Preparation and degradation of highly conducting polyaniline doped with picric acid

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Abstract

Preparation and characterization of highly conducting polyaniline (PANI) doped with picric acid (PA) was proved with the help of various techniques. Elemental analysis, FTIR and XPS spectroscopic measurements confirm that the PA operates as a protonating agent to induce the internal conversion of PANI emeraldine base (PANI-EB) to the PANI emeraldine salt (PANI-ES) with the doping level 50%. Molecular modeling calculations (MM+) showed that the optimum geometric structure of 2PA:1PANI (energy 38.231388 kcal/mol, and gradient 0.065246).

The observed higher conductivity (\(\sigma \sim 150 \text{ S/cm}\)) of PA-doped PANI film prepared at molar ratio 2PA:1PANI (EB) is attributed to the change in the molecular conformation from coil to expanded coil-like. PA-doped PANI is thermally unstable above \(135 \degree C\) and the thermal processing with other insulating matrix is not profitable but the solution casting is highly promising. PA-doped PANI with acrylonitrile-butadiene-styrene copolymer has been fabricated and showed the threshold value 4 wt.% of a conducting material. The reduced PA-doped PANI reveals an ability to store electrical energy of about 110.43 Wh/kg in a condensed lightweight form. The immediate decoloration of the dark green (\(\lambda_{\text{max}} \sim 815 \text{ nm}\)) PANI after addition of 5.5 \(\mu\text{g/ml}\) KMnO\(_4\) in strong acid medium (pH 1.0, H\(_2\)SO\(_4\), 40% DMF) is due to the highest oxidized form of PANI. Increasing the absorbance with increases in the KMnO\(_4\) concentration (\(\mu\text{g/ml}\)) at \(385 \text{ nm}\) has been successfully applied to the determination of trace amount (0.55 \(\mu\text{g/ml}\)) of Mn(VII) in a synthetic solution. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Conducting polymers have attracted much scientific and technological interest in recent years. A significant portion of these studies has been devoted to polyaniline (PANI) which exhibits excellent environmental stability in its conducting form. The protonation of PANI emeraldine base (PANI-EB) or its derivatives with organic acids can be used for the protonation of electrically conducting polymers with improved processability [1–5]. Sulfonic acids have often been employed for the preparation of soluble products: Polyaniline dodecylbenzensulfonate was reported to be soluble in toluene [4,5]. PANI protonated with \(p\)-hydroxybenzenesulfonic acid in dimethylsulfoxide, etc. Protonation of PANI base with cresolsulfonic acid, \(p\)-toluenesulfonic acid, methansulfonic acid, and other sulfonic acids were used to produce electrically conducting polymers partially soluble in various solvents [6–14].

The electrical conductivity of films cast from solutions of PANI-CSA in \(m\)-cresol [5,13,15–17], \(\sigma \sim 10^2 \text{ S/cm}\), is about two orders of magnitude higher than that of PANI protonated with mineral acids \([7,9,15,18,19]\), \(\sigma \sim 10^{-1} \sim 10^1 \text{ S/cm}\), and other organic acids [5]. This observation raised an interest in understanding the conduction mechanism of these materials \([20,21]\). Also the optical properties and morphology of PANI-CSA have been recently investigated [22,23]. We have recently...
observed that, besides sulfonic acids, picric acid (PA: 2,4,6-trinitrophenol) also protonates poly (o-toluidine) base and yields an electrically conducting polymer [24].

As far as back 1974, Pistoia [25] discovered that the yield of polystyrene formed at an anode falls at high current densities (18 mA/cm²), its molecular weight increases sharply and those are small quantities of polymer insoluble in acetone and CCl₄. These could be caused by electrochemical oxidation and further degradation of polystyrene [26,27]. Degradation processes were observed in the study of electrochemical pyrrole polymerization at the anode [28,29]. Investigations of the initial stage of aniline electropolymerization in acidic aqueous solution have established that middle peaks actual reflect the occurrence of oxidative hydrolysis and degradation reactions [30–33].

