

Chemical Lithography of a Conductive Polymer Using a Traceless Removable Group

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In the present Communication, a new modification reaction of polyaniline (PANI), N-nitrosation, is described. The reaction could be reversed with traceless elimination of the incorporated functional group. A simple chemical lithographic process to produce conductive polyaniline images is then demonstrated.

Fabrication of conductive patterns by chemical and photochemical means is of great importance in technologies such as printed board production and microelectronics. The increased use of conducting polymers for electronic and optoelectronic applications¹ requires new patterning methods of conductive polymers.² Holdcroft and co-workers³ synthesized polythiophenes bearing pendant groups which can be hydrolyzed by acids, making them amenable to chemically amplified lithography. Similarly, lithographic patterning of PANI has been achieved using acid⁴ or base photogenerators⁵ which could alter the solubility of the polymer by changing its protonation state. The polymer has to be deposited from the few solvents, like *N*-methylpyrrolidone,⁶ in which PANI is soluble. However, it would be more convenient and useful were it possible to cast PANI films from common organic solvents or water. This has been achieved by covalent binding of functional groups to the backbone rings⁷ or amine nitrogens.⁸ However, the modified polymer usually exhibits inferior properties (e.g., conductivity) as compared to the unmodified material.^{7,8} If the functional group responsible for the increased solubility could be removed after the polymer has been processed (a traceless functional group⁹), then the resultant material will retain its intrinsic properties during processing. Additionally, if the removal of the functional group could be chemically or photochemically driven, direct patterning of the film would then be possible. PANI amide formation/hydrolysis has been previously used to reversibly change polymer conductivity.¹⁰

N-Nitrosated polyaniline (PANI-NO) (2) was prepared by reacting PANI (emeraldine base) (1) with sodium nitrite (1 M) in 1.1 M HCl solution (Scheme 1).¹¹ Up to 43% of N-nitrosation¹² is ob-

Scheme 1. Synthesis and Hydrolysis of Nitrosated Polyaniline (PANI-NO)

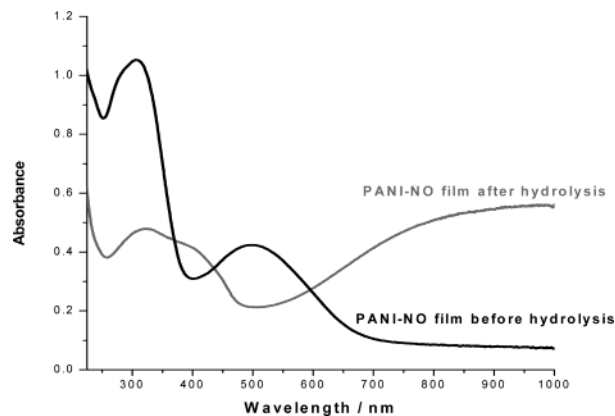
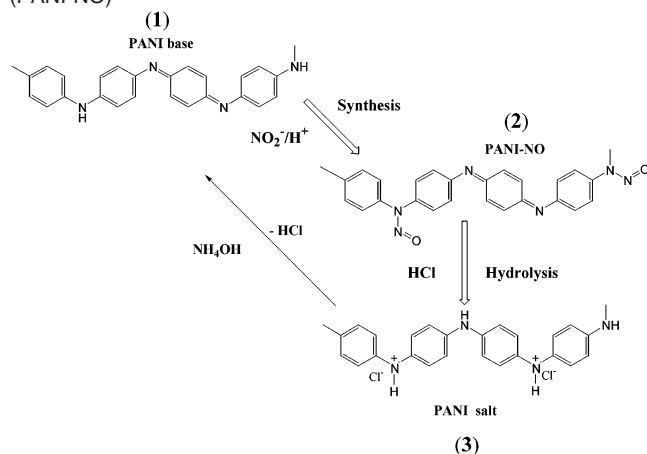


Figure 1. UV-visible spectra of PANI-NO film on quartz before (black line) and after hydrolysis (gray line).

tained. The FTIR spectrum of the product shows bands characteristic of polyaniline (emeraldine base¹³), and new bands are observed at 1508 (str. $-\text{N}=\text{O}$), 1034 (str. $-\text{N}-\text{N}-$), and 757 cm^{-1} (def. $-\text{N}-\text{N}=\text{C}-$),¹⁴ indicating formation of N-nitrosated polyaniline. PANI-NO is soluble in common solvents (CHCl_3 , CH_2Cl_2 , $\text{C}_2\text{H}_4\text{Cl}_2$, secondary amines, DMSO, DMF), giving deep red solutions.

