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Articles

Comparison of the Physical Properties of Polypyrrole Produced by Anodic Oxidation and by Photoelectrochemical Activation of TiO_2

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The conductivity, morphology, and thermal stability of polypyrrole films generated by electrochemical oxidation on stainless steel and by photocatalytic activation on TiO_2 are compared. For the electrochemically produced films, these properties are dependent on the electrolyte anion in the presence of which the film was produced. Conductivity and morphology of the anodic films were interdependent. In contrast, the conductivity and morphology of photoelectrochemically deposited polypyrrole appeared to be less sensitive to electrolyte and showed a significantly lower anion incorporation within the film. The resulting semiconductor–conducting polymer composite was less conducting and thermally less stable than an electrochemically generated polypyrrole film.

Introduction

Polypyrrole, when first produced as a black insulating powder in 1968, was of little use because of its lack of solubility and conductivity.[1] In 1979, however, Diaz and co-workers showed that the polymer could be produced as a conducting (1–200 Ω^{-1} cm^{-1}), continuous free-standing film by anodic oxidation of the monomer.[2] The electrochemically generated polymer was produced in a partially oxidized state with the electrolyte anion incorporated to maintain charge neutrality. Films produced from tetraalkylammonium salts displayed superior mechanical properties and were free of process-poisoning side reactions at the counterelectrode.[3] Electrochemical routes have also proved effective for the production of conducting polymers on Si, GaAs, CdS, and CdSe, where the organic layer can act as a vehicle to inhibit photocorrosion of the semiconductor.[4]

It is now clear that anodic polymerization of pyrrole occurs via a cation radical.[3] Since interfacial electron transfer to a photogenerated hole on the surface of an irradiated semiconductor particle has been shown to form adsorbed cation radicals,[5] photoelectrochemical methods should be viable routes for generating polypyrrole films. Previous investigations have shown that polystyrene, poly(vinylpyrene), and methyl methacrylate can be successfully formed via polymerization of the corresponding monomers via photogenerated radical cations on semiconductor powders.[6–9] Despite a reported unsuccessful attempt to incorporate the suspended semiconductor into the polymer by electrochemical polymerization in an aqueous suspension of TiO_2,[10] several groups have described the photoelectrochemical preparation of polypyrrole on semiconductor surfaces: either on semiconductor wafers in order to develop new imaging materials[4,11–13] or on platinized TiO_2 powders.[14] In no case so far have the resulting polymer's physical properties been characterized.

Although the insolubility of polypyrrole has made detailed structural studies difficult, these polymeric films have several important practical applications that are sensitive to polymer morphology. For example, the polymer can be electrochemically switched between its oxidized (conducting) and its neutral (insulating) states,[3] with an accompanying color change. Thus, its utility in electrochromic displays,[15] in batteries,[16] as an ion gate mem-

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brane,[17] as a medium for controlled-release agents,[18] and as a biomedical sensor[19] has been suggested. If such potential uses are to be exploited, the effect of electrochemical variables that control the physical properties of a given polypyrrole must be clearly defined.

The development of practical applications of polypyrrole has also been inhibited by the lack of a convenient method for producing the polymer in a conducting form by other than electrochemical generation. Some chemical routes involving growth in pillared clays,[20] membranes,[21] and zeolites[22] have been reported, but the conductivities were quite low ($\alpha = 10^{-5}$–10^{-11}) and in some cases almost impossible to measure.

In this paper, we compare the properties of electrochemically and photoelectrochemically generated polypyrrole films. We describe the effect of the counteranion on morphology, conductivity, and thermal stability of both anodically and photoelectrochemically generated polypyrrole and compare the physical properties of such photoelectrochemically deposited films with those obtained by electrochemical routes. We also wished to determine whether polypyrrole, grown by either anodic or photoelectrochemical methodology, could be used as a precursor for morphologically controlled carbon.

