

Electronic Supplementary Information (ESI)

Tin Oxide with Tunable p-n Heterojunction for UV and Visible Light Photocatalytic Activity

Arun Kumar Sinha¹, P.K. Manna², Mukul Pradhan¹, Chanchal Mondal¹, S. M. Yusuf² and Tarasankar Pal^{1*}

¹Department of Chemistry

Indian Institute of Technology, Kharagpur-721302, India

² Solid State Physics Division, Bhabha Atomic Research Centre,

Mumbai 400 085, India

*E-mail: tpal@chem.iitkgp.ernet.in

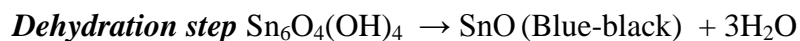
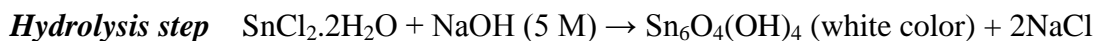
ESI 1:

1. Materials:

All the reagents were of AR grade. Triple distilled water was used throughout the experiment. SnCl₂.2H₂O was obtained from E Merck. NaOH was purchased from BDH Company, Mumbai.

2. Preparation of SnO nanoplate:

Pure SnCl₂.2H₂O was finely powdered by using an agate motor & pestle and a measured amount (10 gm) was mixed with 30 mL NaOH (5.0 M) solution. Within 60 minutes of ultrasonication the white powder changes to a blue-black mass. The blue-black SnO sample was obtained at the solid-liquid interface i.e. the interface between powder SnCl₂.2H₂O and NaOH solution. The hydrolysis and dehydration steps occurred simultaneously.



The blue-black SnO sample was produced slowly from the surface layer of SnCl₂ powder at the interface. The blue-black SnO was formed and washed with copious amount of

water until pH of the washings lowered down to distilled water pH. The blue-black sample was air dried and stored for further characterization.

3. Characterization Instruments:

1.1. UV-Visible study:

All absorption spectra for the degradation reaction were recorded in a chemito spectrophotometer (India) and taking the solutions in a 1 cm quartz cuvette.

1.2. DRS study:

Reflectance spectra were measured using DRS (Diffuse Reflectance Spectra) mode with a Cary model 5000 UV-vis-NIR spectrophotometer.

1.2. XRD-study:

XRD was done in a PW1710 diffractometer, Philips, Holland, instrument. The XRD data were analyzed using JCPDS software.

1.3. Structural computational study:

The analysis of the X-ray diffraction pattern of SnO was done using the FullProf program. This is free software and it is available in internet.

1.4. Raman-study:

Raman spectra were obtained with a Renishaw Raman Microscope, equipped with a He-Ne laser excitation source emitting at a wavelength of 633 nm, and a Peltier cooled (-70 °C) charge coupled device (CCD) camera.

1.5. XPS-study:

The chemical state of the element on the surface was analyzed by a VG Scientific ESCALAB MK II spectrometer (UK) equipped with a Mg K α excitation source (1253.6 eV) and a five-channeltron detection system.

1.6. FTIR-study:

FTIR studies were performed with a Thermo-Nicolet continuum FTIR microscope.

1.7. BET-study:

Nitrogen adsorption-desorption measurements were performed at 77.3 K using a Quantachrome Instruments utilizing the BET model for the calculation of surface areas. The pore size distribution was calculated from the adsorption isotherm curves using the Barrett-Joyner-Halenda (BJH) method.

1.8. FESEM and EDS analysis:

FESEM analysis was performed with a supra 40, Carl-Zeiss Pvt. Ltd instrument and an EDS machine (Oxford, Link, ISIS 300) attached to the instrument was used to obtain the material morphology and composition.

1.9. TEM and HRTEM analysis:

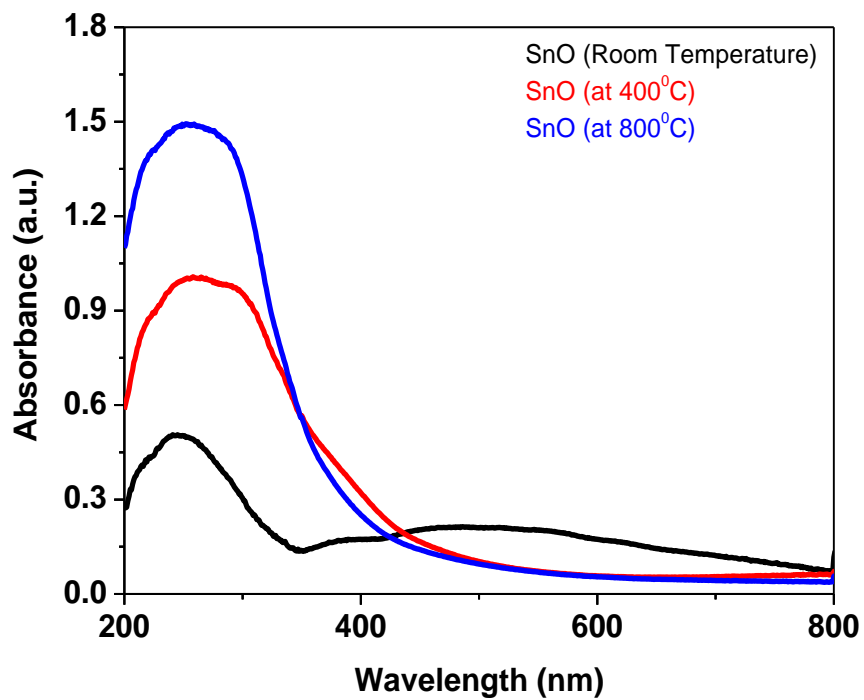
TEM analysis was performed with an instrument H-9000 NAR, Hitachi, using an accelerating voltage of 200 kV.

1.10. Thermo gravimetric analysis:

A differential scanning calorimetry tester (DSC131, Setaram Labsys, France) was used to measure the phase change of SnO nanomaterial. During the test, nanopowders were heated at a rate of 5 °C/min under an O₂ atmosphere.

