Available online at www.sciencedirect.com
ScienceDirect
Reactive & Functional Polymers 68 (2008) 701–709
REACTIVE & FUNCTIONAL POLYMERS
www.elsevier.com/locate/react

Investigations on pyridine-3-sulphonic acid doped polyaniline and polypyrrole: Metal loading through dopant molecules

G. Ramya, C. Renugadevi, Chepuri R.K. Rao *, D.C. Trivedi

Functional Materials Division, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu 630 006, India

Received 24 August 2007; received in revised form 5 November 2007; accepted 12 November 2007
Available online 19 November 2007

Abstract

Polyniline and polypyrrole were chemically and electrochemically synthesized in presence of pyridine-3-sulphonic acid. These conducting polymers were characterized by FT-IR, UV–vis, XRD, TGA and SEM techniques. Polyaniline showed a conductivity of 4×10^{-4} S/cm while polypyrrole exhibited a conductivity of 6.2×10^{-2} S/cm. The presence of pyridine ring in the dopant enabled the polymers to anchor Pd/or PdO through which the composite can work as catalytic material.

Keywords: Polyaniline; Polypyrrole; Doping; Sulphonic acid; Conductivity

1. Introduction

Conducting polymers are excellent candidates for applications in displays, electrochromic mirrors, windows, light-emitting diodes, photovoltaics, near-infrared devices and electrochromic devices [1]. Polyaniline has been known almost for 145 years as an aniline black [2]. However, recent systematic syntheses and structure explorations [3] made this conducting polymer as an advanced functional material. Polyaniline (PAn), though environmentally stable, is intractable due to its metal like conductivity. Polyaniline is built up of reduced (–B–NH–B–NH–) and oxidized (—B—N=Q=N—) repeating units, where B denotes a benzenoid and Q denotes a quinoid ring. The conductivity of polyaniline depends on oxidation state and also on the degree of electronegativity of anions, which are taken up for charge neutrality. Accordingly the chemical and electrochemical behavior of polyaniline depends on the pH and the functionality present in counter ion of the acid doped. The protonation equilibria involves exclusively on the quinone diimine segment of the polymer chain, as two imine nitrogen's have $pK_{a_1} = 1.05$ and $pK_{a_2} = 2.5$ [4,5]. The protons are preferentially added to —N= sites while the number of electrons in the chain remains constant [4,6]. Thus any acid whose pK_a value is around 4.0 can be a useful medium to synthesize polyaniline [5]. The pK_a value of pyridine-3-sulphonic acid (PSA) is 2.9 [7] which indicate that it is a weaker acid compared to its iso-structural

---

* Corresponding author. Tel.: +91 4565 227559; fax: +91 4565 227713.
E-mail address: rkkousik@rediffmail.com (C.R.K. Rao).

1381-5148/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.reactfunctpolym.2007.11.009

benzenesulphonic acid (BSA, with a pK_a value of 0.2). PSA exists as a zwitter ion which can also act as acid (H^+ donor) in presence of even mild bases such as polyaniline-emaraldine base (Pani-EB) which is similar to doping by sulphamic acid [8] (with pK_a of 1.01) known in literature. Recently it has been reported [9] that benzoic acid having a pK_a value of 4.2 can dope Pani-EB to yield conducting polyaniline with a conductivity of 1×10^{-2} S/cm. Therefore, it seemed reasonable to expect that this acid can be useful as a dopant for Pani.

By compositing with metals such as Ru, Pd, Ag, Pt and Au (M-CPs), applications of conducting polymers are broadened [10–16]. In our efforts to synthesize such useful M-CP composites, we demonstrated novel methods to incorporate silver/or palladium/or gold particles into polypyrrole matrix (Ag/Pd/Au–PPy) [17–19]. The Pd–PPy composite can oxidizes hydrazine efficiently even at low Pd loadings [17]. Incorporation of gold nanoparticles involved in an in situ mechanism at water–toluene interphase [18] while simple dip-coating is sufficient to obtain Ag–PPy composite [19] film. When present as the dopant in the polymer chain, PSA may be useful as it has reactive functional site (pyridine group) that can possibly anchor transition metal ions such as Pd^{2+} to form catalytically active conducting polymer composites. This paper presents and discusses the studies on conducting polymers polyaniline and polypyrrole in presence of PSA and anchoring of the palladium/palladium oxide particles to the dopant which yielded polyaniline–Pd and polypyrrole–PdO composites.

2. Experimental

2.1. Materials and methods

All chemicals were analytical grade. Pyrrole, aniline and palladium chloride, ammonium peroxydisulphate (APDS) were obtained from C.D.H chemicals (India). Pyridine-3-sulphonic acid (PSA) was purchased from Aldrich chemical company. Emaraldine base (E.B) form of Pani was synthesized from literature procedure [5]. Elemental analyses were performed on 'Elementar Vario EL III'(Germany) CHNS analyzer. Electrochemical experiments were performed on Solartron SI 1287 interface using three electrode assembly containing platinum foil working electrode (5 mm × 2.5 mm), platinum wire auxiliary electrode and saturated calomel (S.C.E) or Ag/AgCl reference electrode. Purging nitrogen gas before electrochemical experiments effectively deoxygenated the electrolytes. FT-IR spectrum of the polymers ere recorded on model no. Paragaon-500 of Perkin–Elmer after palletizing the sample with solid KBr. SEM images were taken on Hitachi 3000-H instrument by spreading the powdered sample on copper studs. For obtaining better quality SEM pictures at high magnifications, samples were gold sputtered on JEOLFINE COAT ion sputter (model no. JFC-1100) for 3 min. X-ray diffraction experiments were conducted on PANalytical's X'Pert PRO instrument using copper anode material (K-Alpha1 [Å] 1.54060). The conductivity measurements were carried out on pressed pellets (1 cm dia, 3 ton applied pressure) with a four-probe meter connected to Keithley's 2182 nanovoltmeter and 2400 source meter. EDAX data was obtained on THERMO (electron corporation) Super Dry-II system.

