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Improved dye-sensitized solar cells using ionic nanocomposite gel electrolytes

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Abstract

In this study, an effect of addition of nanoparticles into a dye-sensitized solar cells (DSCs) ionic liquid electrolyte was explored. Carbon nanotubes, other carbon nanoparticles and titanium dioxide nanoparticles were dispersed individually into a 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI) ionic liquid electrolyte by grinding. It was centrifuged to form an ionic nanocomposite gel electrolyte. The dispersion of nanoparticles resulted in a substantial increase in their viscosity. Their electric conductivity increased as well. Notable effects were obtained in photocurrent density and voltage measurements of the DSC assembled with them. Energy conversion efficiency of them was significantly improved and increased compared with a DSC using a bare ionic liquid electrolyte.

Keywords: Ionic nanocomposite gel electrolyte; Ionic liquid; Carbon nanotube; Titanium dioxide; Dye-sensitized solar cell

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1. Introduction

Dye-sensitized solar cells (DSCs) constructed using dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have attractive features of high energy conversion efficiency and low production cost and energy [1,2]. Presence of traditional organic liquid electrolytes in such cells has some problems such as a less long-term stability and a need for hermetic sealing. Therefore, solid-state DSCs using p-type semiconductors such as CuI [3] used in attempts to replace DSCs using them [4]. Solid-state DSCs did not need hermetic sealing, but energy conversion efficiency of them decreased in comparison to those of DSCs with traditional organic liquid electrolytes.

Recently room-temperature ionic liquids have attracted growing attention. They have favorable property such as a negligible vapor pressure, thermal stability, high ionic conductivity and a wide electrochemical window [4,5]. Concerning different DSCs have been reported: a DSC with ionic liquid used as an electrolyte [6]; a quasi-solid-state DSC with an ionic gel electrolyte containing dispersed silica nanoparticles [7]; and with an ionic gel electrolyte having a gelator [8,9]. They had the advantage of keeping them stability for a long time because ionic liquid electrolytes do not evaporate in normal temperature, but these cells did not perform as well as DSCs containing traditional organic liquid electrolytes. Furthermore, a DSC used the ionic gel electrolyte fell or had an equivalent performance of a DSC with an ionic liquid electrolyte. A novel way of producing an ionic gel was used: a suspension of single-walled carbon nanotubes (SWCNTs) was grinded in an imidazolium room-temperature ionic liquid [10]. These carbon nanotubes (CNTs) possess unique geometrical, electrical, mechanical and chemical properties. Using carbon nanotubes for DSCs would exhibit a high performance of a solar cell. Although photovoltaic devices using SWCNTs and fullerene (C_{60}) in electrolytes have been studied, DSCs using CNTs to make gel electrolytes have not been reported.

In this study, we prepared ionic gel electrolytes by dispersing CNTs, through the above-mentioned grinding method, into ionic liquid electrolytes and assembled DSCs with these. Expecting similar effects, we tried to disperse other carbon particles instead of CNTs into them. In addition Croce et al. have reported that a polymer electrolyte dispersed titanium dioxide (TiO_2) nanoparticles had higher conductivity than that dispersed alumina (Al_2O_3) and a ceramic free polymer electrolyte [11]. We dispersed TiO_2 nanoparticles into an ionic liquid electrolyte as well.

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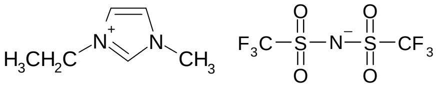
2. Experimental

2.1. Materials

The ionic nanocomposite gel electrolyte was prepared in order to disperse nanoparticles into an ionic liquid electrolyte. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI, as shown in Scheme 1) [5] was used as an ionic liquid. The ionic liquid electrolyte was composed of 1.5 mol/l of 1-ethyl-3-methylimidazoliumu iodide (EMIm-I), 0.1 mol/l of lithium iodide (LiI), 0.15 mol/l of iodine (I_2), and 0.5 mol/l of 4-*tert*-butylpyridine (TBP) in EMIm-TFSI then 0.8 wt.% of deionized water was added. The nanoparticles used to prepare ionic nanocomposite gel electrolytes were these; multi-walled carbon nanotubes (MWCNTs were made through the chemical vapor deposition (CVD) method); carbon black (CB, KETJANBLACK EC600-JD, Ketjen Black International Co.); titanium dioxide (TiO_2, P25, Nippon Aerosil Co. Ltd.); single-walled carbon nanotubes (SWCNTs, purity: 50–70%, MTR Inc.); carbon fibers (CFs, VGCF, Showa Denko KK); and graphite (Nippon Graphite Industries Ltd.). Typically, when a suspension of 1 wt.% of nanoparticles in the ionic liquid electrolyte was grinded in an agate mortar for 10 min and then centrifuged for 1 h (a centrifugal acceleration is about 200 N), an excess liquid phase was separated from a gel phase containing both nanoparticles and the ionic liquid electrolyte.

