Electrochemical Growth of Polyaniline in Porous Sol−Gel Films

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Tetraethyl orthosilicate (TEOS) derived sol−gel films have been utilized for the electrochemical polymerization of aniline. The presence of electroactive polyaniline (PANI) within the porous skeleton of the TEOS sol−gel films has been confirmed using cyclic voltammetry, UV−visible, infrared spectroscopy, and scanning electron microscopic measurements.

Nanomaterials have recently been a subject of increased interest among chemists, physicists, and material scientists.[1−4] This has been largely due to a variety of potential applications of these interesting new electronic materials such as in microelectronics,[5] biosensors,[6,7] photonics, etc.[8,9] It has been suggested that organic microtubules can perhaps serve as a useful replica of various biological systems.[10] In this context, Martin et al.[11−14] have successfully utilized template synthesis for preparation of polymers, metals, and semiconductors on a nanoscopic scale.

Application of conductive polymers such as polyacetylene, polypyrrole, polythiophene, and polyaniline (PANI) entrapped in a sol−gel matrix has recently been proposed.[15−18] However, ease of synthesis, processability, and environmental stability have led to many interesting applications of PANI such as in drug delivery, biomedical devices,[19,20] and nonlinear optical devices[21] including bioencapsulation.[22] It has been proposed that it is possible to entrap conducting polymers in porous ceramic structures, sol−gel films, alumina, and polycarbonate membranes etc.[23−26] Growth of PANI in a sol−gel film may perhaps lead to its application as a nanoelectrode.

In the present paper, we report systematic studies in relation to the growth of PANI into the TEOS sol−gel matrix obtained on an indium tin oxide (ITO) glass using electrochemical technique. Various experimental techniques such as electrochemical, spectroscopic, optoelectrochemical, and scanning electron microscopy have been used to investigate the presence of PANI in a TEOS-derived sol−gel matrix.

Synthesis of Sol−Gel Films. Stock sol−gel solutions were prepared by mixing 4.5 mL of TEOS (E-Merck) with 1 mL of 0.01 M HCl and 0.4 mL of deionized water (Millipore). The total volume (5.9 mL) was placed in a 10 mL airtight glass container and stirred at room temperature (27 °C) at 600 rpm for about 4 h. A clear solution of the gel was thus obtained. About 0.5 mL of the sol was diluted with methanol (1:3) for obtaining the desired solution. This solution having the desired viscosity was spin-coated (3000 rpm) on an ITO glass plate and heated at about 200 °C for about 10 min. This resulted in the evaporation of methanol leaving behind a thin sol−gel film. The thickness of the sol−gel film was measured using a Talystep (Rank Taylor Hobson) and was found to be about 0.25 μm.

Electroentrapment of PANI in TEOS-Derived Sol−Gel Film. The electroentrapment of PANI on TEOS-derived sol−gel films was carried out electrochemically using a three-electrode setup. The working electrode consisted of an ITO glass plate coated with the TEOS sol−gel film (3.25 cm^2) while a platinum plate (2 cm^2) served as an auxiliary electrode. A silver (Ag) wire was used as the reference electrode. The electrolyte consisted of 1 M HCl containing 0.5 M of triple distilled aniline. The polymerization was carried out in the potentiodynamic mode by cycling the potential from 0.0 to 0.8 V with respect to the reference electrode.