2.2. Synthesis of polyaniline and polypyrrole

2.2.1. Oxidative polymerization of aniline and pyrrole in presence of PSA

PSA doped Pani (Pani–PSA) was obtained by oxidizing an aqueous solution of 0.1 M aniline in 1 M PSA using ammonium peroxydisulphate (0.1 M) (APDS). PSA doped polypyrrole (Ppy–PSA) was obtained by oxidizing 0.1 M pyrrole in 1 M PSA solution using ammonium peroxydisulphate (0.1 M) (APDS). In a typical reaction, to 0.9 ml of aniline in 100 ml 1 M aqueous PSA solution was added 2.5 g of APSD dissolved in 10 ml water dropwise. The reaction was continued for 6 h and the resulting green precipitate was filtered, washed with copious amounts water and oven dried at 50 °C. The conductivity of the pellet is 3×10^{-4} S/cm. (The sample is designated as Pani–PSA-A.)

Polypyrrole (PPy–PSA-A) was also prepared by the same procedure as described for polyaniline. The conductivity of the sample is 1 S/cm.

2.2.2. Solution and solid state doping of Pani by PSA

Emaraldine base (E.B, ($C_{24}H_{18}N_4$), 0.9 g, 0.0025 mole) is ground with PSA (0.78 g, 0.005 mole, 1:2 ratio) in an agate mortar for 1–2 h by which time the blue color of the E.B changed into dark green color suggesting that doping by PSA had taken place. The conductivity of the pressed pellet is 2 S/cm. (The sample is designated as Pani–PSA-B.)

For solution doping, exactly weighed E.B and PSA samples (in 1:2 ratio) were stirred in 100 ml water for 6 h at 70–80 °C and the green product was filtered. The dried, pressed sample showed a conductivity of 2.7×10^{-4} S/cm. (sample Pani–PSA-C).

2.2.3. Doping of Pani and PPy with PSA in presence of Pd complex

2.2.3.1. Pani–PSA–Pd(0) composite. Pani–PSA–Pd(0) composite is obtained by solution doping of E.B with $PdCl_2 \cdot (PSA)_2$ complex in 100 ml water for 6 h at 70–80 °C in a two-step process. First, $PdCl_2 \cdot (PSA)_2$ complex solution is obtained by mixing 0.003 mole of $PdCl_2$ and 0.006 moles of PSA in water, heated to 70–80 °C for half-an-hour and filtered to get clear yellow palladium complex solution. To this solution, 0.0015 mole E.B was added and heating (doping) continued for 6 h to get the desired composite material. The conductivity is measured as 4×10^{-4} S/cm. This is designated as Pani–PSA–Pd-D.

2.2.3.2. Ppy–PSA–PdO composite. After preparation of $PdCl_2 \cdot (PSA)_2$ complex solution, pyrrole (0.2 ml, 0.0029 mole) was added and oxidized with APDS (0.0029 mole) solution for 6 h at room temperature. The product was filtered, washed with water and dried at 50 °C. The conductivity was measured to be 0.3 S/cm. This is designated as Ppy–PSA–PdO-B.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. Polyaniline

Thin films of PSA doped Pani can be synthesized by potentiodynamic method by cycling the potential between −0.2 and 0.8 V (with reference to SCE) on a platinum foil at a scan rate of 50 mV/s. The growth of the film is shown for first two scans in Fig. 1a in the form of a cyclic voltammogram where the potential is scanned between −0.2 and 1.0 V. Deposition of the polyaniline was observed in the subsequent scans when the potential was limited to even 0.8 V. The initiation of polymerization, i.e., radical cation formation is observed after 0.8 V as indicated by steep increase in current. The growth pattern of Pani on the platinum electrode showed a different behavior compared to the Pani in sulphuric acid medium. It is known that in presence of sulphuric acid medium, the growth pattern shows well defined cyclic voltammetric peaks [20] at 0.09, 0.36 and 0.625 V (vs.SCE). However in the present case the formation of polyaniline is characterized by an oxidation peak at 0.44 V and a corresponding reduction peak at 0.36 V with a $\Delta E_p = 80$ mV. The peak heights increased and the solution became more greenish with increasing the number of scans. Examination of the electrode after cycling showed that only a thin film is deposited on the electrode. This observation is very similar to the electrochemical polymerization of *m*-anilicacid [21] which is due to the formation of soluble low molecular weight polymers.

The Pani film (0.5 μm) doped with PSA was characterized by electrochemically by performing cyclic voltammetry in 1 M monomer-free PSA solution. The CV is shown in Fig. 1b. Observation of the Fig. 1b shows that the PSA doped Pani exhibits a broad anodic and a cathodic peaks centered around 0.41 V and 0.38 V, respectively.

The Pani–PSA sample obtained by chemical polymerization of aniline in 1 M PSA using APDS was subjected to FT-IR analysis (Fig. 2a). The bands at 1038 cm^{-1} is assigned to the symmetric $-SO_3^-$ stretching, and are the characteristic bands of a sulphonate group present in the dopant. The band at 815 cm^{-1} indicates that there is a head to tail coupling in a polymer that is to say that monomeric units are linked at 1,4-position. This band shifts to 827 cm^{-1} in an undoped emaraldine base, indicating the strong influence of dopant on $C–H_{op}$ vibration.

