



Poly(ethylene-co-acrylic acid)-*g*-poly(ethylene glycol) graft copolymer templated synthesis of mesoporous TiO₂ thin films for quasi-solid-state dye sensitized solar cells

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ABSTRACT

An amphiphilic graft copolymer, poly(ethylene-co-acrylic acid)-*g*-poly(ethylene glycol) (PEAA-*g*-PEG), consisting of a PEAA backbone and PEG side chains was synthesized via an esterification reaction. ¹H nuclear magnetic resonance and Fourier-transformed infrared analysis demonstrated esterification between carboxylic acid of PEAA and hydroxyl group of PEG. Small angle X-ray scattering results revealed that the crystalline domain spacing of PEAA increased from 11.3 to 12.8 nm upon using a more polar solvent with a higher affinity for poly(acrylic acid), while the crystalline domain spacing of PEAA disappeared with PEG grafting, indicating structural change to an amorphous state. Mesoporous TiO₂ thin films were synthesized via a sol-gel reaction using PEAA-*g*-PEG graft copolymer as a structure-directing agent. The hydrophilically-preformed TiO₂ nanoparticles were selectively confined in the hydrophilic PEG domains of the graft copolymer, and mesoporous TiO₂ thin films were formed, as confirmed by scanning electron microscopy. The morphology of TiO₂ films was tunable by varying the concentrations of polymer solutions and the amount of preformed TiO₂. A quasi-solid-state dye-sensitized solar cell fabricated with PEAA-*g*-PEG templated TiO₂ film exhibited an energy conversion efficiency of 3.8% at 100 mW/cm², which was greater than that of commercially-available paste (2.6%) at a similar film thickness (3 μm). The improved performance was due to the larger surface area for high dye loading and organized structure with good interconnectivity.

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1. Introduction

Dye-sensitized solar cells (DSSCs) were reported by the Gratzel group in 1991 [1], after which DSSCs received much attention as a renewable energy alternative to conventional silicon p-n junction solar cells. DSSCs are more attractive in terms of design opportunities, their light weight, flexibility and low cost [2]. DSSCs typically consist of a sensitizing dye, transparent conducting substrates, nanocrystalline TiO₂ film, iodide/iodine electrolyte, and a Pt-coated counter electrode. Considerable attention has been directed toward developing sensitizing dyes [3], electrolytes [4], photoanodes [5–11] and counter electrodes to improve cell performance [12]. In particular, the preparation of mesoporous TiO₂ films with high crystallization and large surface area is important for enhancing the efficiency of DSSCs [5–11]. Research has primarily focused on the development of well-organized TiO₂ films with a large surface area and good interconnectivity because the energy conversion efficiency of DSSCs with well-organized TiO₂ films is much greater than for those with traditional films possessing a less-organized, random morphology [13].

Well-organized mesoporous TiO₂ films have primarily been synthesized using an amphiphilic block copolymer as a structure-directing agent [13–18], which is more effective than a homopolymer as an organic template for the preparation of mesoporous metal oxides. The hydrophilic domains of the copolymer interact with the hydrophilic precursor to form a continuous metal oxide phase, while the hydrophobic domains can generate nanopores after calcination at high temperature. The hydrophobic domains also play an important role as a good support, which provides a sacrificing template without collapse of the final structure.

Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) triblock copolymer is most commonly used and is commercially available under the trade name Pluronic P123 or F127 depending on the length of the PEG chains [13–15]. The Pluronic-templated TiO₂ films typically show a small pore size less than 10 nm due to its low molecular weight, which is less effective for pore-filling of solid electrolytes with a large volume and impedes complete crystallization while maintaining the structural integrity. An alternative block copolymer is poly(isoprene-*block*-ethylene oxide), which has been primarily used by the Snaith and Steiner groups [16–18]. However, these block copolymers are typically synthesized via living anionic polymerization, which is very sensitive to impurities, such as water and oxygen, resulting in a high cost. More importantly, the thickness of a block

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copolymer templated TiO₂ film is limited to the submicron scale because crack formation and disruption of the ordered structure often occur during calcination [13–18]. A multilayer deposition process was introduced to increase the thickness of the crack-free TiO₂ film while maintaining a long-range ordered structure, but several coatings and an additional stabilization step are needed [15].

