 doi:10.20944/preprints201712.0109.v1

Efficiency of FTO/Graphene-based Dye-Sensitized Solar Cell

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Abstract

The focus of this research is to improve the performance of dye-sensitized solar cells (DSSC) through the adoption of high-quality FTO thin films and incorporation of graphene with DSSC photoanode to enhance its electrical transport. In this research, nanostructured FTO films were first grown with homemade Streaming Process for Electroless and Electrochemical Deposition technology (SPEED) using Tin (II) chloride dihydrate and ammonium fluoride and other chemical formulations. The FTO structural property was measured by X-ray diffraction (XRD); the films' optical property was determined with transmittance spectra to curve over the wavelength range of 200-1000 nm measured with a spectrophotometer while scanning electron microscope (SEM) was used to determine the morphological properties of the samples. The electrical transport was evaluated by Hall Effect measurements at room temperature with a four-point probe. The FTO samples with the best structural, optical and electrical properties were employed as electrodes and counter electrodes of DSSC along with titanium dioxide. Thus, effect of graphene on the efficiency of DSSC was investigated. It was shown that a graphene-based DSSC showed an efficiency of 7.98% which is slightly higher than that of DSSC prototype without graphene (6.02%). The higher efficiency obtained with graphene can be credited to the ultrahigh surface area and thermal conductivity of graphene which tend to enhance the charge mobility and photovoltaic performance of DSSC. More research is however required to determine the exact amount of graphene that could achieve optimal DSSC performance. Further studies will also offer an adequate clarification for starting point of the better incorporation of graphene in DSSCs.

Keywords: Graphene, Dye-sensitized solar cell, Efficiency, FTO, SPEED

Introduction

Dye-sensitized solar cell (DSSC) is widely researched due to its low cost, simple preparation techniques and non-toxic [1-2].Considerable efforts have been made so far to enhance the energy conversion efficiency, long-term stability and cost-effectiveness [3-5]of the DSSC. Efforts are still going to further enhance the performance of DSSC [1-6].

Among the DSSC components widely studied is photoanode with well optimized TCO semiconductor [7]. There are a number of factors that make TCO an excellent candidate for DSSC application. Some of them are possession of high optical transparency typically above 80% [7], possession of excellent electron transport, large band gap, stability, good conductivity and high affinity for sensitizer loading [8]. Earlier, some wide gap TCOs such as titanium oxide (TiO_2), undoped tin oxide (SnO_2) and zinc oxide (ZnO) have been having been employed as DSSC photoanode [8]. Optical and electrical properties are two important TCO requirements which cannot be easily increased simultaneously; attempt to increase optical property may degrade the electrical property [10]. Therefore, the present challenge is how optical and electrical properties could be

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increased without tradeoff of any one of them. This challenge has been overcome in this research using a promising technique known as "Streaming Process for Electroless and Electrochemical Deposition technology" commonly referred to as SPEED technique and its chemical formulation (www.sisomtf.com). SPEED is a technique which could rapidly coat a substrate with nanoparticle-based films with minimal scattering of electron carriers. Its home set up approach was employed in this research though, but the result was yet promising due to its nature of excellent chemical formulation as well as ease of optimizing multiple key controlling parameters. Previously, this technique has been employed in fabricating high-quality FTO films materials [16-17; 48-50]. Hence, it will be used in this research to grow high-quality FTO thin films for DSSC application. The resulting FTO films were then incorporated as DSSC photoanode along with TiO_2 and graphene.

Experimental

Optimization of FTO key deposition conditions/parameters

High-quality FTO films for DSSC photoanode application were first grown while optimizing the key deposition controlling parameters. One deposition parameter was kept fixed during the experiment and its effect was assumed negligible during the investigations. It is a very difficult task to adjust all parameters simultaneously and arrive at a common deposition procedure (condition) for the films. Hence to identify the best deposition conditions, each parameter was optimized individually. Table 1 shows the details of optimization of FTO key controlling parameters. These ranges of values were obtained from theories and previous researchers on FTO [16].

2.1.Preparation of FTO materials

Having achieved the best deposition conditions discussed in the previous section, high-quality FTO films were then grown from these conditions using a homemade SPEED technique (fig. 1).The FTO films have been previously grown with original SPEED technique shown in fig. 2 which is more simple, easy and quick to use.

