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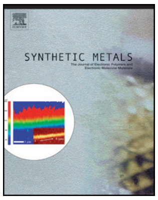

Water soluble polyaniline coated electrode: A simple and nimble electrochemical approach for ascorbic acid detection

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ABSTRACT

We report the design, synthesis, electrochemical stability and electrocatalytic applications of a new kind of water soluble polyaniline (PANI) composite. These water soluble PANI composites are extremely important in electrochemical sensor, semiconducting devices, light-emitting diodes, ultra-thin and flexible display devices, photoconductive sensors, and new fluorescent bio-probes. In the present work, we have prepared water soluble PANI using our designed and synthesized perylene disulphonic acid (PRSA) dopant. This PRSA dopant is a new and superior doping acid for synthesis of water soluble PANI. The PRSA/PANI composite prepared with it exhibits good electrochemical stability and superior electrocatalytic activity. It can sense ascorbic acid, a very important biomolecule, in neutral pH up to mM concentration level at the low electrochemical oxidation potential. Additionally, the modified electrode prepared from aqueous medium of PANI on ITO glass, is reusable and requires only a water rinsing and drying cycle in between measurements. PRSA/PANI composites also show a good semiconducting behavior and follow 1D-VRH (variable range hopping) electron transportation mechanism. The importance and novelty of this method are (i) synthesis of water soluble PANI by 'in-situ' polymerization method, which overcome the major and common problem of PANI processability in water; (ii) high performance electrocatalytic activity and reusability of PANI coated electrode. It also overcomes the electrochemical drawback of PANI synthesis, i.e. low yield, cost effective, limited processabilty etc.

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1. Introduction

L-Ascorbic acid (AA, vitamin C) is the major antioxidant found in many organisms. It is a necessary nutrient which is extensively used as an antioxidant negotiator in foods, beverages and pharmaceutical applications, due to its major participation in several human metabolic reactions [1–4]. So, it is very important to find a method for quantification of ascorbic acid. One possible way is the oxidation of ascorbate ion from ascorbic acid in an electrochemical set-up. However, high potentials are required for the initiation of this reaction using conventional electrodes. Several attempts have been also tried to find chemically and electrochemically modified electrodes showing better electrocatalytic activity and stability with respect to ascorbate oxidation [5].

Polyaniline (PANI), the most important conducting polymer among the conducting polymer family, is used as active component of microelectronics, OLED, optical display, for anticorrosive protection, in bioanalysis, etc. because of its good electrical and optical properties as well as high environmental stability [6]. Due to the poor solubility of PANI in common solvents, coveted technological applications are not seen. So making the water soluble PANI is tremendous interest during the recent years for good application [7,8], particularly in the biological environment.

Usually, acidic condition ($\text{pH} > 4$) is required for the formation of the highly conducting form of PANI (ES) and it seriously restricts its applications in bioelectrochemistry, which normally desires a neutral pH environment. The electroactivity and conductivity of the PANI films in neutral aqueous solutions make them appropriate for catalysis and biotechnology-purpose applications [9,10].

Use of conducting polymer (CP) coated electrode for the purpose of AA oxidation has been investigated since 1989. Conducting polymer and metal binded polymer prepared electrochemically are generally utilized for AA oxidation [11]. However, several problems in electrochemical synthesis of polyaniline are the (i) low yield, that is why it is difficult to characterize and it limits application (ii) costing of such electrodes and (iii) the charge transfer reaction that causes a change in the total number of π-electrons on the conjugated PANI chain and thereby renders its conductivity [12].

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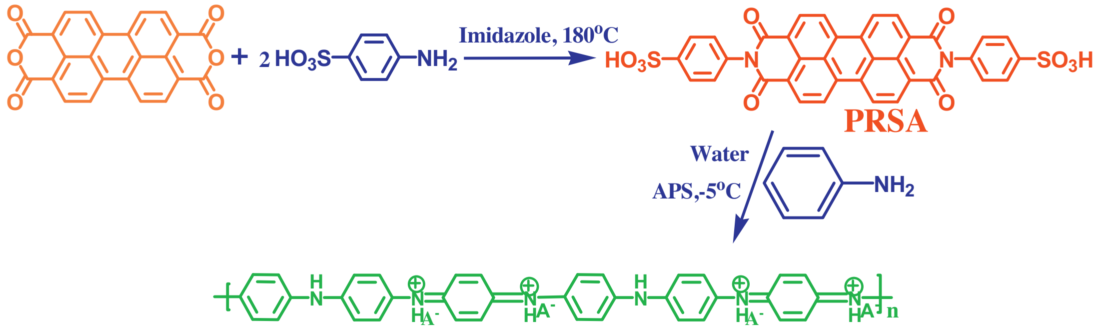

Fig. 1. Schematic presentation of PRSA/PANI synthesis.

