CHAPTER-3

EXPERIMENTAL SECTION

3.1 Chemicals required

3.1.1 Chemicals required for fabrication of DSSC

Electrode material: (TCO22-7/LI)- Low-ion 2.2 mm soda lime glass substrate, 7Ω/sq fluorine-doped tin oxide coating on one side, > 70% transparency from SOLARONIX, Switzerland

Anode material:

Compact layer: Titanium Isopropoxide (TTIP, 97%) from Sigma Aldrich, HCl: Fischer Scientific, Thermo Fischer Scientific India Pvt Ltd,Mumbai, Ethanol from EMSURE Merck, Acetic Acid (100% Glacial) from EMPARATA(R) Merck Science Pvt Limited

Transparent layer: Ti-Nanoxide T/SP, 15-20 nm size, anatase phase from SOLARONIX, Switzerland

Reflective layer: Ti-Nanoxide R/SP, 100-200 nm size, anatase phase, SOLARONIX, Switzerland

Sensitizer: Ruthenizer 535-bis TBA, commonly known as N719 dye, SOLARONIX, Switzerland

Electrolyte: Iodolyte AN-50, Iodide/triiodide, 50 mM, SOLARONIX, Switzerland

Counter electrode material: Plastisol T/SP paste, SOLARONIX, Switzerland

Sealing spacer: Ethylene Vinyl Acetate (EVA) sheet, 0.43 mm thick

Sealing glue: Ethylene Vinyl Acetate (EVA) beats, Toluene, SRL, Sisco Research Pvt Ltd, Maharashtra

3.1.2 Chemicals for synthesis graphene

Graphite powder: SDFCL, S d fine-Chem Ltd, Mumbai, N- Merhyl-2-Pyrrolidone (NMP): SRL, Sisco Research Pvt Ltd, Maharashtra, Dimethyl formamide (DMF), X-Trition, Ethanol: Changushu Hongsheng Fine Chemical Co. Ltd., Changshu City, Jiangsu Province, H_2SO_4: Qualigens, Thermo Fischer Scientific India Pvt Ltd, Mumbai, $NaNO_3$: Fischer Scientific, Thermo Fischer Scientific India Pvt Ltd,

Mumbai, $KMnO_4$: EMPLURA, Merck life science limited, Mumbai, H_2O_2: Qualigens, Thermo Fischer Scientific India Pvt Ltd, Mumbai, L-Ascorbic acid: SRL, Sisco Research Pvt Ltd, Maharashtra, Hydrogen Iodide (HI), Potassium Hydroxide Pallets (KOH), Sodium Hydroxide pallets (NaOH), HCl: Fischer Scientific, Thermo Fischer Scientific India Pvt Ltd, Mumbai, Nafion

3.1.3 Chemicals for preparation of liquid and gel electrolyte

Iodine (I_2): Central Drug House (P) Ltd., Delhi, Potassium Iodide (KI): SIGMA-ALDRICH Co., USA, Acetonitrile (CH_3CN): SDFCL-Gujarat, Valero nitrile (C_5H_9N): Sisco Research Lab., Mumbai, Iodolyte AN-50, Iodide/triiodide, 50 mM, SOLARONIX, Switzerland, Deionized water, agar-agar powder

3.2 Apparatus required

Hot Plate, Spin Coater, Diamond Cutter, Paper Cutter, Clips, Autoclave, Furnace, Dryer, Clips, Connecting probes, Beakers, Magnetic stirrer, Laboratory Pipette, Mortar - pestle, Muffle Furnace, Dryer, Autoclave Reactor, Ultrasonic Bath-Sonicator, Ultrasonic probe-sonicator, Centrifuge, Glass container**,** Heating Plate**,** Magnetic Bud, Desiccator.

3.3 Experimental procedure

3.3.1 Fabrication of DSSC

3.3.1.1 Preparation of solutions

Compact layer using TTIP: 0.1ml HCL was added first in a cleaned and dried glass beaker. Then 0.3ml TTIP is added to it followed by adding 5 ml of Ethanol.

Transparent layer: 2.5 ml ethanol is added to 2 gm Solaronix T/SP. The solution is mixed well and sonicated for 30 minutes.

Reflective layer: 2.0 ml ethanol is added to 2gm Solaronix R/SP. The solution is mixed well and sonicated for 30 minutes.

Liquid electrolyte: 0.2 gm KI, 1 ml Iodine, and 1 ml acetonitrile are addedin a properly cleaned and dried glass vial. The solution is mixed so that KIis dissolved properly.

Liquid electrolyte with dye: 0.36 mg of N719 dye is added to 1 ml of prepared or purchased electrolyte. This solution is sonicated for a minimum of 30 minutes to ensure complete dissolution of N719 dye.

N719 dye Solution: 6.5 mg N719 Dye is added to 10 ml ethanol to make 0.55 mM solution. The solution is mixed properly so that dye particles are completely dissolved.

