

Templated synthesis of mesoscopic titania and its application in the solid-state dye-sensitized solar cells

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Abstract

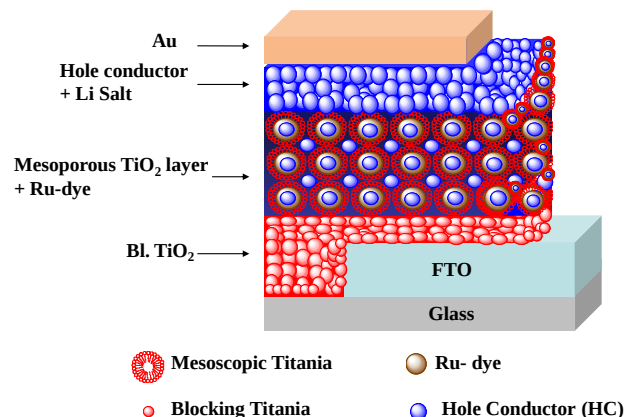
The formation of mesoscopic titania is done by templated mechanism in which the films are prepared by co-assembly of titania precursor species and complexing agent acetyl acetone (acac) and an amphiphilic structure-directing agent, Pluronic F127 (a triblock copolymer). Thinner films of titania having well organized mesoscopic structure were prepared by doctor-blading method. These films were characterized by SEM, TEM, XRD, etc. UV-Vis absorption studies showed good dye intake in very thin mesoscopic titania layers. Prototype photovoltaic device fabricated utilizing the mesoscopic titania films showed reasonable power conversion efficiency and fill factor (FF). The device with mesoscopic TiO_2 layer with thickness as low as 300 nm gave solar cell efficiency 0.31% and FF of 50.2%. This proves the utility of very thin layer of mesoscopic titania fabricated by doctor-blading technique. Such a thin layer may be useful in perovskite solar cells as well. Application of versatile dye molecules, polymers with suitable anchoring functionality could lead to desired high-performance photovoltaic devices. Copyright © 2018 VBRI Press.

Keywords: Mesoscopic titania, dye-sensitization, nanocomposites, organic photovoltaics, doctor-blading.

Introduction

Photovoltaic research in last few years has generated considerable interest focused on hybrid photovoltaic systems because of their great potential to convert solar energy into electrical energy at low cost. These hybrid systems are based on the combinations of an organic chromophore, conjugated polymer or dye, and an n-type inorganic semiconductor.^{1,2} In such system suitable energy levels between the organic and inorganic components ensure the formation of photo-excited electron-hole pairs near the organic/inorganic interface. These electron-hole pairs dissociate into free carriers, with the electrons preferably on one component and the holes on the other.³ Performance of the device is decided by interfacial processes involved in this. The solid-state dye-sensitized solar cells (SDSC), based on nanocrystalline titania ($nc\text{-TiO}_2$), are promising ones in which the light is absorbed in a molecular sensitizer. This sensitizer is chemisorbed to a mesostructured titania electrode with subsequent electron transfer to the TiO_2 .⁴ So far, a maximum efficiency record of 12.3% has been reported with Zn(II) porphyrin sensitizer.⁵ For the fabrication of solid-state dye-sensitized solar cell, we used mesostructured TiO_2 which was prepared by co-assembly of the pluronic F127 template and titania precursor.

The dye molecules (the donor-antenna dye *cis*-di(thiocyanato) (2,2'-bipyridyl-4,4'-dicarboxylic acid)-(2,2'-bipyridyl-4,4'-bis(vinyltriphenylamine) ruthenium (II)-, Ru-TPA-NCS) are contacted on the other side by an organic hole transporting material 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (Spiro-OMeTAD) to which hole-transfer takes place, leaving the regenerating oxidized dye behind. The device architecture with various layers is shown in **Scheme 1**.