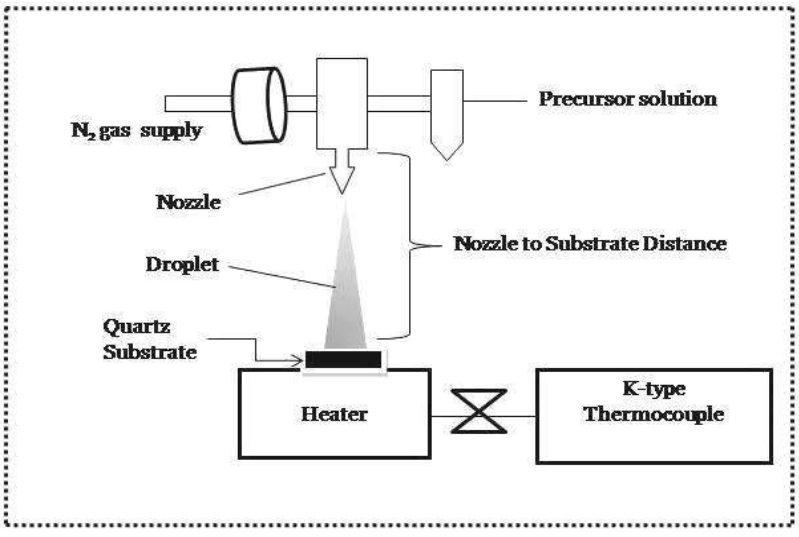

Fig. 1: Schematic diagram of homemade SPEED set up

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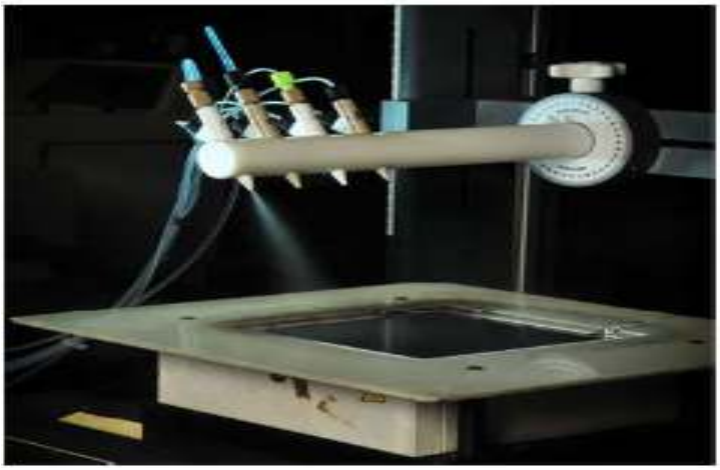

Fig. 2: Photograph of original SPEED spray head [16-18; 48-50]

The adopted chemical formulation belongs to SISOM SPEED LLC (www.sisomtf.com) [16]. Tin (II) chloride dehydrate was used as starting precursor. The precursor was doped with 50% ammonium fluoride NH_4F to enhance its electrical properties. "The precursors were dissolved in a mixed solvent of water, ethanol, isopropanol, and methyl propanol" the detail of chemical formulation and the experimental procedure can be seen in [16].The water acted mostly as solvent and oxygen source, whereas ethanol, isopropanol, and methyl propanol acted mostly as complexing agents for Sn ions. The complexing capability of the mixed solvents was used to control the solution stability and shelf life [16]. The deposition conditions adopted are shown in table 2, that is, substrate temperature (460 ^oC), flow rate (1.2 ml/min), the ratio of F/Sn (0.95atomic ratio), and the substrate to nozzle distance (SND) (30 cm) and so on.

"The precursor solution was put into droplets form by an ICP/MS nozzle, which was specified by the manufacturer to produce droplets in the size range 5 - 15 µm and these droplets were sprayed onto the heated substrate; before deposition, the 5.0 cm × 5.0 cm substrates were cleaned thoroughly with industrial soap, rinsed with deionized water followed by acetone, then rinsed again with deionized water, and hot-air dried" [16].

