



Electrochemical synthesis of nanosize polyaniline from aqueous surfactant solutions

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ABSTRACT

Electrochemical polymerization of aniline was carried out in micellar solutions of camphor sulphonic acid (CSA, anionic surfactant), cetyltrimethylammonium bromide (CTAB, cationic surfactant) and TritonX 100 (Tx100, nonionic surfactant), to reveal the morphology against the nature of the surfactant molecule. The resultant polyaniline film was characterized by Fourier transform infrared (FTIR) spectroscopic and cyclic voltammetric techniques. The surface morphology observed from different surfactant molecules was found to be distinctly different. Polyaniline synthesized from CSA and Tx100 solutions, showed uniform nanosized (100 nm) globular structures.

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1. Introduction

Conducting polymers (CPs) are the important class of materials for the semiconducting and optoelectronic properties [1]. Among the CPs, polyaniline (PANI) is an interesting member since it possesses high environmental stability, ease of preparation, tunable electrical properties and relatively low cost. PANI finds great application in many areas, such as organic conductors, actuators, electromagnetic shielding, light-emitting diodes, coatings and gas-separation membranes [2–5]. PANI nanostructures have been synthesized using various strategies including template assisted, surfactant assisted, phase transfer at interface, etc. Among the available methods, the surfactant assisted synthesis resulted in a controlled morphology of different nanostructures, where the conductivity mainly depends on the surface morphology [6–8]. Relationship between electrical conductivity and phase morphology of polyaniline proved to be inter-dependable and the conductivity might be tunable with the morphology. In the recent past, nanofibrillar morphology was reported for PANI, synthesized by surfactant assisted chemical oxidative polymerization of aniline in dilute aqueous organic acids [9]. Various chemical methods employing “soft templates” such as surfactants [10] that assist in the self-assembly of the PANI nanostructures, and “hard templates” such as porous membranes [11] have been reported.

Polyaniline granules and nanotubes were suspended in solutions of silver nitrate in 1 M nitric acid. The resulting polyaniline–silver composites were reported to have conductivities ranging from 9.3×10^{-5} to 33.2 S cm^{-1} [12]. Stejskal et al. have prepared self-doped polyaniline nanofibers with the diameter of 60–70 nm, and

length up to several micrometers using cetyltrimethylammonium bromide as structure directing agent [13]. The oriented PANI flake arrays are expected to be useful in electrical, optical and electrochemical devices [14]. Self-assembled polyaniline nanorods are reported to be synthesized by facile route of dispersion polymerization [15]. The nanofiber product also shows not only a long nanosized fibril structure with average diameter of $\sim 50 \text{ nm}$ and length of $\sim 4 \mu\text{m}$ but also high crystallinity. It was observed that the nanofibers synthesized using the two oxidants give both high electrical conductivity and high crystallinity compared to polyaniline synthesized using commonly known ammonium peroxydisulfate oxidant [16]. Synthesis of polyaniline/Ag composite nanospheres through UV rays irradiation method [17]. Decrease in the pH of the sub-phase of LB trough increases level of doping (protonation) of polyaniline emeraldine base to emeraldine salt and causes doping induced nanostructure formation [18]. A new post-synthetic method for producing different nanostructures of PANI, especially nanofibers and nano-particles of varying doping (oxidation) states, by simultaneous doping and electro-deposition from electrolyte solutions of undoped PANI (emeraldine bases) and p-toluenesulphonic acid using constant applied voltage and varying deposition time was reported [19]. In this present work, PANI was electrochemically synthesized in the presence of anionic, cationic and nonionic surfactants. This study is carried out to probe the effect of various micellar environments on the morphological behaviour of the PANI film.

2. Experimental

Aniline [E. Merck] was distilled prior to use. Analytical grade (99% pure) reagents such as cetyltrimethylammonium bromide (CTAB) [E. Merck] and TritonX 100 [Aldrich], camphor sulfonic acid (R-CSA) [Aldrich], perchloric acid [E. Merck] were used as received.