Anchoring group: Anchoring group is used in the ratio of 1:10 with dye (11mg Chenodeoxycholic acid is added to 0.55mM dye solution). (only needed when dye shows desorption)

Platinum solution: 20.7 mg of $H_2PtCl_6.H_2O$ is added in 4 ml of ethanol to make 10 mM $H_2PtCl_6.H_2O$ solution.

Sealing Glue: 10 gm of EVA beads is added to 25 ml toluene. The mix is heated at 70˚C for 2 hrs under continuous stirring.

3.3.1.2 Steps to fabricate DSSC

The steps involved are as follows:

1) Cleaning of ITO/FTO
2) Anode preparation
a. Pre-compact layer coating
b. Transparent layer & reflective layer coating
c. Post-compact layer coating
d. Soaking in dye
3) Cathode preparation
4) Sealing and electrolyte filling
5) Cell testing and analysis

1. **Cleaning of ITO/FTO:** The FTO glass substrate is gently cleaned in soap solution using a scrubber. The FTO glass substrate is sonicated for 15 minutes each in soap solution first, then in distilled water, then in acetone, and then in 2-propanol. FTO Glass substrate is cleaned before every coating on the spin coater with 0.5 ml IPA at 2000 RPM for 30 sec.

2. Anode preparation:

a. Pre-compact layer coating: The conducting side of FTO is checked using a multimeter. The compact layer solution is coated on an FTO glass substrate using a spin coater at 2000 RPM for 30 sec then at 4000 RPM for another 100 sec. FTO is (the area where sealing will be done) cleaned with IPA using an earbud or tissue paper. Compact layer coated FTO is sintered at 450˚C in a furnace for 30 minutes by starting at 50˚C and increasing the temperature by 50˚C to 450˚C. Compact layer coated FTO is stored in an airtight container after removing it from the furnace and cooling it.

b. Transparent layer & reflective layer coating: 100µl of transparent layer solution is coated on compact layer coated FTO using spin coater at 2000 RPM for 100 sec. Transparent layer coating is done two more times at the same RPM for the same time to coat 3 layers of it. Now, the transparent layer coated FTO is dried on the hot plate for 15 minutesat 100ºC.

100 µl of reflective layer solution is coated on dried FTO using spin coatedat 3 steps with 1500 RPM for 20 sec, then 3000 RPM for 30 sec, and then5000 RPM for 100 sec. FTO (the area where sealing will be done) is cleaned with IPA. Coated FTO is sintered at 450˚C in a furnace for 30

minutes by starting at 50˚C and increasing the temperature by 50˚C to 450˚C. Coated FTO is stored in air air-tight container after removing it from the furnace and cooling it.

c. Post Compact layer coating: 50µl of compact layer solution is coated on a reflective layer using a spin coater at 2000 RPM for 60 sec. FTO (the area where sealing will be done) is cleaned with IPA. Coated FTO is sintered at 450˚C in a furnace for 30 minutes by starting at 50˚C and increasing the temperature by 50˚C to 450˚C. Coated FTO is taken out at 150˚C for dye soaking.

d. Soaking in dye: Post compact layer coated FTO is taken out from the furnace at 150˚C and soaked in the dye solution for 10 to 12 hours in air-tight container. Dye adsorbed FTO is taken out from the dye solution 12 hours before cell assembly and placed in acetonitrile solvent.

3. **Cathode preparation:** Two small drills are made on FTO using a drilling machine. Plastisol paste is evenly spread on fresh and cleaned FTO using a glass rod. Plastisol paste coated FTO is cleaned from the sides with IPA. Now, FTO is sintered at 450˚C for 15 minutes in a preheated furnace. Coated FTO is taken out from the furnace at 150˚C before cell assembly.

4. **Sealing and electrolyte filling:** The EVA sheet is cut in a square shell (spacer) for the active area. The counter electrode is heated to150˚C for 10 minutes. The spacer is placed over the counter electrode in such a way that drills on it, remains uncovered, and comes between spacer open areas. The anode is placed over a spacer-counter electrode arrangement for at least 2 minutes or till the EVA sheet becomes transparent.

20 µl to 50 µl electrolyte solution is poured into a sealed DSSC assembly from one of the counter electrode drills till the electrolyte comes out fromanother drill on the cathode. The extra electrolyte is wiped out from the counter electrode surface. Drills on the counter electrode are sealed with EVA solution.

Precautions:

- FTO glass substrate should be cleaned twice before every coating using a spin coater at 2000 RPM for 30 seconds with IPA.
- Cleaning from sides on coated FTO should be done after every coating (except transparent layer coating)
- Temperature increment should be gradual during sintering to avoid flacks and cracks in anode coatings.

- Coated FTO should always be removed from the furnace at 150˚C or below it.
- Dye soaking of the anode should always be done at a temperature of more than 100˚C. Containers of dye solution should be closed properly at every use.
- The spacer is properly adhered to the anode and the counter electrode is ensured by it becoming transparent.
- Make sure that there are no air bubbles left inside the active area while filling electrolytes in the DSSC assembly.

