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PAPER

Graphene, carbon nanotube and ionic liquid mixtures: towards new quasi-solid state electrolytes for dye sensitised solar cells

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In this work carbon based nanomaterials in ionic liquids have been studied as potential electrolytes for dye sensitised solar cells (DSSCs). Graphene, single wall carbon nanotubes (SWCNTs) and a mixture of graphene and SWCNTs were incorporated into 1-methyl-3-propylimidazolium iodide (PMII) ionic liquid. The resulting quasi-solid state electrolytes were sandwiched between TiO_2 working electrodes and platinum counter electrodes and subsequent DSSCs were fabricated. Graphene based quasi-solid state electrolytes displayed an increase of light conversion efficiencies in the completed DSSC from 0.16% (for pure PMII) to 2.10%. For SWCNTs, the observed light conversion efficiency increased from 0.16% to 1.43% and for the mixture of graphene and SWCNTs the light conversion efficiency improved from 0.16% to 2.50%. This significant increase occurred because the carbon materials serve simultaneously both as charge transporter in the ionic liquids and as catalyst for the electrochemical reduction of I_3^-. It is also expected that there is an ionic liquid mediated self-organisation of graphene and SWNT nanomaterials into structured networks, which provide an efficient electron transfer. Thermogravimetric analysis (TGA) studies showed that these electrolytes are stable up to 300 °C.

Introduction

Renewable green energy sources such as hydro, wind and solar have been extensively explored over the last few decades. Among all these renewable green energy sources, solar energy has emerged as a most practical and long lasting alternative to conventional fossil-fuel based energy sources.[1] To utilise solar energy for a variety of applications one would need to convert it into electricity using photovoltaic cells. At present silicon based solar cells dominate the market but produce less than 0.1% of the world energy.[2] Silicon solar cells are still too expensive for households due to the costly fabrication process *e.g.* requires high temperatures (400–1400 °C) and high vacuum conditions with numerous lithographic steps. Therefore, the development of new inexpensive solar cells, which can convert maximum solar energy to electricity, is of extreme importance.

The dye-sensitised solar cell (DSSC) is one of the cheapest potential options. Initially the DSSC was developed by Gratzel and O'Regan in 1991.[3] Since then DSSCs have been widely investigated because of their potentially lower costs and simple manufacturing process compared to silicon solar cells.[4] So far, the highest reported efficiency for a small area DSSC (0.25 cm^2) is 11.3%.[1] Although the solar power conversion efficiencies of DSSCs are lower than those of classical crystalline silicon cells, these cells can operate well under diffused light (*e.g.* cloudy day). There is also a high potential for improvement in efficiency of DSSCs.[5] The electrolyte is one of the key components of the DSSC technology and its development is particularly important for further development and commercialisation of DSSCs.

In order to get high cell efficiencies, the electrolyte has to fulfill certain criteria including appropriate viscosity, high diffusion coefficient, high electrochemical and thermal stability, low vapour pressure and ease of sealing.[6–8] Traditional DSSC technology uses a volatile solvent based electrolyte. These electrolytes are characterized by low viscosities and high diffusion coefficients. However, the liquid electrolytes cause a number of problems during manufacturing that limit their applications. The main problems include leakage of electrolytes, corrosion of cells over time, high temperature instability (outdoor conditions) and additional complexity in trying to contain liquids in a solar cell device during manufacturing.[7,8] These drawbacks, as well as the fact that the solvents permeate plastics, are serious obstacles for large-scale outdoor application of DSSCs and their integration into flexible structures. Therefore in the last few years much work has been done to develop new quasi-solid state electrolytes based on ionic liquids (ILs) as a replacement for volatile electrolytes.[8–19] However, the conversion yields obtained with ionic liquids at a full air mass (AM 1.5) solar irradiance have been much lower than those achieved with organic solvent based electrolytes. Various approaches have been made to prepare solid or quasi-solid state electrolytes for DSSCs.[20] For example, p-type inorganic semiconductors,[21] organic hole conducting materials,[10] and

