Bull. Mater. Sci. (2021)44:211
https://doi.org/10.1007/s12034-021-02508-0

Ragi (finger millet) starch-based gel electrolytes for dye-sensitized solar cell application

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MS received 16 January 2021; accepted 6 June 2021

Abstract. Starch was isolated from ragi grains using alkali extraction method. Crystallinity of isolated ragi starch (RGS) was studied using X-ray diffraction technique, and thermal properties of RGS were characterized by differential scanning calorimetry. Novel ragi starch (RGS) based gel electrolyte for dye-sensitized solar cells (DSSCs) was prepared and characterized for the first time. In the first part, the effects of additives guanidinium thiocyanate (GSCN) and N-methylbenzimidazole (NMBI) on the photovoltaic performance of DSSC were investigated. Considerable improvement of open circuit voltage was found in the addition of only NMBI to the electrolyte, while only addition of GSCN has an influence on the short circuit current. Synergetic effects were observed when NMBI and GSCN were used together in the gel electrolyte. In the second part, various weight percentages of multiwalled carbon nanotubes (MWCNTs) were added to observe the cell performance. DSSCs fabricated with the optimum weight percentage (1 wt%) of MWCNT achieved a maximum conversion efficiency of 4.34%, an open circuit voltage (V_{oc}) of 0.803 V, short circuit current density (J_{sc}) of 9.54 mA cm^{-2} and fill factor (FF) of 56.59%. Here we reported the novel ragi starch-based gel electrolytes for DSSC application along with the effect of different additives, such as GSCN, NMBI, and various weight percentages of MWCNTs incorporated into the gel electrolyte.

Keywords. Ragi starch; additives; gel electrolyte; dye-sensitized solar cell.

1. Introduction

Finger millet (*Eleusine coracana*) is a highly nutritious staple food crop cultivated in many parts of India and Africa. It is originated from Ethiopia and belongs to grass family, Poaceae. Finger millet is commonly known as ragi and is one of the important cereals, which is traditionally used to make flour-based products typically in southern India. Ragi has impressive nutritional profile, contains all the essential macronutrients like carbohydrates, fibres, proteins and also it is enriched with major micro-nutrients, such as calcium (344 mg%), phosphorus (283 mg%), iron (3.9 mg%) and many other trace elements that are useful for growth of children, pregnant women and aged persons [1].

Finger millet consists of about 65% of starch and 11.5% of dietary fibre [2,3]. Its starch has amylose and amylopectin fractions in the ratio of 25:75. The seed coat of finger millet contains phytochemicals, which may have health benefits [4].

Recently, researchers focus on cheap, lightweight and environmental friendly materials for electrochemical device applications [5–8]. Use of biopolymers in electrolyte preparation is the current trend and advantage over synthetic polymers [9,10]. Starch is of low cost among all other biopolymers and completely biodegradable [11]. Although different types of starch were used in electrolyte preparation for electrochemical application, until now no attempts have been made to use ragi starch for DSSC application. The basic physical properties of ragi starch, such as solubility index, swelling power and pasting clarity, were thoroughly studied and reported by Wu *et al* [12]. Their studies show that, ragi starch with the highest amylose content had the highest solubility. These results indicate that, ragi starch can be used in application other than the food industry.

In addition to commonly used redox couples, such as iodide/triiodide, incorporation of different additives also affects the performance of dye-sensitized solar cells (DSSCs). Nitrogen heterocyclic compounds, such as 4-*tert*-butylpyridine (4-TBP), *N*-alkylbenzimidazole, etc. have been effectively used to enhance the photoelectrochemical parameters [13–17]. It was reported that the addition of guanidinium thiocyanate (GSCN) to the electrolyte results in a remarkable improvement of open circuit voltage (V_{oc}) because of the reduction of dark current [18]. It was also

Published online: 18 July 2021

reported that the addition of guanidinium cation to the electrolyte could control the self-assembly of the N3 dye at the TiO_2 interface and suppress the dark current. Derivatives of *N*-alkylbenzimidazole have also been widely investigated for DSSC applications [19–23]. A remarkable increase in open circuit voltage (V_{oc}) was also observed by the addition of *N*-methylbenzimidazole (NMBI) to the electrolyte [24].

It is known that the introduction of carbon nanotubes (CNTs) in polymer electrolytes improve the stability and conductivity properties. The highly flexible nature of CNTs may improve the interaction and cross-linking with polymer molecules, which may significantly enhance the morphological and electrical properties of composite electrolytes [25].

