



Improving performance and stability in quantum dot-sensitized solar cell through single layer graphene/Cu₂S nanocomposite counter electrode

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ABSTRACT

In this work, we presented an effective nanocomposite to modify the Cu₂S film by employing single layer graphene (SLG) frameworks via chemical vapor deposition, and utilized this nanocomposite as counter electrode (CE) with CdSe/ZnS core/shell quantum dots for highly stable and efficient quantum dot-sensitized solar cell (QDSSC). Furthermore, Cu₂S film is directly synthesized on SLG framework by electrodeposition method. Using this nanocomposite as CE, we have achieved the high efficiency as high as 3.93% with fill factor of 0.63, which is higher than those with bare Cu₂S CE (3.40% and 0.57). This remarkable performance is attributed to the surface area enhancement by creating nanoflower-shape, the reduction of charge transfer resistance, improvement of catalytic stability, and the surface smoothness as well as good adhesion. More importantly, no visible color change and detachment from surface for the Cu₂S@SLG nanocomposite was observed, demonstrating that the SLG framework is critical role in shielding the Cu₂S structure from sulphur ions into electrolyte, and increasing the adhesion of the Cu₂S structure on surface, thus preventing its degradation. Consequently, the Cu₂S@SLG nanocomposite can be utilized as an effective agent to boost up the performance of QDSSCs.

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1. Introduction

Quantum dot-sensitized solar cells (QDSSCs) have attracted considerable attention in recent years, owing to their tunable band gap, low-cost, easy-fabrication procedure and high theoretically reported power conversion efficiency (PCE) up to 44% [1]. The photoelectrochemical mechanism of QDSSCs exhibits similar behavior to dye-sensitized solar cells (DSSCs), in which the QDs is used instead of the dye molecules as a light absorber layer in QDSSCs [2]. Typically, QDSSC is assembled by a quantum dots-

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sensitized photoanode film, an electrolyte with the inclusion of a redox couple (i.e. S²⁻/S_x²⁻) and a counter electrode (CE) (i.e. Pt, and Cu₂S) [1–3]. Despite these advantages, however, the photovoltaic performance of most QDSSCs is still much lower than those obtained from DSSCs. In order to improve the cell performance, till date many research work has focused on optimizing all the components in QDSSCs. Since one of the main reasons for low efficiency is the loss at electrolyte-counter electrode interfaces, particularly the research efforts have concentrated on the development of compatible CEs for achieving simultaneous high efficiency and stable cells.

Therefore, CEs are amongst the most critical components of the DSSCs since they are utilized to collect charge carriers from the external circuits and provide the reduction of redox electrolyte.

Although platinum (Pt) has a considerably high electrocatalytic activity for iodide/triiodide redox couple in DSSCs [4–9], the utilization of this material in QDSSCs was not successful, as the adsorption of the sulfur on their surface leads to an increment of overpotential, the inefficient interface catalytic activity and low conductivity [10,11]. These factors result in lower current density and fill factor for the QDSSCs [12]. It is therefore necessary to search for alternative Pt-free materials compatible with polysulfide electrolyte as new CEs to further enhance the performance of QDSSCs. Till date, researchers have paid great effort in seeking alternative CE materials compatible with polysulfide electrolytes, such as Cu_xS [13,14], Cu_2S [15,16], CoS [17], PbS [18], Bi_2S_3 [19] and $\text{Cu}_2\text{ZnSnS}_4$ [20]. Among these materials, Cu_2S CEs on brass foil exhibit the highest electrocatalytic activity for reduction of polysulfide species in QDSSCs [1]. Although it appears to be the most effective material in QDSSCs, their charge carrier mobility and stability were not satisfactory, which is mainly due to the fact that the continual corrosion caused by the reaction with sulfide/polysulfide electrolyte over a long time period [21–24].

To avoid the aforementioned problems, the use of fluorine-doped tin oxide (FTO) conducting substrates has started instead of copper brass substrate to produce Cu_2S film. However, these substrates suffer from low electrical conductivity since Cu_2S has a poor conductivity. Therefore, it is of critical importance to attain high catalytic activity and conductivity by modified Cu_2S with conductive agents [25]. Recently, there has been a prominent trend of preparing composite CEs composed of graphene and Cu_2S to enhance the catalytic activity, efficiency and stability of QDSSCs. In 2011, such composite CE based on reduced graphene oxide (reduced-GO)- Cu_2S was reported by Kamat and co-workers, the corresponding properties were investigated [23]. In 2014, CEs composed of Cu_2S microspheres wrapped in reduced-GO nanosheets were introduced using solvothermal process [1]. In 2016, Hessein's group reported hybrid Cu_xS /reduced-GO CEs using the one-pot hydrothermal method [22]. Recently, reduced-GO/ Cu_2S composites have been presented to enhance the CE quality of the QDSSCs [25]. Although it is quite obvious that the composite CE possess remarkable electrocatalytic activity and stability, but the efficiency and the fill factor of these CEs still need to improve. In addition, from the industrial point of view, reduced-GO-based CEs require complex manufacturing routes; therefore they are not wisely attractive for mass production. Moreover, there are no reports yet focused on single layer graphene (SLG) grown by chemical vapor deposition (CVD) and Cu_2S composite material and their integration into CEs in QDSSCs. Comparing with other graphene-based materials, particularly, the multidirectional structure of CVD-grown SLG lead to many perfect performances, such as a large theoretical specific surface area, high-mechanical and thermal properties, corrosion resistance, a huge intrinsic electron mobility and excellent optical transmittance [26,27]. Therefore, we attempted to employ the CVD-grown as interlayer at Cu_2S /FTO interface due to the high surface area of the SLG, and thereby preventing Cu_2S detachment from substrates and passivating sulfur atoms. We speculate that this event has contributed performance and stability of QDSSCs.

