Synthesis of Aniline – Pyrrole Copolymer Nanostructures by the Pulsed Galvanostatic Polymerization 11021

By H Karami
Synthesis of Aniline – Pyrrole Copolymer Nanostructures by the Pulsed Galvanostatic Polymerization

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In this work, aniline- pyrrole copolymer (APC) nanoparticles are synthesized by the pulsed galvanostatic polymerization method. Two cylindrical platinum grid electrodes with diameters of 1 and 3 cm are used as coaxial in the electrochemical cell containing aniline, pyrrole and HCl solution. Aniline and pyrrole are directly oxidized to aniline and pyrrole cation radicals as polymeric precursors on the surface of platinum anode. The effects of synthesis parameters such as pulsed current density, pulse time (t on), relaxation time (t off), temperature and concentrations of aniline, pyrrole and hydrochloric acid are investigated by the “one at a time” method. The optimized conditions include 0.1 M pyrrole, 0.1 M aniline and 0.12 M hydrochloric acid, 9 mA/cm² current density, 1 s t on, 1 s t off and solution temperature of 1°C. The synthesized nanomaterials are filtered and washed with 0.12 M hydrochloric acid solution and finally washed with distilled water. The obtained paste is dried at 80°C for 90 min under vacuum. The synthesized samples are characterized by SEM, TEM, DLS, TGA/DTA, IR spectroscopy, UV- Vis spectroscopy and Cyclic Voltammetry. The optimized sample consisting uniform nanoparticles with average diameter lower than 10 nm.

Keywords: Polymer nanoparticles, aniline- pyrrole copolymer, electropolymerization, pulsed galvanostatic method

1. INTRODUCTION

As an outcome of the developments in polymer technology, conductive polymers can act as substitutes for naturally conductive materials [1]. In last decade, great scientific attention has been paid to the conductive polymers such as polythiophene, polyaniline, PPyr, polyparaphenylene, PANi and etc [2]. Conductive polymers are being commonly used in various applications such as rechargeable...
batteries [3, 4], production of semiconductor photoanodes [5], electrochemical displays [6], data storage devices [7], and biochemical analysis [8].

As a wide application area has inevitably encouraged research in the field of electro-conducting polymers, mainly directed towards obtaining improved properties. The synthesis of copolymers (containing two or more monomers) is the accepted method to change the properties of the polymers and obtain the desired specifications. There are many reports about the synthesis of various copolymers. In all of them, achieving of the desired properties is the main objective. One major problem that limits the availability of conductive polymers is the rareness of the conjugated π-bond containing monomers that are essential for their synthesis. The copolymerization as well as provides better properties, help to overcome this limitation as the number of conductive polymers obtained from the same monomer is increased. Consequently, it becomes possible to pick out superior properties of the individual monomers that polymerizing different environments and combine them together.

Polyaniline (PAni) and Polypyrrole (PPyr) are the famous conductive polymers with appropriate properties such as high electrical conductivities and good stability in the air. Both PAni and PPyr have better performance as cathode of rechargeable batteries [9-13]. The reasonable expectation is that the aniline/pyrrole copolymerization can improve their properties, especially in rechargeable batteries. Copolymerization of aniline and pyrrole can be done through chemical [14-17] and electrochemical methods [1]. The electropolymerization has many advantages including simplicity of preparation and its easy to control the initiation and termination steps of polymerization. The electrochemically synthesized APC is a relatively pure form compared to that obtained from chemical polymerization due to the absence of additional species such as oxidants, surfactants, and so on.

The reported electrochemical methods used in synthesizing conductive polymers include: the constant potential (potentiostatic) [18-25], constant current (galvanostatic) [26, 27], cyclic Voltaammetry [28-33], pulse constant potential (pulse potentiostatic) [34-39], pulse current (pulse galvanostatic) [40-41], and step-wise galvanostatic [44, 45] methods. Pulse galvanostatic electrosynthesis is a powerful technique in controlling the size of the particles and the morphology of the samples. On the other hand, this method can be used in double electrode cells, allowing it to be applicable to laboratory and industrial scales [2].

In this work, APC nanoparticles are synthesized by applying the pulse current (pulse galvanostatic method) into a double-electrode electrochemical cell consisting of aniline, pyrrole and HCl. The parameters affecting the morphology and size of the particles in APC including the pulse height, pulse time, relaxation time, aniline concentration, pyrrole concentration, acid concentration and solution temperature which are investigated and optimized by the "one at a time" method.