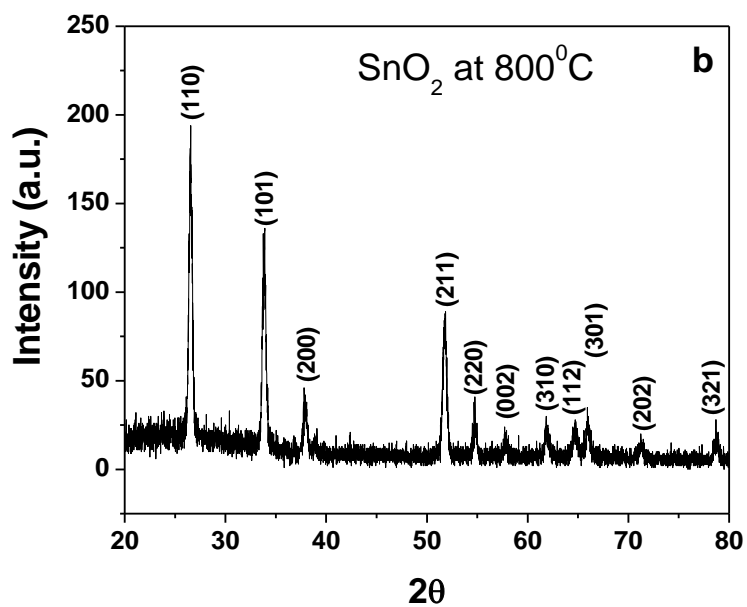
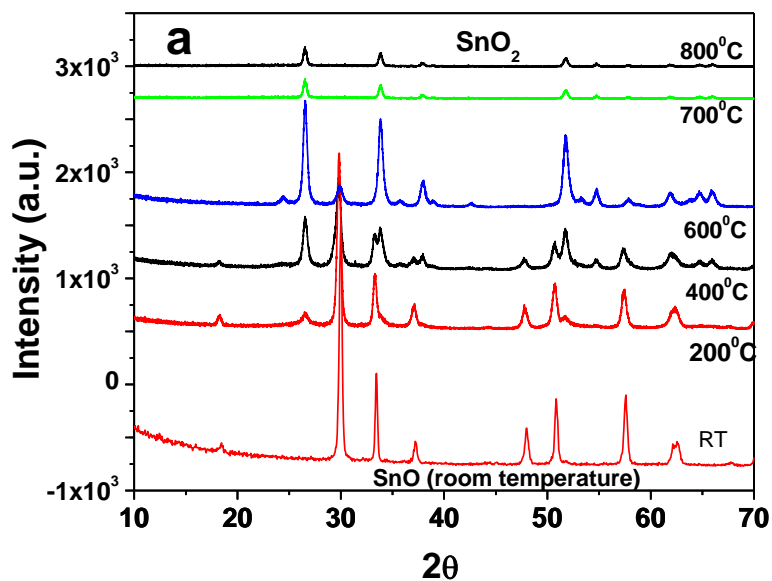
ESI 2.

DR spectra of SnO nanocrystals and heat treated SnO samples

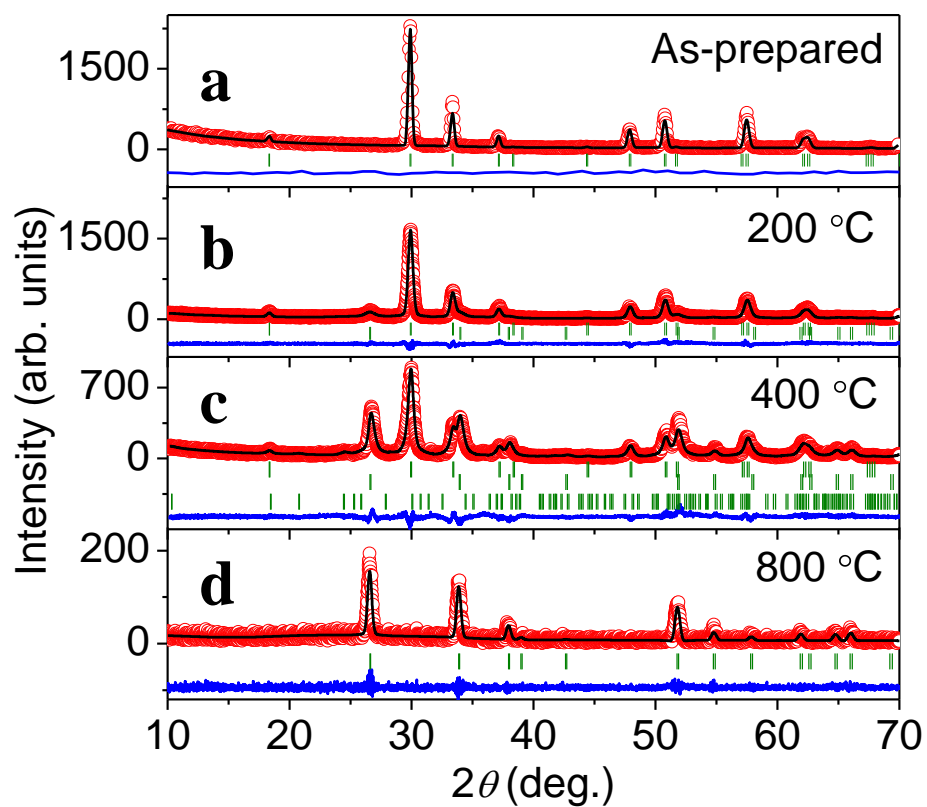


ESI 3:

ESI 3a. XRD pattern of SnO nanoplates showing temperature dependent phase transformation from SnO to SnO₂ (a) and XRD spectrum of rutile phase of SnO₂ obtained after 800°C heat treatment (b).

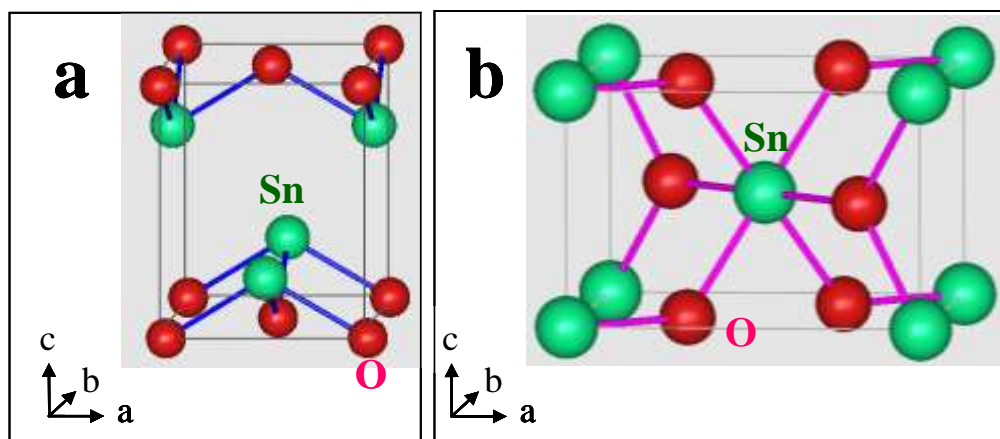


ESI 3b. Rietveld refined, observed (open circle) and calculated (solid line) XRD patterns of (a) as prepared SnO, and SnO annealed at different temperatures (b) 200 °C, (c) 400 °C and (d) 800 °C. The solid line at the bottom shows the difference between observed and calculated patterns. Vertical lines show the positions of the Bragg peaks. The top, middle and bottom layers of vertical lines in figure (c) indicate the Bragg peak positions of SnO, SnO₂ and Sn₃O₄, respectively.