In this work, for the first time, we have developed a one-step, highly stable, and electrocatalytically active Cu_2S @SLG nanocomposite CE on FTO substrate by a facile and scalable electrochemical method for CdSe/ZnS core/shell quantum dots based solar cells. Conductive SLG sheets act as a matrix to support Cu_2S nanoparticles, preventing their self-aggregation, which provides an increment of surface area with more active polysulfide reduction sites. Outstanding photovoltaic performance, a remarkably high PCE of 3.93% and FF of 0.63 was recorded in the case of using Cu_2S @SLG CE with excellent photostability under continuous

operation. This significant photostability was ascribed to the comprehensive coverage of the Cu_2S nanoparticles with the SLG sheets, which is critical in protecting them from the polysulfide electrolyte corrosion.

2. Experimental methods

2.1. Synthesis of CdSe/ZnS core/shell quantum dots

Red-emitting CdSe/ZnS core/shell QDs are synthesized by modifying previously reported synthesis recipe [28–30]. Oleic acid (5 mL), Zn-acetate dihydrate (1.68 mmol) and CdO (1 mmol) chemicals are introduced 4-necked flask with a magnetic stirrer. Three times consecutive degassing with Ar-gas is successively applied to the reaction flask to remove impurities. The reaction vessel is heated to 140 °C and kept for 45 min at this temperature. Then, the flask is cooled to 50–60 °C and octadecene (25 mL) is injected into the solution under gas flow. After injection, the temperature of the solution is increased to 90 °C under vacuum, and then heated to 300 °C under Ar-gas atmosphere. 1M TOP-Se precursor (0.2 mL), which is prepared in glovebox, is swiftly injected into the flask under strong stirring and kept at this temperature for 80 s. After addition of 1-dodecanethiol (300 μL) in the solution, the system was kept for 20 min at 300 °C. At the end, 2 M TOP-S (1 mL) is injected slowly into the system and kept for 10 min. The solution is quickly cooled down using water bath. Hexane (5 mL) is added at 50 °C into the flask and the solution is centrifuged at 5000 rpm. Precipitate is discarded and ethanol added supernatant is precipitated with 5000 rpm for 10 min. Finally, the precipitate is dispersed in hexane.

2.2. Ligand exchange procedure from organic to water phase

Phase transfer from organic phase to water phase has been carried out by using ligand-exchange protocol which is a modified recipe from the literature [31] by using 3-mercaptopropionic acid (3-MPA) as follows:

As synthesized CdSe/ZnS QDs sample was cleaned two times with the mixture of acetone and methanol. Cleaned QDs were dispersed in 10 mL of fresh hexane and concentration of the sample was adjusted to 30 mg/mL, 40 mL of DI water and 15 mL of NH_4OH solution were added on CdSe/ZnS QDs and stirred at room temperature for 3 h. Following, 540 μL of 3-MPA was added on the mixture and kept overnight to realize ligand-exchange procedure efficiently with 3-MPA on the surface of the NCs. Then, the mixture was precipitated and cleaned with ethanol with the volume ratio as 4:1 (ethanol: mixture). The precipitate was dissolved in DI-water and used for device fabrication.

2.3. Synthesis of single layer graphene by chemical vapour deposition (CVD) and Cu_2S by electrochemical deposition technique

In briefly, SLG structures were deposited on polished Cu foils (1.5 \times 1.5 cm^2 area and 25 μm thickness) by MTI OTF-1200 CVD system at 1000 °C, with gas mixture of CH_4 and H_2 (1:2 ratio) for 5 min. After that, SLG films on Cu foils were transferred on the F:SnO₂-coated (FTO) glass substrate (Asahi Glass, sheet resistance: 15 sq^{-1}). Prior to transfer, the FTO substrates were rinsed in an ultrasonic bath for 15 min with pure water, ethanol, acetone and again with pure water, respectively, and then dried by nitrogen flow. The transfer process was carried out by standard poly(methyl methacrylate) (PMMA) process. PMMA film was spin-coated on the SLG/copper foil, and the copper foil was removed by a FeCl_3 etchant. After that, the stack of SLG on PMMA was repeatedly washed by transferring to DI water. Washed FTO substrate was then placed on

top of the stack, lifted from the DI water on a piece of paper, and dried with nitrogen gas flow. Finally, the PMMA was etched by gentle soaking in acetone for 60 min and rinsed with isopropyl alcohol (IPA), and the resultant SLG/FTO sample dried at 60 °C in vacuum furnace for 30 min.

We utilized and modified the electrochemical deposition growth recipe reported by Xu et al. for Cu₂S CE on SLG framework [32]. In a standard synthesis, 3 mmol of Cu(NO₃)₂ and 3 mmol of NaNO₃ were mixed in 60 mL of DMSO. Later, 1.8 mmol of powder sulfur was slowly introduced into the solution. The sulfur was dissolved at 80 °C temperature and was kept at this level during the deposition process. The electrodeposition process was carried out with a potentiostat at −1.05 V under continuous stirring by using three electrode setup which includes Pt stick as CE, Ag/AgCl as reference electrode and SLG/FTO as working electrodes, respectively. After the deposition, prepared films were washed with once hot (at 50 °C) dimethyl sulfoxide (DMSO) and later with ethanol several times. As the last stage, prepared films were dried in vacuum furnace at 80 °C for 1 h.

2.4. Fabrication of CdSe/ZnS QDs sensitized solar cells

Mesoporous TiO₂ film was fabricated according to the previous report [33]. TiO₂ films were prepared using doctor-blading the TiO₂ paste on pre-cleaned FTO-glass. The film was then sintered at 500 °C for an hour for both the removal of the impurities and improving the crystallinity of the film. Then, synthesized CdSe/ZnS QDs were coated to the mesoporous TiO₂ films via drop wise by keeping 18 h under dark conditions. The polysulfide electrolyte was prepared by dissolving sulfur (1M) and sodium sulfide (1M) in DI water:methanol (v:v of 1:3 ratio) before each test. Cu₂S and Cu₂S@SLG CEs based solar cells were assembled using photoanodes, CEs and electrolyte as our previous report [33]. The electrolyte was synthesized freshly for each measurement.

