Electronic Supplementary Information
(ESI)

Shape Preserving Chemical Transformation of ZnO Mesostructures into Anatase TiO_2 Mesostructures for Optoelectronic Applications

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ESI: S-0

Experimental Details:

Materials: The chemical agents were purchased from Aldrich Co. and Merck Chemicals. The $RuL_2(NCS)_2/(TBA)_2$ (N719; L = 2,2′-bipyridine-4,4′-dicarboxylic acid and TBA = tetrabutylammonium) and the fluorine-doped SnO_2 (FTO) electrode (sheet resistance 15 ohm/square) were purchased from Solaronix Co. For the preparation of reference DSSCs, commercial TiO_2 was obtained from Degussa (P25). High-purity water (Milli-Q, Millipore) was used for all experiments. The FTO electrodes were washed with acetone, ethanol, and deionized (18.2 MΩ·cm) water in an ultrasonication bath for 15 min with a final wash in isopropyl alcohol.

Preparation of ZnO Flowers:

The ZnO flowers used in this study were synthesized by hydrothermal route using high purity zinc acetate and NaOH as discussed elsewhere.[1] For obtaining ZnO flower, a 150 ml, 0.01M aqueous solution of zinc acetate was prepared and magnetically stirred for 10 min. After the dissolution of zinc acetate, 6 ml of 6.67 M aqueous solution of NaOH was added to the above solution. Then this solution was transferred into a Teflon lined stainless steel autoclave. It was then sealed and maintained at 180 °C for 2 h. After the reaction a white colored solid powder was recovered by centrifugation followed by washing with distilled water and ethanol to remove the residual ions in the final product. Then the powder was finally dried at 60 °C in air for 5 h.

Preparation of ZnO rods on FTO and ITO:

Zinc acetate, Zinc nitrate, Hexamethylene tetramine (HMT) and Sodium Hydroxide Pellets were used as precursors for ZnO rod growth as discussed elsewhere.[2] Zinc acetate solution (5 mM concentration) was prepared in methanol and was kept under stirring at 65 ^{0}C for 45 min. Then sodium hydroxide solution (30 mM concentration, prepared in Methanol) was added drop wise till the solution attained slight milky color and was used as seed solution. Fluorine doped tin oxide (FTO) and Indium doped tin oxide (ITO) glass plates (2.5 cm ×2.5 cm) were used as substrates for growth of ZnO rods. The substrates were mounted on the spin coater having a preset rotation speed of 2500 rpm for 30 sec and then spin coating was carried out using freshly prepared seed solution. The process was repeated continuously until the transparent substrate turned slightly opaque. Finally the substrates were annealed at 300^0C for 1 hr for better adherence of ZnO nanoparticles which act as nucleating sites for the growth of ZnO rods.

For facile growth of ZnO rods, equimolar solutions of Zinc Nitrate (25 mM) and hexamethylene tetramine (HMT 25 mM)) were separately prepared using de-ionized water as solvent. The seeded substrates were immersed into the solution and the solution temperature was maintained at 95 ^{0}C under slow stirring. The depositions were carried out for time duration of 3 hour. Finally, the deposits were annealed at 300 ^{0}C for 1 hr for removal of moisture and for improving the adhesion.

Preparation of ZnO spheres and flakes:

The ZnO sphere like morphology was synthesized at room temperature by co-precipitation method using zinc acetate, polyvinyl pyrrolidone and sodium hydroxide. 0.02M aqueous solution of zinc acetate was prepared and magnetically stirred for 5minutes. 0.5gm of polyvinyl pyrrolidone (capping agents) was dissolved in 10ml of de-ionized water and added to the zinc acetate solution. Then 10 ml of 2M aqueous solution of NaOH was added drop wise to the above solution. A white colored solid powder was obtained and recovered by centrifugation followed by washing with de-ionized water. Then, the powder was finally dried at 60 °C in air for 10 h. The ZnO flakes were obtained from a commercial source (Smart NanoZ, Pune, India).