The absorption band at 1140 cm^{-1} in the Pani–H_2SO_4 system is said to be due to charge delocalisation on the polymer backbone; this band in the undoped state appears with very weak intensity. In the present study this band is observed at 1128 cm^{-1}. Bands due to aromatic ring breathing mode are observed in the region 1650–1400 cm^{-1}. The characteristic bands of $N–\phi–N$ is observed at 1492 cm^{-1} and the band characteristic of $N{=}\phi{=}N$ is observed at 1580 cm^{-1}. The C–N stretching is observed at 1301 cm^{-1} [22–24]. The aromatic C–H is observed at 2923 cm^{-1}.

The d.c conductivity of electrochemically deposited Pani–PSA film could not be measured due to its fragile nature. The pressed pellet sample of Pani–PSA (Pani–PSA-A) obtained from chemical polymerization showed a conductivity of 3×10^{-4} S/cm whereas Pani–PSA sample (Pani–PSA-B) obtained by simple solidstate doping of

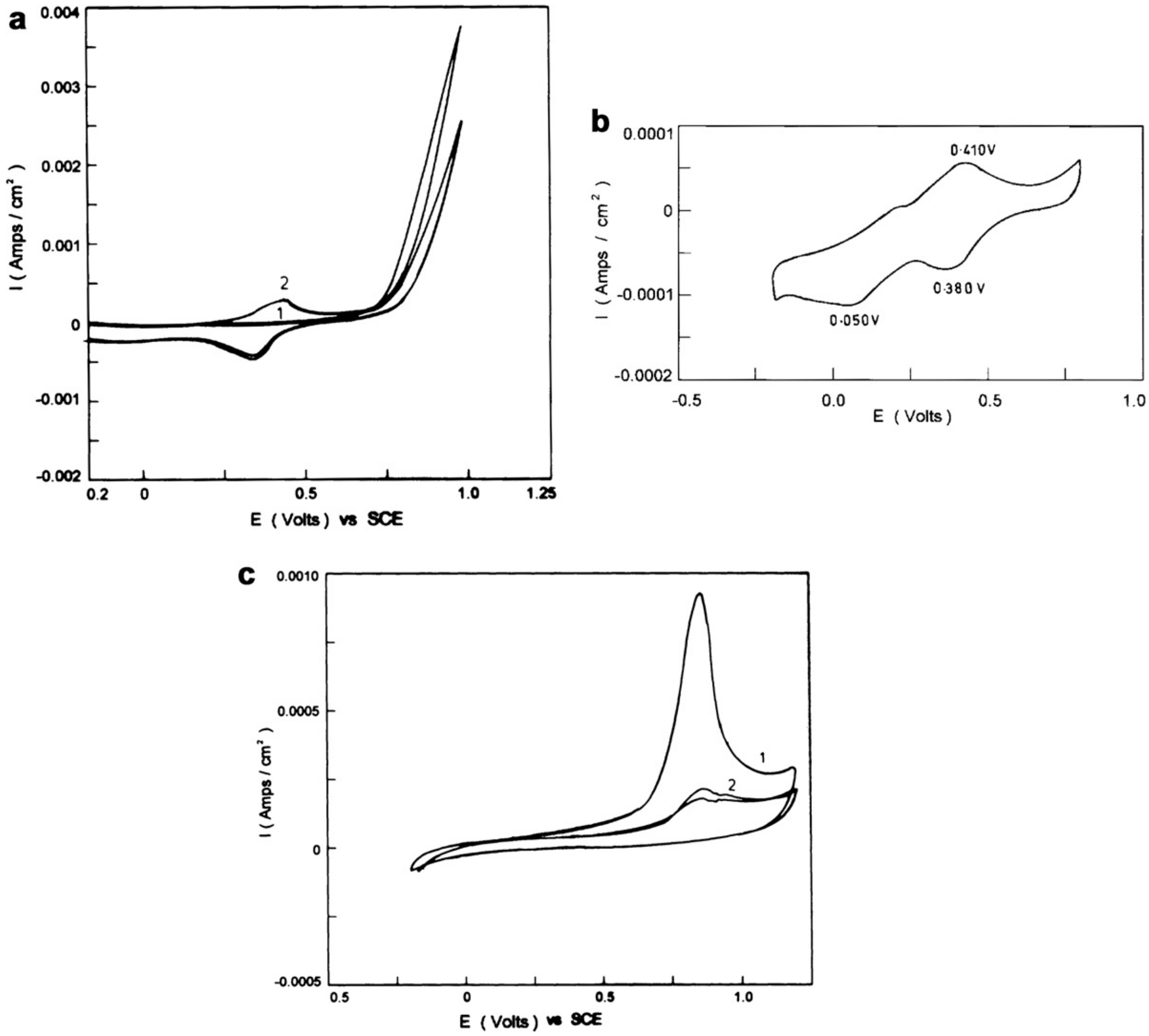


Fig. 1. Growths of (a) Pani–PSA, (b) characteristic CV diagram of Pani–PSA in 1 M pyridine-3-sulphonic acid and (c) Ppy–PSA growth in 1 M PSA. The scan rate is 50 mV/s.