2. EXPERIMENTAL

2.1. Materials

Aniline, pyrrole, hydrochloric acid and dimethyl sulfoxide (DMSO) were purchased from Merck. Next, Aniline and pyrrole were distilled prior to being used and subsequently stored in the dark sealed vessels. Double-distilled water was used in all experiments.
2.2. Instrumental

All the electrochemical experiments were carried out by an electrolyzer equipped with a pulse system (BTE 04, made in Karami technical group, Iran). Cyclic Voltammetry (CV) experiments were done by Autolab (Eco Chimie, PGSTAT-10, Netherlands). The pores of the graphite electrode was mechanically filled with the synthesized APC nanoparticles and was used as the working electrode in all CV experiments. A platinum electrode and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The IR spectrum was recorded using an FT-IR spectrophotometer (JASCO1600, Japan) in KBr pellets and reported in cm\(^{-1}\) to identify the chemical structure of APC nanoparticles. The morphology of the samples was characterized by scanning electron microscopy (SEM, Cam Scan, MV 2300, England). UV-Visible absorption spectra were measured using a double-beam spectrophotometer (GBC 197, Australia). Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Perkin Elmer Thermal analysis, USA) for thermal studies.

2.3. Synthesis procedure

Before each deposition, one pair of cylindrical platinum grid electrodes was placed in the diluted solution for 30 minutes and then rinsed with double-distilled water to clean any surface pollutant. Two cylindrical platinum grid electrodes were coupled together to coaxial form into the electrochemical cell. The smaller electrode was connected to the positive pole of the electrolyzer to act as the anode. The cell was filled with a solution containing 0.1 M aniline, 0.1 M pyrrole and 0.12 M hydrochloric acid at a temperature of 1°C. The Nitrogen gas was passed through the electropolymerization solution to move dissolved oxygen. The current density of 9 mA cm\(^{-2}\), 1 s \(t_{on}\), 1 s \(t_{off}\) and the temperature of 1°C was inserted into the cell for 3 h while the solution was stirred. The synthesized APC nanoparticles was filtered and washed first using 0.12 M hydrochloric acid and finally double-distilled water. The collected paste was then vacuum-dried at 80°C for 24 min. The values of some effective parameters including the pulse time \((t_{on})\), relaxation time \((t_{off})\), were varied and optimized through the “one at a time” method. Finally, all the synthesized samples were studied by SEM. Four samples were selected to more characterize by UV-Vis spectroscopy, cyclic voltammetry and measurement of electrical conductivity. Optimized sample was characterized by IR spectroscopy, TGA, TEM and DLS.

3. RESULTS AND DISCUSSION

In the current study, APC nanoparticles were synthesized by means of the pulsed current method on the Platinum grid electrode from a solution including aniline, pyrrole and HCl. Figure 1 shows a DC current pulse diagram that was used. The pulse diagram reveals that a current pulse has at least three variables: (a) pulse height (pulsed current amplitude or pulse current density), (b) pulse time \((t_{on})\) and (c) relaxation time \((t_{off})\).
Figure 1. The DC current pulse diagram that shows: (a) pulse height, (b) pulse time ($t_{on}$) and (c) relaxation time ($t_{off}$).

Addition to the mentioned parameters in Fig. 1, the present method consisting chemical parameters such as synthesis temperature and aniline, pyrrole and acid concentrations. In this work, the optimized values of some parameters such as pulsed current density (9 mA cm$^{-2}$), pyrrole concentration (0.1 M), aniline concentration (0.1 M) and hydrochloric acid concentration (0.12 M) from previous reports were taken and were constant in all experiments of this work [2,46]. The other parameters were fully studied.

3.1. Optimization of pulse time ($t_{on}$)

The effects of pulse time on the structure and morphology of APC samples were investigated. To investigate the effects of pulse time, five samples were synthesized at different pulse times (0.25 s, 0.5 s, 1 s, 1.5 s and 2 s). In these experiments, the pulse current density, $t_{off}$, temperature, aniline, pyrrole and HCl concentrations were 9 mA cm$^{-2}$, 1 s, 30 $^\circ$C, 0.1 M, 0.1 M and 0.12 M, respectively. Figure 2 shows the SEM images of the APC samples.
Figure 2. SEM images of the APC samples synthesized in 9 mA cm$^{-2}$ pulsed current, 30°C temperature, 0.1 M pyrrole, 0.1 M aniline and 0.12 M hydrochloric acid and with different pulse times 0.25 s (a), 0.5 s (b), 1 s (c), 1.5 s (d) and 2 s (e).