Experimental Section

Materials. Pyrrole (Aldrich Gold Label) was purified by microcolumn chromotography, using activity 1 neutral alumina, immediately before use. Millipore water was used in the polymerizations. Acetonitrile (Aldrich 99%) was stored over molecular sieves for at least 1 week before being distilled under N_2 immediately before use. Tetraethylammonium perchlorate ($TEAClO_4$), tetraethylammonium hexafluorophosphate ($TEAPF_6$), tetraethylammonium fluoroborate ($TEABF_4$), tetrabutylammonium perchlorate ($TBAClO_4$), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), and tetrabutylammonium fluoroborate ($TBABF_4$), all electrochemical grade from Southwestern Analytical, and tetraethylammonium tosylate (TEATs, Aldrich) were stored in a vacuum desiccator or oven before use.

Preparation of Polypyrrole (PPy) Films. A. Electrochemical preparation: All anodically generated films were produced in a 250-mL two-electrode, single-compartment cell equipped with stainless steel electrodes (5050 stainless steel from Reynolds Metals, 6.45 cm^2) separated by 1.0-cm Teflon spacers by using a PAR 173/176 potentiostat/galvanostat in the constant-current mode. Each electrode was polished sequentially with 600-grit wet–dry sandpaper (Buehler Ltd.) and 1.0-μm alumina on a felt polishing cloth (Buehler Ltd.). (In an earlier procedure, sequential polishings with 0.3- and 0.05-μm alumina caused adhesion problems with large electrodes or long electrolysis periods.) After being polished, the electrodes were thoroughly washed with distilled water and were sonicated in distilled water to ensure that no alumina was left on the surface of the electrode.

The electrolyte (0.10 M) was dissolved in 150 mL of a 98:2 mixture of acetonitrile:water which was then purged with N_2 for 3 h. Pyrrole (0.2 M) was then injected into the cell and the nitrogen flow reduced to a rate of approximately 2–3 bubbles/s through no. 20 Teflon tubing. The electrode having been poised initially at +1.0 V, a constant current of 6.45 mA was applied for 4.0 h. The current was then switched off, and the film was rinsed and peeled from the working electrode. Excess monomer and electrolyte were removed by vigorous washing with acetonitrile after removal from the electrode. The film was dried in a vacuum oven at 100 °C for 10 h before being stored in sealed sample vials.

B. Photoelectrochemical preparation: Deposition of polypyrrole on TiO_2 powders (Aldrich, Gold Label, anatase) was accomplished by bandgap irradiation of the semiconductor (1.00 g) suspended in 300 mL of freshly distilled acetonitrile, either with or without electrolyte (0.10 M $TEABF_4$ or TEATs). After the suspension was sonicated in a Pyrex Erlenmeyer flask, the suspension was purged for 1 h with air, before pyrrole (3 mL) was injected. (Little or no polymer could be deposited if the solution was purged with nitrogen.) The mixture was then placed in a Rayonet photochemical reactor (Southern New England Ultraviolet) equipped with 350-nm phosphor-coated low-pressure mercury bulbs and irradiated for 3 days with continual stirring. Every 24 h, 2 mL of pyrrole and 5 mL of acetonitrile were added to compensate for evaporative loss. The resulting light brown material was collected on a 4.5-μm nylon filter and washed with approximately 150 mL of freshly distilled acetonitrile. It was then vacuum dried at room temperature for 10 h and placed in sealed sample vials under argon. Control experiments demonstrate that bandgap irradiation and the presence of oxygen are necessary for polymer film formation. Specifically, pyrrole does not absorb the accessible incident wavelengths under the conditions of the photocatalysis.

Vapor-phase doping with iodine was accomplished by placing a polypyrrole-coated TiO_2 sample (0.2 g) in a 60-mL iodine chamber for 3 days.