Preparation of TiO_2 Nanoparticles:

Nanocrystalline TiO_2 was prepared by using a simple hydrothermal method. 2 ml of Titanium Isopropoxide was hydrolyzed by adding 100 ml of deionized water and then sonicated for 5 minutes. The solution was transferred to Teflon lined autoclave vessel along with 3ml of H_2SO_4 (1M). This autoclave vessel was kept at 175 °C for 24 Hrs. The resulting product was washed thoroughly with deionized water and dried at 50°C in a dust proof environment to produce the powder of TiO_2 nanoparticles.

Fabrication of dye sensitized solar cell:

Doctor blading method was employed to first make the TiO_2 nanoparticle film (thickness ~7 µm) and then an over layer of ZnO flowers film (thickness ~8 µm). The total thickness of the film was ~15 µm. After making such films they were annealed at 450 °C for 60 min. Then these films were treated with $TiCl_4$ solution (50mM) at 70 °C followed by second annealing at 450 °C for 30 min. After $TiCl_4$ treatment, the total thickness of the film was found to be reduced from ~15 µm to ~11 µm. Same thickness (~11 µm) of $TiCl_4$ treated TiO_2 nanoparticle and P25 (Degussa) films were made for comparision. The films were impregnated with 0.5 mM N719 dye in ethanol for 24 h at room temperature. The samples were then rinsed with ethanol to remove excess dye on the surface and were air-dried at room temperature. This was followed by redox electrolyte addition and top contact of Pt coated FTO as discussed elsewhere.[3] The electrolyte used was 1 M 1-hexyl-2, 3-dimethyl-imidazolium iodide, 0.05 M LiI, 0.05 M I_2, and 0.5 M 4-tert-butylpyridine in acetonitrile. The J-V characteristics were measured by exposure to 100 mW/cm^2 (450W xenon lamp, Newport Instruments), 1 sun AM 1.5, simulated sunlight by a solar simulator. The current was measured using a Kiethley 2420 source meter.

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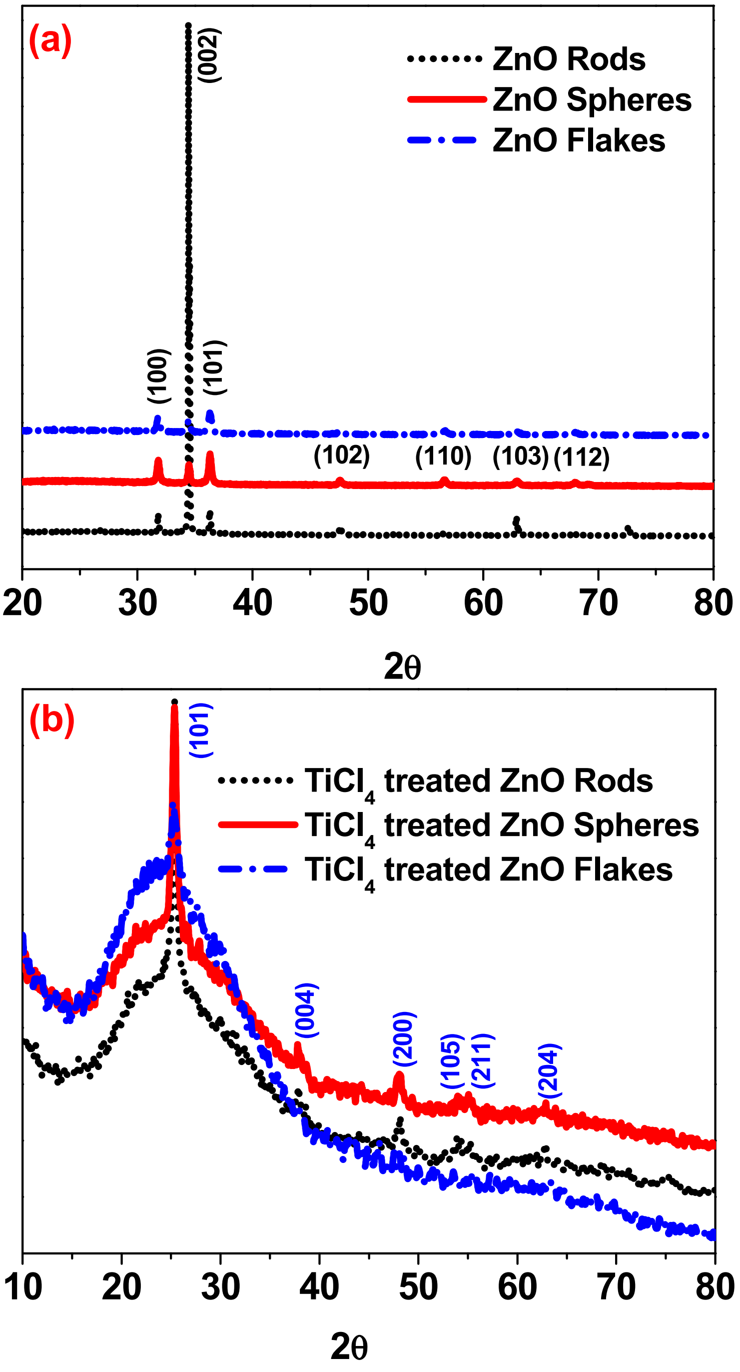