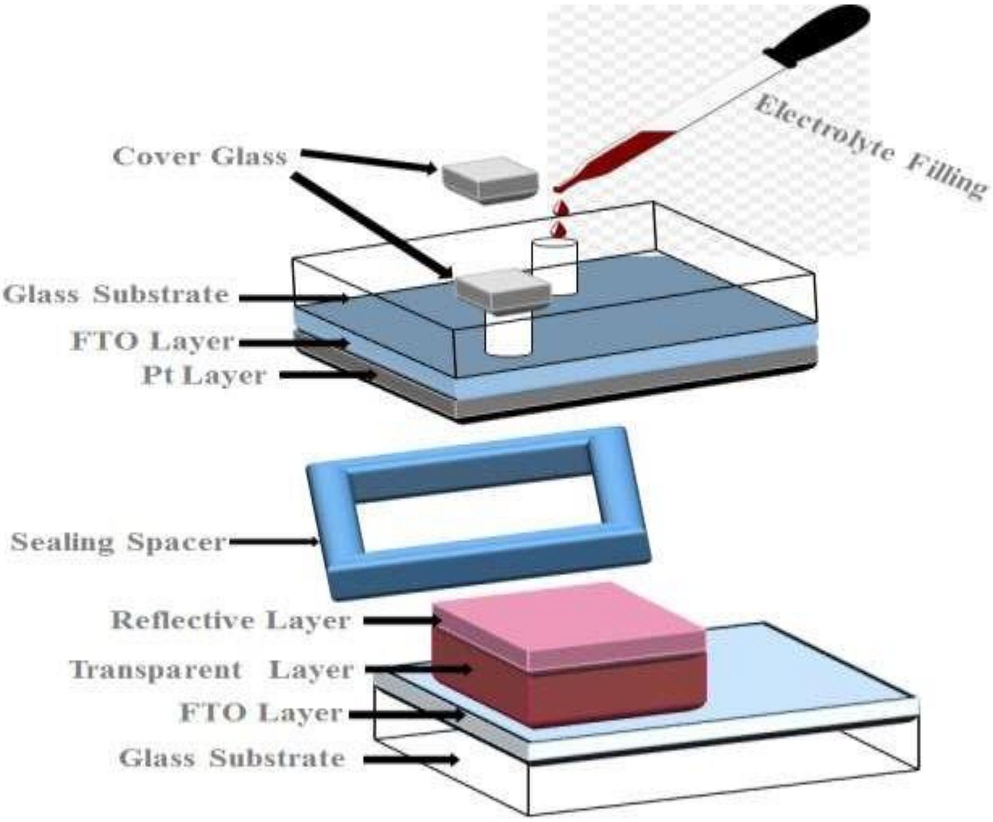

Fig. 6: Schematic of DSSC Fabrication

Fig.7: Fabrication steps of DSSC i.e. images of steps of pre-compact layer coating, transparent layer coating, reflective layer coating, post compact layer coating, dye soaking, Pt coating on CE, anode-cathode assembling and Electrolyte filling & Cell testing.

3.3.2 Synthesis of graphene and its application

3.3.2.1 Synthesis of graphene

3.3.2.1.1 Graphene synthesis via liquid exfoliation route

Graphite powder (3gm) is added to each 30 ml NMP, DMF, Ethanol, and Distilled water with surfactant (30 ml DW+0.1 ml triton) solvents. Each solution is exfoliated using ultra bath sonication and probe sonication for

9 hrs. The resulting exfoliated graphene powder is washed several times. Samples are dried and stored in air-tight containers.

A settling test and EIS study were performed to know the best solvent among NMP, DMF, Ethanol, and Distilled water with surfactant. The results of the study are explained later in the Result and Discussion section.

3.3.2.1.2 Graphene synthesis via oxidation-reduction route

Graphite powder is oxidized by Hummar’s method (explained in detail in section 3.3.2.1.3). Graphite oxide powder is reduced using four different reducing agents namely ascorbic acid, HI, KOH, and NaOH (detailed condition of reduction is explained in section 3.3.2.1.3).

EIS study was performed to find the best reducing agent among ascorbic acid, HI, KOH, and NaoH. The results of the EIS study are explained later in the Result and Discussion section.

3.3.2.1.3 Graphene synthesis via combined exfoliation route

Sample 1 (S1) -Liquid exfoliation synthesis route

Graphite powder (3gm) is mixed with 30 ml NMP solvent. Dispersion of graphite powder and NMP is exfoliated using an ultrasonic bath and ultrasonic probe sonicator for a maximum of 9 hours. The sample is washed multiple times using distilled water. Synthesized graphene is dried and stored in an air-tight container.

