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Polyelectrolyte templated polyaniline—film morphology and conductivity☆

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Abstract

A simple synthesis protocol for stable aqueous colloidal solutions of poly(4-styrenesulfonate) templated polyaniline is developed. The electrical conductivity and submicro/nano features observed in their spin-coated films are shown to be correlated to the polyelectrolyte template molecular weight. This demonstrates the utility of the latter as a new design element for conducting polymer films.

Keywords: Polyaniline; Polystyrenesulfonate; Film morphology

1. Introduction

Polyaniline (PANI) is one of the most extensively studied materials among the conducting polymers. The reasons for this are manifold. Synthesis of PANI is simple and facile, through chemical as well as electrochemical means [1–5], and the polymer shows a high degree of chemical stability. It is conveniently doped using protons to achieve a wide range of optical characteristics and conductivities [2–10], facilitating applications ranging from sensors to smart windows [2,3]. Recently PANI and its composites have been shown to exhibit several submicro and nano architectures [2,9–12] which have significant impact on the materials attributes. The basic problems of solubility and processability of PANI have been addressed through approaches such as self-doping [6,8,13], choice of different counterions [11,12,14] and templating [8,15–18]. The latter technique employing polyelectrolytes is particularly successful in improving aqueous solubility and hence is significant from the point of view of environmental considerations and processing methodology. It has been suggested that polyelectrolytes serve as nanoreactors during the enzymatic oxidative polymerization of aniline [17]. It is of considerable interest to establish correlations between features of the polyelectrolyte template and the electrical conductivity of the film so that new design strategies can be evolved.

We have developed a simple and convenient protocol for the synthesis of poly(4-styrenesulfonate) (PSS) templated PANI (along similar lines as reported in Ref. [19]) and the fabrication of good quality films by adding trace amounts of polyvinyl alcohol (PVA). Interestingly, the electrical conductivity of the films is found to depend on the template molecular weight. Scanning electron microscopic examination of the films reveals submicro and nano level features, which depend on the molecular weight of the PSS used and the amount of the PVA additive, providing insight into the morphology dependence of the electrical conductivity. Many of the microscopic characterizations of soluble PANI in earlier work were on the colloidal state [18,20] or on bulk powders [11,21]. We have focused attention on the films, which would be of direct relevance to most of the practical applications. Our study highlights the role of the template molecular weight as a design element in the fabrication of conducting PANI.

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2. Experimental

2.1. Synthesis

PANI-PSS was synthesized in aqueous solution by the oxidative polymerization of aniline using ammonium peroxodisulfate and hydrochloric acid in presence of poly(sodium 4-styrenesulfonate) (NaPSS). NaPSS with average molecular weights, 100 and 70 kDa were used; the resulting polymers will be denoted respectively as PANI-PSS-100 and PANI-PSS-70. Aniline was distilled twice under reduced pressure. Ammonium peroxodisulfate, NaPSS (MW = 100 kDa (Acros Organics), 70 kDa (Aldrich Chemical Co.)) and other reagents were used as received. Millipore Milli-Q water (resistance = 18 MΩ) was used in all preparations. 0.42 ml (4.6 mmol) aniline was added to 15 ml of 3 M hydrochloric acid. 2.78 g (13.5 mmol of monomers) of NaPSS dissolved in 13 ml of water was added with continuous stirring over 10–15 min. The entire solution was cooled to 0–5 °C and 1.02 g (4.4 mmol) of ammonium peroxodisulfate dissolved in 8 ml of water was added dropwise over 20–30 min. The solution was stirred for 2.5 h to complete the polymerization. The final solution diluted with water (total weight = 43 g) was subjected to dialysis (dialysis bags with 50 kDa cut-off were boiled with EDTA and $NaHCO_3$ prior to use) with aqueous HCl (pH = 4) changed every 20 min, three times. The dialyzed colloidal solution (weight = 48 g) was centrifuged for 90–120 min with the supernatant water removed and replaced with fresh water three times during this period. 17 g of the colloid was diluted by adding 10 ml of water and sonicated for 15 min. 7 g of the resulting solution was mixed with different weights (0.032, 0.064, 0.096, 0.128 g) of aqueous solutions of PVA (1.13 g PVA dissolved in 10 ml water).