A photoelectrode made from TiO_2 paste (nanooxide-T Solaronix SA) was spread, using a doctor-blade technique, over a glass substrate with a transparent conductive oxide (TCO) covering. A fluorine-doped stannic oxide (FTO, 8–10 Ω/sq, Asahi Glass Co. Ltd.) was used as a TCO substrate. The photoelectrode was coated with a second layer of 400 nm light-scattering TiO_2 nanoparticles (Catalysis & Chemicals Ind. Co. Ltd.). After sintering at 623 K for 1 h and cooling to 372 K, a TiO_2 electrode was dye-coated by immersing them into a dye solution (Ruthenium (2,2′-bipyridyl-4,4′-dicarboxylate)$_2$ (NCS)$_2$ generally called N3 Dye Kojima Chemicals Co. Ltd.) at room temperature for 16 h. The electrode was assembled with counterelectrode of a platinum coating FTO substrate applied by sputtering. To form a solar cell, the ionic liquid electrolyte was infiltrated into the space between the electrodes. A DSC using the ionic nanocomposite gel electrolyte was prepared by spreading that on a photoelectrode and then applying a counterelectrode. The photoelectrode was 9 mm × 5 mm in area.



Scheme 1.

2.2. Analyses

The nanoparticles were examined with a scanning electron microscope (SEM, Hitachi S-5200) and a transmission electron microscope (TEM, Hitachi H-9000UHR, 200 kV). Resistances were determined by impedance measurements (frequency range: 1 MHz to 0.1 Hz, alternating current (ac) voltage: 0 V versus open circuit potential (OCP), direct current (dc) voltage: 10 mV) for which an electrochemical interface (SI1286, Schlumberger (Solartron at present)) and impedance/gain phase analyzer (SI1260, Schlumberger (Solartron at present)) were used. A cell for impedance measurements equipped two platinum electrodes had a 1 mm thick spacer with a 5 mm diameter hole between the electrodes. Photocurrent density and voltage characteristics of the solar cells were measured using an *I–V* curve tracer (MP-160, Eiko Seiki) by irradiating them with simulated solar light at AM 1.5 illumination (100 mW/cm^2, ESS-150A, Eiko Seiki).

3. Results and discussion

3.1. Characterizations for the ionic nanocomposite gel electrolyte

SEM images of the nanoparticles dispersed into the ionic liquid electrolytes to prepare the ionic nanocomposite gel electrolytes are shown in Fig. 1. We measured that MWCNTs had a diameter in the range of 10–20 nm, and their lengths were up to 10 μm; CB was a sphere of less than 50 nm in diameter; TiO_2 was a sphere of about 25 nm in diameter; SWCNTs had a diameter in ranges of 2–10 nm, and their lengths were up to 1 μm; CFs had a diameter in

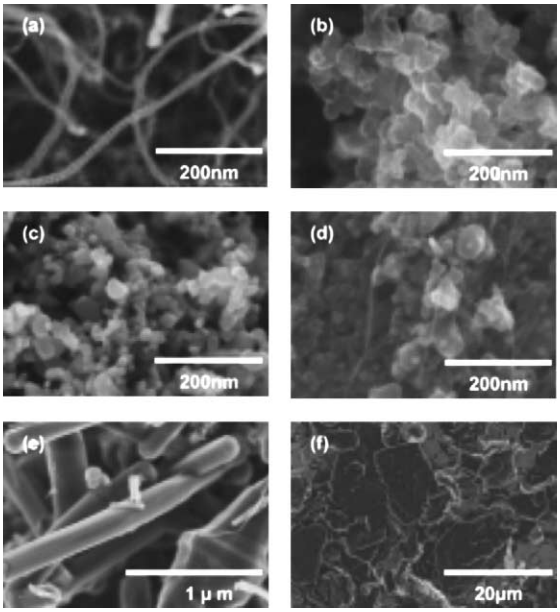


Fig. 1. Scanning electron microscope images: (a) MWCNTs; (b) CB; (c) TiO_2 nanoparticles; (d) SWCNTs; (e) CFs; (f) graphite.

