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Poly(3,4-ethylenedioxythiophene) (PEDOT)-Coated Silica Spheres: Electrochemical Modulation of the Optical Properties of a Hydrogel-Stabilized Core–Shell Particle Suspension

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In situ electrochemical methods involving both oxidative and reductive mediators were employed to modify the oxidation state (doping level) of PEDOT polymers in colloidal PEDOT-coated silica core–shell particles that were prepared as a dispersion encapsulated in a hydrogel matrix. The hydrogel-stabilized PEDOT particle suspensions were prepared as thin films (several hundred micrometers thick) on an ITO electrode surface and were equilibrated with an aqueous electrolyte containing a cocktail of redox mediators prior to mounting in a transmission-mode spectroelectrochemical cell. The modifications of the redox states of the PEDOT coating induced a change in the absorbance characteristics of the hydrogel films. The coated particles exhibited a maximum absorption peak centered at 800 nm in their doped (oxidized) state that could be significantly reduced through the electrochemical de-doping (reduction) of the PEDOT-coating on the particles.

Introduction

Materials research has been actively pursuing the next generation of advanced materials through the development of colloidal crystals, with a specific aim for their use in photonic devices.^{1,2} One area of great interest is in the development of systems that undergo self-assembly to generate three-dimensional periodic dielectric structures that exhibit a photonic band gap.^{3,4} Colloidal particles dispersed in a liquid media have been found to form a three-dimensionally ordered system termed crystalline colloidal arrays.^{5,6}

Ordered colloids containing particles with a core–shell morphology have been developed to enhance the optical performance through an increase in the refractive index contrast in the system.^{7,8} Poly(3,4-ethylenedioxythiophene) (PEDOT) has been used to generate core–shell particles that could be induced to form a self-assembled crystalline colloidal array.⁹ PEDOT and its derivatives are promising

intrinsically conductive polymers because of their high stability, low band gap, high conductivity, and excellent transparency in the doped state.^{10–12}

The stabilization of colloidal arrays by encapsulation of the particles in hydrogel networks³ has furthered the use of these materials in photonic-related applications.^{13,14} When these electrostatically stabilized particles are hydrogel-encapsulated, the colloidal particles are isolated in the hydrogel networks and not in contact with the conductive support; chemical modification of the redox states of the particles must be performed by electrogenerated oxidative/reductive mediators. Mediators can diffusively shuttle electrons between the electrode and the PEDOT coating of the particles. At reductive potentials the mediator would be selectively reduced at the surface of the electrode and then diffuse to the doped PEDOT to undergo rapid electron transfer and dedope the PEDOT; it would then subsequently diffuse back to the electrode surface to be reduced again. This same process would then occur at oxidative potentials in order to redope the PEDOT. The use of mediated electron transfer systems for the development of biosensors has been extensively examined.¹⁵ Coupling the intrinsic absorbance

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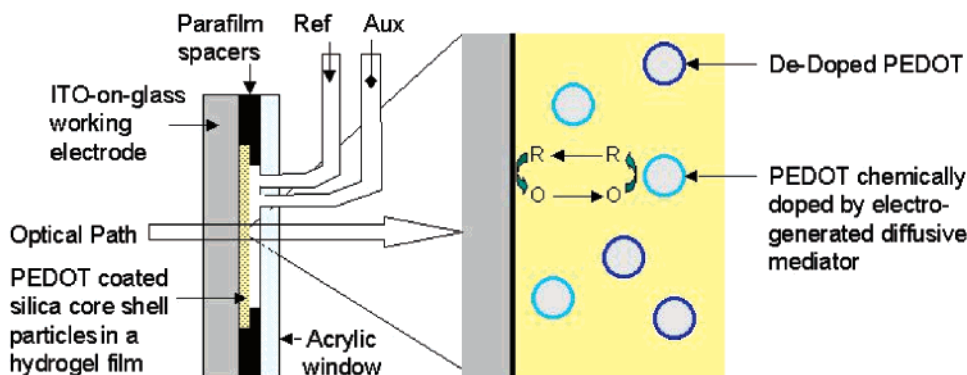


Figure 1. Schematic diagram of the spectroelectrochemical cell used in this work to monitor the electrochemical doping/dedoping of hydrogel-stabilized PEDOT-containing films. Films are initially formed atop ITO-coated-glass working electrodes that are then fitted with spacers and sealed using an acrylic window containing entry ports for the reference and auxiliary electrodes. At right is an enlarged view illustrating the mediated electrochemical doping of PEDOT in the core-shell PEDOT-coated silica particles.

changes caused by switching the oxidation states of PEDOT-coated core-shell silica particles with the Bragg diffraction of a self-assembled colloidal array could lead to interesting optical properties.