2.2. Characterization

FT-IR spectra were recorded on a Jasco FTIR-5300 spectrophotometer. Samples in the form of KBr pellets were made from vacuum dried PANI-PSS. The spectra of PANI-PSS-100 and PANI-PSS-70 are similar. The peaks at 1561 and 1487 cm^{-1} are characteristic of the C=C stretching vibration of the quinonoid and benzenoid rings respectively. The bands at 1294 and 1238 cm^{-1} correspond to C–H bending vibrations. These peaks are similar to those reported earlier [12]. UV–Vis spectra of the PANI-PSS were recorded on a Shimadzu Model UVPC 3101 Spectrometer. Besides the 355 and 418 nm peaks, the polaron absorptions occur at 820 and 783 nm, respectively for the colloidal solutions of PANI-PSS-100 and PANI-PSS-70. XPS analysis of vacuum dried powders of PANI-PSS-100 and PANI-PSS-70 were carried out on a Kratos Axis 165 Spectrometer with a Mg K_α X-ray source (1253.6 eV). The X-ray power supply was run at 15 kV and 5 mA. The pressure in the analysis chamber during the scans was $\sim 10^{-9}$ Torr. The peak positions are based on calibration with respect to the C1s peak at 284.6 eV. The XPS data and spectra are provided in the Supplementary Information.

2.3. Fabrication of films

Glass plates were cleaned with detergent, high purity water and iso-propyl alcohol and dried in a hot air oven at 90 °C. Typical spinning speeds and times employed for the spin coating are 2000 rpm and 30 s. The coated films were dried under dynamic vacuum for 10 h and then in a hot air oven at 80 °C for 1 h. 1 cm^2 pieces of aluminum foils cleaned by rubbing with acetone and dried in hot air oven were used in place of glass substrates in some of the film fabrication.

2.4. Four-probe conductivity measurement

Four-probe room temperature conductivity measurements were carried out on 15-layer films coated on glass. A Keithly Model 224 Constant Current Source and Keithly Model 175 Multimeter were used. Measurements were carried out either by press contact of equally spaced thin wires or by sublimed aluminum contacts. Ohmic conductivity was observed for currents in the range 1–4 mA.

2.5. Scanning electron microscopy

The film morphology was examined using a Philips XL 30 ESEM Scanning Electron Microscope. Gold coating was provided on the films prior to examination. Though the morphological features are similar for films coated on glass and aluminum foil, the latter ones provided better clarity in general. Hence the micrographs presented are of films coated on aluminum foil substrates. 1-layer film is used for the pure PANI-PSS and 5-layer films for the PANI-PSS/PVA cases. Detection of N and S by EDXS was used to confirm that the features observed were due to PANI-PSS.

3. Results and discussion

Our synthesis protocol yielded PANI in the emeraldine salt form. The polaronic bands of the colloidal solutions and spin coated films of PANI-PSS-70 show peaks at 783 and 706 nm, respectively. Addition of PVA has no effect on the former, but causes a further blue shift to 693 nm in the latter. The blue shift observed on film formation possibly arises due to the rigidification of the polymer chains restricting polaron delocalization to smaller segments, which is further enhanced in the film containing PVA. PANI-PSS-100 similarly shows the band maxima at 820 and 722 nm, respectively in the colloidal solution and film. Once again, PVA addition causes a shift in the film alone, with the peak observed at 694 nm. The red shift observed for the solution and film of PANI-PSS-100 (with respect to PANI-PSS-70) signifies relatively longer conjugated segments with less kinks and defects, most likely facilitated by the formation of longer PANI chains. At present we cannot confirm this through the determination of the PANI molecular weight which is complicated due to the coexistence of the strongly bound polyionic chains in PANI-PSS [19].

