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Supporting Information: Structural Studies of Spray Pyrolysis Synthesized Oxygen Deficient Anatase TiO_2 Thin Films by using X-ray Absorption Spectroscopy.†

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Crystallite size of the thin films were calculated using Scherrer formula. The co-ordination number for the particular crystallites were calculated using the following equation: [1]

$$n_{nano} = [1 - \frac{3}{4}(\frac{r}{R}) + \frac{1}{16}(\frac{r}{R})^3]n_{bulk} \quad (1)$$

Table S1 represents the calculated co-ordination numbers considering the crystallite sizes of the films studied in the present manuscript. These nanometer sized crystallites ideally should have co-ordination number $\sim$ 5.9. Hence, it can be concluded that the co-ordination number obtained (see Table 1 and 2 of the article) from the EXAFS analysis is due to oxygen deficiency obtained due to vacuum annealing. Presti *et al.* have calculated the cell parameters (a and c) and cell volume by using PAW, LCGTF and different potentials (Table S4 of Presti et al.[2]) The cell volume of ideal TiO_2 cell calculated by different methods were found out to be 144.3, 137.1, 138.2 ,140.8 Å^3 and oxygen deficient TiO_2 cell were found out to be 144.0, 136.0, 138.1, 140.0 Å^3 by Presti *et al.*[2] We have obtained cell volume $\sim$ 136.0 Å^3(see the last column of Table S1), which suggests the occurrence of oxygen vacancies in the cell.

1 Raman Studies of oxygen deficient TiO_2 thin films

The confirmation of anatase phase in pristine and annealed TiO_2 was studied by using Raman spectra. Raman spectra were recorded using 532 nm excitation with 50ÃŮobjective lens (numerical aperture of 0.8), 1800 gr.mm^{-1} grating as monochromator and thermo electric cooled charged coupled device (CCD) as detector in a in-Via, Renishaw Raman Spectrometer.

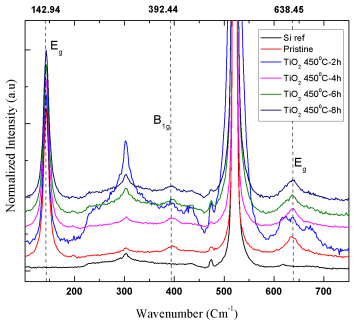

Fig. S1 Raman spectra of pristine and annealed anatase TiO_2 synthesized at 450 °C.

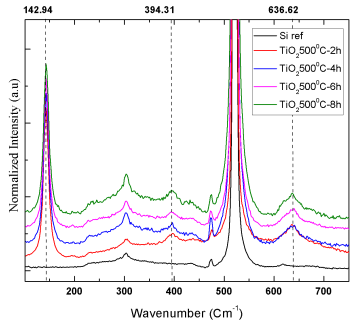

Fig. S2 Raman spectra of pristine and annealed anatase TiO_2 synthesized at 500 °C.

Figure S1 and S2 represents the Raman spectra of pristine and annealed TiO_2 synthesized at 450 °C and 500 °C. The peaks at

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Table S1 Crystallographic parameters and calculated co-ordination number.

Sample id	Crystallite Size (in nm)	Calculated Co-ordination number	Crystallographic cell parameter	Volume(Å^3)
$TiO_2$450 °C-2h	29	5.94	a=3.7842(2)	
			c=9.4907(9)	135.9093(6)
$TiO_2$450 °C-4h	57	5.96	a=3.7801(0)	
			c=9.5263(1)	136.1231(1)
$TiO_2$450 °C-6h	42	5.95	a=3.7827(4)	
			c=9.4795(9)	135.6452(9)
$TiO_2$450 °C-8h	30	5.94	a=3.7794(2)	
			c=9.4651(8)	135.0648(6)
$TiO_2$500 °C-2h	55	5.96	a=3.7775(1)	
			c=9.4657(9)	135.0735(7)
$TiO_2$500 °C-4h	26	5.93	a=3.7789(3)	
			c=9.4670(0)	135.1922(7)
$TiO_2$500 °C-6h	91	5.98	a=3.7806(3)	
			c=9.5077(4)	135.8959(6)
$TiO_2$500 °C-8h	62	5.98	a=3.7809(7)	
			c=9.5001(8)	135.8120(7)

144 cm^{-1} (E_g), 394 cm^{-1} (B_1g), 514 cm^{-1} (A_1g) and 638 cm^{-1} (E_g) peaks represent anatase TiO_2 phase. The presence of most prominent peak at 142.94 cm^{-1} and less intense peak at 392.44 and 638.45cm^{-1} confirms the anatase phase in TiO_2 nanostructures for both the cases. Since, Si used as substrate, the 514 cm^{-1} (A_1g) is merged with Si peak.