In most cases, the PANI film is directly deposited onto the surface of the working electrode at the time of eletropolymerization. The resultant film is integrated and compacted with the surface of working electrode. So, it is very difficult to peel an integrated film off the working electrode. Externally prepared composite film may be helpful for overcoming it [13,14].

We report here a new as well as simple strategy for determination of ascorbic acid using modified PANI electrode prepared by a very quick and simple drop-coating method. Water soluble PRSA/PANI composites have been synthesized in water from the mixture of aniline, PRSA (1:100) and ammonium peroxydisulphate (1:1) by dilute polymerization method. The dilute polymerization is very important for *in-situ* preparation method because the dilute polymer solutions control nucleation and growths resulting good crystallization properties [15,16]. At the initial phase of polymerization, small amount of aniline will be protonated by dopant PRSA slowly to form anilinium ion that can interact with peroxodisulphate to form both monoanilinium peroxydisulphate and dianilinium peroxydisulphate. These anilinium peroxydisulphates convert to anilinium cation-radical to generate the H_2SO_4. As a result, in the reaction medium, the pH of the medium decreases and it proceeds the reaction faster [17–20].

The synthesized nanocomposites are easily dispersed in aqueous media. Aqueous solution (5 μL) has been drop casted on an indium tin oxide (ITO) coated glass slide to prepare PRSA/PANI/ITO electrode [21,22]. After drying in air at room temperature, it has been used as a working electrode for AA oxidation in neutral pH solution. The importance of dopant PRSA in the composite are (i) fluorescence due to the presence of fluorophoric aromatic perylene ring, (ii) the composite is water soluble due to the presence of $–SO_3H$ groups in dopant PRSA and (iii) enhancement of crystallinity, thermal stability etc.

2. Experimental

2.1. Materials

Aniline monomer (Merck Chemicals) was distilled under reduced pressure. Ammonium persulphate $(NH_4)_2S_2O_8$, (APS, Rankem chemicals) as a radical oxidant for PANI and Perylene tetracarboxylic acid-3,4,9,10-dianhydride (PDA) were purchased from Aldrich. Sulphanilic acid, phosphate buffer tablet were purchased from Merck Chemicals. All aqueous solutions were prepared in membrane filtered (Millipore Milli-*Q* system) water of resistivity 18 MΩ cm.

2.2. Synthesis

2.2.1. Synthesis of N,N′-bis(4-benzosulphonic acid)perylene-3,4,9,10-tetracarboxylbisimide (PRSA)

Perylene tetracarboxylic acid-3,4,9,10-dianhydride (2 g, 5.1 mmol), sulphanilic acid (2.6 g, 15.2 mmol), 350 mg of zinc acetate (2.2 mmol), and 15 g of imidazole were taken in round-bottom flask. The reaction mixture was refluxed at 170 °C for 4 h in inert atmosphere. After being cooled at room temperature, it was added to 50 mL of ethanol two times, refluxed and decanted at 80 °C to remove the imidazole from the mixture. The precipitate was collected by filtration. After drying in vacuum, it afforded 3.2 g

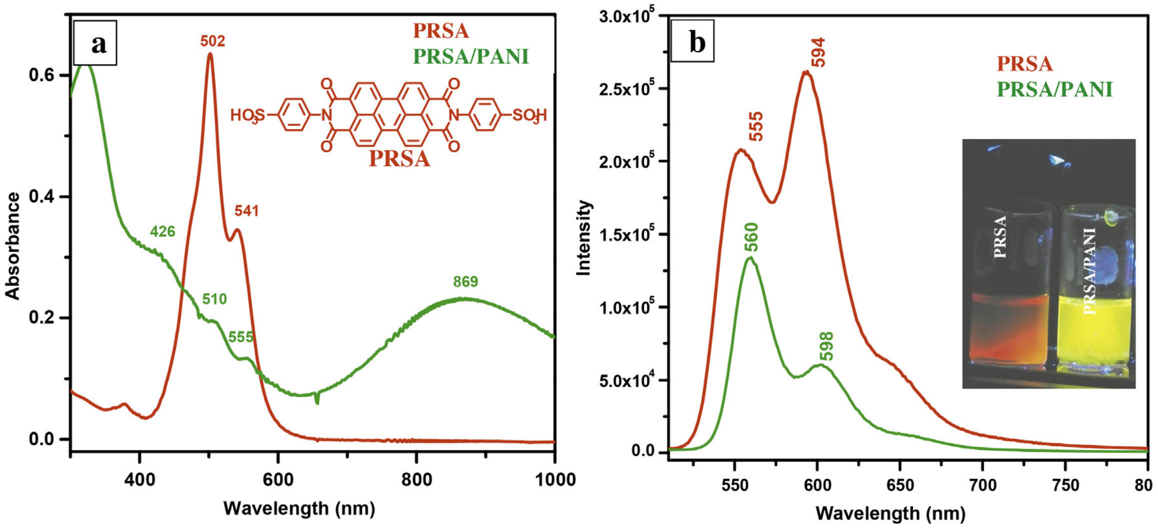

Fig. 2. (a) UV–Vis spectra, (b) fluorescence spectra of PRSA and PRSA/PANI composites from aqueous solution (path length = 1 cm, λ_{ex} = 502 nm).