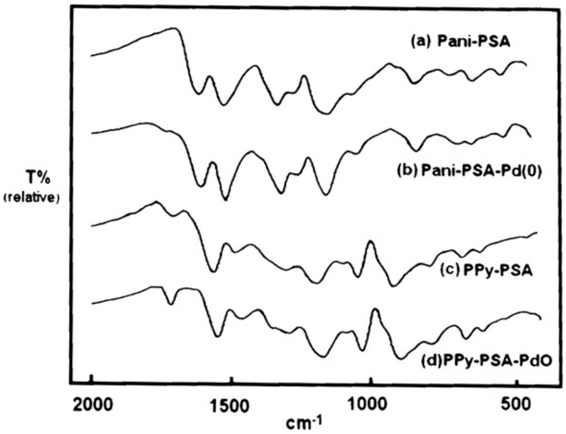


Fig. 2. Segment of FT-IR spectra of (a) Pani–PSA, (b) Pani–PSA–Pd composite, (c) PPy–PSA and (d) PPy–PSA–PdO composite.

EB with PSA showed a very good conductivity of about 2 S/cm (Table 1) and is comparable to electrochemically prepared Pani–benzenesulphonic acid [20]. The higher conductivity in Pani–PSA sample obtained from EB is due to higher molecular weight of pre-formed EB and hence higher doping levels of about 40%. The doping level in chemically synthesized sample (Pani–PSA-A) was found to be only 22%, and hence showed a lower conductivity. The electronic spectrum of Pani–PSA-A dissolved in *m*-cresol is shown in Fig. 3. The green color solution exhibited bands at 326 nm, 423 nm, 569 nm and 1085 nm, similar to the reported Pani-camphor sulphonic acid (or PTSA) system in phenols studied in literature [25,26]. The generally observable elec-

Table 1
FT-IR and conductivity data of the samples

Polyanilines	FT-IR(KBr pellet) ($\mathrm{cm^{-1}}$)							Conductivity (S/cm)
	C–H$_{op}$	R – $\mathrm{SO_3^-}$	C–N	N–B–N	N=Q=N	C–H$_{(arom)}$	N–H	
Pani–PSA	815	1038	1245	492	1580.7	2923	3427.3	3.0×10^{-4}
Pani–PSA–Pd	814	1036	1242	1498	1586	2923	3438	4.0×10^{-4}
Pani–PSA-doped	–	–	–	–	–	–	–	2.0
Polypyrroles	C–H-def		C–H/N–H def		N–H-str	C=C & C–C str		
PPy–PSA	1045		1297		1475	1554		1.0
PPy–PSA–PdO	1042		1304		1446	1551		0.3
Py-PSA(e.c)	–		–		–	–		6.4×10^{-2}

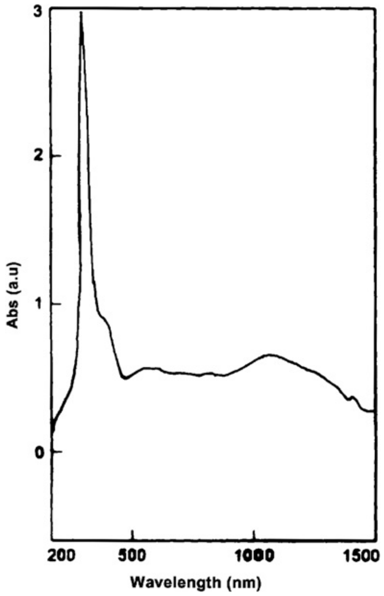


Fig. 3. UV–vis spectrum of Pani–PSA in *m*-cresol.

tronic bands in hydrochloric acid doped Pani at 326, 423 and 826 nm do also appear in Pani–PSA-A/*m*-cresol but some bands are red shifted. The band at 326 nm is attributed to π → π* of benzenoid segments. The bands at 423 or 569 nm are due to cation radicals. The band at 826 nm due to trapped exitons(bipolarons) in Pani–HCl is red shifted to 1085 nm due to secondary doping by *m*-cresol in Pani–PSA system. The X-ray diffraction of the PSA doped Pani (Pani–PSA-A) presented in Fig. 4a shows that there are two main broad peaks located around $2\theta = 19$ and 25 and suggest amorphous nature of the polymer. The morphology and structural characteristics of the polymer is investigated by SEM technique. Fig. 5a shows the SEM of Pani–PSA which consists of 0.1–0.2 μm sized globules and plateau regions.

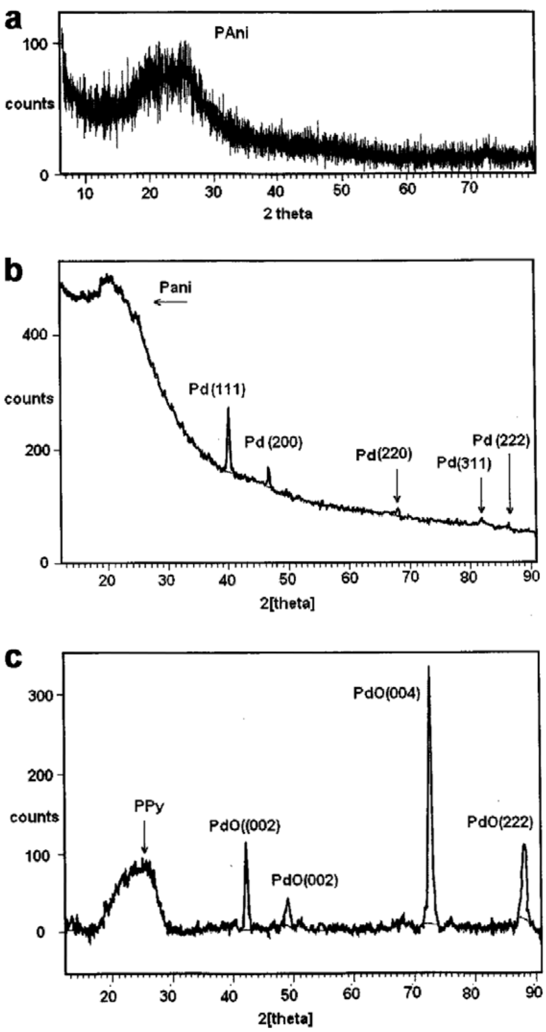


Fig. 4. XRD of (a) pure Pani–PSA, (b) PAni–PSA–Pd composite and (c) PPy–PSA–PdO composite.