Powder samples of PANI-PSS can be obtained by precipitation on addition of acetone or methanol to the colloidal solution or by removal of the water under dynamic vacuum. The dried powder compactions were characterized by XPS analysis; significant data are presented in Table 1. The N(1s) peak is normally deconvoluted into three, with the lowest one at ~399.5 eV assigned to neutral amine/imine sites and the higher ones at >400 eV assigned to protonated N, their exact identities still being a matter of discussion [6,16]. We have deconvoluted the N(1s) peak into two, representing the unprotonated and protonated states (Fig. 1); the relative intensities indicate the extent of protonation of PANI in PANI-PSS-100 and PANI-PSS-70 to be respectively, 0.64 and 0.54. The relatively high values suggest protonation of the imine as well as amine N sites, promoted possibly by the polymeric sulfonic acid template formed from the PSS in the acid medium; it may be noted that even higher protonation levels have been reported for polyaniline–polyelectrolyte complexes [16]. The XPS analysis rules out the presence of Cl but indicates that Na is present in PANI-PSS, implying that SO_3^- groups on the PSS chains are associated with H^+, NH^+ and Na^+. The composition of $SO_3^-H^+$ ($x_{SO_3^-H^+}$) can be inferred from the atomic percentages of sulfur (x_S), all of which exists in the form of SO_3^-, protonated nitrogen (x_{NH^+}) and sodium ions (x_{Na^+}), by imposing the charge balance, $x_S = (x_{SO_3^-H^+} + x_{NH^+} + x_{Na^+})$; the values are presented in Table 1. Based on this, the relative amounts of the amine and sulfonate groups in the protonated state i.e. $x_{NH^+}/x_{SO_3^-H^+}$ can be estimated. Interestingly this ratio appears to be quite similar (~0.8–0.9) in the two polymer samples indicating that the same equilibrium controls the proton distribution in both.

Films of PANI-PSS were fabricated using the colloidal solutions directly or after mixing with small amounts of aqueous PVA solution. Four different blends were prepared containing 0.046, 0.092, 0.138 and 0.184 wt% of PVA. The PVA addition makes the colloids stable for several months. The colloids are spin coated to form films. PANI-PSS without PVA additive does not coat well beyond a single layer. Interestingly, addition of the trace amount (~0.05 wt%) of PVA vastly improves the film quality and facilitates fabrication of multiple coatings; different number of layers were spin coated on glass or aluminum foil substrates. The films are quite uniform, as revealed by the smooth scaling of the film thickness (determined by viewing the film cross-section in an SEM) with the number of layers. We find that the average thickness of a single layer is ~270 nm.

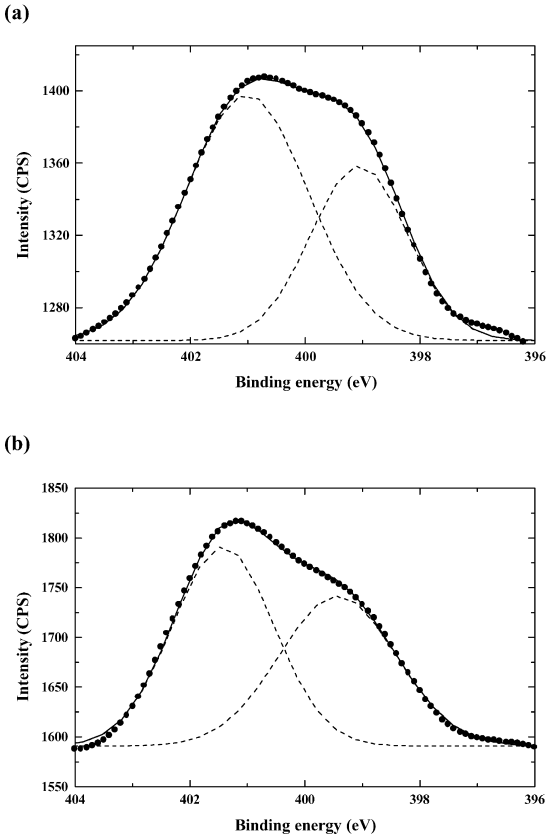

Fig. 1. The N(1s) peaks in the XPS spectrum of (a) PANI-PSS-100 and (b) PANI-PSS-70; the smoothed experimental data (●), the fit using multiple Gaussian functions (—) and the deconvolution (- - -) are shown.

