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PVC-g-PSSA 가지형 공중합체를 이용한 다공성 TiO_2 박막의 합성 및 염료감응 태양전지 응용

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Synthesis of Porous TiO_2 Thin Films Using PVC-g-PSSA Graft Copolymer and Their Use in Dye-sensitized Solar Cells

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요 약: 원자전달 라디칼 중합(ATRP)에 의해 poly(vinyl chloride) (PVC) 주사슬과 poly(styrene sulfonic acid) (PSSA) 곁사슬로 되어있는 양쪽성 PVC-*g*-PSSA 가지형 공중합체를 합성하였다. PVC-g-PSSA 가지형 공중합체 고분자를 템플레이트로 사용하고 졸겔법을 적용하여, 결정성 아타네제상의 미세기공 이산화티타튬 필름을 제조하였다. TiO_2 전구체인 TTIP를 친수성인 PSSA 영역과 선택적으로 작용시켜 TiO_2 메조기공 필름을 성장하였으며, 이를 주사전자 현미경(SEM)과 엑스레이회절(XRD)분석을 통해 분석하였다. 스핀코팅 횟수와 P25 도입에 따른 염료감응 태양전지 성능을 체계적으로 분석하였다. 그 결과 준고체 고분자 전해질을 이용하였을 때, 100 mW/cm^2 조건에서 에너지 변환 효율이 2.7%에 이르렀다.

Abstract: An amphiphilic graft copolymer comprising a poly(vinyl chloride) (PVC) backbone and poly (styrene sulfonic acid) (PSSA) side chains (PVC-*g*-PSSA) was synthesized via atom transfer radical polymerization (ATRP). Mesoporous titanium dioxide (TiO_2) films with crystalline anatase phase were synthesized via a sol-gel process by templating PVC-g-PSSA graft copolymer. Titanium isopropoxide (TTIP), a TiO_2 precursor was selectively incorporated into the hydrophilic PSSA domains of the graft copolymer and grew to form mesoporous TiO_2 films, as confirmed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. The performances of dye-sensitized solar cell (DSSC) were systematically investigated by varying spin coating times and the amounts of P25 nanoparticles. The energy conversion efficiency reached up to 2.7% at 100 mW/cm^2 upon using quasi-solid-state polymer electrolyte.

Keywords: *dye-sensitized solar cell (DSSC), sol-gel, atom transfer radical polymerization (ATRP), titanium dioxide (TiO_2), graft copolymer*

1. Introduction

Polymer electrolytes have been intensively utilized in various applications such as lithium batteries [1], electrochromic devices [2], polymer electrolyte membrane fuel cells [3,4], facilitated transport membranes [5]. Recently, polymer electrolytes were also investigated as a solid electrolyte in dye-sensitized solar cells (DSSC) [6-8]. It is because the use of liquid electrolytes might not be practical for long-term operation due to problems such as electrolyte leakage or evaporation. Thus, many research groups have been searching for alternatives to replace the liquid electrolytes, such as solid hole conductors [9], ionic liquids [10,11], gel electrolytes [12,13], quasi-solid [14,15] and solid polymer electrolytes [16,17].

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DSSCs were first reported by the Gratzel group in 1991 [18], after which they have received much attention due to global warming and the demand for cheap sources of renewable energy. In particular, DSSCs are more attractive than conventional Si-based p-n junction solar cells in terms of great design opportunities, light weight, flexibility and a low cost. DSSCs consist of a sensitizing dye, transparent conducting substrates (F-doped tin oxide), nanometer sized TiO_2 film, iodide electrolyte, and Pt-coated counter electrode. When a dye molecule absorbs light, it excites electrons on the highest occupied molecular orbital to the lowest unoccupied molecular orbital. The excited dye molecule injects an electron into the conducting band of the TiO_2 film. Preparation of mesoporous TiO_2 films with high crystallization and large surface area is of importance for enhancing the efficiency of DSSC. Thus, much prior research has focused on the development of well-organized TiO_2 films in order to an energy conversion efficiency.

