

Transparent Flexible Electrode with Conductive Coating Induced by Proton Implantation of Emeraldine Polyaniline Covalently Functionalized on Polydimethylsiloxane

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ABSTRACT

Transparent thin films of polyaniline covalently fabricated on flexible polydimethylsiloxane substrates by surface modification with *N*-(3-trimethoxysilylpropyl)aniline for robust aniline polymerization could alternatively be redoped by proton implantation without incorporating an undesired labile/hygroscopic dopant acid that tends to compromise operation of encapsulated modules or MEMS components developed for flexible display applications.

1 INTRODUCTION

Due to its ease of synthesis, polyaniline has attracted the interest of many scientists and engineers for technology innovations in various research fields for display applications [1-5]. Polyaniline can be synthesized by electrochemical polymerization or oxidative chemical polymerization [6]. For large-scale synthesis, oxidative chemical polymerization is preferred because it allows for easy scale-up [7]. Among the oxidative chemical polymerization methods used to prepare polyaniline, the polymerization system consisting of aniline and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidizing agent in a 1 M HCl aqueous medium is the most widely used one [8]. This method is also often referred to as the “conventional” oxidative chemical polymerization method. Polyaniline can undergo reversible protonic doping to change its electrical conductivity by up to 10 orders of magnitude [9]. As the polymerization of aniline is pH-sensitive, caution should be taken to maintain appropriate low pH in the reaction media when the synthesis of the “classical” conductive polyaniline is desired [10-12]. In general, an aqueous medium containing a strong protonic acid, such as hydrochloric acid, with a sufficiently acidic concentration is used to ensure that the reaction will follow the desired polymerization mechanism. As polyaniline can undergo reversible protonic doping, conductive polyaniline dedoped by a basic solution, such as ammonium hydroxide solution, can also be further redoped by another acid of choice [13].

With the advance of display technologies based on flexible electronics, it comes with a demand for developing

transparent flexible electrodes that can better tolerate mechanical manipulation. As a polymeric material with electrical conductivity and mechanical flexibility, polyaniline has become a potential candidate for such applications. However, many polymeric flexible electrodes integrated with thin films of polyaniline are mainly fabricated by coating techniques of non-covalent nature. Moreover, the dopant acids used for producing conductive polyaniline may contain labile or hygroscopic groups that are not desired for incorporation in encapsulated modules or MEMS components developed for flexible display applications.

In this study, we demonstrated that transparent thin films of polyaniline could be covalently fabricated on flexible polydimethylsiloxane substrates by surface modification with *N*-(3-trimethoxysilylpropyl)aniline for robust polymerization of aniline. We also found that the dedoped emeraldine polyaniline could alternatively be redoped by proton implantation without using protonic acids.

2 RESULTS

Figure 1 shows the reaction scheme for fabricating the transparent thin film of polyaniline covalently functionalized on the flexible polydimethylsiloxane substrate. To promote the organosilanization of *N*-(3-trimethoxysilylpropyl)aniline on the polydimethylsiloxane substrate surface, the polydimethylsiloxane substrate was treated by oxygen plasma treatment. The oxygen plasma treatment could increase the density of silanol groups on the polydimethylsiloxane surface to further facilitate the chemical reaction for forming covalent linkage between *N*-(3-trimethoxysilylpropyl)aniline and the polydimethylsiloxane surface. After the organosilanization with *N*-(3-trimethoxysilylpropyl)aniline, the polydimethylsiloxane surface became covalently functionalized with aniline monomers. The aniline monomers covalently bound on the polydimethylsiloxane surface could serve as the initiation sites to fabricate a robust transparent thin film of polyaniline by the conventional oxidative chemical

polymerization method. After the oxidative chemical polymerization, the conductive HCl-doped polyaniline coating was obtained. The conductive HCl-doped polyaniline coating could be dedoped to become non-conductive emeraldine polyaniline by a treatment with an aqueous NH_4OH solution. After this dedoping treatment, the color of the polyaniline coating would be changed from green to blue.

Figure 2 shows the result on the polyaniline thin film deposited on the same polydimethylsiloxane substrate by Scotch-Tape peeling test. On the surface of the polydimethylsiloxane substrate, only half of the surface was treated with *N*-(3-trimethoxysilylpropyl)aniline. Even though polyaniline could still be deposited on the whole polydimethylsiloxane substrate surface by oxidative chemical polymerization, it can obviously be seen from Figure 2 that only the part that was subject to the organosilanization treatment with *N*-(3-trimethoxysilylpropyl)aniline could produce robust polyaniline coating on the polydimethylsiloxane substrate surface.