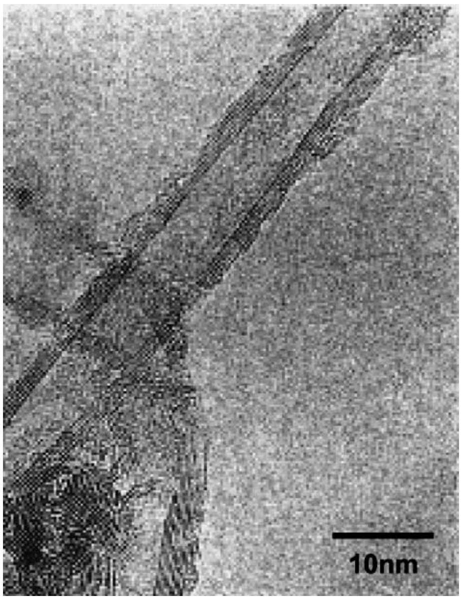


Fig. 2. A transmission electron microscope image of MWCNTs.

the range of 50–200 nm, and their lengths were up to 5 μm; and graphite was a sphere or square ranging between 5 and 20 μm in diameter, respectively. A TEM image shows that an outside and inside diameter of a MWCNT was about 10 and 5 nm, respectively, and about seven graphite layer sheets can be seen in Fig. 2.

An ionic nanocomposite gel dispersed nanoparticles in the ionic liquid is shown in Fig. 3. That did not drop off a centrifuge capsule when this was turned upside down and that could be scooped up with a spoon. A viscosity of EMIm-TFSI was about 1.2 mPa s according to the report [5], by contrast a viscosity of a MWCNT composite gel and CB composite gel was 470 and 110 dPa s, respectively (rotation rate: 0.5 rpm, E-type viscometer). The viscosity of the ionic nanocomposite gels increased more than the ionic liquid alone.

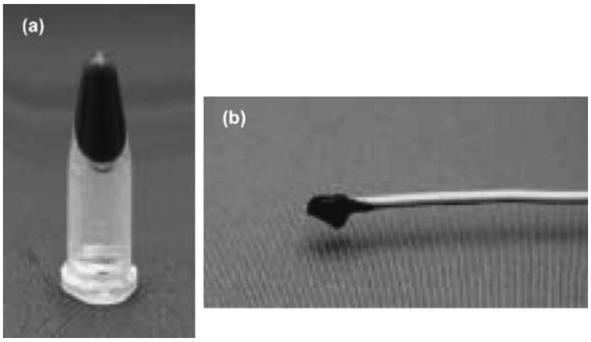


Fig. 3. Pictures of the ionic nanocomposite gel contained MWCNTs. They were ground with EMIm-TFSI in an agate mortar and then centrifuged: (a) it was in the centrifuge capsule turned upside down; (b) it was scooped up with a spoon.

Table 1
Resistances determined by impedance measurements of the original ionic liquid electrolyte and composite gel electrolytes

	Resistance (Ω)
Original ionic liquid	63.6
Ionic liquid electrolytes	76.0
MWCNT composite gel	8.9
CB composite gel	21.3
TiO_2 composite gel	61.0

A cell with platinum electrodes and a 1 mm thick spacer with a 5 mm diameter hole was used.

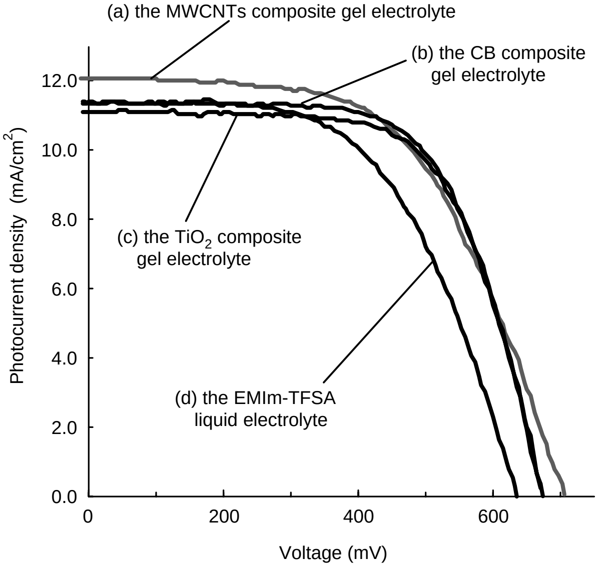


Fig. 4. Photocurrent density–voltage characteristics of the DSCs at AM 1.5 (100 mW/cm^2) illumination.

