Synthesis of Villi-Structured Polyaniline Sheets Using Organic Single Crystal Surface-Induced Polymerization

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Supporting Information

ABSTRACT: Villi-structured polyaniline sheets (VPASs) were synthesized by the organic single-crystal surface-induced polymerization (OCSP) method using sodium decanesulfonate as a template. Aniline hydrochloride is used as a monomer instead of aniline to improve the electrostatic interaction between monomers and hydrated crystals, which reveals that the mechanism of OCSP occurs from the electrostatic force between positively charged monomers and the negatively charged surface of hydrated crystals. Compared with conventional polyaniline ($3.13 \times 10^{-2} S/cm$), VPASs showed higher electrical conductivity ($1.07 \times 10^{-1} S/cm$). The thickness of double-layered VPASs is about 136 nm, and the surface of VPASs shows a random porous structure with a villi-like morphology. This morphological property provides a large surface area, which can be advantageous to various electrochemical applications. The process yields mass-producible inexpensive materials, and the products are suitable for flexible devices because of their characteristic morphology.

INTRODUCTION

Electrically conductive polymers (ECPs), polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene), are well-known materials that possess noticeable advantages, facile synthetic procedure, good conductivity, and competitive price. Among ECPs, polyaniline is a promising conductive polymer because of its relatively low cost, good environmental stability, unique oxidation states with different colors, and reversely controllable electrical conductivity, from the insulating emeraldine base to the conductive emeraldine salt forms, due to an acid–base doping/dedoping response. Because of these merits, polyaniline has been used in various electrochemical applications: dye-sensitized solar cells, chemical sensors, rechargeable batteries, and supercapacitors.

Accordingly, there have been numerous research studies to enhance its electrical properties, and one of the promising methods is to synthesize structured ECPs. Fabricating structured ECPs is a challenging goal for developing a conducting polymer to a better material for electrochemical applications. For example, Wei et al. developed attractive poly/oligoaniline microstructures and characterized with various techniques in details. Sahiner et al. also examined various templated polyaniline synthesis methods using cryogels.

Nanostructures, such as nanoparticles, nanospheres, nanotubes, and nanofibers, can be fabricated by using hard templates, soft templates, or template-free methods. Nano-porous anodic aluminum oxide and zeolite channels, surfactants and block copolymers, and interfacial polymerization or sonochemical methods can be good examples of each method. Among these methods, synthesis of polyaniline hydrogels or cryogels using poly(vinyl alcohol) as a supporting polymer showed attractive viscoelastic and mechanical properties.

Our previous research reported a novel synthesis method called organic single-crystal surface-induced polymerization (OCSP). Unlike the conventional methods mentioned above, OCSP utilizes a hydrated crystal as a soluble template which can be obtained below the Krafft point. Through this polymerization method, micro- or nanostructured conducting polymers, such as polypyrrole hexagonal microplates and ultra-thin polypyrrole nanosheets (UPNSs), can be obtained by a shape-duplicating process, which is performed by electrostatic interactions between negatively charged surfaces of hydrated crystals and cationic monomers or chains. UPNS has a two-dimensional structure, which provides fewer phase boundaries, lower interparticle contact resistance, and higher charge transport efficiency than other nanostructures of polypyrrole. On the basis of these properties, UPNS was
applied for a counter electrode of DSSCs and chemical sensors and showed high efficiency for each application.35−37

In this study, we report the synthesis of villi-structured polyaniline sheets (VPASs) by the OCSP method. Enhancing the electrostatic interaction between monomers and negatively charged surfaces of hydrated crystals, aniline hydrochloride was used as a monomer instead of aniline. We successfully obtained VPASs which have a similar morphology to hydrated crystals of sodium decanesulfonate (SDSn) with nanoscale thickness. The surface of VPASs showed a random porous structure with a villi-like morphology which provides an enlarged surface area. The VPASs present about 3.5 times higher electrical conductivity ($1.07 \times 10^{-1}$ S/cm) than conventional polyaniline.

**RESULTS AND DISCUSSION**

**Synthesis of VPASs.** VPASs were synthesized in hydrated surfactant crystal suspension by chemical oxidation. The polymerization procedure of VPASs is simply described in Figure 1. SDSn was dissolved at 30 °C and started to be recrystallized at around 4 °C while cooling down in 0.01 M HCl aqueous solution. Aniline hydrochloride was stabilized for 1 h to have adequate interactions between anilinium cations and hydrated crystals. The shape-duplicating process by the electrostatic interaction between negatively charged SDSn crystals and cationic pyrrole by oxidation was identified in our previous research. The hydrated SDSn crystals were negatively charged because the surface of crystals consists of sulfonate groups of SDSn molecules.35,37 We also tried to synthesize polyaniline with the OCSP technique; however, for aniline, it was regarded that the electrostatic interaction with hydrated crystals is insufficient. Thus, aniline hydrochloride which can produce anilinium cations in aqueous solution was used as a monomer to enhance the electrostatic interaction. As a result, VPASs were successfully synthesized through the OCSP method. The result shows that anilinium cations were absorbed on negatively charged surfaces of SDSn crystals, and polyaniline chains can grow on surfaces of anionic SDSn crystals by chemical oxidation. After polymerization, the SDSn crystal was dissolved during the washing process at room temperature, and it came out through the cracked or ripped surface of the resulting double-layered VPASs. The product with a dark-green color indicates the formation of an emeraldine salt form.