Figure-S-1 XRD data of (a) ZnO (Rods, Spheres, Flakes), (b) $TiCl_4$ treated ZnO (Rods, Spheres, Flakes)

ESI: S-2

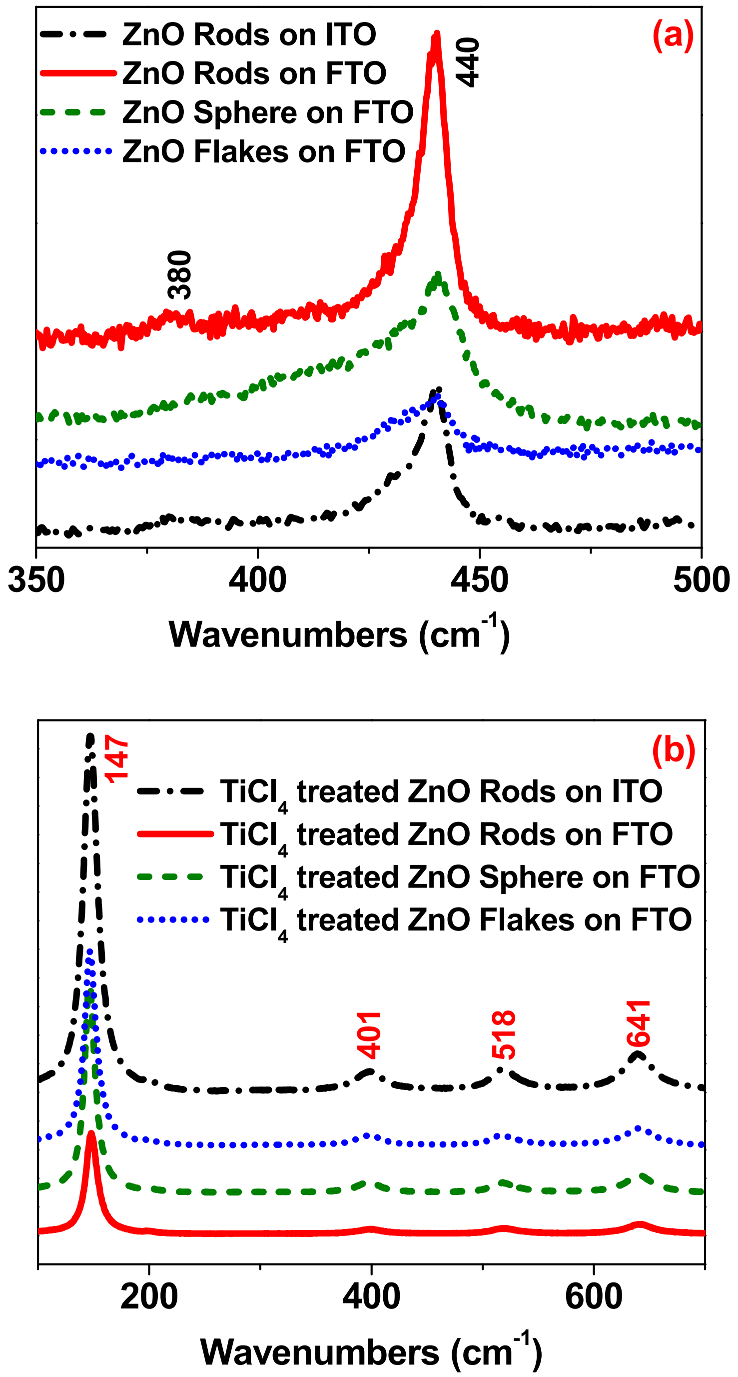

Figure-S-2 Raman Spectra of (a) ZnO (Rods, Spheres