In the present study, incorporation of picric acid into a polyaniline matrix has been investigated. Thermal stability, molecular conformation of PA-doped PANI and fabricated composite consisting of PA-doped PANI (conducting material) and insulating acrylonitrile-butadiene-styrene copolymer (ABS) matrix also discussed here. The reduced PA-doped PANI, can store electrical energy (~110.43 Wh/kg) in a condensed lightweight form. Degradation of PA-doped PANI in strong acid medium, and inorganic oxidizing agent is due to the highest oxidized form of PANI. Beer’s law is obeyed (λ ~ 385 nm) for Mn(VII) in the range 0.0–16.5 μg/ml in a synthetic solution.

2. Experimental

Aniline and picric acid were purchased from Wako Chemical Co., and used as received. All other chemicals and solvents used were of analytical reagent grade. Doubly distilled water was used in the experiments. Polyaniline was synthesized following the previously described procedure [34]. The HCl-doped PANI was converted to the base form (PANI-EB) by treating it with 3% aqueous ammonium solution for 2 h, followed by washing with deionized water until the washing solution was colorless, followed by methanol, and diethyl ether. Glassy carbon (GC) electrodes (Tokai, grade GC-20, diameter 3 mm) were used as working electrodes for the preparation of the PA-doped PANI film. All potentials reported here are referred to an aqueous Ag/AgCl (sat. KCl) electrode. PA-doped PANI films were prepared as follows: Aniline (0.2 M) was polymerized under potentiostatic conditions (+1.0 V) in an aqueous solution containing 0.1 M picric acid. To prepare PA-doped PANI, the emeraldine base form of PANI was mixed with PA in the molar ratio of 1:2 for PANI-EB (tetramer) to PA with an agate mortar and pestle in an inert atmosphere. The 2% (w/w) solution of PA-doped PANI in m-cresol was prepared at 50 °C under ultrasonic irradiation for 1 h. The resulting viscous deep green solution was further utilized for the preparation of composites. The composite solutions with different weight ratios of PA-doped PANI and ABS were obtained by mixing required quantities of both polymers at room temperature. The conductivities of PA-doped PANI and its composite with ABS were measured by using a comb shaped Pt microelectrode. After casting the composite solution on the microelectrode and removing the solvent (m-cresol) at 50 °C, the conductivity was monitored by the two probe method using a Hokuto Denko galvanostat (model HA-501). Thermogravimetric/mass analysis were performed with a JEOL MS-TG/DTA (Model 220) under a helium atmosphere. A given amount of PA-doped PANI was placed in a sample holder, and the temperature was changed from 40 to 610 °C at the programmed heating rate of 5 °C/min. Elemental analysis of PA-doped PANI was carried out on an Elementer analyesysteme (GmbH, Donaasruhr-7, D-63452) Hanau, Germany. Molecular modeling calculations (MM+) was carried out with Hyper-Chem programm version 5.

X-ray photoelectron spectroscopic (XPS) analysis of the PA-doped PANI film was carried with Fisons, ESCALB 210 apparatus using an AlKα X-ray source (1486.6 eV photons). The X-ray source was run at 15 kV, and 20 mA and the energy resolution was better than 0.01 eV at the energy pass chamber was about 10⁻⁶ pa. FTIR spectroscopic measurements in KBr pellets were carried out using a Shimadzu (Type 470) spectrometer. Transmission electron micrograph (TEM) of the PA-doped PANI/ABS composite film were taken with a Hitachi apparatus (H 8000) in which the sample film was directly cast on carbon-coated copper grid. The morphology of the modified PANI deposits was examined with a scanning electron microscope (SEM JEOL JSM, 35). The absorption spectra were recorded on a Shimadzu UV-2101/33101 PC, at 25 ± 1 °C using 1 cm matched stoppered quartz cells. The pH-measurements were carried out using a Fisher Scientific Accument, Digital pH-meter model 810.

3. Results and discussion

3.1. Spectroscopic characterization of PA-doped PANI

A typical N(1s) XPS spectrum of PA-doped PANI is shown in Fig. 1. The spectrum is similar to those doped with other organic functional acids like dodecylbenzenesulfonic acid [35]. The imine nitrogen component, characterized at binding energy ~398.2 ± 0.1 eV in the emeraldine base [36], disappeared completely. The peak located at higher binding energy ~401.9 ± 0.1 eV was assigned to the generated iminium ions (-N⁺H⁻) while...
the one at lower energy centered at \( \sim 399.1 \pm 0.1 \) eV indicates the presence of the radical cation (-N\(^{\ddagger}\)H-). The integrated areas of these two peaks 1:1, is consistent with the intrinsic oxidation state of the polymer with doping level of 50%.