In this effort, we report on the intrinsic absorbance changes caused by switching the oxidation states of synthesized PEDOT-coated core-shell silica particles (150 nm diameter) that were suspended in a colloidal solution and subsequently locked into a hydrogel matrix. We acquired both electrochemical and spectroscopic data for the electrochemical cell developed.

Materials and Methods

Chemicals. Potassium bromide was purchased from Acros. Dimethyl viologen dichloride hydrate, octadecyl trichlorosilane, poly(ethylene glycol) methacrylate (PEG-MA, $M_n=360$), poly(ethylene glycol) dimethacrylate (PEG-DMA, $M_n=550$), toluene, and methanol were purchased from Aldrich. Tris(2,2'-bipyridyl) ruthenium(II) chloride was purchased from Alfa Aesar. Potassium perchlorate was purchased from Baker and Adamson. 3,4-Ethylenedioxythiophene (EDOT) monomer (Baytron M) was purchased from Bayer. Ammonium peroxydisulfate (APS), potassium chloride, potassium phosphate, monobasic, and potassium phosphate were purchased from Fisher. Tris(2,2'-bipyridyl) iron(II) perchlorate was purchased from GFS chemicals. The initiator 2,2-diethoxyacetophenone (DEAP) was purchased from Fluka. Snowtex colloidal silica particles were purchased from Nissian chemicals. All chemicals were used as received from the commercial sources unless otherwise indicated.

Preparation of Poly(3,4-ethylenedioxythiophene) (PEDOT)-Coated Silica Particles. The synthesis of PEDOT-coated silica particles has been described in detail elsewhere.⁹ A brief description is as follows. Commercially available silica particles in an aqueous suspension were centrifuged at 8000 rpm for 30 min to remove smaller particles. The larger particles were collected from the bottom of the centrifuge tubes and then redispersed in deionized water by sonication, leading to a suspension for which the average particle diameter was 135 nm (as measured by dynamic light scattering, DLS).

A 6 g (solid weight) quantity of silica sol with the smaller particles removed as described above was dispersed in 140 mL of deionized water; to this solution was added 0.436 g of EDOT dissolved in 40 mL of methanol. The mixture was stirred for 2 h. Polymerization was initiated by adding 1.81 g of APS oxidant dissolved in 20 mL of deionized water. The reaction was allowed

to proceed at 30 °C for 18 h. Polymerization was terminated by adding methanol to the reaction mixture, and the resulting particles were purified by repetitive centrifugation and redispersion with water and methanol to produce a suspension of PEDOT-coated silica particles with an average particle diameter of 147 nm (as measured by DLS). This particle suspension exhibits opalescence after several cycles of the cleaning processes.

Hydrogel Film Preparation. The preparation of hydrogel-stabilized films containing PEDOT-coated silica particles has also been described elsewhere.⁶ In brief, the hydrogel matrix used to stabilize the colloidal PEDOT-silica particle suspensions was generated from an aqueous solution consisting of PEG-MA monomer, PEG-DMA cross-linker, DEAP photoinitiator, and a particle suspension in water, in a mass ratio of 100:10:1.5:500. The latter mass corresponding to a solution that contained 23 wt % PEDOT-coated silica particles dispersed in deionized water. For the pure-silica-particle hydrogel films, an aqueous dispersion of 23 wt % silica particles was used in place of the dispersion of PEDOT-on-silica particles. In each case, the mixture was placed into a glass cell consisting of two treated glass slides and a 250 μm thick Parafilm spacer with an 18 mm diameter hole cut in the center. The glass-slide surfaces were made hydrophobic prior to use by coating them with a 30% octadecyl trichlorosilane (OTS) in toluene solution after cleaning with piranha reagent. (*Caution: Piranha reagent is an extremely aggressive oxidizing agent and should be used only with proper protection and great care*). Polymerization was initiated by exposure of the mixture to UV light from a Kepro UV exposure frame model BTX-200A for 8 min on each side.