(90.2% yield) as red color product of *N*,*N*′-bis-(4-benzosulphonic acid)perylene-3,4,9,10-tetracarboxylbisimide [23].

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 7.40 (4*H*, d, *J* = 16.8 Hz), 7.75 (4*H*, d, *J* = 16.8 Hz), 8.55 (4*H*, d, *J* = 16.4 Hz), 8.82 (4*H*, d, *J* = 17.2 Hz).

Mass: (MALDI-TOF, dithranol): 702 (M + H) (Fig. 1).

FTIR: γC=O: 1701.1 and 1664 cm^{-1}; C=C (perylene core) 1589.23 cm^{-1}; C=C (benzene core) 1498.59 cm^{-1}; (O=C)N–CH 1429.15 cm^{-1}; (O=C)N 1400.22 cm^{-1}; SO_3^{2-} 1355.86, 1176.5, 1128.35 cm^{-1}; C–H (perylene core) 802.33, 748.33 cm^{-1}.

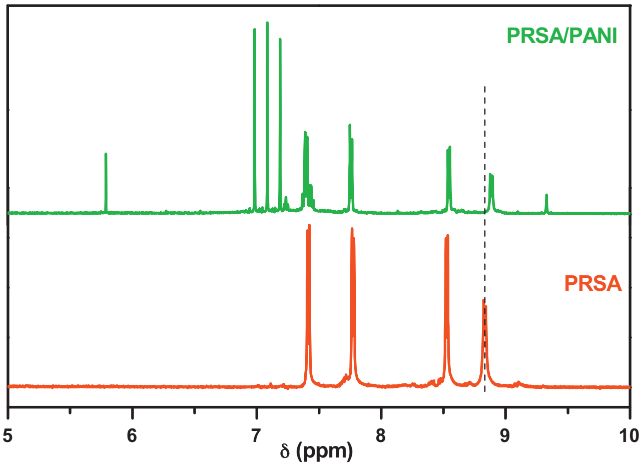

Fig. 3. 1H-NMR spectra of PRSA and PRSA/PANI composite in DMSO-d.

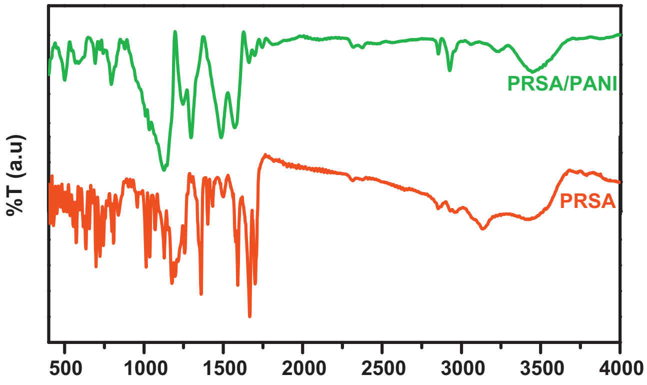

Fig. 4. FTIR spectra of PRSA and PRSA/PANI using KBr pallet.

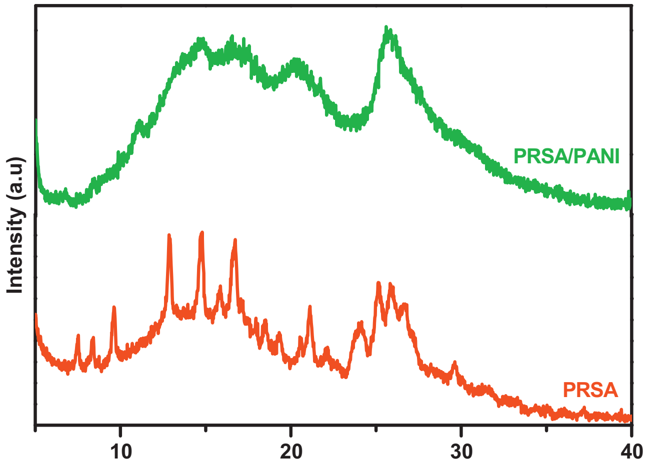

Fig. 5. WXRD pattern of PRSA and PRSA/PANI.