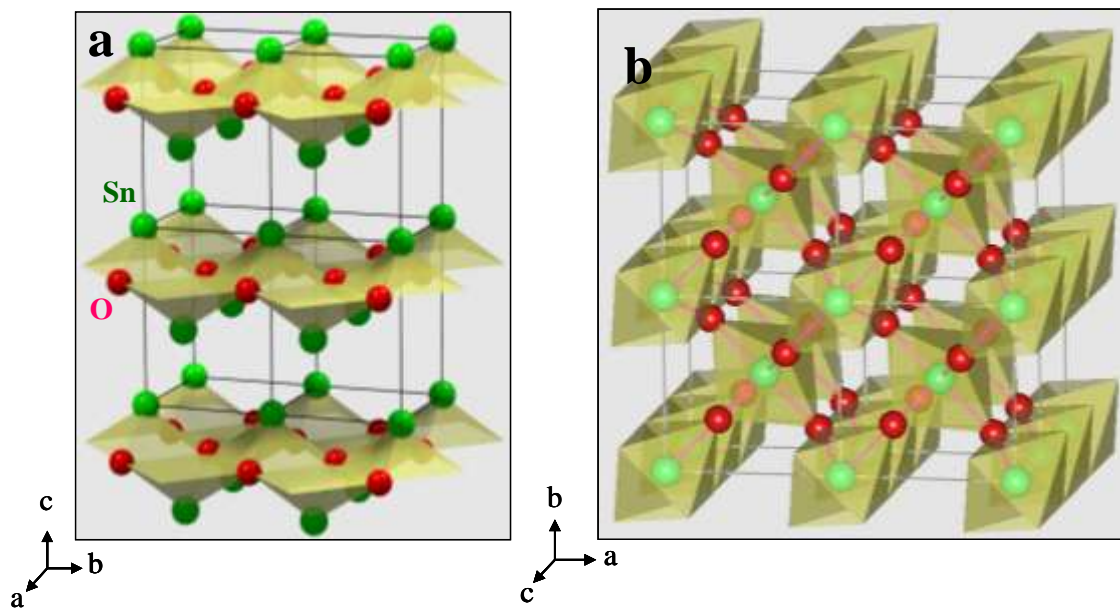


ESI 4:

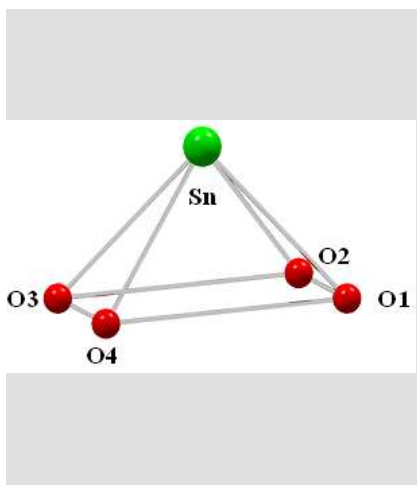
ESI 4a. A comparative view of (a) SnO litharge structure and (b) SnO₂ rutile structure

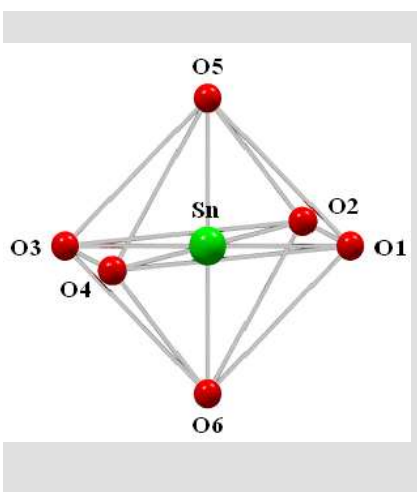


ESI 4b. (a) SnO₄ square pyramidal network in SnO; (b) SnO₆ octahedral network in SnO₂.



ESI 4c: Typical interatomic distances, and angles of SnO and SnO₂, obtained from the Rietveld refinement.

	Bond lengths and bond angles of SnO	Values
Bond length Sn-O1	2.22(3) Å	
Bond length O1-O2	2.69(9) Å	
Bond length O1-O4	3.799 (2) Å	
Bond angles O1-Sn-O2	80.6(7)°	
Bond angles Sn-O-Sn	117.6(1)°	

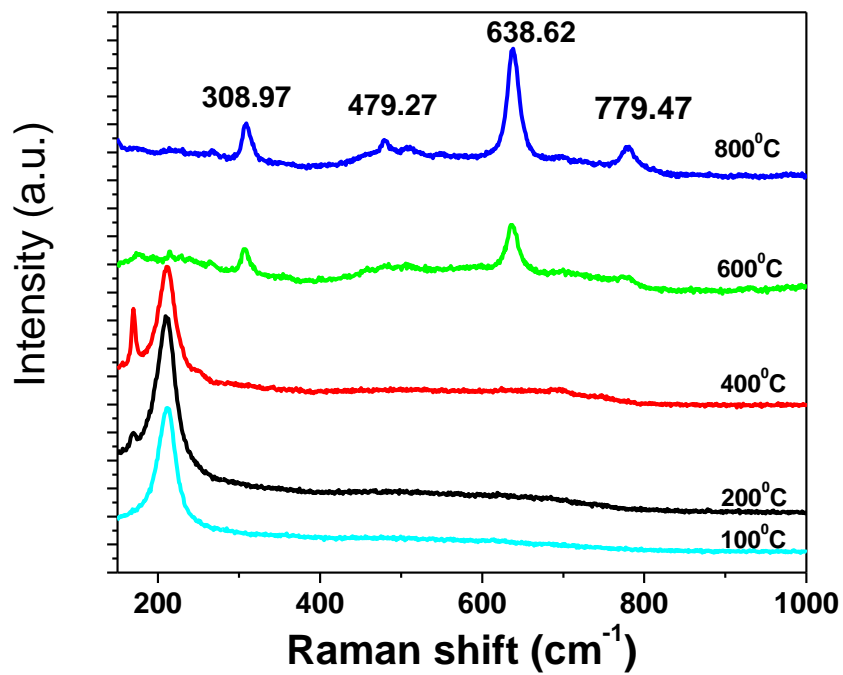
	Bond lengths and bond angles of SnO₂	Values
Bond length Sn-O1	2.06(2) Å	
Bond length Sn-O5	2.04(2) Å	
Bond length O1-O2	2.63(3) Å	
Bond length O1-O5	2.90(3) Å	
Bond length O1-O4	3.187(2) Å	
Bond angles O1-Sn-O2	89.1(9)°	
Bond angles Sn-O-Sn	114.8(3)°	