Scheme 1. Solid-state dye-sensitized solar cell (SDSC) device architecture with various layers of cell fabricated using mesoscopic titania

Recent development of the organic-template assisted growth of materials has created new types of photonic hybrid nanocomposite materials whose structure and function are organized hierarchically. Earlier, Schulz-Ekloff's and Wohrle's group demonstrated inclusion of dye molecules like Oxazine 1, Coumarin 40, and Rhodamine BE50 inside the nanopores.⁶⁻⁸ Several other papers on this topic talk about optimization of the concentration of inclusion effect materials (dye molecules) within the preformed mesopores or during sol-gel synthesis. Frey et al³ prepared mesoscopic titania films by co-assembly of titania precursor, MEH-PPV and an amphiphilic structure-directing agent, F127 but no template was removed. Triblock copolymer (PEO-PPO-PEO) Pluronic P105 was used as templating agent to prepare mesostructured self-assembled titania films by evaporation-induced self-assembly (EISA) to fabricate dye-sensitized solar cells.⁹ Sarkar et al made the perovskite solar cells based on such mesoporous titania and correlated the efficiency enhancement with the pore sizes. Mesoporous films of titania, niobia or tantalum-wide-band gap semiconductor oxides allow an efficient charge carrier transport because of interconnected nanocrystalline particles.⁹ The nature and morphology of nanocrystalline titanium dioxide (nc-TiO₂) films play a significant role in determining the overall efficiency of the SDSC.¹⁰⁻¹³ The desired properties of nc-TiO₂ films for its efficient functioning in SDSC are pure anatase titania phase¹⁴, most advantageous porosity for better filling of hole conductor (HC), high surface area of mesostructured titania for better dye absorption¹⁵ and well-connected nanoparticle network for enhanced electronic percolation.¹⁶ The different preparation methods of nano-TiO₂ leads to different pore size, surface area and morphology of the mesoporous films.¹⁷ For fabricating the best performing TiO₂ mesoporous thin film electrodes, the synthesis of nanocrystalline titania involve tedious and time-consuming procedures running for 2-3 days. Such a long procedure is economically not fitting for industrial production and must be cut short.¹⁸

In this work, we report the fabrication of mesoscopic titania films by templated mechanism and their characterization by various techniques and application of these films in solid-state dye-sensitized solar cell (SDSC) as an electron acceptor. The mesoscopic titania films were prepared by EISA method with the thickness as low as 300 nm and the efficiency of the prototype solar cell fabricated was approximately 0.3% with fill factor 50.2%. Usually in dye-sensitized solar cells, thin films of titania are fabricated only in the range between 1-5 μm approximately. However, with our approach it is possible to fabricate the films as thin as 0.3 μm giving good efficiency which is the proof of the concept. Thinner films of titania having well organized mesoscopic structure were prepared by doctor blading method. Doctor blading method employed for templated synthesis; which resulted in very thin films and can be applicable in various opto-electronic applications. Proposed formation of mesoscopic titania will especially include important topics for organic electronics in near future. Synthetic

method is general and could be easily adapted to other surfactants and inorganic metal-oxide frameworks for a variety of applications.

Experimental

Materials and chemicals

The titania precursor, Diisopropoxytitanium bis(acetylacetonate) (75wt.% in isopropanol) and technical grade Tetraethylorthotitanate (TEOT) was purchased from Aldrich. 2, 2', 7, 7' -Tetrakis-(*N*, *N*-di-4-methoxyphenyl amino)-9,9'-spiro-bifluorene (spiro-OMeTAD) was obtained from Covion Semiconductors, Germany. Lithium bis(trifluoromethyl sulfonyl)imide LiN(SO₂CF₃)₂ (Li salt) and *t*-Butyl Pyridine (TBP) (96%) were purchased from Aldrich and used as received. Pluronic F 127 was purchased from BASF, Germany. Dye molecule, Ru-TPA-NCS was synthesized as per the earlier reported procedure.¹⁹ Common solvents and chemicals were purchased from Aldrich. Glass substrates (Tec 8) covered with ~3 mm fluorine-doped tin oxide (FTO) layer having a sheet resistance of 8 Ω per square were purchased from Hartford Glass Co. Inc., Indiana, USA. The substrates were cut to a size of 25 x 25 mm to suit the solar cell size.