2 Delineating the presence of carbon dopant

A representative XAS spectrum from the data studied in this manuscript was considered to delineate the presence of carbon dopant. Ti-C path from a cubic space group fm-3m was considered for generation of Ti-C scattering path and it is at 2.16 Å. The position of this Ti-C path is shown in figure S3 along with the two Ti-O paths of anatase TiO_2 structure. Since the position of Ti-C path is at the first coordination shell, the fitting is done along with Ti-O paths. If TiC phase is present in the sample, weighted average of both Ti-O paths and Ti-C paths should fit the first co-ordination peak. We have taken the contribution of Ti-O paths as x and Ti-C path as 1-x. The initial value of x is taken as 0.5 with assumption of 50% contribution from each structure. The fitting results shows that the obtained x value is 0.9996, which clearly shows zero contribution of Ti-C path in the first coordination shell. The fitting contribution of Ti-C path and Ti-O paths in the first coordination shell is given in figure S4 of the supplementary information. In addition, X-ray absorption spectroscopy is inherently enabled to delineate between substitutional and interstitial position of the dopant, since it allows the iteration of the bond length during the fitting process . Moreover, TiC crystallises only in cubic phase and the peak of TiC path generated from the available crystal structure is at the first co-ordination sphere. Hence, it can be concluded that there is no carbon dopant in the TiO_2 films.

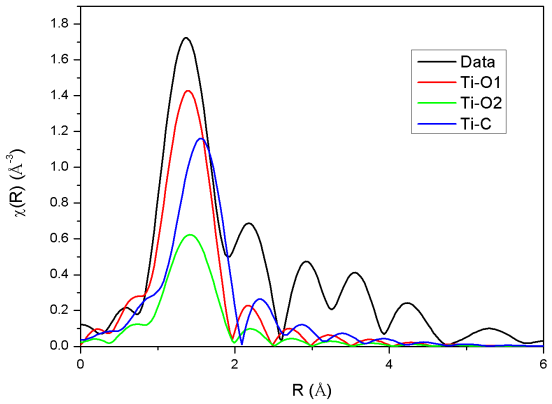

Fig. S3 Ti-O and Ti-C paths along with the spectra of oxygen deficient TiO_2 thin film in R-space .

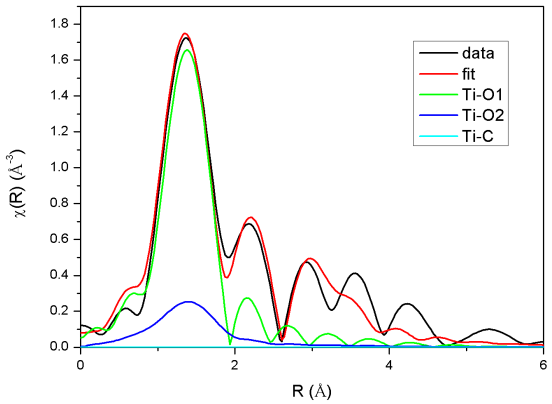

Fig. S4 Extended region fitting of Ti-O and Ti-C paths with the spectra of oxygen deficient TiO_2 thin film in R-space .

3 XAS Full Spectra and Imaginary $\chi(R)$ vs R plots.

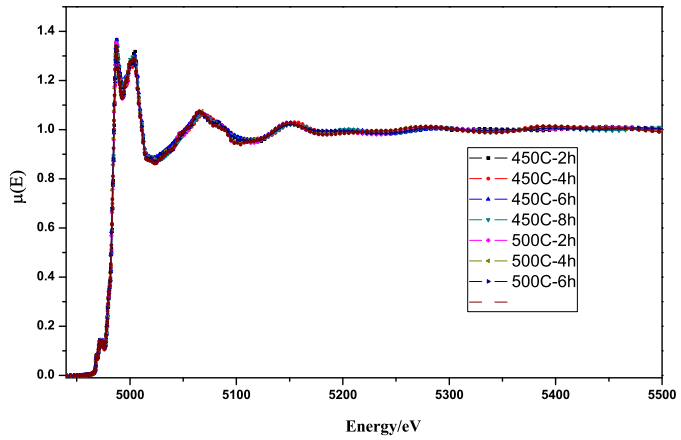

Fig. S5 X-ray absorption experimental curves for the oxygen deficient TiO_2 anatase films.