and Flakes) and (b) $TiCl_4$ treated ZnO (Rods, Spheres and Flakes)

ESI: S-3

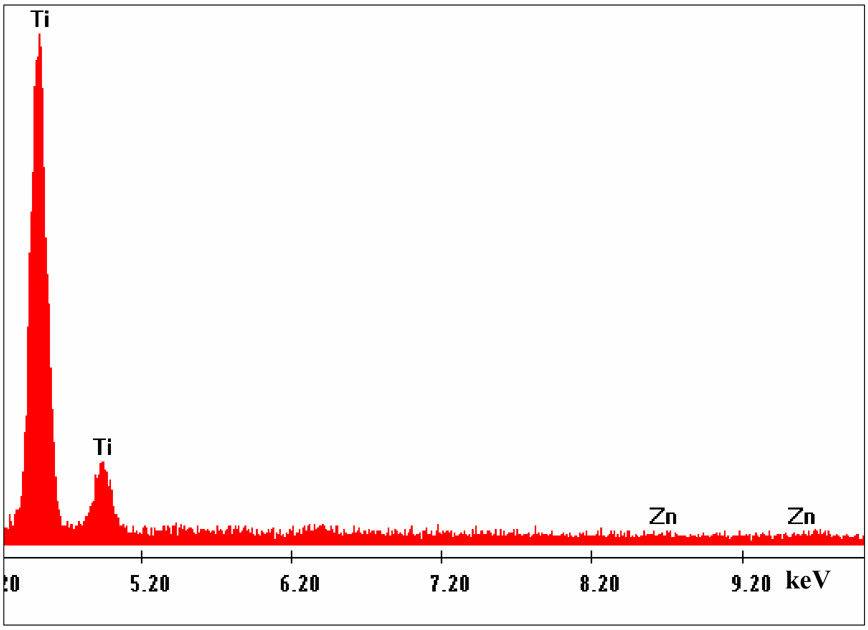

Figure S-3 the energy dispersive x-ray (EDX) data of $TiCl_4$ treated ZnO.