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PANI films were electrochemically deposited on glassy carbon electrode or indium tin oxide glass by potentiodynamic cycles between -0.2 and 1.2 V (versus SCE) at 0.1 V/s from 0.1 M aniline in 0.1 M perchloric acid with the addition of different surfactants. In all the cases the films were grown by five cycles until a polymerization charges of about 5 mC cm^{-2} was reached. After five cycles, the films were rinsed with purified water.

The cyclic voltammetric experiments were performed using a CHI 760C potentiostat (CH Instruments, USA). Electroactivities of the films were studied through cyclic voltammetric scans at 50 mVs^{-1} in 0.1 M perchloric acid.

The measurement of the resistance of PANI film was carried out using a four probe Keithley 614 voltmeter constant-current source system. FTIR spectra were recorded using FTIR spectrometer (Thermo Nicolet Model 670) equipped with a DTGS detector. All spectra were collected for 256 interferograms at a resolution of 4 cm^{-1} . PANI films (coated on ITO glass substrates supplied by Donnelly Corp., USA) were characterized by PicoSPM Atomic Force Microscopy (Molecular Imaging, USA) operated in contact mode. A gold coated SiN_3 cantilever (Force Constant 0.12 N/m) was used as the force sensor and the radius of curvature of the probe tip was about $5\text{--}10 \text{ nm}$. The measurement was made with the "small" 6 mm piezoelectric z-scanner, which was standardized using calibration gratings supplied by M/s Molecular Imaging.

3. Results and discussion

Fig. 1 shows the AFM images of PANI electrochemically deposited from a solution containing perchloric acid in the presence of different surfactant molecules. PANI deposited from a solution containing surfactant molecule shows nanostructures in contrast to the bulk polymeric mass obtained in the absence of surfactants. The as prepared PANI films are globular in nature with a size of 100 nm and it is found to be uniformly distributed within the film. This nano effect results in the resistivity of the film in which the resistivity of the film was measured using a four pin resistivity meter. The film which was deposited from a surfactant solution shows less resistivity.

The conductivity of the different PANI is given as $\text{CSA} = \text{TritonX} 100 < \text{CTAB} < \text{PANI}$.

When aniline was polymerized in the presence of different surfactants, depending on the nature of the surfactant, the surface morphology differed. In the presence of a neutral and anionic molecule, smooth globular structure with a globule size of approx. $0.2 \mu\text{m}$ was observed. In the presence of a cationic molecule, the structure greatly differed. It was earlier reported by Giz et al. [6] that those different sizes of the cationic and chemical nature resulted in different globular morphology. It was observed that anionic and neutral surfactant solutions favoured nanostructure morphology [20].

