

Effect of Structure Texture and Morphology Modulation on Efficiency of Dye sensitized Solar Cells

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Wide band gap semiconductors like TiO₂, ZnO are used as working electrode for dye-sensitized solar cell (DSSC), in present study highly ordered nanoporous TiO₂ materials with crystalline frameworks was successfully synthesized from different concentration of triblock co-polymer (soft templates) like F-127 F-68. Synthesized mesoporous TiO₂ have variation of pore size ranging from 2-5 nm and having high specific surface area from 216 m²/g -352 m²/g. A photoelectrode fabricated using synthesized mesoporous TiO₂ shows increase in photocurrent density (J_{sc}) with increase in pore size as well as surface area and change in Voc with variation in structure texture and morphology of photoelectrode. The DSSC was fabricated using N3 dye as sensitizer and solid polymer electrolyte with KI/I₂ as redox electrolyte. Synthesized samples were characterized by XRD, TEM, and Brunauer- Emmett-Teller (BET). Photovoltaic performance of DSSC overall conversion efficiency (%), fill factor (FF), open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}) from the J-V curves measured with 2400 Keithley Source meter, it was observed that the photoelectric performance is strongly dependent on combined effect of Voc and Jsc which shows the characteristic change with structure texture morphology as well as pore size and specific surface area of fabricated electrode.

Keywords: Nanoporous TiO₂, Dye sensitized solar cell, J-V measurement, Open circuit voltage.

1. INTRODUCTION

Titanium is most abundant transition metal on earth crust, its metal oxide TiO₂ being wide band gap semiconductor is the most promising candidate for lot many applications. As it is wide band gap semiconductor its electronic properties play an important role in various applications such as electronic device fabrication [1] Photo catalysis [2] photovoltaics [3], energy storage, and gas sensing [4] Dye

Sensitized Solar Cell[5-6] Recently a vast amount of research is carried out on TiO_2 as a material for lithium ion battery anodes[7] Though there are some limitations inherent to TiO_2 , researchers have begun to utilize TiO_2 effectively in batteries. As some of the merits of using TiO_2 are clear, e.g. its cost, low toxicity, and density, In many cases, these benefits can only be realized when modifications are made to the various polymorphs of TiO_2 .

TiO_2 based dye-sensitized solar cells (DSSCs) offer one of the most promising alternatives to sustainable, clean, and renewable energy for transferring inexhaustible sunlight into electricity, as they possess advantages such as low cost and environmental friendliness, and they can, in principle, be produced on a large scale.[8] However, electron transport in disordered TiO_2 nanoparticles with a random transit path enhances the possibility of charge recombination and thus reduces the photocurrent and the performance of the device.[9] Thus, designing a photo anode with a fast transport pathway from the photo injected carriers to the electrically conductive electrode would remarkably improve the performance of DSSCs.[10] To enhance electron transport and reduce recombination, several kinds of photoanode materials have been employed in the past decade, including doped TiO_2 ,[11] metal/metal oxide- TiO_2 hybrid, composite and core-shell structures,[12] porous TiO_2 structures,[13] and TiO_2 -carbonmaterials.[14]. Since the discovery of DSSC major group of scientific community working on DSSC are using TiO_2 as working electrode of DSSC. These days to increase efficiency of DSSC number of researchers are working on modification of all the components of DSSCs. Recently lot of efforts are also found on modification of working electrode of DSSC to improve short circuit current density (J_{sc}) as well as open circuit voltage (V_{oc}) Recently, much attention has been devoted to prepare TiO_2 @ reduced graphene oxide for photoanode materials in DSSCs Various TiO_2 @reduced graphene oxide composites with tunable TiO_2 nanostructures (e.g., nanoparticles, nanorods, nanofibers, and nanospheres)[15] doping of carbon, doping of large size crystals of rutile TiO_2 with anatase TiO_2 . Scientist have concentrated to modify structure texture and morphology of these materials by synthesizing nanomaterials with nanoparticles,[16] nanowires (or nanorods),[17] nanotubes,[18] nanobelts,[19] nanosheets,[20] and nanotips.[21] structure by keeping in mind that for the efficient device applications nanomaterials having large specific surface area is the prime need of present scenario, In recent days it is found that nanomaterials with porous morphology is an additional important feature for device application. Very recently nanostructures with highly ordered porous network and having large specific surface area with optimum pore size have been developed like TiO_2 [22-23] ZnO [24-25] SiO_2 [26] SnO_2 [27] most crystalline TiO_2 is most widely used photoelectrode for fabrication of DSSC

As in our recent article[23] we have synthesized highly ordered mesoporous TiO_2 with long range ordering. During the whole study we have observed that concentration of template plays an important role in maintaining long range ordering in and keeping pores in order in porous material we have focused on optimization of template concentration to produce highly ordered porous structure. Also calcinations temperature plays an important role in maintaining ordered porous network by removing carbon residue through thermal decomposition of template. Hence we also introduced shortly the thermal stability of pore wall and effect of calcination temperature on average pore size, specific surface area and orderness of mesoporous structure. Also we have focused on optimization of calcinations temperature to increase the surface area and pore size of mesoporous TiO_2 .

