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# 염료 감응 태양전지를 위한 고급 유기 고분자 – 무기 복합 겔형 전해질의 제조와 특성분석

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# Preparation and Characterization of Advanced Organic Polymer - Inorganic Composite Gel Electrolyte for Dye-sensitized Solar Cells

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Abstract : In this work, polymer – inorganic composites have prepared using polymer such as polyethylene glycol (PEG)/poly (methyl methacrylate, PMMA) and inorganic nanofillers materials such as TiO2 nanotubes (TiNTs)/carbon nanotubes (CNTs). The extensive structural, morphological and ionic properties revealed that the high surface area and tubular feature of nanofillers improved the interaction and cross-linking to polymer matrix which is significantly enhanced the ionic conductivity and electrical properties of composite electrolytes. Comparably high conversion efficiency ~4.5% has been observed by using the newly prepared PEG-TiNTs composite solid electrolyte as compared with PMMA-CNTs electrolyte based DSSCs (~ 3%). The detailed comparative properties would be discussed in term of their structural, morphology, ionic and photovoltaic properties.

Key words : 염료 감응 태양전지, 전해질, 양오봉, Dye-sensitized solar cells, Gel Electrolyte Organic Polymer - Inorganic

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have been investigated intensively because of its lower cost and potential alternatives to traditional photovoltaic device. Light to- electrical energy conversion efficiencies of DSSC have reached 10-11% with liquid electrolytes using organic compound, such as acetonitrile, propylene carbonate and ethylene carbonate as solvent and iodide/triiodide (I-/I3-) redox couple [1,2] under irradiation of AM 1.5. However, the use of liquidjunction cell remains has some problems such as organic solvent evaporation, leakage of liquid electrolytes and low long-term stability which are due to high temperature instability and difficulties in sealing the devices. To overcome these problems, many works have been made to substitute the liquid electrolyte with the room temperature molten salts, inorganic ptype semiconductors, ionic conducting polymers, polymer gel electrolytes and organic hole transport materials [3-6]. Among them, the use of polymer gel electrolytes is most promising materials to solve these problems because it has high ionic conductivities at ambient temperature and its trapping of liquid into polymer cages in a

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host matrix. Presently, several types of gel electrolytes based on the different kind of polymers have already reported in quasi-solid state dye sensitized solar cells [7-11]. In this work, solid electrolytes are prepared by using PEG and PMMA with TiNTs and CNTs as inorganic filler with LiI, $I_2$ and organic solvent. The system has achieve drelatively high conductivity. Further a quasi-solid state dyes ensitized solar cell was fabricated by sandwiching the polymer gel electrolyte.

## 2. Experimental

The polymer composite electrolytes were prepared using 10% polyethylene glycol (PEG) gel solution with different amount of titania nanotubes (TiNTs). In 3 ml of 10% PEG solution, amount of TiNTs 10wt%, 0.5 M LiI, 0.05 M $I_2$ and finally, 0.2M tert - butyl pyridine wasadded. Then, whole mixture was continuously stirred for 18 handagel composite electrolyte obtained. Thus prepared samples were denoted by TiNT10 - PEG as a function of the TiNTs amount. Similarly, thermally prepared CNT-PMMA composite electrolyte swereusing LiI, $I_2$ and TBP inacetonitrile.

For the preparation of $TiO_2$ thin film, $TiO_2$ (P-25,Degussa) slurry was prepared by the incremental addition of aqueous poly ethyleneglycol (Fluka,averageMWof20,000) solution as binder to prevent cracking offilm and control the porosity during preparation of film. Thus prepared uniform slurry was coated on FTO glass(FTO glass, Hartford,8Ω/sq, 80% transmittance) by a doctorblade technique. After natural drying at room temperature, the thinfilm was calcined in staticair at 450°C for 30min. After calcination, the $TiO_2$ electrode was immersed in ethanolicsolution of $3.0x10^{-4}$M cis - $(SCN)_2$ bis (2,2' -bipyridyl- 4,4' -dicorboxylate) Rutheniumdye (535 bis - TBA, Solaronix) at room temperature for 24h in the dark. The electrode was then rinsed with ethanol and dried under $N_2$ stream. Pt electrodes as counterelectrodes were prepared by electronbeam deposition of Pt (60nm thickness) on TCO glass. There sulting dye adsorbed film was sealed with a Pt - coated conducting glass, and then a gel electrolyte solution was introduced into the mesoporous TiO2 film through one of two small holes drilled in the counter electrode by capillary action. TiNTs - PEG and CNT - PMMA gel electrolytes were characterized by field emission scanning electron microscope (FE-SEM, S - 4700 , Hitachi ) , differential scanning calorimetry (DSC), electronic characterization of dye - sensitized solar cells in cluding photocurrent, and IV - curve were measured by using a scanning potentiostat ( EG & G273 ) and conductivity of electrolyte were measured by digital conductometer. The device was connected in a two - electrode configuration: the dye adsorbed $TiO_2$ film on TCO glass was connected as the working electrode and the Pt - coated TCO glass was use dasthepseudo - reference (circuited with the counterelectrode).