Conductivity Measurements. Polypyrrole films (ca. 2.5 cm × 2.5 cm × 5.1 × 10^{-3} cm) and pellets of TiO_2/PPy composites obtained by pressing a 0.20-g composite sample in a standard 13-mm KBr die pressed to 10 000 lbs[23] were mounted on a Teflon block. Conductivities were measured with an Alessi Ind. 641S four-point resistivity probe equipped with osmium tips to minimize contact resistance. A Princeton Applied Research 173/176 potentiostat/galvanostat was used as a precision constant-current source. (A Hewlett-Packard HP6186C precision power supply was used for the TiO_2/polypyrrole samples.) A Fluke Model 77 precision multimeter was used to monitor voltage. An Alessi Ind. conductivity probe station (CPS) test station was used to hold the probe and to connect all components. Thickness measurements (±1 μm) performed with a Sloan-Dektac profilometer were repeated with Brown & Sharpe 599-579-2 precision calipers, with good agreement. Conductivities, σ, were calculated by using the Valdes infinite film approximation,[24] $\sigma = 1/(4.532R_st)$, where R_s is the dc resistance and t is thickness of the film in centimeters.

Spectroscopy. Normal and reflectance infrared (IR) spectra were obtained on a Nicolet 510 P FT-IR spectrometer on samples that had been ground in a mortar and pestle. Absorption spectra were recorded on a Hewlett-Packard 8451A diode array spectrometer. The powdered samples described above were analyzed for signal intensity on an IBM ER 300 electron spin resonance spectrometer.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) studies were conducted on a JEOL JEM 35CX scanning electron microscope at 25 kV at a magnification of 1000× except as noted. All samples were sputtered with gold (10 Å) before imaging and were mounted on the staging platform with conducting metallic tape (3M 1170 OMI tape).

Thermal Gravimetric Analysis. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer Series 7 thermal analysis system. All TGA runs were performed under N_2 (at a flow rate of 40 mL/min) at a scan rate of 20 °C/min from 50 to 725 °C. Onsets, via infection points of the curve, were plotted as the first derivative.

Elemental Analysis. Elemental analyses of the polymers were performed at Desert Analytics, Tucson, AZ, and at Galbraith Laboratories, Inc., Knoxville, TN.

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Table I. Conductivity of TiO_2/PPy Composites[a]

sample	I_2 doping	a,[b] Ω^{-1} cm^{-1}
TiO_2	none	6.6×10^{-6}
TiO_2/PPy Air	none	0.2
TiO_2/PPy Air	yes	0.2
TiO_2/PPyAr	yes	0.2
TiO_2/PPyBF_4	none	0.2
TiO_2/PPyTs	none	0.2

[a] These conductivity measurements were made on pressed pellets of the same weight and size. [b] The values represent the average measurement of two pellets: ±0.1 Ω^{-1} cm^{-1}.

Table II. Elemental Analysis of TiO_2/PPy Composites

	wt %						calcd doping,
dopant	Ti	C	H	N	S	F	%
Air	36.9	3.26	0.28	1.00			
Ts	48.5	3.63	0.27	1.00	0.06		3
BF_4	27.0	3.44	0.27	1.00		0.14	3

[a] Weight fraction of polypyrrole and dopant compared with total composite weight.

Table III. Thermal Stability of Electrochemically Produced Polypyrroles

counterion	wt loss,[a] %	inflection point(s),[b] °C
Ts	40–45	310, 425
ClO_4 ($TEAClO_4$)	50	300
ClO_4 ($LiClO_4$)	55–60	275, 310
BF_4	30–32	410
PF_6	26–28	250, 410

[a] Percent weight loss after thermal decomposition to a temperature of 750 °C as the average of three determinations. [b] Inflection points were obtained by plotting the first derivative of the TGA profile.

Table IV. Thermal Stability of the TiO_2–Polypyrrole Composites

	composite compn				
dopant/ counterion	% TiO_2	% polymer	total wt loss, %	polypyrrole loss,[a] %	inflection point,[b] °C
Air	61.6	38.4	25	66	240, 340
Ts	81.0	19.0	15	78	240, 340
BF_4	45.0	55.0	31	57	240, 340, 370

[a] Percentage weight loss of polypyrrole coating; corrected for TiO_2 composition. [b] Inflection points were obtained by plotting the fast derivative of the TGA profile.