ESI 4d: Structural parameters of SnO and SnO₂, obtained from the Rietveld refinement.

Inorganic Material	SnO	SnO ₂
Space Group	<i>P4/nmm</i>	<i>P42/mnm</i>
crystallographic unit cell	$a = b = 3.799(1) \text{ \AA}$ $c = 4.841(1) \text{ \AA}$	$a = b = 4.738(2) \text{ \AA}$ $c = 3.187(1) \text{ \AA}$
Absolute position And Occupancy number	Sn (2c) $x = 1/4$ $y = 1/4$ $z = 0.238(1)$ <i>Occ = 1</i>	Sn (2a) $x = 0$ $y = 0$ $z = 0$ <i>Occ = 1</i>
Absolute position And Occupancy number	O (2a) $x = 3/4$ $y = 1/4$ $z = 0$ <i>Occ = 1</i>	O (4f) $x = 0.304(5)$ $y = 0.304(5)$ $z = 0$ <i>Occ = 1</i>
chi-square of the pattern	$\chi^2 = 2.13$	$\chi^2 = 1.97$

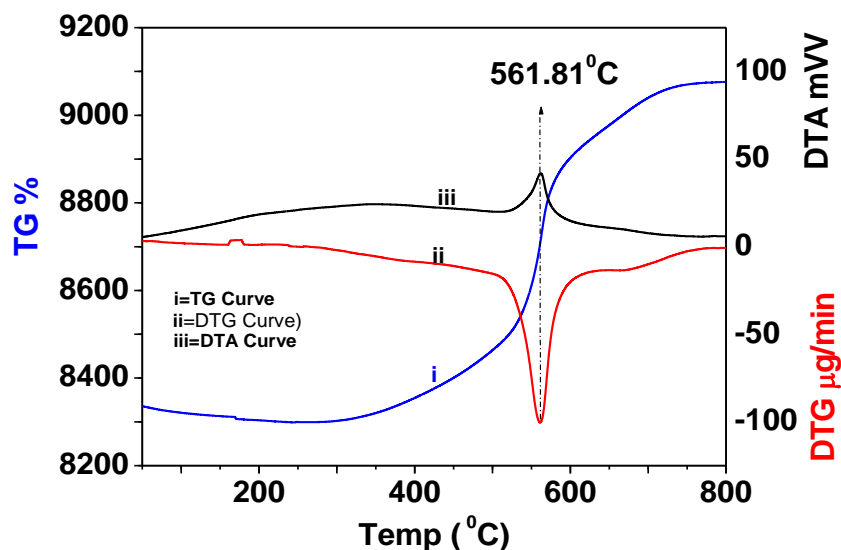
ESI 5.

Raman spectra of heat treated SnO nanoplates examined under laser power 100% (20 mW) and laser exposure time 30 sec.



ESI 6.

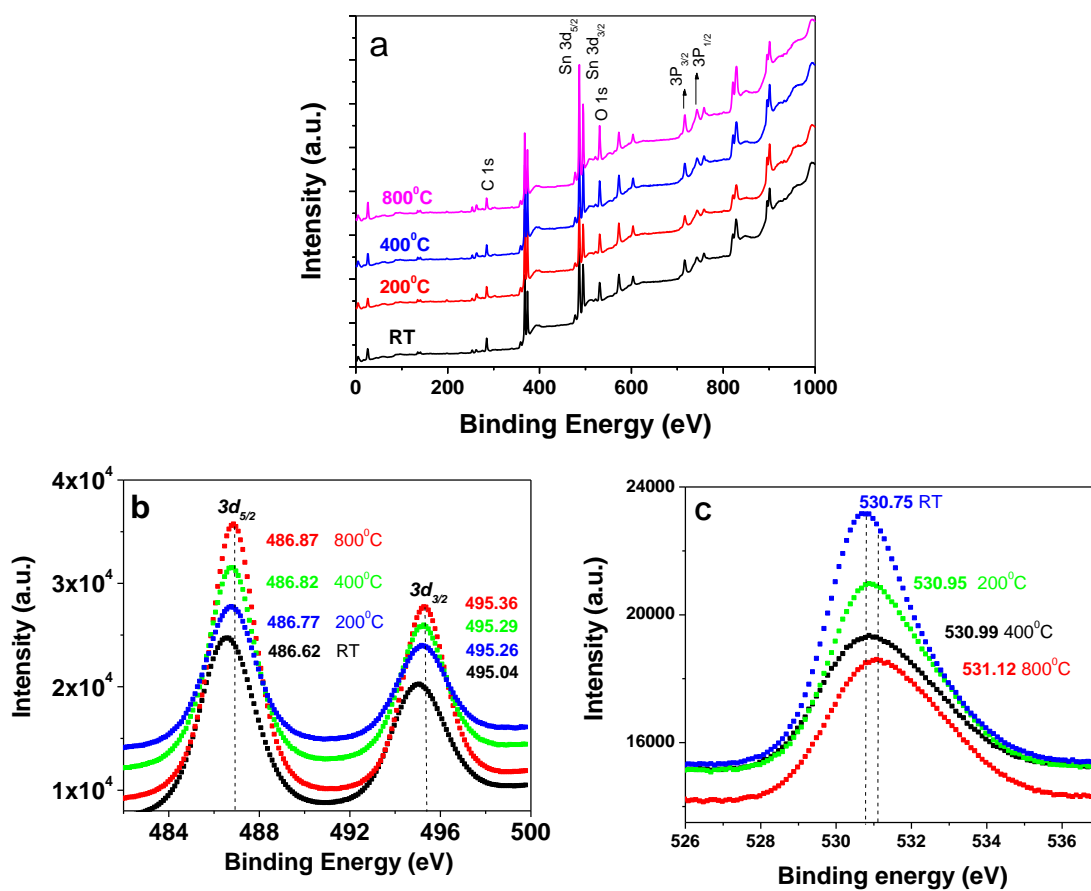
Thermal analysis (TG-DTA) of SnO nameplates