In continuation with this work, In the present article working electrodes of DSSC were fabricated using such modified mesoporous TiO_2 through template concentration variation and also calcinations temperature variation. The effect of such modifications were studied on Voc, Jsc and efficiencies of DSSC it is found that specific surface area and average pore size plays very important role in deciding the increase or decrease in DSSC parameter. Similar results also found in literature on hexagonal rod like structure of TiO_2 synthesized by using other mesoporous materials like mesoporous silica or zeolite as structure directing agent[28]. But no report found on mesoporous TiO_2 Also surface area we reported is very high ranging from $216\text{m}^2/\text{g}$ - $352\text{m}^2/\text{g}$ but other reports show upto $258\text{m}^2/\text{g}$ [28] this is further elaborated in later discussion.

2. EXPERIMENTAL SECTION

2.1 Materials

Titanium tetrabutoxide ($(\text{Ti}(\text{OC}_4\text{H}_9)_4)$, 97.0%, Aldrich), Pluronic F-68 and Pluronic F-127 (extra pure, Sigma Aldrich), ethyl alcohol, ($(\text{C}_2\text{H}_5\text{OH})$, 94.0%, Samchun Chemicals) and HCl (35.0-37.0%, Samchun Chemicals) were used as received without further purification.

2.2 Synthesis

The synthesis of mesoporous TiO_2 were carried through triblock copolymer-templated sol-gel method via an evaporation-induced self-assembly (EISA) process. For preparing Ti-sol, 2.7 ml (0.38M) of titanium tetrabutoxide was dissolved and stabilized in 2.9 ml of 35% HCl solution, under vigorous magnetic stirring for 3 h. Ethanol solutions either of Pluronic F-68 or of Pluronic F-127 were prepared by adding different amounts of either of the copolymers in 15.2 ml of ethanol (94%) under vigorous magnetic stirring for 3 h. The amounts of the Pluronics were varied to vary their concentrations in the final mixture solution as 0.001 M, 0.0025 M, 0.005 M, and 0.01 M. The previously prepared yellowish Ti-sol was then added to the Pluronic solutions dropwise under magnetic stirring. The stirring process was continued for 12 h until the mixture become colorless and transparent. The resulting mixtures aged for humidity at room Temperature for 6-7 days white coloured paste were formed. The resulting mixtures were aged for humidity at room temperature white colored paste were formed which was used to fabricate working electrode of DSSC

2.3 Fabrication of DSSC

The resulting white paste synthesized in by variation of template concentration was then used to fabricate working electrode by doctor blade method on cleaned and blocking layer coated FTO glass and calcinated at $315\text{ }^\circ\text{C}$ for 12 h at heating rate of $1\text{ }^\circ\text{C}/\text{minute}$. Calcinated working electrode then soaked in (0.5 mM in ethanol) dye solution for overnight and washed with ethanol to remove excess of dye adsorbed on surface of electrode. Solid polymer electrolyte was prepared by desolving PEO:PEG

blend in acetonitrile and adding NaI and I₂ with w/w % as 75:25 and 10 w/w % of iodine with NaI dissolved in acetonitrile with 24 h stirring. Also platinum counter electrode was prepared by spin coating of H₂PtCl₆ solution on clean FTO Glass a drop of above prepared electrolyte was sandwiched between fabricated working electrode and counter electrode.

The effect of calcinations temperature was studied by calcining the fabricated working electrodes F-127 (0.001 M) and F-68 (0.005 M) at 260 °C, 280 °C, 300 °C and 315 °C for 12 hrs using the same heating rate.

2.4 Characterizations

Surface area, pore volume, pore size distribution and pore diameter were measured by BET Quantachrome Autosorb AS1win instrument. To analyze pore size sample is outgased at 300 °C for 7 h. The dye sensitized solar cell (DSSC) parameters like open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) and conversion efficiency (η) were measured by Keithley source meter model no. 4200.