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(1) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.
(2) Narang, U.; Bright, F. V.; Prasad, P. N.; Ramanathan, K.; Kumar, N. D.; Kamalasanan, M. M.; Malhotra, B. D.; Chandra, S. *Anal. Chem.* **1994**, *66*, 3139.
(3) Pool, R. *Science* **1990**, *247*, 1410.
(4) Bate, R. T. *Sci. Am.* **1988**, *258*, 96.
(5) Devoret, M. H.; Esteve, D.; Urbina, C. *Nature* **1992**, *360*, 547.
(6) Parthasarathy, R.; Martin, C. R. *Nature* **1994**, *369*, 298.
(7) Pool, R. 101 Uses for Tiny Tubules. *Science* **1990**, *247*, 1410.
(8) Prasad, P. N. *Proc. SPIE−Int. Soc. Opt. Eng.* **1990**, *1328*, 168.
(9) Prasad, P. N.; Williamsuille, N. Y.; Karasz, F. E.; Amherst, M. A.; Pang, Y. U.S. Patent 5,130,362, 1991.
(10) Tabony, J.; Job, D. *Nature* **1990**, *346*, 448.
(11) Martin, C. R. *Science* **1994**, *266*, 1961.
(12) Martin, C. R.; Van Dyke, L. S.; Cai, Z.; Liang, W. *J. Am. Chem. Soc.* **1990**, *112*, 8976.
(13) Brumlik, C. J.; Menon, V. P.; Martin, C. R. *J. Mater. Res.* **1994**, *9*, 1174.
(14) Martin, C. R.; Parthasarathy, R.; Menon, V. P. *Synth. Met.* **1993**, *55−57*, 1165.
(15) Dunn, B.; Mackenzic, J. D.; Zink, J. I.; Stafsudd, O. M. *Proc. SPIE−Soc. Opt. Eng.* **1990**, *1328*, 172.
(16) Wei, Y.; Yeh, J. M.; Jin, D.; Jia, X.; Wang, J.; Jang, G. W.; Chen, C.; Gumbs, R. W. *Chem. Mater.* **1995**, *7*, 969.
(17) Sanchez, C.; Ribot, F. *New. J. Chem.* **1994**, *18*, 1007.
(18) Sanchez, C.; et al. *Sol-Gel Sci. Technol.* **1994**, *2*, 161.
(19) Ramanathan, K.; Annapoorni, S.; Malhotra, B. D. *Sens. Act., B (Chemical)* **1994**, *21*, 165.
(20) Cooper, J. C.; Hall, E. A. H. *Biosens. Bioelec.* **1992**, *7*, 473.
(21) Mattes, B. R.; Knobbe, E. T.; Fuqua, P. D.; Nishida, F.; Chang, E. W.; Pierce, B. M.; Dunn, B.; Karner, R. B. *Synth. Met.* **1991**, *43*, 3183.
(22) Kumaran, R.; Ram, M. K.; Malhotra, B. D.; Murthy, A. S. N. *Mater. Sci. Eng.*, in press.
(23) Wu, C. G.; Bein, T. *Science* **1994**, *264*, 1757.
(24) Mansouri, J.; Burford, R. P. *J. Membr. Sci.* **1994**, *87*, 23.
(25) Parthasarathy, R. V.; Martin, C. R. *Chem. Mater.* **1994**, *6*, 1627.
(26) Feldheim, D. L.; Elliot, M. *J. Membr. Sci.* **1992**, *70*, 9.

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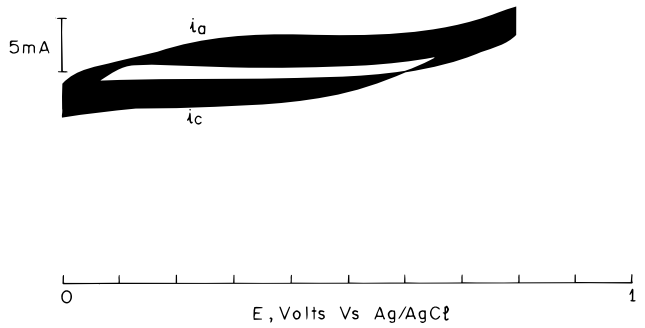

Figure 1. Potentiodynamic growth of PANI in TEOS-derived sol−gel/ITO surface (area = 3.25 cm^2) in the potential region 0.0−0.8 V versus Ag wire at a scan rate = 10 mV s^{-1} for 22 cycles.

The electrochemical polymerization was continued for about 22 cycles until the desired sol−gel films became pale blue.

UV−visible measurements of sol−gel and PANI-entrapped sol−gel films were carried out using a Shimadzu (Model No. 160A) UV−visible double-beam spectrophotometer. Optoelectrochemical measurements were performed in a quartz cuvette with a Teflon holder ITO/sol−gel PANI (0.9 cm^2) and a working electrode (Pt plate). The electrolyte consisted of 1 M HCl solution. Constant potential was applied by a Keithley electrometer (EC 617). In situ UV−visible spectra were recorded by varying the potential from 0.1 to 0.9 V every 3 min at a desired potential. The Fourier transform infrared (FTIR) spectra of the various TEOS sol−gel and the polyaniline entrapped TEOS sol−gel films were recorded using a Nicolet FTIR spectrometer (Model 510P). Morphological studies were carried out using a scanning electron microscope (JEOL, JSM-35).

Figure 1 shows a typical cyclic voltammogram recorded during the electrodeposition of PANI on a 3.25 cm^2 TEOS sol−gel/ITO glass surface. It can be seen that the area under a cyclic voltammogram (CV) increases with increasing number of scans between 0.0 to 0.8 V recorded at 10 mV s^{-1}. However, the redox peaks are not well-defined as one would expect for an electrodynamic growth of PANI on a metallic surface.[27] This peak broadening may be due either to the complex electrochemical processes operating during the diffusion of aniline (0.5 M) into the TEOS sol−gel pores (pore size $\sim$ 500 Å),[28] or to the anchoring of the monomers on the underlying ITO surface (sheet resistance $\sim$ 22Ω), or to the nucleation of PANI along the walls of the TEOS sol−gel pores. Nevertheless, the magnitude of the peak current ($\sim$5 mA) suggests that aniline molecules can easily pass through the porous TEOS network. Since the edges of the sol−gel/ITO films are sealed, the electrodeposition of aniline is unlikely to contribute to the observed CV.