A sol-gel method has many advantages such as an easy deposition on complex shaped substrates, easy control of morphology and simple equipment [19]. The preparation of sol-gel derived nanocrystals has been much investigated due to the versatility and potential for mass production [20]. In this study, we introduced a sol-gel process to synthesize mesoporous TiO_2 thin films templated by a graft copolymer, which is more attractive than a block copolymer due to its low cost and easy of synthesis. An amphiphilic graft copolymer, i.e. poly(vinyl chloride)-graft-poly(styrene sulfonic acid) (PVC-g-PSSA), consisting of PVC backbone and POEM side chains was synthesized via atom transfer radical polymerization (ATRP). The graft copolymer templated TiO_2 films have been characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD), and their efficiencies in DSSC employing quasi-solid-state polymer electrolytes are reported.

2. Experimental

2.1. Material

Poly(vinyl chloride) (PVC, M_n = 55,000 g/mol, M_w = 97,000 g/mol), 4-styrene sulfonic acid (SSA), copper(I) chloride (CuCl), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA), titanium tetraisopropoxide (TTIP, 97%), hydrochloric acid (HCl, 37%) and 1-methy-2-pyrrolidinone (NMP) were purchased from Aldrich. Methanol and dimethyl sulfoxide (DMSO) were purchased from J. T. Baker. All solvent and chemicals were reagent grade and used as received.

2.2. Synthesis of PVC-*g*-PSSA Graft Copolymer

PVC-g-PSSA graft copolymer was synthesized via ATRP, according to a previously reported method [21]. In brief, two grams of PVC was dissolved in 18 mL NMP in a round flask at 70°C. Separately, 14 g of SSA was dissolved in 18 mL DMSO at 70°C and added to the PVC solution. After producing homogeneous solution, 0.04 g of CuCl and 0.1 mL of HMTETA were added and the reaction flask was sealed with a rubber septum. After N_2 purging for 30 min, the reaction vessel was immersed in an oil bath at 90°C. The reaction was allowed to proceed for 24 h. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the graft copolymer was completely dried in a vacuum oven overnight at room temperature.

2.3. Preparation of Mesoporous TiO_2 Films

First, 0.9 g of PVC-g-PSSA was dissolved in 3 mL of DMSO and stirred for 24 h to ensure a clear solution. Separately, 5 mL of TTIP was slowly dropped in 2.5 mL of a HCl aqueous solution with vigorous stirring, followed by adding 2.5 mL of DI-water. After aging for 15 min, 2 mL of the TTIP sol was added to 3 mL of the PVC-g-PSSA polymer solution. The sol was aged under a mild stirring condition at room temperature for 3 h and then spin-coated on the

FTO glass with different coating times, i.e. 2, 4 and 6 times at 1,500 rpm for 20 seconds, named as No. 1, 2 and 3. For the sample of No. 4, P25 (Degussa) nanoparticles of 0.5 g were added to the sol. The resultant sols were well dispersed using speed control Type 37,600 mixer for several seconds. Then, the viscous sols were cast on the FTO-glass using a doctor blading method.

2.4. Fabrication of DSSCs

DSSCs with an active area of 0.4 cm^2 were constructed by drop-casting of electrolyte solution onto the photoelectrode and covering with the counter electrode, according to previous reported procedure [22-24]. In order to prepare photoelectrodes, conductive FTO glasses were first coated by titanium diisopropoxide bis (acetylacetonate) 75 wt% solution in 2-propanol. After drying at 50°C for 30 min, the photoelectrodes were heated at 450°C for 30 min, followed by cooling to room temperature for 8 hours. The Pt counter electrodes were prepared by spin coating hydrogen hexachloroplatinate (IV) hexahydrate solution (H_2PtCl_6) onto the FTO glasses. Then, the counter electrodes were heated to 450°C for 30 min. The photo electrode was spin coated with the solution at 1,500 rpm for 20 sec. The photo electrode was sintered at 450°C for 30 min to obtain mesoporous TiO_2 film. After being sintered, the TiO_2 electrodes were immersed into a solution of an amphiphilic dye (Ruthenium 35-bisTBA, N719, Solaronix SA) in absolute ethanol for 2 hours at 50°C. After drying the dye-adsorbed photoelectrodes at room temperature, polymer electrolyte solutions were cast onto the dye-adsorbed TiO_2 electrodes. A quasi-solid polymer electrolyte solution was prepared by dissolving fumed silica nanoparticles (SiO_2), PEGDME, MPII, and I_2 in acetonitrile [23]. The mole ratio of ether oxygen to iodide salt was fixed at 20, and the iodine content was fixed at 10 wt% with respect to the salt. The cells were placed in a vacuum oven for a day to permit complete evaporation of solvent and were then sealed with an epoxy resin.