2.5. Characterization

Photoluminescence (PL), absorption, structural and Fourier Transformation Infrared (FTIR) properties of CdSe/ZnS core/shell QDs were characterized by Agilent-Cary Eclipse fluorescence spectrophotometer, UV-Vis spectrometer (Thermo Genesys 10S), transmission electron microscope (TEM) (FEI Tecnai G2 F30) and Thermo Scientific Nicolet-6700 spectrometer, respectively. Structural properties of SLG films on FTO, Cu₂S and Cu₂S@SLG films were investigated by Renishaw-INVIA Reflex confocal Raman microscopy. TEM image and selected area X-ray diffraction (XRD-SAED) pattern of SLG were obtained by transferring SLG film on Ted pella 300 mesh copper grid. XRD patterns of Cu₂S CE were obtained using Bruker D8 advance with DAVINCI. Morphological properties of CEs were investigated using Tescan MAIA3 XMU model scanning electron microscope (SEM). Furthermore, elemental composition of Cu₂S film investigated by means of electron dispersive X-ray (EDX) spectroscopy, by using an attachment of SEM instrument. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) studies of CEs were conducted with potentiostat/galvanostat system (Ivium-compact Stat). The (J-V) curves of QDSSCs were measured with sourcemeter (Keithley 4200) under a standard solar irradiation of 300 W m⁻² (Xe lamp with AM 1.5 filter). The wavelength-dependent incident photon to charge carrier efficiency (IPCE) was recorded by Enlitech QE-R equipped with a 75 W xenon arc lamp source. We further monitored the on-off plots of QDSSCs in chronoamperometry mode by alternately irradiating at 30 mW cm⁻² and darkening the device for 180 s.

3. Results and discussions

Water-soluble CdSe/ZnS QDs were obtained by ligand-exchange procedure as described in Synthesis part. Average size of the QDs is about 6.2 nm which is calculated from TEM image as shown in Fig. 1A. Absorbance and (PL) spectra of the sample were given in Fig. 1B. Peak emission wavelength and FWHM of the synthesized water-soluble QDs are 613 nm and 31 nm, respectively. Quantum yield of the water-soluble CdSe/ZnS QDs were measured as 21% by relative QY measurement technique with Rh-6G.

Fig. 1C shows FTIR spectra of the 3-MPA-capped CdSe/ZnS core/shell QDs. The strongest band of absorption in the FTIR spectra was located at 3222 cm⁻¹ and this band indicates the presence of -OH vibrations in 3-MPA. FTIR spectra of the pure 3-MPA has S-H absorption band at around 2568 cm⁻¹, which totally disappeared in 3-MPA-capped CdSe/ZnS QDs due to the bonding and coordinating of thiol group (-SH) on the QD surface [34,35]. Absorption peak at 1566 indicates C=O vibration. IR absorption bands of carboxyl group C-H vibrations observed at 2922–2851–1377 and 1404 cm⁻¹ [34–36]. All these IR absorption bands of 3-MPA-capped CdSe/ZnS core/shell QDs confirm that ligand exchange procedure successfully carried out by using 3-MPA.

To ascertain the overall quality of the SLG present on the FTO substrate, Raman maps were achieved from a (45 × 30 μm²) of the graphene surface. The scaled Raman maps of D, G, 2D bands and I_{2D}/I_G ratio are exhibited in Fig. 2(A–D), respectively and corresponding to marked spots (circle, square and hexagonal), the characteristic graphene Raman spectra with D (~1340), G (~1580 cm⁻¹) and 2D (~2675 cm⁻¹) bands were demonstrated in Fig. 2E. The Raman spectra from all spots (Fig. 2E) shows characteristic features of SLG: (i) a ~2.5 intensity ratio of 2D-to-G (ii) a symmetric 2D band centered at ~2675 cm⁻¹ with a full width half maximum (FWHM) of ~35 cm⁻¹ [37,38]. Furthermore, as shown in Fig. 2D, 2D-to-G ratio, which is above 2.5 over the whole surface, indicating the excellent quality and homogeneity of SLG film grown by CVD method on Cu foil and transferred to FTO substrate [39,40]. On the other hand, the Raman map of D band, which gives an idea about the defect levels in graphene, is uniform and close to the background signal, demonstrating that graphene films with larger domains possess a lower density of defects stem from nucleation centers or interdomains [41]. Moreover, as shown in Fig. 2E, the intensity of the D band is very low (for circle and square spots is absent) relative to intensity of 2D and G bands for all marked spots, showing that SLG structures have low defects and high quality in whole film.

The SEM image of SLG on FTO substrate is given in Fig. 2F. This figure clearly shows the boundary of the SLG. The higher-resolution SEM image shows the presence of SLG in Fig. 2F inset. The Fig. 2(G and H) show TEM image and SAED patterns of SLG film transferred to carbon-coated copper grids (Ted Pella), respectively. The TEM measurement shows that the as-obtained graphene sheets have a relatively smooth and planar structure (Fig. 2G), similar to that obtained by micromechanical cleavage and consist of up to a very large part SLG. Furthermore, one can see from the Fig. 2G there is no contrast difference in whole TEM image, confirming that the graphene formed as a single layer [42]. The bottom right reveals its SAED pattern (Fig. 2H), showing a characteristic split dot set from a SLG sheet. In addition, multiple hexagonal diffraction patterns appear to indicate a wide range of dimensions of the parts forming the SLG film. The direct TEM imaging is fairly consistent with Raman results.