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various types of nano-components[18,22] were dispersed into ILs to solidify them. In the case of p-type inorganic semiconductors and polymers, they cannot properly penetrate into the dye adsorbed porous TiO_2 film, thus the corresponding DSSCs showed lower efficiency compared to traditional DSSCs. Ikeda and Miyasaka fabricated near solid-state DSSCs, where electrolyte contained SWCNTs and derivative of the IL without the addition of volatile components and obtained an efficiency of 1.63% under a simulated sunlight intensity of 100 mW cm^{-2}.[23] Recently Lee *et al.* reported a new promising quasi-solid state electrolyte for DSSCs, which was produced by utilizing a binary ionic liquid and SWCNTs as filler. This research resulted in a cell with a relatively high efficiency of 3.49% without addition of iodine and volatile components in their device.[24] However, similar graphene[25] based electrolyte systems have not been investigated so far.

The main aim of our research is to develop a new type of quasi-solid state electrolyte for DSSCs by incorporating graphene and SWCNTs into ionic liquids such as PMII. We expect that graphene based quasi-solid state electrolytes would give better performance than SWCNTs (1D) based electrolytes due to graphene's 2D nature. In this paper we evaluate various mixtures of graphene and/or SWCNTs in ILs as potential quasi-solid state electrolytes for DSSC applications.

Result and discussion

Preparation and characterisation of graphene

Graphene was prepared by solvent exfoliation according to the procedure reported by Coleman *et al.*[26] The formation of graphene was confirmed by TEM, SEM and Raman spectroscopy analysis. TEM was employed to determine the typical thicknesses of the exfoliated graphene layers in dispersions of graphene/*N*-methyl-pyrrolidone (NMP) and graphene/PMII. TEM of folding at the edges or within the free-hanging sheets gives the number of layers by direct visualization. The number of layers can also be determined by X-ray diffraction.[27] TEM images (Fig. 1) confirmed the exfoliation of monolayer and few layered (up to ten layers) graphene in dispersions.

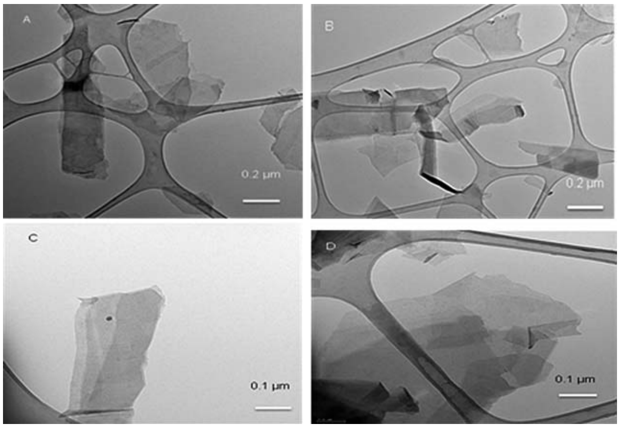

Fig. 1 Representative TEM images of mono- (A and B) and multilayer (C and D) graphene structures observed after 60 hours of sonication.

Raman spectra have been taken from both top and bottom sides of the graphite/graphene films as well as on graphite flakes for comparison. The main features in graphite/graphene Raman spectra are represented by the D, G and 2D peaks.[28] The D peak, so-called after defects, can be found at ~1350 cm^{-1}. The graphite powders displayed a small D band (~1350 cm^{-1}). The D band is indicative of defect or edges. The graphitic G peak located at ~1580 cm^{-1} and the 2D peak located at ~2700 cm^{-1} are usually observed in graphite samples.[29] The graphite's 2D band (~2700 cm^{-1}) always has a shoulder at ~2650 cm^{-1}, representative of graphite.[27] While the absence of a shoulder in the 2D band of the film spectra represents the few layer graphite. Furthermore the shape and height/intensity of the 2D can be used to distinguish single and multilayered graphene in a sample. In monolayer graphene the 2D peak evolves to be roughly 4 times more intense than the G peak.[27] Raman spectra (Fig. 2C) of graphite powder showed only negligible D peak. This suggests that there were no defects in the starting materials, while a shoulder in the 2D peak was observed as one would expect in graphite. Raman spectra of our films showed a large D peak which can either be due to the defect created during sonication of the samples or most likely because of the presence of smaller flakes, *i.e.* edge effect.[26,30] The shape of 2D peak spectra without any shoulder is consistent in all graphene films as shown in Fig. 2A and B, which indicated the presence of few layer thick graphene sheets in films, thus we can also conclude from this analysis that graphene sheets did not aggregate into graphitic stacking in the film.