Photoelectrochemical performance characteristics, including short-circuit current (J_{sc}, mA/cm^2), open-circuit voltage (V_{oc}, V), fill factor (*ff*), and overall energy conversion efficiency (η) were measured using a Keithley Model 2,400 and a 1000 W xenon lamp (Oriel, 91193). The light was homogeneous over an 8 × 8 in^2 area, and its intensity was calibrated with a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si+KG filter, Certificate No. C-ISE269) for a sun light intensity of 1 (100 mW/cm^2). This calibration was double-checked with a NREL-calibrated Si solar cell (PV Measurements Inc.). Photoelectrochemical performance was calculated using the following equations:

$$FF = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}} \quad (1)$$

$$\eta\,(\%) = \frac{V_{max} \cdot J_{max}}{P_{in}} \times 100 = \frac{V_{oc} \cdot J_{sc} \cdot ff}{P_{in}} \times 100 \quad (2)$$

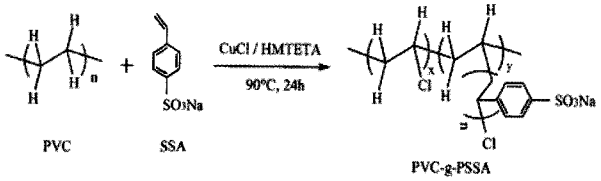
where J_{sc} is the short-circuit current density (mA/ cm^2), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mA/cm^2) and V_{max} (V) are the current density and voltage in the *J-V* curve, respectively, at the point of maximum power output.

2.5. Characterization

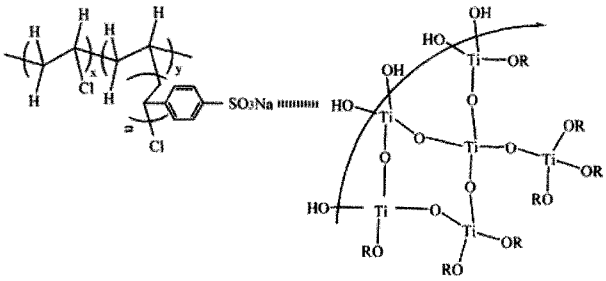
FT-IR spectra of samples were performed on Perkin Elmer spectrum 100, between frequency 4,000~600 cm^{-1} using an ATR. FE-SEM image was obtained to observe the morphology of TiO_2 film from Bruker D8 DISCOVER (Carl Zeiss, Germany). UV-visible spectroscopy was measured with spectrophotometer (Hewlett Packard) in the range of 300 to 800 nm. The XRD experiment was performed on a Rigaku 18 kW rotating anode X-ray generator with Cu-Ka radiation operated at 40 kV and 300 mA.

2.6. Measurement of Dye Adsorption

First, the N719 dye-sensitized TiO_2 photoelectrode was dipped into 10.0 mL of a 10^{-2} M solution of NaOH in ethanol-H_2O (1 : 1). The mixture was stirred until complete desorption of the dye into the liquid



Scheme 1. Synthesis of PVC-g-PSSA graft copolymer by ATRP.