ESI: S-4

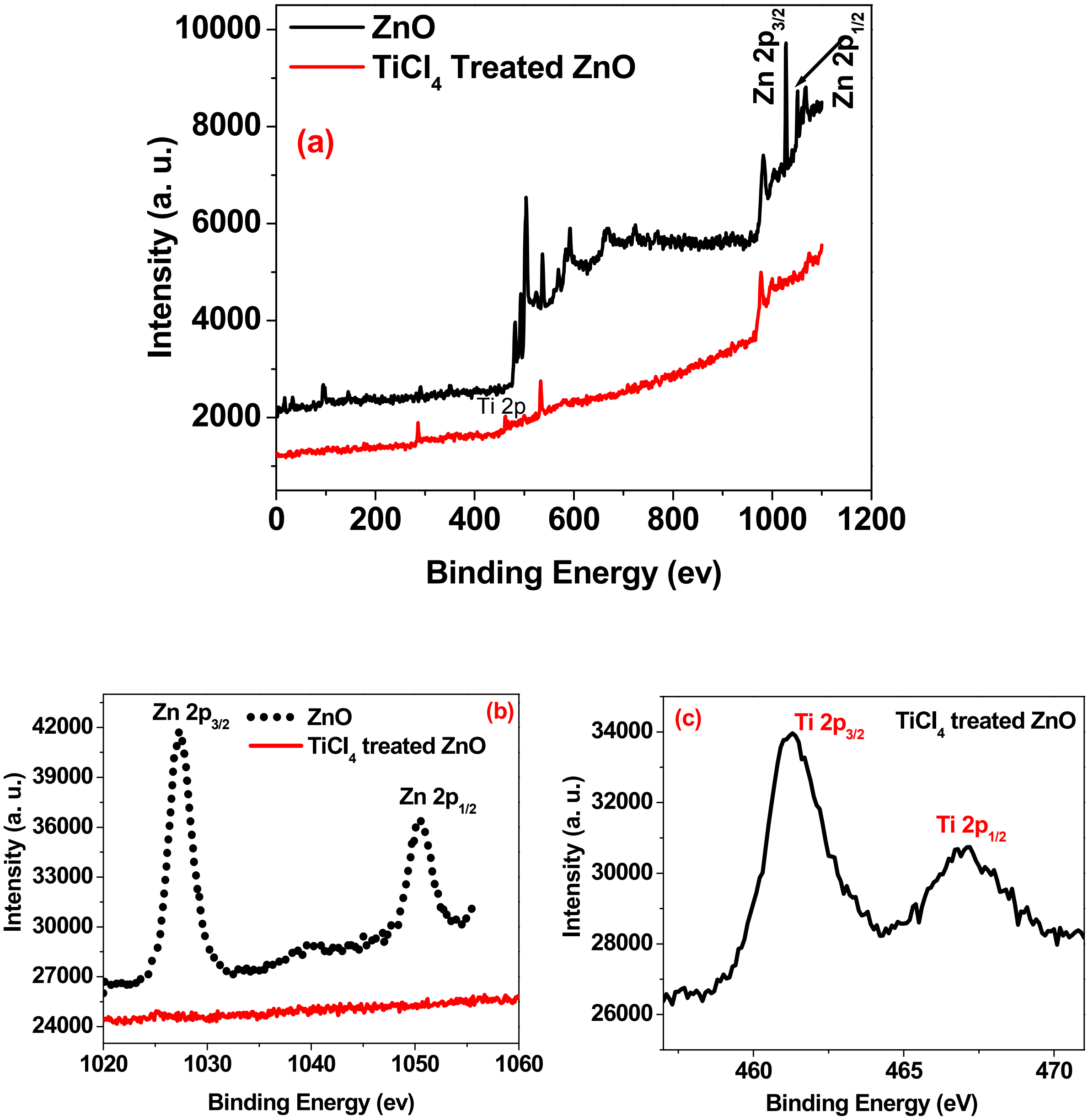

Figure S-4 XPS data of (a) ZnO and $TiCl_4$ treated ZnO, (b) Presence and absence of Zn in ZnO and $TiCl_4$ treated ZnO respectively[4], and (c) Presence of Ti in $TiCl_4$ treated ZnO[5].

ESI: S-5

Figure S-5 (a) and (c) show the SEM images of ZnO rods on ITO substrate which are properly aligned. It is observed that by changing the substrates from FTO to ITO during the synthesis process, the growth and alignment of ZnO rods are different. The $TiCl_4$ treatment of ZnO rods on ITO substrate is shown in figure S-5(b) and (d) which are similar when the same are on FTO substrate. After $TiCl_4$ treatment, all the ZnO rods on ITO are seen to have been converted to TiO_2 hollow rods keeping the alignment conserved. The process of conversion of ZnO rods to TiO_2 rods on ITO keeping the alignment conserved basically follow the same ion exchange mechanism which is discussed in the manuscript.

