Chemically Derived Prussian Blue Sol−Gel Composite Thin Films

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Received September 10, 1998. Revised Manuscript Received October 26, 1998

A Prussian Blue (PB) sol−gel composite thin film was prepared via post-chemical derivatization of a functionalizable sol−gel thin film. Bis[3-(triethoxysilyl)propyl] tetrasulfide (SIS) forms tough and crack-free films by sol−gel process with excellent adhesion on various solid surfaces. The sulfur chain ($-S_4-$) can be chemically oxidized to sulfonic groups ($-SO_3^-$). After oxidation, PB sol−gel composite thin films were prepared by ion-exchange with ferrous ion followed by complexation with ferricyanide. The PB sol−gel composite thin films were characterized by electrochemistry, spectroscopy, and microscopy. Applications in the development of a potassium ion-selective electrode and an optical pH indicator are demonstrated.

Introduction

The unique aspects of sol−gel process, such as mild polymerization conditions and controllable functionalization and properties, not only has offered access to ceramics and glasses with improved or new properties but also has allowed the production of a variety of hybrid inorganic−organic materials. Organic dyes, polymers, and biomolecules have been incorporated in inorganic materials[1] for applications in solid-state dye lasers, catalysts, chemical and biomedical sensors, and electrooptical devices. There are two major approaches to produce sol−gel composites. The simple doping of the sol−gel solution with the desired compound is the most popular technique for immobilization because of its generality, simplicity, and retention of the properties of the compound in the immobilized state. However, a major drawback of this simple processing is the slow leaching of reagents from the doped sol−gel matrixes.[2] On the contrary, covalent bonding by incorporating functional groups into the sol−gel precursor or copolymerization of modified dopants with sol−gel precursors is an effective solution to the leaching problem, though the optimization of preparative parameters is usually an experimental complication.[3]

Although great attention has been paid to hybrid organic−inorganic materials from sol−gel processing by incorporating organic moieties into inorganic materials, inorganic entities in sol−gel materials hold promising applications in tougher environments, such as extreme temperatures or pressures, due to their high thermal, chemical, and mechanical stability.[4] For example, supported metal or metal oxide fine particles for catalysis, entrapped semiconductor nanoparticles for nonlinear optics, and transition metal complexes for solar energy conversion are potential applications. Prussian Blue (PB) is the prototype of a number of polynuclear transition metal hexacyanometalates which form an important class of insoluble, mixed-valence compounds. These compounds have been extensively studied for applications in catalysis, rechargeable batteries, electrochromics, chemical sensing, and photocatalysis.[5] In general, these materials exhibit high chemical stability, facile preparation, low cost, and rich electrochemical, electrochromic, and optical properties. Thin films of PB have now been deposited by chemical, galvanolstatic, potentiostatic, and other electrochemical methods.[6]

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10.1021/cm9806275 CCC: $18.00

Films from direct chemical deposition are usually not robust. Electrochemical methods allow film deposition only on conductive or semiconductive substrates. There are two important aspects to be improved for PB thin film or PB composite thin film deposition, that is, toughness, cracklessness, and high adherence to various solid surfaces.

In this paper, we describe an efficient and simple method to produce PB sol–gel composites via postchemical derivatization of a functionalized sol–gel thin film. The sol–gel composite was prepared using bis[3-(triethoxysilyl)propyl] tetrasulfide (SIS). SIS is an excellent coupling reagent for various surfaces, and the sulfur chain in the molecule has rich derived chemistry. Little literature is available about sol–gel materials prepared from this silane precursor. The PB sol–gel composites were characterized by electrochemistry, spectroscopy, and microscopy. Applications in the development of a potassium ion-selective electrode and an optical pH indicator are demonstrated.

Experimental Section

Materials. SIS was purchased from United Chemical Technologies, Inc. Gilder copper grids (diameter, 3 mm) with standard square mesh were from Electron Microscopy Sciences. Indium-doped tin oxide (ITO) electrodes were a gift from Photran, Inc. Glass slides were from Fisher Scientific. Other reagents were at least analytical grade and used as received. Nanopure water was purified through a Barnstead Milli-Q system.