To investigate structural properties of Cu₂S and Cu₂S@SLG CEs, XRD and Raman measurements have been carried out. In Fig. 3A, the good match of the diffraction peaks of Cu₂S and the standard (JCPDS 26-1116) is presented. XRD pattern does not possess any

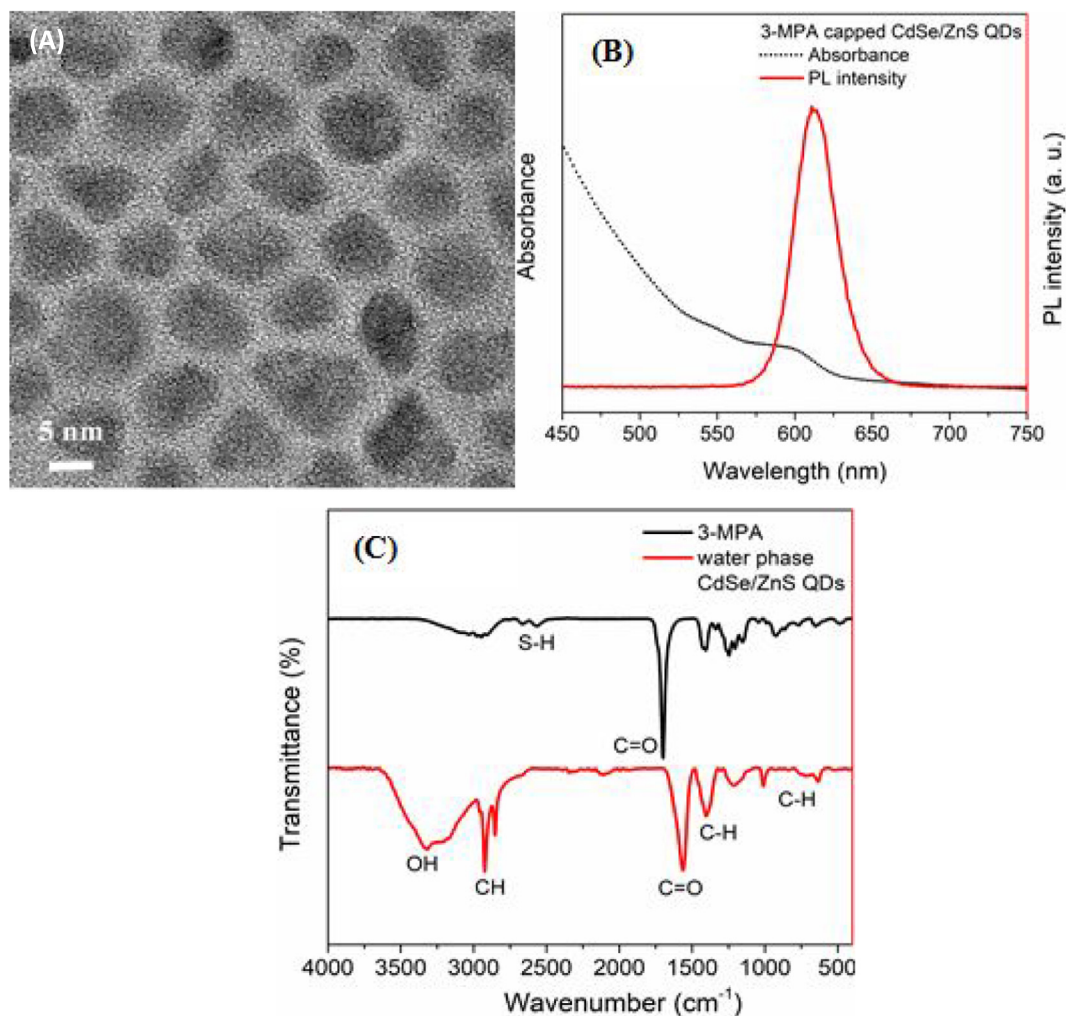


Fig. 1. (A) TEM images of the QDs (B) PL and Abs spectra of the water-soluble CdSe/ZnS core/shell QDs (C) FT-IR spectra of the pure 3-MPA and water phase 3-MPA-capped CdSe/ZnS QDs.

peaks from the bulk sulfur, which represents the formation of pure nanoparticles of chalcocite Cu_2S [43]. Furthermore, the crystallite size of the Cu_2S is calculated by determining the FWHM of main diffraction peak with Debye–Scherrer equation as ~ 14 nm. Fig. 3B shows the Raman spectra of the typical Cu_2S and $\text{Cu}_2\text{S@SLG}$ films. This study revealed the Raman peaks of Cu_2S and $\text{Cu}_2\text{S@SLG}$ are strong and sharp band at ~ 469.3 and 471.5 cm^{-1} , which are in accordance with the results reported for Cu_2S [44,45]. As exhibited in Fig. 3B, by Cu_2S particles growing uniformly on the surface of SLG, Raman peak centered at 469.3 cm^{-1} shift to 471.5 cm^{-1} (up-shift), confirming that the interaction between Cu_2S crystal nucleus and carbon-oxygen groups of SLG structures [46,47]. This interaction proves that adhesiveness and electrical properties of Cu_2S film will improve.