SEM images of the films allowed us to investigate their morphology and graphene layers arrangement in the films (Fig. 3). Again we have carried out SEM investigations both on the top and bottom, and cross-sectional (edge) surfaces of the films. The SEM images showed that these films consisted of few layers of graphene sheets in all cases.

Preparation and testing of graphene based quasi-solid state electrolytes

The quasi-solid state DSSC consisting of graphene and PMII can be represented schematically as shown in Fig. 4. In our work graphene was dispersed in PMII in various amounts (wt%) as described in the Experimental section. The resulting quasi-solid state electrolytes were sandwiched between TiO_2 working

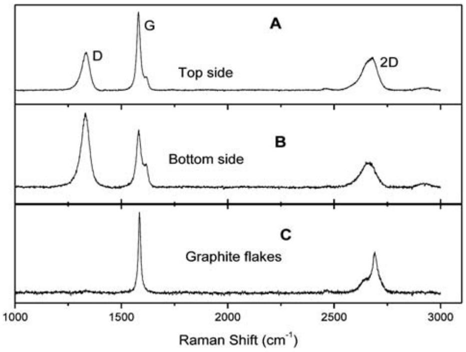

Fig. 2 Raman spectra: (A) top side, (B) bottom side of the graphene film and (C) graphite flakes.

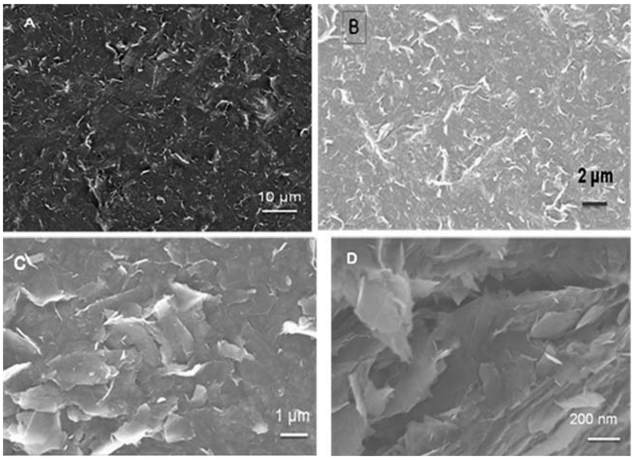

Fig. 3 SEM images of the graphene film top surface (A and B) and the cross-sectional edge (C and D).

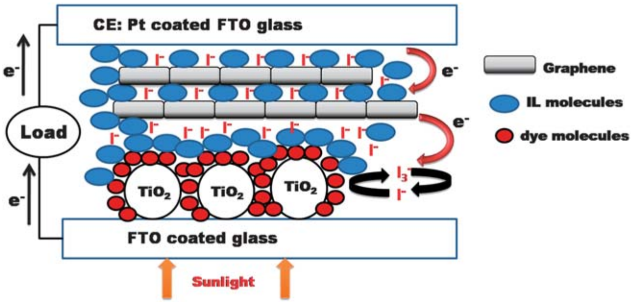

Fig. 4 Schematic presentation of a DSSC with a graphene-IL based quasi-solid state electrolyte.

electrodes and platinum counter electrodes (CE). It is known that an addition of carbon nanomaterials can potentially short circuit a cell.[22–24] In our cells the uncoated TCO area was covered with a 60 μm thick insulator (Surlyn) layer. Besides preventing short circuit, the insulator also has other advantages that is it provides enough space between the working electrode (WE) and CE to hold enough quasi-solid state electrolytes. It also helps to keep the constant space between two electrodes in each cell. Furthermore to avoid short circuiting we only used working electrodes with the TiO_2 layer, which had no pin hole and no scratch after sintering and soaking in the dye (N719) solution. The size of graphene flakes was bigger than that of the pores in the TiO_2 layer as shown in TEM (Fig. 1) and SEM (Fig. 3), therefore this enabled us to prevent the penetration through the TiO_2 layer and potential short circuit in the cell.

