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Conducting Polymer Growth in Porous Sol−Gel Thin Films: Formation of Nanoelectrode Arrays and Mediated Electron Transfer to Sequestered Macromolecules

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We show the templated electrochemical growth of poly(3,4-ethylenedioxythiophene) (PEDOT) into porous sol−gel (PSG) films [50:50 tetraethyl orthosilicate/methyltriethoxysilane (TEOS/MTES)] on indium−tin oxide (ITO) substrates and PEDOT-mediated electron transfer to ferrocene-modified dendrimers encapsulated within these sol−gel matrices. We first describe conditions needed to optimize PEDOT electropolymerization within the porous sol−gel (PSG) films such that barely emergent PEDOT features, ca. 100 nm in diameter, protrude from a PSG thin film surface, functioning as an array of ultramicroelectrodes in diffusion controlled oxidation/reduction reactions of solution probe molecules. We next describe the incorporation of fourth-generation PAMAM dendrimers into these PSG films after (a) conjugation with ferrocenecarboxylic acid (Fc-COOH) to form Fc−PAMAM, (b) conjugation with both Fc-COOH and 3-thiopheneacetic acid (3TAA), or (c) conjugation with both Fc-COOH and 3,4-ethylenedioxythiophenemethanol (2,3-dihydrothieno[3,4-*b*]-1,4-dioxyn-2-yl or EDTM). Oxidation/reduction of the encapsulated Fc−PAMAM units could be voltammetrically detected after PEDOT growth into the sol−gel film, but with different efficiency, depending upon the composition of the encapsulated dendrimer. Background corrected cyclic voltammograms showed that ca. 0.9% of the ferrocene groups became electrochemically active when Fc−PAMAM alone was incorporated into the PSG film. Up to ca. 20% of these Fc−PAMAM units became electrochemically active, with high rates of electron transfer, when EDTM was conjugated to the Fc−PAMAM dendrimer and when the EDOT monomer was codoped into the sol−gel film. These results argue for the direct, facile electrochemical communication of encapsulated Fc,EDTM−PAMAM units to the ITO substrate via the electrochemically grown PEDOT "wires," especially when the conducting polymer and the Fc units are held in close proximity on the dendrimer. This is a new approach to control of the redox chemistry of macromolecules encapsulated in inert porous matrices.

Introduction

Sol−gel-based thin film materials are seeing increasing importance as transducer layers for various optically based chemical sensors and biosensors, owing to the wide variability in properties obtainable by simple modification of the sol−gel composition and by the ease of incorporation of a wide range of macromolecular systems.[1−13] It is well-known that sol−gels based on combinations of either tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) and a chain-termination agent, such as methyltriethoxysilane (MTES), can be engineered to form porous thin films, in which various macromolecules, large biomolecules, etc., can be entrapped.[1−17] Many of these porous sol−gel (PSG) derived transducer layers are used on top of waveguide platforms which provide for substantial enhancements in sensitivity using absorbance and/or fluorescence modes of detection.[1−13,18−21] One can also introduce electroactive coatings to the waveguide platform, such as indium−tin

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oxide (ITO), adding electrochemical modes of detection and the prospect for enhanced selectivity of sensor response.[22−31]

There is substantial interest in adding electrochemical activity to the PSG thin film itself, and the electrochemical applications of sol−gel-based materials have been the topic of several review articles[2,17,32,33] with particular emphasis on the encapsulation of biological materials for chemical and biochemical sensors and catalysts. Electronically conductive materials are, of course, available from sol−gel precursors; however, there are only a few examples where electronic activity has been introduced into an otherwise insulating (e.g. silica-based) sol−gel material.[34−36] Conducting polymers have been added to PSG matrices by two different approaches, yielding electronically active materials with "molecular wires" of the conducting polymer interpenetrating the glass thin film: (i) the polymer is doped directly into the sol before gelation or film casting,[37−39] yielding thin PSG films with high transparency and conductivities ranging from 0.8 S/cm for polyaniline-doped films[37] to 200 S/cm for films containing poly(3,4-ethylenedioxythiophene);[38] (ii) the conducting polymer is incorporated into a thin sol−gel film through a "diffuse and polymerize" scheme in which the planar supported sol−gel film is soaked in a solution of monomer, allowing it to penetrate and diffuse throughout the porous structure;[40−44] electrochemical polymerization[40−42,44] or chemical polymerization[43] is then used to grow the conductive polymer within the sol−gel. The first reported use of this approach involved the electrochemical growth of polyaniline within a PSG film deposited on an underlying ITO electrode.[42] Similar studies have been performed with pyrrole[41] and thiophene[44] derivatives to yield hybrid inorganic−organic composites on electrode surfaces. Other materials have been made by chemically polymerizing aniline or pyrrole within porous glass.[43] In addition to many of the above referenced studies, the ability of conducting polymers to undergo charge transfer with enzymes and biomolecules has been extensively characterized.[45−49] There is interest, however, in further optimization of mediation of electron transfer by conducting polymers and sol−gel encapsulated redox-active molecules, especially to demonstrate vectoral electron transport over substantial PSG film thicknesses.

We report here the characterization of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) grown in porous 50:50 TEOS/MTES sol−gel thin films with specific attention paid to polymer loading and electroactivity. For these studies we primarily used the "diffuse and polymerize" scheme of polymer growth, although monomer doping of the sol was also used to enhance polymer growth. The first stage of these studies demonstrates that conductive polymer "wires" can be grown to high density in a ca. 300 nm thick PSG film over ITO substrates and that emergent conducting polymer wires (ca. 100 nm diameter) act as an ultramicroelectrode array to solution redox probes.