To understand the effects of SLG on morphological properties and growth mechanism of the Cu_2S into composite matrix, SEM analyses were carried out. As demonstrated in Fig. 3C, while Cu_2S CE exhibits nanoparticles morphology, after incorporation of SLG into nanocomposite system the morphology changed to nano-flowers with the diameter of 0.5 – 0.7 μm . In the nanocomposite structure, copper and sulphur ions may accelerate immediately due to the excellent conductivity of SLG layer, resulting in fast and multiple nucleation of Cu_2S at the initial stage of the crystal growth [48,49]. Furthermore, every nucleus can grow up vertically along its

orientation and consequently many of the growth orientations may have shaped flower-like 3-dimensional (3D) Cu_2S nano-architectures [50,51]. This change in morphology brings many advantages for $\text{Cu}_2\text{S@SLG}$ nanocomposite film in CE applications. First, flower-like nanoarchitecture can provide larger surface area compare with particulate, leading to a larger interface contacting with the liquid electrolyte [52]. Second, flower-like nanoarchitecture can be expected as an effective charge transfer network facilitating the accumulation of the charge carriers from the external circuit and transfer of the charge carriers to liquid electrolyte, resulting in higher current density. Third, nanoflower-like CE with especially large surface area can decrease the charge transfer resistances and accelerate the diffusion of the liquid electrolyte, which are the responsible factors for the QDSSC performance [53]. Therefore, the CEs are expected to make an effective contribution to the performance of the QDSSCs. Furthermore, the composition of the electrodeposited Cu_2S nanostructure was investigated with EDX analysis. As shown in the Fig. 3E, the atomic ratio of Cu element is approximately being twice (~ 1.9) higher than that of S element, indicating that Cu_2S structure successfully synthesized by electrodeposition method.

The J–V characteristics of QDSSCs are shown in Fig. 4A and photovoltaic performance of QDSSCs were outlined in Table 1. As presented in Table 1, the open-circuit voltage (V_{oc}) values of the

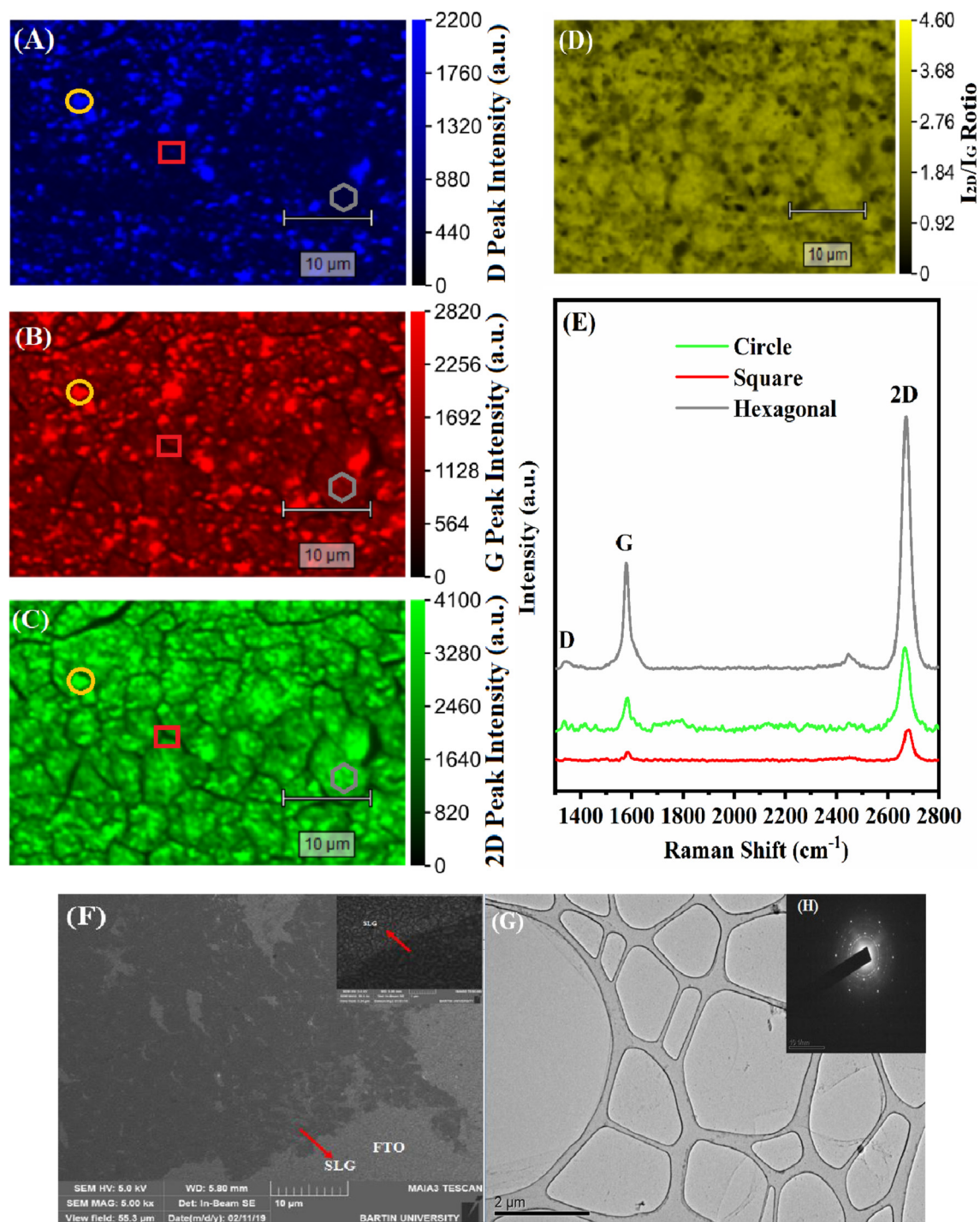


Fig. 2. (A–D) Raman maps of the D, G, 2D bands and I_{2D}/I_G ratio, respectively. (E) Raman spectra from the marked spots with corresponding colored geometrical shapes. (F) SEM image and (G) TEM images (H) SAED patterns of SLG structure.

resultant cells are nearly same with QDSSCs. Generally, V_{oc} is limited by the quasi-Fermi level of quantum dots sensitized TiO_2 and redox potential of electrolyte. In accordance, the QDSSC fabricated with $Cu_2S@SLG$ CE possesses an overall efficiency (η) of 3.93%, which was much higher than that of Cu_2S CE, 3.40%. The increased PCE is primarily derived from the improvement of fill factor (FF) values combine with SLG material. This is attributed to the increment of charge transfer with conductively for $Cu_2S@SLG$ CEs [54]. The obtained from the J–V curves, the short-circuit

current density (J_{sc}) of 3.74 mA/cm^2 was obtained with $Cu_2S@SLG$ CE in the QDSSCs. This value was slightly greater than this obtained Cu_2S CE ($J_{sc} = 3.58$ mA/cm^2).