The curve I represents the TG curve and the inflection region demonstrates the phase change area of SnO material in relation with the temperature change. The significant phase change from SnO to SnO₂ via some intermediate (such as Sn₃O₄) took place at an approximate temperature range of 300°-700°C and at 800°C the transformation of phase becomes complete. In this case, DTA curves (black line) show exothermic peak because there occurs one thermochemical reaction which is oxidative in nature.

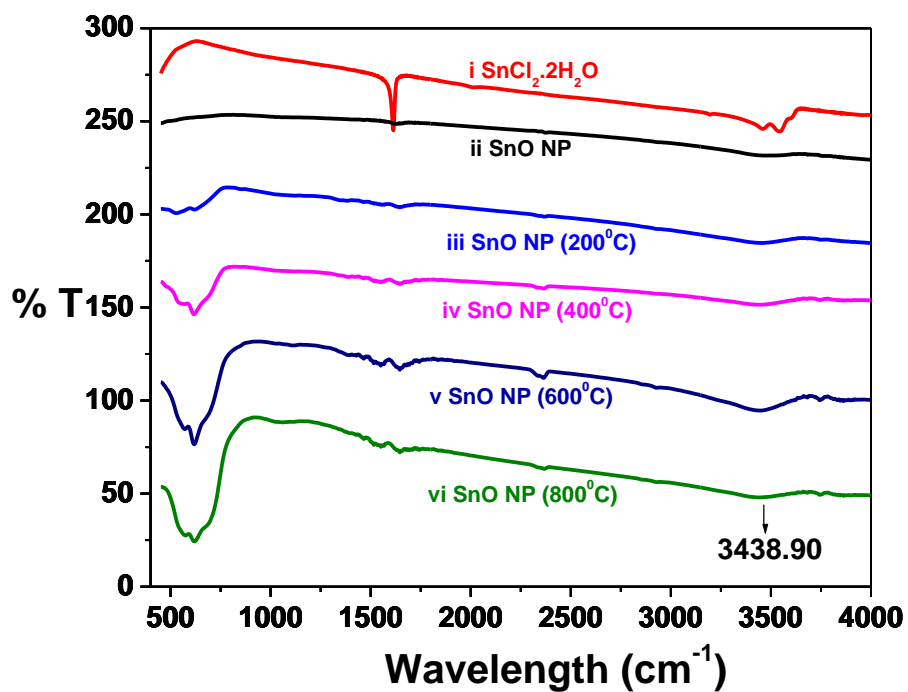
ESI 7.

XPS analysis of SnO nanoplates at different temperature. Survey scan (a), Sn 3d (b) and O 1s (c) core level XPS spectra of SnO (room temperature), SnO (200°C), SnO (400°C) and SnO (800°C) samples.



ESI 8.

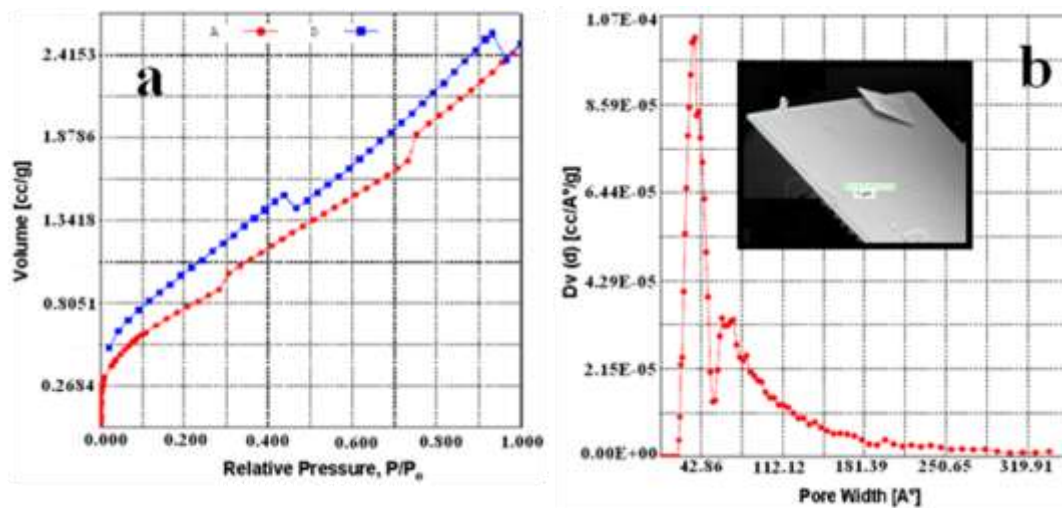
FTIR spectra of powder SnO sample at different temperature. (i) neat $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (ii) as prepared SnO at RT (iii) SnO at 200°C (iv) SnO at 400°C (v) SnO at 600°C and (vi) SnO at 800°C .



ESI 8 shows FTIR spectra SnO nanocrystals but at different temperatures. Thus FTIR conclusively speaks for the non-hygroscopic behavior of SnO material. It is also observed that as SnO is oxidized to SnO_2 and the sample became hygroscopic. So a broad band at 3438.90 cm^{-1} appeared for SnO_2 material at 600 and 800°C .

ESI 9.