We have found that the addition of only 1 wt% of graphene changes the colour of PMII from yellow to black. It was found that 1–15 wt% of graphene has almost no effect on the viscosity of PMII and can only result in a gel like material. However, 20–40 wt% resulted in a quasi-solid state product. PMII fills the mesoscopic interior of the sensitised porous TiO_2 layer where no space is available for the graphene to occupy and PMII functions as a carrier mediator between the sensitised porous TiO_2 and graphene.

A reference DSSC was made with PMII only. Table 1 summarises photovoltaic parameters of the DSSCs with quasi-solid state electrolytes containing different amounts (wt%) of graphene. The light conversion efficiency of the reference DSSC without graphene additives was found to be only 0.16%. Initially we tried to keep graphene at a low concentration, significantly below the percolation threshold. After the addition of 1 to 10 wt% of graphene the light conversion efficiencies of DSSCs increased very little (up to 0.21% only). However, a dramatic increase in the light conversion efficiencies was observed for cells containing 15–30 wt% of graphene in PMII electrolyte. It seems that at low concentrations the graphene flakes are too far away from each other and do not provide sufficient charge transfer. As the concentration increased the graphene flakes are arranged in more dense structures resulting in an efficient electron transfer, hence viscous quasi-solid state electrolytes show higher light energy conversion. The light conversion efficiencies increased from 0.16% (without graphene) to 2.10% with 30 wt% of graphene concentration.

It has been previously reported that the addition of carbon nanotubes and carbon nanoparticles into ILs increases the conductivity of ILs.[22] The greater conductivity of the IL electrolyte can be attributed to the presence of electron-rich carbon nanoparticles or nanotubes which interact with the imidazolium cations in the ILs. In classical DSSCs the tri-iodide ion (I_3^-) physically diffuses toward Pt CE where it is reduced back to iodide ion ($I_3^- + 2e \rightarrow 3I^-$). Therefore, the physical diffusion of tri-iodide ion in the electrolyte is an important parameter that influences the performance of a DSSC.[14,17] However, the presence of a carbon based nanomaterial in ILs enables to achieve a direct link between CE and dye/TiO_2 layers of WE, providing an extended electron transfer material (EETM).[24] In our case graphene plays the role of EETM and facilitates electron transfer from counter electrode to tri-iodide ions, which are close to WE enabling the I^-/I_3^- redox couple to work more efficiently than in the absence of these carbon based materials in ILs. In addition graphene is electrocatalytically active toward I^-/I_3^- couple as it has been previously reported.[31] Thus we believe that an increase of light conversion efficiency of the cell with graphene is attributed to the dual functions of graphene, *i.e.* mediating charge transfer in the electrolyte and electrocatalyzing the I_3^- reduction. However, a further increase of graphene in PMII (35 to 40 wt%) had reduced the conversion efficiencies of DSSCs. When the amount of graphene was increased up to 35 to 40 wt%, the light conversion efficiencies decreased to 0.59% and 0.48% respectively. These reduced light conversion efficiencies are most likely because at 35 to 40 wt% graphene cannot be properly exfoliated and dispersed in PMII that results in a non-homogeneous electrolyte composite.

Table 1 presents the effect of graphene content on short-circuit current density (J_{sc}), fill factor (FF) and open-circuit voltage (V_{oc}) of quasi-solid state DSSCs respectively. From the results shown in Table 1, it can be seen that J_{sc} of DSSCs increased with increase in the amount of graphene (wt%) in PMII. This indicates that an increased amount of graphene also results in higher conductivity of PMII in quasi-solid state DSSCs. Previously Kang *et al.*[32] have described that J_{sc} is strongly dependent on the ionic conductivity of the electrolyte. The highest FF (0.49) was obtained with 30 wt% of graphene. This reflects a relatively high internal electric resistance because a thick composite layer was used between WE and CE of quasi-solid state DSSCs. V_{oc} also

Table 1 Photovoltaic parameters of the DSSCs with quasi-solid state electrolytes containing various amounts of graphene (wt%) in PMII. Light intensity: 78 mW cm^{-2}. Cell active area: 0.8 cm^2

