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Enhanced adhesion of polypyrrole film through a novel grafting method

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A new method for the deposition of polypyrrole (PPY) thin films on a metal oxide surface through a grafting polymerization has been developed for the purpose of enhancing adhesion of the deposited PPY films to the substrates.

Since the 1970s, much has been reported regarding organic conducting polymers (OCPs), (*e.g.* polyaniline, polypyrrole, polyacetylene). These 'synthetic metals,' which can reversibly switch their oxidation states, have led to the increasing displacement of both conventional metals and inorganic materials in a variety of applications, *e.g.* optical displays, sensors, rechargeable batteries, membranes, electromagnetic interface shielding, nonlinear optics, and microelectronics.[1]

The further application of these materials has been dwarfed by the technical challenges they pose. Most OCPs are unstable in air, and are insoluble. However, new process technology has been developed to address some of the materials' inherent problems.[2] In addition, development work has been shifted from its original base such as batteries and electronics component to coatings such as corrosion-resistant coating and electrostatic dissipation coating.[3]

Polypyrrole (PPY) thin films have been shown to work quite well in coatings as protective layers, sensors, and adsorbents for protein separations.[4,5] However, the adhesion of PPY films to surfaces is a major obstacle to be solved for industrial applications. Recent reports have shown that the adhesion problem in PPY coating can be addressed by using *N*-(3-trimethoxysilylalkyl)pyrrole which can be chemically adsorbed on hydrated metal oxide surfaces and ω-(*N*-pyrrolyl)alkanethiols which can be chemically adsorbed on gold surfaces.[6] However, those chemicals are very expensive for industrial scale production. Therefore, a new inexpensive procedure to improve adhesion without sacrificing the electrical properties of PPY is in high demand.

In this paper, the new method (Fig. 1) for formation of PPY coatings on silica using less expensive 3-(trimethoxysilyl)-propyl methacrylate (TSM) self-assembled monolayers as grafting sites is reported. The resulting PPY grafted onto the surface of glass plates has been characterized using AFM, SEM, and electrical conductivity measurements.

Pyrrole (98%, Aldrich) was purified by passing it through a short column of basic alumina, activity grade I (Sigma). *p*-Xylene, acetone, and 3-(trimethoxysilyl)propyl methacrylate (TSM) (Aldrich) were used without further purification. Glass microscope slides (Fisher) were cut (2 cm × 1 cm) and cleaned by soaking in a 6 M HCl solution for 24 h, and these plates were then placed in a large volume of double distilled water (resistivity $\geqslant 13$ M cm^{-1}). Silicon dioxide particles (356 mesh) were purchased from Aldrich and calcined at 900 °C before use. Ammonium persulfate (99.99+%, Aldrich) as an oxidant was used without further purification.