Spectroelectrochemical Cell and Measurements. The cell used to acquire both electrochemical and spectroscopic data consisted of an indium-doped tin oxide (ITO)-coated glass working electrode, a platinum wire auxiliary electrode, and a silver wire quasireference electrode. Two Parafilm spacers, each 250 μm thick, were stacked in the cell to give an overall cell thickness of 500 μm . The first spacer holds the PEDOT film against the ITO electrode and defines the active region of the electrode surface as an 18 mm diameter circle. The second spacer has a slightly smaller diameter of 17 mm, such that the PEDOT-containing hydrogel film is held securely against the ITO electrode surface. An acrylic top is firmly placed on top of the spacer stack to create the thin-layer cavity, and the entire cell is sealed with epoxy prior to use. Figure 1 illustrates this cell design. The total cell volume, not including the inlet tubes for the reference and auxiliary electrodes, is approximately 120 μL . The cell was typically filled with a buffer solution consisting of 25mM KCl, 25 mM KClO_4 , and 50 mM phosphate at pH 7.2.

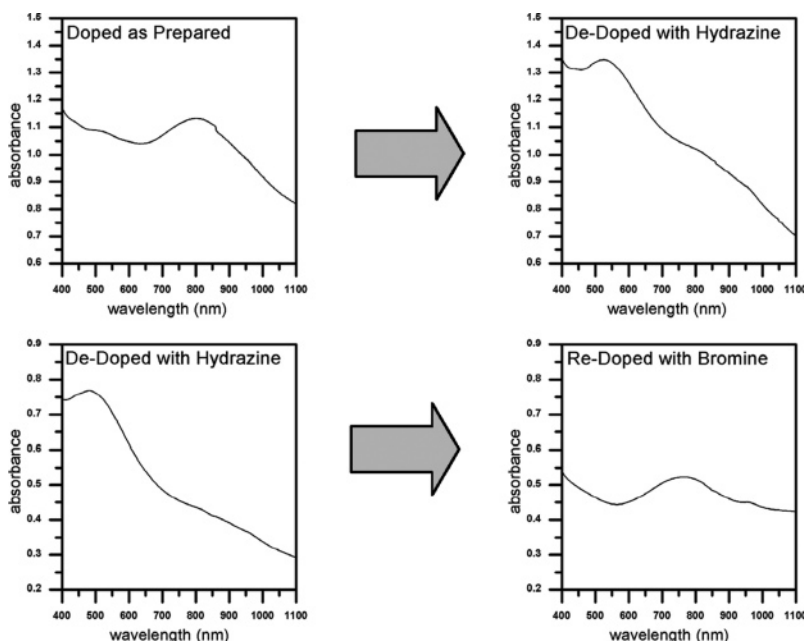


Figure 2. Absorbance spectra of PEDOT-coated silica particles dispersed in deionized water and treated with chemical oxidizing and reducing agents. Top, chemical dedoping of the PEDOT in the suspended particles is accomplished using 100 mM hydrazine. Bottom, chemical redoping of PEDOT in the dedoped suspended particles is accomplished using aqueous 100 mM bromine.

In some cases, redox mediators and/or potassium bromide were also present in the buffer solution. When redox mediators were present, their concentrations were as follows: 0.1 mM of reductive mediator (dimethyl viologen dichloride, MV^{2+}) and 0.1 mM of oxidative mediator (tris(2,2'-bipyridine) ruthenium(II) chloride, $Ru(bpy)_3^{2+}$). When bromide was present in the buffer solution, it was added as 25 mM KBr. Hydrogel-stabilized films containing PEDOT-coated silica particles on ITO glass were prepared for spectroelectrochemical experiments by gently shaking them in the various redox mediator-containing buffer solutions on a Vari-mix shaker for 12 h. The films were placed in fresh mediator solutions that were nitrogen-purged to remove ambient oxygen and then sealed inside the electrochemical cell using epoxy. A CH Instruments model 660B electrochemical workstation was used for acquiring cyclic voltammograms and for applying the requisite potential programs while the optical absorption data were simultaneously acquired on a Perkin-Elmer Lambda 900 UV-vis absorption spectrophotometer. The spectrometer was set to automatically acquire an absorption spectrum every 10 min at a scan speed of 150 nm per minute scanning from 400 to 1100 nm. A hydrogel-stabilized film containing only silica particles, with no PEDOT, with the same particle concentration as for the films containing PEDOT-coated silica particles was used as the spectral reference.