Results

Conductivity. A. Electrochemically produced films: Conductivity of electrogenerated polypyrrole depends on the identity of the counterion,[23,24] with significantly larger conductivity observed in the presence of tetraalkylammonium tosylate (~70 Ω^{-1} cm^{-1}) than with perchlorate, tetrafluoroborate, or hexafluorophosphonate (~20 Ω^{-1} cm^{-1}). Despite high sensitivity to the incorporated anion, changing the electrolyte cation had little effect on the observed conductivity. Irrespective of counterion, the previously reported spectroscopic features of oxidized polypyrrole[26,27] (IR[28] 3400 (br), 1610, 800 cm^{-1}; ESR[29] $g = 2.0028$, with bandwidth dependent on the degree of exposure of the sample to oxygen; absorption,[30] neutral 384 nm, oxidized from 850 nm tailing to ca. 550 nm, as a film on indium tin oxide coated glass in contact with acetonitrile) were present in all samples.

B. Photoelectrochemically produced films: Elemental analysis showed that particles obtained after bandgap irradiation of TiO_2 in the presence of dissolved pyrrole are composites of TiO_2-coated polypyrrole. This TiO_2–PPy composite exhibited enhanced conductivity (by several orders of magnitude, compared to the native metal oxide powder) and the expected[26–30] IR, ESR, and visible absorption spectra, demonstrating that the polymer was indeed in its conducting form. Different electrolyte dependence on conductivity was observed in the polypyrrole films prepared by photoelectrochemical routes on TiO_2 than in the electrochemically generated films. Coating TiO_2 with polypyrrole changed the conductivity of the suspended particles from semiconducting in native anatase to conducting in the photoelectrochemically grown composite, but comparable conductivities were observed in films produced with or without added electrolyte (Table I). Iodine doping did not further improve the conductivity of the composites.

The rate of photoelectrochemical polymer deposition, however, was dependent on electrolyte. Elemental analysis of these composities (Table II) confirmed that the heaviest coating, for a constant irradiation period, was produced in a BF_4^--containing solution. Doping levels obtained in this photoelectrochemical polymerization were obtained by normalizing this data to reflect the composition of the polymer alone.

Morphology. A. Electrochemically produced films: The morphologies of the variously prepared polypyrrole films were examined by scanning electron microscopy (SEM). Film morphology depended on the identity of the dopant anion: the smoothest films (at 1000× magnification) with the highest conductivities were produced in the presence of tosylate. The electrolyte cation had no appreciable effect on the morphology of the electrochemically produced films, in parallel to the observations in the conductivity study. Only with a drastic change in the cation (TEA^+ to Li^+) was an appreciable change in morphology obtained.

B. Photoelectrochemically produced films: A SEM study of the composite TiO_2–polypyrroles revealed complete surface coverage of the metal oxide. The poor quality of images obtained even at 10000× magnification, however, made further SEM description difficult. Loosening by the electron beam of the particulate composite mounted on the viewing platform made it virtually impossible to focus the microscope for the time needed for imaging of smaller features. Nonetheless, it is clear that no morphological similarities could be seen between the photochemically and electrochemically produced polypyrroles. That is, much less porous films were formed via photoelectrochemical deposition.

Thermal Stability. A. Electrochemically produced films: Thermal gravimetric analysis (TGA) was used to correlate thermal stability to dopant anion and to provide insight into the interconnections between thermal stability, conductivity, and morphology. Plots of both the thermal

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profile itself and its first derivative were reproducible within 3% for samples prepared months apart. Each polypyrrole anion pair exhibited a distinctive TGA profile with a characteristic inflection point and weight loss, Table III.[25,26]

B. Photoelectrochemically produced films: TGA profiles of the TiO_2/polypyrrole composites showed different weight losses and TGA infection points (Table IV). Elemental analysis showed that the polymer had incorporated dopant anion, but substantial shifts in the infection points for the photoelectrochemically generated composites indicate quite different structural stability, as was implied as well by the SEM imaging.