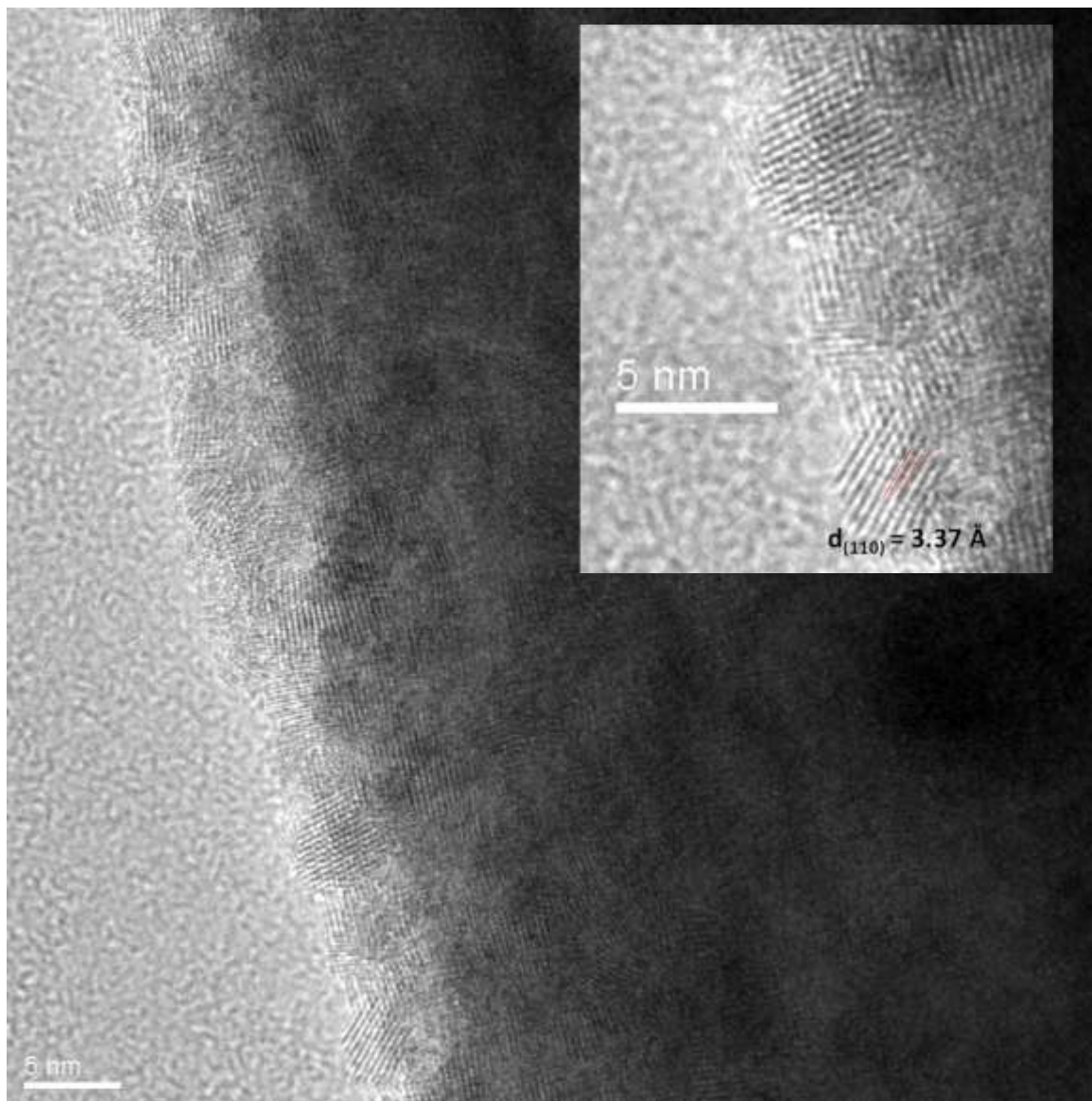
Nitrogen adsorption–desorption isotherm and the BJH pore size distribution of SnO nanoplates



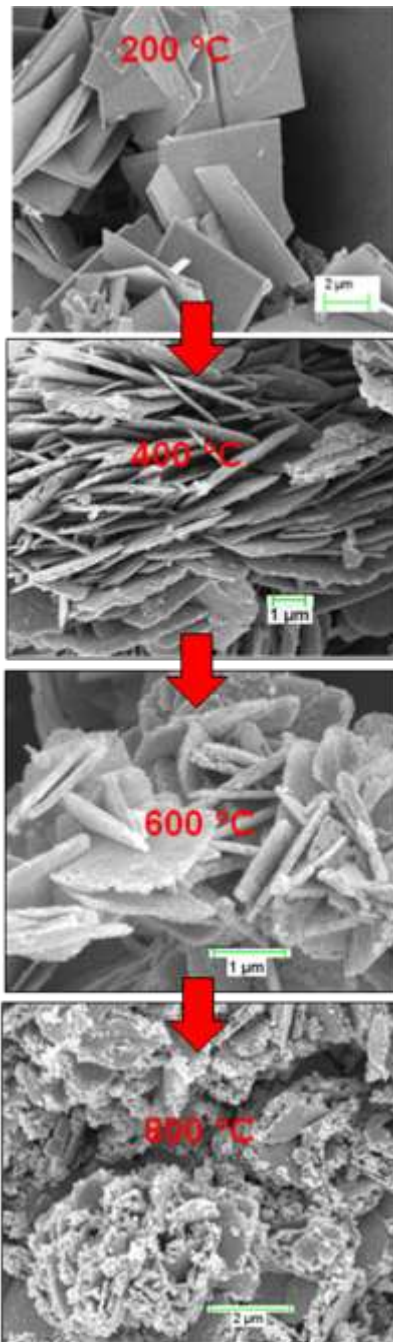
The N₂ adsorption–desorption isotherm and the pore size distribution of SnO nanoplates. The BET specific surface area of the SnO plates is found to be 2.99 m²/g.

ESI 10.

HRTEM image of SnO sample annealed at 200°C. A polycrystalline SnO₂ nanoparticles are formed on the surface of SnO.



ESI 11:
Morphology SnO nanoplates at different temperature



ESI 12:

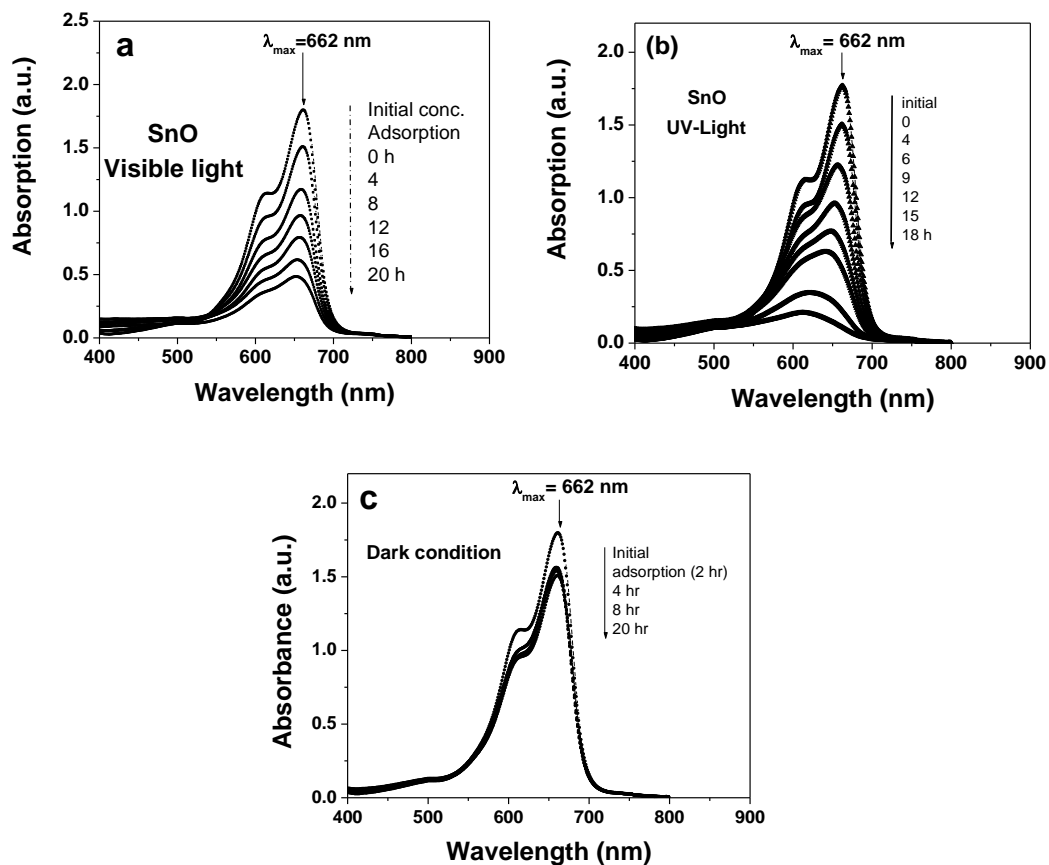
Photodegradation experiment

To carry out the photoreaction, one 100 mL capacity photoreactor was used. The photoreactor was kept at 30°C circulating cold water during the photoreaction to avoid heating effect on the reaction mixture. Reaction mixture was prepared in the photoreactor using 0.025 g of the as prepared SnO powder and 50 mL aqueous solution of MB so that the final concentration of MB becomes 3×10^{-5} M. The MB solution was allowed to stand for 2 h for aging to reach an adsorption-desorption equilibrium on the surface of SnO before light irradiation. We have used commercial visible light source (i.e. 200 W and 500 W tungsten light) and commercial UV-light source (365 nm). The reaction mixture was well stirred at 500 rpm during photoreaction due to passing of air O₂ into the reaction mixture.

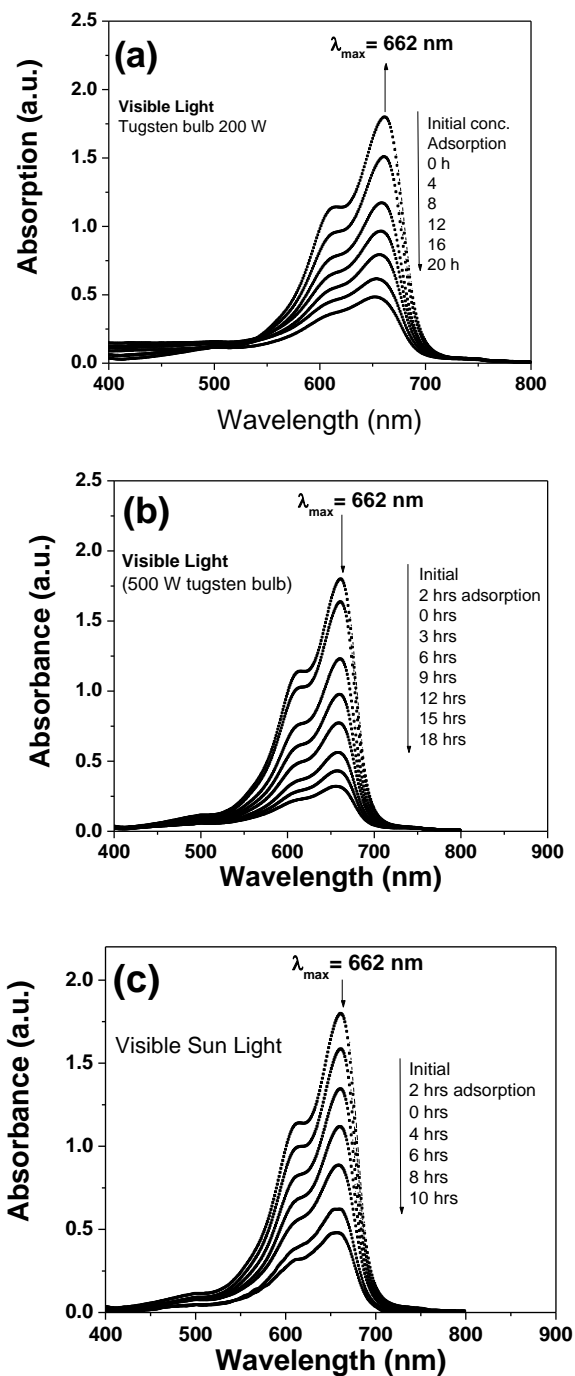
The time dependent photocatalytic reaction was monitored spectrophotometrically. During the absorption measurement of the reaction mixture containing the exposed dye solution and SnO material, methylene blue solution was separated by centrifugation (5000 rpm for 10 min) to avoid light scattering due to the dispersed SnO nanocrystals in the aqueous phase. In the similar fashion, we have also used annealed tin oxide samples for photodegradation of methylene blue by UV-light (365 nm)

ESI 13.