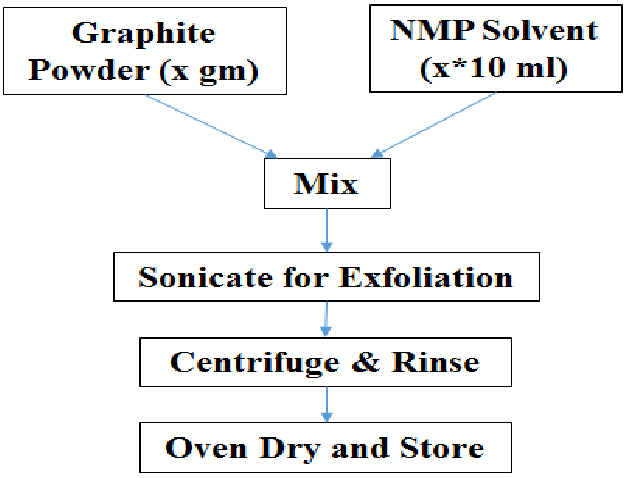

Fig.8: Schematic of graphene synthesis via liquid exfoliation route

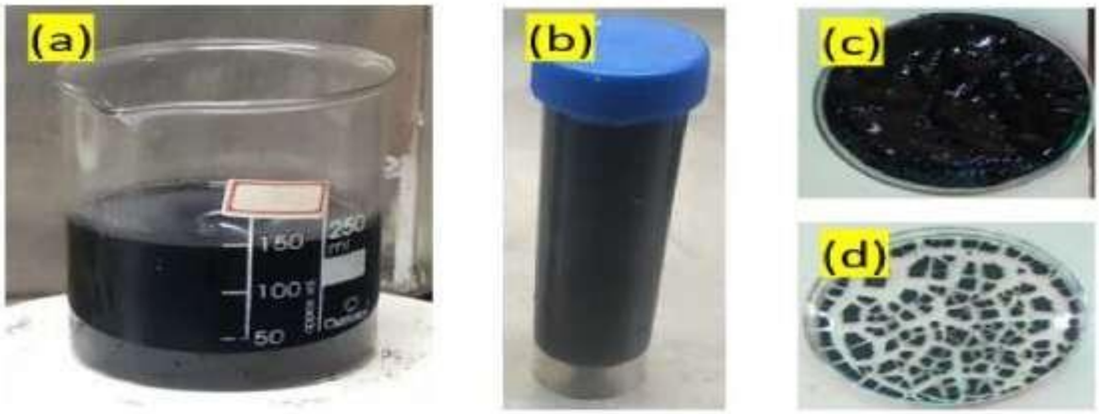

Fig.9: Graphene synthesis via Liquid phase Exfoliation: (a) Mixing of Graphite powder in NMP solvent (b) Mixture in centrifuge tubes for washing (c) Graphene paste after washing (d) Resultant hard solid graphene

Sample 2 (S2) - Oxidation-Reduction synthesis route

Graphite is oxidized by Hummer's method. 98% H_2SO_4 (138 mL) is added to a mixture of graphite powder (3.0 g) and $NaNO_3$ (3 g), and the mixture is stirred for 1 hour at 800 RPM. $KMnO_4$ (18.0 g) is added slowly in ice bath conditions with continuous stirring to keep the reaction temperature below 20 °C. The reaction is warmed to 35 °C and stirred for 24 hours, after which Distilled water (112.5 mL) is added slowly. The reaction mix was kept at 85 °C for 30 min. Additional water is added and 30% H_2O_2 (3-10 mL) is added to remove excess $KMnO_4$ until the yellow color appears. The reaction mix is left overnight for gravity settling and air cooling. The reaction mix is washed multiple times with 5% HCl solution. The reaction mix is dried at 110 °C in a dryer for 10-12 hours.

Fig.10: Schematic of Hummer's Method

Oxidation of Graphite to Graphite Oxide (GO) via HUMMER'SMETHOD

$$KMnO_4 + 3H_2SO_4 \longrightarrow K^+ + MnO_3^+ + 3HSO_4^-$$

$$MnO_3^+ + MnO_4^- \longrightarrow Mn_2O_7$$

The resultant hard solid graphite oxide (GO) is ground and stored in an airtight container. GO (x gm) and ascorbic acid (2x gm) are mixed in distilled water. Then, the Reduction of GO is achieved in the basic medium by heating at 110 °C for 1 hour under continuous stirring. The reaction mix is washed, dried, and stored.

