Preparation of Nanostructured Conjugated Polymers Using Template Electrochemical Polymerization in Supercritical Fluids

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The electrochemical coating and filling with conjugated polymers in porous templates were carried out in supercritical fluids. The use of the special properties of the fluids such as higher diffusivity and lower viscosity enabled the effective monomer transport into the porous template and the nanoprecise coating and filling with the polymers.

The development of nanotechnology will be one of the key engines that drive our technological society in the 21st century. This rapidly growing area focuses on tailoring a nanomaterial structure for specific and unique properties.[1]

The nanostructured conjugated polymers are one potential class of materials for nanodevices and nanosensors.[2] Electrochemistry is a conventional method for synthesizing conjugated polymers on electrodes.[3] Although various fabrication methods of nanostructures of conjugated polymers using electrochemistry, nanoprecise electrochemical coating and filling in porous templates are elegant approaches for this purpose.[4] However, the nanostructure fabrication of conducting polymers using porous templates was carried out with great difficulty owing to poor monomer transfer typically associated with liquid-phase electropolymerization. Hence, the nanostructure fabrication using template electrochemical deposition has still remained a challenging target.

A supercritical fluid exhibits larger diffusivility and lower viscosity compared to those of conventional liquids, since physicochemical properties of supercritical fluids are intermediate between those of gases and liquids.[5] Moreover, supercritical fluids such as supercritical trifluoromethane (scCHF_3) can be used as electrolytic media for electrosyntheses without any additives like polar solvents because of their relatively high solubilizing ability and dielectric constant.[6]

We envisioned that the use of scCHF_3 as an electrolytic medium for template electrochemical polymerization would enable the effective monomer transport into the porous template and the nanoprecise coating and filling with the polymers. In this paper, we wish to report our results indicating that this concept works.

Rectangular graphite felt ($1 \times 1 \times 0.5\,cm^3$, GF-20-5F, Nippon Carbon Co.) was used as porous templates and anodes for electrochemical deposition of conjugated polymer like a polythiophene (PT) in scCHF_3.[7] For a comparison, electrochemical deposition of PT was also carried out in a conventional liquid-phase medium like an acetonitrile solution.

Figure 1 shows SEM photographs of the fibers outside and inside the felt electrodes after the polymerization in an acetonitrile solution and scCHF_3. Large grains of PT could be observed at the surface of the fiber outside of the graphite felt after the polymerization in an acetonitrile solution (Figure 1a), while almost no grain was observed at the surface of the fiber inside the felt (Figure 1b). In sharp contrast, nanoscale coating of PT on individual graphite fibers could be observed both outside and inside the felt polymerized in scCHF_3 (Figures 1c, 1d, and 1e). These facts suggest that monomer penetration into the porous template was enhanced by the use of scCHF_3 as a medium, and consequently nanoprecise coatings of uniform PT layers on individual fibers could be formed even inside the graphite felt.

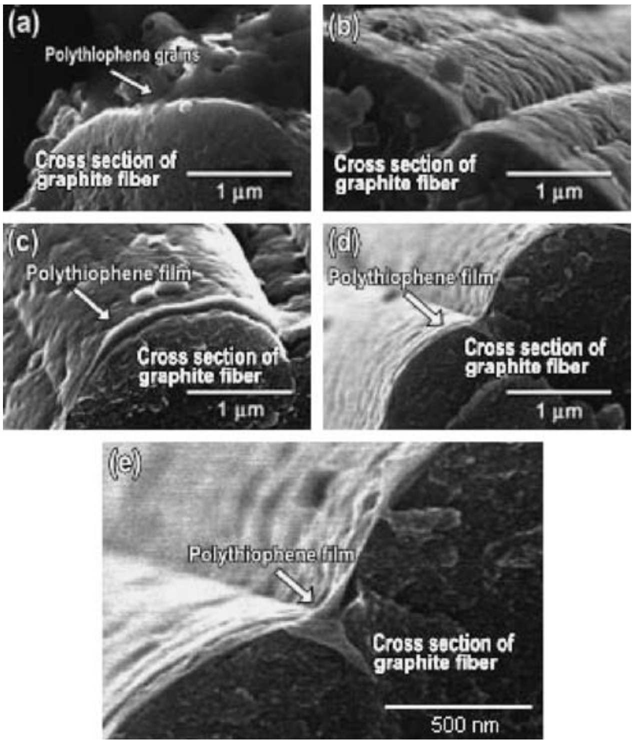

Figure 1. SEM images of the graphite fibers outside and inside the graphite felt electrodes after the electrochemical polymerization in an acetonitrile solution (a and b, respectively) and scCHF_3 (c and d, respectively). Figure 1e shows a higher magnified image of Figure 1d.