Synthesis of Templated TiO₂ Nanocomposite

0.35 mL of 12 M HCl was added to tetraethylorthotitanate (TEOT) (1.07 gm, 4.7 mmols) which was solidified while stirring, so kept in sonicator at 40°C for about ten minutes to get the clear solution. Then acetyl acetone (acac) (0.35 mL, 3.4 mmols) was added dropwise and solution color changed to yellow-brown. Separately, solution of Pluronic F 127 (BASF) (0.162 g) in 4.56 mL dry THF was prepared. This surfactant solution was carefully added to the above solution slowly while stirring, resulting in nanocomposite solution. The solution color turned reddish after some time. Stirring continued for 2 h. This solution was used for doctor blading to get mesoscopic titania layer.

Fabrication of Solid-state Dye-sensitized Solar Cell (SDSC)

Fluorinated tin oxide (FTO) substrates were coated with compact layer of TiO₂ (bl-TiO₂) by spray-pyrolysis (about 20 spraying cycles) from the mixture of Diisopropoxytitanium bis(acetylacetonate) (Aldrich) (5.0 mL) and ethanol (45.0 mL). These substrates were subsequently sintered at 400°C for an hour and later cooled down to room temperature. The fairly accurate thickness of the bl-TiO₂ layer was 115 nm (see SEM transverse section of device prepared). After cooling, the substrates were coated by doctor-blading with templated mesoporous titania nanocomposite solution (60 μL) prepared above. The films were dried under vacuum overnight and were sintered at 500°C for three hours with programmed heating and allowed to cool down. When the temperature of the substrate reached around 80°C while cooling, it was kept into Ruthenium-dye (Ru-TPA-NCS)

solution (28.90 mg in 50 mL dry DMF) for chemisorption for about 16 hours. The 'warm-condition' of the sample (80°C) prevented moisture from being absorbed in the cavities, which can otherwise reduce the surface area available for Ru-dye molecules self-assembly. Thereafter the physisorbed dye molecules were rinsed away by dimethyl formamide solvent and substrates were kept under vacuum for an hour at room temperature. The UV-visible absorption spectra of these films were recorded.

Application of hole-transport layer (HTL)

Solutions of Spiro-OMeTAD in chlorobenzene (0.16 M, 75 μ L), *t*-Butyl Pyridine (TBP) (1.25 μ L), LiN(SO₂CF₃)₂ salt in dry cyclohexanone (30mM, 1.25 μ L) were prepared separately. These solutions were mixed resulting in a yellowish solution. 50 μ L of this was deposited on dye/TiO₂ layer by spin-coating technique. The substrate with hole-transport layer (HTL) was kept under vacuum for about two-three hours and later the gold electrode was deposited on top. Thickness of the gold layer was about 40 nm.

Instrumentation

UV-vis absorption spectra were recorded on a Hitachi 3000 spectrophotometer. X-ray diffraction (XRD) patterns of the films were recorded using Cu-K α radiation on PANalytical X'Pert PRO MRD system equipped with X'Celerator Scientific RTMS detector. The patterns were taken from thin films on quartz substrates. Images (including cross sectional features) of the films were examined using LEO 1530 Gemini field emission scanning electron microscope (FE-SEM). The photovoltaic current-voltage (*I*-*V*) characterization measurements have been carried out by a Keithley 6517 Source-Measure unit under AM1.5 G conditions (Xenon arc lamp, Air Mass 1.5 Filters from Oriel). The representative area of each cell was 0.1 cm².

Results and discussion

To prepare semiconducting mesostructured titania, a titania precursor, tetraethylorthotitanate, was allowed to react with acetyl acetone (acac) slowly. Formation of yellow brown solution confirmed the complex formation. Then this complex was allowed to react with polyethylene oxide triblock copolymer Pluronic F 127 in dry THF. The solution turned reddish after some time and was used to form mesoscopic titania layer (as-made) by doctor blading. Films of this layer finally sintered at 500°C for three hours to remove the template.