PANI-PSS without any PVA additive where only single layers could be coated, showed high resistance; therefore conductivity could not be measured reliably. However, four-probe conductivity measurements could be carried out on thicker films (15 layers on glass) of PANI-PSS containing different amounts of PVA. The conductivity changes very little with the PVA composition in the case of PANI-PSS-100 and even less in PANI-PSS-70 (Table 2). This is

Table 1
Selected XPS data for PANI-PSS films

Sample	Peak/eV [atom %]				Protonation level of N	Atom % $SO_3^-H^+$
	S	N	NH^+	Na^+		
PANI-PSS-100	168.37 [8.20]	399.06 [0.93]	401.02 [1.66]	1071.23 [4.70]	0.64	1.84
PANI-PSS-70	168.04 [7.40]	399.43 [1.50]	401.42 [1.72]	1071.04 [3.44]	0.54	2.24

Table 2
Four-probe room temperature conductivity of PANI-PSS films containing different amounts of PVA additive

Weight % of PVA	σ (10^{-2} S cm^{-1})	
	PANI-PSS-100	PANI-PSS-70
0.046	8.3	4.5
0.092	8.3	3.6
0.138	9.1	3.6
0.184	12.5	3.7

primarily due to the fact that the quantity of PVA added is very small. It is also consistent with observations that conducting polymers manifest self-assembly leading to little interference to the conducting pathways from the electrically insulating additive [5,17]. The more significant observation presented in Table 2 is the sensitivity of the film conductivity to the molecular weight of the template polyelectrolyte; the higher molecular weight PSS leads to improved conductivity in the film. Together with the shift of the polaronic band with the molecular weight of the template noted earlier, this observation suggests that the polyelectrolyte acts as a nanoreactor template, controlling the polymerization process [17]; the longer PSS chains promote the formation of more extended and possibly better aligned PANI chains.

We have examined the morphology of the films to gain insight into its influence on the conductivity. Fig. 2 shows scanning electron microscope pictures of PANI-PSS-100. The influence of PVA addition is clearly visible. The morphology is nearly circular disc-like in the absence of PVA (Fig. 2(a)); the packing density is low since, as noted earlier, a single layer alone is coated. The shape resembles those observed in similar instances reported earlier [18] and the diameter is approximately 250–350 nm. It turns into a distinct rod shape when 0.09 wt% of PVA is added (Fig. 2(c)). At this stage the rods are typically 80–100 nm wide and 220–400 nm long. As the PVA content is increased the rod length goes up to ~1 µm with small increase in the average width (Fig. 2(d)). However the packing density is reduced at higher PVA content. The morphology of the PANI-PSS-70 are shown in Fig. 3. The trends with PVA