2.2.2. *Synthesis of PRSA/PANI*

Water soluble PANI composites were synthesized in water from the mixture of aniline (102 mg, 1.1 mmol) and PRSA (0.01 mmol) with constant stirring for one hour (Fig.1). After cooling the mixture at 12 °C, aqueous solution of ammonium peroxydisulphate ($(NH_4)_2S_2O_8$, APS), 248 mg, 1.1 mmol in 5 mL) was added drop wise and the mixture was allowed to stand for 24 h at low temperature. The resultant precipitate was centrifuged using 8000 rpm 10 times with water and methanol to remove APS and oligoaniline [24–26]. Finally, it was dried under vacuum for 24 h to receive black color PRSA/PANI composites [14].

2.3. *Apparatus and characterizations*

FTIR spectra were recorded in an FTIR-8400S instrument (Shimadzu) using the KBr pellets of the samples. The UV–Vis spectra of all samples were studied with Hewlett–Packard UV–Vis spectrophotometer (model 8453). Photoluminescence (PL) studies of all samples were carried out in a Horiba Jobin Yvon Fluoromax 3 spectrometer. XRD of the all samples were measured on Bruker AXS diffractometer (D8 advance) using Cu*K*α radiation (λ = 1.54 Å), a generator voltage 40 kV and current 40 mA. Samples were scanned in the range of 2θ = 5–40° at the scan rate of 0.5 s/step with a step width of 0.02°. Fluorescence lifetimes were measured using a time-correlated single-photon-counting fluoremeter (Fluorecule, Horiba Jobin Yvon). Average fluorescence lifetimes for exponential iterative fitting were calculated from the decay times and the relative amplitudes. Cyclic voltammetry measurement was done with an Electrochemical Workstation, Princeton Instrument. The working electrode was prepared by drop casting the aqueous solution of PRSA/PANI on ITO coated glass. Ag/AgCl electrode and Pt plate were used as reference electrode and the counter electrode, respectively. A Keithley 617 digital multimeter was used for current voltage and conductivity measurement using two probe methods at room temperature. The temperature dependence conductivities were measured using (high field measurement system) HFMS-J2468, Cryogenics Limited instrument by two probe method. The sample was prepared for *I–V* measurement by pressed pellet method.

3. Results and discussion

3.1. *Spectral studies*

Absorption spectra of PRSA/PANI aqueous solution are shown in Fig. 2, in which three absorption bands at 323, 426 and 869 nm are for PANI. The peak position ~323 nm (3.84 eV) for π–π^* transition,

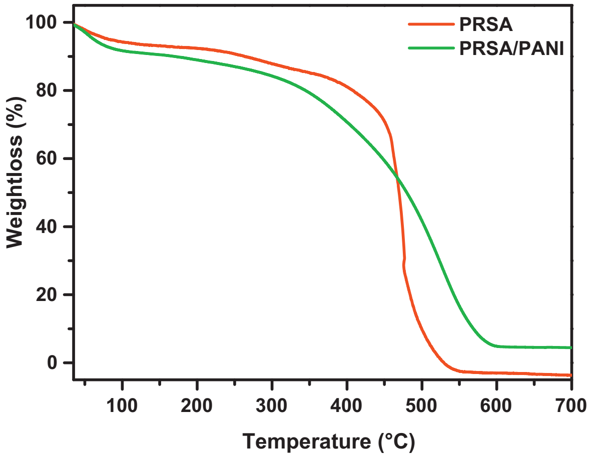

Fig. 6. TGA spectra of PRSA and PRSA/PANI.

~426 nm (2.91 eV) for polaron-π^* and at ~832 nm (1.49 eV) for the π-polaron transition are supporting the formation of PANI. A long tail in the NIR region points out the occurrence of the conductive emeraldine salt of PANI [9]. Appearance of peak (510 nm and 555 nm) in the UV–Vis spectra indicates the presence of the dopant acid in the PRSA/PANI composite. The absorbance intensities of the dopant peaks are small with respect to the polymer because of the lower doping level of the dopant in composite. Two peaks of PRSA at 502 and 541 nm are red shifted to 510 and 555 nm in composite and it implies a strong interaction of the dopant with polymer chains. The PL spectra (Fig. 2b) and bottle picture under UV-light (Fig. 2b inset) of the composite confirm the presence of PRSA in PANI. Intensities of the PRSA peak are comparatively low and peak pattern does not change in composite with respect to free PRSA. The red shifting of the emission peak of PRSA (from 555 nm and 594 nm to 560 nm and 598 nm) in the composite is owing to the interaction of PRSA with PANI and π–π stacking of PRSA in composite [27].