Table 1: Optimization of key controlling parameters

Parameters	**Range**	1	2	3	4	5	6
F/Sn atomic ratio (mole)	0-1.5	0	0.35	0.55	0.75	0.95	1.15
Flow rate ml/min	0.6-2.4	0.6	1.2	1.8	2.4		
NSD (cm)	25-32	24	27	30	33		
Water addition (%)	0-1.5	0	0.5	1.0	1.5		
Precursor qty (cm^3)	15-45	10	20	30	40		
Substrate temp(^oC)	400-500	400	420	440	460	480	500
Ageing (hours)	6-24	6	12	24			

Table 2 shows the best deposition conditions obtained after several optimization experiments and trials. These conditions were utilized to deposit high-quality FTO samples for DSSC photoanode component. This is fully discussed in the next section.

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Table 2: Parameters and deposition conditions for the best FTO material

	Parameters	Deposition conditions
1.	Starting precursor	$SnCl_4$ doped with ammonium fluoride
2.	Flow Rate	1.2 ml/min
3.	Substrate temperature	460 ^oC
4.	F/Sn concentration	0.95 atomic ratio
5.	Substrate to Nozzle Distance (SND)	30 cm
6.	Deposition Time	30 minutes
7.	Films thickness	150 nm
8.	Aging of precursor	12 hrs
9.	Pressurized	0.75 bar

Characterization of FTO film samples

X-ray diffraction (XRD) system at 2θ values from 20 to 80 degrees with 30 kV, 40 mA, Cu Ka radiation ($\lambda = 0.1540598$ nm) was employed to record the films crystallinity.

Scanning electron microscopy (SEM) was used to characterize the particle morphologies using a Zeiss Ultra 55 SEM at 5 kV.

A 5000 Digital Atomic force microscopy (AFM) Instruments model system in a contact mode was used to study surface topology.

A Perkin-Elmer Lambda 900 spectrophotometer collected transmittance spectra T over the wavelength range 200-1000 nm. The absorption coefficient was calculated according to equation 1.

$$\alpha = (1/d) \ln (1/T) \quad (1)$$

The optical band gap of the material was deduced from the absorption coefficient spectrum. The resistivity, mobility, and carrier concentration were evaluated by Hall Effect measurements at room temperature in a Van der Pauw [21] four-point probe configuration.

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Results and Discussions

FTO's optical and electrical properties

The X-ray diffraction of FTO grown with the key controlling parameters of table 1 is shown in fig. 3. The FTO film shows the most obvious reflection at (200) orientation. Other discernible orientations are 110, 211, 310 and 301 planes. This implies that the FTO film is highly crystalline with tetragonal structure [22]. Other peaks traceable to another crystal or phase are not discernible in the structure.

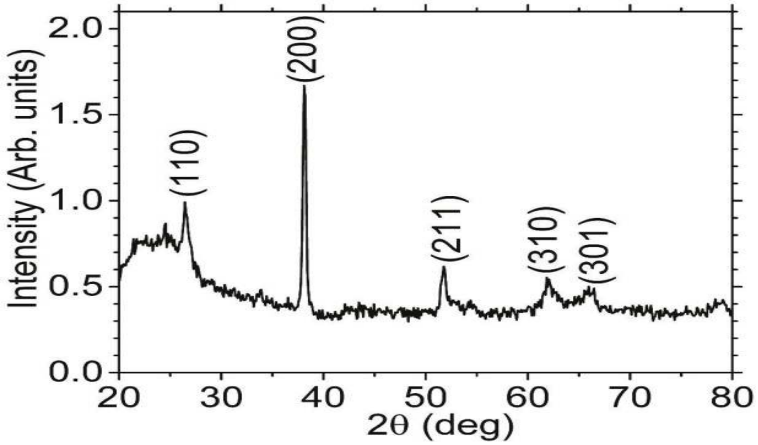

Fig. 3: X-ray diffraction of the FTO films or best FTO materials

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Fig. 4 shows the transmittance curve for FTO film deposited from the highly optimized and key deposition parameters shown in table 1. The measurement was taken in the wavelength range 250 to 1000 nm. From the scanning electron microscopy (SEM) and AFM (fig.4).This structure is appropriate for maximizing sensitizer loading of DSSC. The film microstructure is less than ~100 nm and is smaller than the wavelength, so that little scattering is expected [16]. The grain size is uniformly distributed with relatively scanty holes and voids. Fig. 4 also shows the transmittance of the FTO film. An average transmittance of 83% of FTO film taken in the visible range was measured. This value implies that the film is highly transparent in the visible-UV range. This value shows that the film is highly transparent. High transmittance is significant for DSSC in allowing the movement of incident sunlight down to the active region of DSSC photoanode [20-23].