Results and Discussion

Figure 2 presents the spectral changes observed in a 1 wt % suspension of PEDOT-on-silica core-shell particles in deionized water as a function of the PEDOT doping state, with doping/dedoping accomplished using chemical oxidizing and reducing agents in solution. The top two spectra show the absorbance changes that were seen on addition of 100 mM of hydrazine (N_2H_4 , a reducing agent for which $E^0 = -1100$ mV vs SHE)¹⁶ to an aqueous suspension of core-shell particles. The absorbance peak near 800 nm that is charac-

teristic of the as-prepared PEDOT particles in the doped (oxidized) state disappears following hydrazine treatment and is replaced by an absorbance peak near 550 nm that is characteristic of the dedoped (reduced) PEDOT material.

The bottom two spectra in Figure 2 illustrate that the spectral changes observed on dedoping are reversible. Treatment of a hydrazine-dedoped suspension with a 100 mM aqueous solution of bromine (Br_2 , an oxidant with $E^0 = +1087$ mV vs SHE)¹⁷ causes reappearance of the absorbance peak near 800 nm, indicating redoping of the PEDOT polymer. Note that the absorbance magnitudes in the two pairs of spectra differ because they are for different samples. The relative changes on dedoping and redoping are always similar to those shown, though a residual doping of PEDOT, as evidenced by spectroscopic means, has been indicated to occur even with exposure to hydrazine.²² Nonetheless, these spectral changes are similar to those that have previously been observed for a wide variety of polythiophenes including PEDOT in a variety of formats,¹⁸ thereby establishing that the chosen oxidizing and reducing agents are adequate for accomplishing PEDOT doping and dedoping in these core-shell particles.

A key aim of the present work was to show that the same spectral changes that are obtained using chemical oxidizing/reducing agents to change the PEDOT doping state in core-

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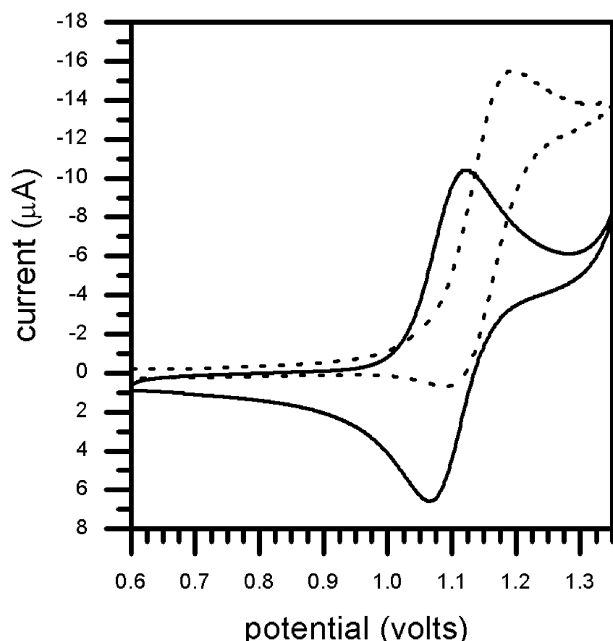


Figure 3. Cyclic voltammograms illustrating the electro-oxidation of Ru(bpy)₃²⁺ mediator (0.1 mM) in the absence (solid line) and presence (dashed line) of bromide. Each voltammogram was recorded at a scan rate of 5 mV/s at an ITO electrode in the cell shown in Figure 1, in a solution that also contained 0.1 mM methyl viologen, 25 mM KCl, 25 mM KClO₄, and 50 mM phosphate buffer adjusted to pH 7.2. When bromide was present (dashed line), it was added as KBr at a concentration of 25 mM.

shell particle suspensions in water may be obtained using electrogenerated redox mediators with suspensions of isolated PEDOT-containing particles that are dimensionally stabilized in a polyether hydrogel matrix. The hydrogel-stabilized PEDOT particle suspensions were prepared as thin films (several hundred micrometers) on ITO electrode surfaces as described above and were equilibrated with an aqueous electrolyte containing a cocktail of redox mediators prior to mounting in the transmission-mode spectroelectrochemical cell (Figure 1). A mediator cocktail consisting of a mixture of redox mediators to accomplish dedoping (reduction) and doping (oxidation) was used. For the dedoping (reduction) process, methyl viologen (MV²⁺, $E^0 = -446$ mV vs NHE)¹⁹ was chosen as the redox mediator. Viologens as a class are often used as reductive redox mediators, and the formal potential for methyl viologen is similar to that for hydrazine and is quite negative enough to accomplish PEDOT dedoping.