## 3. Results and discussion

In general, the penetration and filling of gel electrolyte into the pores of the $TiO_2$ layer allows good interfacial contact between the dye absorbed $TiO_2$ layer and electrolyte [12]. Fig.1 shows the cross - sectional and surface FESEM images of $TiO_2$ electrode saft erfilling of gel TiNT - PEG electrolytes.

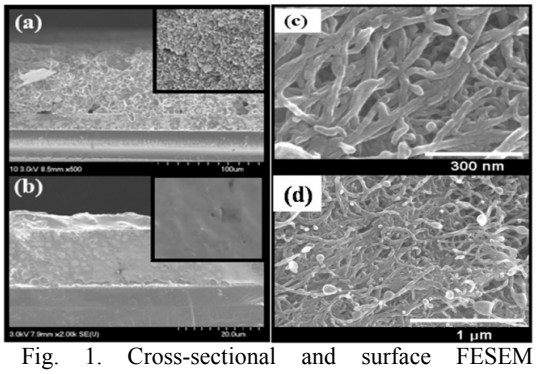


Fig. 1. Cross-sectional and surface FESEM images of $TiO_2$ electrolyte after filling of (a) TiNT5- PEG and (b) TiNT 10- PEG gel electrolyte. (c) and (d) shows the high and low magnification FESEM images of CNT - PMMA.

These images explain the degree of penetration and filling of gel electrolytes The penetration of the composite electrolyte into the mesoporous $TiO_2$ film. TiNT 10- PEG exhibited high penetration and complete filling of the electrolyte in to the pores of $TiO_2$ film (Fig.1b). The filling and penetration of electrolytes resulted from the good gelation of TiNT swith the polymer. On other hand, the lower concentration of TiNTs is not able to make proper gelation with PEG and well filling of TiNT - PEG gelelectrolytes, as shown in Fig.1 a. Hence, penetration and pore filling of the TiNT10 - PEG composite electrolytes in to the $TiO_2$ are crucial for the determination of photovoltaic properties. Similarly, after polymerization of MMA t o CNT - PMMA composite, the CNTs are aggregated to each other an dincreased the diameter from or iginalsize of CNTs by about ~ 17 - 20nm, as in Fig.1(c,d). This result reveal sthat CNTs were completely covered or coated by PMMA molecules (Fig.1d).

Fig. 2 shows the HR-TEM images of bare TiNT and PEG-TiNT composite electrolytes as a function of TiNTs wt%. Bare TiNTs (Fig. 2a) has shown typical fringes well grown to [101] direction with the dimension of 5 nm (ID) x 8 nm (OD) and 700 − 800 nm length. The introduction of TiNTs into the polymer electrolyte matrix appeared the dark spots on the surface of TiNTs. As increasing the amount of TiNTs into composite electrolytes, the dark spots increased on the pore of TiNTs.

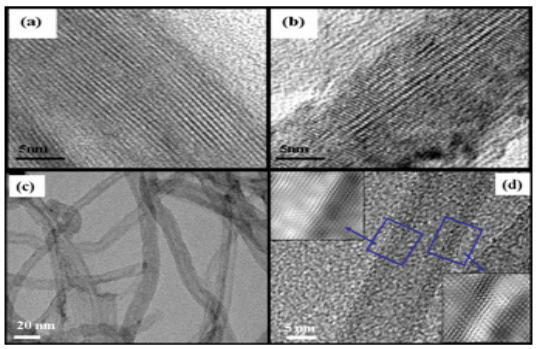


Fig. 2. HR-TEM images of (a)TiNTs and (b) TiNT5 - PEG. TEM and HR TEM images of (c) and (d) of CNT-PMMA composite electrolyte film.