Polymer solutions in dichloromethane show bands at 298 (4.15 eV) and 495 nm (2.50 eV). The band at 298 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the aniline ring.¹⁵ The band at 495 nm is assigned to the excitation from HOMO of the benzenoid rings (π_b) to the LUMO of the quinoid rings (π_q) in the quinoneimine units.¹⁶ The spectrum of PANI-NO solution in NMP exhibits two bands at 316 (3.92 eV) and 490 nm (2.52 eV). The UV band occurs at 327 nm in PANI, indicating a hypsochromic shift in PANI-NO for the $\pi \rightarrow \pi^*$ transition due to the NO group. The band in the visible region shifts to higher energy in PANI-NO (490 nm, 2.52 eV) as compared to PANI in NMP (630 nm, 1.96 eV¹⁶). This is probably due to the electron-withdrawing effect of the NO group.

By evaporation of solutions, it is possible to produce films on quartz with UV-visible spectra similar to those in solution (Figure 1).

PANI-NO films are nonconductive as expected for an undoped polyaniline derivative (Scheme 1). The films are stable for months in the dry state or basic media. However, it is known that aryl nitrosamines are sensitive to acids, hydrolyzing to arylamines.¹⁷ Therefore, it would be possible to obtain PANI from PANI-NO by acid hydrolysis.¹⁸ The FTIR spectrum of PANI-NO powder treated with 5% HCl for 1 min is indistinguishable from that of PANI salt,¹⁹ indicating that the N-nitrosated polyaniline could be hydrolyzed and films of PANI salt (3) or base (1) could be recovered from PANI-NO films (Scheme 1). Treatment of PANI-NO films with 5% HCl for 1 min renders films which show an optical absorption spectrum similar to those of PANI salts (Figure 1). The films are conductive as expected from PANI salt films.

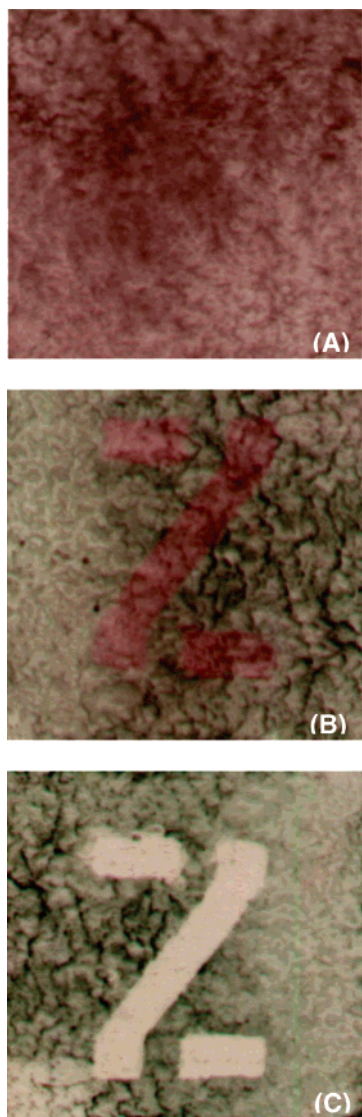


Figure 2. PANI image formation by hydrolysis of a PANI-NO film. (A) PANI-NO film on PET. (B) PANI-NO film on PET exposed to HCl vapors with a region protected by a PMMA image sprayed through a mask. (C) PANI image after washing the film shown in (B) with dichloromethane.

Because the removal is chemically driven, a lithographic process was designed to produce PANI patterns (Figure 2). First, a PANI-NO coating was deposited onto a plastic (poly(ethylene terephthalate), PET) plate (Figure 2A). The red film was then covered with a metal mask, and an image of a protective layer was produced by spraying a solution of an inert polymer (poly(methyl methacrylate), PMMA) through the mask. The plate was then exposed to HCl vapor. The PANI-NO layer hydrolyzes into PANI except in the protected region, leaving a positive image of the mask in PANI-NO surrounded by a PANI salt region (Figure 2B). The plate is then washed with CH_2Cl_2 , removing the protective layer together with the unexposed PANI-NO, leaving a negative image of the mask (Figure 2C) in PANI salt.²⁰ The exposed region is conductive, while

the unexposed region shows high resistivity ($> 100 \text{ M}\Omega$), suggesting that PANI-NO has been completely removed. The process could be easily extended to photolithography because the inert polymer image could be created by conventional photolithography or an acid photogenerator used to promote PANI-NO hydrolysis.

It has been shown that polyaniline could be easily converted into nitrosated polyaniline by reaction with nitrite ion in acids. The product is soluble in common solvents and could be deposited into thin films. The nitrosated polyaniline could be converted back into polyaniline by acid hydrolysis. On the basis of those properties, a chemical lithographic process to produce conductive polyaniline images is designed.

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Supporting Information Available: Details of nitrosated polyaniline synthesis, and FTIR and UV-vis spectra of **1** and **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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