Instruments. UV–vis measurements were done in a HP 8452A diode array spectrophotometer. Fourier transform infrared reflection–absorption spectra were obtained with a Nicolet 710 spectrometer equipped with a MCT detector. X-ray photoelectron spectra (XPS) were obtained on Perkin-Elmer PHI 560 ESCA/SAM system. Optical microscopy was done with a Nikkon Alpha Photo YS model 146695. Transmission electron microscopy was performed with a Philips TEM 201. Electrochemical measurements were conducted with a BAS 100W/B (Bioanalytical Systems) with platinum wire as the counter electrode and a Ag/AgCl as the reference electrode. A Beckman ϕ50 pH meter was used for pH measurements.

Film Formation. A 10% (v/v) SIS sol solution was prepared in *N*,*N*-dimethyformamide (DMF). The molar ratio of SIS:H_2O was 1:8, using 0.1 M HCl as the catalyst. SIS sol–gel films on glass slides and ITO and glassy carbon electrodes were prepared by spin-coating (4000 rpm). Ultrathin SIS sol–gel films on gilder copper grids were prepared by dip-coating. Oxidation of the SIS sol–gel films was accomplished by putting a drop of concentrated nitric acid or Piranha solution (***Caution***: *Piranha solution is strongly oxidizing and may detonate upon contact with organic materials!*) on the film surface for 5 s and then washing with water. The PB sol–gel composite films were prepared by dipping the oxidized film into 0.1 M $FeSO_4$ solution for 5 min, rinsing with water, and then dipping in 0.1 M $K_3Fe(CN)_6$ solution for 5 min.

Results and Discussion

Formation of the PB Sol–Gel Composite Films. SIS sol–gel films were prepared by spin-coating onto various solid surfaces, such as ITO and glassy carbon electrodes and glass slides. The oxidation of SIS sol–gel thin film by concentrated nitric acid produces a brown gas with an odor characteristic of NO_2. Figure 1 shows the XPS of SIS sol–gel film before (A) and after (B) nitric acid oxidation. A binding energy of 163.3 eV was observed for S2p of the pristine SIS sol–gel film. After oxidation, two peaks were observed with binding energy of 163.3 and 167.9 eV. The second peak is characteristic of $-SO_3^-$ species.[7] The oxidized SIS sol–gel films were first soaked in $FeSO_4$ solution for 5 min, rinsed with water, and then transferred into $K_3Fe(CN)_6$ solution; Prussian Blue formed immediately throughout the sol–gel film as noted by the blue coloration of the surface. Upon reversing the experimental sequence, i.e., soaking the film first in $K_3Fe(CN)_6$ solution and then in $FeSO_4$ solution, no PB was formed. This confirms the role of the ion-exchange process during the formation of the PB sol–gel composite. Figure 2 shows the proposed mechanism for the composite formation.

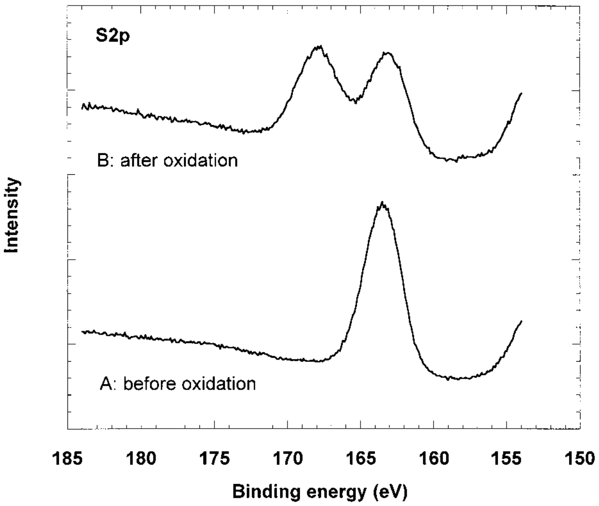

Figure 1. XPS of a SIS sol–gel film on ITO before (A) and after (B) nitric acid oxidation.