3.1.2. Polypyrrole

The electrochemcial growth of polypyrrole is shown in Fig. 1c. The initiation of polymerization took place around 0.86 V. However in contrast to the general formation of thick films of polypyrrole, only thin films of PPy–PSA are observed. According to the numerical calculations based on charge consumed in the electropolymerisation reaction of pyrrole that 500 mC/cm^2 gives about 1 μm thick polypyrrole film [27,28], the thickness of the film estimated is 0.07 μm. Attempts to grow thicker films in presence of neutral salt NaPSA also failed. Indeed it is observed that the formation of radical cation and subsequent growth of the polypyrrole film are identical in PSA and NaPSA. The cyclic voltammogram of a thin film of Ppy–PSA in a monomer-free 1 M PSA solution showed a capacitative behavior. The conductivity of these thin films were found to be low, in the range 6.4×10^{-2} S/cm (Table 1) showing low levels of doping by PSA.

IR spectrum (Fig. 2c) of the PSA doped polypyrrole (Ppy–PSA-A) obtained from oxidation of pyrrole in PSA solution by APDS showed charge carriers, bipoloron bands at 920 and 1196 cm^{-1} indicating the Ppy formed is in oxidized state [29,30]. The peaks at 1690.7, 1553 and 1475 cm^{-1} are assigned to fundamental vibrations of pyrrole rings [31,32]. The broad hump at 3400 cm^{-1} is assigned to N–H stretching vibration from pyrrole. The Raman spectrum for this compound exhibited bands as follows: The C=C stretching is found at 1605 cm^{-1}. The C–N-antisymmetrical stretching observed at 1380 cm^{-1} in pure polypyrrole [33] is shifted to 1400 cm^{-1}. The other bands found are due to symmetrical C–H in-plane bending associated with dication at 1080 cm^{-1}, ring deformation associated with dication at 950 cm^{-1}. The electronic spectrum of PPy–PSA recorded in diffused reflectance mode showed a peak between 350 and 390 nm, assigned to $\pi \rightarrow \pi^*$ transition associated with benzenoid ring. The band due to cation radicals lie between 400 and 1000 nm as broad rising band. The tail of this band extends to the infrared region indicating that the charge carriers are bipolarons. The absorption peak around 1300 nm can be related to a transition from the valance band to the half filled polaron bonding level. The peak around 457 nm corresponds to the transitions from valance band to the antibonding polaron state.

3.2. Studies on anchoring of palladium through dopant PSA

Doping polyaniline-E.B by PSA in presence of palladium chloride demonstrates the utility of dopant PSA for anchoring Pd^{+2} ions. For this purpose, first a $PdCl_2[PSA]_2$ complex is generated by heating $PdCl_2$and PSA (1:2 ratio) in water at 70–80 °C, as described in Section 2. The formation of the complex is evident from yellowish color due to the formation of a square-planar complex, (Scheme 1) akin to many Ni(II) complexes (UV–vis spectrum showed 369 nm LMCT band) [34]. Addition of E.B to the complex solution and heating for 3 h (70–80 °C) gave Pd containing PSA doped polyaniline (Pani–PSA–Pd-D). During the course of reaction, it is noticed that Pd^{+2} ions are reduced to Pd(0) state. This can be anticipated as the Pd^{+2} ions are known to undergo reduction with even mild reducing agents (due to the noble nature, i.e., higher positive reduction potential of Pd(II)/Pd(0) couple 0.95 V vs NHE). Palladium(0) state is confirmed from X-ray diffraction profile for the composite (Fig. 4b). The composite exhibited reflections due to planes of (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) at $2\theta = 40.11$, 46.50, 67.95, 81.79, 86.40 in accordance with literature (JCPDS FILE 5-0681). The conductivity of the composite (PAni–PSA-D) is 4×0^{-4} S/cm (Table 1) with a doping PSA level of 22.6 wt%. The conductivity of the composite is slightly more than the pure PAni–PSA-C (2.7×10^{-4} S/cm, Table 1) prepared under similar experimental conditions (i.e., heating at 70–80 °C for 3 h) with doping level remaining unchanged. The increase in the conductivity of composite is due to the presence of Pd(0) particulates. The FT-IR spectrum of the sample shown in Fig. 2a resembles the pristine polymer except for decrease of (about 3 cm^{-1}) C–N and increase for other bands frequencies indicating possible interaction of Pd particles with polyaniline nitrogens. The analysis of the composite by EDAX (Fig. 6a) showed that Pd is present in the composite with other elements such as Al, Cu and Au which arise due to base material (copper stud) and gold sputtering on the sample. Fig. 5(c) shows the scanning electron micrograph of the composite with loosely packed, porous sponge like structure of polyaniline. This is in contrast to the morphology of the pristine polymer (Fig. 5(a)) where the polymer is tightly packed and non-porous and somewhat crystalline. The porous and spongy nature of the Pani–PSA–Pd composite is desirable and a promising character to function as a catalyst.

