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Enhanced Adhesion of Deposited Polypyrrole Ultra-Thin Films Through Self-Assembled Polymeric Monolayers

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A novel method for the deposition of polypyrrole (PPy) thin films on a metal oxide surface using self-assembled polyethylene glycol (PEG) monolayers as reaction media has been developed. This method lends to increased adhesion of the deposited PPy films to the substrates and an increase in its electrical conductivity. The procedure consists of several simple steps. First, the surface of glass substrate is functionalized with the isocyanate group. Then, a PEG monolayer is formed on the surface through the reaction of its hydroxy group with the isocyanate group. Finally, a polypyrrole film is grown in the self-assembled PEG monolayer by adding oxidant. The resulting PPy thin films were characterized by measuring the electrical conductivity, adhesion, and surface morphology. It was found that the deposited PPy films show higher conductivities (13 S/cm) and superior adhesion compared to simply deposited PPy films.

Keywords: polypyrrole thin films; self-assembled monolayers

INTRODUCTION

Fabrication of thin conducting polymer films is an important technique for advanced applications. Thin conducting polymer films can be easily prepared either chemically or electrochemically in various media^[1-3]. Among conducting polymer coatings, polypyrrole (PPy) thin films have been shown to work quite well as protective layers, sensors, and adsorbents for protein separation. However, the adhesion of PPy films on a surface is a major obstacle to be solved in industrial applications. Recent reports have shown that the

adhesion problem in PPy coating can be solved by grafting polymerization of pyrrole on chemically adsorbed *N*-(3-trimethoxy-silyl) alkyl pyrrole or ω -(*N*-pyrrolyl) alkanethiols on the surface of substrates^[4]. However, those chemicals are quite expensive for industrial scale production. Therefore, an alternative inexpensive procedure without sacrificing the electrical properties of PPy is in high demand. In this paper, a new method for enhancing adhesion at PPy coating on glass through an interaction between doped PPy and a template will be reported.

EXPERIMENTAL

Materials. HPLC grade *p*-xylene (99+%), 3-(triethoxysilyl)propyl isocyanate (TPC, 95+%), methylene chloride (anhydrous, 99.8%), polyethylene glycol (PEG, Mw 3400), and acetonitrile (99.9+%) were purchased from Aldrich and used without further purification. Stannous 2-ethyl-hexanoate, a catalyst, and pyrrole (98%) were purchased from Sigma and Aldrich, respectively. Glass microscope slides were obtained from Fisher and used after rinsing thoroughly with soap solution, acetone, ethanol, and water. Doubly-distilled water was used in preparing polypyrrole thin films.

SAMs preparation. Surface modification of glass using TPC was carried out based on a previously reported method^[5]. Those surface modified glasses are characterized using contact angle meter, and surface reflection IR. A FT-IR spectrophotometer (SRIR) (FTIR-7100, Shimadzu Co., Ltd., 2 cm⁻¹ resolution) equipped with custom-designed optics similar to that described in the literature with an 83° incidence angle using *p* polarization was used. All samples were kept under N₂ atmosphere. SAMs of PEG were simply prepared by adding PEG onto the surface modified glass which was subsequently immersed in a methylene chloride solution containing catalytic amount of stannous 2-ethyl-hexanoate, under N₂ atmosphere. The resulting PEG self-assembled monolayer on glass was washed several times with acetonitrile and characterized using contact angle meter, and surface reflection IR.

PPy thin film formation. Both the PEG self-assembled glass and bare glass were placed vertically in the synthesis vessel (polypropylene tube) containing various amounts of pyrrole. After adding ammonium persulfate into the aqueous pyrrole solution, it was kept at room temperature for 4 h. The resulting PPy films were characterized using SRIR, SEM, cyclic voltammetry (CV), and temperature-dependent conductivity measurements. The same measurements were made for samples polymerized in the absence of self-assembled PEG layers for comparison. In addition, adhesion of

the deposited PPY films was simply tested by the Scotch tape method.

RESULTS

The results for the contact angles of bare glass, TPC modified glass, and PEG self-assembled glass are 0° , 105° , and 30° respectively. All reported values are the average of at least five measurements taken at different locations on the glass surfaces. If we consider that the contact angle of the completely hydrophobic surface of polyethylene is 120° and the end group of TPC on glass is the cyanate group ($-N=C=O$), it is reasonable to conclude that almost perfect packing of TPC on glass was achieved. In addition, after PEG self-assembles on TPC modified glass, the advancing contact angle is lower than that of TPC modified glass. Considering the hydrophilicity of PEG, the observed contact angle for the PEG self-assembled glass is a reasonable one. In addition, IR spectra for the TPC and PEG modified glass were taken. For the TPC modified glass, the characteristic frequency of the cyanate group at 2156 cm^{-1} was observed with a weak intensity. For PEG modified glass, the characteristic C-O stretching peak at 1130 cm^{-1} was observed with a strong intensity.

PPy films both on self-assembled PEG (PSP) and bare glass (PBG) were easily deposited under aqueous solution using oxidants. To investigate the influence of PEG self-assembled monolayers on thickness and morphology of thinly-deposited PPy films, the surface and cross-sectional SEM images were taken for 0.2 mmol of initial pyrrole concentration. From the cross-sectional SEM images, both PSP and PBG have almost same thicknesses about 140 nm.

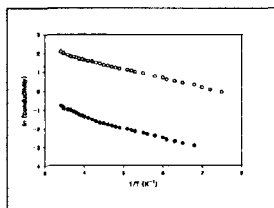


Fig. 1. Temperature dependent conductivity of PSP (open sphere) and PBG (filled sphere).

However, PSP have more stable and higher conductivity than the PBG (Fig. 1). Since SRIR studies of PSP show stronger "doping induced" bands (1200 cm^{-1} and 1000 cm^{-1}) than those of PBG, we speculate that the higher conductivity of PSP may be due to their stabilized doped PPy by ethyloxide ($\text{CH}_2\text{CH}_2\text{-O}$) units of PEG. In addition, the adhesion of PSP is superior than that of PBG due to the interaction between doped PPy and ethyloxide ($\text{CH}_2\text{CH}_2\text{-O}$) units of PEG (Fig. 2). The interaction of doped PPy and PEG unit was proved by CV studies

(Fig. 3). Furthermore, after the electrical reduction PSP, the deposited PPy could be completely removed by using a Scotch tape. Then, the intensities of "doping induced" bands from the SRIR investigation were reduced to the same as those of PBG. Those results are indirectly support the role of PEG in enhancement of the adhesion of PPy ultra-thin films.

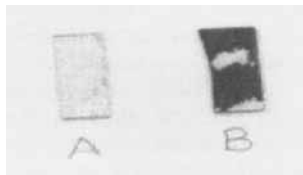


Fig. 2. Photograph of PPy films remaining after attempted removal scotch tape : A for PBG, B for PSP.

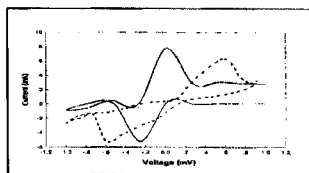


Fig. 3. Cyclic voltammogram for PSP (solid line) and PBG (dotted line).

CONCLUSION

In summary, we have prepared strongly adhered PPy thin films on glass plates using a simple surface polymerization of pyrrole in self-assembled PEG monolayers as templates. In this process, the ionic interactions between dopants of PPy and ethyloxy units of self-assembled PEG monolayers play a key role in enhancing electrical conductivity and adhesion of deposited PPy thin films.

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