3.2. Effects of the ionic nanocomposite gel electrolyte

Table 1 shows resistances of the ionic liquid and the nanocomposite gel electrolytes were determined by impedance measurements. The ionic nanocomposite gel electrolytes had the lower resistances than the bare ionic liquid electrolyte. Fig. 4 shows photocurrent density and voltage characteristics of the solar cells with the ionic nanocomposite gel electrolytes. Characteristics of the solar cells are summarized in Table 2. Their performance improved significantly. The increase of energy conversion

Table 2
Characteristics of DSCs with each of electrolytes

Electrolyte	V_{oc} (mV)	J_{sc} (mA/cm^2)	η (%)	FF
Ionic liquid	648	11.57	4.21	0.56
MWCNTs composite gel	706	12.02	4.79	0.57
CB composite gel	672	11.02	4.83	0.65
TiO2 composite gel	675	11.45	5.00	0.65
SWCVTs composite gel	695	10.78	4.60	0.62
CFs composite gel	688	11.11	4.97	0.65
Graphic composite gel	681	10.60	4.57	0.63

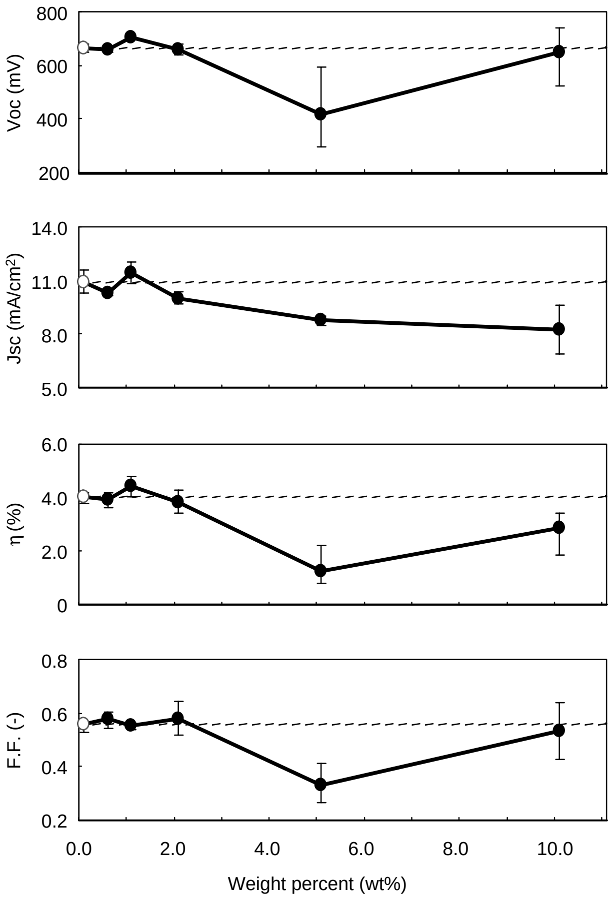


Fig. 5. The plots of V_{oc}, J_{sc}, η, FF vs. the concentration of MWCNTs. A white circle and a dashed line show the value of the DSCs with ionic liquid electrolytes alone ($n = 3$).

efficiency (η) probably resulted from improvements of an open-circuit voltage (V_{oc}) and/or a fill factor (FF). Fig. 5 shows V_{oc}, FF, a short-circuit photocurrent density (J_{sc}) and η with different weight percentages of MWCNTs dispersed into them to prepare ionic MWCNT composite gel electrolytes. V_{oc}, J_{sc} and η reached their peak at 1 wt.% MWCNTs, respectively. The result suggested that the photoelectrode and counterelectrode short-circuited in an ionic nanocomposite gel electrolyte with a large amount of MWCNTs and did not perform as well in that containing a small amount of MWCNTs.

3.3. *Effects of different kinds of nanoparticles*

It is considered that CNTs have their potentials as molecular wires such as ballistic transport, quantized resistance or Coulomb blockade, among others. We expected that the DSCs with MWCNTs and SWCNTs composite gel electrolytes exhibited performance better than that of other carbon composite gel electrolytes. CNTs were compared with CB from the difference in the form of spheres and ropes. The DSCs with MWCNTs composite gel electrolytes showed high V_{oc} and they with SWCNTs composite gel electrolytes showed high V_{oc} and FF. In contrast they with CB composite gel electrolytes showed high FF. However, they had almost same η (Fig. 6). When MWCNTs were compared with CFs from the difference in the particle size such as a diameter and length, the variation of the DSCs with CFs composite gel electrolytes in η was wider than them with MWCNTs. The large particle size did not pose the wide variation in the performance because graphite with larger the particle size had the narrow variation in the performances. The variation in their length rather than the difference in their particle size probably had an effect on the variation in the performance. If we controlled the length of CNTs or CFs, the DSCs with their composite gel electrolytes would exhibit the better performances than them. The difference in some kinds of carbon particles could not result in significant different effects. Performance of DSCs with them improved when they had the lower resistances and as such, they included conductive particles that had lower resistances than ionic liquid electrolytes.