To understand the interaction of the –NH proton of the PANI with –SO_3H group of dopant, ^1H-NMR experiment was performed from the DMSO-d_6 solvent in 500 MHz NMR instrument. There are four types of doublet peak in PRSA. Two peaks are at δ 7.40 ppm and 7.75 ppm for the perylene core and remaining two peaks at δ 8.55 ppm and 8.82 ppm (ortho to $-SO_3H$ group) are for the benzene ring, respectively. Besides four peaks of PRSA moiety, there are also the presence of three characteristic peaks of PANI at δ = 5.78 ppm, 6.98–7.18 ppm and 9.32 ppm. The peak position at 5.78 ppm is attributed to the –NH proton resonance of PANI (Fig. 3). A triplet with a coupling constant of $^1J_{NH}$ = 51.1 Hz having integral area ratio of 1:1:1 with equal intensity at 7.18 ppm, 7.08 ppm and 6.98 ppm is for the free radical NH+ proton resonance. The singlet peak located at δ 9.32 ppm is for intermolecular hydrogen bond of PRSA with PANI. A small down field shift of the benzene peak closer to –SO_3H group is observed from 8.82 ppm to 8.88 ppm after polymerization. Deshielding of proton is possibly originating from the intermolecular H-bonding between PRSA and PANI chain [28,29].

3.2. Structural studies

Corresponding IR spectra of the composite support the formation of PANI and also the presence of PRSA in the composite. IR bands at 1697, 1571, 1487, 1298, 1245, 1126, 1010, 1035, 812, and 780 cm^{-1} are attributed to PRSA/PANI composites. Peaks present at 1010 and 1035 cm^{-1}, (symmetric and asymmetric S=O stretching of –SO_3H group) and 1697 cm^{-1} (the imide >C=O group) confirm the presence of PRSA moiety in the composite. A broad peak ~3500 cm^{-1} corresponding to the H-bonded N–H stretching of the polymer with PRSA (Fig. 4) is also noted [30].

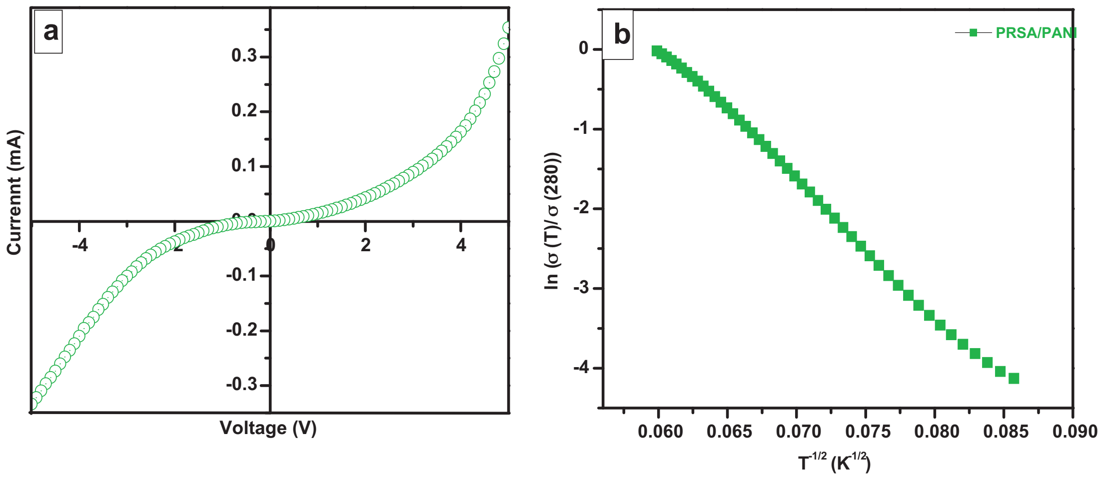

Fig. 7. Electrical study of PRSA/PANI (a) *I–V* curve and (b) temperature dependence conductivity of the composite.