Fourth-generation PAMAM dendrimers, conjugated with ferrocenecarboxylic acid (Fc-COOH) to form Fc−PAMAM, were next incorporated into these PSG films, to explore redox mediation by electropolymerized PEDOT wires. Initial results showed that electrochemical communication between encapsulated Fc−PAMAM and PEDOT was obtained as the electropolymerization process loaded the PSG films with PEDOT wires. A much higher fraction of Fc−PAMAM centers became electroactive within this environment when the Fc−PAMAM was first conjugated with an EDOT monomer (2,3-dihydrothieno[3,4-*b*]-1,4-dioxyn-2-yl, otherwise known as 3,4-ethylenedioxythiophemethanol, EDTM). This conjugation provides for sites for the growing PEDOT chain to directly link to many of the Fc−PAMAM dendrimers, providing for direct electrochemical communication of these macromolecules with the ITO substrate.

Experimental Section

Modified PAMAM Dendrimers. Generation 4 PAMAM dendrimer (Aldrich, 10% in methanol) was labeled with ferrocenecarboxylic acid (Aldrich, 97%), 3-thiopheneacetic acid (Aldrich, ≥98%), or EDTM. EDTM was synthesized in the Molecular Synthesis Facility at the University of Arizona according to previously published procedures.[50] Linkages were made using *N*,*N*′-dicyclohexylcarbodiimide (DCC) (Aldrich, 99%) or

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1,1′-carbonyldiimidazole (CDI) (Aldrich) as the coupling agent in solvents that were dried over Na_2SO_4 (anhydrous) or molecular sieves. Activation of the label molecules by DCC took place in ethanol or dimethyl sulfoxide solution by mixing the components in an equimolar ratio and reacting at room temperature for 1 h. In a separate vial, the methanol in the PAMAM solution was evaporated under a stream of nitrogen and replaced with ethanol or dimethyl sulfoxide. The PAMAM solution was then added to the activated label solution in a 5:1 label:PAMAM ratio and allowed to react at room temperature overnight.

The reaction mixture was then quenched with an excess of water to precipitate the unreacted materials and insoluble products. The solids were separated by centrifugation at 10 000 rpm for 20 min. The supernatant was removed, mildly acidified with hydrochloric acid, and placed in a separatory funnel with diethyl ether. Ether extractions were continued until the ether layer appeared colorless, signifying the removal of unreacted ferrocenecarboxylic acid. Further purification, concentration, and solvent exchange of the labeled dendrimer was carried out in an Amicon model 8050 stirred ultrafiltration cell with a YM3 (3000 MW cutoff) filter under nitrogen pressure.

Mass spectroscopic data of the labeled PAMAM dendrimer in a dithranol MALDI matrix indicate an approximate labeling ratio of 5:1 label:dendrimer for the ferrocenylated product (Fc−PAMAM) and a 5:5:1 ratio for PAMAM conjugates containing both Fc and 3TAA (Fc,3TAA−PAMAM) and the ferrocenylated/EDTM product (Fc,EDTM−PAMAM). To avoid complications due to the changing molar absorptivity of ferrocene upon linkage to the dendrimer, solution concentrations of bound ferrocene were measured by atomic absorption (AA) spectroscopy. Measurements were performed on a TJA UNICAM 969 AA spectrometer at 248.3 nm using an air/acetylene flame. Quantitation of the ferrocenyl iron was performed against a standard curve of ferrocenecarboxylic acid.

Substrate and Sol−Gel Preparation. Indium tin oxide (ITO) substrates were obtained from Colorado Concept Coatings with a resistivity of ∼16 Ω per square and root-mean-square surface roughness of ca. 2.5 nm. Substrates were cleaned by first lightly scrubbing with Alconox cleaner on a cotton pad and then rinsing with deionized water (18 MΩ·cm Barnstead/Thermolyne Nanopure). Substrates were then blown dry with nitrogen and cleaned in an air plasma (Harrick PDC-3XG) for 15 min at 15 W. Substrates were used immediately upon removal from the plasma cleaner.

Sol−gel thin films and monoliths were made from a precursor sol formulation consisting of 500 μL of tetraethyl orthosilicate (TEOS) (Aldrich, 99.999%), 500 μL of methyltriethoxysilane (MTES) (Aldrich, 99%), 300 μL of ethanol, 311 μL of deionized water, and 12 μL of 0.25 M HCl as catalyst. EDOT-doped precursor sol contained 0.14 M EDOT. Solutions were vigorously stirred at room temperature for 4 h to yield the precursor sol, which was used within 4 h of preparation to ensure desired properties. For bulk monoliths, the solution was added to a glass vial, capped, and allowed to gel and cure at room temperature for several months.

Optimized thin film doping and film casting was carried out by mixing the precursor sol in a 1:1 volume ratio with a buffer solution (0.1 M pH 7 TRIS) containing the labeled PAMAM dendrimer (6.0, 6.5, and 4.2 mM ferrocene for Fc−PAMAM, Fc,3TAA−PAMAM, and Fc,EDTM−PAMAM, respectively). Films were cast immediately after mixing by pipetting 200 μL of the doped sol−gel solution onto an ITO substrate and spin casting at 3000 rpm for 1 min in 10% humidity. Films were allowed to cure at room temperature and humidity (∼20%) for approximately 48 h prior to electrochemical characterization. Bulk sol−gels of the above formulation typically exhibit 80% shrinkage in volume upon drying. For thin films, this degree of shrinkage was assumed in order to estimate analyte concentrations within the films. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies have shown that this procedure yields films 200−300 nm thick with a 0.3 nm root-mean-square surface roughness.

AFM measurements were performed in tapping mode on a Digital Instruments Multimode III instrument. Tapping mode etched silicon probes (TESP) were purchased from Digital Instruments and tuned between 300 and 400 kHz. SEM measurements were performed in the University of Arizona Department of Materials Science and Engineering on a Hitachi S-4500/Thermo-Noran field-emission SEM for digital imaging/EDS equipped with a cold field emission electron gun. Images were acquired with an accelerating voltage of 4.0 kV and 150 000× magnification. AFM and SEM images were acquired at several locations on each sample, and the images shown here represent the typical characteristics of each sample.