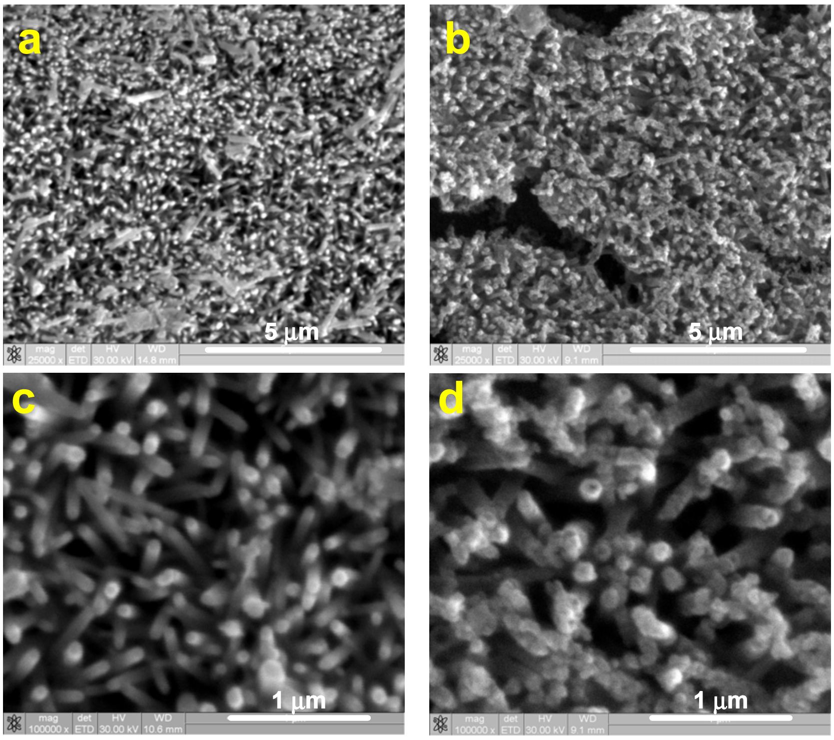

Figure S-5 SEM Data of ZnO rods (a) & (c) and $TiCl_4$ treated ZnO Rods (b) & (d) on ITO.

ESI: S-6

The SEM images of the hierarchically structured ZnO synthesized at room temperature by using poly vinyl pyrrolidone as capping agent are shown in figure S-6(a) and (c). The inset of figure S-6(c) is the magnified SEM image of the ZnO mesostructure. These hierarchically structured ZnO were converted to anatase TiO_2 with diameter ranging from 1 µm to 2 µm by $TiCl_4$ treatment keeping the morphology broadly conserved, as shown in figure S-6(b) and (d). The zoomed version of one of the TiO_2 mesostructure is shown in the inset of figure S-6(d).