As it is not possible to dope polypyrrole chemically like as described above for polyaniline, another in situ method is chosen for loading Pd into polypyrrole. Polymerization of pyrrole in the

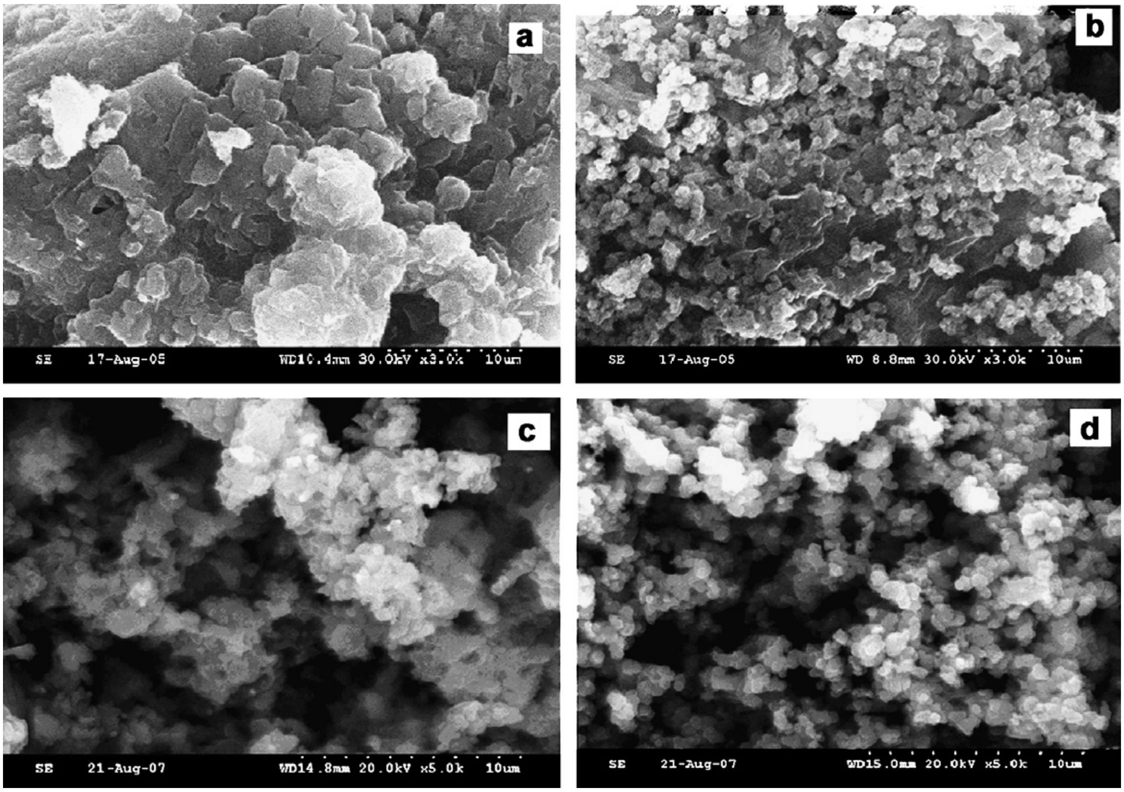
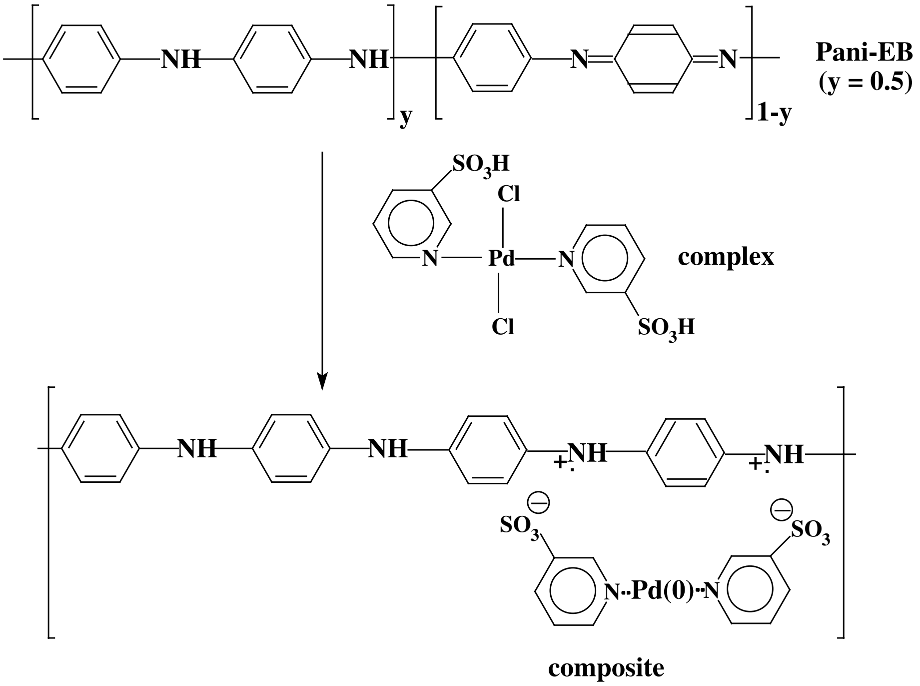


Fig. 5. Scanning electron micrographs of (a) Pani–PSA, (b) Ppy–PSA at ×3000, (c) Pani–PSA–Pd composite and (d) PPy–PSA–PdO composite at ×5000 magnification.



