

Preparation of Porous TiO₂ Thin Films by Poly(vinyl chloride)-*graft*-poly(N-vinyl pyrrolidone) and Their Applications to Dye-sensitized Solar Cells

Seung Hyeon Yeon, Rajkumar Patel, Jong Kwan Koh, Sung Hoon Ahn, and Jong Hak Kim*

Department of Chemical and Biomolecular Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, South Korea

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Abstract : Mesoporous titanium dioxide (TiO₂) thin films were prepared using poly(vinyl chloride)-*graft*-poly(N-vinyl pyrrolidone) (PVC-g-PVP) as a templating agent via sol-gel process. Grafting of PVC chains from PVC backbone was done by atom transfer radical polymerization (ATRP) technique. The successful grafting of PVP to synthesize PVC-g-PVP was checked by fourier-transform infrared spectroscopy (FT-IR) and gel permeation chromatography (GPC). The carbonyl group interaction of PVC-g-PVP graft copolymer with TiO₂ was confirmed by FT-IR. The porous morphologies of the TiO₂ films generated after calcination at 450°C was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mesoporous TiO₂ films with 580 nm in thickness were used as a photoelectrode for solid state dye sensitized solar cell (DSSC) and showed an energy conversion efficiency of 1.05% at 100 mW/cm².

Keywords : Polymer electrolytes, Dye-sensitized solar cell, Graft copolymer, Titania (TiO₂), Sol-gel

1. Introduction

Polymer electrolytes are materials that consist of metal salts dissolved in a solid polymeric matrix containing polar groups such as ester, ether, amide linkages. The interaction between a metal salt and a polymer matrix directly determines the dissolution behavior of the metal salt and consequently the concentration of free ions, which are responsible for the ionic conductivity, mass transport properties, and nanostructural properties. Polymer electrolytes have been utilized in various electrochemical devices such as lithium batteries,¹⁾ electrochromic devices,²⁾ polymer electrolyte membrane fuel cells,^{3,4)} facilitated transport membranes,⁵⁾ and dye-sensitized solar cells (DSSC).^{6,7)}

After O'Regan and Gratzel invented a new type of solar cell in 1991,⁸⁾ DSSCs have been extensively studied due to relatively lower cost than silicon based solar cell and potential use of flexible panels. An energy conversion

efficiency of more than 11% has been achieved in DSSC using an organic liquid-based electrolytes containing triiodide/iodide, i.e. I₃⁻/I⁻ as a redox couple.⁸⁾ However, utilization of liquid electrolytes in DSSC is not practical for long-term operation due to problems associated with electrolyte leakage or evaporation. Thus, many research groups have been searching for alternatives to replace the liquid electrolytes, such as inorganic or organic hole conductors,⁹⁾ ionic liquids,^{10,11)} gel electrolytes,^{12,13)} quasi-solid¹⁴⁻¹⁶⁾ or solid polymer electrolytes.^{17,23)}

The porosity of TiO₂ electrode is one of the most important factor that determines the photoelectron transport and dye adsorption. The physical properties of TiO₂ mainly depend on the morphology, type and size of its crystallites. There are several methods to prepare TiO₂ nanoparticle such as hydrothermal process,²⁴⁾ surfactant directed,²⁵⁾ and sol-gel approaches.²⁶⁻³⁰⁾ Among them, sol-gel methods are usually used to prepare targeted material due to the easy control of their structural and morphological behavior. Structure directing agents such as surfactants or amphiphilic block copolymer are often introduced to prepare well-defined porous thin films.²⁶⁻³⁰⁾

*E-mail: jonghak@yonsei.ac.kr

However, graft copolymer is more economical than block copolymer as well as the method of synthesis is simple. In our previous paper, poly(vinylidene fluoride-*co*-chloro trifluoroethylene)-*graft*-poly(oxyethylene methacrylate) (P(VDF-*co*-CTFE)-*g*-POEM)³¹⁾ and poly(vinyl chloride)-*graft*-poly(oxyethylene methacrylate) (PVC-*g*-POEM) were used as a structure directing agent to synthesize mesoporous TiO₂ films.^{31,32)}