3. RESULTS AND DISCUSSION

3.1 Dye Sensitized Solar Cells (Template Concentration Variation)

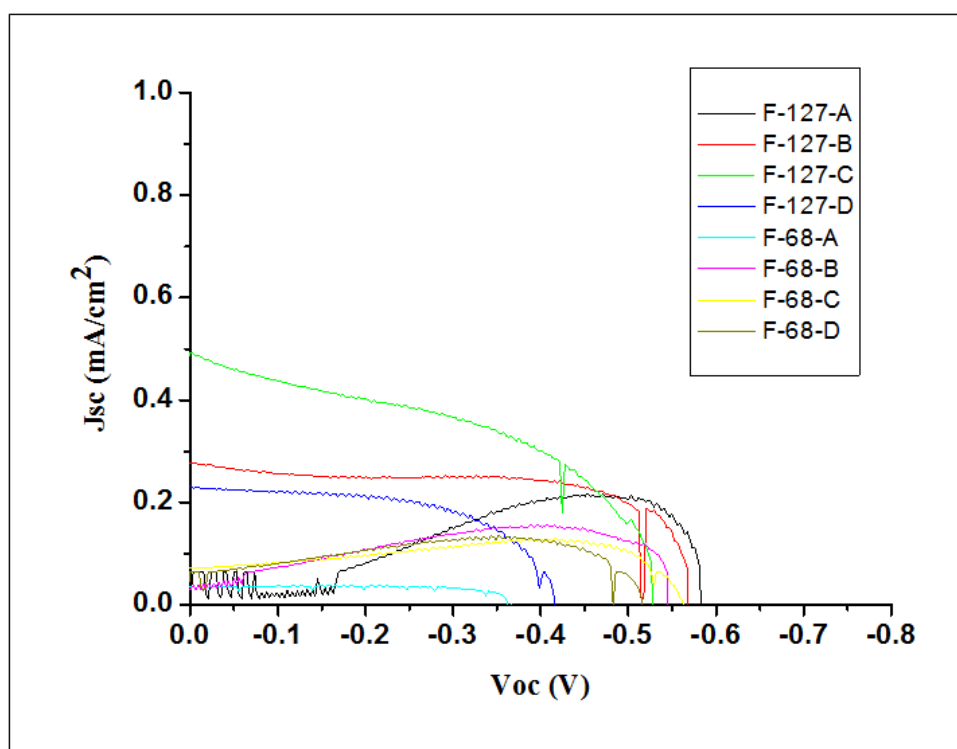


Figure 1. J-V curve for the mesoporous TiO₂ sample synthesized using different concentration wiz. a) 0.001 M, b) 0.0025 M, c) 0.005 M and d) 0.01M for both pluronics and calcinated at 315 °C for 12 h recorded at 1 sun condition using Keithley 2400 sourcemeter.

The synthesized TiO₂ paste from different concentrations of both platonics was used to fabricate working electrode of DSSCs and calcinated at 315 °C for 12 h. The photo current density–voltage (J–V) characteristics of the DSSCs fabricated with the different morphologies of TiO₂ photoanodes are measured by using keithley 2400 sourcemeter and analysed under 1 sun condition which are shown in Figure1. And all the parameters are summarized in following Table1.

Table 1. Comparison of Specific Surface area average pore size also DSSC parameters (Voc Jsc and Effeciencies) with variation of template concentration of both pluronics in TiO₂ samples

Template	Samples	Specific Surface area (m ² /g)	Average Pore size (nm)	Voc (V)	Jsc (mA/cm ²)	Effeciency (%)
F-127	0.001 M	216.2	3.15	0.582	2.183X10 ⁻¹	0.107
	0.0025 M	251	4.5	0.568	2.773X10 ⁻¹	0.104
	0.005 M	287.6	4.78	0.528	4.939X10 ⁻¹	0.122
	0.01M	348.4	4.11	0.417	2.306X10 ⁻¹	0.056
F-68	0.001 M	224.4	2.63	0.593	3.84 X10 ⁻²	0.0637
	0.0025 M	259.5	2.93	0.579	1.566 X10 ⁻¹	0.0665
	0.005 M	315.3	4.12	0.545	3.453 X10 ⁻¹	0.0874
	0.01M	352.5	3.57	0.516	1.350 X10 ⁻¹	0.0519

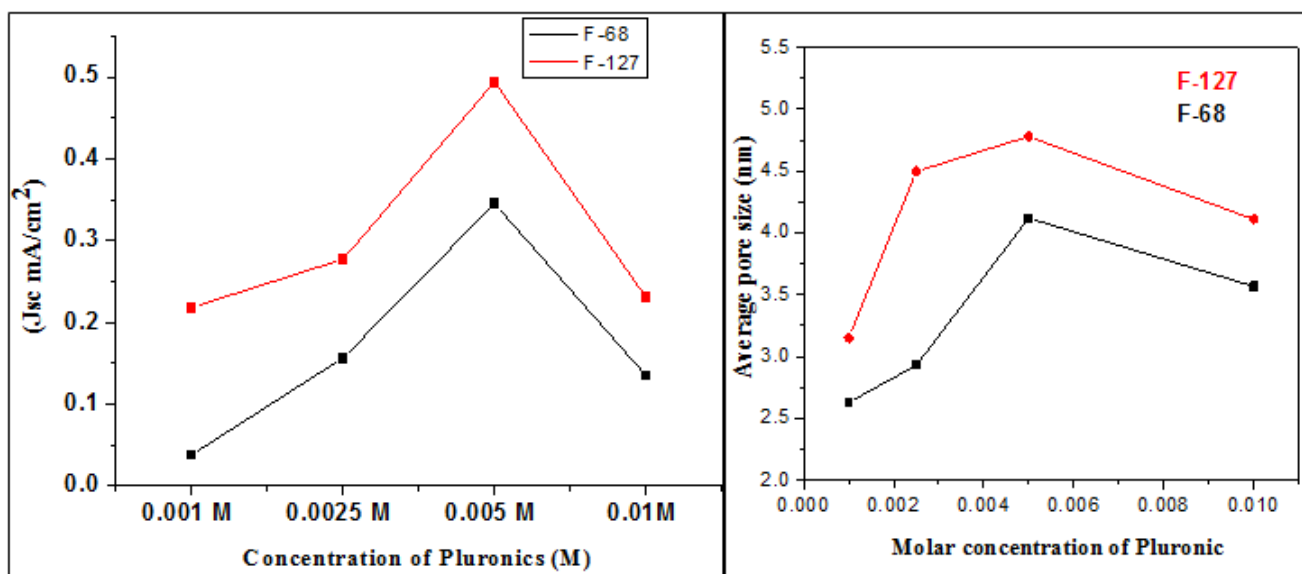


Figure 2 a). Variation of Short circuit current density (Jsc) versus molar concentration of pluronics b) variation of avourage pore size versus molar concentration of pluronics

