

# 3

## METHODOLOGY

### 3.1 Materials and preparation

#### 3.1.1 Transparent conducting oxide glass

Transparent conducting oxide (TCO) substrate used in this work was fluorine-doped tin oxide (FTO) glass. The substrate was procured from Solaronix, Switzerland. This FTO conducting glass was used as substrate for both working and counter electrodes. The properties of the TCO are as shown in Table 3.1.

Table 3.1 Properties of FTO conducting glass.

Type	Thickness	Conducting layer	Surface resistivity
TCO30-8	3.0 mm	SnO <sub>2</sub> :F	~ 8 ohm/sq.

### 3.1.2 Compact layer

A compact layer was first deposited on the conducting substrate of the working electrode. Di-isopropoxytitanium bis (acetylacetonate) solution (Sigma-Aldrich) which has been diluted with ethanol to obtain a 0.38 M solution was dripped dropwise and spin coated on the conducting surface of the TCO. Spin coating was performed at 3000 rpm for 10 seconds. The compact layer was prepared in 2 cycles of spin coating. The spin coated TCO was then sintered at 450 °C for 30 minutes. The resulting layer serves as a blocking layer for electron recombination between the electrolyte and the conductive FTO surface. It also improves adhesion of the subsequent TiO<sub>2</sub> film to the substrate [1].

### 3.1.3 Mesoporous TiO<sub>2</sub> layer

There are various types of titanium dioxide (TiO<sub>2</sub>) paste available in the market. Among the widely used TiO<sub>2</sub> pastes are supplied by JGC C&C (Japan), Solaronix (Switzerland), Dyesol (Australia) and P25 Degussa (Germany). In a separate study (not reported here), TiO<sub>2</sub> paste supplied by JGC C&C (Japan) appeared to produce a better solar cell performance when used for QD sensitization. As such, TiO<sub>2</sub> of PST-18NR as supplied by JGC C&C (Japan) was used as the wide-bandgap metal oxide in this work.

TiO<sub>2</sub> paste was deposited on top of the sintered compact layer electrode (as prepared in section 3.1.2) using the doctor blade method. 3M Scotch tape was used as the guide for depositing the TiO<sub>2</sub> paste. It had an average thickness of 60 μm. The deposited TiO<sub>2</sub> paste was then sintered at 450°C for 30 minutes. To obtain a good and uniform TiO<sub>2</sub> layer, oven temperature profile as shown in Table 3.2 was used. The

purpose of sintering process is to remove organic residues and moisture as well as obtaining a porous TiO<sub>2</sub> layer.

Table 3.2 Temperature profile for sintering TiO<sub>2</sub> layer.

Profile step	Stage	Temperature (°C)	Duration (min)
1	Ramp up	250	10
2	Stabilize	250	10
3	Ramp up	350	5
4	Stabilize	350	15
5	Ramp up	450	10
6	Stabilize	450	30
7	Cool down	25	60 - 120

## 3.2 Fabrication of QD sensitizers via successive ionic layer adsorption and reaction (SILAR)

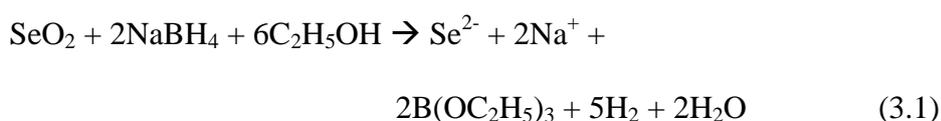
### 3.2.1 CdS QD

Two solutions were prepared in the fabrication of CdS QD via the SILAR technique. Solutions used were Cd(NO<sub>3</sub>)<sub>2</sub> in ethanol and Na<sub>2</sub>S in methanol. Cadmium nitrate tetrahydrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) was procured from Sigma-Aldrich while sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O) was obtained from Bendosen, Germany. In general, a TiO<sub>2</sub> coated electrode was first dipped into the Cd(NO<sub>3</sub>)<sub>2</sub> ethanolic solution for a defined period. The optimum period has been defined in the optimization study as reported in Chapter 4. This was followed by rinsing with ethanol and drying. The electrode was then dipped into the Na<sub>2</sub>S methanolic solution for the same defined period. The single dipping cycle was completed after rinsing with methanol and drying. The