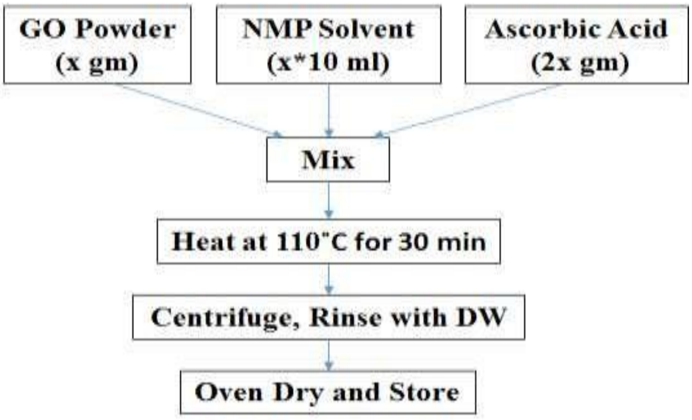

Fig.11: Schematic of Graphite Oxide (GO) reduction

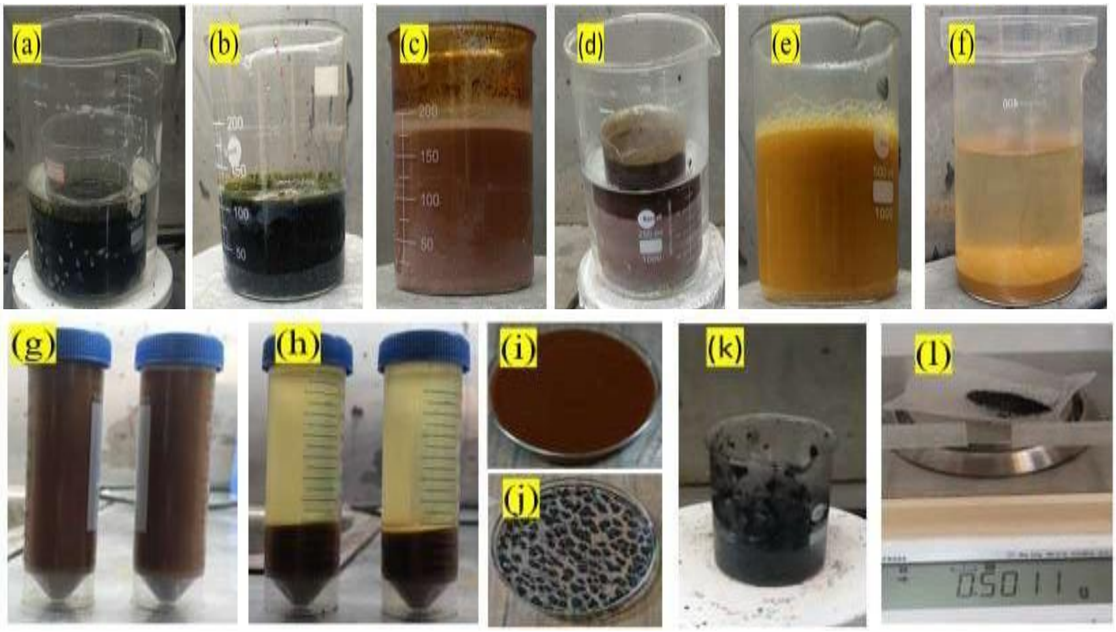

Fig.12: Graphene synthesis via chemical exfoliation method: (a)Slow addition of $KMnO_4$ in the mixture of Graphite, $NaNO_3$, and H_2SO_4 under an ice bath (b) Heating of mixture for 24 hours at 35 °C, (c) Addition of distilled water producing large exotherm, (d) Removal of excess heat in an ice bath, (e) Addition of additional water and H_2O_2 to remove excess $KMnO_4$, (f) Gravity settling of the mixture, (g) & (h)Washing in centrifuge tubes (i) & (j) Graphene oxide paste before andafter drying, (k) Reduction of GO powder in ascorbic acid (l) Resultant Reduced graphene oxide powder

Sample 3 (S3) - Oxidation followed by exfoliation followed by reduction during exfoliation

Oxidation of graphite to graphite oxide is done in the same manner as done for sample S2. Graphite oxide is exfoliated in NMP solvent for 9 hours using an ultra-bath and probe sonication. Graphene Oxide GO (x gm) is reduced by adding ascorbic acid (2x gm) in the above dispersion. The reaction mix is heated at 110 °C in the basic medium for 1 hour under continuous ultra-probe sonication. The reaction mix is washed multiple times and dried. The resultant hard solid reduced graphene oxide (RGO) is ground properly and stored in an airtight container.

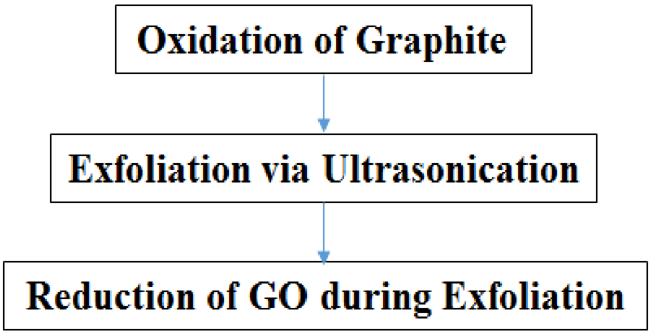

Fig.13: Schematic of S3 synthesis via combined exfoliation route

Sample 4 (S4) - Exfoliation of graphite during oxidation followed by exfoliation followed by exfoliation during reduction

98% H_2SO_4 (138 mL) is added to a mixture of graphite powder (3.0 g) and $NaNO_3$ (3 g), and the mixture is exfoliated via ultra-bath sonication for 5 hours. The rest oxidation process is done in the same manner as it is done for sample S2. Exfoliation and Reduction are done in the same manner as it is done for sample S3.

