Structural Changes in Polyaniline upon Reaction with DPPH

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Polyaniline (PANI) powder was prepared using ammonium persulfate (APS) as the oxidant with an APS to aniline (ANI) ratio of 1.5. The powder was then reduced by hydrazine or dedoped using an aqueous ammonium solution. The antioxidant properties of these polymers were investigated through their reaction with the stable and intensely coloured DPPH radical. The highest DPPH scavenging activity was shown by reduced PANI, followed by PANI as-prepared, with the least radical scavenging shown by dedoped PANI. The reaction of PANI and DPPH radicals causes structural changes in PANI, with a transformation of –NH– and N\(^+\) groups to –N=.

Keywords: Polyaniline; Conducting polymer; DPPH; Radical scavenging

I. INTRODUCTION

Conducting polymers (CPs) have been reported to demonstrate free radical scavenging activity [1]. Polyaniline (PANI) is one of the most promising CPs for a range of applications, including potential antioxidant properties [2]. DPPH\(^•\) is a stable free radical which is commonly used to evaluate the antioxidant activity of molecular compounds. The DPPH radical scavenging of PANI has been demonstrated previously [3, 4], and it is of interest to investigate the structural changes of PANI during reaction with the DPPH radicals.

In this study, changes in the structures of PANI have been examined using mainly spectrometric methods, including FTIR, XPS and ESR. Cyclic Voltammetry was also used to examine the redox properties of the PANI powders.

II. EXPERIMENTAL

A. preparation PANI powders
Aniline (ANI) was distilled under reduced pressure and stored in the dark under nitrogen. PANI powder was chemically synthesized by adding 25 mL of APS solution (0.3M) into 25 mL of milli-Q water containing 5\(\times\)10\(^{-3}\) mol of ANI with vigorous stirring for 24 hours. The PANI powder was then filtered, washed several times with distilled water and methanol, and dried in a vacuum oven at 35\(^°\)C. PANI powder (30 mg) was reduced by reacting with 2 mL of hydrazine in 10 mL of Milli-Q water and dedoped (deprotonated) with 10 mL of 15% ammonium water for 48 hrs.

B. DPPH assay
The DPPH free radical scavenging capacity of each sample was carried out by adapting methods used previously for soluble forms of conducting polymers [2]. The procedure involved adding 1.0 mg of each test powder, measured using a 5 digit balance to ensure a weight in the range between 1.00 and 1.05 mg (weighing error <5%), to 20.0 mL of a 255 \(\mu\)M methanolic DPPH solution, which was left to stand for various times with shaking for the first 6 hours from one to 24 hours at room temperature. After centrifugation, the supernatant was removed and the absorbance at 516 nm was measured using a Schimadzu UV-1700 UV-visible spectrophotometer, with all analyses run at least in duplicate. The number of \(\mu\)moles of DPPH which reacted over a 24 hour period was then calculated after subtracting away the background loss of a DPPH solution without added PANI.

C. Spectroscopy
IR spectra were recorded using a Perkin-Elmer Spectrum 1000 FTIR spectrometer on samples prepared as KBr discs. The oxidation state and the protonation levels of PANI powders were determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were made on a Kratos Axis Ultra spectrometer with an Al K\(\alpha\) source (1486.7 eV). Electron Spin Resonance (ESR) spectra of 12.0 mg of the PPy powders were measured at ambient temperature using a JEOL JES-FA 200 ESR spectrometer in an ESR quartz tube.

D. Cyclic Voltammetry
The electrochemical properties of the sample powders were determined using a BAS100B electrochemical analyzer. Sample powders were dispersed in CHCl\(_3\) (2 mg in 2 mL) and the dispersion was then dropped onto a 3 mm diameter glassy carbon working electrode to form a film. The cell filled with 0.1 M HCl was purged with N\(_2\) for approximately 10 min. Cyclic voltammograms were recorded in the potential range from −300 to +850 mV.
III. RESULTS AND DISCUSSION

A. DPPH free radical scavenging activity of PANI powders

Polyaniline (PANI) powder was synthesized using APS as oxidant, and reduced by hydrazine and dedoped with ammonium hydroxide. The formation of different oxidised structures for PANI (including radical polarons and bipolarons) are presented in Fig. 1. The DPPH free radical scavenging activities of the sample powders was determined for the reaction of 1.0 mg of PANI with 5.1 µmole of DPPH radicals. As seen in Fig. 2, the reduced PANI and as-prepared PANI powder removed 76% and 72% respectively of the DPPH radicals, while the dedoped PANI only removed 54% of DPPH•. The results indicate that –NH– and N+ groups are important reacting units for PANI, when they act as DPPH free radical scavengers. The possible mechanism of the reaction is that –NH– and N+ groups are oxidized through –N= species [5, 6]. The change in the structure of PANI being an oxidation process has been indicated in previous studies [7, 8].