X-Ray diffraction (XRD) analysis of the nanocomposite thin films of both as-made and calcined samples showed broad and intense Bragg peaks in the low 2 θ region, characteristic of periodic mesoscopic titania structure (Fig. 1). There was no change in the XRD peak position for the heat-treated (calcined) sample which indicates that the nanocomposite is intact even after thermal treatment at higher temperatures. Titania mesostructure has remarkable property of the channel

formation because of the crystallization and thermal shrinkage that are induced by calcination at temperatures higher than 400°C²⁰ and that is why we observe intense XRD peaks in low 2 θ region indicating periodic, short-range structural order for the nanocomposite film. Thermal treatments at temperatures range of 400 and 600°C give a high surface area mesoporous nano-anatase coating, presenting channel-voids which are very interesting for dye-sensitized solar cells.

Transmission Electron Microscopy (TEM) images (Fig. 2) show mesoscopic nature of the composite formed. Images reveal that as-made as well as calcined composites have uniform periodic mesostructure. It also shows that the structure is intact after removal of pluronic F127 template by calcination (Fig. 2b).

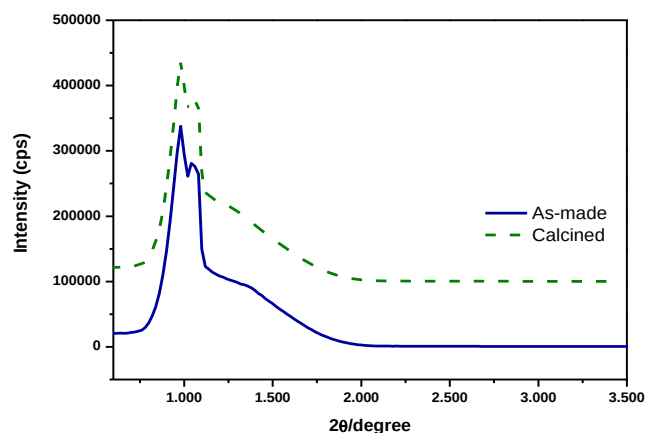


Fig. 1. X-ray diffraction spectra of mesoscopic TiO₂ film before and after calcination.

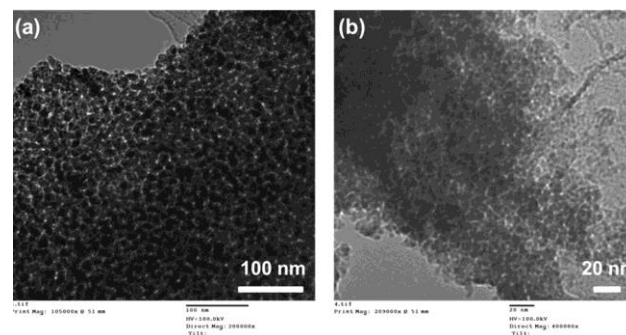


Fig. 2. Transmission electron microscopy images of mesoscopic titania synthesized (a) before and (b) after pluronic F127 template removal by calcination.

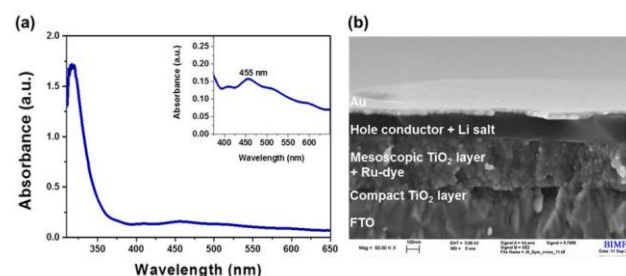


Fig. 3. (a) Absorption spectra of 0.3 μ m thick mesostructured titania film sensitized by Ru-TPA-NCS dye (with inset enlarged between 350-650 nm of dye absorption peaks) (b) Scanning electron microscopic image cross-section of the SDSC fabricated.