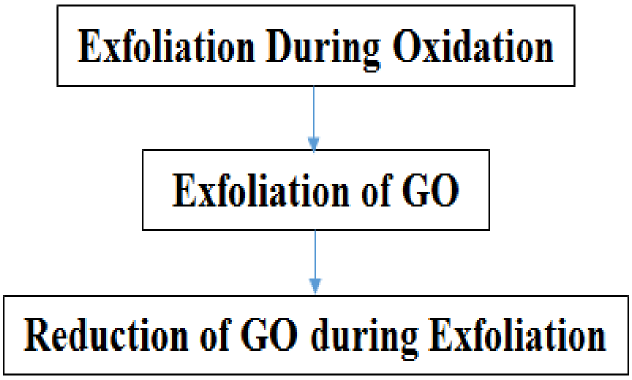

Fig.14: Schematic of S4 synthesis via combined exfoliation route

Sample 5 (S5) - Exfoliation of graphite followed by exfoliation during oxidation followed by exfoliation followed by exfoliation during reduction

Exfoliation of graphite powder is done in the same manner as it is done for sample S1. Exfoliation during oxidation is done in the same manner as it is done for sample S4. Exfoliation followed by exfoliation during reductionis done in the same manner as it is done for sample S3.

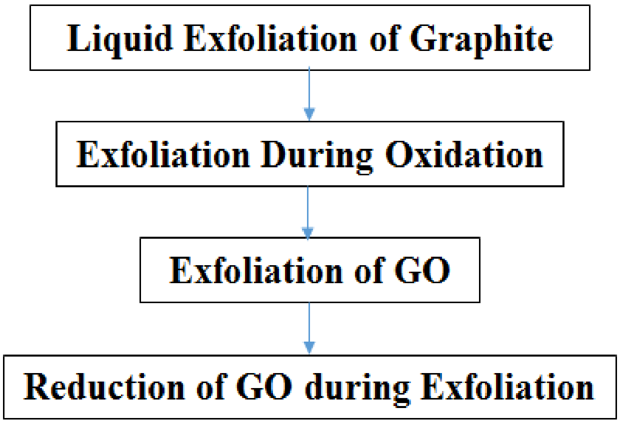

Fig.15: Schematic of S3 synthesis via combined exfoliation route

3.3.2.2 Preparation of graphene counter electrode (CE) and Cell assembly

3.3.2.2.1 Preparation of graphene solution

Graphene solution is prepared using S1 and S4 samples. 0.5 gm graphene (either S1 or S4) sample is added to 1 ml of ethanol and 100µl Nafion is added to it in a centrifuge tube and then sonicated for a minimum of 1 hour in a bath-sonicator.

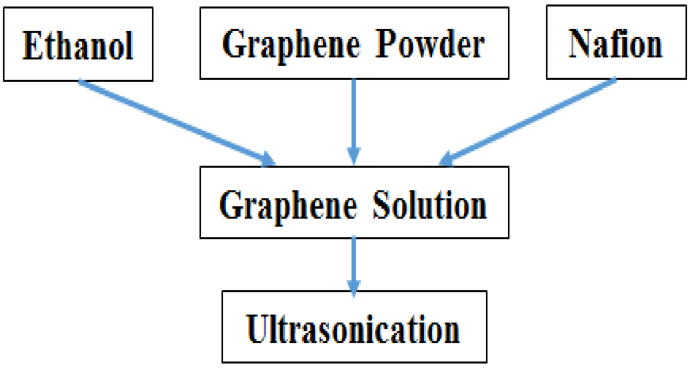

Fig.16: Schematic of graphene solution preparation

3.3.2.2.2 Coating of graphene solution on FTO

After sonication, S1 and S4 solutions are coated on a cleaned FTO glass substrate using a spin coater at 1500 RPM for 30 sec, so that a thin layer of graphene coat is obtained. Graphene solutions from the sides are cleaned with IPA. Coated glass substrates were heated in a vacuum furnace at 300°C for 1 hour. Graphene coated substrates are cooled to 150°C and then are used as a counter electrode in DSSC fabrication.

Fig.17: Preparation of graphene cathode: Picture of (a) graphene solution, (b), (c)& (d) coating of graphene solution on FTO using the spin coating method, (e) graphene coated substrate, (f) heating of graphene cathode.