After protonation of the PANI base form with PA at equimolar protonation, the 1593 and 1498 cm\(^{-1}\) are ascribed to quinoid and benzenoid rings (PANI-EB) [3] respectively. These wave numbers are shifted to 1550 and 1480 cm\(^{-1}\) respectively for PA-doped PANI. Such a red shift indicates the delocalization of quinoid and benzenoid structures to the semiquinoid form (polaron) in polymer chain [24], confirming the protonation of the emeraldine base. Elemental analysis of PA-doped PANI also indicated that the PANI was doped (doping level 50%) with PA (% found: C, 52.06; H, 2.96; N, 17.46 and O, 27.96). According to the MM\(^+\) it is possible to determine the lowest energy (38.231388 kcal/mol) and gradient (0.065246) of the optimum geometric structure (Scheme 1) of polyaniline doped with picric acid (2PA: 1PANI). Calculations were carried out for the other possible configurations, but they are less stable.

3.2. Morphology of PA-doped PANI

It is conceivable that surface morphology of the copolymer is related to the PA content. Therefore, SEM was used to obtain the morphological information as shown in Fig. 2. Pure PANI exhibits a granular structure in Fig. 2a, and the granular deposit is not entirely uniform over the electrode, indicating that the granule is the preferred site for further polymer growth. The PA addition [mole fraction (f\(^U\)) of PA to ANI is 1:0.12] increases the number of porous structures on the polymer film (Fig. 2b). Examination of the polyaniline (Fig. 2b) reveals more branching and less granules. These results indicate that PA may act as a cross-linking agent in its modification of polymer film morphology. Thus, PA molecules influence the growth mechanism of polymer film [37], leading to more branching networks. Fig. 2c, is a SEM micrograph for PA addition of 0.333 (f\(^U\)) which reveals the absence of a granular and a significant crack deposit. The distinct change in surface characteristics of
these polymers from granular to a crack network would result from a strong electrostatic interaction between the (-O\(^{-}\)) and cation radical nitrogen atoms (-N\(^{\ddagger}\)H-) or amine hydrogen.

The TEM observation of the composite containing 20 wt.% of PA-doped PANI is shown in Fig. 3. As seen from this figure, the ABS composite with this content of PA-doped PANI exhibits fine rod-shape particles of size ranging from 20 to 80 nm embedded in insulating ABS. These particles are seen to be located very closely to each other and electron hopping is facilitated, thereby enhancing the conduction process in this composite.

3.3. Thermal behavior of PA-doped PANI

The thermal behavior of PA-doped PANI is illustrated by the DTG curve in Fig. 4. The weight loss in the first step (~1.82%) is attributed to the description of superficial water molecules associated with the doped PANI. The mass spectra presented in Fig. 5, reveals an intense fragment (m/z:18) corresponding to water molecules stage I (Fig. 4). The PA-doped PANI then remains stable up to ~135 °C. The second step, extending up to 200 °C with the weight loss of ~16.37%, indicates the loss of picric acid and the polymer is completely dedoped at ~320 °C. The intensity of the fragments observed at m/z: 62, and 199 corresponding to NO\(_3\) and C\(_6\)H\(_3\)N\(_2\)O\(_6\), were significantly enhanced, indi-
cating the picrate ions were readily detached from the polymer backbone (Fig. 5 t2). On the other hand, the fragments with the mass spectra, \( m/z \): 77, 92, 117, and 163 are related to the polymer chain decomposition. The intensity of these fragments is not so high indicating that the polymer degradation just started at this temperature (Fig. 5 t2). More interestingly, at 320 °C, the mass spectra do not show any signal fragment resulting from the decomposition of PA, suggesting that the acid was completely dedoped from the polymer, and the total weight loss was found about \( \sim 60\% \). At higher temperature (Fig. 5 t3), appearance of fragments \( m/z \): 28, and 44 are due to the formation of \( \text{N}_2 \) and \( \text{CO}_2 \) indicating full-scale polymer degradation.