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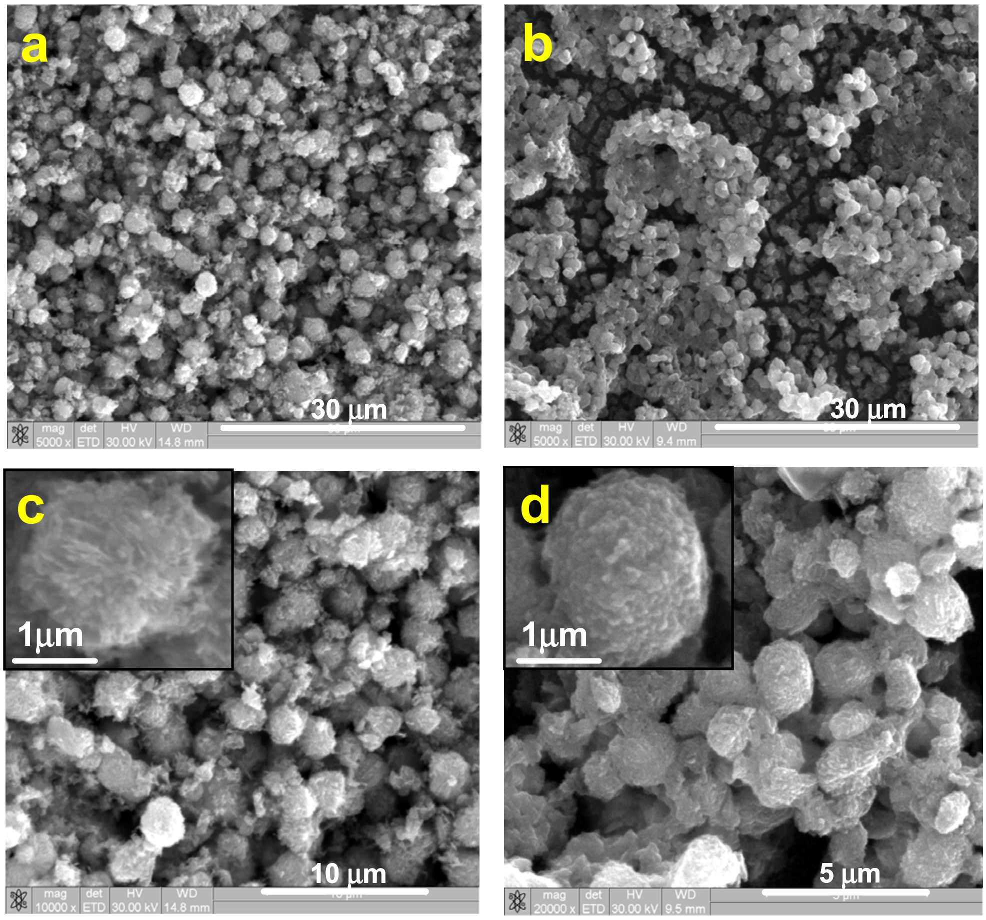

Figure S-6 SEM Data of ZnO capped with PVP (a) & (c) and $TiCl_4$ treated ZnO capped with PVP (b) & (d) on FTO

ESI: S-7

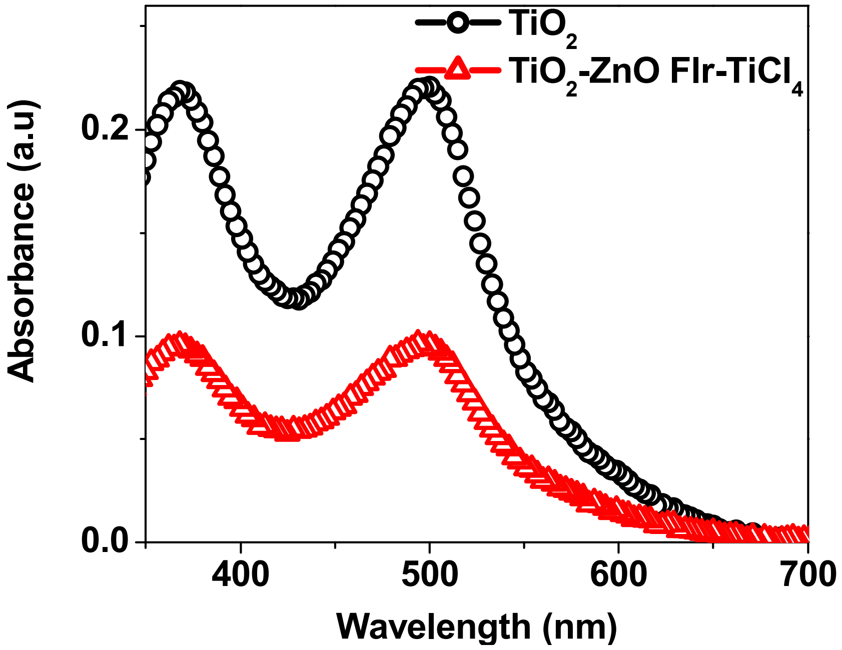

Figure S-7 Optical Absorption of solutions containing dye detached from doctor bladed films of different cases of interest (film area of 1.6 cm^2 dye extracted in 10 mL of 1 mM KOH).