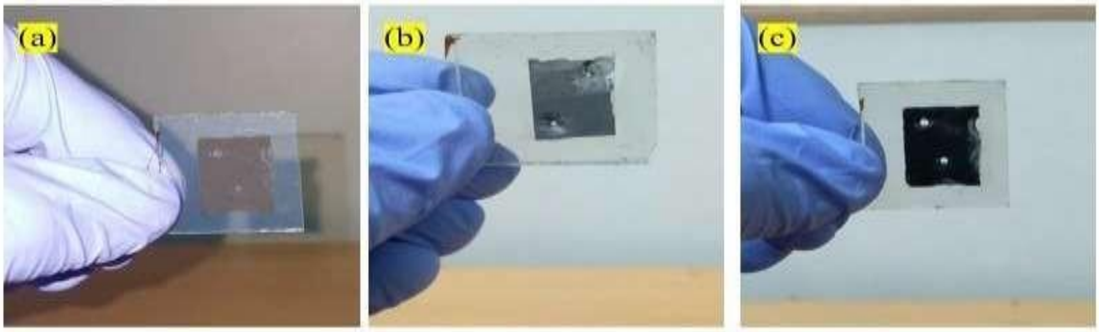

Fig.18: Pictures of fabricated Graphene counter electrode (a), (b) from S1 solution and (c) from S4 solution

3.3.2.2.3 Cell assembly

For assembling graphene coated CE refer section 3.3.1.2

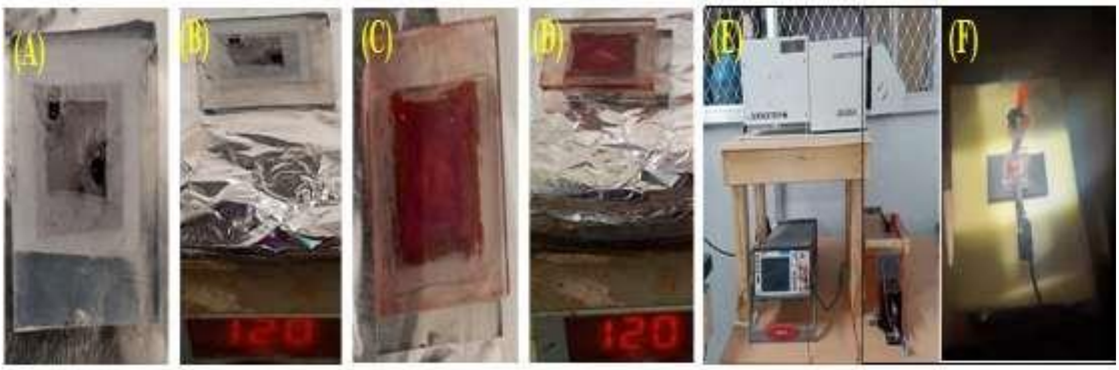

Fig.19: Cell Assembly with Graphene coated CE: (A) Placing space on graphene coated CE, (B) Heating of space on CE, (C) Placing anode on space-CE assembly, (D) Assembled Cell, (E) & (F) testing of DSSC

3.3.2.3 Preparation of graphene liquid electrolyte

0 mg, 2.5 mg, and 5.0 mg of S4-RGO sample are added to 0.2 ml each of Iodolyte AN-50 solutions in 3 centrifuge tubes and placed in an ultra-bath sonicator for a minimum of 1 hr. Sonication is done so that RGO samples disperse uniformly in electrolyte.

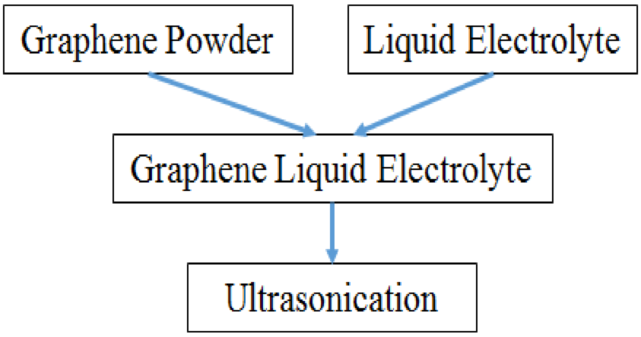

Fig.20: Preparation of Graphene Liquid Electrolyte

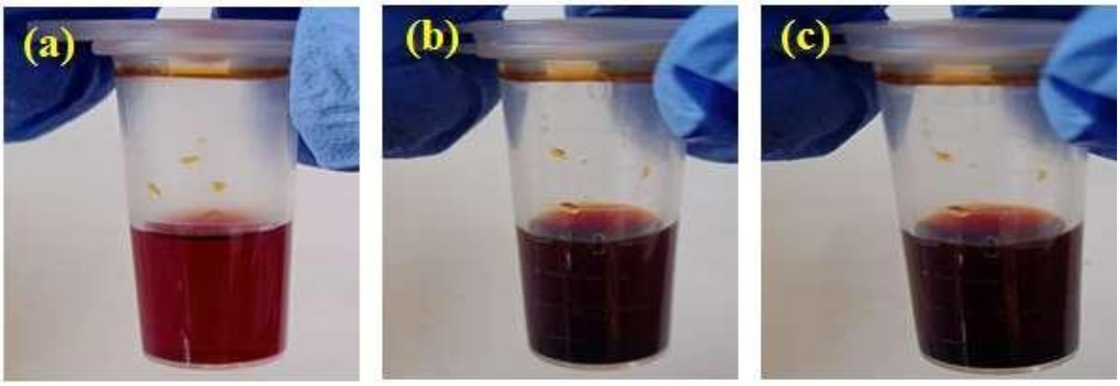

Fig.21: Pictures of liquid electrolyte with graphene conc. (a) 0 mg/ml, (b) 2.5 mg/0.2 ml & (c) 5.0 mg/0.2 ml