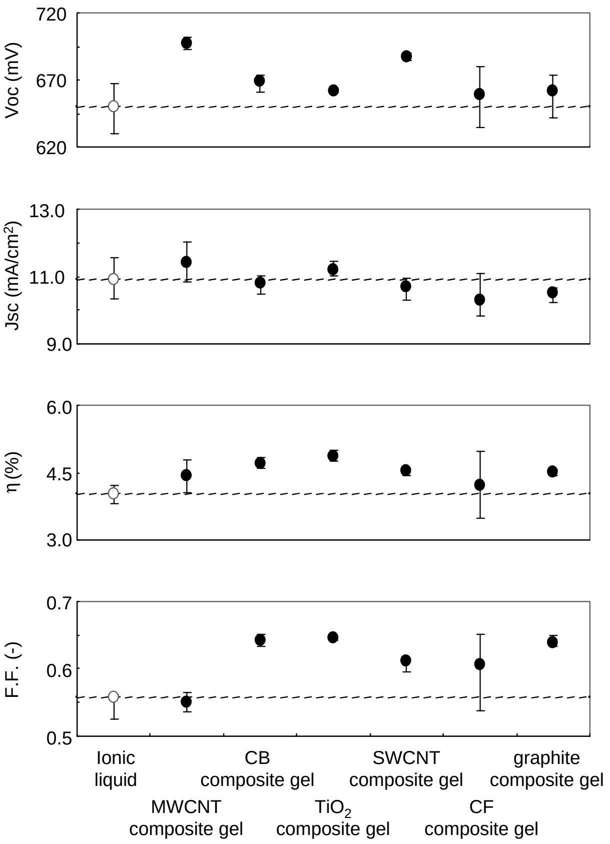


Fig. 6. The plots of V_{oc}, J_{sc}, η, FF vs. the ionic liquid electrolytes and the ionic nanoparticle gel electrolytes. A white circle and a dashed line show the value of the DSCs with ionic liquid electrolytes alone ($n = 3$).

In the case of TiO_2 nanoparticles dispersed into ionic liquid electrolytes, TiO_2 is not a conductor, but rather a semiconductor. It was difficult to think that TiO_2 nanoparticles acted as conductive particles and TiO_2 nanoparticles themselves reduced the resistance of the electrolytes. The movement of electrons in the inside of the electrolyte in

DSCs may be performed by diffusion and an electron exchange reaction (or referred to a Grotthus-like exchange mechanism [7]) between I^- and $I_3{}^-$ [12]. The movement of electrons by diffusion did not increase since a viscosity of an ionic nanocomposite gel electrolyte was going up. Here we supposed that presence of TiO_2 nanoparticles enhanced the electron exchange reaction. The adsorption of imidazolium cation on TiO_2 surfaces has reported by Kambe et al. [13]. Similarly an explanation might be that 1-ethyl-3-methylimidazolium cation ($EMIm^+$) was adsorbed on TiO_2 surfaces. While the $EMIm^+$ was adsorbed on TiO_2 particles surfaces, an I^- and $I_3{}^-$ of anion gathered around the $EMIm^+$ through the Coulomb attraction. Subsequently concentration of an I^- and $I_3{}^-$ increased locally and nanoscale local ordering of an $I^-/I_3{}^-$ redox couple was formed, consequently it seemed that it was enhanced. Fukushima et al. reported that a possible “cation-π” interaction between imidazolium cations and SWCNTs surfaces occurred [10]. As FF of the DSCs with TiO_2 composite gel electrolytes rose seemed to result in improvement of their η, η of the DSCs with each of the carbon composite gel electrolytes seemed to improve by FF of them improved. Therefore, it is possible that the electron exchange reaction was enhanced when each of the carbon nanoparticles was present.

4. Conclusion

Through the dispersion of the following nanoparticles: carbon nanotubes, carbon fibers, carbon nanoparticles and TiO2 nanoparticles, individually into a DSCs ionic liquid electrolyte (EMIm-TFSI), viscosities and conductivity of the ionic nanocomposite gel electrolyte increased. The energy conversion efficiency of DSCs prepared using them improved (mainly by increase of FF and V_{oc}) from 4.21% for the bare ionic electrolytes to 5% at the maximum value for the electrolytes containing dispersed TiO_2 nanoparticles. Similar effects were also observed in them with dispersed carbon nanotubes or other carbon nanoparticles. They offer to be useful to DSCs with ionic liquids. Thus they will enable assembled DSCs free of leakage and obtain high photovoltaic output.

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