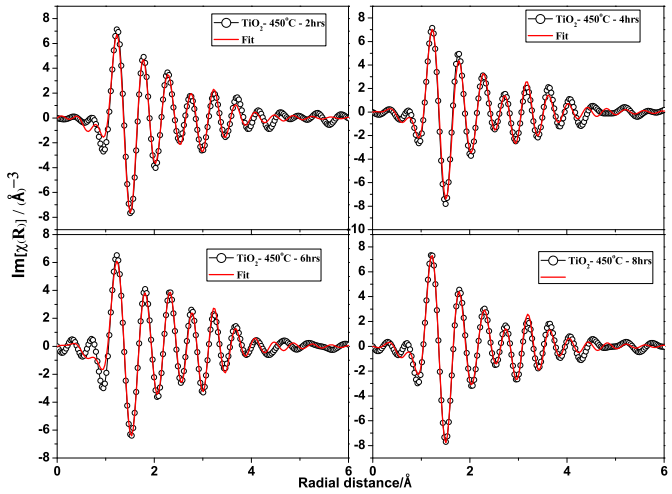

Fig. S6 Imaginary $\chi(R)$ vs R plots for the films synthesized and annealed at 450°C.

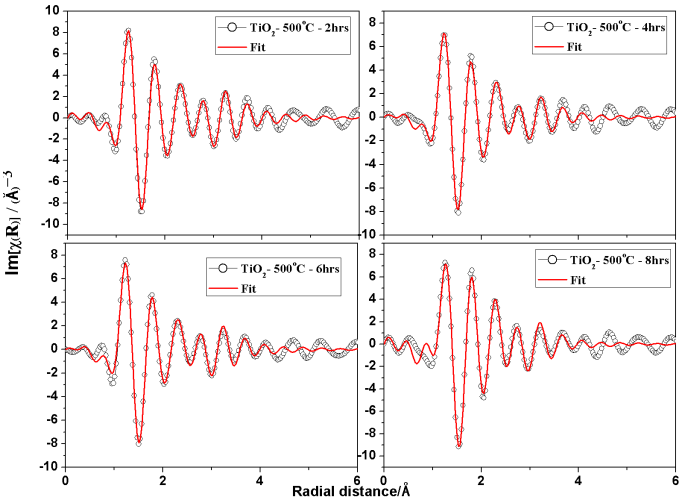

Fig. S7 Imaginary $\chi(R)$ vs R plots for the films synthesized and annealed at 500°C.

3.1 Correlation of peak height and peak position.

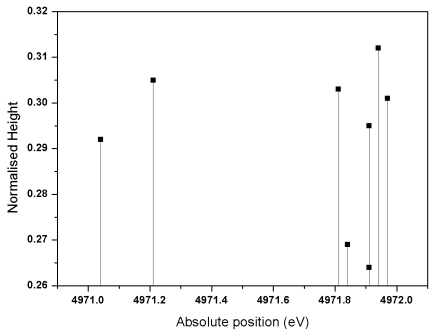

Fig. S8 Plot of normalized height vs energy of the Ti pre-edge feature(A_2 peak)

A comparison of the above figure with the Figure 6 of ref[3] reveals that the samples considered in the present study contains both 5 and 6 co-ordinated Ti species.

Notes and references

1 A. I. Frenkel, A. Yevick, C. Cooper and R. Vasic, *Annual Review of Analytical Chemistry*, 2011, **4**, 23–39.

2 L. Lo Presti, M. Ceotto, F. Spadavecchia, G. Cappelletti, D. Meroni, R. G. Acres and S. Ardizzone, *The Journal of Physical Chemistry C*, 2014, **118**, 4797–4807.

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