In this study, poly(vinyl chloride)-*graft*-poly(N-vinyl pyrrolidone) (PVC-*g*-PVP) graft copolymer was synthesized by using atom transfer radical polymerization (ATRP) technique. It is because PVP is a hydrophilic polymer that can coordinate to TiO₂ precursor while PVC is a hydrophobic polymer, which would provide good phase-separated morphology. The graft copolymer was characterized by FT-IR, NMR and the self assembly behaviour was analyzed by transmission electron microscopy (TEM). This graft copolymer solution was mixed with titania isopropoxide (TTIP) sol-gel precursor to form in situ TiO₂ thin films, followed by calcination at high temperature. The thin films were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. Finally, the porous thin TiO₂ films were used as a photoelectrode for quasi-solid-state dye-sensitized solar cell (DSSC) fabrication.

2. Experimental

2.1. Materials

Fumed silica nanoparticles (SiO₂, 14 nm), poly(ethylene glycol dimethyl ether) (PEGDME, M_n = 500 g/mol), iodine (I₂), titanium (IV) bis(ethyl acetoacetato) diisopropoxide, chloroplatinic acid hexahydrate (H₂PtCl₆), titanium (IV) isopropoxide (TTIP, 97%), hydrogen chloride solution (HCl, 35 wt%), and sodium hydroxide solution (NaOH, 0.1 N) were purchased from Aldrich. Distilled water was obtained with a water purification system made by Millipore Corporation. 1-Methyl-3-propyl imidazolium iodide (MPII) and ruthenium dye (535-bisTBA, N719) were purchased from Solaronix, Switzerland. Acetonitrile, butanol, 2-propanol, chloroform, and ethanol were purchased from J.T. Baker. Fluorine-doped tin oxide (FTO) conducting glass substrate (TEC8, 8 ohms/sq, 2.3 mm thick) was purchased from Pilkington, France. Poly(vinyl chloride) PVC, Mw ~ 97,000 g/mol, Mn ~ 55,000 g/mol, PDI 1.76), N-vinyl pyrrolidone (VP, ≥ 99%), 1,1,4,7,10,10-

hexamethyltriethylene tetramine (HMTETA, 99%), and copper(I) chloride (CuCl, 99%), are procured from Aldrich. 1-methyl-3-propylimidazolium iodide (MPII), lithium iodide (LiI), were purchased from Aldrich chemicals and used as received without further purification.

2.2. Synthesis of PVC-*g*-PVP

Six grams of PVC and 18 g of VP were dissolved in 50 mL of NMP together in a round bottom flask. 0.1 g CuCl catalyst and 0.23 mL of HEMTA ligand was added to the round bottom flask. The whole system was deoxygenated by purging of nitrogen into the system for half an hour. Then the temperature was raised to 90°C with stirring and the reaction continued for 18 h. The resultant product was diluted with THF and passed through activated Al₂O₃ column to remove catalyst and then precipitated in methanol. The product was purified by dissolving in THF and reprecipitated in methanol. The product was dried in vacuum oven at 50°C overnight. PVC-*g*-PVP with 64:36 wt ratio were obtained.

2.3. Preparation of photoelectrodes

Transparent glass, coated with conductive FTO, was used for the photoelectrode. The neat glass was cleaned by sonication in isopropanol and then in chloroform. The clean conducting surface of the FTO glass was blocked by a layer of titanium (IV) bis(ethyl acetoacetato) diisopropoxide using spin coating, followed by heating to 450°C for 2 h, holding for 30 min, and cooling to 30°C for 4 h. 0.05 mL of HCl (37%) was added slowly to 0.3 mL TTIP solution in THF under vigorous stirring. In another vial, PVC-*g*-PVP graft copolymer was prepared in 1 wt% THF and added to the TTIP/HCl/THF solution slowly to make a clear sol-gel solution. The solution was aged by stirring at ambient temperature for at least 3 h. The film was casted on a FTO glass with blocking layer at 2000 rpm for 30 sec. The organic compounds were completely removed via sintering by heating to 450°C for 4 h, holding at 450°C for 30 min and cooling to 30°C for 8 h. The nanocrystalline TiO₂ layers were then sensitized with a 10⁻⁴ mol dm⁻³ alcoholic ruthenium solution at 50°C for 2 h in darkness. Finally, the dye-sensitized photoelectrodes were rinsed with absolute ethanol and dried in a vacuum oven.