Visible and IR Spectra. Figure 3 shows the UV–vis spectra of the PB sol–gel composite film deposited on a glass slide. The absorption band centered at 690 nm is characteristic of PB films[8] in the form of $Fe_4[Fe(CN)_6]_3$, since other forms, i.e., Prussian White, Everitt's salt, and Prussian Yellow, do not adsorb in the 500–800 nm range. Furthermore, both the oxidized and reduced forms of PB are unstable in air and water; however, no obvious change was observed for the UV–vis spectra of the PB sol–gel composite film after half a year of preparation. From the infrared spectra, a strong absorption band at 2080 cm^{-1} was observed, which has previously been associated with the bridging cyanide stretches.[9]

Microscopy. We have shown that SIS sol–gel ultrathin membranes can be cast on gilder copper grid with standard square mesh as the supporting film for TEM applications.[10] These sol–gel films have micro-

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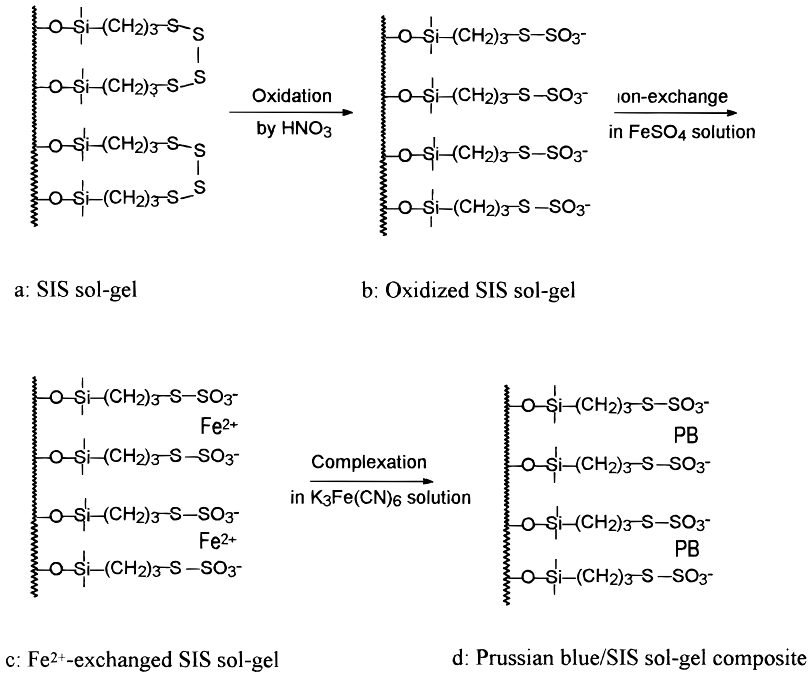

Figure 2. Proposed mechanism for the formation of PB sol–gel composite.

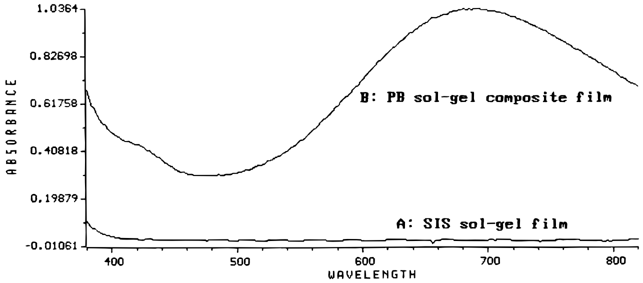

Figure 3. Visible spectra of a SIS sol–gel film (A) and the PB sol–gel composite film (B) on a glass slide.

structure down to nanometer scale and transmittance similar to Formvar supporting film. By chemical derivarization, we have prepared ultrathin PB sol–gel composite films and characterized them by optical microscopy and TEM. Figure 4A shows the optical microscopy of a composite film. A uniform and homogeneous structure is observed at this magnification (1000×). The TEM micrograph at a higher magnification (70000×) shows a much finer structure (shown in Figure 4B). It shows that PB nanocrystallites formed throughout the sol–gel film. Compared with PB films prepared by electrochemical means, where many cracks occurred,[11] the quality of this PB sol–gel composite film is considerably improved. Besides oxidation by nitric acid, we have also tried to oxidize the sulfur chain in the SIS sol–gel film with a strong oxidant, piranha. Figure 4C shows the TEM micrograph of the PB sol–gel composite film prepared by piranha oxidation. Obviously, the vigorous oxidation leads to highly porous fibril-like microstructure. Besides the sulfur chains, the organic hydrocarbon chains might have also been at least partially oxidized by piranha, forming a rougher morphology. This highly porous composite with high specific surface area could be useful for applications in photocatalysis.