Discussion

Conductivity. Both anodic and photoelectrochemical oxidation of pyrrole led to conductive polymeric films whose physical properties were dependent on the conditions of their formation. Conductivity of the electrochemically produced films was particularly sensitive to the identity of the electrolyte, while the photoelectrochemically prepared materials were less sensitive to the dopant anion.

A. Electrolyte effects: The influence on observed conductivity of the dopant anion in electrochemically generated polymer films corresponds to the previously reported order,[25-27] but we observed a somewhat lower sensitivity to the identity of the electrolyte cation. The films produced electrochemically were well behaved and stable in our hands, despite a suggestion in the literature that conductivity is age-dependent,[31] possibly because our films were stored under vacuum after they were produced. This process most likely anneals the films to a thermodynamically static state.

B. Photoelectrochemically generated films: In contrast, the photoelectrochemically produced films appeared to be less sensitive to the presence of anions or cations, with nearly uniform conductivities being observed irrespective of the electrolyte present (Table I). Elemental analysis (Table II) indicated a low level of anion incorporation and thus lower conductivities than from the anodically generated films. Thorough washing did not dislodge the counterion, and the TGA studies (Table III) showed that the dopant anions, although found in low amounts, where indeed bound into the polymer. The observed conductivities may be ascribed to intrinsic polymer doping (by the negatively charged TiO_2 particle itself or by intimately associated anionic surface sites) or to oxygen-derived anions formed by electron trapping. The elemental analyses show sufficient production of polypyrrole (compared with intrinsic surface sites) to suggest that at least some of the latter route is likely to be involved. The lower electrolytic anion incorporation was most likely caused by the lower effective oxidative current density available during photoelectrochemical deposition, which probably also produced a smoother polymer layer. Conductivity also depends on carrier mobility, as well as doping level. The polymer produced in this composite may have increased carrier mobility as a result of the different morphology achieved in the photoelectrochemical polymerization.

The possibility that the observed conductivity changes can be completely assigned to reduced TiO_2 is unlikely. Spectral signatures clearly indicate the presence of oxidized polypyrrole on the composites. That some of the charge balance may come from reduced species (TiO_{2-x} or H_xTiO_2), however, remains a viable possibility, to augment doping effects by reduced oxides or incorporated counterions.

The presence of dopant anions during the photodeposition of the film did, however, improve the yield of the polymer, presumably by varying the ionic strength and hence the surface charge of the photocatalytically active surface. The decreased yield observed for polymerization in the presence of tosylate did not arise from competitive light absorption by that anion (λ_{max} = 215 nm). Apparently, the photoelectrochemical deposition alters the preference for anion incorporation observed in anodic polymerization.

The insensitivity of the photocatalytically produced composites to iodine doping was surprising, for such doping usually improves the conductivity of polypyrrole films by 1–2 orders of magnitude.[3] Thus, the morphologically smooth, photoelectrochemically produced polymer, which is self-doped during formation, differs significantly from electrochemically produced films.

Morphology. A. Electrochemically generated films: The morphology of the various anodically prepared polypyrrole films depends on the identity of the dopant anion: the smoothest films with the highest conductivities were produced in the presence of tosylate. The observed oxidation level of the polymer was proportional to the obtained conductivities and the level of counterion incorporation.[25,26]

B. Photoelectrochemically generated films: Experimental difficulties with the polypyrrole-coated TiO_2 samples made defining specific morphological features of the composites problematic, but clearly the electrolyte-dependent morphological features that were obvious in the electrochemically generated samples were absent in the photoelectrochemical films. This is also consistent with the conductivity measurements that showed a lower level of electrolyte incorporation, which might have produced the anodic structural changes. Furthermore, the semiconductor surface appeared to be completely covered, with no residual surface domains exposed.