ESI: S-8

The **Diffused Reflectance Spectra** of TiO_2 films (with and without dye) on FTO were recorded with illumination from the TiO_2 side. Higher reflectance for $TiCl_4$ treated ZnO (TZFT film) (Fig. S-8 (a)) shows higher capability of these mesostrucures to back reflect light which is then responsible for better light harvesting. Reflectance of dye loaded TiO_2 films is also recorded with TiO_2 side facing illumination. In this case dye-loaded TZFT film shows higher reflectance than the dye-loaded TiO_2 film which shows its less dye adsorption and higher reflecting abilities resulting in better light harvesting in actual solar cell architecture.

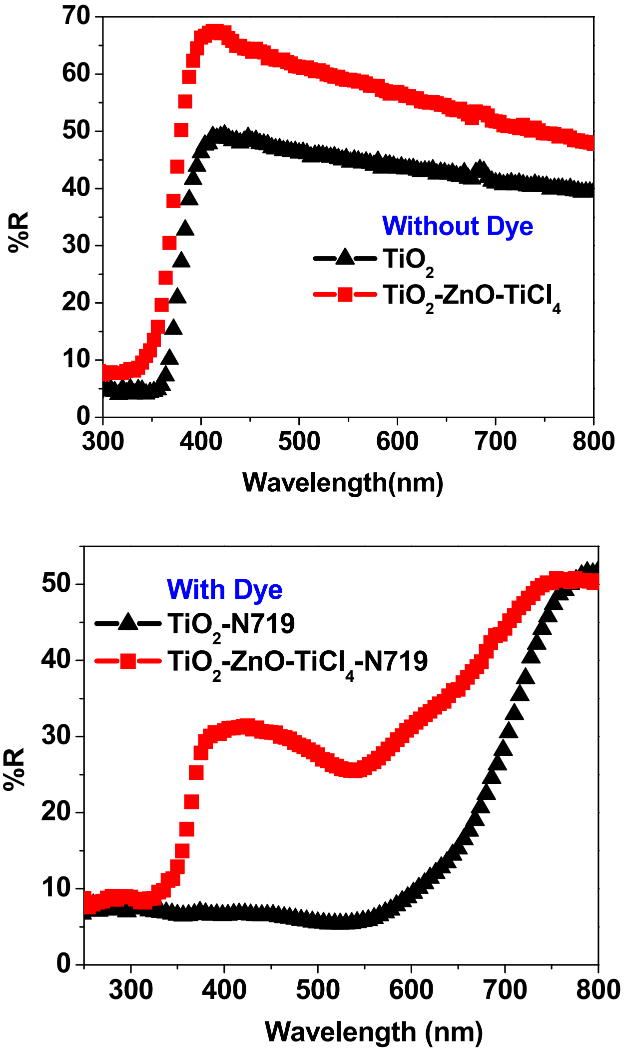

Figure S-8 Diffused reflectance spectra of the nanocrystalline TiO_2 and TZFT films (a) without and (b) with adsorbed N-719 dye.

ESI: S-9

Table-1

The BET Surface area measurements of ZnO Flr and $TiCl_4$ Treated ZnO Flr.

Name	Surface Area(m^2/g)
ZnO Flr	5.9
$TiCl_4$ treated ZnO Flr	30.5

Table-2

Photovoltaic properties of dye-sensitized solar cells.

Name	Voc(V)	Jsc (mA/cm^2)	Fill factor(FF)	Efficiency (η) %
Degussa P25	0.67	12.9	60.5	5.2
TiO_2	0.66	14.0	58.1	5.4
1st layer TiO_2 + 2nd layer $TiCl_4$ treated ZnO Flr	0.78	14.0	62.8	6.9

The thickness of all films of DSSC were ~11 µm

References:

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