2.4. Preparation of counter electrode

Transparent glasses coated with a conductive FTO were used for counter electrodes. These glasses were cleaned by sonication in isopropanol and then in chloroform. The counter electrodes were prepared by spin coating 4 wt% H_2PtCl_6 propanol solution onto the conductive FTO glass and sintering at 450°C for 2 h, holding for 30 min, and cooling to 30°C over 8 h.

2.5. Preparation of polymer electrolytes

A polymer electrolyte solution was prepared by dissolving fumed silica nanoparticles (SiO_2), PEGDME, MPIL, and I_2 in acetonitrile. 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.³³⁾ After casting polymer electrolyte solution onto photoelectrode, the solvent was evaporated very slowly to allow penetration of the electrolytes through the mesopores of TiO_2 layer. Both electrodes were then superposed together and pressed between two glass plates in order to achieve a thin electrolyte layer. The cells were placed in a vacuum oven for 1 day for complete evaporation of the solvent.

2.6. Fabrication of DSSC

DSSCs with an active area of 0.24 cm^2 were constructed by drop-casting of electrolyte solution onto the photoelectrode and covering with the counter electrode, according to the following procedure.³¹⁻³⁴⁾ 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 2400 and a 1000 W xenon lamp (Oriel, 91193). The light was homogeneous over an $8 \times 8\text{ in}^2$ 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 ($100\text{ mW}/\text{cm}^2$). This calibration was double-checked with a NREL-calibrated Si solar cell (PV Measurements Inc.).

2.7. Dye adsorption amount

The N719 dye-sensitized TiO_2 photoelectrodes were dipped into 10 mL of 0.01 M aqueous ethanolic (1:1)

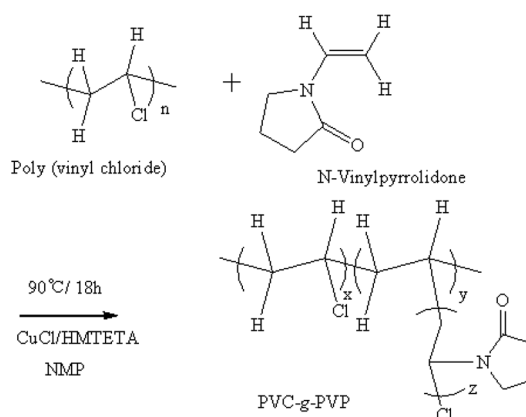
alkaline solution of NaOH. The mixtures were stirred until complete desorption of the N719 dye. The volume of the alkali solution containing the fully desorbed dye was carefully measured by UV-visible spectroscopy (Hewlett-Packard, Hayward, CA) at 515 nm. The adsorbed dye was calculated according to the Beer-Lambert law.

2.8. Characterization

FT-IR measurements were performed on Perkin Elmer spectrum 100, between frequency $4000\text{--}600\text{ cm}^{-1}$ using an ATR. The XRD experiment was performed on a Rigaku 18 kW rotating anode X-ray generator with Cu-K α radiation operated at 40 kV and 300 mA. UV-visible spectroscopy was measured with a spectrophotometer (Hewlett Packard) in the range of 200 to 800 nm. TEM images were obtained from JEM 1010 which was made by JEOL. For getting TEM images, the polymer was dissolved in THF with 0.3 wt% concentration, and then cast a drop of solution on the copper grid. Morphological characterization for mesoporous TiO_2 thin films was carried out using a field-emission scanning electron microscope (FE-SEM, S-4700, Hitachi).

3. Results and discussion

The PVC-g-PVP amphiphilic graft copolymer having hydrophobic PVC main chain and hydrophilic PVP side chain was synthesized by ATRP, as shown in Scheme 1. This technique has been used to prepare a graft copolymer having well defined structures.^{35,36)}



Scheme 1. ATRP synthesis of PVC-g-PVP graft copolymer.

