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Synthesis of Chiral Polyaniline Films via Chemical Vapor Phase Polymerization

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Electrically and optically active polyaniline films doped with (1R)-(-)-10-camphorsulfonic acid were successfully deposited on nonconductive substrates via chemical vapor phase polymerization. The above polyaniline/R-camphorsulfonate films were characterized by electrochemical and physical methods, such as cyclic voltammetry (CV), UV-vis spectroscopy, four-point probe conductivity measurement, Raman spectroscopy, circular dichroism spectroscopy, and scanning electron microscopy. The polyaniline films grown by this method not only showed high electrochemical activity, supported by CV and Raman spectrum, but also exhibited optical activity corresponding to the polymer chains as observed by circular dichroism spectra.
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Synthesis of optically active (chiral) conducting polymers has continued to attract considerable attention because of their potential applications in various areas such as electrochemical asymmetric synthesis,[1] electroactive chiral membranes for the separation of enantiomeric chemicals,[2] electrodes for performing bioelectrosynthesis,[3] and microwave absorbents.[4] Among these conducting polymers, polyaniline (PAn) is a unique and promising material due to its stable electrochemical activity, environmental stability, and high conductivity. Further it can be reversibly switched between three different oxidation states, as well as undergo rapid acid-base equilibria.[5]

According to the previous study on chiral polyaniline by Wallace and co-workers, and Kaner and co-workers,[6-9] camphorsulfonic acid (CSA) doped optically active polyaniline salts have been successfully synthesized as films or colloids by electrochemical polymerization and chemical oxidation. However, electrochemical polymerization of chiral polyaniline on conducting substrates is rarely suited for large-scale applications and cannot be used for nonconducting surfaces. Chemical oxidation has a limitation related to the design of the coating process. One way to achieve both polymerization of aniline on nonconducting substrates as well as freedom in the process design is to apply the oxidant by solvent coating on nonconducting substrates and subsequently expose the coated surfaces to monomer vapor, a process that has been coined vapor-phase polymerization (VPP).[10]

In this paper, we report the successful direct deposition of the optically active PAn films onto nonconductive substrates [poly(ethylene terephthalate) (PET) foils and glass slides] doped with (1R)-(-)-10-camphorsulfonic acid (R-CSA) as a chiral dopant through a chemical vapor phase polymerization process. The polyaniline/R-camphorsulfonate (PAn/R-CSA) films were characterized by cyclic voltammetry (CV), Raman spectroscopy, scanning electron microscopy (SEM), UV-visible spectroscopy, four-point probe conductivity measurement and circular dichroism spectroscopy (CD).

Experimental

Aniline (BDH) was distilled and stored below −4°C prior to use. All other chemicals, R-CSA, Aldrich), Fe(III)$Cl_3 \cdot 6H_2O$ (BDH), Fe(III) toluenesulfonate (Fe(III) tosylate) (40% solution in butanol, Baytron C), ethanol (Ajax), butanol (APS), sodium chloride (Sigma), and sulfuric acid (Ajax) were used as received. Glass slides or PET foils were used as substrates for chemical vapor phase polymerization of polyaniline/R-camphorsulfonate (PAn/R-CSA).

Fe(III)(1R)-(-)-10-camphorsulfonate (Fe(III)R-CSA) was prepared according to the following procedure: $FeCl_3 \cdot 6H_2O$ was dissolved with three times the molar amount of R-CSA in butanol. The mixture was heated (90°C) until the solvent was evaporated. Thereafter the Fe(III)R-CSA was redissolved in butanol. This procedure was performed twice to remove HCl the solution. We cannot exclude the possibility that there were traces of HCl remaining in the solution, as it has not been analyzed. But it has not influenced the formation of crystal-free films.