Graphene content (wt%)	J_{sc}/ mA cm^{-2}	V_{oc}/V	FF	Maximum power point/W	Efficiency (%)
0% (only PMII)	0.370	0.575	0.64	0.000104001	0.16 ± 0.01
1%	0.850	0.507	0.30	0.000101249	0.16 ± 0.01
5%	0.749	0.561	0.36	0.000116000	0.18 ± 0.01
10%	0.790	0.561	0.39	0.000133001	0.21 ± 0.02
15%	3.910	0.538	0.31	0.000492280	0.79 ± 0.02
20%	4.000	0.521	0.34	0.000563456	0.90 ± 0.05
25%	4.800	0.535	0.37	0.000746530	1.20 ± 0.06
30%	5.300	0.624	0.49	0.001304600	2.10 ± 0.10
35%	3.910	0.460	0.27	0.000370600	0.59 ± 0.02
40%	3.520	0.464	0.24	0.000298340	0.48 ± 0.02

slightly increased from 0.575 to 0.624 V. Overall the addition of graphene up to 30 wt% did not affect too much the V_{oc} of DSSCs. However, the value of V_{oc} decreased when the amount of graphene was increased to 35 to 40 wt%. This shows that electrolyte with up to 30 wt% of graphene can easily penetrate into the TiO_2 layer but further increase of graphene wt% results in very high viscosity liquid, which cannot penetrate into the TiO_2 layer.

Overall, apparently graphene based IL electrolyte is a facile and low-cost alternative to iodine-containing liquid and other quasi-solid state electrolytes. In addition to promising photovoltaic parameters above this highly viscous electrolyte can hold together both electrodes and does not show any leakage even without sealing. We also believe that this approach to quasi-solid-state DSSCs can potentially be applied for a large scale fabrication of DSSCs by a screen-printing method.

Preparation and testing of SWCNTs based quasi-solid state electrolytes

SWCNTs were dispersed in PMII in various amounts (wt%) as described in the Experimental section. The resulting mixture was used as an electrolyte to fabricate DSSCs. Table 2 presents the summary of photovoltaic parameters of SWCNTs based quasi-solid state electrolytes. In our experiments we found that 1 weight% of SWCNTs can make a viscous gel like material but does not affect the viscosity of PMII. The addition of 1 wt% of SWCNTs increased conversion efficiency of DSSCs from 0.16% to 0.25% only. However, the dispersion of 7 wt% of SWCNTs in PMII produced a highly viscous black gel. The resulting quasi-solid state electrolyte demonstrated the highest conversion efficiency (1.43%) in corresponding DSSCs. It has previously been reported that SWCNTs form buckygels with highly structured networks in ionic liquids.[33] We believe that these self-organised networks provide a very good electron transfer, which is achieved at 7 wt% of nanotubes. High J_{sc} (5.19 mA cm^{-2}) indicates the increase of the conductivity of PMII electrolyte. Furthermore, at 7 wt% of SWCNTs the viscosity of the electrolyte is not too high and the electrolyte can penetrate into the sensitized porous TiO_2 layer. Further increase of SWCNTs loading from 10–16 wt% produced much more viscous gels. DSSC containing dispersions with 10, 13, and 16 wt% of SWCNTs gave conversion efficiencies of 0.56, 0.46 and 0.40% respectively. This decline in efficiency can be explained by the poor dispersion and aggregation of SWCNTs at concentrations above 7 wt%. In fact the SWCNT aggregates can easily be seen even by naked eye. In addition perhaps at high loading SWCNTs based quasi-solid state electrolytes are too viscous and cannot achieve sufficient penetration into the porous TiO_2 layer.