Cyclic Voltammetry. Figure 5A shows the cyclic voltammogram of PB sol–gel composite thin film coated on an ITO surface in 0.1 M KCl solution. There are two redox processes[12,5b,5g] corresponding to PB reduction to Everitt's salt (ES) and PB oxidation to Berlin Green (BG):

$$\mathrm{Fe_4{}^{III}[Fe^{II}(CN)_6]_3 + 4e + 4K^+ \Leftrightarrow K_4Fe_4{}^{II}[Fe^{II}(CN)_6]_3} \quad (1)$$

$$\mathrm{Fe_4{}^{III}[Fe^{II}(CN)_6]_3 - 3e + 3A^- \Leftrightarrow Fe_4{}^{III}[Fe^{III}(CN)_6A^-]_3} \quad (2)$$

These two redox processes are comparable to those of electrochemically deposited PB on ITO,[12] indicating that the PB in the composite enhances the electrical conductivity of the intrinsically insulating sol–gel material. The peak currents are proportional to the scan rate, indicating the surface-confined redox behavior of immobilized PB. The redox processes are quasireversible with a peak potential difference of 30 mV for PB reduction and 60 mV for PB oxidation. Differences in cathodic and anodic peak potentials of a few tens of millivolts are typical for species immobilized on silanized metal oxide electrodes.[13] The redox potential of the wave at 0.2 V varies with the KCl concentration in solution, as shown in Figure 5B. These rigid and tough inorganic polymer (silica network) thin-film-modified electrodes are a good alternative to the swellable and flexible organic polymer-film-modified electrodes in applications under harsh environment.

An all solid-state thin film electrochromic system is attractive for flat panel displays, swichable optical smart windows, controllable light-reflective or light-

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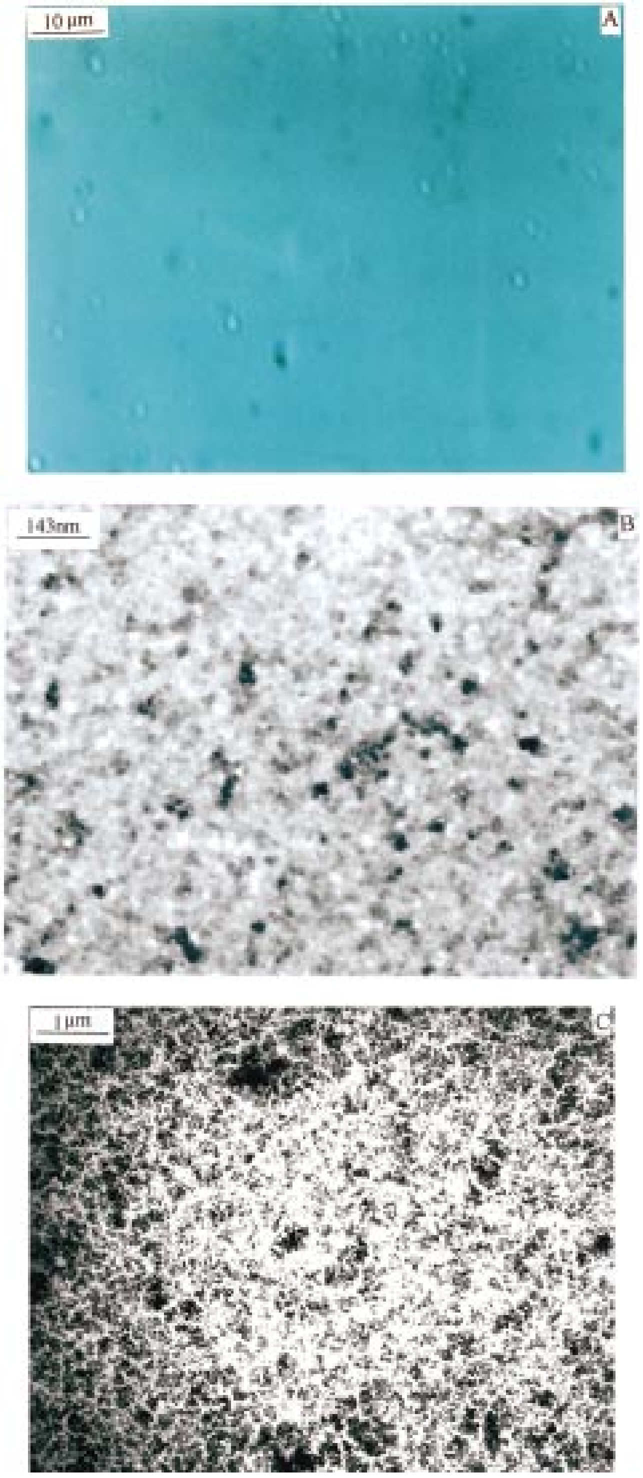