Scheme 2. Interaction between PVC-g-PSSA graft copolymer and TiO_2 sol-gel solution.

occurred. The volume of the NaOH solution containing the fully desorbed dye was then carefully measured by UV-visible spectroscopy. The amounts of the NaOH solutions were recorded, and the absorption value at 515 nm (as a function of wavelength) was used to calculate the number of adsorbed N719 dye molecules according to the Beer-Lambert law, $\mathbf{A} = \epsilon lc$, where A is the absorbance of the UV-visible spectra at 515 nm, ϵ = 14,100/M cm is the molar extinction coefficient of the dye at 515 nm, l is the path length of the light beam, and c is the dye concentration [23].

3. Results and Discussion

PVC-g-PSSA graft copolymer was synthesized via one-step ATRP, as illustrated in Scheme 1. This copolymer was combined with a TiO_2 precursor, i.e. TTIP to produce graft copolymer/TiO_2 hybrid via a sol-gel process. Because of hydrophilicity, TTIP is preferentially incorporated into the hydrophilic PSSA domains of the graft copolymer and grows to form TiO_2 nanoparticles [25]. Upon calcination, the hydrophobic PVC domains were completely burn out to generate pores whereas PSSA/TTIP produced the TiO_2 matrix, as shown in Scheme 2.

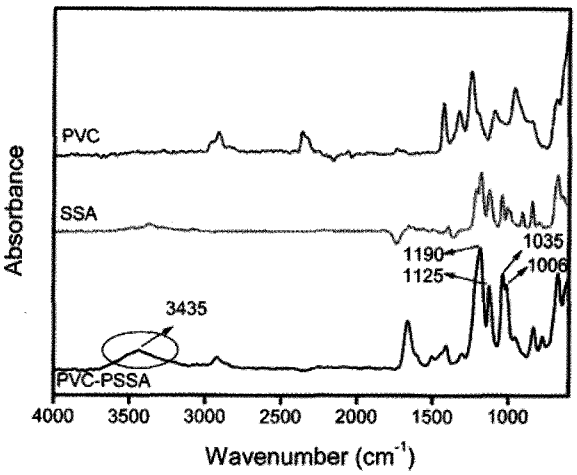


Fig. 1. FT-IR spectra of pristine PVC, SSA and PVC-g-PSSA graft copolymer.

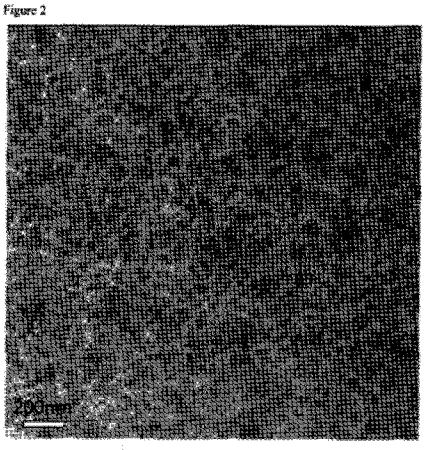


Fig. 2. TEM image of PVC-g-PSSA graft copolymer.

Fig. 1 shows the FT-IR spectra of pristine PVC and its graft copolymer with PSSA. Compared to the pristine PVC, the PVC-g-PSSA graft copolymer exhibited the strong absorption bands at 1,190, 1,125, 1,035 and 1,006 cm^{-1}. These bands result from the stretching vibrations of phenyl rings substituted with sulfonate groups and sulfonate anions attached to phenyl ring [26]. The broad absorption band at around 3,435 cm^{-1} is attributed to the water bounded to ionic groups of the graft copolymer.

TEM analysis was carried out to characterize the

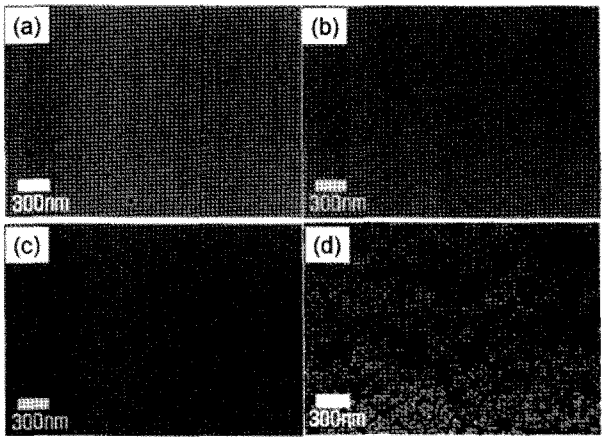


Fig. 3. SEM images of mesoporous TiO_2 films prepared with different compositions of PVC-g-PSSA and TTIP; (a) No 1, (b) No 2, (c) No 3 and (d) No 4.