Herein, we report the novel ragi starch-based gel electrolytes for DSSC application along with the effect of different additives, such as guanidinium thiocyanate (GSCN), *N*-methylbenzimidazole (NMBI) and various weight percentages of multiwalled carbon nanotubes (MWCNTs) incorporated into the gel electrolyte.

2. Experimental

2.1 *Materials and methods*

Ragi was purchased from local market in Mysore, India. Sodium iodide (98.5%) (NaI), sodium hydroxide (NaOH), guanidinium thiocyanate (GSCN), *N*-methylbenzimidazole (NMBI) and dimethyl sulphoxide (99%) (DMSO) were purchased from Merck. Iodine (99%) (I_2), acetonitrile (99.5%) AR grade and tert-butyl alcohol (99%) were purchased from SD Fine-Chem Limited, India. MWCNTs with diameter of 20 nm, length 20 μm and purity >99.9% were purchased from United Nanotech Innovations Pvt. Ltd. India. N719 dye (Solaronix), Surlyn film (25 μm) (Solaronix) and platinum paste (PT-1) were purchased from Global Nanotech, Mumbai, India.

2.2 *Isolation of starch from ragi grains*

Starch was isolated from ragi grains by removal of protein using alkali extraction method, as described by Vasantha Kumar *et al* [26]. Powdered grains were steeped in 0.25% of NaOH solution at room temperature for 24 h to soften the endosperms. After 1 day of steeping, the liquid portion was drained off and the endosperms were ground lightly in small fractions successively, with the help of a mortar and pestle. The slurry was then diluted to 500 ml using 0.25% NaOH. The mixture was centrifuged at 3000 rpm for 20 min. The cloudy supernatant was removed and the sediment was diluted to the original volume with NaOH solution. The process was repeated until the supernatant showed a negative reaction to the biuret test for protein. Then the starch obtained was suspended in distilled water. The suspension was passed through a 100–200 mesh nylon cloth and repeatedly washed with water until the supernatant no longer gave any pink colour with phenolphthalein. The starch was separated by sedimentation and the white portion was collected and dried in a cabinet drier below 40°C.

2.3 *Preparation of gel electrolyte*

(i) Three different systems with ragi starch (RGS) incorporating NMBI, GSCN and NMBI+GSCN were performed. The system with RGS/GSCN was designated as RGS_{GSCN}, RGS/NMBI as RGS_{NMBI} and combined electrolyte (RGS/NMBI+GuNCS) as RGS_{BOTH}. For each sample 5 ml of DMSO was used as solvent. A quantity of 1 wt% of RGS was added into DMSO and heated to 70°C until to get uniform gelatinization. After gelatinization, suitable amounts of NMBI (0.5 M), GuNCS (0.1 M) and NMBI+GuNCS were added. The mixture is stirred till all the salts were dissolved. Finally, 0.5 M of NaI and 0.05 M of I_2 were added to the above solutions.

(ii) MWCNT-RGS based gel electrolytes were prepared by adding 0.5, 1 and 1.5 wt% of MWCNTs in RGS gel. It was continuously stirred for about 1 h and subsequently sonicated for 30 min. Finally, 0.5 M of NaI and 0.05 M of I_2 were added to the above solutions.

2.4 *Dye-sensitized solar cell fabrication*

Commercial TiO_2 nanocrystalline powder (P25) was mixed in alpha-teripenol and ethyl cellulose mixture to form uniform TiO_2 paste. Approximately 10 μm thick TiO_2 layer was coated on conducting surface of FTO with an active area of 0.25 cm^2 by doctor-blade technique. TiO_2-coated photo-anode was annealed at 500°C for 30 min and then soaked for sensitization in an 0.3 mM N719 dye/(1:1) ratio of tert-butyl alcohol and acetonitrile solution at room temperature for 12 h. A counter electrode was prepared by doctor-blade coating of the platinum paste on to the fluorine-doped tin oxide (FTO) surface, which was subsequently annealed at 400°C for 10 min. A 25 μm thick Surlyn film was used to fabricate cell. DSSC was completed upon the injection of the electrolyte through the pre-drilled hole.