As shown in Fig. 4B, the incident photon-to-current efficiency (IPCE) spectra were measured different photovoltaic performance of these two CEs between 350 and 700 nm wavelength regions. The IPCE value of $Cu_2S@SLG$ based QDSSC at the wavelength region of 350–700 nm was about 45%, which was higher than Cu_2S QDSSC. This result agrees with the current density values of QDSSCs

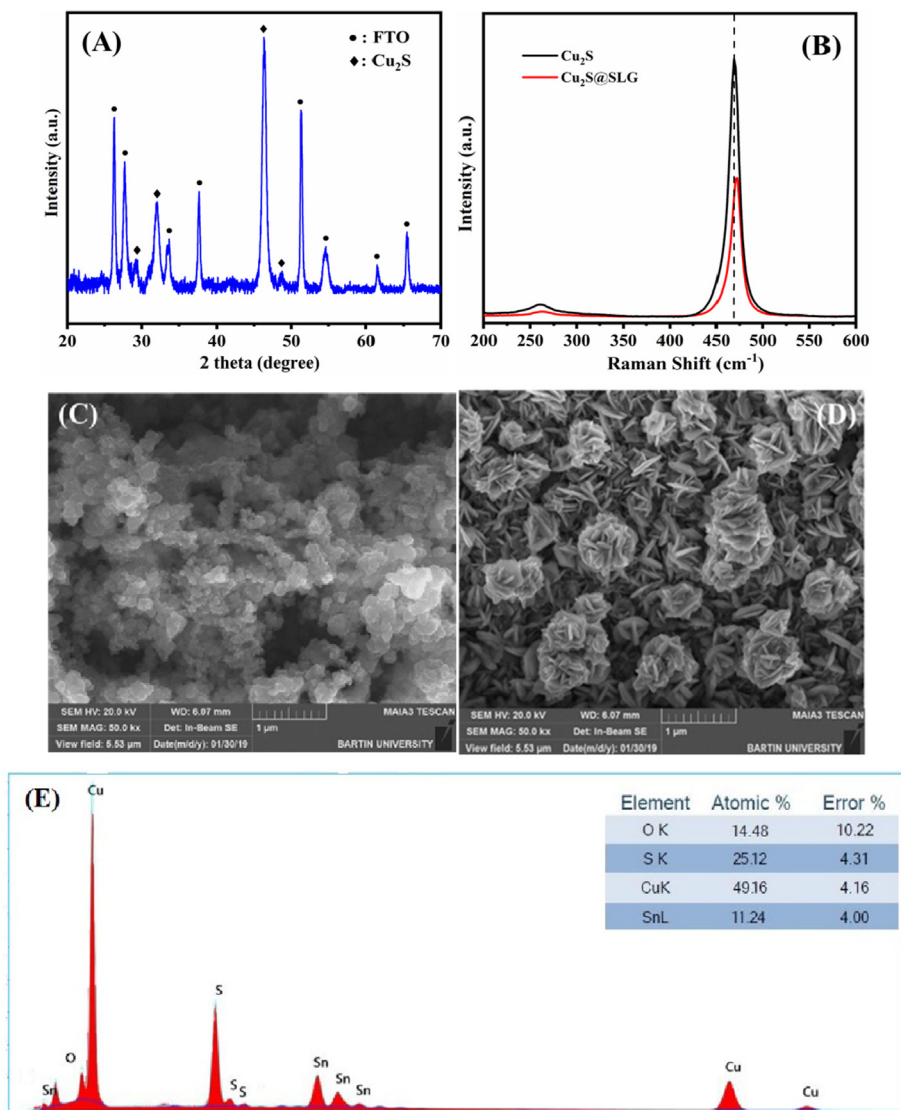


Fig. 3. (A) XRD pattern of Cu_2S on FTO substrate, (B) Raman spectra of Cu_2S on FTO substrate, (C) SEM images of Cu_2S film, (D) SEM images of $\text{Cu}_2\text{S}@$ SLG nanocomposite films and (E) EDX of Cu_2S film.

presented (see Table 1). We can also infer from here that the $\text{Cu}_2\text{S}@$ SLG layer and the FTO substrate have a better contact at their surface.

We have further conducted EIS measurements to monitor the catalytic activity of the CE, with a symmetrical cell constructed with two CEs (Cu_2S and $\text{Cu}_2\text{S}@$ SLG). The equivalent circuit, including the series resistance (R_s), charge transfer resistance (R_{CT}) and interfacial capacitance (C), and resultant EIS plots of these different CEs are shown in Fig. 4C. The EIS parameters are outlined in Table 1. At the low-frequency, the charge transfer resistance (R_{CT2}), estimated by measuring the radius of second semicircle, give us information about CE/electrolyte interface. The R_{CT2} values of the Cu_2S and $\text{Cu}_2\text{S}@$ SLG electrodes were 57.9 and 42.5 Ω , respectively. It clearly indicates that the $\text{Cu}_2\text{S}@$ SLG CE has lower value of charge transfer resistance than Cu_2S CE. The fact that lower value of charge transfer resistance reflects the superior charge transfer and electrocatalytic ability at the CE/electrolyte interface [54]. The meaning difference is largely because the existence of SLG in $\text{Cu}_2\text{S}@$ SLG composite can serve as a structure to firmly hold the Cu_2S nanostructure which also act as an efficient channel to transport charges which provided