2.1 Proton Implantation of Emeraldine Polyaniline

Figure 3 shows the effect of proton implantation on a sample with emeraldine polyaniline covalently bound on a flexible polydimethylsiloxane substrate. As the polyaniline coating would be in its HCl-doped state when it was produced by the reaction scheme shown in Figure 1, the sample was treated with an aqueous NH_4OH solution to form emeraldine polyaniline for this experiment. Meanwhile, the color of the polyaniline would change from green to blue. As can be seen in Figure 3, when the sample with emeraldine polyaniline was subject to proton implantation (8.03 MeV, 1.01×10^{15} ions/cm² for 52 minutes), the color of the polyaniline coating in the peripheral area blocked by the aluminum sample holder still remained blue while the color of the polyaniline coating in the central area not blocked by the aluminum sample holder turned green, indicating that proton implantation could similarly cause emeraldine polyaniline to undergo the state conversion conventionally known to be induced by protonic acids.

2.2 Spectroscopic Analysis

Figure 4 shows the UV-Vis spectra of the emeraldine polyaniline before and after proton implantation. Essentially, the change in spectral features of the emeraldine polyaniline sample upon proton implantation was consistent with the well-established conversion found for polyaniline emeraldine base treated with protonic acids during the protonic doping process. The result suggests that anion-free *protons* in the form of an irradiation beam alone could also convert non-conductive emeraldine polyaniline into a conductive polymeric material.

Figure 5 shows Raman Spectra for samples of emeraldine polyaniline coated on polydimethylsiloxane upon proton implantation with energy ranging from 2.04

MeV to 9.99 MeV. As is shown in Figure 5, a peak at $\sim 1410 \text{ cm}^{-1}$ appeared when the samples were subject to proton implantation with higher energy. The peak at $\sim 1410 \text{ cm}^{-1}$ is attributed to the phenazine structure, which has previously been found in emeraldine polyaniline subject to a thermal treatment that caused segmental C-N crosslinking of polyaniline chains [14]. The result suggests that, while providing proton source to dope emeraldine polyaniline by proton bombardment, the onset of proton implantation might concomitantly generate negatively-charged species/segments out of the polyaniline molecules to help maintain and stabilize the proton-irradiated polyaniline without using protonic acids.

3 CONCLUSIONS

We demonstrated in this study that transparent thin films of polyaniline could be covalently coated on flexible polydimethylsiloxane substrates by a robust reaction scheme involving surface modification with *N*-(3-trimethoxysilylpropyl)aniline for subsequently initiating the polymerization of aniline on the polydimethylsiloxane surface using the conventional oxidative chemical polymerization method. Our results also suggest that proton implantation could alternatively redope the non-conductive emeraldine polyaniline into a conductive polymeric material without incorporating labile/hygroscopic dopant acids that tends to compromise the operation of encapsulated modules or MEMS components developed for flexible display applications.