2.5 *Characterizations*

X-ray diffraction (XRD) was done using Rigaku ultima-IV diffractometer with Cu Kα radiation (40 kV, 30 mV) wavelength 0.15406 nm. Diffraction recorded in the range of 5° to 50° at a scan rate 2° s^{-1}. Fourier transform infrared (FTIR) spectra of starch were measured using Thermo

Nicolet FTIR spectrometer (Model 5700, Madison, USA). Spectra were measured from 4000 to 650 cm^{-1} using a single bounce attenuated total reflectance (ATR) accessory with a ZeSe crystal. Thermogravimetric anlysis (TGA) was carried out using TA Instruments, USA, to determine the thermal stability of ragi starch under the nitrogen atmosphere. About 10 mg of the samples were analysed in the temperature range 30–600°C. Differential scanning calorimetric measurements were carried out using thermal analyst 2100 system. A quantity of 10 mg of freeze-dried samples were placed on DSC sample pans and hermetically sealed. Each sample pan was heated from 50 to 220°C at a heating rate of 10°C min^{-1}. The electrochemical impedance spectroscopy (EIS) was measured using CH Instrument CHI608C from frequency range from 1 Hz to 1 MHz with signal amplitude of 5 mV. Symmetric dummy cells were fabricated by two platinum-coated FTO glasses with a gap of 25 microns. Electrolytes were injected into the cell through pre-drilled holes. The morphological characterization of starch was carried out using field emission scanning electron microscope (FESEM, Carl Zeiss). Photoelectrochemical measurements of DSSCs were measured in the dark and under simulated solar light conditions (Oriel Sol3A, 1600 W). The output power was calibrated to 1 sun by using NREL certified silicon photodiode. The conversion efficiency of DSSC based on photocurrent *vs.* voltage (*I–V*) curve was recorded with a Keithley 2400 source metre. All measurements were carried out at room temperature, 25°C. The various types of experimental errors in the present experimental investigations are counting statistics, multiple scattering, sample impurity and non-uniformity of the sample. The total error was determined by adding all the errors and it was found to be below 3–4% in all cases.

3. Results and discussion

3.1 *XRD studies of isolated ragi starch*

XRD pattern of isolated starch from ragi grains is shown in figure 1. The diffraction pattern of the isolated starch having a typical 'A' type crystalline structure with diffraction peak at 15.1°, unresolved doublets between 17.2° and 17.8° as well as between 20.5° and 25.2°. There is also a small peak at 19.5°. This is in agreement with the reports that starch from cereals are in general having A-type crystalline structure [27,28].

3.2 *FTIR analysis of isolated ragi starch*

FTIR spectra of raw ragi powder and ragi starch are reported in figure 2. In a starch source amide (II) bond of protein present is visible at 1580–1680 cm^{-1}, as shown in figure 2. The absence of this band in extracted ragi starch indicates that the extracted starch is devoid of any proteins [26]. The ragi starch spectrum shows characteristics peaks at 3300–3290 cm^{-1}, corresponding to –OH stretching vibrations. The stretching vibration of C–O, C–O–H and C–O–C groups of the glucose ring appeared at more or less 1150, 1077 and 1020 cm^{-1}, respectively. The characteristic peak of ring vibration of ragi starch was found to be at 760 cm^{-1} (figure 2).

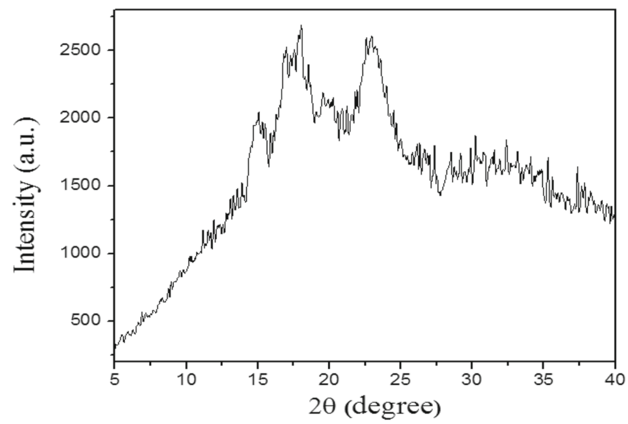

Figure 1. X-ray pattern of ragi starch.