optimum solution concentration, dipping time and cycle number are reported in Chapter 4. Upon completion of SILAR, the electrodes were sintered at 400°C for 10 minutes under nitrogen gas flow in order to obtain a homogeneous growth of the QDs.

### 3.2.2 CdSe QD

For the fabrication of CdSe QD, SILAR process was performed in a glove box filled with argon gas. The process is critical to normal atmospheric gas due to instability of  $\text{Se}^{2-}$  solution. The synthesis procedure was adapted from the work of Lee *et al.* [2]. Cationic solution was prepared by dissolving  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in ethanol. Meanwhile,  $\text{Se}^{2-}$  solution was prepared by reacting one part of selenium dioxide ( $\text{SeO}_2$ ) with two parts of sodium borohydride ( $\text{NaBH}_4$ ). All the chemicals used in this process were supplied by Sigma-Aldrich. In the preparation of  $\text{Se}^{2-}$  solution,  $\text{SeO}_2$  was reduced by  $\text{NaBH}_4$  in ethanol as shown in reaction (3.1). During the reduction process, the solution was constantly stirred for one hour. A gradual colour change from orange red to transparent was observed which indicated the reduction of  $\text{SeO}_2$  (+4) to  $\text{Se}^{2-}$  (-2).



The optimum solution concentration, dipping time and cycle number are reported in Chapter 4.

### 3.2.3 ZnS, ZnSe and ZnTe QDs

Zinc sulfide (ZnS) was applied as the last layer on the QDs which acted as passivation layer. The passivation layer helps in reducing electron recombination at the QD/electrolyte interface [3,4]. ZnS was fabricated by the SILAR technique in zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) ethanolic solution and sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) methanolic solution. SILAR was performed in 0.1 M concentration at 1 minute in both solution. In this work, 2 SILAR cycles were performed.

For the fabrication of ZnSe and ZnTe QD layer, zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in ethanolic solution was used as cationic precursor. A concentration of 0.03 M was required. This concentration was based on the optimum concentration of CdSe SILAR study as reported in Chapter 4. The preparation of anionic precursor was based on the procedure described in section 3.2.2 where  $\text{SeO}_2$  or tellurium dioxide ( $\text{TeO}_2$ ) was reduced by  $\text{NaBH}_4$ . The amount of  $\text{SeO}_2$  and  $\text{TeO}_2$  required was 0.03 M. In the case of fabricating ZnSe, 0.06 M of  $\text{NaBH}_4$  was used while for ZnTe, about 0.12 M of  $\text{NaBH}_4$  was required due to the slow reduction process. During the reduction process, the solution was stirred for about an hour (for  $\text{Se}^{2-}$ ) and 2 hours (for  $\text{Te}^{2-}$ ) respectively. SILAR was performed for 30 seconds in both cationic and anionic precursors. In the reduction of  $\text{TeO}_2$ , a light pink color solution would change to grey indicating the success of the reduction process. All the chemicals used in this procedure were procured from Sigma-Aldrich except  $\text{Na}_2\text{S}$  which was supplied by Bendosen, Germany.

### 3.2.4 Safety and precautions

Due to the toxicity of the materials used, especially  $\text{Cd}^{2+}$ ,  $\text{Se}^{2-}$ , and  $\text{Te}^{2-}$ , proper personal protective equipments such as gloves and goggles need to be worn throughout the experiment work. The material safety data sheets of the materials as provided by the suppliers should also be read and complied accordingly. In any event, laboratory safety guidelines are to be strictly adhered. All waste solutions shall not be disposed in laboratory sink. The waste solutions shall be stored in individual bottle or container with clear label and kept in a dry, designated place before being collected by third party contractor for disposal.