Jsc obtained from different cells of Mesoporous TiO₂ are plotted against sample synthesized with different concentration of both pluronics as shown in figure.2a, and it is observed that the obtained Jsc values follows the same trends which is followed by pore size (refer pore size plot in figure 2b the explanation for variation of pore size is already discussed in article 23) also it is observed that the sample synthesized using F-68 template have smaller pore size compared with sample synthesized using template F-127 (due to smaller chain length of template) the value of short circuit current also small i.e the cells fabricated using photo-electrode with higher pore size value of Jsc is high and at lower pore size value of Jsc is low as pore size increase the Jsc value also increases and as pore size decrease Jsc also decrease This is due to radius of gyration of Polymers used in electrolyte. As we know it is very important that there should be direct contact or penetration of electrolyte inside pore to increase the exchange of electron and to increase the Jsc. as pore size increase there are lot of chances of polymer chain to penetrate inside the pores of electrode and exchange of electrons with dye molecule adsorbed on surface of electrode as well as the dye molecule inside pore get reduced through polymer electrolyte and hence photocurrent get increased, as pore size decreases it is difficult for polymer chain to penetrate inside pore and make exchange of electrons with dye molecule adsorbed in side pores resulting photocurrent may decreased. Similar reports on hexagonal rod likeTiO₂ structure formation is there but author have not commented on variation of Voc and Jsc compared with respect to pore size and surface area[28]. Author only discussed on increase or decrease in overall efficiency with thickness of electrode.

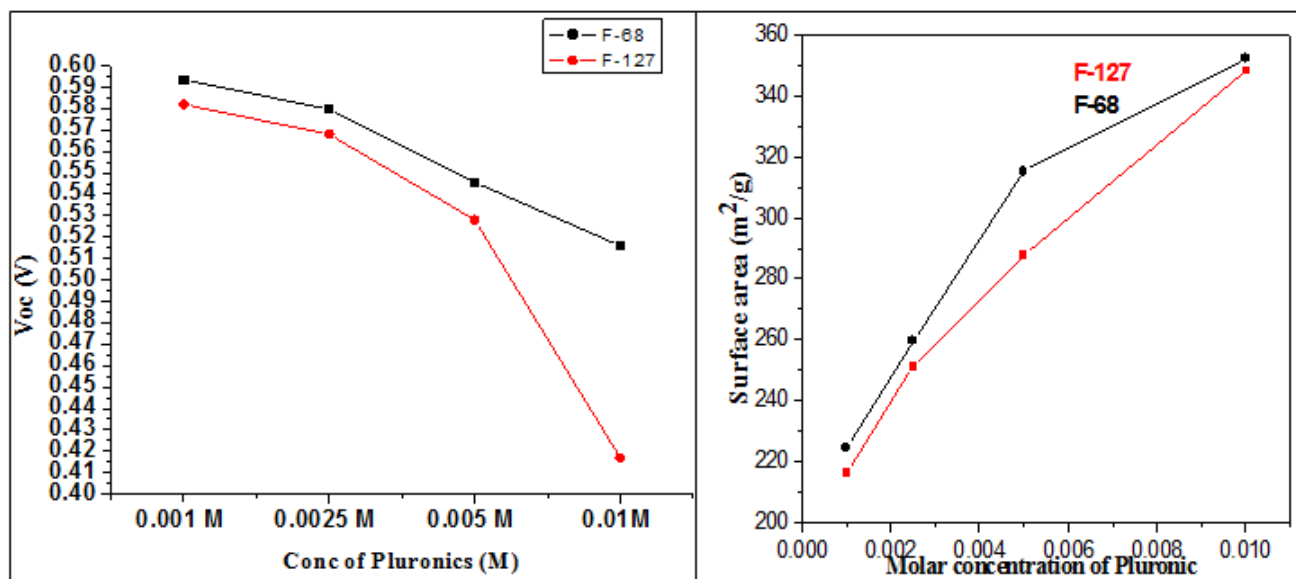


Figure 3 a). Variation of Open circuit voltage (Voc) versus the molar concentration of pluronics 3b) Variation of specific surface area versus molar concentration of pluronics

figure3a. Shows variation of open circuit voltage (Voc) versus the mesoporous TiO₂ samples synthesized using different concentration of both Pluronics. The samples were calcinated at 315 °C for 12 h. from this plot it is observed that the Voc follow the reverse trend of specific surface area i.e as

surface area increases Voc decreases and as surface area decrease Voc increases (refer surface are plot in figure 3b the explanation for variation of specific surface area is already discussed in article 23) as we know that Voc is resultant product of interface between electrolyte and working electrode so in this case as surface area increases that is number of pores present on TiO₂ surface increases and direct contact of TiO₂ surface to electrolyte decreases due to the pores present on TiO₂ surface as a result extend of formation of interface between electrode-electrolyte decreases and ultimately Voc also decreases but at lower surface area number of pore formed on surface of TiO₂ are less and hence more surface of TiO₂ is exposed to direct contact of electrolyte which results in good extend of formation of electrode electrolyte interface and ultimately Voc increases .