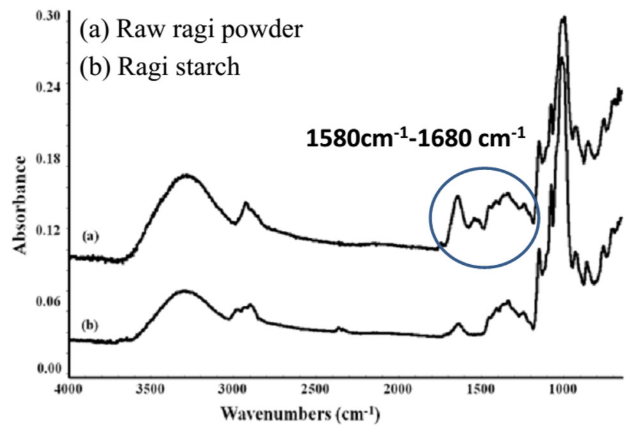

Figure 2. FTIR spectrum of raw ragi powder and ragi starch.

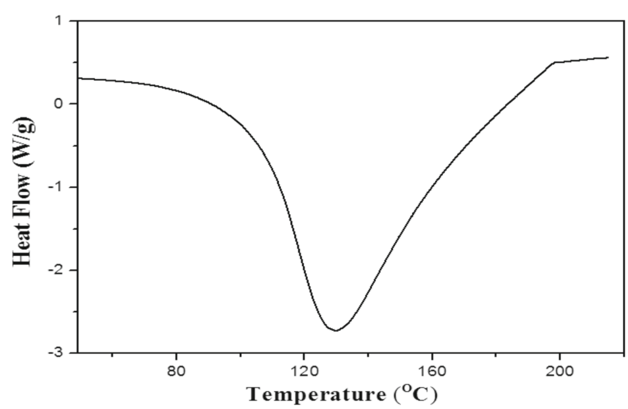

Figure 3. DSC thermograms of extracted ragi starch.

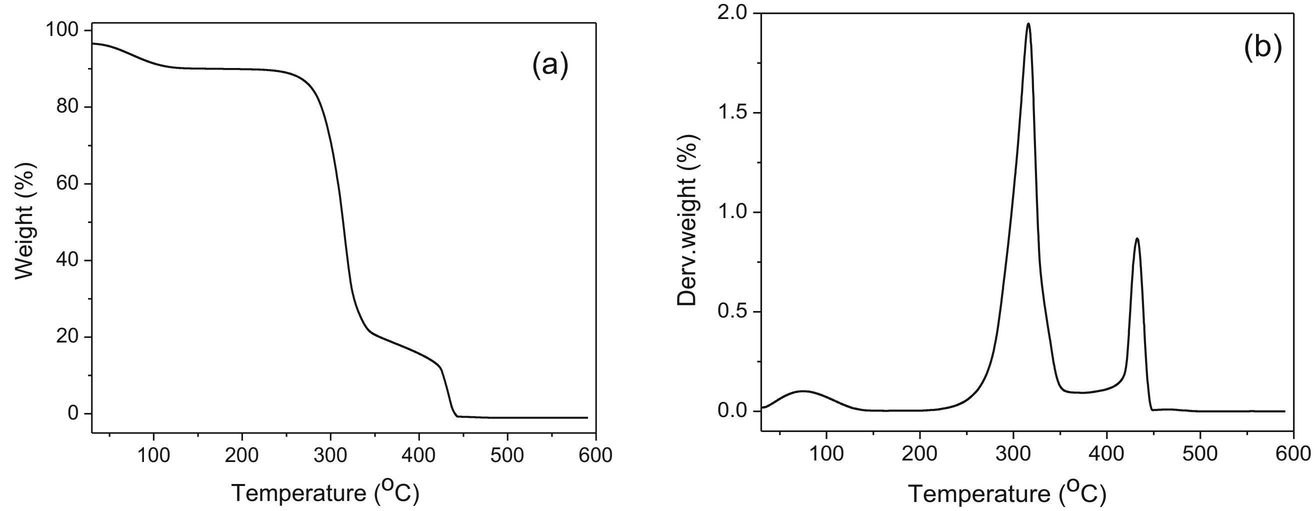

Figure 4. TGA and DTGA thermograms of ragi starch.

3.3 *DSC analysis of ragi starch*

DSC plots of ragi starch are shown in figure 3. For dry starches the maximum endothermic peak ranged between 120 and 150°C, which is consistent with a previous study. This temperature range is below expectations as the theoretical melting point of perfect crystallites without water is estimated at 160–210°C. This might be due to the presence of residual moisture in our sample.