These dark sports may be ascribed the presence of polymer molecules and embedded on the surface of TiNTs. From fig. 2 (d), the HR-TEM result clearly indicates that PMMA moieties were embedded in the CNTs. Additionally, the fringes of CNT-PMMA composites are not clear with highly damaged outer walls and quite distorted inner wall of tubes, which increases the fringes distances.

Table 1 is shown the differential scanning calorimetry (DSC) and ionic conductivity of TiNT-PEG and CNT-PMMA composite electrolytes. Generally, the addition of nanofillers improves the transport properties, recrystallization, enhancement of ionic conductivity due to the enlargement of the amorphous phase in polymer network and the electrode to electrolyte stability [13]. It can be seen that as increasing the amount of TiNTs in polymer matrix, the values $T_m$and$\Delta H_m$ (area integration of $T_m$ peak) decreased to the minimumin TiNT10- PEG .Incase of CNT-PMMA composite, the $T_m$ and $\Delta H_m$ are 81.2$^o$ Can d97.8J/g, respectively, which are lowered than that of bare PMMA[14]. The lower values of $T_m$ and $\Delta H_m$ indicates that the prepared TiNT-PEG and CNT - PMMA composite electrolytes are have high amorphicity due to prevention of the recrystallization of polymer inpresence of TiNTs and CNTs as nan of illers. It is well known that the high degree of crystallinity is unfavorable for

**Table 1** Summary of DSC, ionic conductivity and photovoltaic performance results.

| Samples | DSC data | | Conductivity | Photovoltaic performance | | | |
|---|---|---|---|---|---|---|---|
| | Tm ($^o$C) | Δ Hm (J/g) | $10^{-3}$x (S/cm) | $J_{SC}$(mA/cm$^2$) | $V_{OC}$ (V) | FF (%) | η (%) |
| PEG | 49.2 | 32.6 | 0.81 | 8.20 | 0.624 | 57.7 | 2.9 |
| 10TiNT-PEG | 40.2 | 19.9 | 2.44 | 9.36 | 0.725 | 65.3 | 4.5 |
| CNT-PMMA | 81.2 | 97.8 | 2.3 | 8.9 | 0.57 | 61.8 | 3.0 |

ion conduction of polymerelectrolyte[15]. These composites exhibited very high ionic conductivities of $2.44\times10^{-3}$S/cm in PEG-TiNT10 and $2.3x10^{-3}$S/cm inCNT-PMMA.

Table 1 also exhibits summary of the current-voltage curves of the DSSC fabricated with the TiNT-PEG and CNT-PMMA composite electrolytes in the simulated sunlight irradiance of 100 mW/cm$^2$ .DSSC fabricated with TiNT10 -PEG achieved the maximum overall energy conversion efficiency of 4.4%, shortcircuit current density($J_{SC}$) of 9.4 mA/cm$^2$, an opencircuit voltage($V_{OC}$) of 0.73V and fillfactor(FF) of 65.3%. Contrary, DSSC fabricated with CNT- PMMA showed th e improved overall conversion efficiency of 2.94%, short circuit current density($J_{SC}$) of 8.9mA/cm$^2$, an opencircuit voltage ($V_{OC}$) of 0.567 volt and fillfactor(FF) of 61.8%. The high $J_{SC}$ and conversion efficiency of DSSCs is attributed to the high ionic conductivities and amorphicity of composite electrolytes. The high penetraton of gel electrolyte in to the porous $TiO_2$ film is provides good interfacial contacts between electrolyte layers to $TiO_2$ layer, which is capableto execute advanced photovoltaic properties and high conversion efficiency of devices.

## 4. Conclusions

Novel composite gel electrolytes for DSSCs were prepared by introducing TiNTs and CNTs as the nano fillers into PEG and PMMA matrixes. The TiNTs-PEG and CNT-PMMA composite gel electrolyte showed improved morphological, amorphicity and ionic conductivity due to the highly crystalline nature of TiNTs and CNTs. The DSSCs fabricated with the optimal composite gel electrolyte, PEG-TiNT10, showed an improved efficiency of 4.43%, which was maintained for 30 days without any significant decrease. On the other hand, DSSCs fabricated with CNTs-PMMA composite electrolytes achieved relatively high conversion efficiency of 2.9% with short circuit current ($J_{SC}$) of 8.9mA/cm$^2$ and fillfactor of 61.8%, which is attributed to formation of high amount of $I_3^-$, enhanced amorphicity and ionicconductivity due to the formation of strong bonding between CNT and PMMA.

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