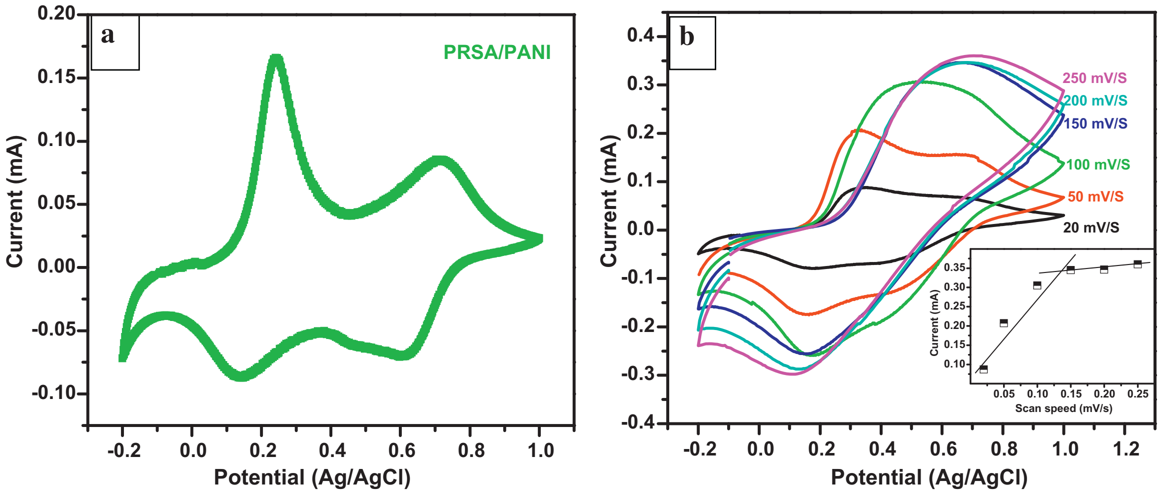

Fig. 8. Electrochemical study of PRSA/PANI in 1 M H_2SO_4 (a) CV study of PANI thin film on ITO electrode at a scan rate 50 mV/s. (b) Cyclic voltagrams of PANI at different scan rate and plot of peak current vs scan speed (inset).

WXRD studies of free PRSA and PRSA/PANI samples are depicted in Fig. 5. The three main diffraction peaks at $2\theta = 6.75°$ ($d = 13.07$ Å), $20.7°$ ($d = 4.28$ Å), $25.5°$ ($d = 3.48$ Å) of the crystalline PANI are observed. The peak at $2\theta = 6.75°$ represents the periodicity along the PANI chain, $2\theta = 20.7°$ for the periodicity in the direction parallel to PANI chain and $2\theta = 25.5°$ due to the periodicity in the direction perpendicular to PANI chain [30–32].

Thermo gravimetric analysis (Fig. 6) indeed confirms the improvement of the thermal stability of composites with respect to PRSA only [33,34]. It shows a weight loss starting at ~190 °C probably due to the elimination of some sulphonic acid groups and after 450 °C breaking of PANI chain starts. All these observations indicate the formation of PANI in presence of PRSA as well as the composite is a special due to its solubility in water.

3.3. I–V properties

I–V characteristics (Fig. 7) show semiconducting behavior of PRSA/PANI composite. The conductivity decreases with decrease of temperature. It indicates that the conduction in the PRSA/PANI composite is obeying one-dimensional variable range hopping (VRH) model proposed by Mott.

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right]$$

where σ_0 is the conductivity pre-factor, T is the temperature, characteristic temperature $T_0 = 4\pi/3N(E_F)k_B a^3$, where $N(E_F)$ is the density of state at the Fermi level, k_B is the Boltzmann constant and a is the number of nearest neighbor chain [27,33,35–37]. The conductivity of the sample is 0.0032 S/cm that is close to the conductivity of polyaniline sulphate [25].

3.4. CV properties

Electroactivities of PRSA/PANI composites are checked by cyclic voltammetry (CV). The working electrode was prepared by drop casting the aqueous polymer solution on measured area of ITO coated glass and subsequently air dried. The free standing film was compact in nature and water insoluble, it did not dissociate from ITO electrode during measurement [38,39]. CV curve of PRSA/PANI shows two couple of redox peaks, corresponding to redox transitions of leucoemeraldine form (semiconductor)/polaronic emeraldine form (conductor) and Faradic transformation of emeraldine/pernigraniline form (Fig. 8a). Scan dependent studies show that both the oxidation and reduction peak currents increase with the increasing scan rates. However, the peak potentials are almost independent of the scan rates 20–150 mV/s. This indicates that the electron transfer rate is very fast. The plot of peak currents versus scan rate is linear in the range of 20–150 mV/s which is indicative of the surface reaction process (Fig. 8b) [40,41].