Recently, our group reported the use of amphiphilic graft copolymers as an alternative structure-directing agent for organized mesoporous TiO₂ films [19–22]. A graft copolymer is more advantageous than a block copolymer as it is economical and has a simple synthetic method. A poly(vinyl chloride)-*graft*-poly(oxyethylene methacrylate) graft copolymer was synthesized via atom transfer radical polymerization (ATRP) with a copper/ligand complex that functions as a reaction catalyst. The PVC-*g*-POEM graft copolymer worked well as a structure-directing agent due to a well-defined, microphase-separated structure, resulting from the flexible, hydrophilic properties of rubbery POEM and the rigid, hydrophobic properties of glassy PVC chains. Additionally, the amorphous nature and high molecular weight of PVC-*g*-POEM could generate large pores, which facilitate deep infiltration of solid electrolytes and promote complete titania crystallization while maintaining the structural integrity.

Poly(ethylene-co-acrylic acid) (PEAA) is a cheap random copolymer synthesized with a major component of polyethylene (PE) and a minor component of poly(acrylic acid) (PAA). However, the physico-chemical properties of PEAA are not significantly different from those of PE due to a small portion (~15 wt.%) of PAA. Here, thus, to provide amphiphilic properties of a polymer, a poly(ethylene-co-acrylic acid)-*graft*-poly(ethylene glycol) (PEAA-*g*-PEG) graft copolymer was synthesized via an esterification reaction, which is much easier and less sensitive than an ATRP reaction. The additional hydrophilicity of PEG would help to increase the interaction between the titania precursor and polymer template in the sol-gel reaction medium, which may lead to a better morphology. The synthesized PEAA-*g*-PEG graft copolymer was characterized using ¹H nuclear magnetic resonance (NMR), Fourier-transformed infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and small angle X-ray scattering (SAXS). The PEAA-*g*-PEG graft copolymer templated TiO₂ films were characterized using scanning electron microscopy (SEM) and utilized as a photoanode in quasi-solid-state DSSC (qssDSSC).

2. Experimental details

2.1. Materials

Poly(ethylene-co-acrylic acid) (PEAA, acrylic acid 15 wt.%), methoxy poly(ethylene glycol) (M_n = 550 g/mol), N,N'-dicyclohexylcarbodiimide (DCC), titanium(IV) chloride (TiCl₄), benzyl alcohol, iodine (I₂), titanium(IV) bis(ethyl acetoacetato)diisopropoxide, chloroplatinic acid hexahydrate (H₂PtCl₆), titanium(IV) isopropoxide (97%), fumed silica nanoparticles (SiO₂, 14 nm), poly(ethylene glycol dimethyl ether) (PEGDME, M_n = 500 g/mol), hydrogen chloride solution (HCl, 35 wt.%), and sodium hydroxide solution (0.1 N) were purchased from Aldrich. 1-Methyl-3-propylimidazolium iodide (MPII) and ruthenium dye (535-bisTBA, N719) were purchased from Solaronix, Switzerland. High purity solvents of tetrahydrofuran, N-methyl pyrrolidone (NMP), butanol, acetonitrile, 2-propanol, chloroform, and ethanol were purchased from J.T. Baker. All solvents and chemicals were used as received without further purification. The fluorine-doped tin oxide (FTO) conducting glass substrate (TEC8, 8 X/sq, 2.3 mm thick) was purchased from Pilkington, France.