Results of preliminary physical measurements yield the value of bulk density of PANI/TEOS sol−gel matrix as 1.965 g cm^3 in agreement with the value reported in literature.[29] Besides this, the percentage of polyaniline entrapped in TEOS sol−gel matrix has been determined to be about 13.8%.

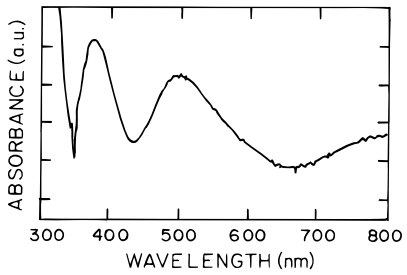

Figure 2. UV−visible spectra of PANI/TEOS derived sol−gel/ITO in the region 300−800 nm after correcting the background signal with the native TEOS derived sol−gel film.

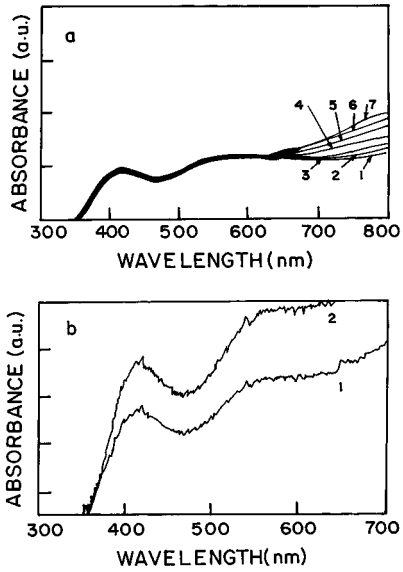

Figure 3. (a) Optoelectronic spectra of PANI/TEOS-derived sol−gel/ITO film in 1 M HCl as a function of applied potential: (1) 0.1−0.3, (2) 0.4, (3) 0.5, (4) 0.6, (5) 0.7, (6) 0.8, and (7) 0.9 V versus platinum wire as pseudoreference electrode. (b) Magnified view of the optoelectronic spectra of PANI/TEOS-derived sol−gel/ITO film in 1 M HCl as a function of applied potential: (1) 0.1 and (2) 0.9 V versus platinum wire as pseudoreference electrode.

To confirm the growth of PANI within TEOS sol−gel films, UV−visible measurements in the region 300−800 nm (Figure 2) were undertaken. The background signal emanating from the native TEOS sol−gel film was corrected from the UV−visible spectrum of the PANI-entrapped sol−gel film. The UV−visible spectrum clearly shows two peaks at 380 and 500 nm, respectively.[30] The presence of these peaks corresponding to the electronic transitions in polyaniline points out the presence of tubules in polyaniline within the TEOS sol−gel network. Any effect resulting due to physisorption of PANI oligomers on TEOS sol−gel film was overcome by repeated washing of the film with HCl (1 M). The value of the bandgap estimated using the $\pi-\pi^*$ transition was found to be 3.2 eV in agreement with the reported value for PANI wires in porous structures.[31] To investigate the effect of an applied electric field on the electronic spectra of PANI tubules, optoelectrical measurements were performed. Figure 3a exhibits the effect of application of voltage (0.1−0.9 V) on the UV−visible spectra of PANI sol−gel films recorded in 1 M

(27) Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 2385.
(28) Braun, S.; Rappoport, S.; Zusman, R.; Avnir, D.; Ottolenghi, M. *Mater. Lett.* **1990**, *10*, 1.
(29) Maeda, S.; Armes, S. P. *Synth. Met.* **1995**, *73*, 151.
(30) Huang, W. S.; MacDiarmid, A. G. *Polymer* **1993**, *34*, 1833.
(31) Boudreaux, D. S.; Chance, R. R.; Wolf, J. F.; Shacklette, L. W.; Bredas, J. L.; Themans, B.; Andre, J. M.; Silbey, R. *J. Chem. Phys.* **1986**, *85*, 4584.

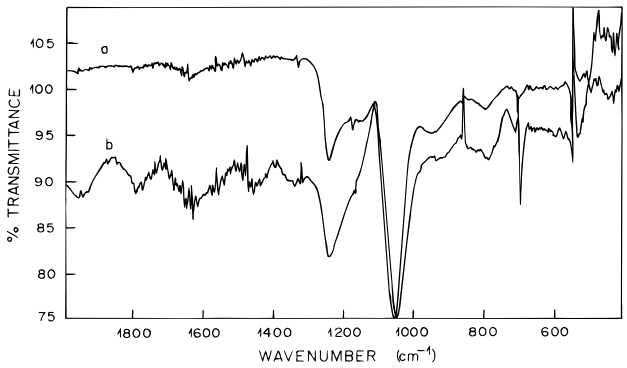

Figure 4. FTIR spectra recorded in the region 1987−406 cm^{-1} at a resolution of 4 cm^{-1} on (a) native TEOS-derived sol−gel film on ITO and (b) PANI/TEOS-derived sol−gel/ITO film in the reflection mode.