As we know that the photocurrent conversion efficiency in DSSC is the resultant product of Voc and Jsc so overall increase and decrease in conversion efficiency for all samples mesoporous TiO₂ are due to increase or decrease in Voc as well as Jsc which are presented in following figure.4

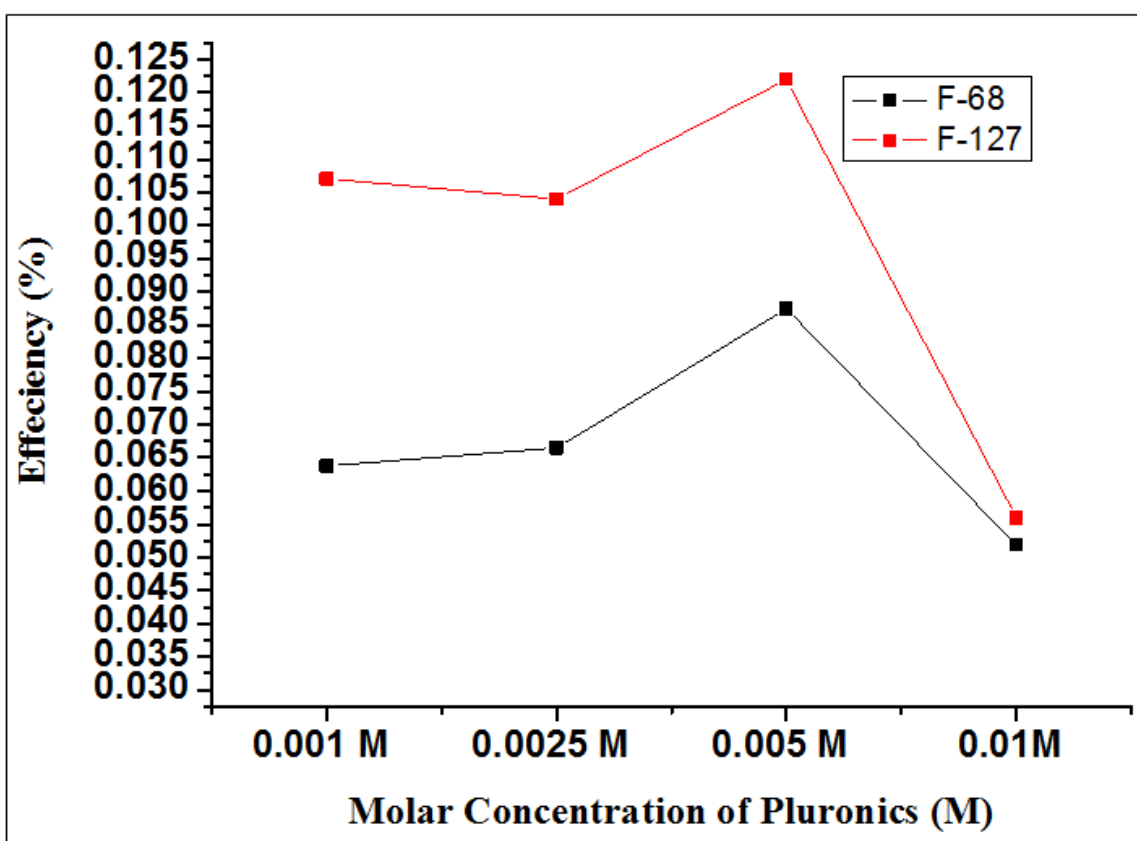


Figure 4. Variation of photocurrent conversion efficiency versus molar concentration of pluronics

3.2. Dye Sensitized Solar Cells (DSSC's) (Calcinations Temperature Variation)

The synthesized TiO₂ paste from both platonic's was used to fabricate working electrode of DSSC and fabricated electrodes were calcinated at different temperatures wiz. a) 260 °C b) 280 °C, c) 300 °C and d) 315 °C for 12 h. The photo current density–voltage (J–V) characteristics of the DSSCs

fabricated with the different morphologies of TiO₂ photoanodes were measured with Keithley 2400 sourcemeter and measured under one sun condition.