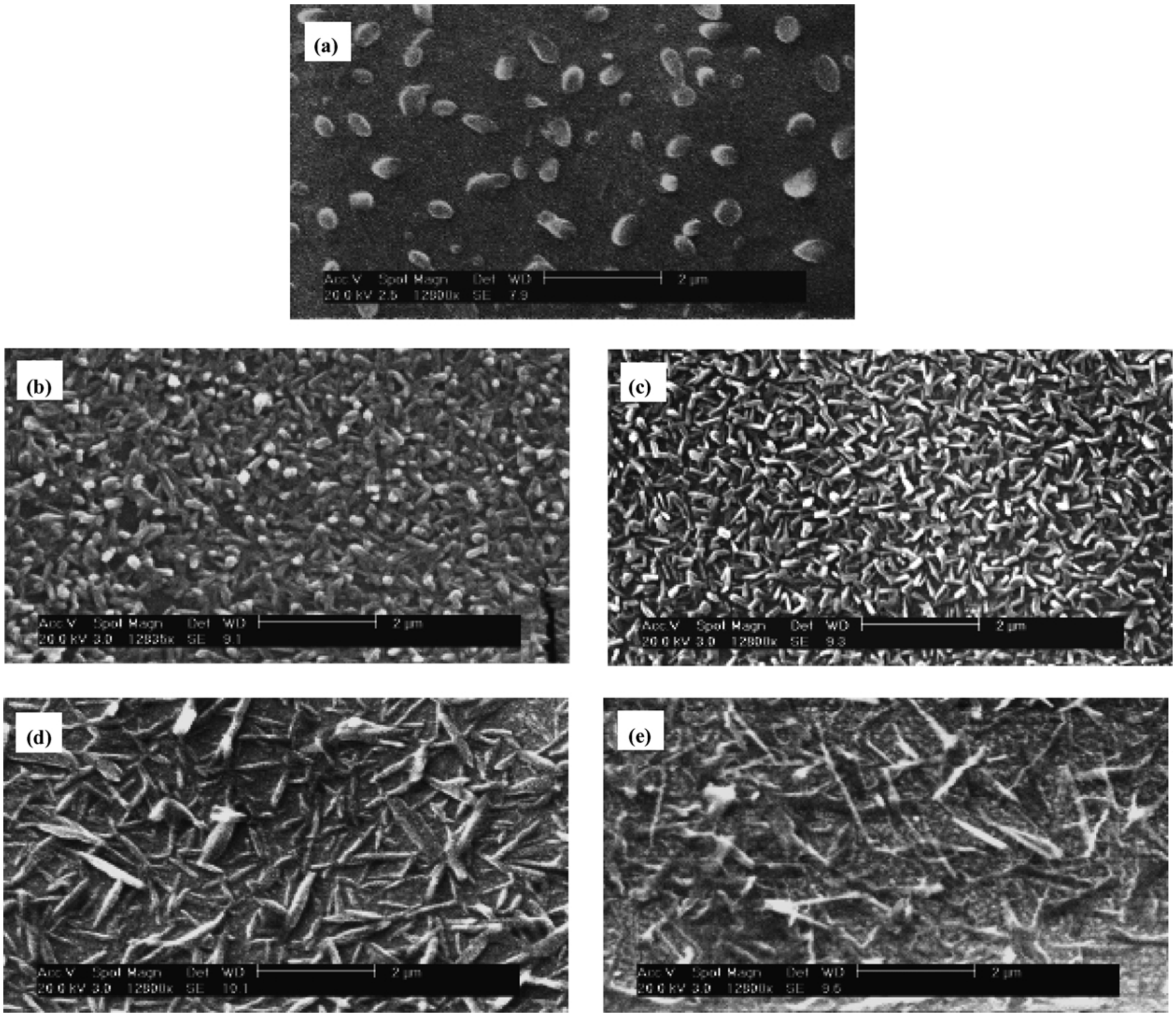

Fig. 2. Scanning electron micrographs of PANI-PSS-100 containing (a) 0.000, (b) 0.046, (c) 0.092, (d) 0.138 and (e) 0.184 wt% of PVA additive.