HCl medium. It is interesting to see that the 400 nm peak remains unaffected. However, the 500 nm peak shows a distinct shift of about 50 nm toward the higher wavelength. Besides this, the values of the absorbance obtained at 400 and 560 nm peaks show an increase of about 4 units (Figure 3b) when the applied voltage is increased from 0.1 to 0.9 V, respectively, with respect to the reference electrode. As the TEOS sol−gel films are insulating in nature, it appears that the observed effect is perhaps due to the electrical changes occurring within the PANI tubules. From these results it can be tentatively concluded that the PANI tubules are sensitive to the application of a dc field. The value of the dc conductivity obtained using the van der Pauw[32] technique for a given PANI/sol−gel film has been found to be 6.8×10^{-3} S cm^{-1}.

As an additional evidence pertaining to the presence of PANI tubules within the transparent TEOS sol−gel films, FTIR measurements on TEOS sol−gel films and PANI entrapped sol−gel films were carried out in the transmittance mode. The FTIR spectrum of a PANI/TEOS sol−gel film (curve b, Figure 4) shows characteristic peaks at 1600, 1500, and 1300 cm^{-1} assigned to C═C benzenoid, C═C quinonoid and the C−N vibrations, respectively. These peaks are, however, absent in the FTIR spectrum of the native TEOS sol−gel film (curve a). The decreased peak intensity in the FTIR spectrum may however be attributed to the low concentration (13.8%) of PANI tubules within the TEOS sol−gel films. The results of the morphological studies conducted on a TEOS sol−gel film (Figure 5a) show a smooth, homogeneous surface whereas a PANI-entrapped sol−gel film (Figure 5b) exhibits a semigranular texture indicating the presence of PANI in the TEOS sol−gel matrix.

It has been revealed that TEOS derived sol−gel films can be used as nanomaterials for the electrochemical

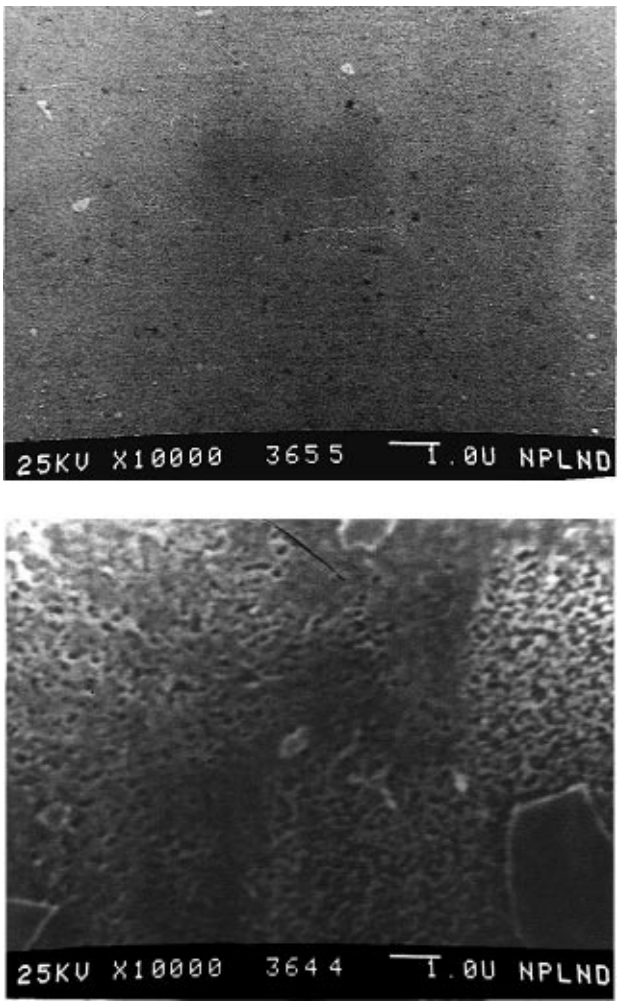

Figure 5. SEM pictures of (a, top) TEOS-derived sol−gel film and (b, bottom) PANI/TEOS derived sol−gel film.

growth of PANI tubules. Keeping these results in view, it should be interesting to carry out detailed studies on the physical measurements such as surface area and pore size distribution of PANI-entrapped TEOS sol−gel films for their potential application as "molecular wires".

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(32) Valdes, A. *Proc. IRE* **1954**, *1954*, 421.