As can be seen in Fig. 2, the pulse time can strongly change the morphology and particle size of the samples. Based on the presented SEM images, pulse time of 1 s brings about more uniform nanoparticles with a smaller diameter than the others (Fig. 2c). Each current pulse contains a calculable number of electrons whose number varies depending on the pulse time [2]. During the application of the pulse, aniline-pyrrole copolymer nanoparticles are formed. Any variation in the number of electrons can affect the morphology and the size of the sample particles. At the beginning of each pulse, the nucleation process is faster than the particle growth [47]. Conversely, at the end of each pulse, it is the particle growth that is faster than the nucleation process [2]. Therefore, the pulse time is an important parameter affecting the morphology of and the size of the particles in the samples.

When a current pulse is exerted into the cell, this is a big impedance against electron transmission, which causes the cell potential to increase and overcome this impedance. In each pulse, a major part of the pulse time is spent on increasing the potential [2]. Once the cell potential has reached the suitable degree, the oxidation of aniline and pyrrole will start. Therefore, the effective period of the optimized pulse time is below 1 s.
3.2. Optimization of relaxation time ($t_{off}$)

To investigate the effects of relaxation time on morphology and the structure of the synthesized APC, we apply different relaxation times (0, 0.25 s, 0.5 s, 1 s, 2 s and 3 s). In these experiments, the pulse current density, $t_{on}$ temperature, aniline, pyrrole and HCl concentrations were 9 mA cm$^{-2}$, 1 s, 30°C, 0.1 M, 0.1 M and 0.12 M respectively. Figure 3 shows the SEM images of APC samples which were synthesized at different relaxation times. SEM images indicate that when the $t_{on}$ is 1 s, it leads to more uniform nanoparticles and smaller diameters than the others. Pulse on time, plays an important role in controlling chain size and chain defects [48]. The relaxation time in pulse electropolymerization is the main factor affecting the mechanism of the particle growth [2]. At low relaxation times, aniline-pyrrole copolymer nanoparticles are more agglomerated; further, they are not completely isolated because the relaxation between two consequent pulses is so short that before the particle formation is completed in the first pulse, the next pulse is applied and another particle begins to be formed and, as a result, gets connected to the last particle. At the longer relaxation time, the synthesized nanoparticles have rearrangement to further. Thus, using the longer relaxation time than 1 s cause the non-desirable morphology of synthesized samples. Therefore, relaxation time of 1 s can be used as the suitable amount in synthesizing uniform nanoparticles.
Figure 3. SEM images of the APC samples synthesized in 9 mA/cm² pulsed current, 1 s t_on, 30°C temperature, 0.1 M NiCl₂, 0.1 M aniline and 0.12 M hydrochloric acid and with different relaxation times: 0 s (a), 0.25 s (b), 0.5 s (c), 1 s (d), 2 s (e) and 3 s (f).

3.3. Optimization of synthesis temperature
As demonstrated by our previous studies [2, 46, 49-54], the temperature of electrosynthesis solution is an important parameter that can affect the morphology and the size of the particles of the final product. Five samples were synthesized at different temperatures (1 °C, 10 °C, 20 °C, 30 °C and 40 °C). In these experiments, the pulse current density, \(t_{\text{on}}\) \(t_{\text{off}}\), aniline, pyrrole and HCl concentrations were 9 mA cm\(^{-2}\), 1 s, 1 s, 0.1 M, 0.1 M and 0.12 M, respectively. Figure 4 shows the SEM images of APC samples which were synthesized at different temperatures.

The SEM images indicate the synthesis temperature can change the morphology and particle size of APC. Based on the previous report, electropolymerization temperature has a substantial influence on the mechanical characterization as well as on conductivity and redox properties of the final sample [55]. It should be noted that a decrease in the redox properties is observed as the temperature increases. At higher temperatures, side-reaction such as solvent discharge and nucleophilic attacks on polymeric radicals cause the formation of more structural defects, resulting in lower conducting APC. In general, higher conductivities are obtained at lower temperatures [56, 57]. In acidic medium, the overall process is favored by lower reaction temperatures [58]. Based on Fig. 4, the sample synthesized at 1 °C has the smallest and most uniform nanoparticles. Therefore, to obtain an APC sample with the highest conductivity and smallest particles, synthesis can be done at the lowest temperature (1°C). In this temperature, the produced sample was black in color.