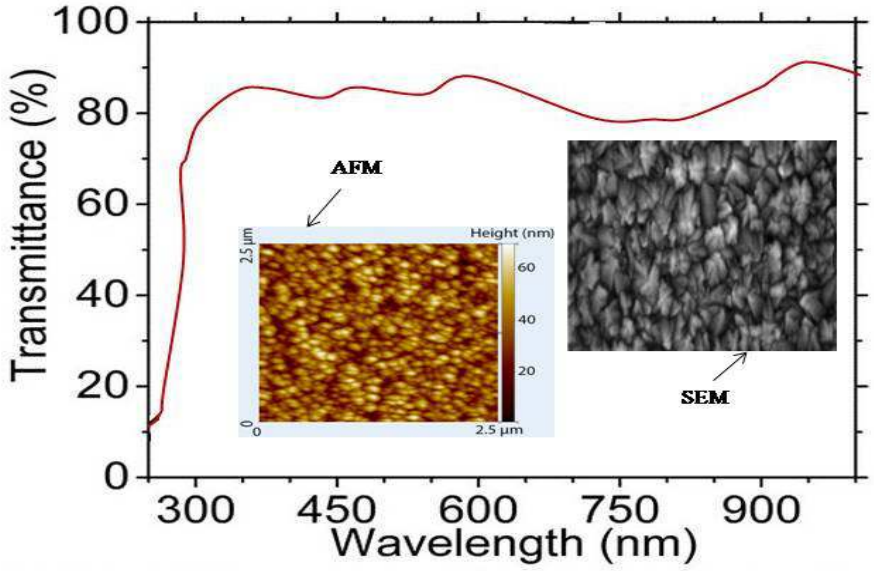

Fig. 4: Transmittance, SEM, and AFM of the FTO films

The absorption coefficient (2) is related to the incident photon energy by:

$$\alpha h\nu = C.\ (h\nu - Eg)^{1/2} \qquad (2)$$

where C is a constant, E_g band gap energy, hν is the photon energy [24]. Plotting $\alpha h\nu^2$ against hν and extrapolating the linear portion to zero gives the bandgap of 3.8eV as shown in Fig. 5. The previous band gap measure with FTO films is within the range of 3.9-4.6 eV [25].

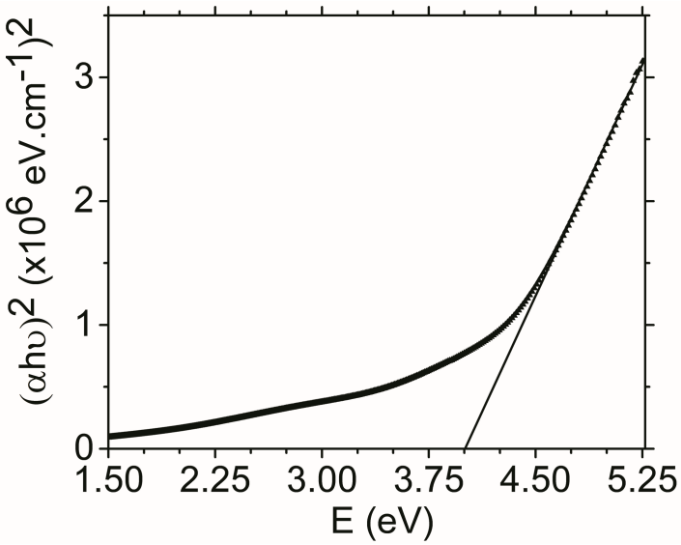

Fig. 5: Plot of $(ahv)^2$ as a function of photon energy (hv) to estimate band gap

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Electrical properties

Table 3 shows the summary of electrical properties of FTO films deposited using the key controlling parameters in table 1. The average resistivity (ρ) of 6.89×10^{-4} was achieved, Hall Effect measurement revealed a carrier concentration (n) value of 1×10^{20} (cm^{-3}) while 9.4 (cm^2/V-s) was measured as the films' election mobility (μ). These values show that the FTO film is of high quality and can be a good candidate for DSSC application as seen in the next section.