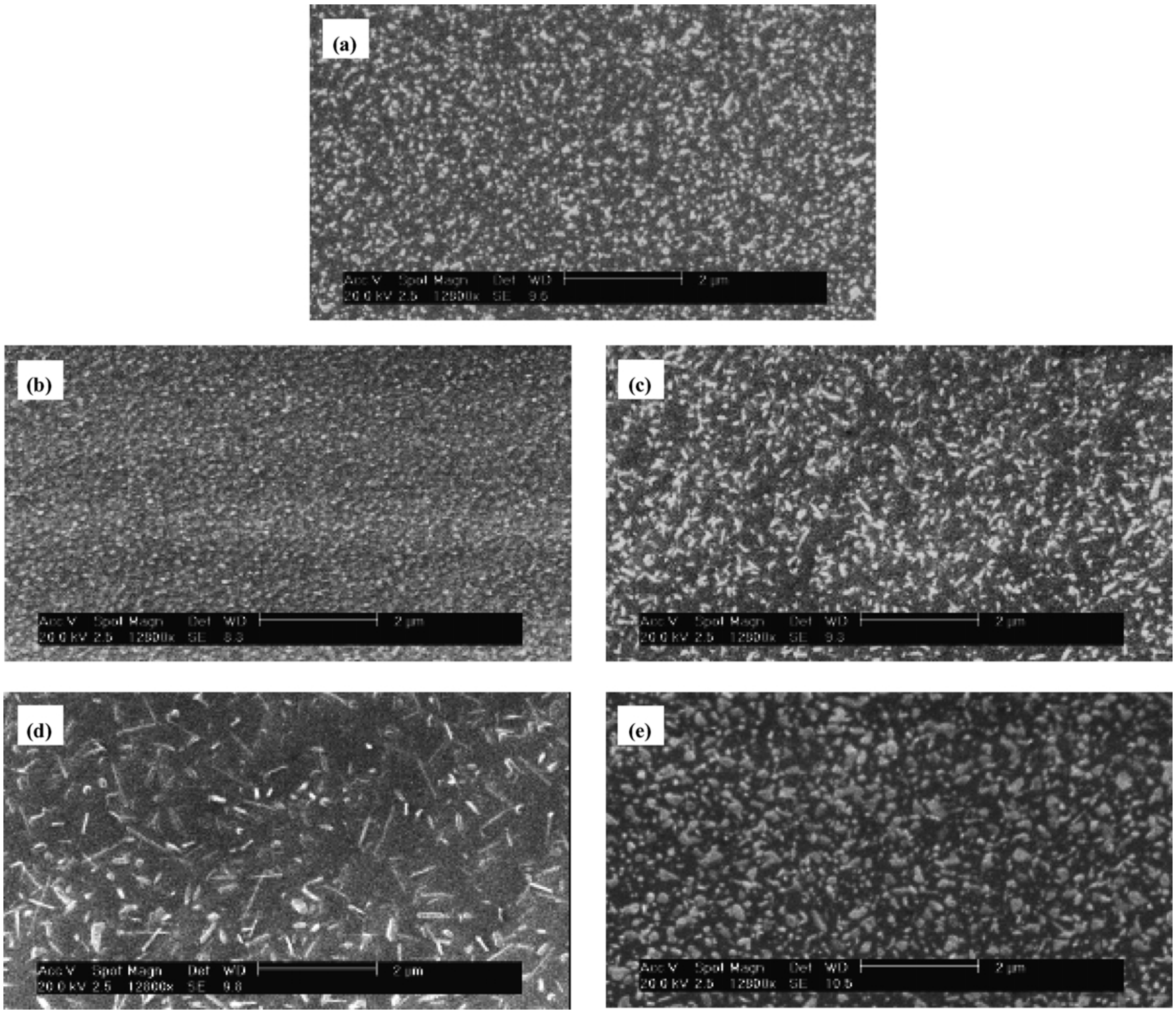

Fig. 3. Scanning electron micrographs of PANI-PSS-70 containing (a) 0.000, (b) 0.046, (c) 0.092, (d) 0.138 and (e) 0.184 wt% of PVA additive.

addition are similar to those in the previous set, though less dramatic. More significantly the sizes of the different features are distinctly smaller. For example, the discs in Fig. 3(a) show average diameters of 30–60 nm and the rods in the case of films with 0.09 wt% of PVA (Fig. 3(c)) are typically 55–70 nm wide and 120–300 nm long. The former are slightly larger than the sizes reported earlier for PANI-PSS [19]. At the highest PVA content, a mixture of rods and discs are observed.

It is instructive to analyze the possible role of PVA in the morphology changes and its impact on the conductivity of the PANI-PSS films. In view of its extremely small mol ratio with respect to PANI-PSS, PVA is likely to be engaged only in some surface level molecular interactions with PANI-PSS aggregates. Such a picture is consistent with its stabilizing influence on the PANI-PSS colloid and further suggests that the assembly of the aggregate structures observed in the spin-coated films may be initiated in the colloidal state itself. The H-bond interactions between PVA and PANI/PSS chains at the periphery of the aggregates, possibly promotes an organized assembly leading to the rod-like morphology which becomes more prominent with increasing PVA content. The conductivity does not show any strong dependence on the percentage of PVA, which may be understood in terms of the simultaneous increase in the size of particles and decrease in their packing density. The slightly higher sensitivity of the conductivity in the case of PANI-PSS-100 compared to PANI-PSS-70 is consistent with the larger morphology changes in the former, noted above. Compared to PANI-PSS-70, the extent of protonation in PANI-PSS-100 deviates more from the optimal 0.50. In spite of this the latter shows higher conductivity, which appears to result from the larger size of the features observed in these films. We infer that the longer PSS chains promote the growth of more extended PANI chains, eventually leading to larger structures in the spin-coated films.

4. Conclusions

The synthesis protocol we have developed allows the preparation of stable colloidal solutions of PANI using the environmentally friendly aqueous route and the formation of good quality polyelectrolyte templated PANI films. The morphological characterization reveals interesting features at the submicro and nano levels and their sensitive dependence on the amount of the PVA additive. The investigation also reveals the correlation between the morphology and the electrical conductivity of the films. Preliminary studies in our laboratory suggest that these PANI-PSS films exhibit sensitive and fast resistivity change responses to the presence of ammonia vapors. Their sensor characteristics are currently under exploration.

5. Supplementary Information

XPS data and spectra for PANI-PSS (2 pages).

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