For the doping (oxidation) process, a combination of tris-(2,2'-bipyridyl) ruthenium(II) chloride (Ru(bpy)₃²⁺, $E^0 = 1050$ mV vs Ag/AgCl)²⁰ and bromide ion, present as

potassium bromide, was used. The Ru(bpy)₃³⁺ trication is a potent oxidant that is readily formed via electro-oxidation of Ru(bpy)₃²⁺ at an ITO electrode;²⁰ in the presence of bromide, it can easily generate elemental bromine, which can serve to dope the PEDOT polymer. Figure 3 illustrates this fact via a pair of cyclic voltammograms showing Ru(bpy)₃²⁺ oxidation, one in the absence of bromide and the other in the presence of bromide. The voltammogram in the presence of bromide shows an enhanced oxidative current on the forward scan and a diminished reductive current on the reverse scan. Both of these observations are consistent with a catalytic regeneration electrode mechanism²¹ involving oxidation of bromide to bromine by the electrogenerated Ru(bpy)₃³⁺ trication. Control experiments attempting to accomplish direct electrooxidation of bromide to bromine at ITO electrodes consistently failed because of slow kinetics of bromide electrooxidation at ITO (data not shown). It is for this reason that we adopted the mediator cocktail consisting of both bromide and Ru(bpy)₃²⁺. This mediator cocktail (also including MV²⁺ for accomplishing mediated reductions) was employed in all of the work described in the following sections.

(The apparent positive shift in formal potential for Ru(bpy)₃²⁺ oxidation on addition of potassium bromide to the electrolyte that is evident in Figure 3 is believed to be an artifact associated with a shift in the rest potential of the silver wire quasireference electrode. It is important to note that this shift has occurred; however, it is relatively modest in magnitude and is not considered to be of major consequence to subsequent experiments because the applied oxidative potentials were always sufficiently positive to oxidize Ru(bpy)₃²⁺ at the mass-transfer-limited rate, regardless of the modest shift in reference potential.)

Figure 4 presents a series of spectra acquired for one film in the spectroelectrochemical cell in Figure 1 showing that PEDOT dedoping and redoping are readily accomplished in the hydrogel-stabilized particle suspensions using electrochemically generated species. The spectrum at left corresponds to a hydrogel-stabilized film with PEDOT in the doped, as-prepared form. The film resides in the cell with the working electrode at the open circuit. The spectrum in the center was acquired after application of a reducing potential (−775 mV vs Ag wire) to the working electrode for 150 min. The spectral changes are quite similar to those in Figure 2 following hydrazine treatment of an aqueous particle suspension and clearly indicate that application of

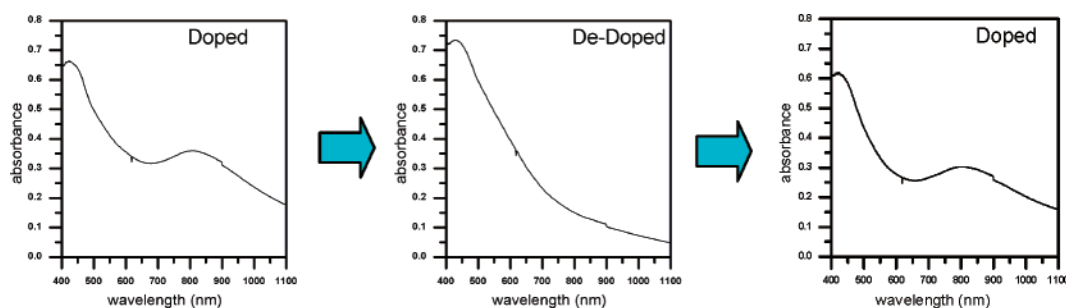


Figure 4. Electrochemical dedoping/redoping of PEDOT in a hydrogel-stabilized film of PEDOT-coated silica particles on an ITO electrode in the presence of a MV²⁺/Ru(bpy)₃²⁺/Br[−] redox mediator cocktail. Dedoping was accomplished by application of a reducing potential to the ITO electrode for 150 min, and redoping was accomplished by subsequent application of an oxidizing potential to the ITO electrode for 150 min.