### 3.4. Electrochemical characterization of PA-doped PANI

Fig. 6 shows the cyclic voltammogram (CV) of PA-doped PANI in strong acid medium. The two redox complexes (\( p_{a1}/p_{c1} \) and \( p_{a2}/p_{c2} \)) could be explained as:

The first redox:

\[
(C_6H_4NH_2^+)(PA^-) \leftrightarrow (C_6H_4NH)^+ + e^- \tag{1}
\]

The second redox is due to the deprotonation of the imine nitrogen producing an uncharged matrix with expulsion of protons and anions according to the Eq. (2)

\[
(C_6H_4NH)^+ + (C_6H_4=NH-C_6H_4-N=) + H^+ + PA^- + e^- \tag{2}
\]

PA\(^-\) is the picrate anion.

A similar result was reported with the CV and electrochemical quartz microbalance of PANI doped with other organic sulfonic acids, [38,39]. Good linearity between the peak height (first and second) for the reduction current and the square root of the scan rate in a range of 5–100 \( \text{mVs}^{-1} \) of the PA-doped PANI film, suggested that the electron transfer is diffusion controlled.

It is interesting to note in Fig. 7 that the maximum electrical conductivity of PA-doped PANI (\( \sigma \sim 150 \text{ S/cm} \)) is about 11 orders of magnitude higher than that of PANI [3] base form (\( \sigma \sim 4.3 \times 10^{-9} \text{ S/cm} \)). In fact, MacDiarmid et al. [40], have demonstrated that the conformational change in polymer chain results in the significant change in conductivity of polymer. A plot of the conductivity vs. doping level (%) of PANI (EB) to PA (Fig. 7) revealed a similar observation to the case of CSA-doped PANI [41]. The observed higher conductivity (\( \sigma \sim 150 \text{ S/cm} \)) of PA-doped PANI films prepared at molar ratio of 2PA to 1PANI, i.e., (50% doping level), indicates the complete protonation of PANI to produce polysimquinone radical cation.
The electroactivity of PA-doped PANI is very important for many possible applications such as energy storage (ES) and batteries, and is expressed as the amount of charge that can be stored per kilogram of polymer [42]. The energy storage of PA-doped PANI can be calculated if the weight (W or Mwt/kg) of the electroactive species is known as [43]:

$$\text{ES} = \frac{\Delta Q}{\Delta V} \frac{\text{Am h}}{\text{kg}} = \frac{\text{Wh}}{\text{kg}}$$

Fig. 8 showed that the reduced PA-doped PANI reveals an ability to store electrical energy of about 110.43 Wh/kg in a condensed lightweight form. This would solve a current problem of redox-flow energy-storage systems, which require huge reservoirs to store electroactive material in solutions. The electroactive species can be used to generate the electric power, then the reservoir capacities can be much smaller than those required for the redox-flow systems based on the current design.

3.5. Induced electrical conductivity into ABS by the incorporation of PA-doped PANI

By utilizing functionalized protonic acid, such as picric acid, one can design the conducting polyaniline complex to be soluble in a specific solvent. After doping of PANI with PA, the conducting PANI is soluble in m-cresol. Conducting polyblends can be made by co-dissolving the PANI/PA complex and the bulk polymer (ABS). Fig. 9 shows the conductivity of the composite plotted vs. the weight percent of PA-doped PANI in ABS matrix, showing the percolation threshold at ~4 wt.% of a conducting material (PA-doped PANI). This percolation threshold is considerable lower than that (~16 vol.%) reported [44]. Cao et al. [4] have proved that in the composite with counter ion-induced conducting polymer the conductivity initiates at a concentration that is at least one order of magnitude below than the classical percolation threshold (~16 vol.%). Such a low threshold is attributed to conducting channels formed in the composite through which electrons can easily travel leading to the observed conductivity. Fizazi et al. [45] have studied the conducting poly(3-octyl-thiophene) (P3OT) doped with iodine in polyethylene (PE) gel, and found evidence about the connected conducting paths but with no indication of percolation threshold. They discussed their results in terms of adsorption of the P3OT onto the PE gel network which subsequently organizes the P3OT into the connected paths. This view is consistent with our results obtained here.