Table 3: Summary of electrical properties of the FTO samples

ρ (Ω.cm)	n (cm^{-3})	τ (%)	μ (cm^2/V-s)
6.89×10^{-4}	1×10^{20}	83	9.4

Preparation of graphene

Graphene (GR) is a material with promising photoelectric properties. It has a fast electron transfer, good charge-carrier mobility, and high conductance [26].Therefore; it is adopted here to enhance the performance of the DSSC along with the grown FTO samples. A 7:2 mixture of 98% of H_2SO_4 and phosphoric acid (82%H_3PO_4) (221:8mL) was refrigerated at a temperature of about 4°C. It was then mixed with about 3.5g of graphite flakes and 13.5g of $KMnO_4$ (97%). The detail of preparation procedure can be found in [27-28]. The solution'' temperature was controlled by cool 320ml H_2O together with 4mL hydrogen peroxide. The mixture was centrifuged at 4200 for 5hours after being washed with distilled water, hydrochloric acid (HCl) and ethanol.

To prepare the SnO_2-RGO hybrid. The glass beaker containing 85 mL DI water at 8mg of GO content was "ultrasonicated" for 3hrs after which about 1.7 g of $SnCl_2 \cdot 2H_2O$ was mixed with 220 mL of 0.12M HCl solution [27-28]. The GO dispersion was mixed with the tin (II) chloride solution and then stirred for 25 minutes. The mixtures were then reacted under 550 W for 5 minutes. The sample was then incorporated into FTO sample grown in the last section for DSSC photoanode application

Incorporation of grown FTO and graphene as photoanode

The FTO samples grown above were immersed in a 40 mM of titanium chloride at a temperature of 73°C. The mixture after being treated with FTO electrodes was coated with the SnO_2 and SnO_2-RGO pastes using a technique known as "doctor blade" [29]. A film thickness of about 16 μm was achieved with adhesive scotch tape on the FTO electrode. The optimum condition of photoanode thickness to achieve high DSSC performance is 2-16 μm [30-32]. Both photoanode and counter electrodes were prepared using the high-quality FTO coated with graphene. Another experiment was set up but this time without graphene to study the effect of graphene on the performance of DSSC. After the deposition of SnO_2 and SnO_2-RGO pastes onto the FTO substrates, the photoanode films were gradually heated under an air flow at 125°C for 30 min, followed by cooling to room temperature. For preparing DSSC counter electrode, a hole with a diameter of 7 mm was drilled on the FTO. Then the FTO glass was washed as described above for FTO working electrode but instead for 6 min. The FTO was heated to 470 °C for 15 min. Electrolyte iodolyte R-150 was introduced drop by drop through the one side of the two small holes, thereafter, the edges of the two holes were cleaned with acetonitrile and the holes were then sealed with 50:50 amoxil A and B gum, let dry at room temperature. Silver paint was applied on the conducting side of each electrode to ensure optimal electrical connections or contact [33]. The active area was 4.55cm^2. Fig. 6 shows the assembled DSSC solar cells. The effect of graphene incorporation on the photoanode was repeated using photoanode with FTO only (no graphene incorporation). The efficiency of both experiments was calculated using I-V characterization discussed in the next section.

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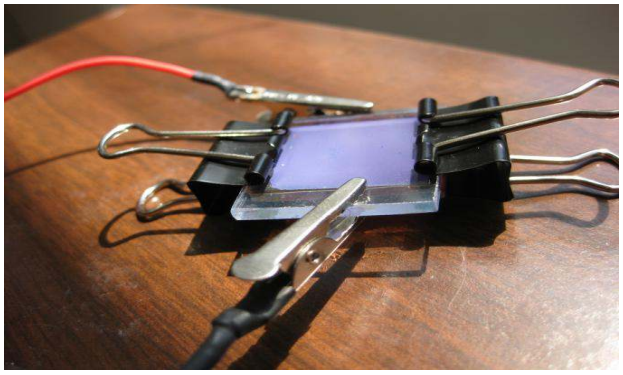

Fig. 6: Images of the DSSCs prototype with TiO_2 and FTO electrodes

Measurement of DSSC efficiency

"The I-V characteristics were recorded by varying an external potential compensating the photovoltage. The integral photocurrent (short-circuit current) was obtained without the external potential. The photoelectric efficiency was calculated with respect to the solar spectra through a calibration of the Light Drive 1000 lamp with direct sunlight" [34].

