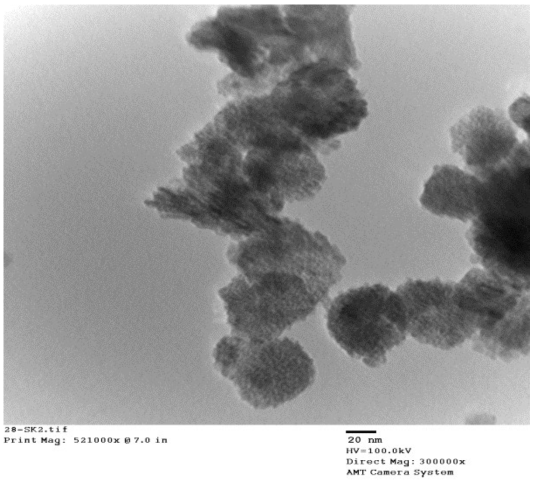
TEM images of samples prepared by using AIL $[HO_3S(CH_2)_3MIM][CF_3SO_3]$:



(a) S-1



(b) S-3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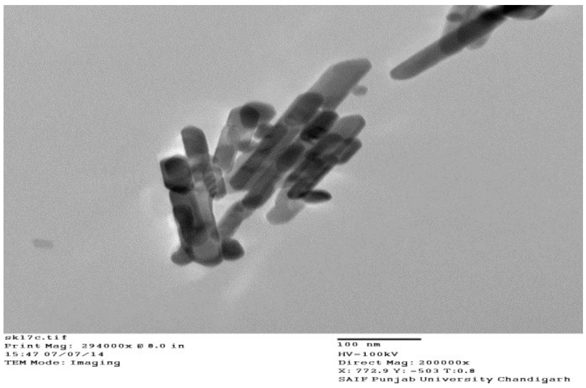
20 nm
HV=100.0kV
Direct Mag: 300000x
AMT Camera System

(c) S-5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15:47 07/07/14
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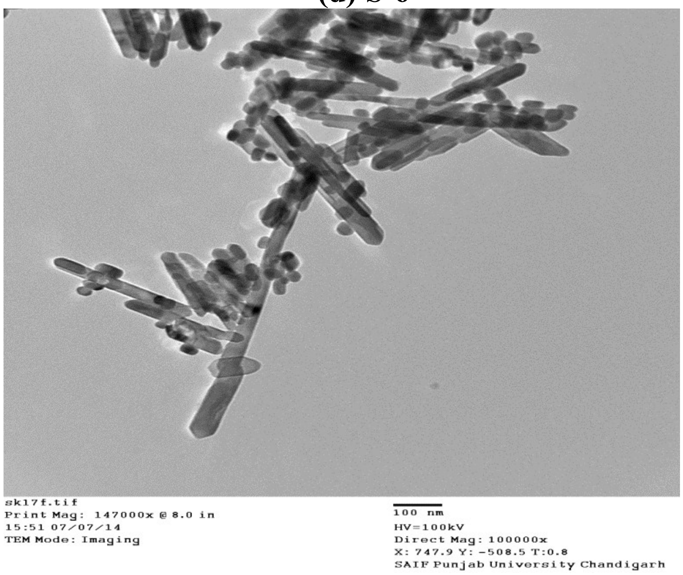
HV=100kV
Direct Mag: 200000x
X: 772.9 Y: -503 T:0.8
SAIF Punjab University Chandigarh