Electrochemical characterization was done using an electrochemical hardware system comprised of an EG&G PAR 363 potentiostat/galvanostat, a MacLab 400 with EChem v 1.3.2 software (ADInstruments), and a PC computer. A three-electrode electrochemical cell was used which comprised a working electrode [PAn/R-CSA modified (by VPP) gold-coated glass electrode ($0.1\ cm^2$)], a platinum mesh auxiliary electrode, and an Ag/AgCl (3 M NaCl) reference electrode with salt bridge.

Scanning electron microscopy (SEM) of polyaniline/R-camphorsulfonate was carried out using a Leica-stereo SS 440 microscope.

UV-visible spectra of polyaniline/R-camphorsulfonate film were obtained using a Shimadzu UV1601 spectrophotometer and scanning over the range of 300–1100 nm.

Circular dichroism (CD) spectra of chiral polyaniline/R-camphorsulfonate were recorded using a Jobin Yvon Dichrograph 6 from 325 to 800 nm.

Raman spectra of polyaniline/R-camphorsulfonate were obtained using a Jobin Yvon HR800 confocal Raman system with 632.8 nm diode laser excitation on 300 lines/mm grating at room temperature.

Results and Discussion

Fe(III)R-CSA (20 wt %) was coated on PET foils from a butanol solution. When the coating was almost dry, the samples were put into an oven at 60°C. After heating for between 30 s and 3 min the color of the coating changed to a darker yellow, indicating that the solvent was evaporated. This procedure eliminated crystal formation in the Fe(III)R-CSA coatings. The samples were then exposed to aniline vapor at room temperature. After 2 h, the samples were removed from the VPP chamber; as the color had changed from yellow to green indicating the formation of polyaniline films. During this polymerization period the Fe(III)R-CSA may well have formed crystal structures, that influence both the formation of optical active polyaniline as well as the smoothness and conductivity of the films.

After another 30 min of drying in air, these PAn modified PET foils or glass slides were washed twice in ethanol for 10 min. Using this method, light green films were obtained with conductivities in the order of 1 S/cm (ranging from 0.6 to 1.8 S/cm). This conduc-

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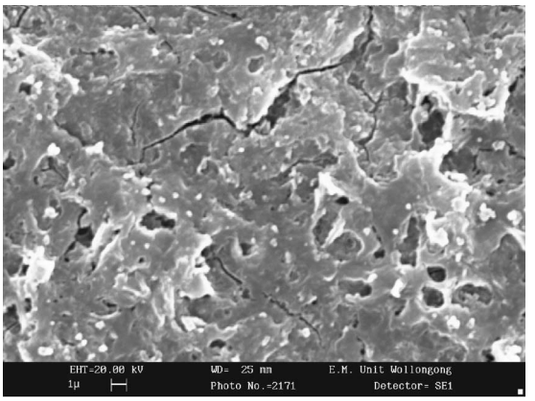

Figure 1. SEM image of PAn/R-CSA film.

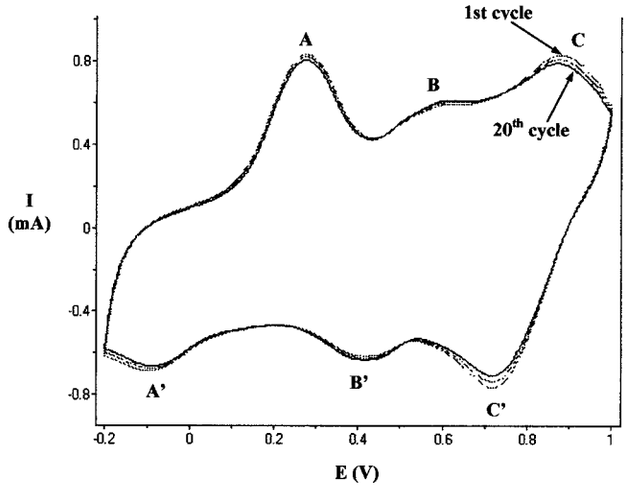

Figure 3. Postpolymerization CVs of PAn/R-CSA film grown by VPP on a gold-coated glass electrode (0.1 cm^2) in 1.0 M H_2SO_4/H_2O. Reference electrode: Ag/AgCl (3 M NaCl). Scan rate: 100 mV s^{-1}.

tivity is at the low end of what has been reported for (nonchiral) polyaniline, which can be possibly due to the synthesis method, VPP. However, as seen from the SEM image of PAn/R-CSA film deposited on quartz slide (Fig. 1), the surface morphology has a noneven, porouslike structure, which may partially explain the lack of conductivity.