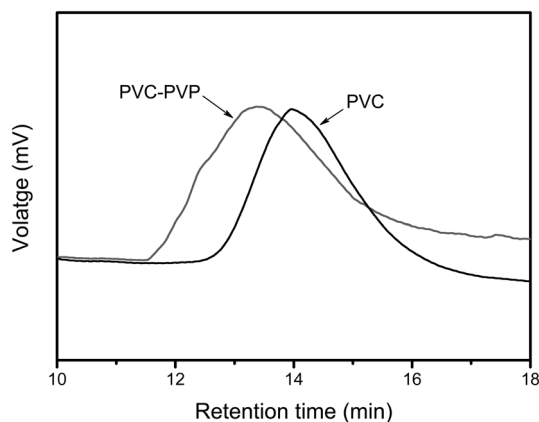


Fig. 1. GPC traces of pristine PVC and PVC-g-PVP graft copolymer.

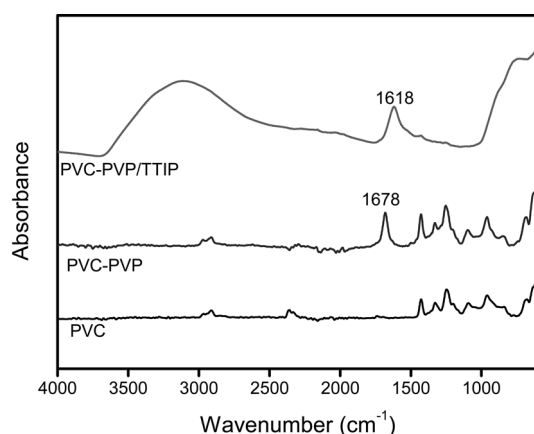
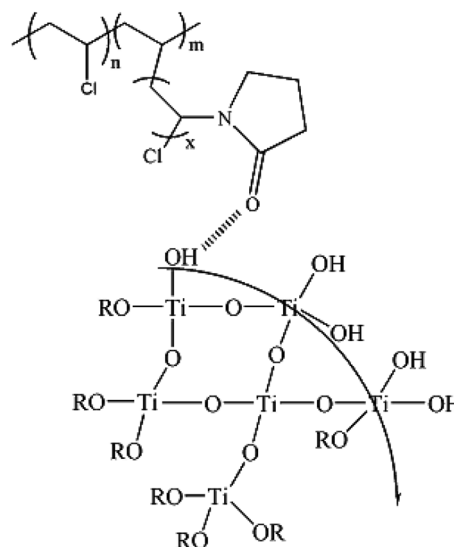


Fig. 2. FT-IR spectra of pristine PVC, PVC-g-PVP graft copolymer and PVC-g-PVP/TTIP film before calcination.

GPC traces for pristine PVC and PVC-g-PVP graft copolymer are presented in Fig. 1. The grafting of PVP from PVC backbone led to distribution shifted up in molecular weight relative to the PVC: number-average molecular weight (M_n) increased from 6.6×10^4 to 7.8×10^4 g/mol whereas weight-average molecular weight (M_w) increased from 1.6×10^5 to 2.2×10^5 g/mol. Accordingly, polydispersity index (PDI) value increased from 2.4 to 2.8. The molecular weight distribution for PVC-g-PVP graft copolymer was monomodal, indicating no evidence of homopolymer contamination or coupling reactions. Fig. 2 shows the FT-IR spectra of pristine PVC, PVC-g-PVP graft copolymer and PVC-g-PVP/TTIP film before calcination. The sharp peak at 1678 cm^{-1} in PVC-g-PVP is



Scheme 2. Interaction between PVC-g-PVP graft copolymer and TTIP sol-gel solution.

assigned to the stretching vibration of carbonyl ($\text{C}=\text{O}$) group in PVP, indicating the successful grafting of PVP from PVC backbone.