Figure 4. Optical microscopy (A) and transmission electron microscopy (B, C) of the PB sol–gel composite thin films: (A and B) by nitric acid oxidation and (C) by piranha oxidation.

transmissive devices for optical information and storage, etc.[14] A PB–Nafion-based solid-state device has been designed.[14a] For this system, device fabrication involved chemical, rather than electrochemical, formation of the PB on immersion of a membrane of the solid polymer electrolyte Nafion (a sulfonated polytetrafluoroethane polymer) in aqueous solutions of $FeCl_2$ and then $K_3Fe(CN)_6$. The resulting PB-containing Nafion composite was sandwiched between two ITO plates. An all solid-state *inorganic* thin film electrochromic system based on a PB sol–gel composite film should possess more advantages; for example, inorganic polymer electrolytes tend to exhibit a better long-term UV stability than organic ones, and the silane-derived electrolyte also fulfills an important secondary role as a binder between glass plates.[14c] The feasibility of the construction of such devices is being studied.

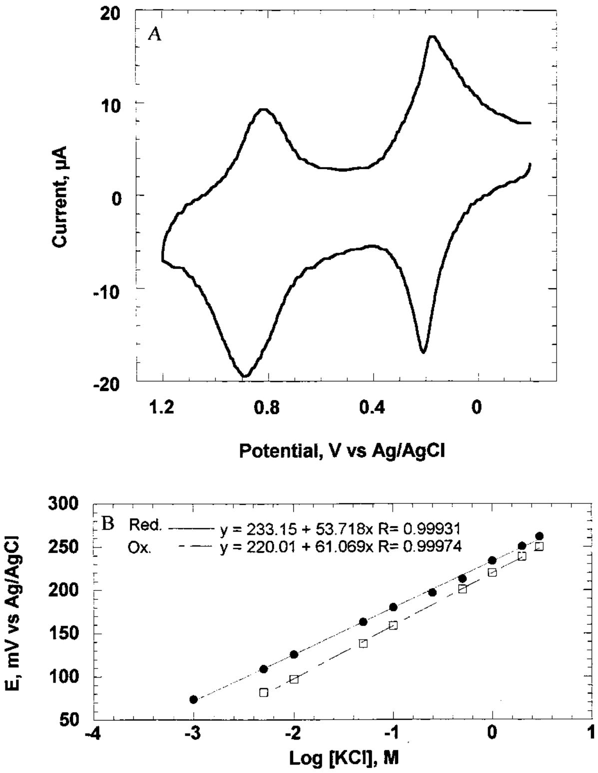

Figure 5. (A) Cyclic voltammogram of PB sol–gel composite film deposited on an ITO surface in 0.1 M KCl solution and (B) dependence of the PB redox potential on the concentration of KCl in solution; sweep rate, 50 mV/s.