2.2. Synthesis of the PEAA-*g*-PEG graft copolymer

The PEAA-*g*-PEG was synthesized via esterification between the carboxylic acid of PEAA and the hydroxyl group of PEG. Three grams of PEAA was dissolved in 45 ml of NMP in a round flask at 100 °C for an

hour, 1 mL of PEG was then added, followed by the addition of 0.25 g of DCC as a catalyst. The reaction flask was sealed with a rubber septum. The homogenous mixture was stirred at 100 °C for 24 h. The product was precipitated in methanol and washed several times to remove any unreacted chemicals. The final product was dried completely in a vacuum oven at 50 °C for 24 h.

2.3. Synthesis of preformed TiO₂ nanoparticles

TiCl₄ (1.5 mL) was added to 10 mL of toluene and stirred for a few seconds to produce a homogeneous, red-colored solution. The solution was added drop-wise to 50 mL of benzyl alcohol and stirred for more than 2 h. The transparent yellowish solution was heated in a convection oven at 70 °C for 12 h. White precipitates were then obtained in the bottom of the solution. The precipitated TiO₂ nanoparticles were isolated by centrifugation at 12,000 rpm for 30 min [21,22].

2.4. Preparation of mesoporous TiO₂ films

FTO glass was coated with a 75% titanium diisopropoxide bis(acetylacetonate) solution in 2-propanol to prepare a blocking layer. After drying at 50 °C for 30 min, the FTO glass was heated at 450 °C for 30 min, followed by cooling to room temperature for 8 h. The FTO glass with a dense TiO₂ blocking layer was used for preparing a mesoporous TiO₂ photoanode. The amphiphilic PEAA-*g*-PEG graft copolymer was dissolved in 4 and 8 wt.% NMP at 80 °C. Different weight percents of preformed TiO₂ nanoparticles were added to the polymer solution. After 12 h of aging, the solutions were deposited on FTO glass by a doctor blade method and then sintered at 500 °C for 30 min. The mesoporous TiO₂ film prepared using a 4 wt.% polymer solution and 0.2 g of preformed TiO₂ was named TiO₂-1, while that using the 4 wt.% solution and 0.3 g of preformed TiO₂ was named TiO₂-2. TiO₂-3 and TiO₂-4 were prepared using the 8 wt.% solution and 0.2 and 0.3 g TiO₂, respectively. To each of these, 0.1 mL of dilute HCl was added and stirred until a homogenous TiO₂ sol-gel solution was produced. The TiO₂ film thickness was approximately 2.6–3 μm.

2.5. Device fabrication

qssDSSCs with an active area of 0.16 cm² were constructed by drop-casting the electrolyte solution onto the photoanode and covering with a counter electrode, according to a previously reported procedure [23–25]. The Pt counter electrodes were prepared by spin coating a hydrogen hexachloroplatinate(IV) hexahydrate solution (H₂PtCl₆) onto the FTO glasses, followed by calcination at 450 °C for 30 min. The TiO₂ electrodes were immersed in a solution of amphiphilic dye (Ruthenium 535-bisTBA, Solaronix SA as referred to N-719) in absolute ethanol for 2 h at 50 °C. After drying the dye-adsorbed photoanodes at room temperature, the polymer electrolyte solution was cast on the electrode. A quasi-solid polymer electrolyte solution was prepared by dissolving fumed silica nanoparticles (SiO₂), PEGDME, MPII and I₂ in acetonitrile. The introduction of fumed silica nanoparticles can increase ionic conductivity and the viscosity of electrolyte resulting in the formation of quasi-solid-state electrolyte [23,25]. 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 one day to permit complete evaporation of the solvent and were sealed with an epoxy resin.

2.6. Characterization

¹H NMR measurements were performed with a Bruker AV400 NMR spectrometer (400 MHz) using CDCl₃ as the solvent and tetramethylsilane as the internal reference. The FT-IR spectra of the samples were collected using a 6030 Mattson Galaxy Series FT-IR spectrometer in the frequency range of 4000–400 cm⁻¹ with an attenuated

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