

2

AD-A248 806



DTIC
ELECTE
APR 21 1992
S C D

TEMPLATE-SYNTHESIS - A METHOD FOR ENHANCING THE IONIC AND
ELECTRONIC CONDUCTIVITY IN ELECTRONICALLY CONDUCTIVE POLYMERS

Charles R. Martin*, Leon S. Van Dyke, and Zihua Cai

Department of Chemistry

Colorado State University

Fort Collins, CO 80523

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

*Corresponding author

92-10040



98 4 20 099

Abstract

Template-synthesis entails the synthesis of an electronically conductive polymer (or other material) within the pores of a microporous membrane. The membranes used have cylindrical pores of equivalent pore diameter; as a result, polymeric fibers are obtained, where the diameters of the fibers are determined by the diameter of the pores in the template membrane. We show in this paper that template-synthesized polypyrrole fibers show faster rates of charge-transport, during electrochemical "undoping," and dramatically higher electronic conductivities, than conventional forms (e.g. electrochemically-synthesized film) of this polymer.

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 66

Template-Synthesis - A Method for Enhancing the Ionic and Electronic Conductivity in Electronically Conductive Polymers

by

Charles R. Martin, Leon S. Van Dyke and Zhihua Cai

Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

Prepared for publication

in

Electrochimica Acta

April 16, 1992

Reproduction in whole or part is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

*This statement should also appear in Item 10 of Document Control Data - DD Form 1473. Copies of form Available from cognizant contract administrator

Approval For	
NTIS GRANT	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT APPROVED FOR PUBLIC DISTRIBUTION, DISTRIBUTION UNLIMITED.			
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR TECHNICAL REPORT #66		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research			
6a. NAME OF PERFORMING ORGANIZATION Dr. Charles R. Martin Department of Chemistry	6b. OFFICE SYMBOL (if applicable)	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217			
6c. ADDRESS (City, State, and ZIP Code) Colorado State University Ft. Collins, CO 80523		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract # N00014-82K-0612			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS			
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Template-Synthesis - A Method for Enhancing the Ionic and Electronic Conductivity in Electronically Conductive Polymers					
12. PERSONAL AUTHOR(S) Charles R. Martin, Leon S. Van Dyke and Zhihua Cai					
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 1992, 4, 16		15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Conductive polymers, template synthesis, microtubules		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Template-synthesis entails the synthesis of an electronically conductive polymer (or other material) within the pores of a microporous membrane. The membranes used have cylindrical pores of equivalent pore diameter; as a result, polymeric fibers are obtained, where the diameters of the fibers are determined by the diameter of the pores in the template membrane. We show in this paper that template-synthesized polypyrrole fibers show faster rates of charge transport, during electrochemical "undoping," and dramatically higher electronic conductivities than conventional forms (e.g. electrochemically-synthesized film) of this polymer.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak			22b. TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL	

INTRODUCTION

We have coined the term "template-synthesis" to describe the process whereby electronically conductive polymers (or other materials) are synthesized within the pores of a microporous support membrane (1-8). The membranes employed have cylindrical pores of equivalent pore diameter. These pores act as templates for the nascent conductive polymer. Because the pores are cylindrical, narrow polymeric fibers are obtained. The fiber diameter is defined by the diameter of the pores in the template membrane. The fiber length is defined by the thickness of the template membrane (1-8).

We have used the template method to prepare microscopic fibers of polypyrrole (1,5,7,8), poly(N-methylpyrrole) (3,5), poly(3-methylthiophene) (5), and polyacetylene (2). We have also shown that this approach can be used to synthesize organic microtubules (3,6). Furthermore, we have used this method to make microscopic fibers of Au and Pt; these metal fibers were used as ultramicroelectrodes (9) and as transparent metal films (10). Finally, we have recently shown that this method can be used to obtain Au microtubules (4,6). There are several previous examples in the literature of depositing materials within the pores of such microporous membranes. For example, Bean filled the pores of nuclear track/etched membranes with AgCl which was subsequently converted to Ag (11). Various other metals have also been deposited into the pores of such membranes (12,13)

This paper will focus on fibers composed of electronically conductive heterocyclic polymers (1,5,7,8). We will show that these fibers show much higher effective rates of ion-transport (7,8) and dramatically higher electronic conductivities (1,5) than conventional forms (e.g. electrochemically-synthesized films) of the analogous polymers.

EXPERIMENTAL

Ion-Transport. The fibers used for these investigations were synthesized electrochemically. Anopore microporous alumina filters (200 nm-dia. pores) were used as the template membranes (2,4). Synthesis was accomplished by converting one surface of the membrane into an electrode by covering the surface with a layer of Au (4,8,10). This electrode was then used to conduct electropolymerization of polypyrrole (PPy) within the pores of the membrane (8). Details of this electrochemical template method can be found in (8).

After electropolymerization of the PPy fibrils, the alumina template was dissolved away by exposing the membrane to 0.2 M NaOH. This yielded an array of isolated PPy fibers, connected at their bases to the substrate Au layer (Figure 1). Exposure to strong base has a deleterious (but reversible) affect on the electrochemistry of PPy (14). In order to reverse the effects of exposure to strong base, the isolated fibers (Figure 1) were immersed in a 1% solution of HBF_4 prior to use (7,8).