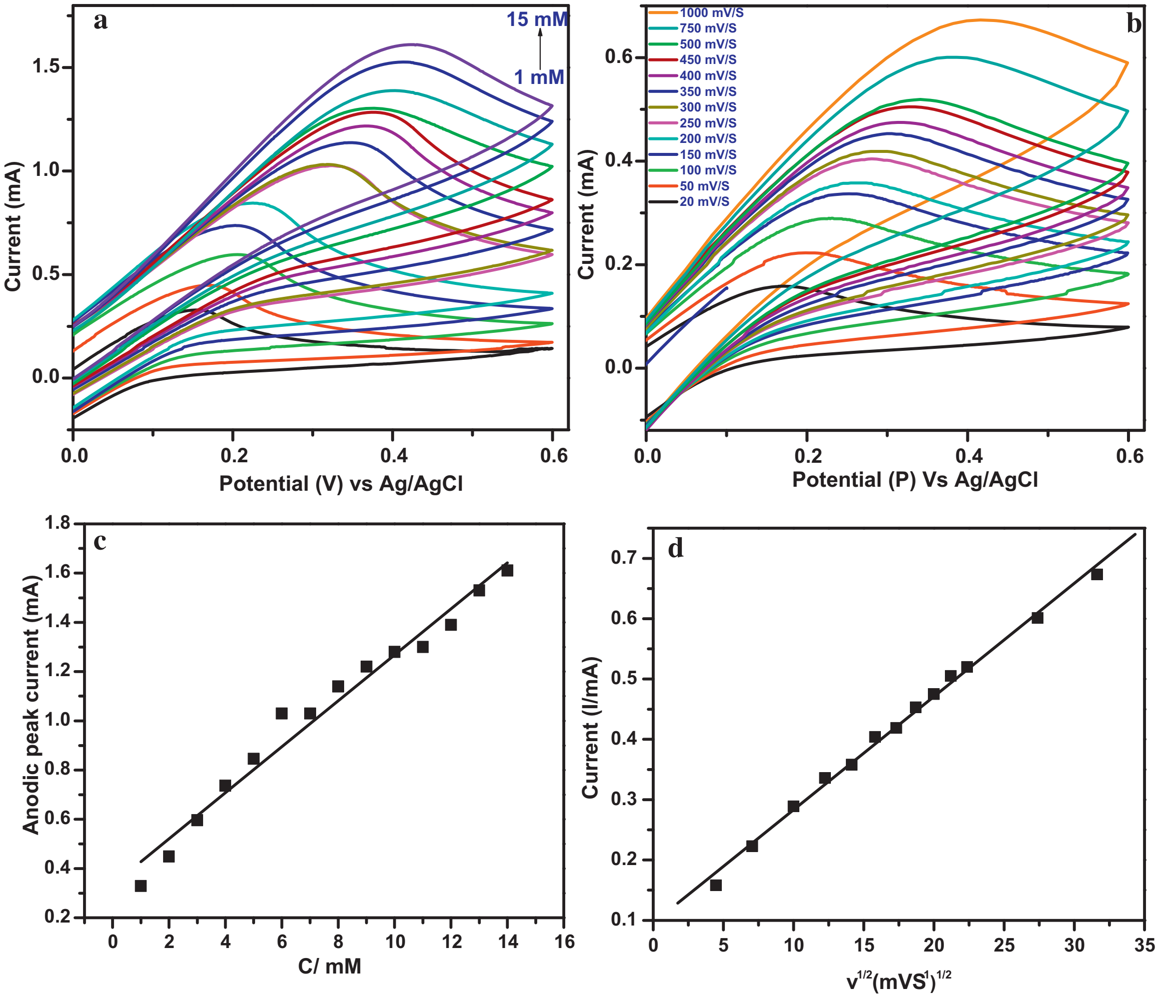

Fig. 9. (a) CV of different concentrations of AA at PRSA/PANI/ITO electrode in 0.1 M PBS (7.0), (b) CV of 1 mM AA at different scan rates (c) dynamic response of the composite polymer modified electrode to successive addition of ascorbic acid in 0.1 mM steps at a constant potential of 0.2 V, and (d) Plot of the anodic current function (I) vs square root of scan rate ($v^{1/2}$).

However, the linearity deviates at higher scan rates, revealing the kinetic irreversibility of the redox processes [42].

CV of PRSA/PANI/ITO modified electrode has been measured using different concentration of AA (Fig. 9a) and the composite electrode has a potential application to detect mM concentration of ascorbic acid. The transport characteristic of AA in PRSA/PANI/ITO modified electrode has been measured from the CV using 1 mM AA at different scan rates (Fig. 9b). It is seen that the anodic peak current increases with concentration of AA, which is attributed to the considerable catalytic reaction by electrochemically.

To establish whether the current is exclusively mass transport controlled at low AA concentration or not, we have investigated by changing the scan speed at 1 mM AA concentration. The corresponding linear plots of the CV peak current as a function of the square root of scan speed indicate that the current is mass transport controlled at low AA concentrations (Fig. 9d). From the slope of the linear fit plot peak current as a function of the square root of scan speed (20–150 mV/s) and assuming the number of electrons transferred (n) is 2, the diffusion coefficient of AA is $0.61 \times 10^{-6}\ \mathrm{cm^2/s}$ that is close to the literature value of $6.6 \times 10^{-6}\ \mathrm{cm^2/s}$ obtained for a poly(pyrrole) coated electrode [4,43].

Reduction of ascorbic acid by PANI has also been supported by kinetics data measured with UV–Vis spectrometer in presence of 1 mM AA solution (Fig. 10a). The spectra show that with time the absorbance intensity of π-polaron peak decreases, indicating the transformation of conducting ES of PANI to insulating pernigraline form and simultaneously AA to dehydrated AA [44]. In amperometric experiments, the current passed through the PRSA/PANI/ITO electrode at 0.3 V was measured as a function of concentration of AA in 0.1 M phosphate buffer solution (Fig. 10b) [42,45]. The spectra reveal a rapid current response to AA addition. At each addition, a steady current is obtained. Rapid response times are also significant from the viewpoint of practical applications.