## 3.3 Assembly of solar cell

### 3.3.1 Cell assembly

A sandwich-type solar cell was assembled by clamping the working electrode (QD-sensitized  $\text{TiO}_2$  electrode) with the counter electrode (CE). Parafilm (130  $\mu\text{m}$  thickness) was used as spacer to prevent the liquid electrolyte from leakage. Counter electrodes were prepared by spin coating a thin layer of platinum catalyst solution on a FTO conducting glass. The platinum catalyst solution was supplied by Solaronix, Switzerland under a product named Plastisol. The spin coated electrodes were sintered at  $450^\circ\text{C}$  for 30 minutes.

Prior to the cell assembly, a few drops of polysulfide liquid electrolyte were placed on the surface of QD-sensitized  $\text{TiO}_2$  film within the aperture of the spacer. Unless otherwise specified, polysulfide liquid electrolyte for CdS QDSSC was prepared

by dissolving 0.5 M  $\text{Na}_2\text{S}$ , 2 M  $\text{S}$  and 0.2 M  $\text{KCl}$  in methanol/water (7:3/v:v) solution following the work of Lee *et al.* [5]. The optimized polysulfide liquid electrolyte for CdSe QDSSC is reported in Chapter 5. The overall architecture of the solar cell assembly is shown in Figure 3.1. The effective working area of the cell was  $0.25 \text{ cm}^2$ . During the characterization process, solar cells were monitored if there was any leakage of liquid electrolyte. The monitoring was performed via visual inspection of the liquid electrolyte contained within the parafilm spacer as well as observation of droplets formed at the edge of the cells.

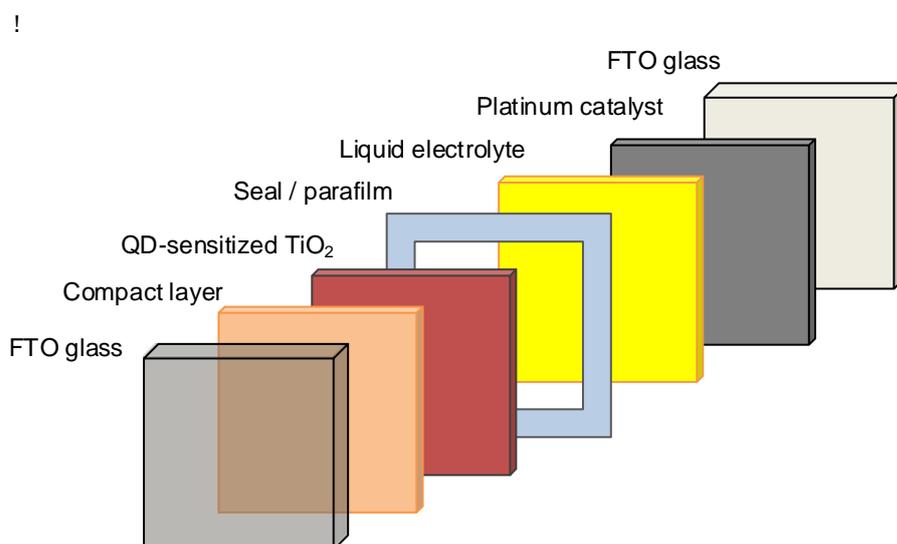


Figure 3.1 Architecture of the solar cell assembly.