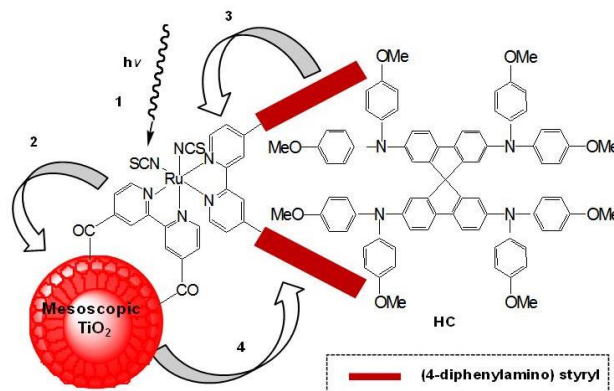
The UV-Vis spectra (**Fig. 3a**) of the 0.3 μm thick mesoscopic titania film impregnated by Ru-TPA-NCS dye showed absorption peaks at 325 and 455 nm. An additional extended band beyond 500 nm is attributed to the $d_{\pi} \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT) transition and is caused by NCS ligands which causes extension of the absorbance of the dye at longer wavelength ($\sim 500\text{-}600\text{ nm}$). This is gainful for better light harvesting in SDSC. The UV-Vis spectra give direct indication of the successful impregnation of the dye within the film. The interface between the Ru-dye and the surface of the titania mesoporous walls forms a heterojunction where we can observe photo-induced charge transfer (CT) and separation. The generation of electronic charge is activated by the excitation of the dye that causes the excitation of electron from the metal to carboxylate bipyridyl ligand (see **Scheme 2**). Use of Ru-TPA-NCS dye have following effect: (a) extended π -conjugation in ligands to obtain high molar extinction coefficients; (b) introduction of trylamine groups with low HOMO energy values than Ru(II) core as donor molecules in order to transfer the hole from Ru(II) core to the donor groups and finally to the hole conductor in a multi-step charge transfer cascade, and (c) to achieve compatibility between donor-antenna groups and hole conductor molecules so that the discrepancy in polarity between dye-coated TiO_2 and hole conductor is minimized.¹⁹ Wetting behavior of the hole conductor is also improved. Li-salt is added to increase conductivity as well as to enhance the surface potential of TiO_2 for injection.

Since the Ru-TPA-NCS dye has extremely high molar extinction coefficient,¹⁷ it is possible to use thinner TiO_2 layers. An attempt by Innocenzi et al⁹ to fabricate titania films by dip-coating and doctor blading techniques could not yield the films thinner than 1 μm . **Fig. 3b** shows the scanning electron microscopic image cross-section of the SDSC fabricated. It shows transverse section of solar cell with various layers of clear thickness. From the darker area and diminished contrast it is evident that the adsorption of dye and filling of HC is efficient in such a thin layer of mesostructured titania.

Heteroleptic complexes such as Ru-TPA-NCS carrying donor groups show significantly broad absorption bands and unusually high extinction coefficients.

TPA units in the dye molecules guarantee a polarity match between the relatively non-polar hole conductor (Spiro-OMeTAD) and highly polar Ru-dye. This improves the interfacial wetting and contact with mesostructured titania. A complete spectroscopic study of the type of anchoring of analogous donor-antenna dyes on nanocrystalline TiO_2 has revealed that such dye molecules generally anchor on nanocrystalline TiO_2 surface using carboxylic acid ($-\text{COOH}$) group via bridging or bidentate type of linkage.²¹

The power conversion efficiency (η) is governed by three parameters namely open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and fill factor (FF). These are summarized in **Table 1**.



Scheme 2. Schematic representation of Mesoscopic TiO_2 -donor-antenna Ru(II)-dye-Hole Conductor system. Physical processes in an antenna dye-sensitized solar cell (1) absorption of light, (2) electron injection into mesoscopic TiO_2 , (3) regeneration of Ru-dye via hole transfer to antenna group and to hole conductor, HC and (4) slow recombination caused by spatial separation of charges at the interface.