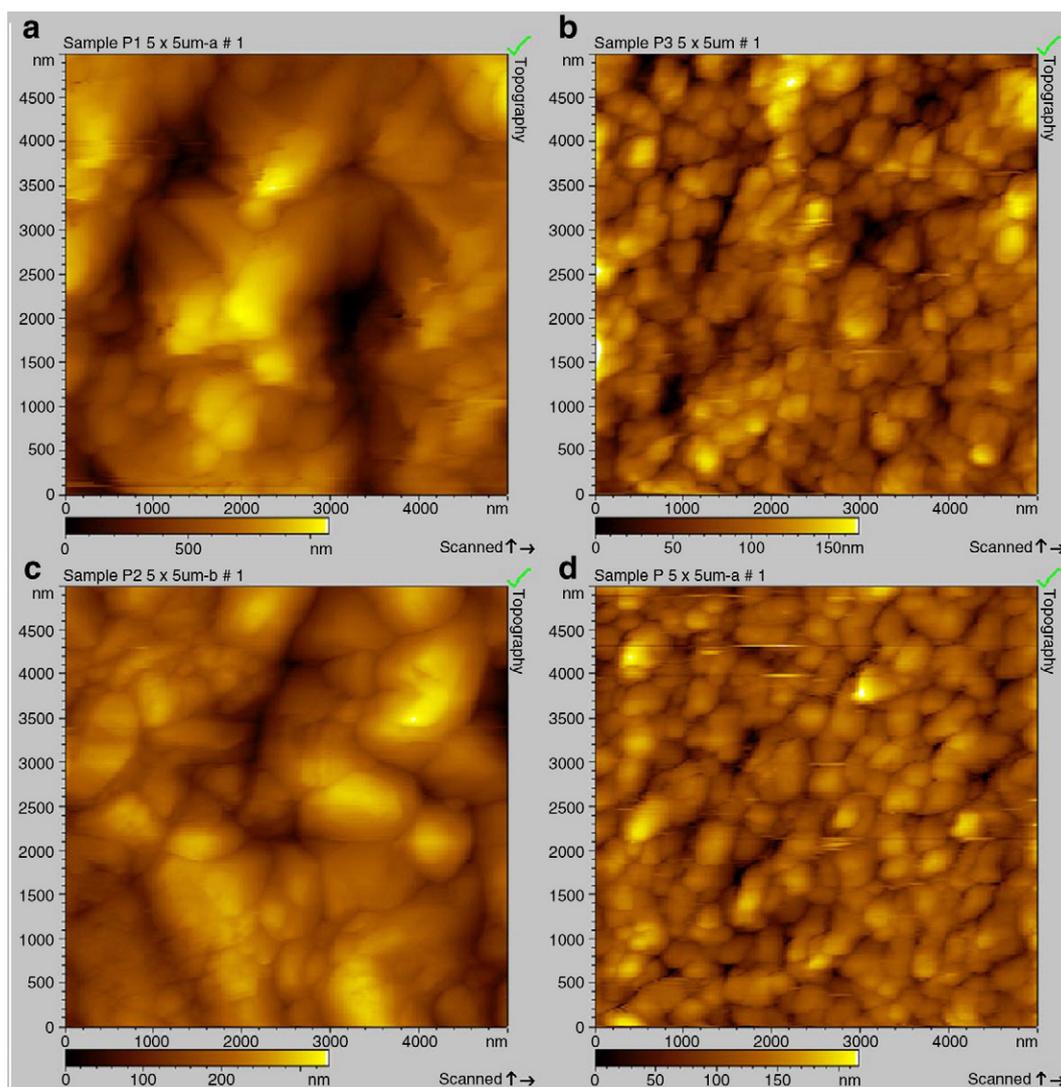


Fig. 1. Atomic force microscopy images of PANI films deposited with (a) perchloric acid, (b) perchloric acid + CSA, (c) perchloric acid + CTAB and (d) perchloric acid + TritonX 100.

Fig. 2 shows the FTIR spectra of PANI deposited from different surfactant solutions in the region from 2000 to 400 cm^{-1} . The bands at around 1600 and 1500 cm^{-1} are due to quinone and benzene ring deformation, respectively, and the band at 1310 cm^{-1} is assigned to C–N stretching of a secondary aromatic amine. The two bands become visible at 1030 and 1000 cm^{-1} and are due to the asymmetric and symmetric stretching of SO_3^- , indicating the presence of SDBS in the sample. These results are in good agreement with the previous spectroscopic characterization of polyaniline [21].

The oxidation level of PANI is qualitatively estimated by the intensity ratio of the IR absorption peaks for quinoid ring stretching around 1600 cm^{-1} and for benzenoid ring stretching at 1500 cm^{-1} . The FTIR spectrum of the base form of (Fig. 2a) shows that the relative intensity of benzenoid ring stretching at 1493 cm^{-1} is higher than that of the quinoid ring stretching vibration at 1584 cm^{-1} . The value of the imine-to-amine ratio, calculated from the FTIR data, is between 0.4 and 0.5, whereas the ratio is between 0.9 and 1.0 for PEB. These facts indicate that the synthesized PANI films exist in an oxidation state lower than PEB.

The characteristic absorption bands of PANI appear at 1293 and 1569 cm^{-1} , corresponding to the stretching mode of C–N and CN bands affirming the presence of leucoemeraldine and pernigraniline components [22].