B. IR spectra of PANI

The FTIR spectra of polyaniline powders were recorded using KBr pellets (Fig. 3). The peaks at 1576 and 1498 cm\(^{-1}\) are assigned to C=C stretching vibration of quinoid (C=C (Q)) and benzenoid ring (C=C (B)) [9–11]. The absorbance at 1140 cm\(^{-1}\) is due to the stretching vibration of N=Q=N [10]. The band at 1294 cm\(^{-1}\) corresponds to the stretching vibration of the imine group C=N [12] and the band at 822 cm\(^{-1}\) to the bending vibration of C–H. As seen in Fig. 3, the peak at 1576 cm\(^{-1}\) increased and the peak at 1498 cm\(^{-1}\) declined due to the reaction with DPPH•. The increase of the C=C (Q)/C=C (B) ratio, representing the transformation of –NH– to –N=, indicates that PANI was oxidized during reaction with DPPH• (see Fig. 1).
TABLE I: Elemental analysis of PANI before (A) and after (B) reaction with DPPH free radicals, according to XPS wide spectra.

| At %        | S/N (%) |
|-------------|---------|
| N 1s   | 10.28  | 78.14  | 9.87  | 1.71  | 16.6  |
| C 1s   | 80.27  | 9.11   | 0.89  | 9.1   |
| O 1s   | 9.87   | 9.11   | 0.89  | 9.1   |
| S 2p   | 1.71   | 0.89   | 9.1   |

At %: relative atomic concentrations (%)

FIG. 4: ESR spectra of PANI (a) before and (b) after reaction with DPPH•.

C. XPS investigation of the PANI powders

An elemental analysis of the PANI powders before and after reaction with DPPH radicals is presented in Table I. The S/N ratio of PANI decreased by 46%, from 16.6 to 9.1, after reaction with DPPH• for 24 hrs. The lowering of the S/N ratio indicates a loss of N+ species in the PANI powders, since the sulfur (S) is derived mainly from the dopant HSO4−/SO2−4 [13], as has been applied previously to estimate the level of doping and protonation of PANI [14]. The result provides further evidence for an oxidation or deprotonation process moving from N+ to –N=.

D. ESR spectra of PANI

20 mg of PANI powder was mixed with 200 mL of DPPH solution (510 µM) for 24 hours. The PANI powders before and after reaction with DPPH free radicals were then investigated by Electron Spin Resonance (ESR) spectrometry. The spectra of these two samples are presented in Fig. 4, which shows that the PANI powder contains 45% less free radicals (polaron) after reaction with DPPH•. The diminution of the polaron signal confirms the results obtained from the XPS investigation, indicating a loss of N+ species during reaction with DPPH•.

FIG. 5: Cyclic voltammograms of PANI powders (a) before and (b) after reaction with DPPH•, cast on a glassy carbon working electrode and cycled in 0.1 M HCl at a scan rate of 20 mV·s⁻¹.

E. Cyclic Voltammetric investigation

The electrochemical properties of the PANI samples were evaluated by cyclic voltammetry as shown in Fig. 5. The voltammogram of the as-prepared PANI powder showed oxidation peaks at +121, +247 and +446 mV and reduction peaks at +62 and +420 mV, at a scan rate of 20 mV·s⁻¹. The first anodic peak at 121 mV is assigned to the oxidation of the leucoemeraldine to the emeraldine form of PANI (Fig. 1(a)), and the peak at 446 mV to the oxidation from emeraldine to pernigraniline (Fig. 1(b)). The presence of an intermediate peak at 242 mV points to the presence of branched chains and/or shorter oligomeric species which are being oxidized in the 100-300 mV region. After reaction with the DPPH radicals, the same level of electroactivity was not readily obtained on the cast films, and the possibility of further cross-linking reactions resulting from reaction with DPPH in addition to internal PANI redox processes needs to be explored further.

IV. CONCLUSION

The radical scavenging activity of reduced PANI, as-prepared PANI and dedoped PANI was evaluated through their reaction with DPPH free radicals. The reduced PANI was the most efficient scavenger (with a greater capacity to be oxidised), followed by as-prepared PANI and dedoped PANI. The reaction of PANI with DPPH radicals leads to the transformation of –NH– and N+ groups through to more fully oxidized –N=–. Spectroscopic evidence from FTIR and ESR showed the change from –NH– to –N=– and a lowering of the content of N+ groups. The decline of clearly defined oxidation peaks in voltammograms of the PANI powders confirms that structural changes had occurred in the PANI powders during reaction with DPPH radicals.
Acknowledgments

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