3.4. Characterization of synthesized aniline-pyrrole copolymer nanoparticles

Based on the optimization experiments (sections 3.1 to 3.3), the optimum condition for the synthesis of APC nanoparticles by the pulse electropolymerization method are 9 mA cm\(^{-2}\) current density, 1 s relaxation time, 1 s pulse time, 1°C solution temperature, 0.1 M, 0.1 M pyrrole and 0.12 M hydrochloric acid.

Figure 5 shows the SEM images of the optimized APC nanoparticles in four magnifications.
Figure 5. SEM images of the optimized APC nanoparticles in four magnifications: 15000 (a), 30000 (b), 60000 (c) and 100000 (d).

Based on these SEM images, the optimum sample contains nanoparticles with 20 nm average diameter. For more clarifications, the optimum sample was analyzed by TEM and DLS. Figure 6 shows the DLS diagram and TEM micrograph. TEM and DLS results show that the sample containing nanoparticles with average diameter lower than 10 nm.

Figure 7 displays the FT-IR spectrum of the optimized APC nanoparticles. FT-IR spectroscopy was incorporated to characterize the molecular structure of the optimized APC nanoparticles.

According to [44], 500 to 900 cm\(^{-1}\) absorption bands attributed to the bend vibrations of C-H bonds and 1350 to 1000 cm\(^{-1}\) absorption bands attributed to C-N bonds [50]. Vibration bands of the ring are located at 1547 and 1461 cm\(^{-1}\) [60]. According to another study [60], absorption band at 3425 cm\(^{-1}\) attributed to aromatic N-H bonds stretching vibrations in PPy, but in this study, position of this absorption bond has low change and is 3432.67 cm\(^{-1}\). Also, in other study [61], the absorption band of C=C bonds stretching, vibrations benzenoid rings in PANi reported at 1490 cm\(^{-1}\), but in this study, position of this absorption bond has low change and it is 1427.07 cm\(^{-1}\). Therefore, this changes
in position of this absorption bands can related to the bonding between aniline and pyrrole in synthesized APC.

![TEM image and DLS diagram for APC nanoparticles](image)

**Figure 6.** TEM image and DLS diagram for APC nanoparticles

![FT-IR spectrum of the APC nanoparticles](image)

**Figure 7.** FT-IR spectrum of the APC nanoparticles synthesized in the optimum conditions

### 3.5. Electrochemical studies

To investigate the effect of morphology on the electrochemical behavior of APC, four experimental conditions from the experimental set (section 3.1 to 3.3) were chosen (Table 1) and four APC samples were synthesized in the selected conditions.
Table 1. Four different synthesis conditions selected for synthesizing of different APC samples for electrochemical studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pulse current (mA cm⁻²)</th>
<th>t_on (s)</th>
<th>t_off (s)</th>
<th>Aniline (mol dm⁻³)</th>
<th>2Pyrrol (mol dm⁻³)</th>
<th>HCl (Mol dm⁻³)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>9</td>
<td>1.00</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.12</td>
<td>1</td>
</tr>
<tr>
<td>b</td>
<td>9</td>
<td>0.25</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.12</td>
<td>30</td>
</tr>
<tr>
<td>c</td>
<td>9</td>
<td>1.00</td>
<td>3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.12</td>
<td>30</td>
</tr>
<tr>
<td>d</td>
<td>9</td>
<td>2.00</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.12</td>
<td>30</td>
</tr>
</tbody>
</table>

*(optimized sample)*

Figure 8 shows the SEM images of the selected samples that synthesized according to the Table 1. As it can be seen in Fig. 8, the APC sample have different morphologies and particles sizes.

Figure 2: SEM images of four APC samples which synthesized under the different conditions according to Table 1. The a, b, c and d samples were introduced in Table 1.

Many factors, including the electrolyte type, potential scan rate and aniline- pyrrol copolymer morphology can change the CV shape of APC nanoparticles.
To investigate the effect of electrolyte on the CVs, four electrolytes including 0.1 M barium perchlorate, 0.2 M sodium benzoate, 1 M potassium chloride and 0.12 M hydrochloric acid, were used for obtaining of CVs of the APC samples1 with 100 mV/s potential scan rate in the potential range of 0.8 V to 1.1 V versus Ag/AgCl reference electrode. Figure 9 displays CVs of the synthesized samples of Table 1 in the different electrolytes.

![Graphs showing CVs](image)

**Figure 9.** The effect of electrolyte type on the CVs of the synthesized APC samples: (A) barium perchlorate 0.1 M, (B) sodium benzoate 0.2 M, (C) potassium chloride 1 M (D) hydrochloric acid 0.12 M. In all curves, a, b, c and d are the samples labels according to Table 1. All CVs were taken with 100 mV/s potential scan rate.