Electrochemical Studies. All measurements were performed using an EG&G 263A potentiostat. The electrochemical cell consisted of a Ag/AgCl reference electrode (Bioanalytical Systems) and a platinum wire counter electrode (Aldrich, 99.99%) in a 2.5 mL Teflon cell. All stated potential values are relative to the Ag/AgCl electrode. The ITO surface served as the working electrode with an exposed surface area of 0.5 cm^2. Contact was made with the ITO through a brass foil contact. Electropolymerization of 3,4-ethylenedioxythiophene (EDOT) was performed in an aqueous solution containing 10 mM EDOT, 10% (v/v) methanol, and 0.1 M $LiClO_4$. Unless otherwise stated, before electropolymerization, sol−gel films were equilibrated for 5 min at open circuit potential to allow the EDOT monomer to diffuse throughout the film. Stepped-potential electropolymerizations were performed by equilibrating the electrode at +0.6 V for 15 s, followed by a step to +1.15 V and holding for 10 s. Cyclic voltammetric data was obtained in 0.1 M $LiClO_4$ (aq) in the absence of EDOT monomer. Cyclic voltammograms were background-corrected by subtraction of the baseline estimated from the capacitive background current. Unless otherwise stated, cyclic voltammograms were obtained at 10 mV/s utilizing a built-in 5.3 Hz I/E filter.

The amount of polymer loading, defined as the molar concentration of EDOT monomer units polymerized in the film, was determined by integration of the charge passed during electropolymerization, assuming 2.3 electrons transferred for each EDOT unit.[51] The polymer loading was found to be highly variable and dependent on the exact sol−gel curing conditions. At high relative humidity (>50%) or longer curing times (>1 week), polymer loading by electropolymerization was almost undetectable. At low relative humidity (<10%) or short curing times (<24 h), the degree of polymer loading could be extremely high, such that the background capacitive current of PEDOT itself overwhelmed the voltammetric signal of the encapsulated Fc−PAMAM units. Optimal sensing of the electrochemical activity of the encapsulated Fc−PAMAM dendrimers was achieved with the curing conditions noted above, and these optimized films exhibited an effective concentration for PEDOT loading between 0.03 and 0.10 M.

Results and Discussion

Electrochemical Growth of Emergent PEDOT Features through Porous Sol−Gel Films. Figure 1 shows a schematic view of the progress of conductive polymer growth from the ITO/PSG interface outward toward the solution, along with the estimated loading of PEDOT within the PSG film

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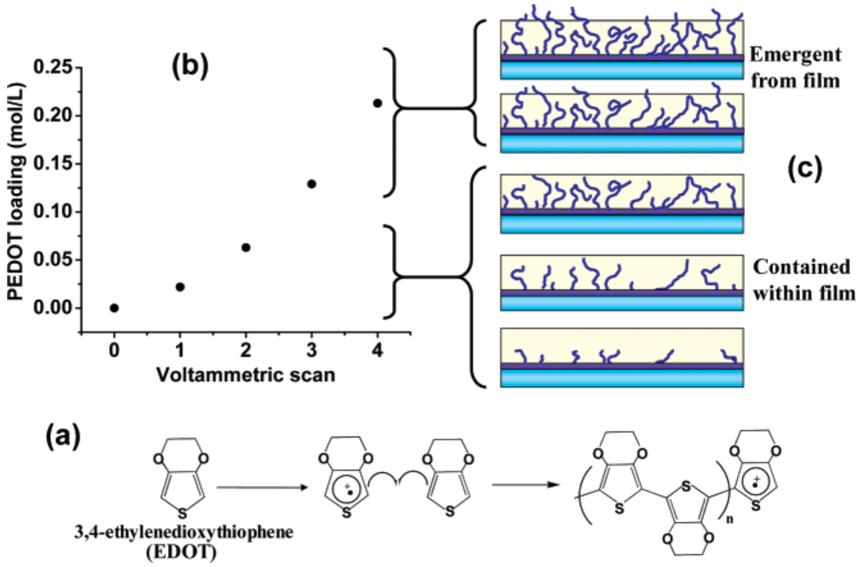

Figure 1. Overview of the formation of PEDOT wires and cables encapsulated in porous sol−gel (PSG) films on ITO. (a) Schematic view of the PEDOT electropolymerization process. (b) Estimated loading of PEDOT in the PSG film as a function of the number of voltammetric scans used to form these encapsulated conducting polymer chains. The loading was estimated from a coulometric analysis of these voltammetric scans; comparable results were obtained when potential step electropolymerization conditions were used. (c) Schematic view of the PEDOT wires and cables growing up from the ITO substrate, emerging finally to form nanoelectrode and microelectrode arrays (see Figures 2 and 3).

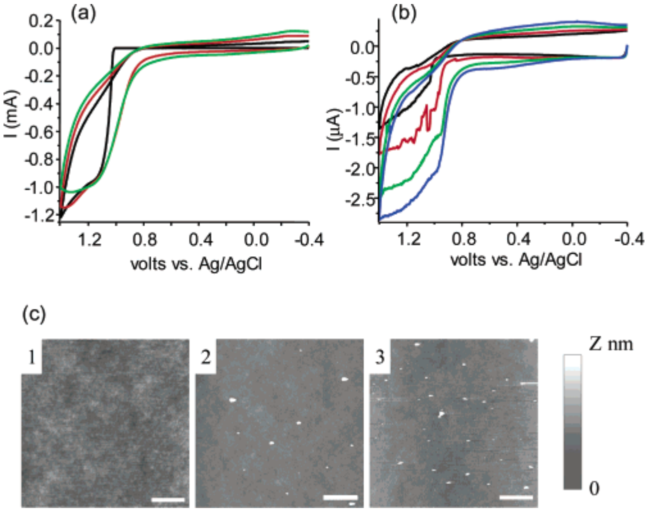

Figure 2. Voltammograms for the growth of PEDOT on (a) bare ITO and (b) ITO with a ca. 300 nm TEOS/MTES PSG film; (c) AFM images of the PSG prior to any PEDOT growth (image 1) and the PSG film after four and five electropolymerization scans (images 2 and 3, respectively) to produce emergent PEDOT features. The vertical (*Z*) scale bar in image 1 is 2.5 nm; for images 2 and 3, *Z* = 40 nm. The *X*,*Y* scale bar in each image is 1 *μ*m.