the improvement of electrocatalytic activity of $\text{Cu}_2\text{S}@$ SLG electrode [1,23]. To examine the electrochemical catalytic activity of Cu_2S and $\text{Cu}_2\text{S}@$ SLG CEs in polysulfide electrolyte, CV was performed, as shown in Fig. 4D. The relative catalytic activity of the obtained CEs can also be understood from the CV curve, by focusing on current density peak value. The negative current is attributed to the reduction reaction of Sn^{2-} to S^{2-} , and the positive current is attributed to the oxidation of S^{2-} in electrolyte [55,56]. The value of reduction peak current density (J_{red}) of $\text{Cu}_2\text{S}@$ SLG CE is slightly higher than that of Cu_2S CE. As compared to the conventional Cu_2S CE the proposed $\text{Cu}_2\text{S}@$ SLG CE structure has provide highly superior electrochemical stability and enhanced corrosion resistance [1,57]. Besides, one can see from Fig. 4D, $\text{Cu}_2\text{S}@$ SLG CE possesses a lower peak-to-peak potential (E_{pp}) value than that of Cu_2S CE, exhibiting superior electrocatalytic activity of $\text{Cu}_2\text{S}@$ SLG CE compare to Cu_2S [58].

The fast start-up and multiple start/stop cycling of QDSSCs are important to understand their photostability. In order to examine the repeatability of the device, photo-response study has been analyzed by chronoamperometry technique under light

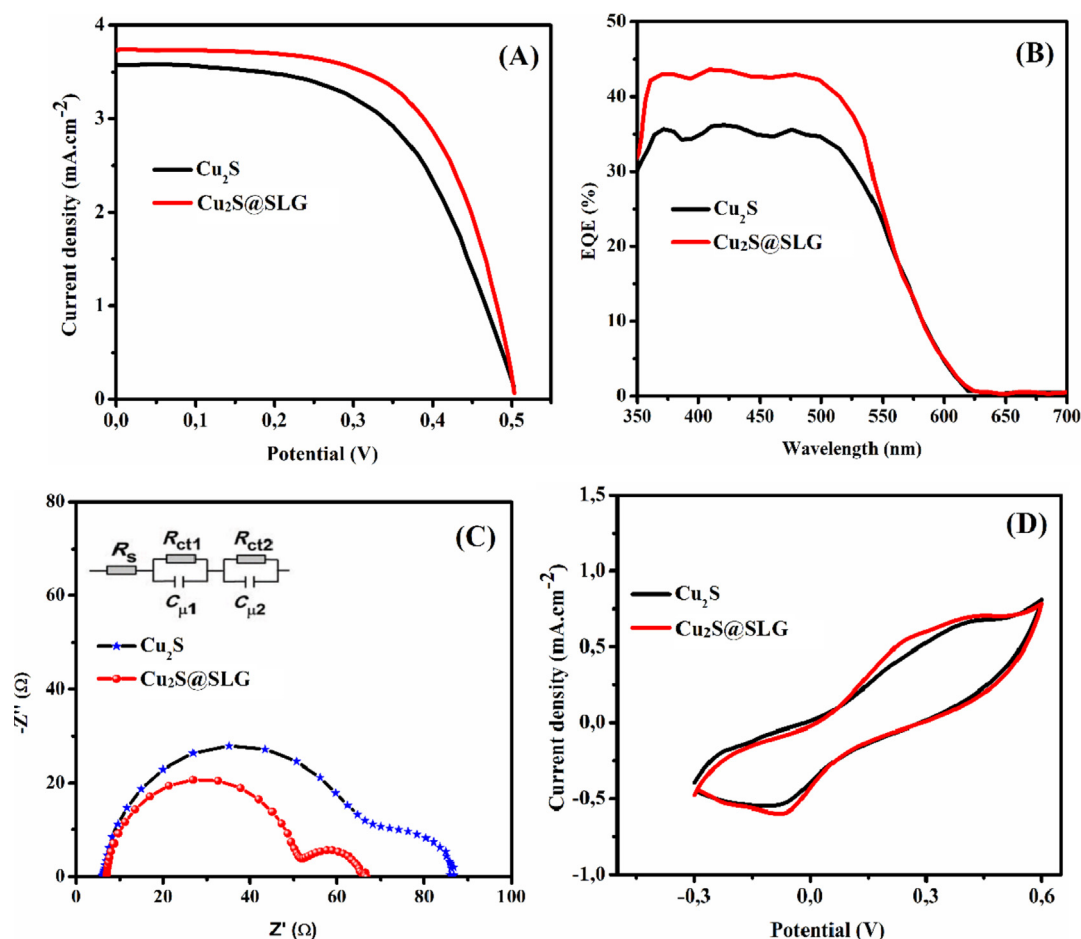


Fig. 4. (A) J–V characteristics, (B) IPCE spectra, (C) EIS measurements of QDSSCs, (D) CV of Cu_2S and $\text{Cu}_2\text{S}@SLG$ CEs.

Table 1
EIS and photovoltaic performance of QDSSCs.

Samples	R_s (Ω)	R_{ct1} (Ω)	R_{ct2} (Ω)	C_1 (mF)	C_2 (mF)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
Cu_2S	7.17	57.90	20.00	130.0	10.70	3.58	0.50	0.57	3.40
Graphene/ Cu_2S	7.65	43.50	13.30	517.0	7.42	3.74	0.50	0.63	3.93