Scheme 1. Scheme showing doping process by palladium complex and the structure of polyaniline–palladium composite.

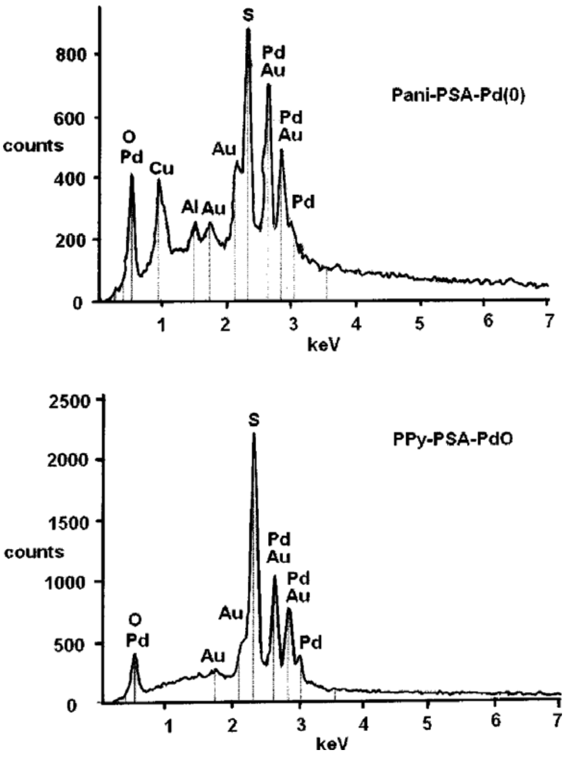


Fig. 6. EDAX profile of the composites.

solution of $PdCl_2(PSA)_2$ complex with APDS yielded Pd–PPy composite (Ppy–PSA–PdO-B). However, as the Pd(II) is also subjected to oxidation by strong oxidant APDS during the reaction, the resultant composite contained PdO particles instead of Pd as confirmed by X-ray diffraction profile (Fig. 4c). The peaks at $2\theta = 42.10$, 49.17, 72.59 and 88.38 are assigned for the reflections due to (002), (200), (004) and (222) by palladium oxide particulates in the polymer. The conductivity of the composite is 0.3 S/cm (Table 1). EDAX analysis (Fig. 5b) of the sample also confirmed the presence palladium. Elemental analyses (C, H, N and S, Table 2) performed on these two composites suggest that one Pd(0)(or one PdO) and two PSA molecules exists in the four-rings extended PAni (or PPy) chain (Scheme 1). The stability of the Pani and Ppy composites were investigated by TG analysis (Fig. 7). The analysis showed that there is a weight loss of 8–10% at 100 °C due to moisture. The percentage is little higher and is due to incomplete drying of the samples. The Pani and PPy composites are stable up to 250 and 300 °C, respectively. The decomposition of the composites starts at these temperatures and continues upto 490 °C for Ppy composite with 70% overall loss, which is mainly due to the loss of dopant molecules. The decomposition for Pani composite is found to be faster between 300 and 500 °C with a overall loss of 95%. As the weight of the doped PSA is almost same in both composite, the final residual weights of these composites (8.5 wt% for PPy and 6.5% for Pani) suggest that the loading of Pd into PPY composite is higher by about 2%. The exothermic peak in their DTA curves at 498 °C for PPy and 470 °C for Pani may arise due

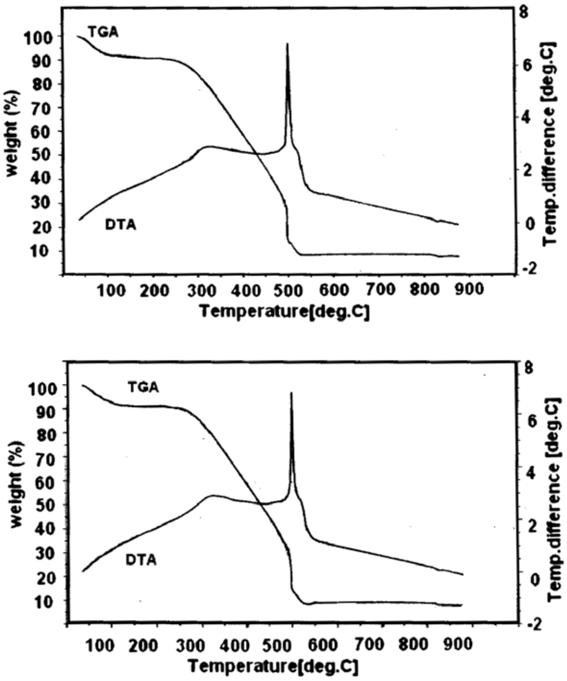


Fig. 7. TGA curves for Pani–PSA–Pd (above) and Ppy–PSA–PdO (below) composites.

Table 2
Elemental data of the composites

Composite	C%	H%	N%	S%
Pani–PSA–Pd($C_{34}H_{28}N_6$ O_6PdS_2)	54.3(54.1)	3.71(3.71)	11.07(11.1)	3.8(4.20)
PPy–PSA–PdO ($C_{26}H_{20}N_6$ O_7PdS_2)	47.6(47.4)	3.16(3.06)	12.32(12.76)	4.3(4.86)

Numbers in parentheses are calculated values.

to sintering of Pd(0) particles [35]. The morphology of the composite is shown in the scanning electron micrograph (Fig. 5(d)) which shows that the uniform sized globules of polypyrrole is loosely packed resulting in porous structure. The composites can be useful as catalysts for C–C bond forming coupling reactions and electrocatalytic reactions [36–38]. These procedures for inclusion of metal particles through dopant PSA paves a way to load various other transition metals/ions into the conducting polymer matrices.