Table 2 Photovoltaic parameters of the DSSCs with quasi-solid state electrolytes containing various amounts of SWCNTs in PMII. Light intensity: 78 mW cm^{-2}. Cell active area: 0.8 cm^2

SWCNT content (wt%)	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	Efficiency (%)
0% (only PMII)	0.370	0.575	0.64	0.16 ± 0.01
1%	0.524	0.573	0.70	0.25 ± 0.01
7%	5.19	0.540	0.41	1.43 ± 0.13
10%	2.15	0.616	0.36	0.56 ± 0.02
13%	1.64	0.614	0.41	0.46 ± 0.02
16%	2.09	0.541	0.32	0.40 ± 0.02

Hybrid graphene–SWCNTs based quasi-solid state electrolytes

Two kinds of hybrid quasi-solid state electrolytes with different graphene to SWCNTs ratios have been produced. One consisted of 3 wt% of graphene and 12 wt% of SWCNTs and the second one consisted of 3 wt% of SWCNTs and 12 wt% of graphene in PMII. Table 3 summarises photovoltaic parameters of hybrid graphene and SWCNTs based DSSCs. A highest efficiency of 2.50% was obtained with 3% of SWCNT and 12% of graphene quasi-solid state electrolytes. This increase is higher than that for both pure graphene–PMII and pure SWCNT–PMII based quasi-solid state electrolytes. It has been previously reported in the literature that conductivity of the graphite/graphene composite can be increased by addition of small quantities of SWCNTs.[34] We think that this might be the reason in our case as well. This can be confirmed by the J_{sc} data obtained. The highest J_{sc} (7.32 mA cm^{-2}) was achieved for the sample with 3% of SWCNT and 12% of graphene, therefore the ionic conductivity of this particular electrolyte is higher than all other types of quasi-solid state electrolytes prepared in this work. We also believe that there is an ionic liquid mediated self-organisation of graphene and SWNT nanomaterials into highly structured networks,[33] which provide an efficient electron transfer. Fig. 5 shows the representative I–V curves of the three most efficient quasi-solid state electrolytes of each type of sample and reference DSSCs (PMII)s which are fabricated in this work.

Table 3 Photovoltaic parameters of the DSSCs with quasi-solid state electrolytes containing various amounts of graphene and SWCNTs in PMII. Light intensity: 78 mW cm^{-2}. Cell active area: 0.8 cm^2

SWCNT/graphene weight content (%)	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	Efficiency (%)
0% (only PMII)	0.370	0.575	0.64	0.16 ± 0.01
SWCNT (3%) + graphene (12%)	7.32	0.594	0.44	2.50 ± 0.10
SWCNT (12%) + graphene (3%)	4.66	0.561	0.43	1.39 ± 0.10

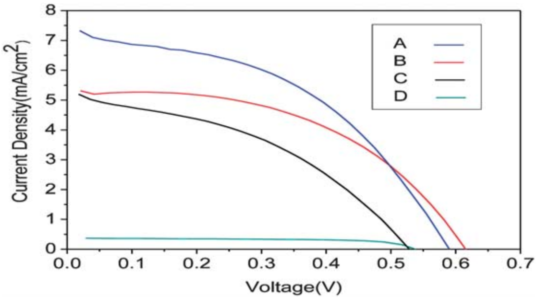

Fig. 5 Photovoltaic curves (*J–V*) of the DSSCs with (A) graphene (12 wt%) and SWCNTs (3 wt%), (B) graphene (30 wt%), (C) SWCNTs (7 wt%) and (D) PMII only, light intensity 78 mW cm^{-2}.

Thermogravimetric analysis (TGA) of electrolytes

To investigate the thermal stability of the quasi-solid state electrolytes, the three most efficient quasi-solid state electrolytes were selected from each type and characterized by TGA. The TGA study shows that our quasi-solid state electrolytes and all their components are perfectly stable at quite high temperature condition, up to 300 °C (Fig. 6). Therefore these electrolytes should be very promising for DSSC applications.

