Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

For

Studies on interstitial carbon doping from Ti precursor in hierarchical TiO_2 nanostructured photoanode by single step hydrothermal route

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1. Growth mechanism

As discussed in our previous reports [1–3] the preparative parameters like time, pH and reaction temperature decides the appearance of the TiO_2 nanostructures. More specifically time determines the growth of the structures while pH and temperature determines the diameter and length of the TiO_2 nanorods. In present study we have varied the Ti precursor concentration. From study it is observed that the precursor concentration does not affect directly or indirectly on the appearance of the TiO_2 nanostructures. In typical synthesis the FTO molecules from substrate serve as an initial nucleation sites for rutile TiO_2 nanorods which gives rise to initial base layer of compactly and well aligned TiO_2 nanorods. The further increase of concentration of Ti precursor causes increment in the thickness of thin film i.e. it enhances the length of the TiO_2 nanorods in the based layer. The outgrowth of TiO_2 nanorods from the exposed tip of the base layer nanorods gives rise to symmetrical microflower like structure. The growth of microflower like structure increase with increment in precursor concentration from 0.3ml to 0.7ml amount of Titanium (IV) Isopropoxide (TTIP) in solution containing 10 ml HCl and 10 ml double distilled water. After 0.7ml of TTIP further increment in the concentration level leads in to too bulky layer of TiO_2 microflowers which are unable to sustain on the surface of the film and gets peeled out. So the 0.7ml Ti precursor in 20ml hydrothermal solution (10ml HCl and 10ml H_2O) is the maximum concentration of TTIP at which we can deposit thin film of TiO_2.

2. Photoelectrochemical performance

PEC properties mainly linear sweep voltammetry was measured using potentiostat with three electrode configuration, where Ag/AgCl/NaCl is used as the reference electrode. Pt wire and deposited TiO_2 thin films are used as a counter electrode and working electrode respectively, while 1 N NaOH was used as an electrolyte. The Xenon lamp with simulated intensity of 100mW/cm^2 was used for the illumination. Potential values were transformed from Ag/AgCl to the reversible hydrogen electrode (RHE) scale using following formula,

$V_{RHE} = V_{Ag/AgCl/NaCl} + 0.201 + 0.059\ pH$

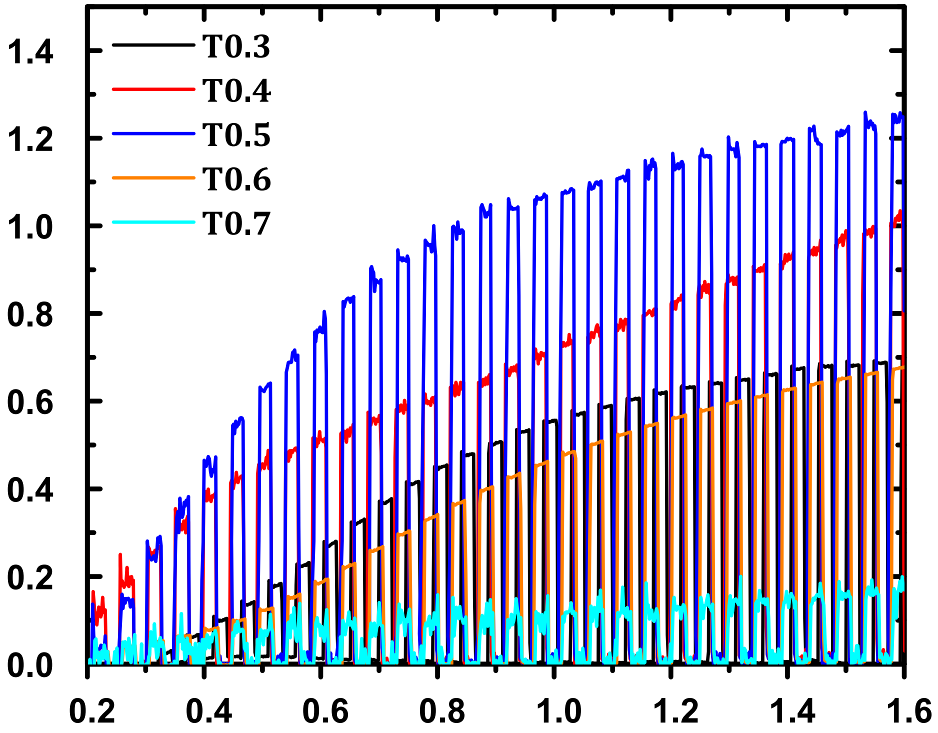

Fig. S1 Linear Sweep Voltammetry plots of TiO2 samples deposited with varying TiO_2 samples deposited with varying Ti precursor concentration (T0.3 to T0.7 samples) on FTO under illumination (100 mW/cm^2).