(estimated coulometrically from the data in Figure 2), as a function of the number of voltammetric scans used to drive electropolymerization. Parts a and b of Figure 2 show the voltammetric responses of a bare ITO electrode and a PSG-coated ITO electrode, respectively, in contact with 0.010 M EDOT/10% MeOH/H_2O solutions. The first voltammetric scan shows an onset potential for the initiation of PEDOT growth of ca. +1.1 V vs Ag/AgCl. On the second and subsequent scans the onset potential for oxidative electropolymerization is decreased by ca. 0.5 V and the reversible oxidation/reduction of PEDOT is then seen growing in size in the voltage window from 0.00 to +0.50 V vs Ag/AgCl.[52] At the bare ITO electrode each voltammetric scan deposits approximately equivalent amounts of PEDOT, whereas increasing amounts of PEDOT are deposited with each scan at the PSG-coated ITO electrode. The decrease in current density for electropolymerization of PEDOT on TEOS/MTES sol−gel coated ITO substrates is dramatic, with maximum current densities reduced by a factor of ca. 400 times for the PSG-coated versus bare ITO electrodes; the qualitative current/voltage responses, however, are the same as seen on the bare ITO electrodes.

Figure 2c shows a series of AFM images of (left) a ca. 300 nm PSG thin film deposited on ITO prior to any polymer growth and (middle; right) PSG-coated ITO electrodes with differing extents of electropolymerization of PEDOT. The bare ITO surface initially shows an rms roughness of 2.5 nm versus 0.3 nm for the PSG coating, which allows the emergent PEDOT features to be easily detected. After the fourth voltammetric electropolymerization scan in Figure 2b (a total charge passed of ca. 275 $\mu C \cdot cm^{-2}$), emergent PEDOT features were observed, 73 ± 23 nm in apparent diameter, ranging in height from 3 to 35 nm. After an additional voltammetric scan (total charge passed of ca. 450 $\mu C \cdot cm^{-2}$), additional similarly sized emergent PEDOT features were observed, with total PEDOT feature densities from 5×10^8 to $2 \times 10^9/cm^2$, constituting a total area change from approximately 0.1−0.2 μm^2. After extensive electropolymerization, the electrochemical behavior of the films displayed diffusion-controlled peaks due to PEDOT formation, similar to that for a PEDOT film grown over bare ITO. This suggests that the PEDOT features converged, forming an electroactive, continuous PEDOT film over the entire surface.

Figure 3 shows an SEM cross-sectional image of two emergent PEDOT features (b and c) of ca. 120 nm height and ca. 100 nm diameter, from a carefully fractured ITO/PSG electrode in which PEDOT had been grown, similar to the conditions used in Figure 2. Note that column

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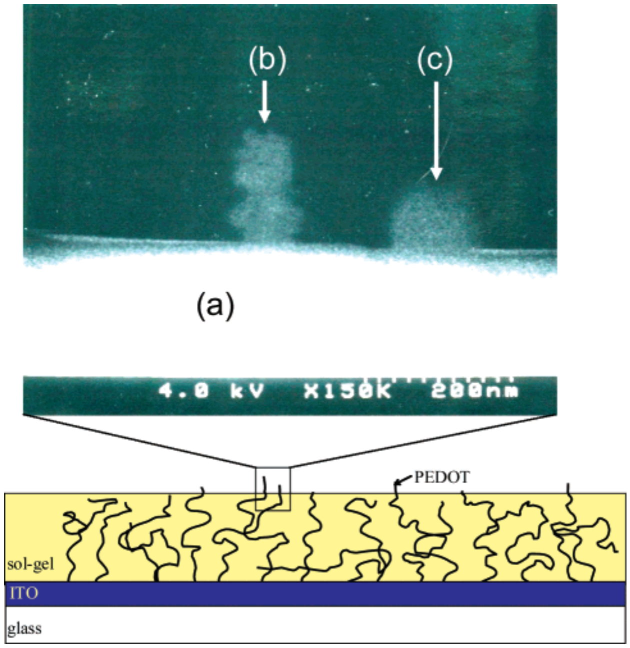

Figure 3. SEM images of two emergent PEDOT chains (b and c) from the PSG film (a). The electron beam focus and image focus conditions were optimized at a higher magnification and then the image above was acquired at this magnification. Some damage appeared to occur to chain b versus chain c. The average diameter of both chains appears to be ca. 100 nm, but the initial SEM images suggest a smaller diameter and less roughening than seen in the PEDOT features here.

b is significantly roughened in contrast with column c. In initial higher resolution SEM images this column was less structured, but during the course of image optimization, at higher magnification, some thermal degradation of this feature apparently resulted. Once SEM optimization was achieved, a lower resolution image was obtained; however, these PEDOT features quickly changed in appearance with continued exposure to the electron beam.