4. Conclusions

Pyridine-3-sulphonic acid doped polyaniline and polypyrrole thin films can be prepared on platinum electrodes. We have demonstrated a new route to load catalytic metals like Pd into the polymer matrix through the dopant. The presence of Pd in composites were confirmed by XRD and EDAX techniques. The new composites can find catalytic applications in organic synthesis.

References

[1] Gursel Sonmez, J. Chem. Soc., Chem. Commun. (2005) 5251.

[2] H. Letheby, J. Am. Chem. Soc. 15 (1862) 161.

[3] A.G. Macdiarmid, J.C. Chiang, M. Halporn, W.S. Huang, S.L. Mu, N.L. Somasiri, W. Wu, S.I. Yaniger, Mol. Cryst. Liq. Cryst. 121 (1985) 173.

[4] W.S. Haung, A.G. MacDiarmid, A.J. Epstein, J. Chem. Soc., Chem. Commun. 784 (1987).

[5] D.C. Trivedi, in: H.S. Nalwa (Ed.), Hand Book of Organic Conductive Molecules and Polymers, vol. 2, John Wiley, New York, 1997, pp. 505–572.

[6] L.W. Shackelete, J.F. Wolf, S. Gould, R.H. Baughman, J. Chem. Phys. 88 (1988) 3955.

[7] sixth ed., J.J.G. Cadogon (Ed.), Dictionary of Organic Compounds, vol. 6, Chapman & Hall, London, UK, 1996, p. 5519.

[8] S.K. Dhawan, D.C. Trivedi, J. Appl. Electrochem. 22 (1992) 563.

[9] C.A. Amarnath, S. Palaniappan, Polym. Adv. Technol. 16 (2005) 420.

[10] Y. Li, G. Shi, J. Phys. Chem., B 109 (2005) 23787.

[11] X. Feng, G. Yang, Q. Xu, W. Hou, J.-J. Zhu, Macromol. Rapid Commun. 27 (2006) 31.

[12] S.K. Pillalamarri, F.D. Blum, A.T. Tokuhiro, M.F. Bertino, Chem. Mater. 17 (2005) 5941.

[13] Y. He, J. Yuan, G. Shi, J. Mater. Chem. 15 (2005) 859.

[14] Anthony P. O'Mullane, Sara E. Dale, Julie V. Macpherson, Patrick R. Unwin, J. Chem. Soc., Chem. Commun. (2004) 1606.

[15] M.C. Henry, C.C. Hsuch, B.P. Timko, M.S. Freund, J. Electrochem. Soc. 148 (2001) D155.

[16] R. Gangopadhyay, A. De, Chem. Mater. 12 (2000) 608.

[17] Chepuri R. K Rao, D.C. Trivedi, Catal. Commun. 7 (2006) 662.

[18] Chepuri R.K. Rao, D.C. Trivedi, Synth. Metals 157 (2007) 432.

[19] Chepuri R.K. Rao, D.C. Trivedi, Synth. Metals 155 (2005) 324.

[20] S.K. Dhawan, D.C. Trivedi, Polym. Int. 25 (1991) 55.

[21] A. Kitani, K. Satoguchi, H.Q. Tang, S. Ito, K. Sasaki, Synth. Metals 69 (1995) 129.

[22] Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima, T. Kawagoe, Macromolecules B 21 (1988) 1297.

[23] A.J. Epstein, A.J. MacDiarmid, Mol. Cryst. Liq. Cryst. 160 (1988) 165.

[24] N.S. Sariciftci, H. Kuzmany, H. Neugebauer, A. Neckel, J. Chem. Phys. 92 (1990) 4530.

[25] A.G. MacDiarmid, A.J. Epstein, Synth. Metals 69 (1995) 85.

[26] S. Geetha, K.K. Satheesh Kumar, D.C. Trivedi, J. Compos. Mater. 39 (2005) 647.

[27] Y. Liu, B. Hwang, W. Jian, R. Santhanam, Thin Solid Films 374 (2000) 85.

[28] O. Inganas, R. Erlandsson, C. Nylander, I. Lundstrom, J. Phys. Chem. Solids 45 (1984) 427.

[29] B. Tian, G. Zerbi, J. Chem. Phys. 92 (1990) 3892.

[30] A. Chen, H. Wang, Xiaoyu Li, J. Chem. Soc. Chem. Commun. (2005) 1863.

[31] J. Liu, M. Wan, J. Polym. Sci., A 38 (2000) 2734.

[32] T. Nguyen, A. Diaz, Adv. Mater. 6 (1994) 858.

[33] Y. Furukawa, S. Tazawa, Y. Fujii, I. Harada, Synth. Metals 24 (1988) 329.

[34] (a) A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984 (Chapter 6);
(b) F.A. Cotton, G. Wilkinson, Advanced Inorganic chemistry, John Wiley, 1988 (Chapter 19).

[35] Chepuri R.K. Rao, D.C. Trivedi, Mater. Lett. 60 (2006) 3165.

[36] M. Moreno-manas, R. Pleixats, Acc. Chem. Res. 36 (2003) 638.

[37] K.M. Mangold, F.M. Juttner, Synth. Metals 144 (2004) 221.

[38] A. Malinauskas, Synth. Metals 104 (1999) 75.