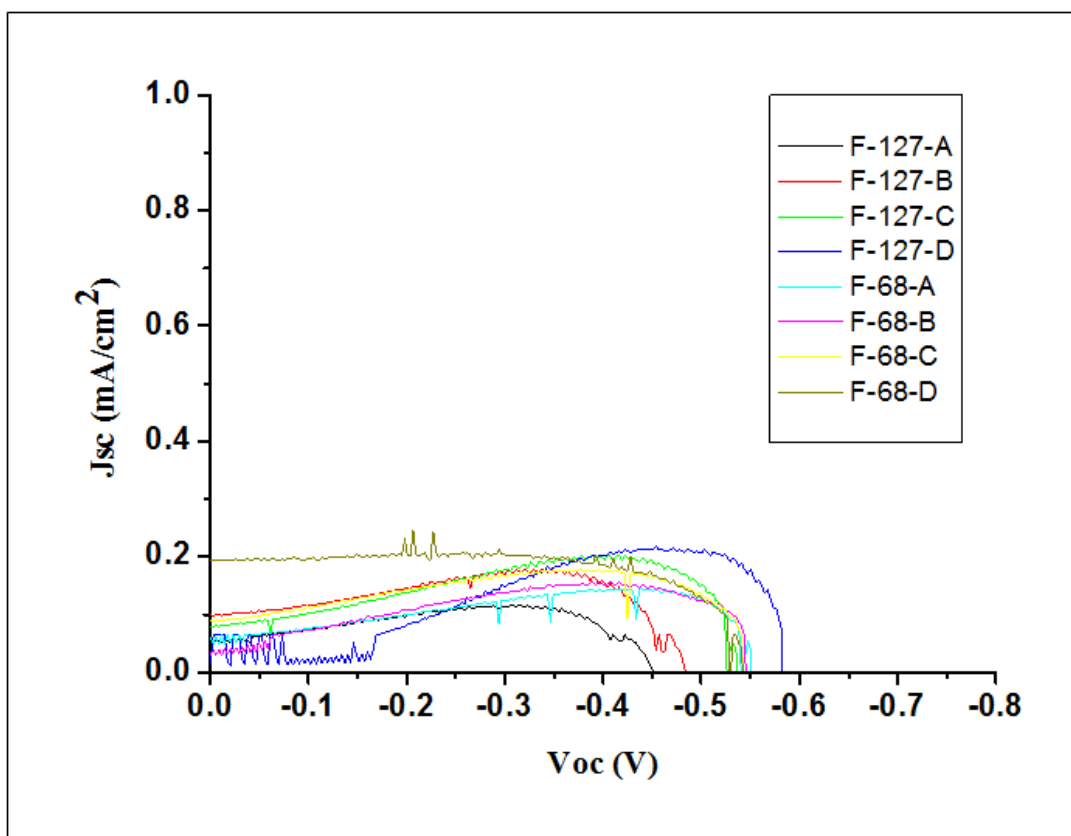


Figure 5. J-V curve for the mesoporous TiO₂ sample synthesized using F-68 and F-127 triblock copolymer as template and calcinated at a) 260 °C b) 280 °C, c) 300 °C and d) 315 °C for 12 h.

Which are shown in Figure5 and all the parameters are summarized in following Table2.

Table 2 Comparison of Specific Surface area also DSSC parameters (Voc Jsc and Efficiencies) with variation calcinations temperature for both pluronics in TiO₂ samples

Template	Samples	Specific Surface area (m ² /g)	Average Pore size (nm)	Voc (V)	Jsc (mA/cm ²)	Effeciency (%)
F-127	260 °C	151.8	1.03	0.452	0.0117	0.039
	280 °C	155.3	2.29	0.484	0.018	0.064
	300 °C	188.7	2.80	0.537	0.0203	0.087
	315 °C	216.2	3.15	0.582	0.0218	0.107
F-68	260 °C	287.6	1.66	0.527	0.0144	0.066
	280 °C	293.1	2.31	0.542	0.0177	0.075
	300 °C	296.5	3.04	0.556	0.0245	0.086
	315 °C	315.3	4.12	0.570	0.0345	0.087

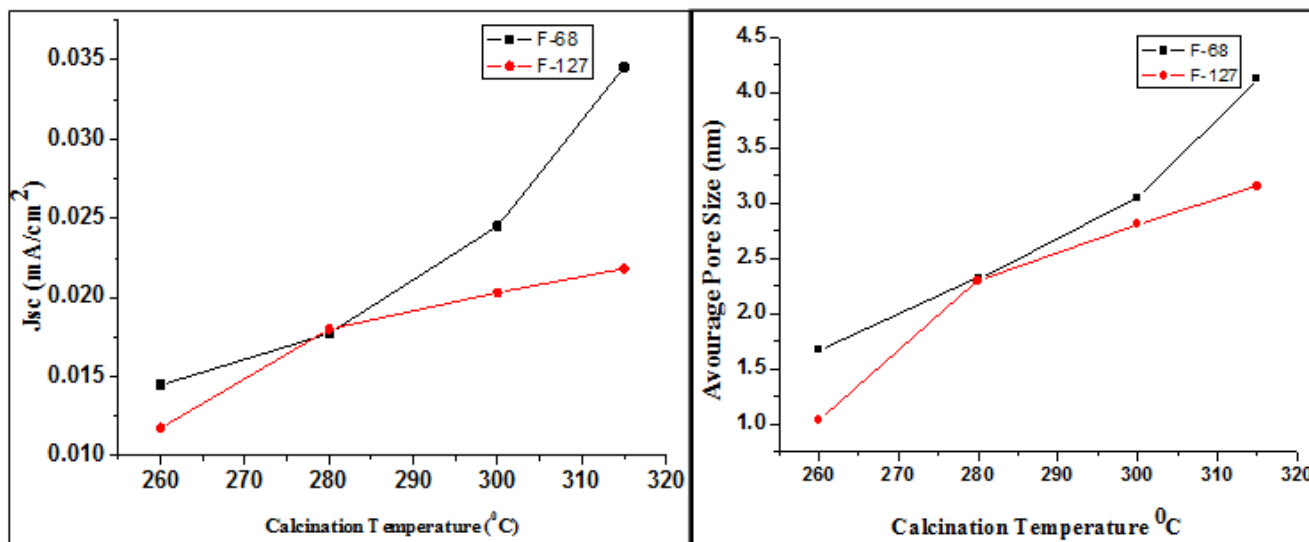


Figure 6. a) Variation of Short circuit current density (J_{sc}) b) variation of average pore size versus the calcination temperature of mesoporous TiO_2 synthesized using both plurionics