These PEDOT features display excellent electrochemical contact with the ITO surface and exhibit voltammetric behavior characteristic of ultramicroelectrode arrays. Figure 4a shows the background-subtracted cyclic voltammetry of such a PEDOT-modified PSG/ITO electrode in response to oxidation/reduction of solutions of ferrocenylated PAMAM dendrimer (Fc−PAMAM), shown schematically in Figure 4b. This ferrocene-modified dendrimer is too large to enter the pores in the sol−gel[1] and shows no voltammetric response of the Fc/Fc$^+$ redox couple prior to the growth of PEDOT in the film, confirming that the 50:50 TEOS/MTES films are free of pinholes, which would support diffusion controlled electrochemistry. After PEDOT growth the oxidation and reduction of PAMAM-bound ferrocene could be seen as sigmoidal curves with distinct current plateaus. This shows that the PEDOT is behaving as a “molecular wire” through 300 nm of insulating sol−gel film, with the emergent columnar structures behaving as an array of nanoelectrodes. The sigmoidal response and steady-state current are characteristic of hemispherical diffusion processes and indicate that each electrode behaves independently in this array with nonoverlapping diffusion zones.[53] Furthermore, the current plateau height increases with consecutive polymerization steps, due to the increase in the number of emergent columnar structures (shown in Figures 2c and 3) and the resulting increase in overall electrode area. On the basis of the changes in plateau height, the electroactive area increases approximately 27% between the second and third polymerization steps and another 37% between the third and the fourth steps.

Variable scan rate cyclic voltammetry was used to further characterize the electrochemical response of the PEDOT nanoelectrode arrays. The scan rate dependence was evaluated against a solution of 0.027 M potassium ferricyanide. The use of a small molecule (as opposed to Fc−PAMAM) as the electrochemical probe decreases the influence of slow molecular diffusion on the measurements, while the negatively charged ion is prevented from penetrating the sol−gel by ionic repulsion with surface hydroxyls in the film.[54] At slow scan rates (10 mV/s, Figure 4c) the voltammograms again display diffusion-limited current plateaus with no discernible voltammetric peaks.[53] As the scan rate is increased, several changes in the voltammograms are observed. The non-Faradaic background increases linearly with scan rate as expected for a charged conductive polymer layer.[55−59] However, the magnitude of the steady-state current plateau from the Faradaic component, measured from baseline, remains independent of scan rate, as expected for voltammetry at ultramicro- or nanoelectrodes.[60] At higher scan rates, the plateaus become noticeably more peak-shaped with a broad anodic peak at 350 mV, suggesting the onset of linear diffusion voltammetry, resulting from the overlap of the hemispherical diffusion zones.[53]

Mediated Redox Processes for Encapsulated Fc−PAMAM and Fc,3TAA−PAMAM Dendrimers. A series of TEOS/MTES PSG films were next doped with Fc−PAMAM dendrimers or Fc−PAMAM dendrimers previously modified with either 3TAA or EDTM, to demonstrate that PEDOT wires in the PSG film could electrochemically communicate between the ITO substrate and an entrapped macromolecule. When added directly to the sol solution, modified dendrimers of this size are effectively immobilized within the pores of the sol−gel and do not leach from the dried film.[1] For the voltammetric responses shown below, PEDOT was electropolymerized through the PSG film; between each electropolymerization step the voltammetric response was characterized at a sweep rate of 10 mV·s^{-1}.

Figure 5a (scan 1) shows a single voltammogram without background subtraction, and Figure 5b shows background-subtracted voltammograms acquired before and after a total of zero, one, three, and five electropolymerization steps (intermediate voltammograms have been removed for clarity), for a PSG film doped with Fc−PAMAM and immersed

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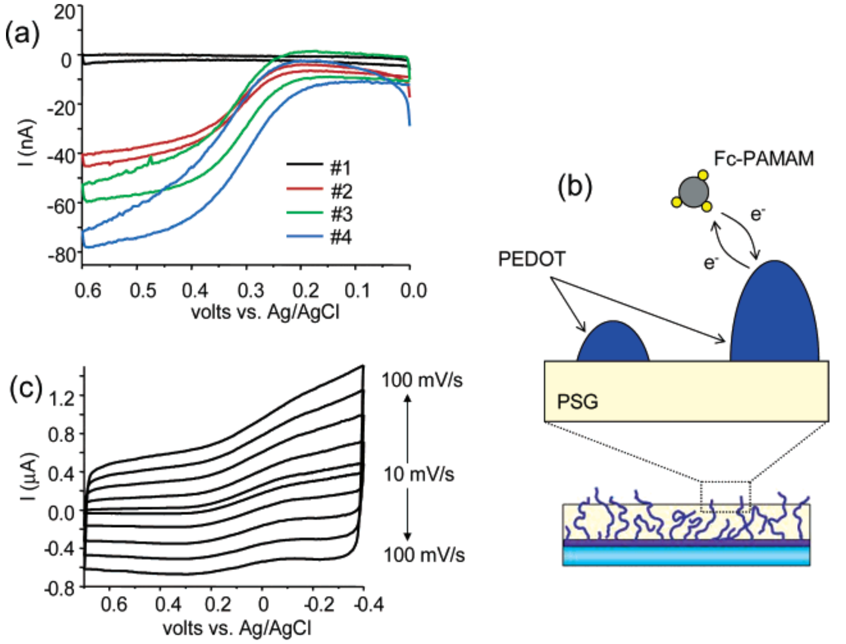

Figure 4. (a) A series of 10 mV/s voltammograms of a PSG-coated ITO electrode in electrolyte with 3.4 mM Fc−PAMAM dendrimer, which is too large to permeate the PSG film (schematically shown in (b)). Voltammogram 1 shows the response prior to PEDOT electropolymerization in the PSG film; voltammograms 2−4 show the voltammetic oxidation/reduction of solution Fc−PAMAM at the "nanoelectrode arrays" formed by the emergent PEDOT features, as described in Figures 2 and 3, as more PEDOT is grown in the PSG. (c) Voltammograms as a function of sweep rate for reduction/oxidation of 0.027 M ferricyanide at the same electrode after final formation of emergent PEDOT wires. In the absence of emergent PEDOT, the voltammetric response was negligible, since ferricyanide does not permeate the sol−gel films due to electrostatic repulsion with surface hydroxyl groups in the sol−gel film.[54]