3.3.3 Preparation of gel electrolyte and its modification

3.3.3.1 Synthesis of aqueous gel electrolyte:

0.75 gm agar-agar is added to 25 ml of distilled water. The solution is heated at 150˚C for 20 min under continuous stirring. The solution is cooled down to room temperature. As the mixture cools, it will start to solidify into a gel. 2ml liquid electrolyte is added into the agar solution. Solutions are mixed properly so that agar-agar solution and liquid electrolyte can be mixed thoroughly. Now, it can be used in DSSC as a gelelectrolyte.

3.3.3.2 Synthesis of non-aqueous gel electrolyte:

0.15 gm of agar-agar was added to 5 ml of liquid electrolyte solution (either prepared or purchased). The solution is heated at 150˚C for around 30 minutes under continuous stirring. The solution is cooled down to room temperature. As the mixture cools, it will start to solidify into a gel. Now, it can be used in DSSC as a non-aqueous gel electrolyte.

Precautions:

- Any Gel electrolyte either aqueous or non-aqueous, should be poured in DSSC in flowing condition, otherwise once solidified, it can’t be poured in DSSC assembly.

- When making the agar gel, it is important to stir continuously to ensure that the agar powder dissolves fully. Otherwise, the gel may not form.
- Always follow proper safety procedures when working with liquid electrolytes, as it can be corrosive and toxic. Wear protective gear and work in a well-ventilated area.

3.3.3.3 Synthesis of non-aqueous gel electrolyte with N719 dye:

Refer to **liquid electrolyte with dye** in section 3.3.1.1 to make a liquid electrolyte with dye. Refer to section 3.3.3.2 to prepare a non-aqueous Gel electrolyte with dye.

3.3.3.4 Synthesis of non-Aqueous gel electrolyte with N719 dye and RGO (S4) Sample:

3.6 mg N719 dye and 1.1 mg RGO (S4) sample are added in 1 ml of liquid electrolyte solution (either purchased or prepared). Electrolyte solution with N719 dye and RGO (S4) sample is sonicated for a minimum of 30 minutes. Ultra-sonication will ensure the complete dissolution of N719 dye and uniform dispersion of the RGO (S4) sample. Now, non-aqueous gel with dye and graphene is prepared by following section 3.3.3.2.

3.4 Characterization performed

3.4.1 Characterization performed for DSSC

The UV–visible absorbance spectrum of samples was obtained using ELICO UV VIS Absorption Spectrophotometer, SL 210, India. The J-V characterizations of the DSSC cell assembly were performed on the SCIENCETECH solar simulator using a Keithley-2400 source meter at 1000 W/m^2 power input. Gel conductivity was measured using four probe instruments. Thickness and morphology of different layers were obtained using AFM-NTEGRA Prima, NT-MDT Service & Logistics Ltd., Particle size of T/SP and R/SP particles were obtained using Melvern (Zeta-sizer Pro) instrument.

3.4.2 Characterization of graphene

The surface morphological changes of all formed samples were analyzed using an SEM Instrument, and the chemical composition of the synthesized photocatalysts was analyzed by EDAX analysis; both analyses were done on an SEM instrument (Nova Nanosem 450, FEI, USA).

The X-ray diffraction (XRD) was carried out using a Bruker D2 Phaser diffractometer system with Cu Kα radiation source ($\lambda = 1.5406$ Å) at 40 kV. The XRD scan was carried out for 2θ in the range from 3° to 90° with a step size of 0.02°.

The Raman spectrum of different samples was taken using Renishaw in-Via Raman Spectrophotometer (Germany) at a semiconductor laser wavelength of 532 nm.

The number of sheets, d-spacing, and crystal structure were observed by high-resolution transmission electron microscopy (HRTEM) using the TEM instrument (Model 20 G2 Tecnai, FEI, USA).

The electrochemical nature of the synthesized samples was taken using Versastat 3 instruments. EIS (Electro-chemical impedance spectroscopy) was performed in 1 M KOH aqueous electrolyte. Resistance like solution resistance or equivalent series resistance (Rs), resistance due to charge transfer (Rct), diffusion resistance, or Warburg impedance (w) was calculated. -

The UV–visible absorbance spectrum of samples was obtained using ELICO UV VIS Absorption Spectrophotometer, SL 210, India. Band gaps were calculated using absorbance data using the Tauc plot.

Particle size distributions and zeta potential values were obtained using the Malvern Zetasizer Pro instrument.