3.6. Spectrochemical stability of conducting PA-doped PANI for oxidizing agent

Stability and degradation of polymers are of importance, since environmental pollution due to plastic wastes have become increasingly serious. In a number of studies, however, authors proceeded even further to application of the degradation process for polymer reclamation, conversion or imparting it with new useful properties [46-49].

Fig. 10 shows spectrochemical degradation of HCl-doped PANI and PA-doped PANI (100 μmol/l⁻¹) by
inorganic oxidizing agent (KMnO₄) in strong acid medium (pH 1.0 adjusted by H₂SO₄, 40% DMF). The immediate decoloration of dark green ($\lambda_{\text{max}} = 815–385$ nm) PA-doped PANI after addition of $100 \mu\text{mol}\cdot\text{L}^{-1}$ KMnO₄ is due to the highest oxidized form of PANI obtained (the quinoid one) which undergoes a hydrolysis reaction to produce $p$-hydroquinone (H₂Q) by the mechanism similar to Schiff-base hydrolysis [50]. The possible mechanism of these processes are presented in Scheme 2. The end group hydrolysis of PANI is more preferable than chain group hydrolysis. The oxidation-reduction reaction of KMnO₄/PANI for a tetramer (for example) unit of aniline can be written as follows:

$$
5\text{R-PANI (tetramer)} + 16\text{KMnO}_4 + 24\text{H}_2\text{SO}_4 \\
\rightarrow 5\text{R-NH}_2 + 20\text{NH}_3 + 20\text{H}_2\text{Q} + 8\text{K}_2\text{SO}_4 \\
+ 16\text{MnSO}_4 + 24\text{H}_2\text{O} \quad (4)
$$

The number of electrons required for complete degradation is expected to be 3.0 for dimer, 2.5 for tetramer and 2.0 for octamer per unit of aniline [51].

3.7. Spectroanalytical sensitivity of PA-doped PANI for inorganic oxidizing agent

The addition of oxidizing agent (KMnO₄, $\mu\text{mol}\cdot\text{L}^{-1}$) to PA-doped PANI (10 $\mu\text{mol}\cdot\text{L}^{-1}$) in strong acid medium (pH 1.0 adjusted by H₂SO₄, in 40% DMF) is not only important for understanding the degradation of polymer matrix, but also useful for analytical purpose. This procedure was applied for determination of manganese (VII) in a synthetic solution using spectrophotometric technique. The significant increases of the absorbance at $\sim 385$ nm during addition (10–300 $\mu\text{mol}\cdot\text{L}^{-1}$) of Mn(VII). Fig. 10, was analyzed using a least-square program. The absorption spectra remains unchanged for at least 24 h. At the optimum conditions (cf. Experimental), Beer’s law is obeyed over a range of 10–300 $\mu\text{mol}\cdot\text{L}^{-1}$ of Mn(VII) without the need for any separations. The molar absorptivity ($\epsilon$) and the relation coefficient are $4.87 \times 10^4$ $\text{mol}^{-1}\cdot\text{cm}^{-1}$ and 0.995, respectively. The reproducibility of the method was checked by testing two
series of solutions containing 100 and 300 μmol\(^{-1}\) of oxidant. The relative standard deviation was found to be less than 2% for ten experiments. The proposed method has been successfully applied to the determination trace amount (0.55 μg/ml) of Mn(VII) in a synthetic solution.

4. Conclusions

Polyaniline in its base form can be protonated with picric acid. The structural changes induced by the protonation are reflected in elemental analysis, FTIR, and XPS measurements. These results were confirmed by MM+ calculations. The reduced PA-doped PANI reveals an ability to store electrical energy about 110.43 Wh/kg in a condensed lightweight form. The immediately decolorization of dark green PA-doped PANI after addition of oxidizing agent (100 μmol\(^{-1}\), of KMnO\(_4\)) is due to the highest oxidized form of PANI undergoing a hydrolysis reaction. The useful concentration range (10–300 μmol\(^{-1}\)) of Mn(VII) for Beer’s law is widened. The results obtained in this work show that the proposed method is applicable to determine trace amount (0.55 μg/ml) of Mn(VII) in a synthetic sample and that the method is simple, selective, and accurate, suggesting the possible application in real samples.

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