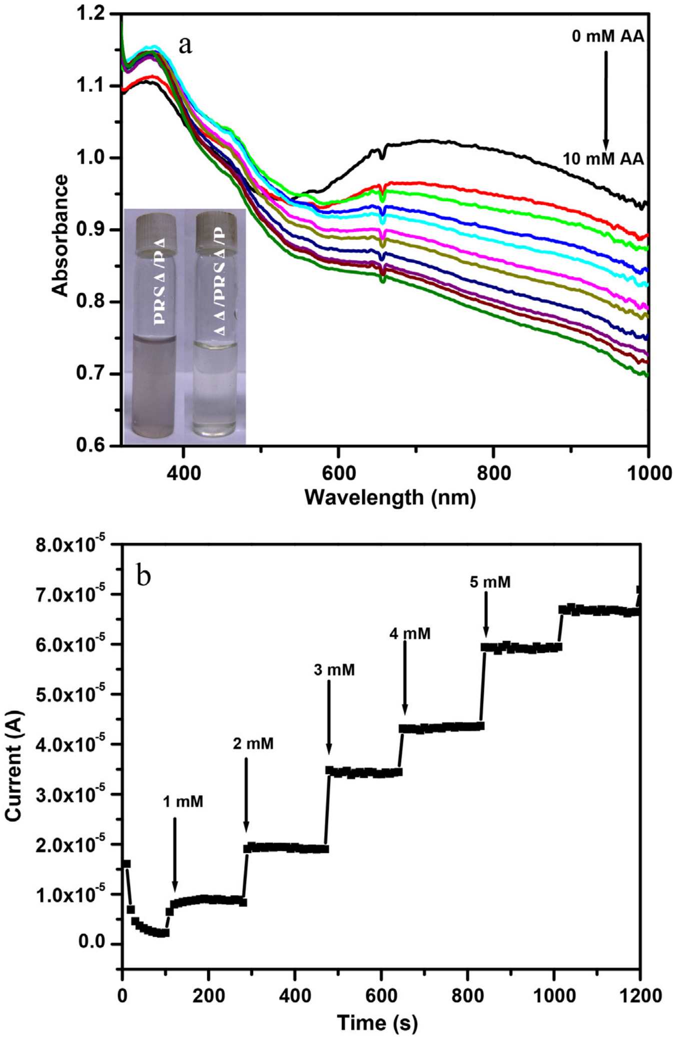

Fig. 10. (a) UV–Vis spectra of PANI/PRSA after addition of 1 mM AA in aqueous medium and (b) Amperometric titration of AA.

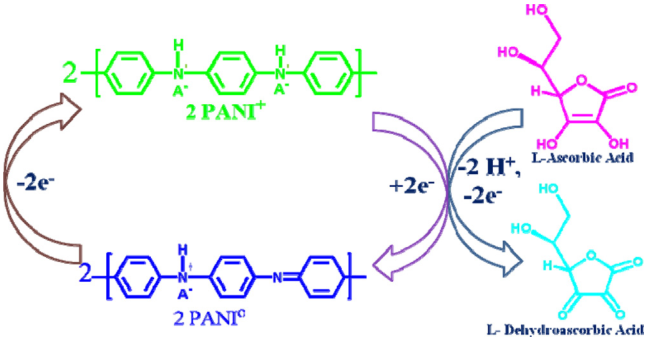

Fig. 11. Schematic representation of L-ascorbic acid (AA) oxidation mechanism.

The mechanism of the AA oxidation is explained by the following facts (Fig. 11). The oxidation of L-ascorbate to dehydro-L-ascorbic acid involves the transfer of 2 electrons and one proton. At first, AA is absorbed on the surface of PRSA/PANI electrode and changed into AA radical by losing one electron. The second hydroxyl group of the radical intermediate is further absorbed at the surface of electrode and a stable hydrogen bond is formed between the radical intermediate and PANI chains. The loss and conduction of a second electron is easier with the decrease of the activation energy. Finally, the intermediate is frequently losing an electron and a proton and the dehydrogenated ascorbic acid is formed [21,42].

4. Conclusion

Water soluble PRSA/PANI composite is a promising semiconducting material which follows 1D variable range hopping mechanism. The PRSA/PANI is electrochemically, thermally and photochemically stable. The PRSA/PANI coated electrode measures ascorbic acid in physiological condition as well as exhibits good electrocatalytic activity. We believe that these water soluble polyaniline composites have great potential application for electrochemical device.

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