**Morphology.** The morphology of the VPASs synthesized via OCSP on SDSn hydrated crystals is revealed by optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Figure 2 is OM images of organic crystals of SDSn and VPASs synthesized through the OCSP method. The OM image in Figure 2a shows the morphology of hydrated crystals of SDSn after the addition and stabilization of aniline hydrochloride. Hydrated SDSn crystals were formed in a hexagonal shape with a width of ∼20 μm, a length greater than 30 μm, and used as templates for adsorption of anilinium cations. Figure 2b shows the morphology of polyaniline synthesized by the OCSP method when aniline was used as a monomer. Because the electrostatic interaction between aniline monomers and SDSn hydrated crystals is not sufficient, aniline monomers were not able to be adsorbed on the surface of a crystal, and therefore, they form amorphous morphology, as shown in Figure 2b. On the contrary, the sample polymerized with aniline hydrochloride monomers well-duplicated the morphology of hydrated crystals of SDSn after the addition and stabilization of aniline hydrochloride. Hydrated SDSn crystals were formed in a hexagonal shape with a width of ∼20 μm, a length greater than 30 μm, and used as templates for adsorption of anilinium cations. Figure 2c shows the morphology of polyaniline synthesized by the OCSP method when aniline was used as a monomer. Because the electrostatic interaction between aniline monomers and SDSn hydrated crystals is not sufficient, aniline monomers were not able to be adsorbed on the surface of a crystal, and therefore, they form amorphous morphology, as shown in Figure 2b. On the contrary, the sample polymerized with aniline hydrochloride monomers well-duplicated the morphology of hydrated crystals of SDSn (Figure 2c). Aniline hydrochloride has anilinium cations, which can increase the possibility to interact with negatively charged surfaces of organic crystals. The size and the morphology of synthesized polyaniline on SDSn crystal templates duplicate those of SDSn crystals well, meaning anilinium ions interact with negatively charged surfaces of organic crystals successfully. As a result, anilinium cations were able to perform OCSP by electrostatic interaction, whereas aniline monomers were not able to, and the result well-corresponds to the hypothesis of our previous research.
Conductivity of VPASs. Electrical conductivities of VPASs, HCl-redoped VPASs, and conventional polyaniline are presented in Figure 5. To identify the optimal concentration of HCl solution for the highest electrical conductivity, various concentrations of HCl solution were used in the redoping process. Figure 5a displays the curve of electrical conductivity of HCl-redoped VPASs. The highest electrical conductivity was observed to be 6.49 S/cm at 0.4 M HCl concentration. At higher concentrations of HCl, a decrease in electrical conductivity occurs which is due to overprotonation of polyaniline chains causing a decrease in the delocalization length. Conclusively, the effective HCl concentration for redoping VPASs is 0.4 M.38 Figure 5b shows that the sample of VPASs is outstanding in electrical properties because electrical conductivity of VPASs was nearly 3.5 times higher than that of conventional polyaniline.

X-ray diffraction (XRD) patterns in Figure 6 describe why VPASs show a higher conductivity than conventional polyaniline. In the case of the conventional polyaniline sample, crystalline peaks appeared around 2θ = 20° and 25°. The XRD pattern of VPASs shows that the peak around 15° is discovered and the peaks around 25° are sharpened, compared to conventional polyaniline. The peaks that appear at 15, 20, and 25° are three representative peaks of pure crystalline polyaniline, indicative of (011), (020), and (200) crystalline planes of the emeraldine salt form.39 This result suggests that no additional crystalline order has been introduced by other materials, and the packing of polyaniline main chain was increased by OCSP and made VPASs more electrically conductive.39−41

XPS Analysis of VPASs. To confirm doping levels of VPASs, Figure 7 shows N 1s core X-ray photoelectron spectroscopy (XPS) spectra of VPASs. The binding energy peak of benzenoid-amine (−NH−) is observed around 399.4 eV. The quinoid-imine peak (−N═N−) can be found around 398.1 eV. The peak above 400 eV corresponds to positively charged nitrogen (−•NH−).42,43

Figure 7a presents the XPS spectrum of VPASs. The peak above 400 eV is deconvoluted to two peaks at 400−403 eV, and the doping level of VPASs is revealed to be 23.3%. The doping level of polyaniline is defined as [Cl]/[N_{total}].24 It can be also calculated that the ratio of the area of doped nitrogen peaks to the total peak area of nitrogen ([N]/[N_{total}]) indicates the doping level because chloride ions have almost an equivalent amount of positively charged nitrogen in polyaniline.10 The doping level of dedoped VPASs was measured to be 2.82% as shown in Figure 7b. Dedoped VPASs present a dark-blue color of the emeraldine base form (EB) and electrically insulating. These indicate that the dedoping procedure was well-proceeded. Figure 7c shows the XPS N 1s core-level spectra of redoped VPASs at the 0.4 M HCl concentration. The doping level of redoped VPASs by 0.4 M HCl solution was measured.
to be 39.3%. This result indicates that VPASs were properly redoped by HCl solution.