J_{sc} obtained from different cells of Mesoporous TiO_2 synthesized using both co-polymers and calcinated at different calcinations temperature are presented in figure 6a. From figure it is observed that the variation of J_{sc} with calcinations temperature follow same trend as like variation of average pore size with calcinations temperature (refer pore size plot in figure 6b the explanation for variation of pore size is already discussed in article 23). At lower calcinations temperature short circuit current density (J_{sc}) is also low, as calcinations temperature increases J_{sc} values also increases. As we know that the most ordered porous structures are formed on calcinating the samples at 315 °C. In the samples calcinated at lower temperature, a good fraction of the pores remained blocked with the carbon produces through the thermal dissociation of the copolymer template, which results in decrease in their specific surface area and average pore size which have been supported from their nitrogen adsorption/desorption result presented in figure 6b that is at lower calcinations temperature the carbon residue remains inside the pores and pores remain blocked however as calcinations temperature increases the pores get opened, when calcinations temperature increases more number of pores get open and hence pore size increases. when pore size increase the J_{sc} value also increases and as pore size decrease J_{sc} also decrease This is due to radius of gyration of Polymers used in electrolyte as pore size increase there are lot of chances of polymer chain to penetrate inside the pores of electrode and exchange of electrons with dye molecule adsorbed on surface of electrode as well as the dye molecule inside pore get reduced through polymer electrolyte and hence photocurrent get increased, as pore size decreases it is difficult for polymer chain to penetrate inside pore and make exchange of electrons with dye molecule adsorbed in side pores resulting photocurrent may decreased.

If we compare J_{sc} values between F-127 and F-68 templates it is observed that the value of J_{sc} is higher for the samples synthesized using template F-68 the reason behind this is sample synthesized using pluronic F-68 template have large pore size than sample synthesized with pluronic F-127 (reason for higher pore size is already discussed in our previous article) So that the sample synthesized using pluronic F-127 templat have higher current (J_{sc}) than the sample synthesized using plurionics F-68.

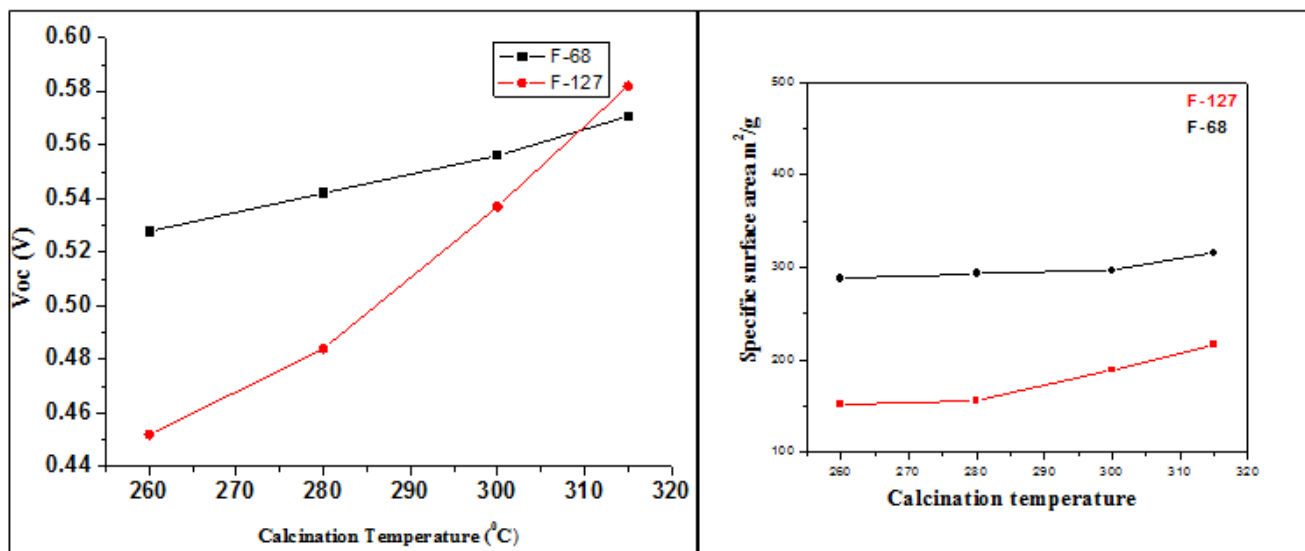


Figure 7 a). Variation of Open circuit voltage (Voc) b) variation of specific surface area versus the the calcination temperature of mesoporous TiO₂ synthesized using both pluronics

Figure 7a. Shows Variation of Open circuit voltage (Voc) versus the mesoporous TiO₂ samples synthesized using different calcinations temperature for both Pluronics. from this plot it is observed that the Voc increase as calcinations temperature increases.