Scheme 2 shows the hydrogen bonding interaction between the PVP of the PVC-g-PVP graft copolymer and TiO_2 nanoparticles formed from TTIP in the sol-gel solution. The interaction of PVP hydrophilic part of the amphiphilic graft copolymer without any surfactant addition leads to the selective affinity between the TTIP and the PVP chains of PVC-g-PVP graft copolymer.^{37,38} This selective interaction may result in specific morphology formation in PVC-g-PVP/TTIP film. The hydrogen bonding interaction between the hydroxyl group of titania and the carbonyl group of the PVP chains was investigated, as seen in Fig. 2. The presence of broad peak at 3119 cm^{-1} in PVC-g-PVP/TTIP film is due to the stretching vibration of $\text{Ti}-\text{OH}$ groups. The hydroxyl group results from the incomplete polycondensation reaction of TTIP. The hydrogen bonding interaction between the carbonyl group of PVP chains and the hydroxyl group result in lowering of stretching vibration mode of carbonyl ($\text{C}=\text{O}$) group in PVC-g-PVP from 1678 cm^{-1} to 1618 cm^{-1} . This indicates the presence of hydrogen bonding interaction between the hydroxyl group present in uncondensed TTIP and the carbonyl group of the PVP moiety.³⁹

XRD analysis was performed to investigate the structural pattern of pristine PVC, PVC-g-PVP graft copolymer and crystallized mesoporous TiO_2 thin film templated by PVC-g-PVP, as seen in Fig. 3. Pristine PVC exhibited some weak peaks at 18° , 25° and 40° , indicating its amorphous state. Upon grafting of PVP from PVC backbone, two peaks at 18° and 25° gradually merged to a single broad peak centered at 19° , demonstrating more structureless morphology of the graft copolymer. The mesoporous TiO_2 thin film showed several crystalline sharp peaks at 25.3° , 48.2° and 54.5° (2θ value which are assigned to (101), (200), and (211) planes, respectively, of the anatase TiO_2 phase.^{40,41}) The rest of the peak arises from FTO glass. This result demonstrates that the structural changes and phase transformation of TiO_2 to crystalline anatase occur around 450°C . By using Scherrer equation,⁴²) the crystallite size of the TiO_2 film templated by PVC-g-PVP graft copolymer was determined from the diffraction peak broadening: $D = K\lambda/\beta \cos \theta$, where D is the crystallite size of the particles, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the (101) crystalline peak, $K = 0.9$ is a coefficient, and θ is the diffraction angle. The average crystallite size of the mesoporous TiO_2 thin film was calculated to be about 20 nm.

TEM and SEM analysis were performed to characterize microphase-separated morphology of graft copolymer and porous structures of TiO_2 thin film, as shown in Fig. 4. Unstained TEM sample provided a

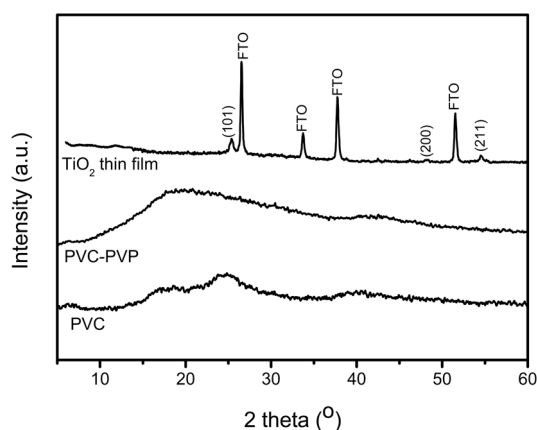


Fig. 3. XRD patterns of pristine PVC, PVC-g-PVP graft copolymer and PVC-g-PVP/TTIP film after calcination 450°C .

clear image contrast due to large difference of electron densities between the PVC backbone and the PVP side chains. Dark area shows the hydrophobic domains of PVC backbone whereas bright region represents the hydrophilic PVP side chains. The PVC-g-PVP graft copolymer showed microphase-separated morphology which molecularly self-assembled into the continuous nanophase domains of PVC interweaved with the hydrophilic domains of PVP (Fig. 4a). Fig. 4b shows