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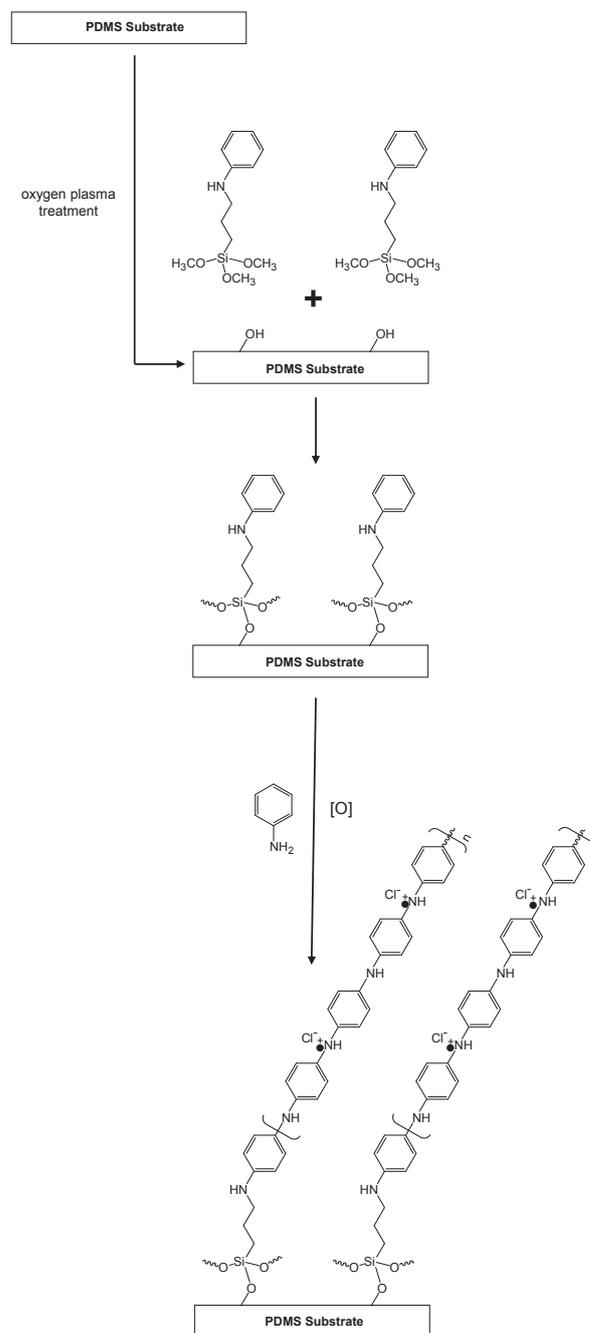


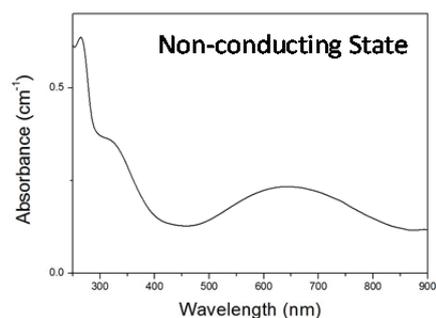
Fig. 1

Reaction scheme for covalently fabricating polyaniline coating on polydimethylsiloxane surface



Fig. 2

Scotch-Tape peeling test showing the result that the polyaniline deposited on the left side of the polydimethylsiloxane surface with *N*-(3-trimethoxysilylpropyl)aniline treatment still remained on the surface, while the polyaniline deposited on the right side of the polydimethylsiloxane surface without *N*-(3-trimethoxysilylpropyl)aniline treatment was peeled off from the surface (Prior to the test, the polyaniline was dedoped so that it became emeraldine polyaniline with blue color.)



**Proton
Implantation**

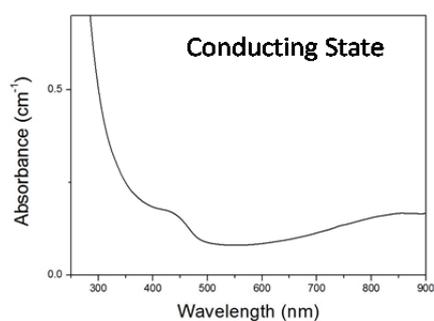


Fig. 4

UV-Vis spectra of emeraldine polyaniline before and after proton implantation



Fig. 3

The result of proton implantation on emeraldine polyaniline covalently coated on polydimethylsiloxane showing that the color of the polyaniline coating in the peripheral area blocked by the aluminum sample holder still remained blue (non-conducting state), while the color of the polyaniline coating in the central area not blocked by the aluminum sample holder turned green (conducting state)

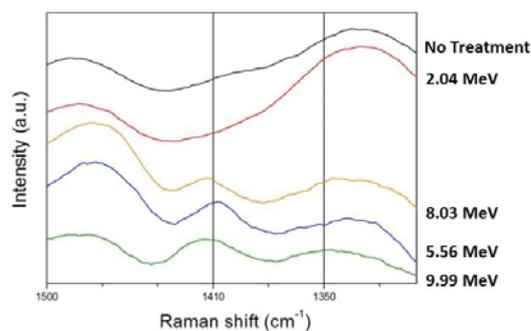


Fig. 5

Raman spectra of emeraldine polyaniline coated on polydimethylsiloxane subject to proton implantation with energy ranging from 2.04 MeV to 9.99 MeV