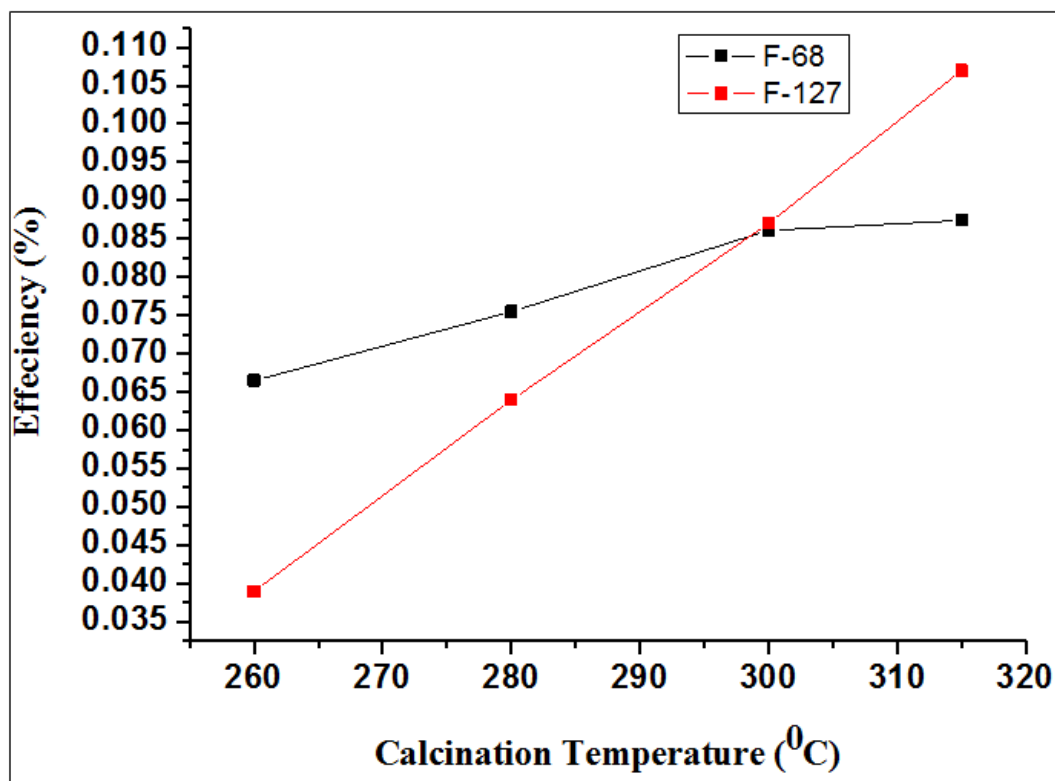


Figure 8. Variation of photocurrent conversion efficiency versus the calcination temperature of mesoporous TiO₂ synthesized using both pluronics

Which follows same trend as variation of specific surface area versus calcinations temperature (refer specific surface area plot in figure 7b the explanation for variation of specific surface area is already discussed in article 23) V_{oc} is the resultant product of interface between electrolyte and working electrode i.e TiO_2 (wide band gap semiconductor). When extend of interface between working electrode and electrolyte increases, V_{oc} also increases and as extend of interface decreases V_{oc} decreases. As calcinations temperature increases more and more pores get open and carbon residue formed during decomposition of template inside pores get removed. Which results more surface of TiO_2 is exposed to direct contact with electrolyte and hence good extend of formation of electrode electrolyte interface takes place and ultimately V_{oc} get increased at higher calcinations temperature.

The photocurrent conversion efficiency in DSSC is the resultant product of V_{oc} and J_{sc} so extend of increase and decrease of V_{oc} as well as J_{sc} reflects in increase or decrease in overall conversion efficiency. For all samples of mesoporous TiO_2 variation in photocurrent conversion efficiency are due to increase or decrease in V_{oc} as well as J_{sc} which are presented in following figure8.

4. CONCLUSIONS

We have introduced synthesis strategy of mesoporous TiO_2 powder in bulk amount through triblock copolymer-templated sol-gel method via an evaporation-induced self-assembly (EISA) process. As we know powdered photocatalyst are efficient in its catalytic activity due to its simplicity. As surface area and pore size both of these factors play an important role in efficiency of photocatalysis. In the present work we have modified the working electrode of DSSC. We have modified the structure texture and morphology of mesoporous TiO_2 . We have successfully synthesized mesoporous TiO_2 with highest specific surface area and variation of pore size Also we have studied the effect of increase or decrease in pore size on short circuit current of DSSC and effect of increase or decrease in specific surface area on open circuit voltage of DSSC.

Also simultaneously we have introduced shortly the thermal stability of pore wall and effect of calcination temperature on average pore size, specific surface area and orderness of mesoporous structure. Working electrodes of DSSC were fabricated using such modified mesoporous TiO_2 and effect of such modifications were studied on V_{oc} , J_{sc} and efficiencies of DSSC These findings will helps us as well as scientific committee to work further more on such types of porous materials

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