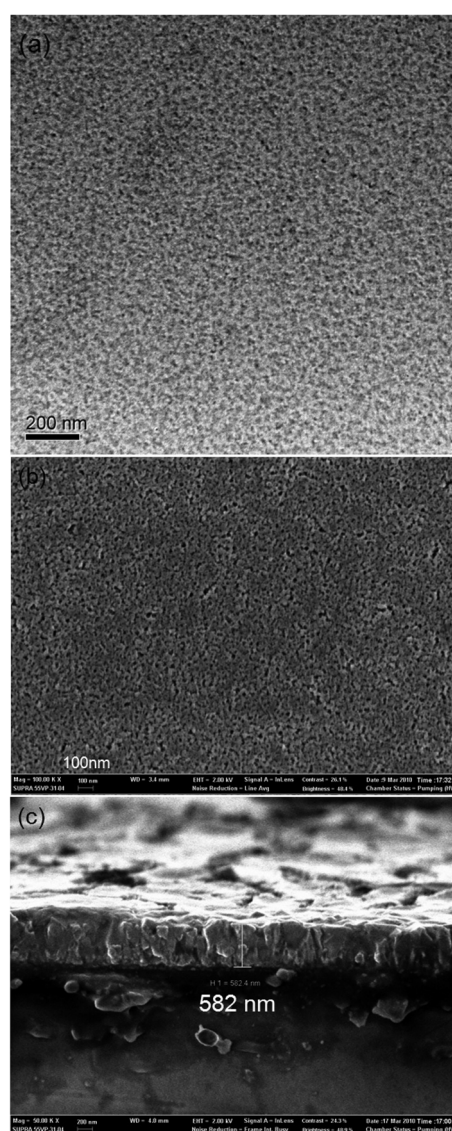


Fig. 4. (a) TEM image of PVC-g-PVP graft copolymer and SEM images of (b) surface and (c) cross-section of TiO_2 film templated by PVC-g-PVP graft copolymer.

the SEM image of mesoporous TiO_2 thin film templated by PVC-g-PVP graft copolymer which involves a sol-gel process based on the hydrolysis and condensation of TTIP. The cylindrical worm-like micelles formed around PVC chains were burned out under calcination to form the worm-like pores of 30-40 nm in diameter. The TiO_2 film was 582 nm in thickness, as characterized by cross-sectional SEM image (Fig. 4c).

There are some advantages of quasi-solid-state DSSC than liquid based one due to flexibility, lightness and long term stability. Thus, quasi-solid-state polymer electrolyte was employed to make solar cell and the cell performance was measured using linear sweep voltammetry, as represented in Fig. 5. The polymer electrolyte consisting of PEODME, fumed nanosized silica (SiO_2), ionic liquid (MPIL) and I_2 was used to due to its higher conductivity and higher energy conversion efficiency.³³⁾ The DSSC performances such as J_{sc} , FF and efficiency were summarized in Table 1. The DSSC fabricated using 582 nm-thick mesoporous TiO_2 film and PEODME/ SiO_2 /MPIL/ I_2 polymer electrolyte exhibited cell performance with J_{sc} of 2.87 mA/cm^2 , V_{oc} of 0.75 V, FF of 49% and overall conversion efficiency of 1.05%. The dye adsorption value was also measured using UV-visible spectroscopy.

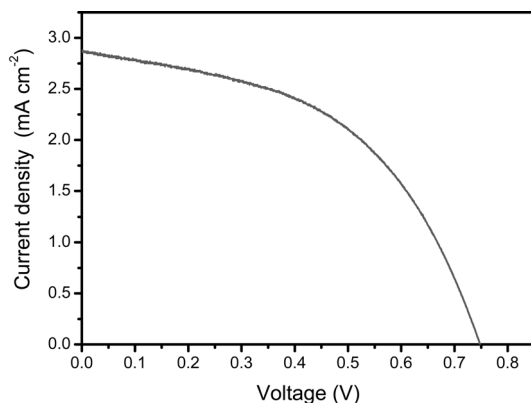


Fig. 5. J-V curve of DSSC fabricated using TiO_2 film templated by PVC-g-PVP graft copolymer and PEGDME/ SiO_2 /MPIL/ I_2 polymer electrolyte at 100 mW/cm^2 .

Dye adsorption onto mesoporous TiO_2 film was determined to be 26.35 nmol/cm^2 , which was 0.031 mg/cm^2 .