illumination on/off for a total time of 180s when the polysulfide electrolyte is present and shown in Fig. 5A. When the light is turned on photocurrents are reached to $3.58 \text{ mA}/\text{cm}^2$ and $3.74 \text{ mA}/\text{cm}^2$ for Cu_2S CE and $\text{Cu}_2\text{S}@SLG$ CE, respectively. The photocurrent-time curve observed for the QDSSCs are well agreement with its corresponding photocurrent-voltage character. Under illumination with light, a prompt and stable photocurrent density was observed in $\text{Cu}_2\text{S}@SLG$ CE, implying that the collecting electron in $\text{Cu}_2\text{S}@SLG$ can be rapidly transferred from CE to polysulfide electrolyte, which effectively prevents the recombination of electron-hole pairs. The QDSSC assembled with the Cu_2S CE suffered from instability as can be seen from the rapid drop in J_{sc} that reached about 85% after 180s light soaking. This drop was mainly due to the degradation and poisoning of the Cu_2S surface by sulfur ions. To examine the repeatability of the Cu_2S and $\text{Cu}_2\text{S}@SLG$ CEs under certain irradiation, the J_{sc} of the assembled QDSSCs was also collected under irradiation around 180s. In Fig. 5B, the QDSSC with the $\text{Cu}_2\text{S}@SLG$ as the CE exhibited no apparent change in J_{sc} , remaining ~98% of the initial value, during 180s, which shows its remarkable photostability. The achieved photostability of the QDSSC device was

attributed to the high chemical durability of the $\text{Cu}_2\text{S}@SLG$ CE which is due to the Cu_2S nanocrystals embedded within the SLG framework. On the other hand, the QDSSC based on the Cu_2S CE was not able to complete 180s photostability test. The J_{sc} was observed to be greatly suppressed. In comparison with the conventional Cu_2S CE, the results presented offers relatively better repeatability of the QDSSCs with a $\text{Cu}_2\text{S}@SLG$ CE. Fig. 5C and D presents the color alteration of cells before/after exposing the polysulfide electrolyte. As presented in Fig. 5C and D, we have shown that the control devices degrade significantly within few hours, while the $\text{Cu}_2\text{S}@SLG$ nanocomposite shows no discernible color change and detachment from surface, indicating that the SLG framework is critically important to protect the Cu_2S structure from sulphur ions penetrating into electrolyte, and to increase the adhesion of the Cu_2S structure on surface, thus preventing its degradation.

4. Conclusions

In this study, relatively highly electrocatalytic, repeatable and

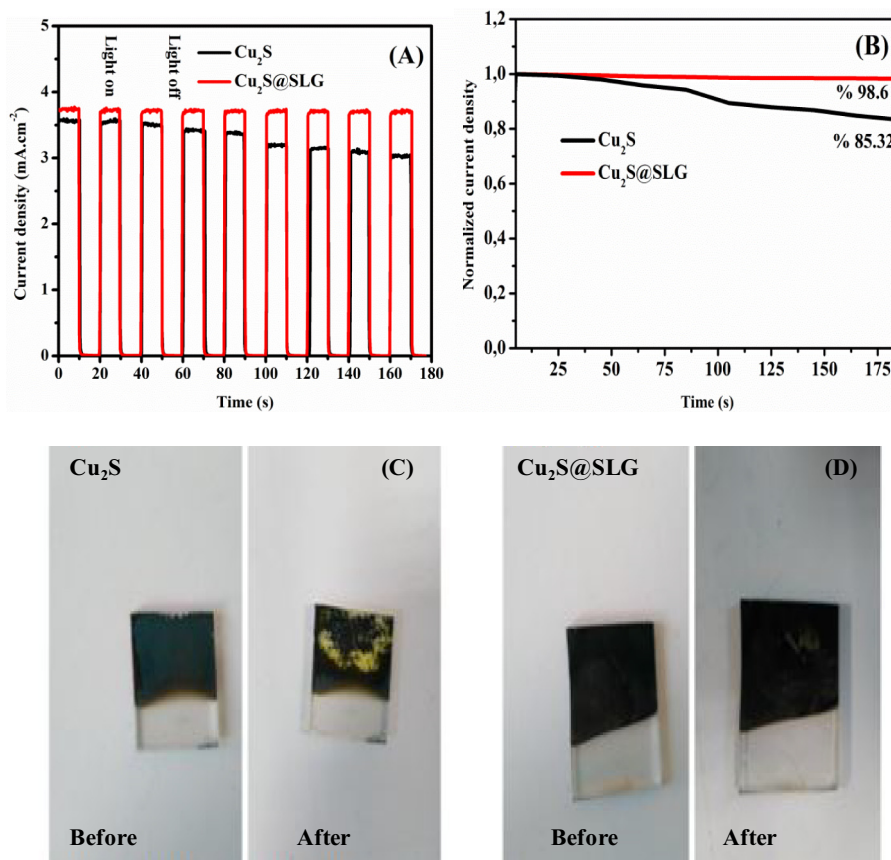


Fig. 5. (A) On-off test and (B) Time dependent stability of QDSSCs, and Digital pictures of (C) Cu_2S and (D) $\text{Cu}_2\text{S@SLG}$ CEs before/after cell fabrication.

stable $\text{Cu}_2\text{S@SLG}$ composite CE has been developed. The results indicated that with replacement of CE from Cu_2S to $\text{Cu}_2\text{S@SLG}$, J_{SC} , FF and η values shift from 3.58 mA/cm^2 to 3.74 mA/cm^2 , 0.57 to 0.63 and 3.40%–3.93%, respectively. The development reasons of these photovoltaic parameters have been explained by EIS analysis, CV studies and the on-off test characterizations. The electrochemical measurements showed that the $\text{Cu}_2\text{S@SLG}$ CE had superior electrocatalytic activity for polysulfide reduction to the Cu_2S CE. This is attributed to the large number of Cu_2S active sites and the rapid electron transport through the conductive SLG framework in the $\text{Cu}_2\text{S@SLG}$ nanocomposite. Moreover, the repeatability measurement of the Cu_2S and $\text{Cu}_2\text{S@SLG}$ CEs was examined for certain time. The obtained result indicates relatively more repeatability and stable of the solar cell with a $\text{Cu}_2\text{S@SLG}$ CE in comparison to Cu_2S CE. All of the results have displayed a promising of $\text{Cu}_2\text{S@SLG}$ composite employed as the CEs in QDSSCs.

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