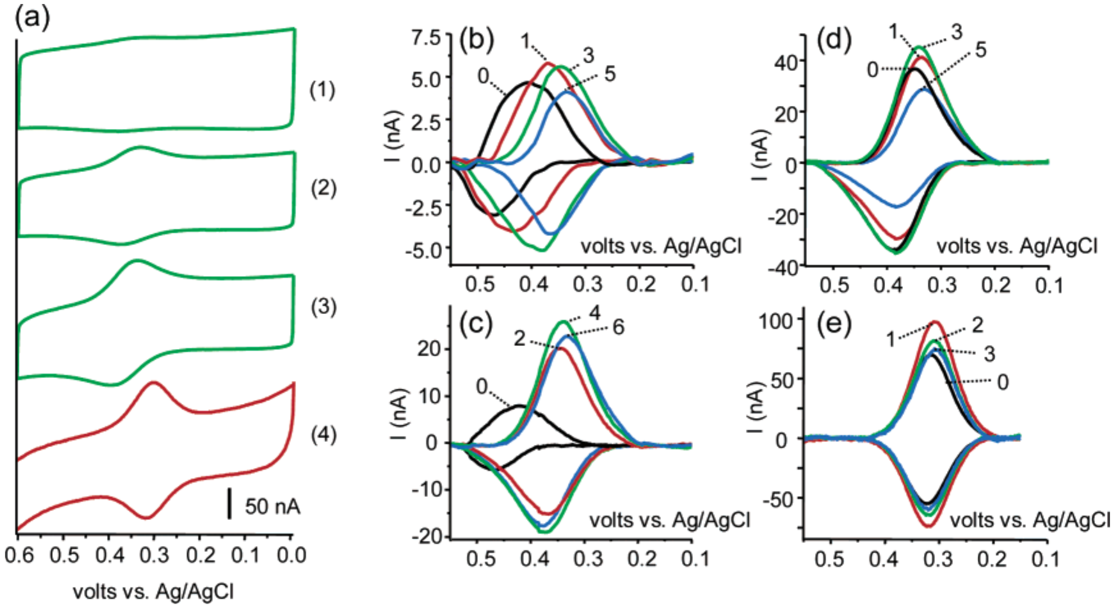

Figure 5. (a) Voltammetric responses (without background correction), at maximum efficiency, of ca. 300 nm PSG films on ITO with entrapped Fc−PAMAM dendrimers. (b−e) Background-corrected voltammetric scans for the same samples. The numbers in b−e correspond to the number of voltammetric steps performed while the film was soaked in 0.01 M EDOT solution. Scan 1 in part a corresponds to scan 3 in part b (the voltammetric response of the PSG/ITO film with only entrapped Fc−PAMAM). As PEDOT is grown through the PSG film, the voltammetric response improves, but the fraction of electroactive ferrocene units was only ca. 0.9%. Scan 2 in part a corresponds to scan 4 in part c (the PSG/ITO film with entrapped Fc,3TAA-PAMAM). The fraction of electroactive ferrocene increased to ca. 4% of available ferrocene. Scan 3 in part a corresponds to scan 3 in part d (a PSG/ITO film with entrapped Fc,3TAA-PAMAM and entrapped EDOT, both added during the gelation process). The percentage of electroactive ferrocene units increased to ca. 7%. Scan 4 in part a corresponds to scan 1 in part e (Fc,EDTM−PAMAM dendrimers were entrapped in PSG/ITO films, along with EDOT). The voltammetic activity indicates greatly enhanced rates of electron transfer to the entrapped ferrocene units, with up to ca. 20% of these units in electrochemical contact with the ITO substrate.

in a 0.01 M solution of EDOT. Before any PEDOT had been grown through the film (Figure 5b, scan 0), some voltammetric activity could be seen for encapsulated Fc−PAMAM (corresponding to ca. 0.2 μC·cm^{-2} oxidative charge for the Fc/Fc^{+} redox couple), with a midpoint potential of +0.44 V and a voltammetric peak separation (ΔE_{peak}) of 0.07 V, corresponding to redox activity of Fc−PAMAM units that are apparently encapsulated within a few nanometers of the ITO electrode surface. As PEDOT was electrochemically grown through the film, the midpoint potential for the Fc−PAMAM/Fc^{+}−PAMAM redox couple decreased to +0.34 V and exhibited a smaller ΔE_{peak} of 0.02 V. The shift in midpoint potential represents an apparent change in the interface where electron transfer occurs from the bare ITO electrode to a PEDOT/ITO electrode surface. There was only a factor of 2 increase in the amount of electrochemically active ferrocene after the growth of PEDOT throughout the sol−gel matrix; the charge passed on the oxidation sweep increased to ca. 0.4 μC·cm^{-2} after the third electropolymerization step, corresponding to electron transfer to ca. 0.9% of the total amount of ferrocene units available in the film.

In the next set of experiments, 3TAA was covalently attached to Fc−PAMAM dendrimers, yielding a product containing both pendant ferrocene and thiophene groups (Fc,3TAA−PAMAM), with approximately five ferrocene and five thiophene groups per PAMAM dendrimer. FTIR studies of thick PEDOT films formed on ITO in the presence of 3TAA showed no signs of a covalent incorporation of thiopheneacetic acid into the PEDOT chains at the polymerization potentials used in these experiments. This is not surprising, since the oxidative polymerization of the thiophene parent monomer occurs at potentials positive of the potential for oxidative polymerization of EDOT.[61] Despite the lack of a covalent interaction between 3TAA and PEDOT, differences were still noted in the voltammetric response of encapsulated Fc,3TAA−PAMAM, arising from an apparently increased interaction with the growing PEDOT chains. Scan 2 in Figure 5a and the background-corrected voltammograms in Figure 5c show the responses of entrapped Fc,3TAA−PAMAM in the PSG film, after several different electropolymerization steps (+1.15 V for 10 s). The EDOT solution was removed after each electropolymerization step, replaced with electrolyte, and the cyclic voltammograms were acquired. The midpoint potential for the Fc/Fc$^+$ redox couple shifts from +0.45 to +0.34 V after several polymerization steps, with the major shift taking place after the first polymerization step. The decrease in ΔE_{peak} is relatively small, 54−48 mV after nine electropolymerization steps. The integrated charge from oxidation of the ferrocene units reaches a maximum after four polymerizations steps, corresponding to 1.7 μC·cm^{-2} or 4% of the available ferrocene monomer units, and begins to decline after the fifth polymerization step. This apparent decline in the efficiency of charge transfer with encapsulated ferrocene was observed in all systems studied and occurs at levels of polymer loading in excess of ca. 0.1 M. This level of PEDOT loading is significant in that (1) the PSG is effectively saturated with PEDOT and the columnar structures described above (Figures 2c and 3) begin to emerge from the top of the PSG/ITO film, and (2) at loading levels exceeding 0.1 M there is a sharp decline in the degree of oxidative doping of PSG-encapsulated PEDOT.[62] This decline in oxidative doping represents an overall decrease in the conductivity of the encapsulated PEDOT, resulting in the observed decline in the efficiency of charge transfer between PEDOT and the encapsulated dendrimer.