Thermal Stability. A. Electrochemically generated films: Polymer stability is sensitive to the included counterion,[25,26] Table III. From the observed weight loss profiles, a decomposition scheme for these polymers could be proposed in which the polymers lose their dopant anion and nitrogen atoms upon pyrolysis. For PPyTs and $PPyClO_4$, this would result in weight losses of approximately 45% and 60%, respectively, i.e., the percent residual carbon for each polymer based on known doping levels. The TGA weight loss values for these two polymers were very close to the predicted values. For $PPyPF_6$ and $PPyBF_4$, however, the observed weight losses were much lower than expected, with pyrolysis inducing about a 30% instead of the expected 50% weight loss. Therefore, these polymers follow a decomposition path differing from that of PPyTs and $PPyClO_4$. Similarly, PpyTs and $PPyClO_4$ films showed relatively sharp transitions in their TGA profiles, while $PPyBF_4$ and $PPyPF_6$ films, showed gradual, but continual, weight loss throughout the temperature range tested.

The weight losses for each of these polymers were too great and the residual carbonaceous material too fragile to be used for ceramic applications.

B. Photoelectrochemically generated films: The photoelectrochemically produced polymers were much less stable than electrochemically prepared polypyrroles (Table IV). This instability probably derives both from the different structure of the photoelectrochemically generated

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films and from their dispersion on the surface of TiO_2, a catalyst known to be thermally and photochemically reactive with adsorbed, oxidizable organic substrates.[5] The larger fractional weight loss associated with the thermal decomposition of the polymers in this composite indicates that the decomposition pathway proposed for anodic PPyTs and $PPyClO_4$ (loss of anions and nitrogen to form residual activated carbon films) does not apply to the photoelectrochemically generated films, where further decomposition of the carbonaceous film proceeds. However, the relative order of thermal stability of the photoelectrochemically generated composites mirrored that in the anodic films, with $PPyBF_4$ being more stable than PPyTs.

Conclusions

The conductivity, morphology, and thermal stability of electrochemically generated polypyrrole films were predictable, reproducible, and dependent on the electrolyte in the presence of which they were produced. Although these properties could be altered by either the cation or anion, greater sensitivity to the dopant anion was observed. An interdependence of conductivity and morphology was clear: polypyrrole with the smoothest morphology (at 1000× magnification) had the highest conductivity. Thermal stability and conductivity were independent, although both of these properties showed some dependence on morphology.

Polypyrrole could be produced in a conducting form by photoelectrochemical deposition on TiO_2. The physical properties of resulting polymer composites differed significantly from those of the anodically grown polymers. The presence of dopant anions during the photoelectrochemical polymerization influenced the yield of polymer but not its conductivity or morphology. The polymeric film in the resulting composite was smoother, more uniform, and less thermally stable than the electrochemically generated films. Neither technique appears applicable for the synthesis of polypyrrole films that can be thermally decomposed to highly crystalline carbon fibers.

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Pyrolysis Chemistry of an Organometallic Precursor to Silicon Carbide

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The cross-linking reactions and decomposition of a vinylic polysilane precursor to silicon carbide were systematically investigated in the course of thermolysis to 1000 °C in N_2. The polymer-to-ceramic conversion chemistry was studied by means of thermogravimetry, infrared spectroscopy, solid-state NMR spectroscopy (^{1}H CRAMPS; ^{13}C and ^{29}Si magic-angle spinning), X-ray powder diffraction, and elemental analysis of isolated solid intermediates. Gaseous byproducts were analyzed by gas chromatography, mass spectrometry, and infrared spectroscopy. The polymer primarily undergoes cross-linking through the vinyl groups below 300 °C, although there is evidence for some hydrosilylation. Decomposition reactions consist of chain scission, with production of radical species, and methylene insertion, which converts the polysilane backbone to polycarbosilane. Crystallization to carbon-rich β-SiC ceramic occurs above 750 °C.

Introduction

Silicon carbide is an advanced ceramic material with high thermal and chemical stability, low density, high mechanical strength and hardness, and high thermal conductivity. SiC is also a high-temperature semiconductor. These attributes combine to make SiC attractive for use as fiber and matrix materials in advanced composites, oxidation resistant coatings, mechanical abrasives, furnace elements, and electronic components.[1-3]

Several researchers have prepared SiC-containing ceramics by the thermal decomposition of organosilicon polymeric precursors.[4-9] Such precursors offer potential

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