The overall efficiency η of a photovoltaic cell was calculated from the expression:

$$\eta = \frac{J_{Sc}V_{oc}FF}{P_s} \text{ or } \frac{P_{out}}{P_{in}} \quad (4)$$

where J_{sc} is the integral photocurrent density (current obtained at the short-circuit condition, divided by the area of the cell), V_{oc} is the open circuit voltage, P_s is the intensity of the incident light. FF is the fill factor (related to the series resistance for a practical solar cell) and was obtained from equation (4).

$$FF = \frac{I_{MP}.V_{MP}}{I_{SC}.V_{OC}} \quad (5)$$

The parameters I_{MP}, V_{MP}, I_{SC}, and V_{oc} were obtained from fig. 7 which illustrates the current-voltage characteristics of the prepared DSSC sample with graphene-based FTO and FTO only. Using the information in fig. 7 for the calculation of efficiency, an energy conversion efficiency of 7.98 % at 100 mW/cm^2 light intensity is obtained with graphene incorporated DSSC while the energy conversion of 6.02% was obtained with only FTO (no graphene incorporation). The difference in efficiency is significant and depicts an improvement in the performance of DSSC. While some reports emphasize that there have not been an acceptable explanation and theories on graphene enhancing role in DSSC, [35] asserted that the enhancement may be attributed to the ultrahigh theoretical surface area of 2600 m^2/g and high thermal conductivity of 5×10^3 W/m K of graphene which allows for perfect electron mobility.

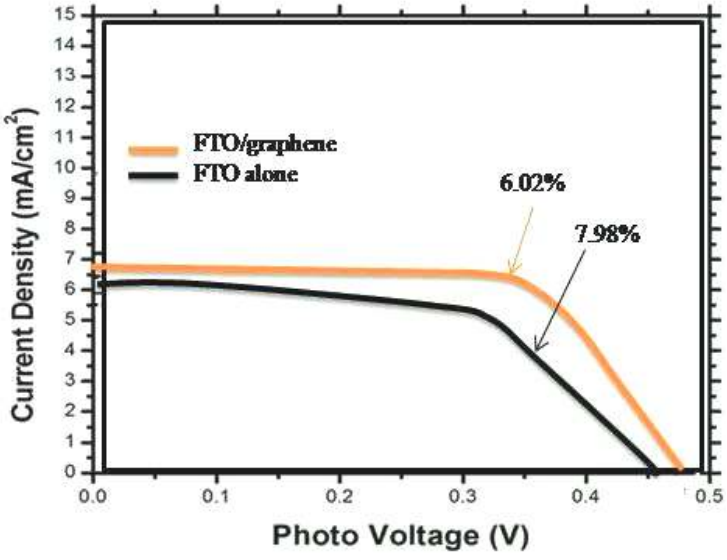

Fig. 7: Current-voltage of both FTO/graphene and FTO alone photoanode

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Furthermore, [41-42] opined that there are many grain boundaries in TiO_2nanoparticle, leading to faster charge recombination at the TiO_2/electrolyte interface. Therefore, low dimensional materials such as carbon nanostructures (carbon nanotube (CNT)) and graphene sheets incorporated into semiconductor electrodes could improve the charge collection and photovoltaic performance of DSSC [43-44].This is because they possess band gaps which could align with those of TiO_2 and FTO to produce a more efficient pathway for collection and transport of photogenerated electrons [45-46]. This may be responsible for the increase in performance in graphene-based DSSC in this research.

Conclusion

This research has demonstrated that incorporation of graphene into DSSC and the usage of high-quality FTO thin films could jointly enhance the DSSC efficiency. High-quality FTO thin film samples were first grown with homemade SPEED technique using Tin (II) chloride dihydrate and ammonium fluoride as starting precursors. The first FTO sample (photoelectrode and a counter electrode) was prepared with graphene along with TiO_2 while the second FTO samples without graphene were used as a control. The graphene-based DSSC showed an efficiency of 7.98% whereas the DSSC fabricated without graphene showed a lower efficiency of 6.02%. The higher efficiency obtained when graphene was incorporated could be attributed to the ultrahigh surface area and thermal conductivity of graphene which tend to enhance the charge mobility and photovoltaic performance of DSSC. More research is however required to determine the exact amount of graphene that could achieve optimal DSSC performance. Further studies will also offer an adequate clarification for starting point of the better incorporation of graphene in DSSCs.

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