Comparative stability study of electrolytes in DSSCs

To investigate time-dependent stability of the quasi-solid state based DSSCs, the three most efficient quasi-solid state DSSCs were selected from each type of electrolyte. In addition reference additive free cells with PMII only were also tested. These four DSSCs (open cell) were stored in desiccators. The *I–V* curves of all the DSSCs were measured at intervals of 120 hours for 1000 hours. Fig. 7 shows a summary of the stability studies of DSSCs. It was noticed that the cell efficiency in all cases decreased after five days and then stabilized for some period of time. This was followed by another gradual decrease as shown in Fig. 7. These results indicate that after 1000 hours the overall light conversion efficiencies of the quasi-solid state electrolyte 1 (SWCNT), quasi-solid state electrolyte 2 (graphene), and quasi-solid state electrolyte 3 (graphene + SWCNTs) were decreased from 1.43% to 1.02%, 2.10% to 1.61% and 2.50% to 1.55% respectively. The efficiency of the reference cell made with PMII was initially increased after 120 hours but then gradually decreased and reached 0.50% after 1000 hours. Among all the various types of quasi-solid state DSSCs, the graphene based DSSC was the most stable. One reason for the stability could be that the high loaded graphene electrolyte makes a protective layer over the dyed TiO_2 layer. Another possible reason is the 2D structure of these graphene based electrolytes firmly sticks to the TiO_2 layer and thus protects dyed TiO_2 and PMII from moisture/humidity and other contaminations. From the first glance apparently it looks like the cell made using pure PMII is more stable than the rest. However, it is clear that even at 1000 hours of aging all the nano-carbon filled electrolyte samples still have much higher efficiencies than that of pristine PMII at the same aging level.

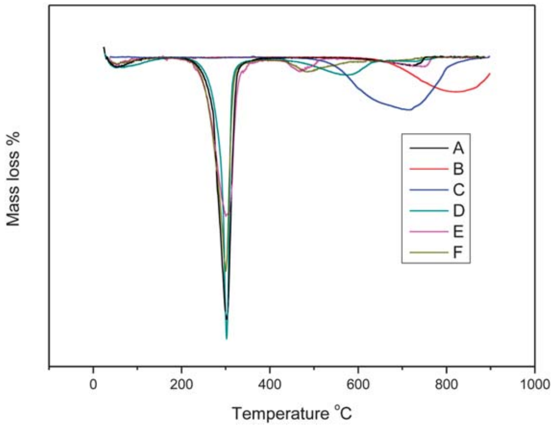

Fig. 6 DTGA curves of: (A) PMII, (B) graphene, (C) SWCNTs, (D) graphene (30%) + PMII, (E) SWCNT (7%) + PMII and (F) graphene (12%) + SWCNT (3%) + PMII.

Experimental

General procedures

Powdered graphite was purchased from Branwell (Branwell natural graphite). 1-Methyl-3-propylimidazolium iodide (PMII) was purchased from Iolitec. Working electrodes (TiO_2 layer with 10 μm thickness), counter electrode (Pt coated) and dye (N719) were supplied by Dyesol limited. Sealant/spacer (Meltonix 1170-60 series) was purchased from Solaronix SA. SWCNTs were supplied by Elicarb (SWCNT, PR 0925, 10g). *N*-Methyl-pyrrolidone (NMP) and ethanol were supplied by Sigma-Aldrich.

Graphene samples were prepared according to the Khan *et al.* method.[26] Ultrasonic Bath Grant XB6 (200 W) was used in all sonication experiments. The TEM of the samples was performed using a Jeol 2100, operated at 200 kV. TEM sample preparation involved dropping the graphene dispersions onto a holey carbon grid (400 mesh). Raman spectra (633 nm) were recorded on a Horiba Jobin Yvon LabRAM-HR (100× objective lens). SEM images of the dry film have been taken using a Zeiss Ultra plus SEM. The electron beam generator was a thermal field emission tungsten tip, with a sintered reservoir of zirconium oxide in the shank. For these samples, the electrons were accelerated between 2 and 5 kV. Thermogravimetric analysis was done using a Perkin Elmer Pyris 1 TGA. TGA experiments were carried out under air.

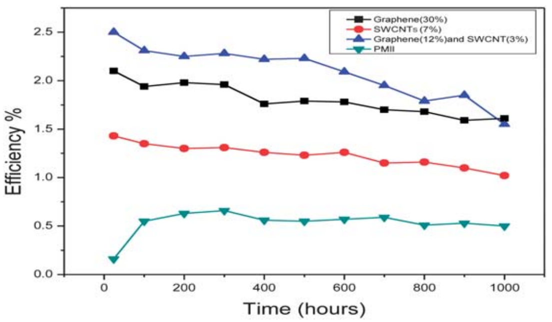

Fig. 7 Stability study of efficiencies of DSSCs based on graphene, SWCNTs, graphene + SWCNT electrolytes and reference DSSCs (PMII only).