Figure S1 shows LSV plots of samples T0.3, T0.4, T0.5, T0.6 and T0.7. The magnitude of the J_{sc} was 0.630, 0.834, 1.150, 0.564 and 0.128 mA/cm^2 at 1.23 V (vs RHE) for the samples T0.3, T0.4, T0.5, T0.6 and T0.7 respectively. For sample T0.5 maximum photocurrent of 1.150 mA/cm^2, at 1.23 V (vs RHE) applied potential was observed. Now let's consider the most dominated factors related to the photoelectrochemical applications; the first one is effective light harvesting and second one is effective charge transport; both these play very important role in determining the overall photoelectrochemical performance of any photoelectrode. In particular case of thin film based photoelectrodes, effective light harvesting depends on the absorption coefficient of the material and secondly on thickness of the thin film. The absorption coefficient is intrinsic property of the material which does not change until and unless we do some chemical modifications in the pure material. So in case of thin films of same material the phenomena of light harvesting is highly depend on the thickness of the thin film. The second thing i.e. effective charge transport is depending upon the extent of uniform pathways (nonuniformities are: defects, grain boundaries and interfaces) provided by material to the charge carriers i.e. electrons and holes. So, generally TiO_2 thin films having more thickness harvest more light and consequently generate more electron hole pairs under light illumination.TiO_2 with well aligned and compactly arranged structures results in a better charge transport as compared to loosely bound structures. In present case, the observation of SEM images reveals that sample T0.3 and T0.4 are seems to be most compactly arranged as compared to other samples. But first two samples lacks the microflower like structures which are present in the remaining samples, this microflower like structures actually enhance the active surface area of the photoelectrode during the electrochemical reactions. The T0.5, T0.6 and T0.7 samples have almost same type of symmetrically developed compact microflowers. Now if we compare thickness of all the samples, we could easily find that the thickness goes on increasing with respect to increasing precursor concentration. So light harvesting also goes on increasing from sample T0.3 to T0.7. The second factor which also contributes positively in the increased absorption of T0.3 to T0.7 samples is the fact that as we move from T0.3 to T0.7 sample the red shift in the band gap energy is also increased accordingly which is due to the carbon doping as mentioned in the main manuscript. So, The PEC performance of TiO_2 thin film goes on increasing from T0.3 to T0.5 but it eventually decreases for further samples. The T0.5 sample has better PEC performance than T0.3 and T0.4 samples since it posses microflower like structures on the surface of the thin film which are not present in T0.3 and T0.4. But still the PEC performance of the T0.6 and T0.7 samples are low instead of the fact that these two samples also have the same microflower like structures on the their surface and their band gaps are also low due to probable carbon doping. This may be due to the extra high thickness of the films, which inhibits the effective charge transport through the material. The extra thickness cause the increased distance to be travel by photogenerated electron to escape to the external circuit and this extra distance enhances the probability of recombination of electrons with the holes present in the material. As observed in the **Figure S1** the decrement in the PEC performance is mainly due to the decrement in the photogenerated current and this decrement can clearly be justified on the basis of increased recombination.

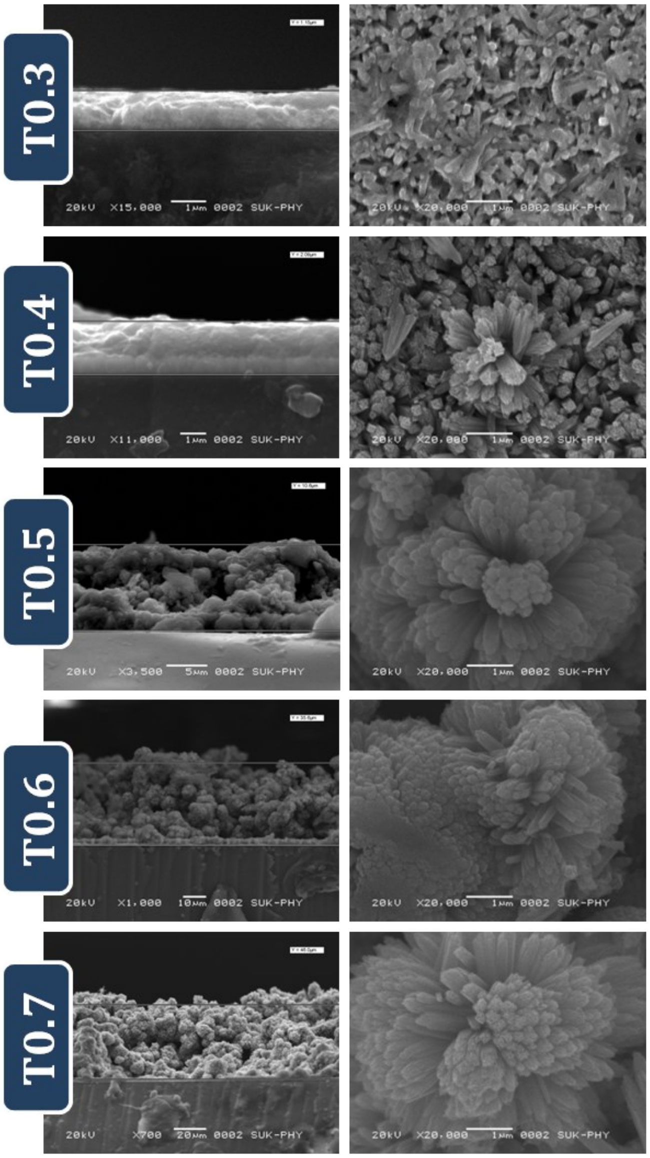

Fig. S2. Cross section Scanning Electron Microscope images of all TiO_2 samples.

References:

1 V. V. Burungale, V. V. Satale, A. M. Teli, A. S. Kamble, J. H. Kim and P. S. Patil, *J. Alloys Compd.*, 2016, **656**, 491–499.

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