Figure 2 presents the Raman spectrum of polyaniline/R-camphorsulfonate (PAn/R-CSA) film grown by VPP, which was taken with 682 nm diode laser excitation on 300 lines/mm grating at room temperature. It displayed a typical Raman spectrum of polyaniline containing bands related to the PAn oxidation state (1000–1700 cm^{-1}) and conformation dependent features (400–900 cm^{-1}).[11-13] This confirms the successful deposition of PAn film on PET foil by VPP. This Raman spectrum confirms that this is the fully oxidized structure of polyaniline.

The cyclic voltammograms (CVs) of PAn/R-CSA in 1 M H_2SO_4/H_2O solution are shown in Fig. 3 for the potential range of −0.2 to +1.0 V, and display three stable redox couples labeled A/A′, B/B′, and C/C′ after 20 cycles. The first redox couple (A/A′) corresponds to the conversion of amine units to radical cations (semiquinones), and the third redox couple (C/C′) is attributed to the conversion of the radical cation into the fully oxidized form of the PAn (complete quinoidal structure).[14] The second (middle) redox couple has been identified as the one belonging to water-soluble degradation products. It can be concluded that a highly electrochemically active PAn film had been deposited successfully on PET foil by the VPP method.

The UV-visible spectrum of PAn/R-CSA film VPP deposited on PET foil is shown in Fig. 4, and displays one optical absorption peak at 350 nm, which is assigned to the $\pi-\pi^*$ transition band of the benzenoid rings of PAn, and other two optical absorption peaks at 430 and 815 nm without the localized peak at 650 nm, which have been interpreted as excitations of valence electrons to the polaron band formed when emeraldine base is doped to the conducting emeraldine salt form.[15] The UV-vis spectrum of this kind of PAn/R-CSA film is consistent with that of PAn/R-CSA in *n*-methyl pyrrolidone (NMP) solution.[16] This again confirms the formation of PAn/R-CSA on PET foil. Thus, it can be concluded that this PAn/R-CSA film formed by VPP deposition is fully doped and optically active.

Further evidence obtained from the CD spectral measurement (Fig. 5) proved again that this kind of PAn/R-CSA film by VPP exhibits optical active properties and is chiral PAn (Fig. 5a), while PAn/tosylate film (using Fe(III) tosylate as oxidant) by VPP does not show any response in the CD spectrum (Fig. 5b). As shown in Fig. 5a, the CD spectrum of PAn/R-CSA film shows three distinctive

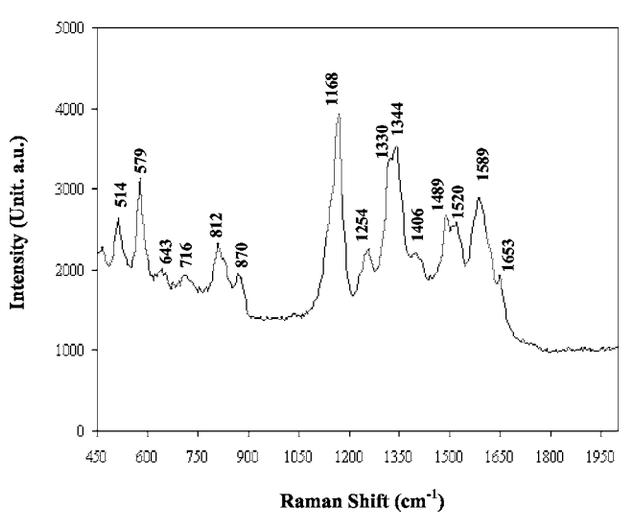

Figure 2. Raman spectrum of PAn/R-CSA film at 632.8 nm diode laser excitation on 300 lines/mm grating at room temperature.