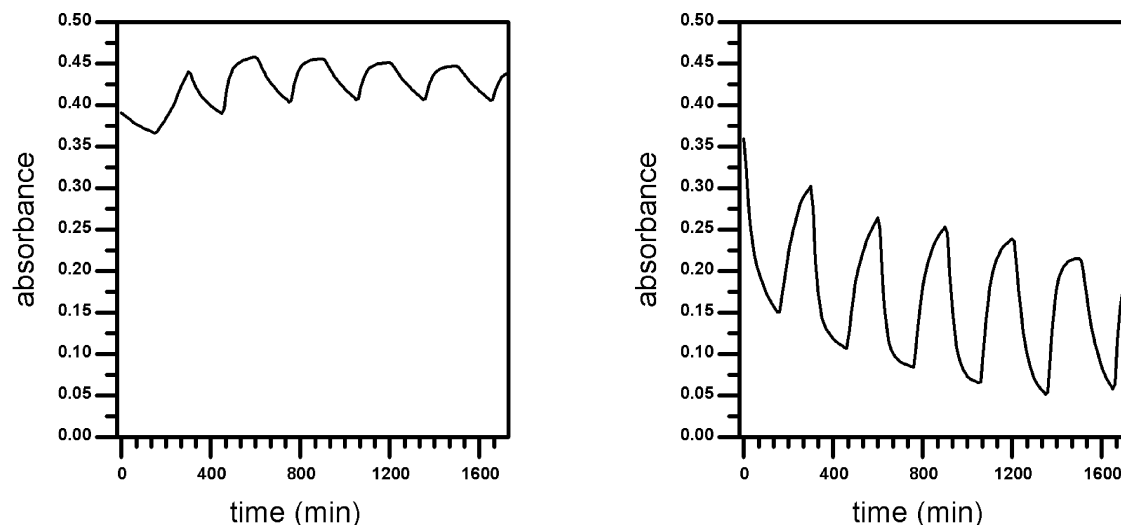


Figure 5. Absorbance change at 800 nm for a hydrogel-stabilized film of PEDOT-coated silica particles in the spectroelectrochemical cell shown in Figure 1. The cell was filled with a 50 mM phosphate buffer at pH 7.2 containing 25 mM KCl, 25 mM KClO_4 , and 25 mM KBr. The film underwent five complete cycles, each consisting of a reductive step at -755 mV for 150 min followed by an oxidative step at 1275 mV for 150 min. Left, absorbance changes in the absence of the $\text{MV}^{2+}/\text{Ru}(\text{bpy})_3^{2+}$ redox mediators. Right, absorbance change for a similar film in a buffer solution that also contained the $\text{MV}^{2+}/\text{Ru}(\text{bpy})_3^{2+}$ redox mediators.

the reducing potential has caused the PEDOT in the particles to be dedoped. The spectrum at far right was acquired after a subsequent application of an oxidizing potential of $+1275$ mV vs Ag wire for 150 min. The spectral feature of the initial spectrum is recovered, indicating that the PEDOT has been redoped. Taken together, these spectra provide strong evidence for electrochemical adjustment of the doping state in these films despite the fact that the individual PEDOT particles are dispersed throughout the film and are not in physical contact with each other.

For monitoring the dynamics of electrochemical doping/dedoping/redoping of PEDOT in these films, it is useful to construct plots of absorbance vs time at a specific wavelength; the scans are acquired during application of a potential program to the ITO electrode, which accomplishes sequential PEDOT dedoping and redoping. Inspection of the absorbance spectra in Figures 2 and 3 suggests that monitoring absorbance vs time at 800 nm will be informative, because at this wavelength, the doped PEDOT absorbs strongly but the dedoped PEDOT absorbs hardly at all. We note that control spectroelectrochemical experiments showed nearly zero absorbance at this wavelength for solutions containing only the redox mediator cocktail of MV^{2+} and $\text{Ru}(\text{bpy})_3^{2+}$, each at 0.1 mM, and no PEDOT, over the full range of potentials applied in this work.