EIS is very powerful technique to define recombination life time and resistive elements on the photovoltaic performance. Nyquist plot was used to investigate resistance relation for charge transfer process at the Pt counter electrode, resistance for TiO_2 /electrolyte interface and Nernst diffusion in the electrolyte. The Nyquist plot of DSSC with AC amplitude of 0.02 V and light intensity of 100 mW/cm^2 is presented in Fig. 6a. In general, the impedance spectra can be interpreted and modeled using equivalent circuits. Each equivalent

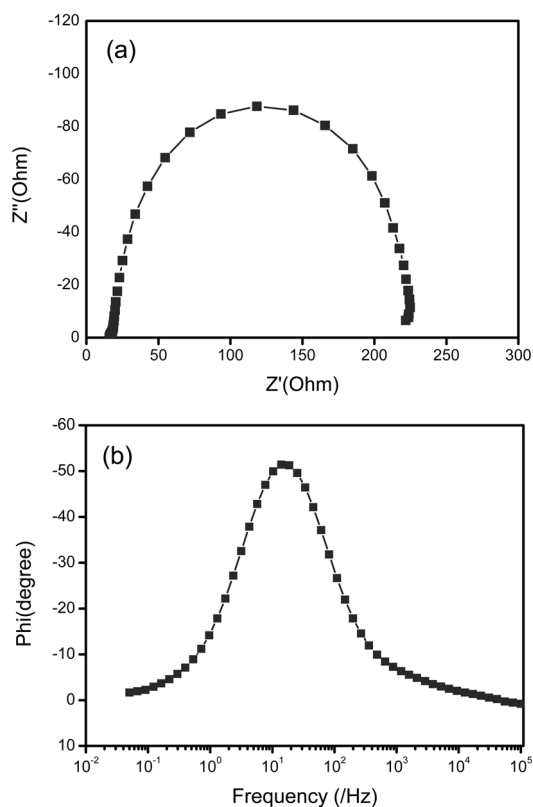


Fig. 6. EIS data of DSSC fabricated using TiO_2 film templated by PVC-g-PVP graft copolymer and PEGDME/ SiO_2 /MPIL/ I_2 polymer electrolyte at 100 mW/cm^2 ; (a) Nyquist plot and (b) Bode plot.

Table 1. Cell performance of DSSC fabricated using TiO_2 film templated by PVC-g-PVP graft copolymer and PEGDME/ SiO_2 /MPIL/ I_2 polymer electrolyte at 100 mW/cm^2 .

V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency (%)	Dye adsorption (nmol/cm^2)	Dye adsorption (mg/cm^2)
0.75	2.87	0.49	1.05	26.35	0.031

Table 2. EIS results of DSSC fabricated using TiO₂ film templated by PVC-g-PVP graft copolymer and PEGDME/SiO₂/MPII/I₂ polymer electrolyte at 100 mW/cm².

Characteristic frequency (Hz)	Electron lifetime (ms)	R ₁ (Ω)	R ₂ (Ω)
13.9	11.45	4	200

circuit consists of several components: ohmic resistance (R_s), charge transfer resistance at counter electrode/electrolyte (R_1), charge transfer resistance at photoelectrode/electrolyte (R_2), resistance at the Warburg diffusion of redox I^-/I_3^- couple in electrolyte (W_s). However, the sample had two semi-circles, in the high frequency region and low frequency region. The semi-circle for Nernst diffusion and resistance for TiO₂/electrolyte interface was overlapped because our TiO₂ layer is very thin (<600 nm) and polymer electrolyte has higher resistance than liquid electrolyte. The characteristic frequency peak (10^{-2} - 10^6 Hz) in the Bode phase plot is shown in Fig. 6b. The characteristic frequency is related to the inverse of the recombination lifetime (τ_r) or electron lifetime (τ_e), in the TiO₂ film.^{43,44} Electron lifetime of DSSC fabricated using mesoporous TiO₂ film and PEGDME/SiO₂/MPII/I₂ polymer electrolyte was found to be 11.45 ms.

4. Conclusion

PVC-g-PVP graft copolymer was synthesized by ATRP method by using the labile chloride group as the initiating site. The synthesis of graft copolymer was characterized by FT-IR, GPC and TEM analysis. The PVC-g-PVP graft copolymer was used as a template to synthesize in situ mesoporous TiO₂ thin film, which was characterized by XRD and SEM. The resultant TiO₂ porous films were efficiently used as a photoelectrode for fabricating quasi-solid-state DSSC and the maximum energy conversion efficiency of 1.05% at 100 mW/cm² by using PEGDME, fumed nanosized silica, MPII/I₂ as a polymer electrolyte.

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