Table 1. Photovoltaic performance of Ru-TPA-NCS dye in SDSC under standard AM 1.5 spectral conditions and at 100 mW/cm^2 light intensity.

V_{oc} (mV)	I_{sc} (mA/cm^2)	FF (%)	η (%)
705	0.89	50.2	0.316

The higher absorption arising from extended conjugation in ligands leads to efficient light harvesting, which in turn results in higher short-circuit current.¹⁹

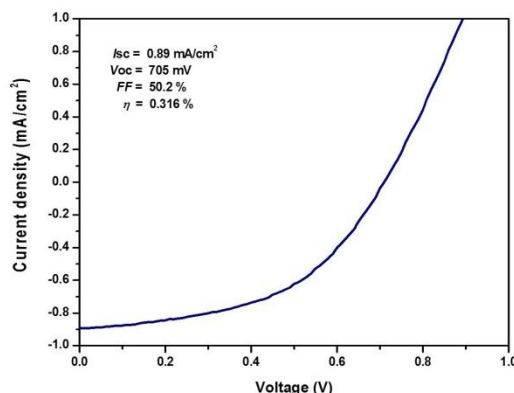


Fig. 4. I-V characterization curve of the solid-state dye-sensitized solar cell device fabricated using mesoporous TiO_2 layer sensitized with Ru-dye.

The reason for lesser short circuit current ($0.89\text{ mA}/\text{cm}^2$) in our device may be that thickness of the titania layer is too less to have maximum dye intake on the surface of nc- TiO_2 . However, V_{oc} (705 mV) and FF (50.2%) are significantly good. That is because there could be continuous network of the nc- TiO_2 and absorbed dye throughout the mesoporous layer and is evident from the SEM image cross section of the SDSC device shown in **Fig. 3b**. Frey et al³ fabricated the solar cells with pristine films prepared by co-assembly of titania precursor species, MEH-PPV and an amphiphilic structure-directing agent, Pluronic F127, from a THF based precursor solution. However, with this configuration they got the power conversion efficiency of 0.034% with a fill factor of 30% only. The presence of the

long F127 surfactant at the MEH-PPV/titania interface inside the mesostructure might pose a barrier for exciton dissociation into free carriers. The prototype device we prepared showed better power conversion efficiency of 0.31% which is almost ten times higher. This is because removal of the F127 template led to the better exciton dissociation of the free carriers throughout the mesoscopic layer and this has reflected into significantly higher fill factor, viz., 50.2%.

Conclusion

In conclusion, we report the fabrication of mesoscopic titania semiconducting electrode for the fabrication of solid-state dye-sensitized solar cell. The formation of this mesoscopic titania is done by templated mechanism in which triblock copolymer Pluronic F127 is used as template. The films are prepared by co-assembly of titania precursor species and complexing agent acetyl acetone (acac) and an amphiphilic structure-directing agent, Pluronic F127. This synthetic method is general and could be easily adapted to other surfactants and inorganic metal-oxide frameworks for a variety of applications. Prototype photovoltaic device fabricated utilizing the mesoscopic titania films showed reasonable power conversion efficiency and fill factor. With the continuous research on the synthesis of versatile dye molecules, polymers with suitable anchoring functionality could lead to the desired high-performance photovoltaic devices. The device with mesoscopic TiO₂ layer with thickness 0.3 µm gave solar cell efficiency 0.31% and FF of 50.2%. This proves the utility of very thin layer of mesoscopic titania fabricated by templated synthesis. The increase in mesoscopic titania thickness and with optimizations the dye intake should increase which will ultimately enhance the device performance. Such a thin layer may be very useful in perovskite solar cells as well.

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Author's contributions

Conceived the plan: cjb; Performed the experiments: yp, gth; Data analysis: cjb, yp, gth; Wrote the paper: cjb. Authors have no competing financial interests.

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