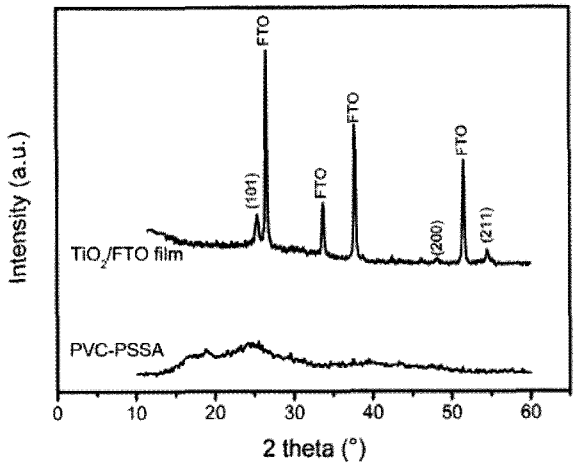


Fig. 4. XRD patterns of PVC-g-PSSA graft copolymer and mesoporous TiO_2 film (No 3).

morphology of PVC-*g*-PSSA graft copolymer, as shown in Fig. 2. The large difference of electron densities between the PVC main chains and the PSSA side chains produces amphiphilic property and thus provides clear image contrast between two domains [17]. Dark regions represent the hydrophobic domains of PVC main chains whereas lighter regions do the PSSA side chains. The PVC-*g*-PSSA graft copolymer self-assembled into the hydrophobic domains of PVC main chains with the hydrophilic domains of PSSA brush layer, resulting from chemical dissimilarity between the two polymer segments.

SEM analysis was used to characterize the morphology of PVC-*g*-PSSA/TTIP films after calcination at 450°C. A TiO_2 precursor, TTIP is selectively incorporated into the hydrophilic PSSA domains of the graft copolymer and grows to form TiO_2 nanoparticles, as illustrated in Scheme 2. The SEM images of Fig. 3 shows randomly distributed pores at film surface and their size is approximately 30 nm. Fig. 3(a)~(c) shows the effect of coating time on the TiO_2 morphology. Generally, the number of pores increased with an increase in coating time of sol-gel solution. Upon the introduction of P25 powder (Fig. 3d), spherical particles grew up uniformly and covered the whole surface of TiO_2 film.

The structural patterns of PVC-g-PSSA graft copolymer and the crystallized mesoporous TiO_2 thin film templated by PVC-g-PSSA were investigated using XRD analysis, as presented in Fig. 4. Neat PVC-g-PSSA graft copolymer exhibited some weak peaks at 16.7°, 18.9°, and 24.6°, indicating its amorphous state. The mesoporous TiO_2 thin film showed several crystalline sharp peaks at 25.3°, 48.2° and 54.5°, which are attributed to (101), (200), and (211) planes, respectively, of the anatase TiO_2 phase [27,28]. It represents that the structural changes and phase transformation of TiO_2 to crystalline anatase occurred at around 450°C. The rest of the strong peaks arose from the FTO glass. There was no amorphous peak from graft copolymer in the mesoporous TiO_2 thin film, indicating complete calcination of the organic template.

The efficiency of DSSC strongly depends on the amount of dye adsorption, which is related, in turn, to the structure of the TiO_2 film. The dye adsorption of the mesoporous TiO_2 films were measured by adsorption-desorption experiments. Fig. 5 shows the UV-visible absorption spectra for dye adsorption onto the TiO_2 films and their results were summarized in Table 1. The strong absorption at around 515 nm is attributed to N719 dye molecules. The amount of dye adsorption was different depending on the kind of TiO_2 films and affected by the number of spin coating times and the presence of P25. The amount of dye adsorption was