Potassium Ion-Selective Electrode. Solid-state films and membranes from PB and its analogues have been reported for the construction of potassium, cesium, and ammonium ion-selective electrodes.[15] The suitability of these metal cyanometalates for ion-selective electrodes has been well-documented due to their great selectivity, simple preparation, low cost, longevity, and stability in various solutions including nonaqueous media. They can basically be divided into two types: directly electrochemically deposited PB film on solid electrode surfaces (e.g., Pt, Au, GC) and PB/polymer (PVC, silicone, polystyrene, epoxy resin) composite membranes attached to electrode surfaces. The electrochemically deposited films are usually not strongly

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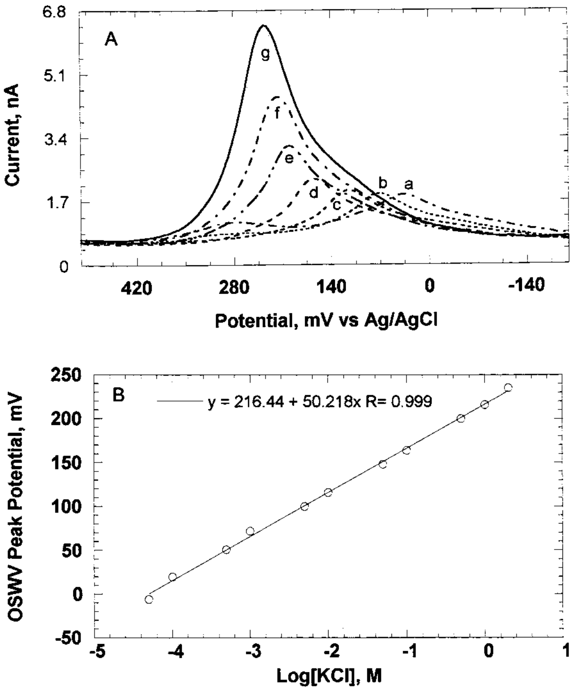

Figure 6. Osteryoung square wave voltammertry (A) of a PB sol−gel composite-film-modified glassy carbon electrode in (a) 0.0001 M, (b) 0.001 M, (c) 0.01 M, (d) 0.1 M, (e) 0.5 M, (f) 1.0 M, and (g) 2.0 M KCl solution and the corresponding plot (B) of peak potential vs potassium activity; sweep rate, 60 mV/s; square wave amplitude, 25 mV.

adherent and, consequently, lack mechanical stability. The physically blended PB/polymer composites are not microscopically homogeneous and are neither thermally stable nor solvent resistant.

Besides the dependence of the redox potential of the PB reduction process (reaction 1) on potassium concentration in solution by cyclic voltammetry, we found that the peak potential of the PB sol−gel composite film prepared on a glassy carbon electrode was also dependent on potassium activity by Osteryoung square wave voltammetry (OSWV) (shown in Figure 6). This provides a more rapid (a few seconds) and practical technique for an ISE operation, and the pulse-based model operation can be accomplished by more economic and compact electronic devices, like the commercially available glucose electrochemical sensors. The PB sol−gel composite thin-film-modified glassy carbon electrode was also used as a potentiometric potassium ion-selective electrode. By connecting the modified electrode to a pH meter, the steady-state potential of this electrode was found to be proportional to the potassium concentration in solution. Figure 7 shows the Nernst plot for the PB sol−gel composite-film-modified glassy carbon electrode. A linear range is obtained between 3×10^{-4} and 3.0 M with a slope of 48 mV/decade. This type of all solid-state electrode is rather robust due to its high chemical, thermal, and mechanical stability. Robust ion-selective electrodes such as the glass membrane pH electrode could be constructed from sol−gel composite membranes.

Optical pH Indicator. Though PB strongly absorbs in the vis−NIR range and potential changes in its optical properties can be expected as a result of the various physicochemical processes in which PB is involved, only one report has been made very recently[16] exploiting the protolytic properties of PB and its application in an optical pH sensor based on chemically derived PB/*N*-substituted polypyrroles composite films. Compared to PB-based electrochemical sensors, the PB films can be deposited on nonconducting supports or even prepared as free-standing membranes for optical sensors instead of onto conducting or semiconducting substrates. The report presented a new and simple method for the composite film deposition on polystyrene surfaces. However, only pyrroles which are difficult to chemically polymerize can be used for the preparation of such composite films, and the intrinsic adsorption properties of polypyrroles in the vis−NIR range may prevent some optical applications. On the contrary, sol−gel derived silica films, membranes, and monoliths are inherently suitable for optical applications, and the