### 3.3.2 Preparation of different counter electrode materials

In Chapter 6, four other types of counter electrodes (CEs) were prepared. CEs were prepared from graphite, carbon,  $\text{Cu}_2\text{S}$  and reduced graphene oxide (RGO). Graphite layer was obtained by rubbing pencil lead on the conducting glass surface. To obtain carbon layer, the conducting glass was placed over a candle flame for a few seconds so that black carbon soot formed readily on the surface.  $\text{Cu}_2\text{S}$  electrode was prepared according to the procedure given in the literature [6]. In this procedure, a brass electrode was immersed in hydrochloric acid at  $70^\circ\text{C}$  for 5 minutes and then the treated

brass was dipped into polysulfide aqueous solution (1 M Na<sub>2</sub>S and 1 M S) for 10 minutes. Upon the solution treatment, Cu<sub>2</sub>S would be formed on the brass surface as a thin black layer. To prepare CE with RGO, RGO powder (Timesnano) was suspended in the N-methyl-2-pyrrolidone (NMP) solution with 10 wt. % of polyvinylidene difluoride (PVDF). The suspension was then cast on the conducting glass and allowed to dry at 70°C.

### 3.4 Characterization

#### 3.4.1 UV-vis spectroscopy

Optical characteristics of the QD sensitized photoelectrodes were obtained with Shimadzu PC3101 UV-Vis NIR spectrophotometer. Samples were prepared on a transparent glass where the same QD-sensitized TiO<sub>2</sub> layer was deposited on the glass (without the compact layer). The wavelength response used was from 800 – 400 nm. The spectra obtained were used to assess the absorbance intensity of the QDs as well as to determine their energy band gap. QD size could also be estimated from the results. Details of the data interpretation are provided in Chapter 4.

#### 3.4.2 Surface morphology

Surface morphology of the QD-sensitized electrode was examined with field emission scanning electron microscopy (FESEM, Jeol JSM-7600F) and high resolution transmission electron microscopy (HR-TEM, Jeol JEM-2100F). Elemental analysis was performed using the EDX instrument as supplemented to the FESEM. For FESEM and

EDX analysis, samples were prepared as per usual photoanode preparation as described in section 3.2. For TEM analysis, sample was prepared by scrapping off the QD-sensitized TiO<sub>2</sub> film into an ethanol solution (~ 1 ml). The solution was then sonicated for 5 seconds so that the QD-sensitized TiO<sub>2</sub> particles were uniformly suspended. A droplet of the suspension was then placed onto a copper grid with a carbon support. The droplet was then allowed to be evaporated in air at room temperature. The prepared copper grid was then submitted for TEM viewing. The change in TiO<sub>2</sub> particle size upon sensitized by QDs could be confirmed with FESEM images while the elements of the QD materials were acquired via EDX and TEM analysis.

#### 3.4.3 Photoelectrochemical measurement

Photocurrent-voltage (*I-V*) characteristics of the QDSSCs were measured using a Keithley 2400 electrometer under illumination from xenon lamp at the intensity of 1000 Wm<sup>-2</sup>. Efficiency was calculated from the equation

$$\eta = (J_{SC} \times V_{OC} \times FF) / P_{in} \quad (3.2)$$

where  $J_{SC}$  is the short circuit photocurrent density,  $V_{OC}$  is the open-circuit voltage, FF is the fill factor and  $P_{in}$  is the power density of the incident light. *I-V* measurements for each cell were repeated three times to ensure the consistency of the data. The best result is reported in the work.

#### 3.4.4 Electrochemical impedance spectroscopy (EIS)

EIS study was performed using an Autolab potentiostat/galvanostat. EIS analysis forms an extended characterization of solar cell devices with the interpretation of the kinetics behind the solar cell mechanism. The resistance and chemical

capacitance at the interfaces within the solar cell could provide an invaluable information for understanding the solar cell performance. Measurement was performed with cells under dark and illumination. Light illumination was provided by a xenon lamp at the intensity of  $1000 \text{ Wm}^{-2}$ . Unless otherwise specified, the cells were biased at the  $V_{OC}$  of the highest cell performance with a 15 mV RMS voltage perturbation. Frequency range was  $10^6$  Hz to 0.01 Hz. The output was plotted in Nyquist plot where the curve fitting was performed on *ZSimWin* software.

### 3.5 References

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