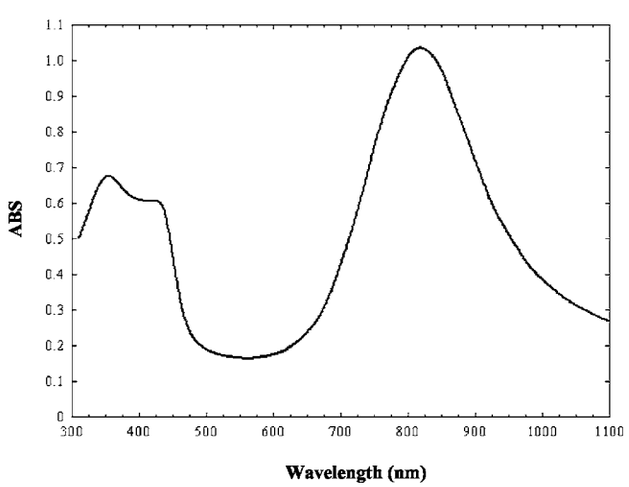

Figure 4. UV-vis spectrum of PAn/R-CSA film grown by VPP on a glass substrate.

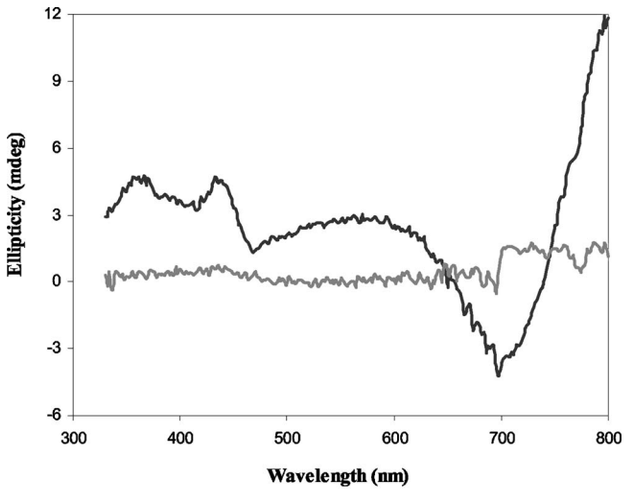

Figure 5. CD spectra of (a) PAn/R-CSA and (b) PAn/tosylate films grown by VPP on a glass substrate.

bands at 365, 440, and 580 nm. This indicates that PAn/R-CSA film formed by VPP has a chiral structure of polymer chains. These visible peaks observed in the CD spectrum are attributed exclusively to optical activity in the polymer chains of PAn/R-CSA film while the incorporated chiral dopant R-CSA does not exhibit any CD band at wavelengths longer than 300 nm. Moreover, the CD bands at 365 and 440 nm may be assigned to the exciton-coupled CD bands associated with the absorption band shown at 430 nm (Fig. 4), while the broad CD band centered at 580 nm is probably due to the exciton-coupled CD band associated with the polaron absorption band at 815 nm (Fig. 4).[17,18] Thus it can be concluded that optically active chiral PAn/R-CSA has been deposited successfully onto nonconductive substrates, PET foil, and glass slides, by chemical VPP. It is believed that the optical activity of chiral PAn arises from the electrostatic binding of the chiral R-CSA$^-$ anions to $-$NH-$^+$ centers along the polymer backbone.[19]

Conclusion

Stable, optically active PAn films can be deposited successfully on conducting and nonconducting substrates via the chemical VPP of aniline using Fe(III)(1R = CSA) as oxidant. According to the post-polymerization CV and CD spectral measurement, these PAn films show very stable electrochemical activity in the acidic environment and also show optical activity. This process has offered a simple route to prepare chiral PAn film with large surface area and stable electrochemical properties readily and efficiently onto different substrates.

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