**CONCLUSIONS**

VPASs were successfully synthesized by the OCSP process using aniline hydrochloride. Lowering the temperature of micellar solution below the Krafft point, hydrated SDSn crystals were obtained and used as a template for electrostatic interaction between anionic surfaces of hydrated crystals and cationic monomers or oligomers. Aniline hydrochlorides, which are ionized to anilinium cations in water, were used instead of aniline; thus, the OCSP method was successfully performed by enhancing the electrostatic interaction. Polyaniline was synthesized on the surfaces of SDSn crystals and formed hexagonal-shaped sheets, which has a morphology similar to SDSn crystals. Combined thickness of top and bottom VPAS layers was around 136 nm. Surfaces of VPASs showed a random porous structure and a villi-like morphology, which can provide a large surface area. With the most suitable HCl doping concentration for VPASs, the optimized electrical conductivity was obtained as 6.49 S/cm. VPASs showed 3.5 times higher electrical conductivity than the conventional polyaniline because of increased packing of polyaniline chains.

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**Figure 5.** (a) Graph and (b) actual values of electrical conductivities of VPASs with different HCl concentrations and the conventional polyaniline sample measured by a four-probe method.

**Figure 6.** XRD patterns of conventional polyaniline and the VPAS sample.

**Figure 7.** XPS N 1s core-level spectra of (a) VPAS, (b) dedoped VPAS, and (c) redoped VPASs by 0.4 M HCl solution.
**EXPERIMENTAL SECTION**

**Materials.** Aniline hydrochloride (Sigma-Aldrich, 99%) was used as a monomer. Ammonium persulfate (APS) (Sigma-Aldrich, 98%) was used as an oxidant with no further purification. Sodium 1-decanesulfonate (SDSn) (TCI, 98%) was used as a redoping agent. HCl aqueous solution and ammonium hydroxide solution (Sigma-Aldrich) were used as a doping and dedoping agent, respectively.

**Synthesis of VPASs.** VPASs were synthesized by dissolving 8 mmol of SDSn (1.95 g) in 80 mL of 0.01 M HCl aqueous solution. The solution was stirred at 30 °C for 30 min with a constant temperature circulator and cooled down to 0 °C. To recrystallize of SDSn, the solution was stabilized for 30 min with vigorous stirring. 8 mmol of aniline hydrochloride (1.04 g) was added to the solution and stabilized for 1 h. An oxidant solution was produced by dissolving 8 mmol of APS (1.83 g) in 0.01 M HCl aqueous solution (20 mL) at room temperature. Preventing template dissolution by temperature difference between APS solution and organic crystal suspension, APS solution was precooled at 0 °C and added to the solution at a rate of 10 mL/h using a syringe pump. The solution was polymerized for 5 h with stirring. The product was washed with 0.01 M HCl aqueous solution, methanol, and acetone several times using a polytetrafluoroethylene (PTFE) membrane filter with 100 nm pores. After washing, VPASs were obtained as an emeraldine salt form. Conventional polyaniline was prepared for comparison, in the same condition of VPAS synthesis except the presence of templates.

**Dedoping and Redoping of VPASs.** After washing, the product was immersed in 1 M ammonium hydroxide solution for 24 h at room temperature, and the VPAS emeraldine EB (VPAS-EB) was obtained. VPAS-EB was filtered with an aspirator and a PTFE membrane filter.

Filtered VPAS-EB was immersed in 0.2 M HCl aqueous solution to redope for 24 h at room temperature. For comparison, VPAS-EB was redoped in various concentrations of HCl aqueous solution (0.4, 0.6, and 0.8 M) for the same number of hours. Redoped products were washed with each redoping concentration of HCl aqueous solution, methanol, and acetone.

**Characterization.** The morphology of organic crystals of SDSn and VPASs was observed by an OM (Nikon ECLIPSE and acetone). The thickness and the surface morphology of the SDSn and VPASs was observed by an XRD analyzer (Rigaku Ultima IV) and an electronic spectrometer (Jasco V-570). The dichroic ratio of the electronic spectra of the VPAS samples was analyzed by a JASCO UV-visible spectrophotometer (V-570) using a quartz cell with a path length of 0.1 cm.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website atDOI: 10.1021/acsomega.7b01024.

J–V curves of DSSCs and table of photovoltaic parameters, UV–vis spectra and table of transmittance values, TEM images, fabrication procedures of VPAS CEs and DSSCs, and characterization (PDF)

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**Notes**

The authors declare no competing financial interest.

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