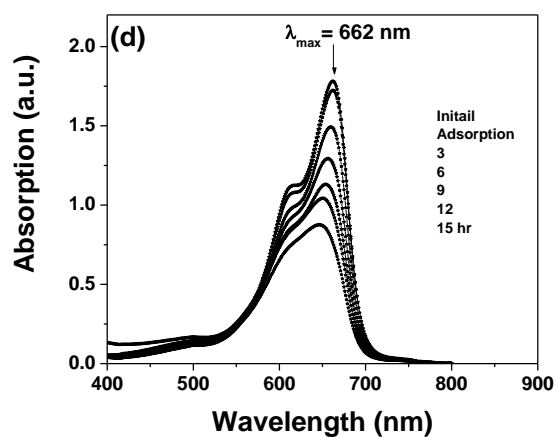
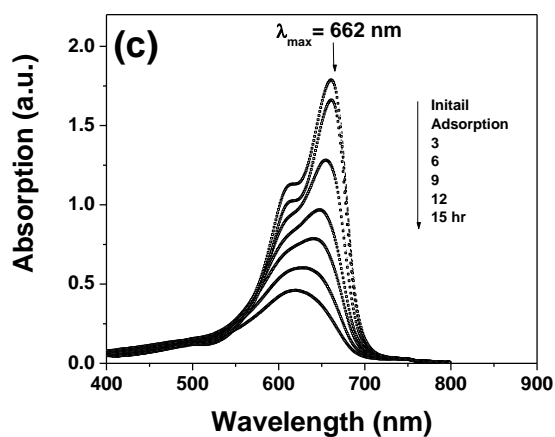
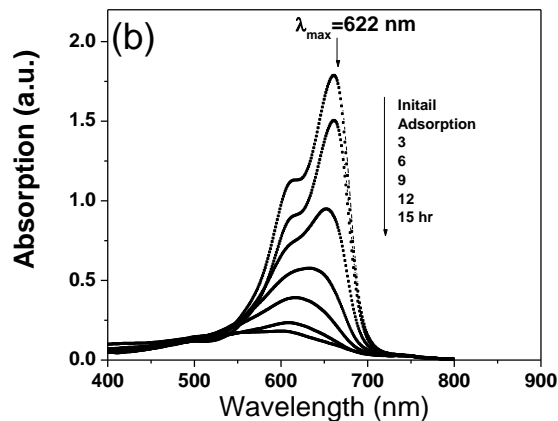
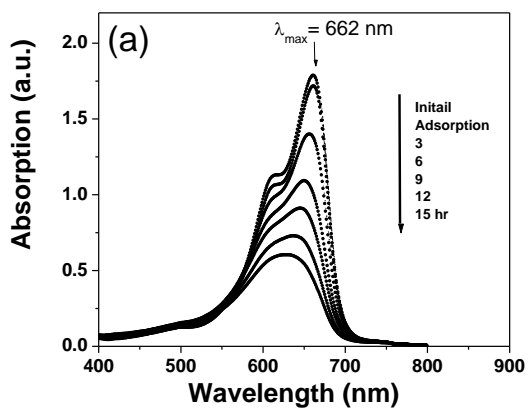
Photocatalytic degradation of MB on SnO nanoplates in presence of visible light (tungsten light 200 W) (a), UVlight (365 nm) (b), and in the dark condition (c)



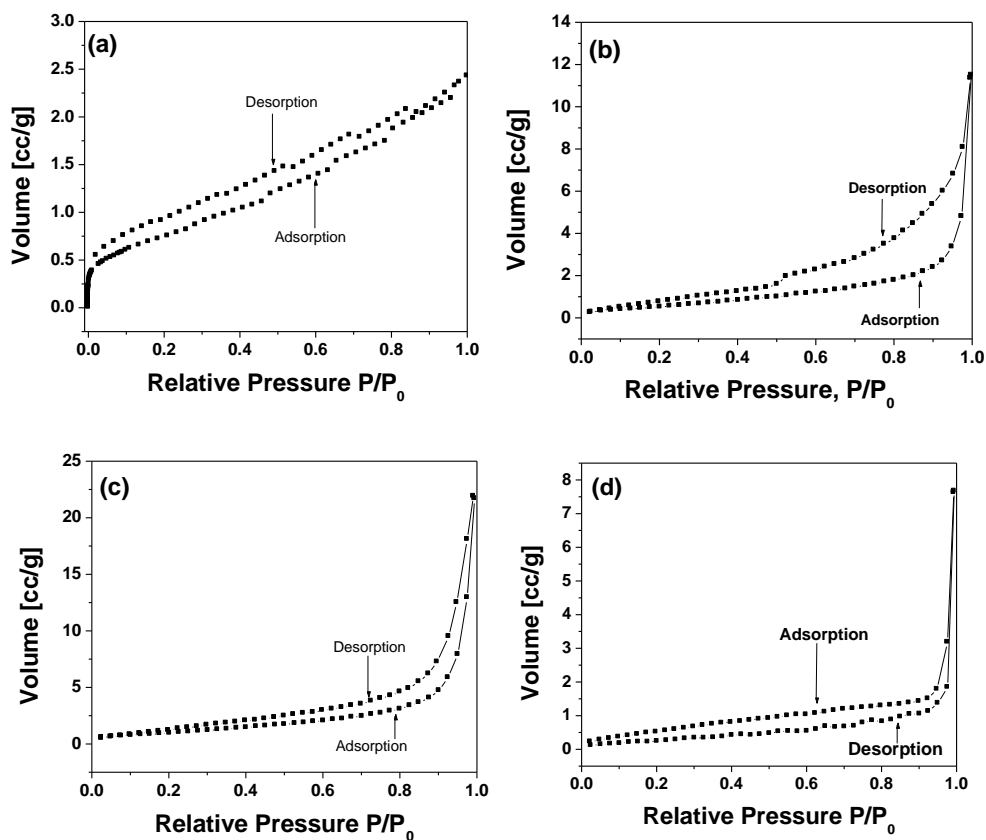
ESI 14. Photocatalytic degradation of MB in presence of tin oxide nanoplates under different visible lights



ESI 15. Photocatalytic degradation of MB (3×10^{-5} M) in presence of annealed tin oxide samples (0.025 g) by UV-light (365 nm): SnO at 200°C (a), SnO at 400°C (b), SnO at 600°C (c) and SnO at 800°C (d).



ESI 16. Nitrogen adsorption–desorption isotherm for the SnO at 200°C (a), SnO at 400°C (b), SnO at 600°C (c) and SnO at 800°C and their comparative BET surface area and pore volume.



The BET surface area of the annealed SnO sample (at 200°C, 400°C, 600°C and 800°C) is changed and the result is tabulated as bellow.

Annealed SnO	BET surface Area
Sample	(m ² /g)
SnO (200°C)	2.85
SnO (400°C)	2.194
SnO (600°C)	3.816
SnO (800°C)	1.133

ESI 17: Determination of VB position of SnO and SnO₂ from the survey scan of SnO and SnO₂ material.