(d) S-6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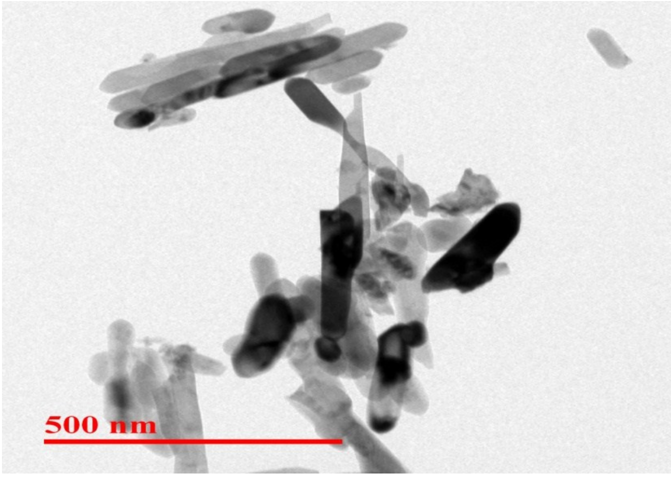
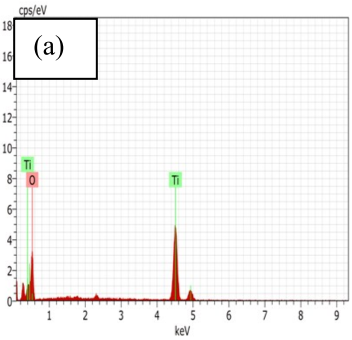
100 nm
HV=100kV
Direct Mag: 100000x
X: 747.9 Y: -508.5 T:0.8
SAIF Punjab University Chandigarh

(e) S-8

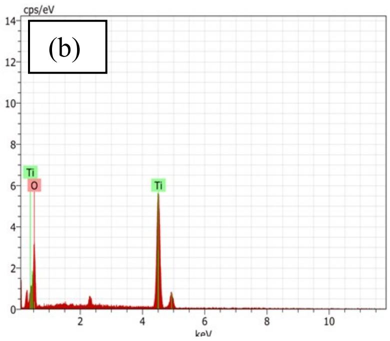


(f) S-10

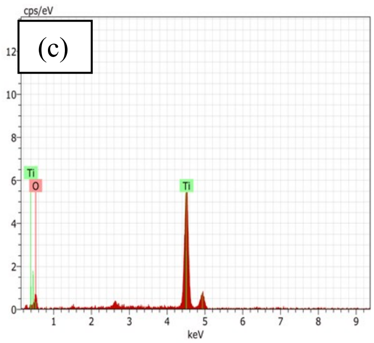
EDS Spectra of samples prepared by using AIL $[HO_3S(CH_2)_3MIM][CF_3SO_3]$:



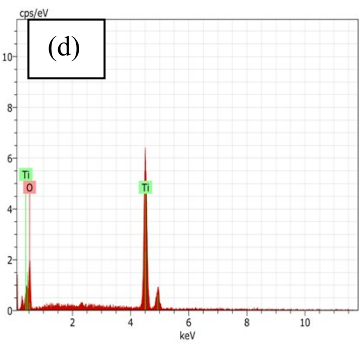
(a) S-1



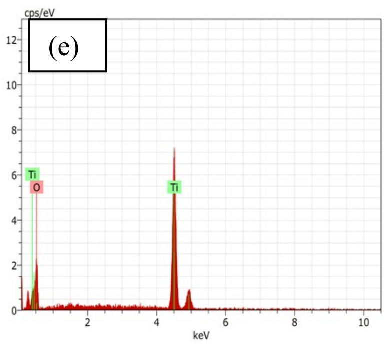
(b) S-3



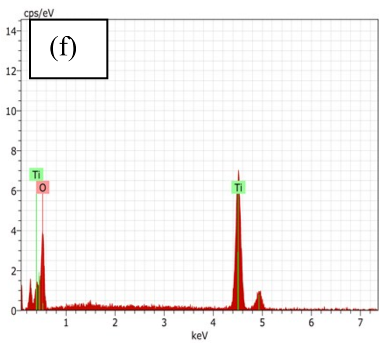
(c) S-5



(d) S-6



(e) S-8



(f) S-10

Photocatalytic degradation curve:

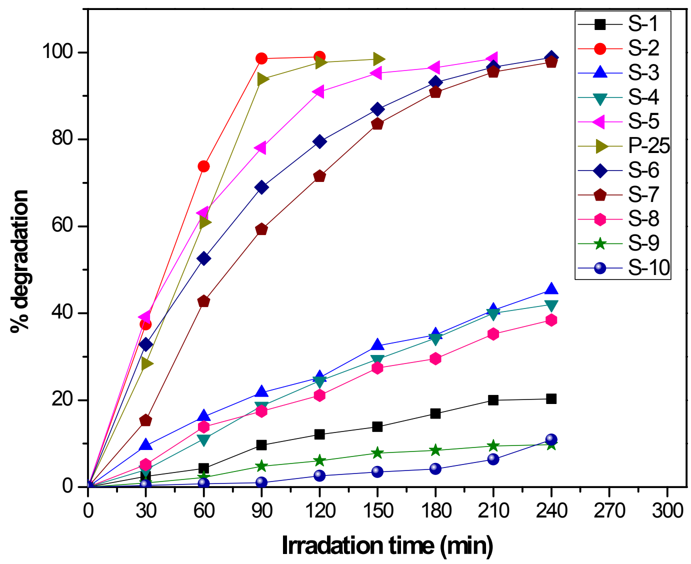


Figure 8 Photocatalytic degradation of methyl orange dye % degradation versus irradiation time with TiO_2 samples (S-1 to S-10) and Degussa P-25.

Table 1 Structural information of the anatase TiO_2 nanoparticles

Samples	Average thickness (nm)	Average length (nm)	Percentage of {001} facet
S100	0.09	0.10	25.8
S350	0.09	0.09	22.9
S550	0.09	0.13	33.3
S750	0.49	0.46	21.6
H-1	6.36	10.16	36.2
H-2	7.48	17.43	47.5
H-3	6.01	5.48	20.5
H-4	9.75	7.57	16.6
H-5	10.55	6.76	12.3
S-5	6.69	6.71	23.03
S-4C	29.91	33.48	26
S-5C	25.37	23.71	21.2
S-6	33.18	32.60	22.4
S-7	37.08	30.05	17.6
S-8	36.63	22.99	11.9

Table 2 Comparative study of previous studies with the present report

Precursor and Fluorine source	Synthesis route and conditions	Morphology and Particle size	{001} facet %	Photocatalytic activity	Ref.
Titanic acid nanobelts and HF	Solvothermal; 200°C; 24h	Nanosized	40 to 77%	Nanocrystals with 77% {001} facets exhibited high photocatalytic activity for photodegradation of MO, MB and RB	33
TiN and HF	Hydrothermal; 200°C; 18h	Microsheets Size:3.5μm	65%	Large visible light photocatalytic activity for CO_2 reduction	34
TTIP and [bmin][BF4]	Hydrothermal; 200°C; 24h	Cubic anatase Size: 100±13nm	25% {001} and 75% {100}	Higher photocatalytic CO_2 reduction	30
TBT and HF	Hydrothermal, 200°C, 24h	Nanosheets to nanoparticles Size: along [001] direction-10-80nm Along [100] direction-30-85nm	89-64%	Photocatalytic degradation of acetone in air. The rate constant exceeded by a factor of 2.1	18
TBT and HF	Hydrothermal; 180/200°C; 24h	Nanosheets Size: 30-130nm	68-89%	TiO_2 nanosheets exhibited a gradually accelerating degradation rate and are more efficient than P25 TiO2	17
TBT and HF	Hydrothermal, 180°C , 24h	Nanosheets Size:50-100nm	61-78%	TiO_2 with 70% {001} facet exhibited highest photocatalytic activity for photocatalytic oxidation decomposition of acetone in air	35
$TiCl_4$ and AILs	Sol-gel and hydrothermal	Nanosized Size: 4.5 to 36.5nm	11.5 to 47.5%	TiO_2 with highest facet percentage exhibited higher photocatalytic activity in the degradation of methyl orange	Present report