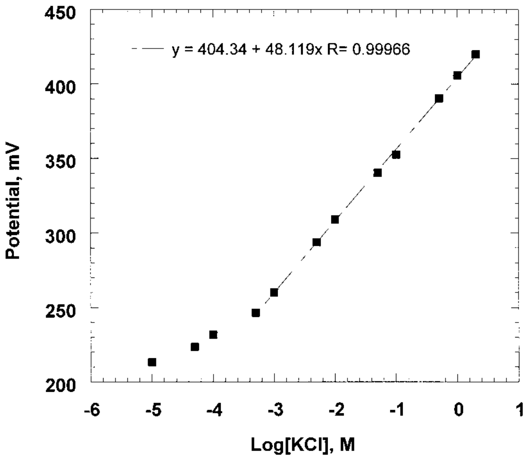

Figure 7. Nernstian response for a potentiometric sensor made from a PB sol−gel composite film on a glassy carbon electrode.

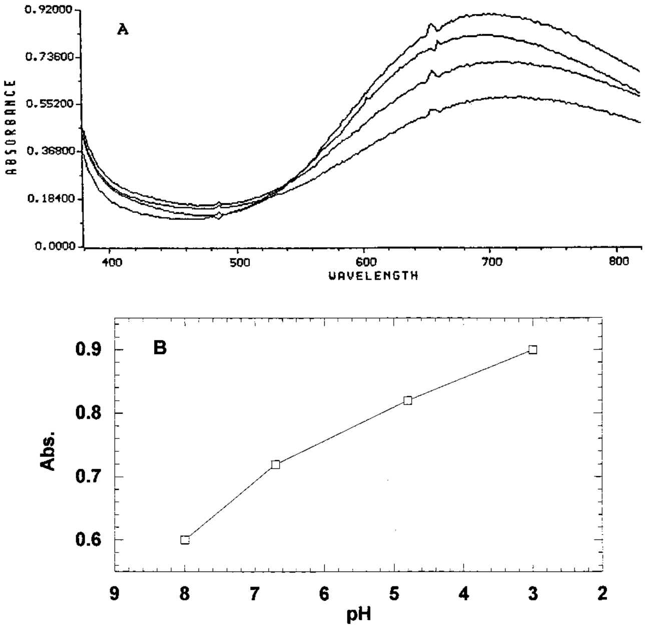

Figure 8. UV−vis spectra (A) of a PB sol−gel composite film deposited on a glass slide in buffers with pH = (a) 3.0, (b) 4.8, (c), 6.66, (d) 8.0 and the corresponding plot (B) of the maximum absorption versus solution pH.

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chemical derivatization to functionalized sol−gel composites is versatile. The feasibility of the PB sol−gel composite thin film deposited on a glass slide surface for optical pH indicator is demonstrated. Figure 8 shows the UV−vis spectra of the PB sol−gel composite film in buffers of pH 3.0, 4.8, 6.66, and 8.0, respectively. It shows that a linear dependence of the maximum absorption on the solution pH can be established within a certain range. The optical response to pH changes of the PB film is reversible in the pH range tested ($3.0 \le \mathrm{pH} \le 9.0$). As proposed,[16] the reversible hydrolysis of PB occurs according to

$$\mathrm{Fe_4[Fe(CN)_6]_3} + 3\mathrm{H_2O} \Leftrightarrow \mathrm{Fe(OH)_3} + 3\mathrm{Fe[Fe(CN)_6]^-} + 3\mathrm{H^+} \quad (3)$$

Conclusion

A novel method for preparing Prussian Blue composite films from functionalized sol−gel materials has been described. Electrochemical, spectroscopical, and microscopical characterization of the PB composite film was done. Applications of the composite film as a potassium ion sensor and optical pH indicator were demonstrated. By combining the facile preparation and unique performance of sol−gel films, this chemical derivatization method provides a new and versatile approach to produce functionalized semiconducting or conducting sol−gel coatings for electronic and magnetic applications.

Acknowledgment. The financial support of DOE-EPSCoR (046138) is greatly appreciated. Special thanks to Eng. Camillo Cagani, at the Research Center for Minority Institutions (RCMI, RP-03051), UPR-Medical Science Campus, and Janet Figueroa, at the Materials Characterization Center, UPR-Río Piedras Campus, for their help with the TEM and FTIR measurements, respectively.

CM9806275