The degree of entrapped ferrocene redox activity could be further increased if EDOT was doped into the sol−gel solution, along with Fc,3TAA-PAMAM, prior to film formation (scan 3 in Figure 5a, and Figure 5d). In this case the charge passed on the oxidative wave, after PEDOT electropolymerization, increased to ca. 3.2 μC·cm^{-2}, or ca. 7% of the available ferrocene monomer units. As a control experiment to accompany the characterization of these EDOT predoped films, we attempted to determine whether there is spontaneous formation of PEDOT during the sol−gel formation process. In bulk sol−gels, doping of the precursor sol with EDOT monomer was shown to produce some PEDOT upon gelation, as evidenced by a dark green/blue coloring of the cured sol. The absorption spectrum of the CH_2Cl_2 extract from a HF digestion of a monolithic EDOT-doped sol−gel is available in the Supporting Information of this paper. A large absorbance peak was observed at 260 nm representing residual EDOT, along with absorption bands at 363, 479, 580, 732, and 851 nm, due to the presence of partially oxidized PEDOT oligomers.[63] Some PEDOT chains are therefore likely to exist in PSG films in which EDOT was incorporated before the gelation and spin-casting stages and may even play a role in templating the further growth of PEDOT wires in the dried PSG film.

Mediated Redox Processes for Encapsulated Fc,EDTM−PAMAM Dendrimers. Unlike 3TAA, the methanol-substituted EDOT monomer, EDTM, can copolymerize with EDOT at the potentials used in this experiment to form a hydroxy-substituted PEDOT.[64] EDTM was therefore conjugated to Fc−PAMAM dendrimers in order to provide a site for close interaction between pendant ferrocene groups and PEDOT, through copolymerization of pendant EDTM directly into the growing PEDOT chain. MALDI mass spectrometry indicated the presence of approximately five EDTM groups per PAMAM dendrimer. As before, the Fc,EDTM−PAMAM dendrimers were encapsulated in the spin-cast (0.14 M EDOT doped) PSG film, and PEDOT was electropolymerized using potential steps, in 0.01 M EDOT solutions. After each potential step, the electrode was placed in blank electrolyte and the voltammetric response characterized.

Scan 4 in Figure 5a and the series of scans in Figure 5e show the voltammetric response obtained for Fc,EDTM−PAMAM-doped PSG films before and after several PEDOT electropolymerization steps. The voltammetric responses of these films were dramatically improved over all previous Fc−PAMAM modified PSG films. Each background-corrected voltammogram is nearly ideal in its symmetry, and the midpoint potential (+0.31 V vs Ag/AgCl) is shifted to less positive potentials than all previous Fc−PAMAM-modified PSG/ITO films. As seen from the change in current scale in these voltammograms, there was an impressive enhancement in the fraction of Fc−PAMAM units in electrical communication with the ITO substrate. After one polymerization step the fraction of ferrocene units electrochemically communicating with the ITO substrate is nearly

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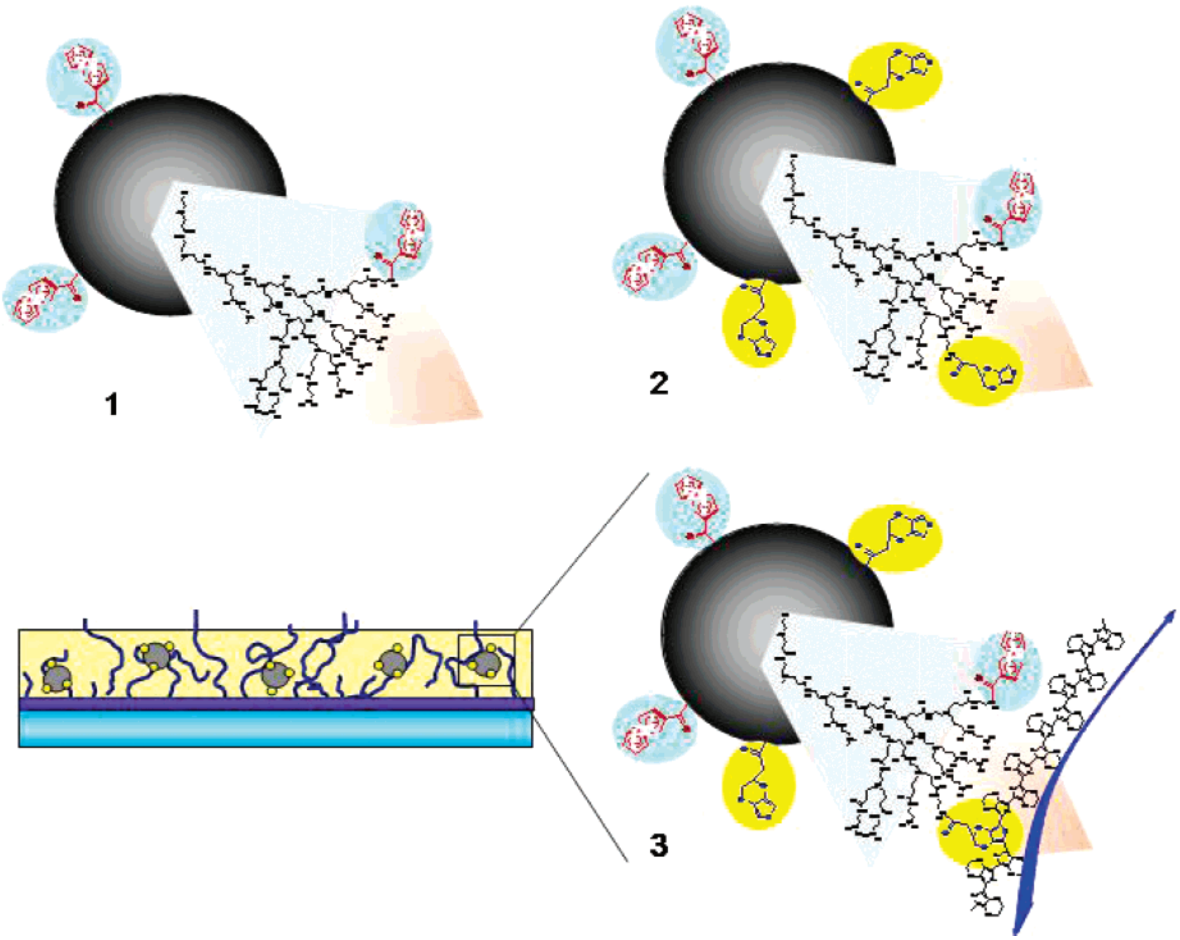