Figure 5 presents two such plots of absorbance at 800 nm vs time for two different hydrogel-stabilized PEDOT-silica core-shell particle films, each of which was subjected to five cycles of a potential program involving the initial application of a reducing potential (-775 mV vs Ag wire) for 150 min, followed by application of an oxidizing potential ($+1275$ mV vs Ag wire) for 150 min. For the film at left, the solution contained buffer and electrolyte, including some potassium bromide, but no viologen or ruthenium mediators, whereas for the film at right, the solution contained both of the redox mediators. Both films show absorbance changes that correlate with the periodic application of reducing and oxidizing potentials to the ITO electrode, but the changes

are much greater in magnitude and occur much more rapidly when the redox mediators are present than when they are absent. It seems likely that this observation reflects the action of the mediators in shuttling oxidizing and reducing equivalents between the ITO electrode and the PEDOT-silica particles throughout the film, thereby promoting oxidation/reduction of PEDOT in particles that are not in direct contact with the electrode.

The absorbance changes that were observed in the absence of mediators are believed to be caused by direct PEDOT oxidation/reduction in a small population of PEDOT-silica particles that may have settled onto the ITO electrode surface during the hydrogel curing step and/or that may have formed a percolating particle network in which direct electrooxidation/reduction could occur within the network of contacting particles. Such networks could easily form in a disordered suspension such as those that were the focus of this work; however, they would be highly unlikely in an ordered suspension such as that which would form when making a hydrogel-stabilized crystalline colloidal array (CCA) of the PEDOT-silica core-shell particles. Future studies will be directed at these optical materials, for which the present studies lay important groundwork.

Finally, a close inspection of the absorbance vs time trace in Figure 5 acquired in the presence of bromide and the redox mediator cocktail reveals that the absorbance corresponding to redoped PEDOT never fully recovers to its initial value following electrochemical dedoping and redoping. Figure 6 presents the absorbance of the PEDOT-coated particles with time, which more thoroughly considers this latter observation. The absorbance data in Figure 6 were acquired over a very long time (over 70 h) following a single oxidative potential step at a hydrogel-stabilized PEDOT-silica core-shell particle suspension on ITO in the presence of the $\text{MV}^{2+}/\text{Ru}(\text{bpy})_3^{2+}$ /bromide mediator cocktail. The absorbance increases slightly during the first hour, as expected if application of an oxidative potential resulted in a small increase in the doping level of the PEDOT polymer; however, after