Preparation of quasi-solid state electrolytes

Preparation of graphene based quasi-solid state electrolytes. The graphene samples were triturated in a vial and again dried in an oven for 4 hours at 65 °C to remove the traces of NMP, if any remained present in graphene powder. After that the graphene powder was dispersed in PMII at concentrations of 1%, 10%, 15%, 20%, 25%, 30%, 35% and 40% by weight. In all cases graphene samples were added in small portions, followed by sonication for 30 minutes. After this, all samples were sonicated in closed glass vials in the ultrasonic bath for further 4 hours until homogeneous quasi-solid state electrolytes were obtained.

Preparation of SWCNT based quasi-solid state electrolytes. SWCNTs were dispersed in PMII in quantities of 1%, 7%, 10%, 13% and 16% by weight. Each sample was sonicated by an ultrasonic tip Bandelin Sonopuls HD 2200 at 20% power for 10 minutes. After this, all samples were sonicated in the ultrasonic bath in closed glass vials for further 4 hours.

Preparation of hybrid graphene/SWCNTs based quasi-solid state electrolytes. Two samples of hybrid graphene and SWCNTs quasi-solid state electrolytes were prepared: one with 12% of graphene and 3% of SWCNTs by weight was dispersed in PMII and the second one with 12% of SWCNTs and 3% of graphene was dispersed in PMII. Both samples were sonicated using an ultrasonic tip at 20% power for 10 minutes and then sonicated in an ultrasonic bath for further 4 hours.

Fabrication and characterization of DSSCs

The TiO_2 coated electrodes (WEs) were sintered at 450 °C in an oxygen atmosphere in a furnace and then cooled to 80 °C. After that, electrodes were soaked in 3×10^{-4} M solution of N719 dye in ethanol in a closed container at room temperature for 24 hours. After dye adsorption white TiO_2 film became reddish. Dyed TiO_2 films were washed with ethanol to remove the excess dye which was not firmly bound to the surfaces of $TiO_{2.}$ Then 60 μm thick Surlyn was coated around the uncoated TiO_2 film area with the help of iron solder. Various types of electrolytes were then applied to these WEs and DSSCs were fabricated by closing them with the Pt coated FTO glass counter electrode.

Measurements of I–V curves were performed using a digital source meter (Keithley 2400) and a standard solar simulator (Oriel 92193), which was equipped with a 1.5G air mass filter and calibrated with a silicon-based reference cell. DSSC power conversion efficiency was calculated according to the equation below:

$$\eta = \frac{V_{oc} I_{sc} FF}{A_c I_l}$$

where η = overall power conversion efficiency, V_{oc} = open circuit voltage, I_{sc} = short-circuit current, FF = fill factor, I_l = light intensity of the incident light, and A_c = surface area of the cell.

Conclusion

In conclusion, a series of quasi-solid state electrolytes were prepared by the incorporation of: (1) graphene or (2) SWCNTs or (3) a combination of SWCNTs and graphene into PMII. Using these new electrolytes, significant increases in light conversion efficiencies of DSSCs were achieved. The maximum efficiency in graphene based quasi-solid state electrolytes was 2.1%. This is an increase by a factor of 13 (an increase from 0.16%). While in the case of SWCNTs based quasi-solid state electrolytes the light conversion efficiency showed a more modest increase from 0.16 to 1.43%. However, the best efficiency of 2.50% (an increase by a factor of 15) was achieved when SWCNTs and graphene were mixed in PMII. The corresponding cells demonstrated the best light conversion efficiencies among all DSSCs that prepared in this work. We believe that the increase in efficiencies is attributed to the fact that these filler materials act as extended electron transfer surfaces (EETS). The incorporation of carbon based nanomaterials has enhanced the cell efficiency, most likely due to augmented electron transfer from the counter electrode to the PMII (ILs) resulting in reduced charge diffusion length. In fact we believe that carbon nanomaterials can serve simultaneously both as charge transporters in the ILs and as catalysts for the electrochemical reduction of I_3^-.

Acknowledgements

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