Table 1. Dye adsorption amounts and performance parameters of DSSC fabricated with different types of TiO_2 photoelectrodes at 100 mW/cm^2

Sample	Thickness (μm)	Dye adsorbed (nmol/cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
No 1	0.7	14.2	0.22	1.27	0.30	0.08
No 2	1.5	18.3	0.61	1.92	0.58	0.68
No 3	3.8	27.3	0.76	2.69	0.56	1.15
No 4	12.0	118	0.77	6.21	0.55	2.64

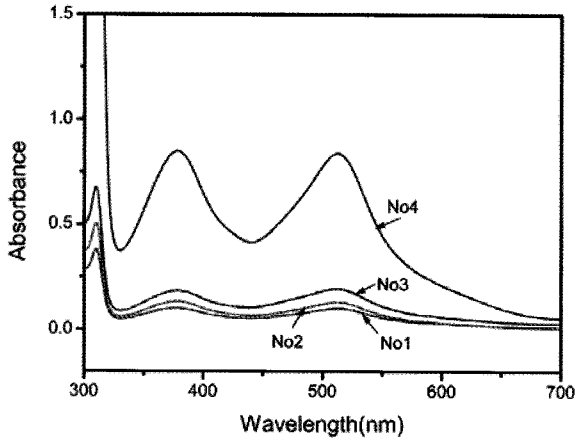


Fig. 5. UV-visible spectra for the dye adsorption in mesoporous TiO_2 films prepared with different compositions of PVC-g-PSSA and TTIP.

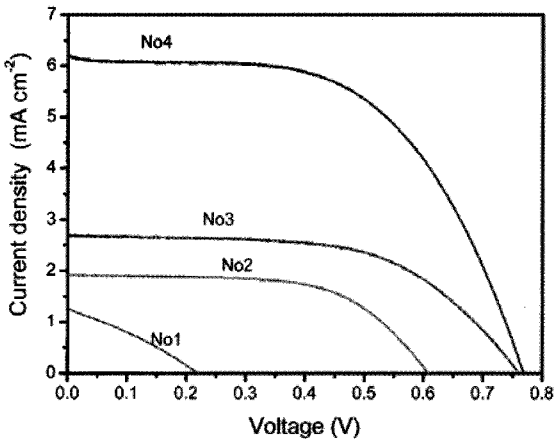


Fig. 6. Current-voltage characteristics of DSSC fabricated with different types of TiO_2 photoelectrodes at 100 mW/cm^2.

arranged in the following order: No 1 < No 2 < No 3 < No 4.

In order to examine the photoelectrochemical performance, the photocurrent density-voltage characteristics of DSSC were measured at 100 mW/cm^2 as shown in Fig. 6 and summarized in Table 1. The energy conversion efficiency continuously increased with the thickness of TiO_2 film, which was also related to the amount of dye adsorption. The performance of DSSCs was arranged in the following order: No 1 < No 2 < No 3 < No 4, which is consistent with the sequence of amount of dye adsorption. The DSSC of No 4 showed improved the J_{sc} and V_{oc} values and a better performance of 2.64% at 100 mW/cm^2. It results from the large amounts of dye adsorption due to larger thickness of mesoporous TiO_2 film.

4. Conclusions

Amphiphilic PVC-g-PSSA graft copolymer was synthesized via ATRP technique using PVC backbone as a macroinitiator and used as a template for the preparation of mesoporous titanium dioxide (TiO_2) film for DSSC. Synthesis of microphase-separated PVC-g-PSSA graft copolymer was successful via a grafting-from method using ATRP. The graft copolymer was molecularly combined with a TiO_2 precursor, TTIP to produce graft copolymer/TiO_2 nanocomposite membranes via a sol-gel process. A hydrophilic TTIP was selectively confined into the hydrophilic PSSA domains of the graft copolymer and grew to form TiO_2 nanoparticles. The porosity of mesoporous TiO_2 film and the effect of spin coating times were investigated. As a result, the DSSS of No 4 with large spin coating time and the presence of P25 nanoparticles showed the highest

energy conversion efficiency of 2.64% at 100 mW/cm^2.

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