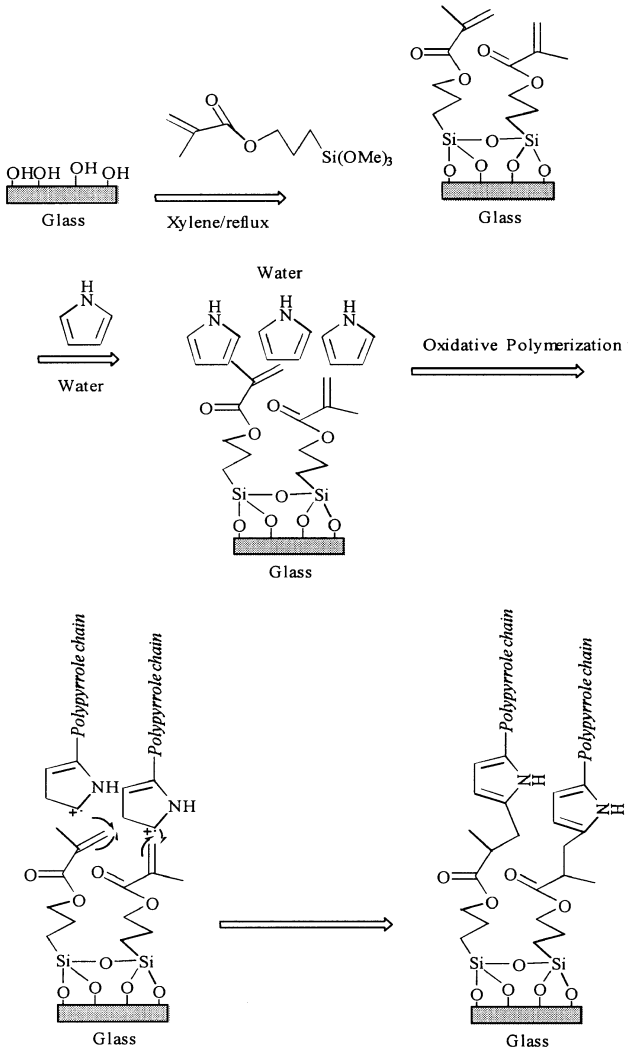

Fig. 1 A schematic illustration for the preparation of PPY-grafted glass.

Surface modification of both glass plates and silicon dioxide particles was carried out based on the previously reported method.[7] Cleaned glass plates or 5 g of silicon dioxide respectively were put into a 100 mL round bottomed flask, and 70 mL of xylene solution (contained 20 mmole of TSM for glass plates and 200 mmol of TSM for silicon dioxide particles) was added. The mixture was heated to reflux for 24 h and methanol was removed through an 80 °C water condenser. These glass

plates and silicon dioxide were then washed several times with acetone and dried in a vacuum oven at 30 °C for 48 h.

Contact angles were measured with sessile drops on the surface of the modified glass and a bare glass substrate in a microscope equipped with an environment-controlled transparent chamber. The advancing water contact angle (H_2O) was obtained by measuring the tangent to a 2 mL drop at its intersection with the surface.[8] The average value of six measurements taken at different locations on the surface showed a maximum standard deviation of 3°.

Diffuse reflection FT-IR (Shimadzu 8700 instrument) was used to prove that grafting sites (vinyl group of TSM) had not reacted themselves during the surface modification by using modified silicon dioxide particles. The surfaces of the modified glasses were also characterized after grafting polymerization of pyrrole on the surfaces. The grafting polymerizations of pyrrole from aqueous solution on surfaces were initiated by adding an equimolar amount of ammonium persulfate (based on pyrrole) to the sample solution. In this work, we used a glass plate with 10 mL of water and various pyrrole concentrations. For comparison, polypyrrole films were deposited on bare glass plates under the same conditions. Scanning electron microscopy (SEM) was used to measure the thickness of the PPY films grafted onto the glass plates. The morphology of the PPY grafted on glass plates was investigated by using atomic force microscopy (AFM). The electrical conductivities of PPY films deposited on glass plates were measured by using the 4-probe method.

After the surface reaction of TSM at the xylene and glass plate interfaces, the surfaces of the glass plates became hydrophobic. The contact angle of the modified glass surface was 117° while the bare glass surface was 0°. Based on the results of the contact angle measurement, we can speculate that TSM was homogeneously held on the surface by chemical bonds. In addition, it was shown that the methyl methacrylate groups of TSM on the surface were not affected during the surface reaction by using diffuse reflection FT-IR. We observed the carbonyl stretching band from modified silicon dioxide particles; characteristic IR bands of TSM appeared at 1690 cm^{-1} in the diffuse reflection FT-IR spectra. If the vinyl group of TSM had reacted, the carbonyl peak of TSM would have been observed about 1700 cm^{-1}. Indeed, the carbonyl peak at 1713 cm^{-1} was observed after adding the initiator and heating the modified silicon dioxide particles for overnight. Therefore, based on the above experimental results, we can confirm that TSM is homogeneously anchored on the glass surface through covalent bonds as a monolayer and the vinyl group of TSM is present as a reactive site on the surface.