3.4 *TGA analysis*

TGA analysis indicates weight loss of ragi starch with increase in temperature in an inert atmosphere. Weight loss curves of ragi starch as a function of temperature are shown in figure 4a. Thermal degradation (T_d) of ragi starch ranged from 282.77 to 287.85°C as shown in figure 4b.

3.5 *Morphological studies of isolated starch*

Figure 5a shows the FESEM image of the isolated starch, and the shape of the obtained starch from ragi is polyhedral structure. The average particle size evaluated was $\sim$10 µm. Figure 5b shows the images of MWCNTs. The average diameter of the MWCNTs is found to be 25 nm.

3.6 *J–V characteristics*

The *J–V* characteristics of RGS-based electrolyte with three different combinations of additives, such as GuCNS, NMBI and NMBI+GuCNS, are shown in figure 6. From figure 6 and table 1, it is observed that, pure RGS electrolyte without any additives show the lowest J_{sc}, V_{oc} and η. When NMBI is added to the electrolyte pure RGS, V_{oc}

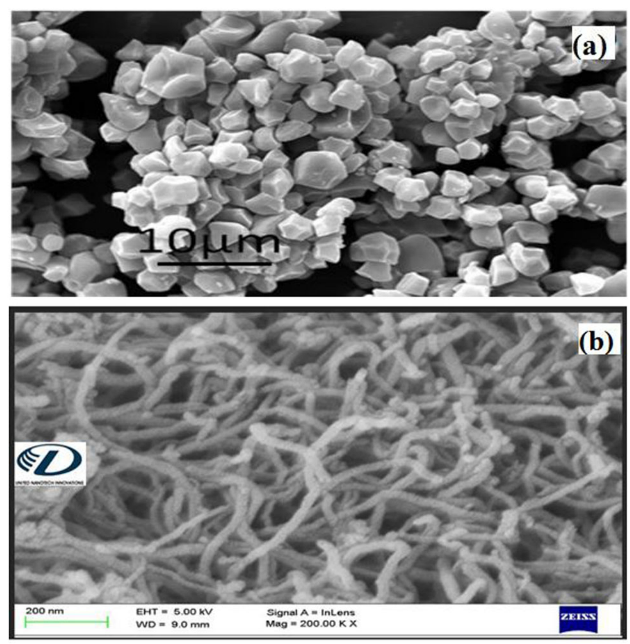

Figure 5. SEM images of (**a**) the isolated starch and (**b**) MWCNT.

increased drastically compared to pure RGS. However, addition of only GSCN to the gel electrolyte has a pronounced influence on the short circuit current (J_{sc}) and improved fill factor (FF) owing to the positive shift of the conduction band edge potential. This corresponding to increased efficiency of GSCN based cell compared to cells with NMBI additive.

Enhancement of FF and efficiency of cells was due to reduction of series resistance (R_s), thereby increases in the electron transport mechanism in the DSSCs. Table 1 shows the definite correlation between FF and efficiency, both are highest for RGS_{GSCN} based gel electrolyte. Synergistic effects were observed when both NMBI and GSCN

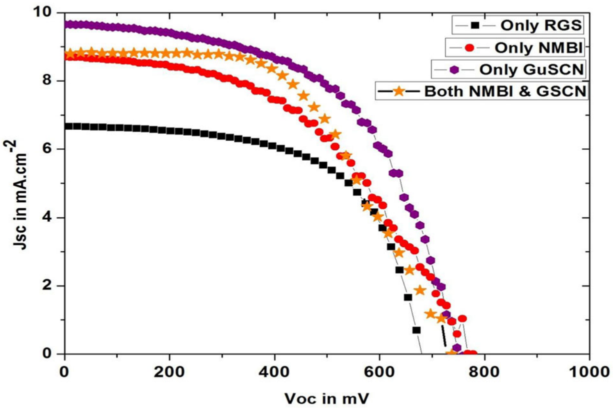

Figure 6. Characteristic *J–V* curves of DSSCs with RGS/NMBI, RGS/GuNCS and RGS/NMBI+GuNCS electrolytes.