The electrochemical characteristics of these template-synthesized fibers were compared to conventional electrochemically-synthesized PPy film (15). The PPy film contained the same quantity of polymer as in the array of template synthesized fibers. This was accomplished by using the same total amount of charge to synthesize both the film and fibers (190 mC). The electrochemical instrumentation and cell used were identical to those used in our previous studies on the electrochemistry of conductive polymers (15).

We are interested in the rate of the electrochemical "switching reaction" for PPy (15). This reaction converts the polymer from its electronically insulating state to its electronically conductive state (or vice versa). The rate of this reaction is usually controlled by the rate of

ionic diffusion in the polymer phase (15). In order to obtain relative measures of the rates of this reaction for the fibrous and film materials, identical quantities of each material were first quantitatively oxidized at 0.15 V vs. SCE. The fibrous and film samples were then reduced by stepping the potential to -0.65 V vs. SCE. The rate of the reduction reactions were followed by recording the charge-time transients associated with the reduction processes.

Electronic Conductivity. Fibers for these studies were chemically synthesized within the pores of microporous polycarbonate filters (Nuclepore) (1,5). We have recently published a correspondence which describes this chemical template synthesis (1). A full paper on this subject has been submitted for publication (5). The electronic conductivity for these fibers were measured by leaving the polycarbonate template membrane in tact and measuring the resistance across this membrane/fiber composite. Because the fibers within the pores of the polycarbonate membrane are the only electronically conductive paths through the membrane, the bulk resistance of the composite provides the electronic conductivity of the fibers (1,5).

RESULTS AND DISCUSSION

Ion-Transport. Figure 2 compares the charge time transient associated with the reduction of an array of 200 nm-diameter PPy fibers with the analogous transient for the identical quantity of conventional electrochemically-synthesized film. The rate of reduction of the fibrous material is significantly higher. As indicated earlier, the rate of charge-transport in PPy is limited by the rate of ion-transport in the polymer (15). In the film form of the polymer, the distance over which ions must diffuse in the polymer is determined by the film thickness (in this case, Figure 2, 1.0 μm). In contrast, in the fibrous form, the distance over which ions must diffuse in the polymer is limited to the radius of the fiber, which is significantly smaller

(100 nm). Put another way, the surface to volume ratio for the fibrous material is significantly higher than for the film.

We have demonstrated that the fibrous versions of PPy retain the switching rate advantage (e.g. Figure 2) for fibers as long as $3.08 \mu\text{m}$ (8). The thickness of the film containing an equivalent quantity of PPy, in this case, was $2.0 \mu\text{m}$. We have not yet investigated longer fibers. Because the membranes employed for these investigations are available in only one pore diameter (200 nm), we have not yet investigated other fiber diameters. We are currently synthesizing membranes with smaller pore diameters.

Electronic Conductivity. Figure 3 shows plots of conductivity vs. diameter for PPy fibers synthesized at two different temperatures. Conductivity increases dramatically in the fibers with the smallest diameters. Furthermore, fibers synthesized at lower temperatures show higher conductivities than analogous fibers synthesized at higher temperatures (Figure 3). We have used this approach to synthesize 30 nm-diameter poly(3-methylthiophene) fibers with conductivities of $6,600 \text{ S cm}^{-1}$ (5). We have found that this enhanced conductivity results from longer conjugation lengths and greater polymer chain orientation in the template-synthesized materials (5). We are currently conducting syntheses at lower temperatures and investigating conductivity in fibers composed of other conductive polymers.

Acknowledgements.

This work was supported by the Office of Naval Research and the Air Force Office of Scientific Research.

References.

1. Z. Cai and C.R. Martin, *J. Am. Chem. Soc.* 1989, 111, 4138.
2. W. Liang and C.R. Martin, *J. Am. Chem. Soc.* 1990, 112, 9666.
3. C.R. Martin, L.S. Van Dyke, Z. Cai, and W. Liang, *J. Am. Chem. Soc.* 1990, 112, 8976.
4. C.J. Brumlik and C.R. Martin, *J. Am. Chem. Soc.* 1991, 113, 3174.
5. Z. Cai, J.T. Lei, and C.R. Martin, *Chem. Materials*, submitted for publication.
6. C.R. Martin, *Advanced Materials*, accepted for publication.
7. L.S. Van Dyke and C.R. Martin, *Synth. Met.* 1990, 36, 275.
8. L.S. Van Dyke and C.R. Martin, *Langmuir* 1990, 6, 1118.
9. R.M. Penner and C.R. Martin, *Anal. Chem.* 1987, 59, 2625.
10. M.J. Tierney and C.R. Martin, *J. Phys. Chem.* 1989, 93, 2878.
11. C.P. Bean, U.S. Patent 3,483,095, 1969.
12. G.E. Possin, *Rev. Sci. Instr.* 1970, 41, 772.
13. N. Giordano, *Rev. Sci. Instr.* 1984, 55, 410.
14. W. Wernet and G. Wegner, *Makromol. Chem.* 1987, 188, 1465.
15. R.M. Penner, L.S. Van Dyke, and C.R. Martin, *J. Phys. Chem.* 1988, 92, 5274.

Figure Captions

Figure 1. Electron micrograph of an array of polypyrrole fibers.

Figure 2. Charge-time transients for the reduction of fibrous (upper) and film (lower) PPy.

Figure 3. Conductivity vs. fiber diameter for PPy fibers synthesized at two temperatures.