Although there is no information available to prove grafting of PPY onto the vinyl group of methyl methacrylate, grafting can be indirectly proved by an adhesion test. Adhesion of PPY films to the surface of a glass plate was found to be drastically increased when a monolayer of TSM was present. We observed that PPY films on TSM modified glass were not removed at all by the Scotch tape method. Shown in Fig. 2 is a photograph of both a PPY-grafted glass plate (PMG) (A) and PPY-nucleated glass plate (PDG) (B) after attempted removal of the PPY films with Scotch tape. As shown in Fig. 2, while PPY films grafted on TSM modified glass could not be completely removed by the Scotch tape (A), PPY films nucleated on bare glass could be removed by the Scotch tape method (B). Furthermore, after the treatment of TSM modified glass under ammonium persulfate solution at 80 °C for 24 h, PPY deposition was carried out on treated TSM modified glass. The deposited PPY film was easily peeled off as we observed for the PDG. To further confirm the grafting of PPY, triethoxyoctylsilane was used to modify the surface of bare glass and the resulting surface of the modified glass was very hydrophobic (as shown by the contact angle of 120°). The triethoxyoctylsilane modified (TOM) glass was used to deposit PPY under the same conditions mentioned previously. The deposited PPY films on TOM glass were completely removed by the Scotch tape method as well. In addition, it

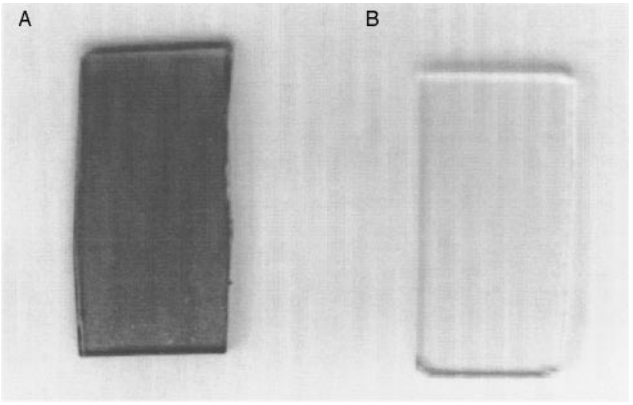

Fig. 2 Photograph of PPY films remaining after attemped removal with Scotch tape: A, PMG; B, PDG.

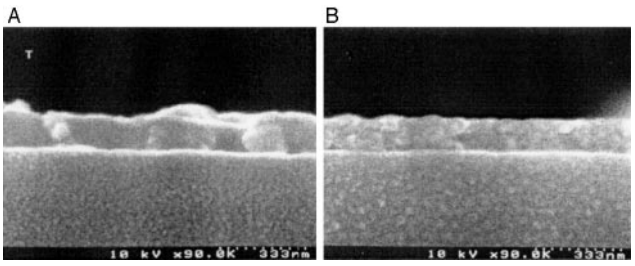

Fig. 3 Cross-sectional SEM image of PPY grafted (A) and nucleated (B) films on glass.

has been known that the adhesion between PPY thin films and polymers with hydrophilic surfaces was often enhanced while, notably, PPY thin films on hydrophobic surfaces of polymers were completely transferred to the adhesion tape.[9] Therefore these results strongly support the argument that PPY is indeed grafted to the methyl methacrylate group of TSM on the surface.

Based on available information[9] and our results, we can speculate on a possible PPY grafting mechanism (Fig. 1). Due to the hydrophobic properties of TSM modified glass, pyrrole will be condensed on the surface of TSM modified glass from the aqueous phase and consequently polymerized by adding ammonium persulfate as oxidant. As pyrrole is used up the active PPY chain ends may graft onto the vinyl group of TSM (Fig. 1). The elucidation of the exact mechanism of grafting is under investigation at our laboratory.

For comparison of the conducting properties between PPY grafted modified glass plate (PMG) and PPY deposited bare glass plate (PDG), we investigated the conductivity of both PMG and PDG using 4-probe measurements. Although the thickness of the PMG is the same as that of PDG (130 nm) (Fig. 3), the PMG shows an electrical conductivity of 1.3 S cm^{-1}, while the PDG has a conductivity of 0.18 S cm^{-1}. Surface-bonded polymer chains may have better regularity resulting in higher conductivity as has been observed by other authors.[10] However, AFM of the PPY-grafted glass shows a typical granular type surface morphology.

In summary, we have prepared strongly adhered PPY thin films on glass plates through a grafting polymerization method. In this process, the grafting sites on the glass plate were simply prepared by surface reaction of TSM which results in a strong adhesion of PPY films deposited on the substrate. The surface morphology of the resulting PPY thin films was a typical granular shape and very smooth. The electrical conductivity was 1.3 S cm^{-1} for thin films (130 nm thickness).

Acknowledgements

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