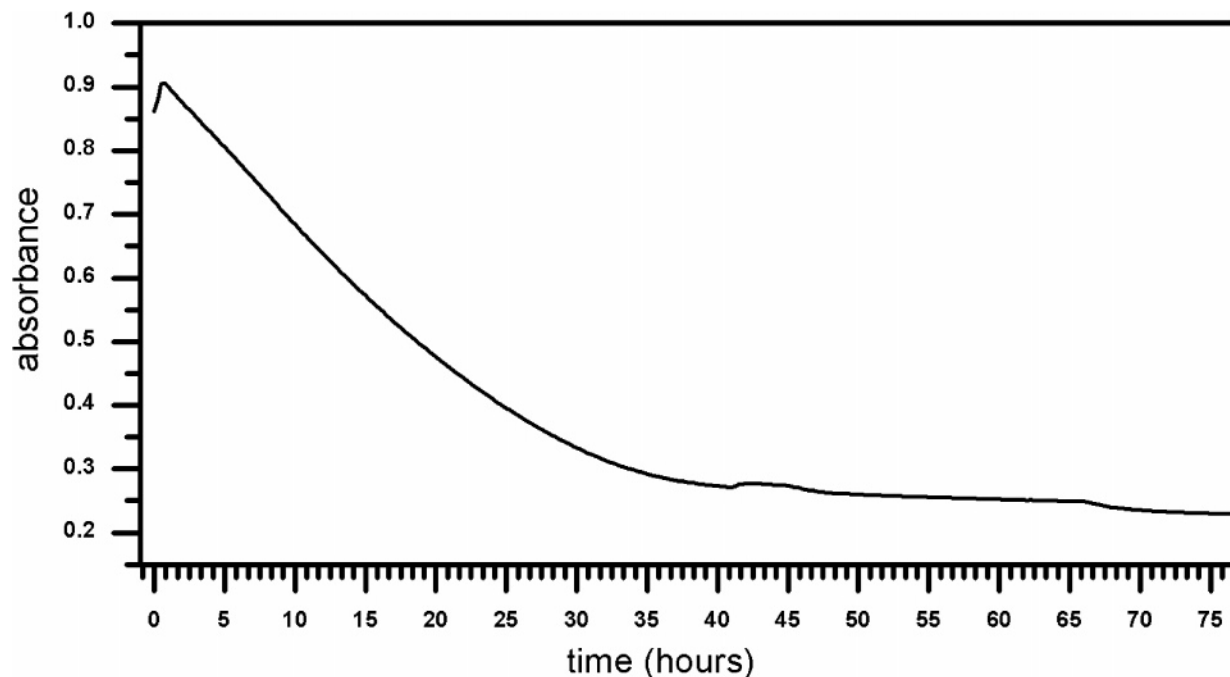


Figure 6. Absorbance vs time corresponding to electro-oxidation at 1275 mV for 77.75 h of a 250 μm thick film of hydrogel-stabilized PEDOT-coated silica particles. The mediator solution in the electrochemical cell contained 0.1 mM methyl viologen, 0.1 mM tris(2,2'-bipyridyl) ruthenium (II), 25 mM KBr, 25 mM KCl, and 25 mM KClO_4 in 50 mM phosphate buffer at pH 7.2.

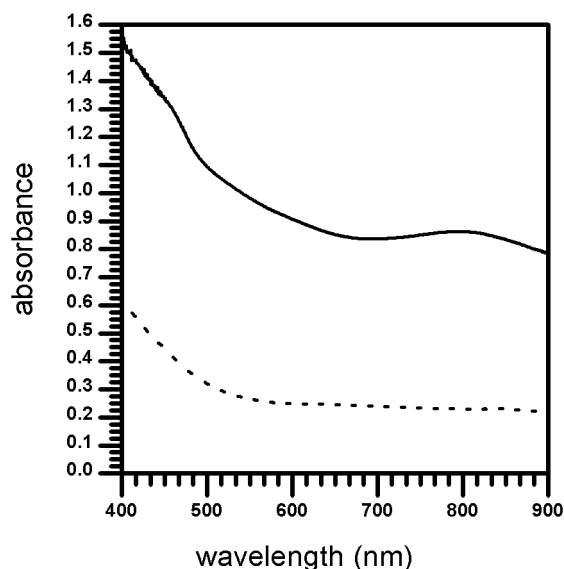


Figure 7. Absorbance spectra corresponding to the film from Figure 6 at time zero (solid line) and 77 h (dashed line), illustrating the bleaching of the PEDOT absorption following a long time scale exposure to oxidizing potentials in the mediator-containing electrolyte solution.

this first hour, the absorbance peaks and then begins to gradually decrease, eventually reaching a much reduced value after several days. Figure 7 shows the full absorption spectra acquired before and after this extended electro-oxidative treatment, which confirm that the end result of such treatment is a complete bleaching of the PEDOT absorbance. Apparently, the electrogenerated bromine can dope the PEDOT on a short time scale (tens of minutes), but on a longer time scale, it can irreversibly oxidize the polymer, perhaps via a mechanism involving irreversible bromination of the PEDOT

unsaturated bonds. This over-oxidation process apparently renders the material colorless. Control experiments revealed that a very long time scale treatment of a PEDOT-silica core-shell particle suspension in water with bromine also results in bleaching of the PEDOT optical signature. We learn from this result that schemes designed to accomplish reversible doping/dedoping of PEDOT-based materials must utilize oxidizing agents that are able to oxidatively dope the PEDOT without also irreversibly oxidizing it so as to bleach the optical signal.

Conclusions

This work demonstrates electrochemical modulation of the optical properties of PEDOT-on-silica core-shell particle suspensions in a stabilizing polyether hydrogel matrix using electrogenerated oxidizing and reducing agents. Changes in absorbance at 800 nm are correlated with electrochemical dedoping and redoping of PEDOT-containing particles in spatially isolated regions by electrogenerated redox mediators that diffuse between the ITO electrode where they are generated and the isolated PEDOT-containing particles throughout the hydrogel film. Extension of this work to include hydrogel-stabilized crystalline colloidal arrays of PEDOT-containing particles, for which redox mediation offers the only alternative for electrochemically modulating optical properties, is anticipated.

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