Figure 6. Schematic view of (1) the Fc−PAMAM dendrimer with three appended Fc groups, (2) Fc−PAMAM with added EDTM thiophene groups, and (3) Fc,EDTM−PAMAM with PEDOT strands able to copolymerize with the EDTM groups appended to the PAMAM dendrimer, placing the growing PEDOT strands in close proximity to the Fc groups.

20% of the available units, and the charging current (scan 4, Figure 5a) is only ca. 40% of that seen for previous PSG films. With subsequent electropolymerization steps, the number of electrochemically active Fc−PAMAM units in the PSG/ITO film decreased slightly, while the charging current (not shown) increased to nearly the same level as seen for previous PEDOT-loaded PSG films. These results suggest that the initial PEDOT electropolymerization step occurs preferentially along routes in the PSG film that are decorated with the Fc,EDTM−PAMAM dendrimers and that subsequent polymerization steps load the PSG film with additional PEDOT which is not proximate to these dendrimer units.

Electron-transfer rates at maximum electrochemical communication efficiency for the entrapped Fc units were estimated according to methodology presented by Laviron.[65] To apply this method, the following assumptions were applied: (1) the electrode surface consists of encapsulated PEDOT; (2) since maximum efficiency was observed at PEDOT saturation in the PSG film, the PEDOT concentration, and therefore the total electrode surface area, is equivalent in all films studied; (3) there is less than monolayer coverage of adsorbed PAMAM on the electroactive surface of encapsulated PEDOT; and (4) we assume a electron-transfer coefficient (α) value of 0.5. Using this approach, electron-transfer rates were ca. 1.5 s^{-1} for entrapped Fc,EDTM−PAMAM compared to 0.1−0.4 s^{-1} determined for Fc−PAMAM and Fc,3TAA−PAMAM-modified PSG/ITO films.

Figure 6 shows a schematic view of the proposed interaction of a growing PEDOT chain with a segment of the PAMAM dendrimer to which both Fc and EDTM units have been conjugated. Our electrochemical studies suggest that conjugation of sufficient EDTM monomers with Fc−PAMAM units will provide sites for direct linkage with PEDOT, especially in the earliest stages of PEDOT wire growth through the PSG matrix. PEDOT chains that grow in close proximity to the dendrimer site are expected to provide improved electron transfer rates, relative to cases where the PEDOT chain is only occasionally proximate to the bound ferrocene center. What is not yet clear, however, is the extent to which more than one ferrocene unit per PAMAM dendrimer becomes electroactive when the PEDOT chain grows, i.e., whether there is through space electron transfer between Fc units on the same dendrimer.

Conclusions

As a result of the studies shown here, and other recent electrochemical studies of PSG films,[37−44] it is clear that a wide variety of electroactive conducting polymer/glass hybrid materials can be formed, with good retention of the elec-

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trochemical activity of the entrapped macromolecule or nanoparticle. These environments are appealing for some biological molecules, whose stability and activity might be compromised by simple adsorption to an electrode surface, and show potential for the development of new photoelectrochemical materials.[66] It is clearly desirable to increase the fraction of electronically active entrapped units within the PSG film, without sacrificing the site isolation that comes from entrapping them in the PSG environment. Control of the fraction of entrapped material that can be rendered electrochemically active is strongly dependent upon modification of the macromolecule to provide for intimate contact with a conducting polymer wire. We have also recently observed that we can finely control the number of emergent conducting polymer features and then independently interrogate their electrical properties with conducting-tip AFM, suggesting a means to characterize the electronic and electrochemical properties of PSG encapsulated macromolecules and nanoparticles.[67] Future studies will focus on further characterization of the optimum concentration of redox centers on the dendrimer, the type of conducting polymer used, the number of monomer units per dendrimer, the optimum concentration of PAMAM units within the sol−gel matrix, etc., with the intent of increasing the concentration of electroactive units without sacrificing the insulating, protective features of the sol−gel environment.

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Supporting Information Available: UV−visible absorbance spectrum of CH_2Cl_2 extract from cured EDOT-doped sol−gel monoliths. This material is available free of charge via the Internet at http://pubs.acs.org.

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