The electrochemical properties of the polyaniline are characterized by cyclic voltammetry. Fig. 3 shows the cyclic voltammograms (CV) of the films of (a) PANI, with CSA and TX100 shows only one set of broad redox peaks at $E_{1/2}$ 0.50 V. This redox peak corresponds to the transformation of polyaniline from protonated emeraldine to pernigraniline. In the case of CTAB assisted polymerization, it shows another set of peak corresponding to leuco emeraldine to protonated emeraldine then to pernigraniline form. This was quite similar to that of PANI doped with common protonic acid.

Thus, it is interesting to note that the cationic surfactant induces the formation of leucoemeraldine form whereas the other type of surfactant induces the formation of protonated emeraldine form of PANI with different microstructures.

4. Conclusion

In this study, we have demonstrated that various polyaniline nanostructures could be synthesized by varying the micellar environ-

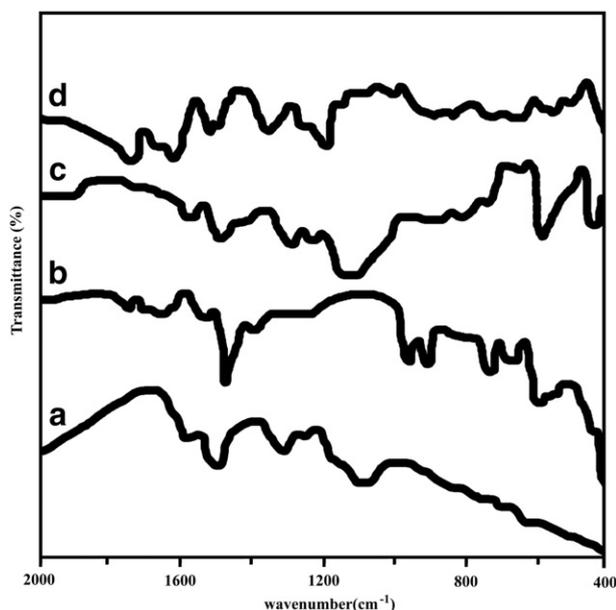


Fig. 2. FTIR spectrum of polyaniline films deposited with (a) perchloric acid, (b) perchloric acid + CSA, (c) perchloric acid + CTAB and (d) perchloric acid + TritonX 100.

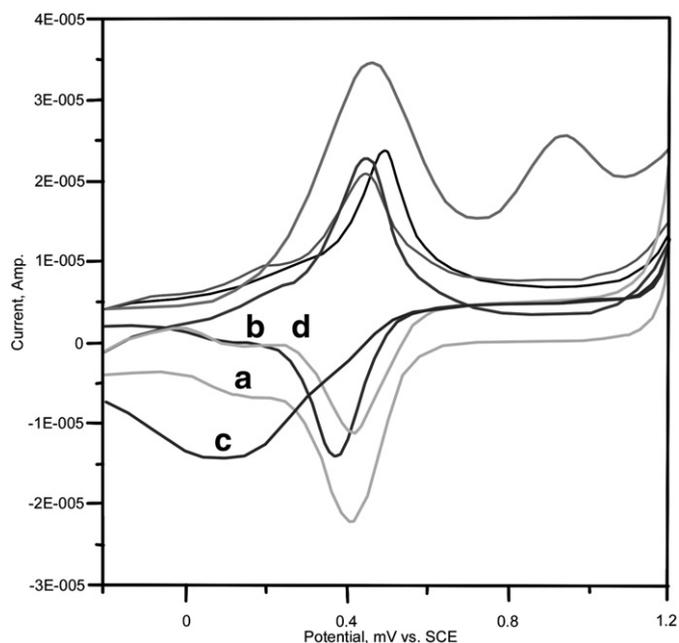


Fig. 3. Cyclic voltammetric behaviour of polyaniline films deposited with (a) perchloric acid, (b) perchloric acid + CSA, (c) perchloric acid + CTAB and (d) perchloric acid + TritonX 100.

ments during the electrochemical polymerization. Further it is interesting to note that the resistivity of the film is also tunable with the deposition environment. It was also found that the morphology, chemical structure and electrical properties depend on the polymerization conditions. The present method may be a simpler, less expensive and more convenient route to synthesize PANI nanostructures with tunable electrical properties.

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