To demonstrate the generality of this new methodology, the electrodeposition of PT into another template was also carried out in scCHF_3. Nanoporous alumina membranes are widely utilized as templates for the deposition of nanocylindrical materials[8] such as nanorods[9] and nanotubes;[10] hence, the alumina membranes (60-µm thick, 200-nm pore size, Anodisc 13, Whatman) coated on one side with evaporated Pt (ca. 500-nm thick) were employed as another template for PT electrodeposition into pores.[7] Figure 2 shows cross-sectional views of nanoporous membranes filled with PT (dark area) electrodeposited at 2.6 V vs. Ag wire in an acetonitrile solution and scCHF_3, respectively. Although the PT-filled volume (dark area) increased with time of deposition in both media, the deposition rate was apparently fast-

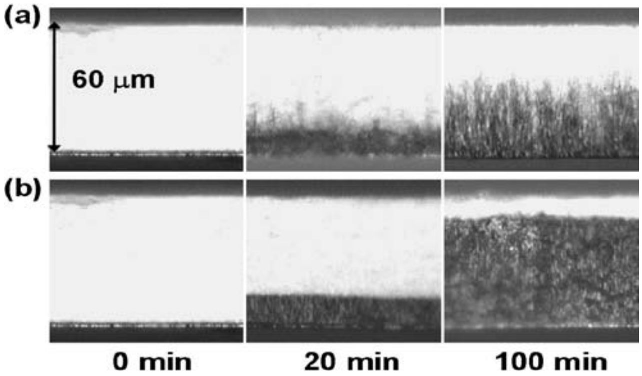

Figure 2. Optical microscope images showing cross sections of nanoporous membranes (60-μm thick, 200-nm pore size) filled with PT electrodeposited at 2.6 V vs. Ag wire for several time periods (indicated) in an acetonitrile solution (a) and $scCHF_3$ (b).

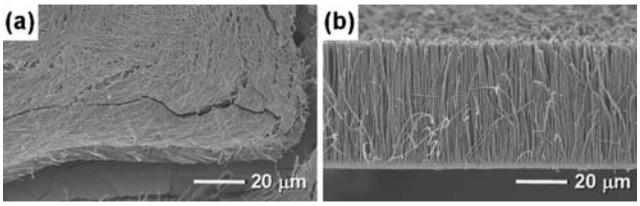

Figure 3. SEM images of cylindrically shaped PT electrodeposited at 2.6 V vs. Ag wire for 100 min in an acetonitrile solution (a, oblique view) and $scCHF_3$ (b, cross-sectional view).

er in $scCHF_3$ than in an acetonitrile solution. Calculations based on the charge passed during electrodeposition for 100 min indicate that the deposition rate in $scCHF_3$ is ca. seven times as fast as that in acetonitrile solution. Furthermore, the height of the PT wires electrodeposited in $scCHF_3$ is appreciably uniform compared with that deposited in an acetonitrile solution, and the height is found to be correlated exactly with the deposition time. These results can be also ascribed to a large diffusivility of $scCHF_3$. The diffusivility of media used for the electrodeposition also affected on strength and structures of the cylindrically shaped PT obtained by dissolving the alumina membrane in 4 M aqueous NaOH solution. Thus, in the case of the deposition in an acetonitrile solution, the PT wires fell down after the removal of the membrane, as shown in Figure 3a. This result can be ascribed to the formation of hollow structures due to a low monomer diffusion rate into the pores. In sharp contrast, by the use of $scCHF_3$ as a reaction medium, PT electrochemical growth occurred uniformly and steadily in the pores, and consequently, as shown in Figure 3b, the solid PT "nanobrush" could be obtained because the diffusion of the monomer in the pores was no longer the limiting parameter of the deposition process in $scCHF_3$.

In summary, we have developed a novel fabrication method of nanostructures of conjugated polymers using template electropolymerization in supercritical fluids. This new methodology has many practical advantages and characteristics: (a) the effective monomer transport into the porous templates by a large diffusivility of supercritical fluids; (b) very smooth electrochemical deposition of conjugated polymers in porous templates; (c) the nanoprecise coating and filling with the polymers in the templates. It is hoped that the present methodology will be applied to various template electrochemical syntheses that are useful for nanodevice technology.

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