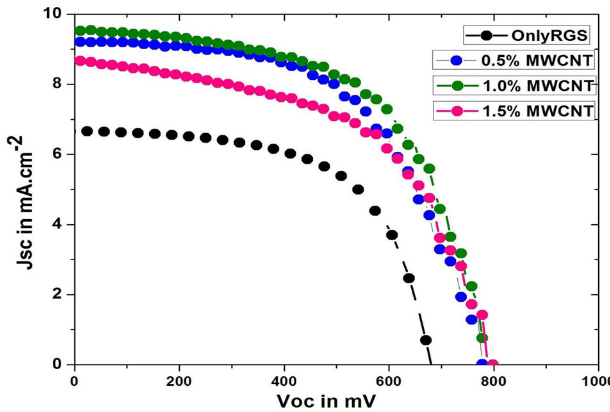

Figure 7. *J–V* characteristics of MWCNT-RGS based gel electrolytes.

Table 1. DSSC parameters for RGS, RGS_{NMBI}, RGS_{GSCN} and RGS_{BOTH} systems.

Samples	Conductivity (σ) (mS cm^{-1})	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	η (%)
Pure RGS	0.81	6.65	678	60.45	2.72
RGS_{NMBI}	1.52	8.69	773	47.16	3.17
RGS_{GSCN}	1.84	9.65	755	54.51	3.97
RGS_{BOTH}	1.61	8.80	736	53.12	3.44

(RGS_{BOTH}) were used together in the gel electrolyte. Previous reports on the synergistic effect of NMBI and GSCN on the performance of DSSCs also indicate the similar results [17]. DSSC containing the electrolyte RGS_{GSCN} shows the highest conversion efficiency, even higher than that of DSSC with the electrolyte RGS_{BOTH}.

The current density (*J*)–voltage (*V*) characteristics of DSSCs fabricated with MWCNT-RGS gel electrolytes are shown in figure 7 and summarized in table 2. The conversion efficiencies of DSSCs are significantly increased by using MWCNT-RGS electrolytes in comparison with pure RGS gel electrolyte. Introduction of MWCNT into RGS matrix may reduce the ohmic contact to increase electron transport in the RGS matrix. In general, conductivity plays crucial role in the enhancement of J_{sc} and FF for DSSCs. The highest conversion efficiency of 4.34% and J_{sc} of 9.54 mA cm^{-2} achieve in the DSSCs with 1% MWCNT-RGS electrolyte.

It is observed from table 2 that, in comparison with pure RGS gel electrolyte, J_{sc} gradually increased up to 1% MWCNT-RGS and then decreased for 1.5% MWCNT-RGS as subsequent increase in MWCNT concentration in gel electrolyte. Introduction of MWCNT into RGS matrix may reduce the ohmic contact, thereby increases the J_{sc}, FF and almost no variation in V_{oc} of DSSCs.

Table 2. DSSC parameters for RGS with MWCNT additive systems.

Samples	Conductivity (σ) (mS cm^{-1})	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	η (%)
Pure RGS	0.81	6.65	678	60.45	2.72
0.5% MWCNT-RGS	2.06	9.22	788	55.24	4.10
1% MWCNT-RGS	2.25	9.54	803	56.59	4.34
1.5% MWCNT-RGS	1.73	8.67	799	53.92	3.73

4. Conclusion

Ragi starch was isolated from ragi grains using alkali extraction method. Novel ragi starch (RGS) based gel electrolyte was prepared and characterized for DSSCs for the first time. The effects of the additives *N*-methylbenzimidazole and guanidinium thiocyanate on the photovoltaic performance of DSSCs have been investigated thoroughly. When only NMBI is present in the RGS-based gel electrolyte, a significant improvement of the open circuit voltage is observed, which can be attributed to the combined effect of a negative shift of the conduction band edge potential and the longer electron lifetime in the TiO_2 film under open circuit conditions. The short circuit current is dramatically enhanced when only GSCN added into the electrolyte. A significant synergistic effect is observed when both NMBI and GSCN are added to the pure electrolyte. Further, various weight percentages of MWCNT were added to pure RGS gel electrolyte and characterized for DSSC application. The addition of MWCNTs into RGS networks improved the interaction and cross-linking between MWCNT and RGS molecules, resulting in increased ionic conductivity. DSSC fabricated with 1 wt% of MWCNT in RGS gel electrolyte achieves maximum efficiency of 4.34%, which is much higher compared to other biopolymer–MWCNT composites.

Acknowledgements

We are thankful to the Indian Nanoelectronics User Program (INUP), IISc, Bengaluru, for their characterization support. This study was supported by the Vision Group of Science & Technology (VGST), Karnataka.

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