According to Fig. 9, the 0.12 M hydrochloric acid is suitable electrolyte for this cyclic voltammetry studies, because the cyclic voltammetry diagrams of this electrolyte have more obvious
peaks than other diagrams. The observed result is related to this fact that the doping and decrapping of polymer depends strongly on hydrogen and chloride ions. The hydrochloric acid solution can provide enough both hydrogen and chloride ions. Therefore redox reactions can be fastly carried out. As it can be seen in Fig. 9, in all cyclic voltammograms (CVs), two pairs of redox peaks are observed. The first pair of redox peaks occurs in the potential range of -0.3 V to 0.4 V (vs. Ag/AgCl reference electrode) indicates the reversible transformation 45 Leucoemeraldine into Emeraline salt in PANi department of aniline-pyrrole copolymer. During conversion 45 Leucoemeraldine to Emeraline salt, both oxidation and doping of chloride ions are done. The second pair of redox peaks occurs in the potential range of 0.4 V to 1 V which is attributed to the transformation of emeraldine salt into permigraniline in PANi [2]. These 32 s are characteristic of PANi’s conversions between the different doping states [62]. The width of the peaks suggests that these doping and undoping processes are complex [63]. Therefore, According to the CVs shown in Fig. 9, the optimized APC (sample a) has a higher redox kinetics (based the peak cut 40 ). The obtained result is related to the smaller particles of sample a than those of other samples. The improved performance of polymer is attributed to the presence of a lesser density of defects in polymer structure during polymerization by pulsed technique.

For more study, the effect of potential scan rate was investigated on the CVs of the sample a (The optimized sample in Table 1). Eventually, scan rates of 20, 40, 60, 80, 100, 120, 140 and 160 mV/s were used for cyclic voltammetry of the optimized sample in 0.12 M hydrochloric acid electrolyte and -0.8 V to 1.1 V potential range of scan respectively (Fig. 10).

![Graph showing CVs of the optimized sample at different scan rates](image)

**Figure 10.** CVs of the optimized sample (sample a in Table 1) in different scan rates in 0.12 M HCl electrolyte.
According to Fig. 10, the 140 mV/s is suitable scan rate for the cyclic voltammetry studies, because the cyclic voltammetry diagrams of this scan rate have more obvious peaks than other diagrams.

3.6. Additional studies

3.6.1. UV-Vis spectroscopic studies

UV-Vis spectroscopy is a powerful technique to show any change in the molecular structure and chromophore groups. Figure 11 shows the spectrums of the samples a, b, c and d as well as PAni and PPyr.

![UV-Vis spectrums for PAni nanopowder, PPyr nanopowder and APC samples a, b, c and d according to Table 1. All samples were dissolved in DMSO to obtain saturated solution for UV-Vis spectrometric studies.](image)

Figure 11. UV-Vis spectrums for PAni nanopowder, PPyr nanopowder and APC samples a, b, c and d according to Table 1. All samples were dissolved in DMSO to obtain saturated solution for UV-Vis spectrometric studies.

Figure 11 shows the UV-Vis spectrums of four APC samples synthesized under different conditions, according to Table 1. PPyr nanopowder [46] and PAni nanopowder [2]. Samples a, b, c and d have the same spectrums but with different absorbances because these samples have different solubilities in MSO. According to a, b, c and d's spectrums, the peak at 260 nm represent the $\pi-\pi^*$ transition of the pyrrole rings in APC. The peak at 300 nm can attributed to the $\pi-\pi^*$ transition of the benzenoid segment of PAni in APC. The peak at 390 nm can related to the protonated emeraldine form of PAni or polaron form of PPyr in APC. There are blue shifts for the peaks of aniline and pyrrole in all APC samples in the presented UV-Vis spectrums in comparison with those of pure
PAni and PPyr nanoparticles. The seen blue shifts is due to the bonding between aniline and pyrrole rings in APC formation.

3.6.2. Thermal analysis

Thermal gravimetric analysis (TGA) and Differential thermal analysis (DTA) were utilized for additional studies of the optimized APC (sample a in Table 1). Figure 12 shows the TGA/differential copolymer sample which was synthesized under optimum conditions.

Figure 12. TGA/DTA thermographs of the optimized APC sample

Figure 12 shows that the APC is relatively stable in the thermal range of 25 to 850 °C. TGA diagram for the synthesized sample under optimum conditions. The decomposition temperature is higher than those of the previous reports [1, 17]. The decomposition temperature of pure PAni and pure PPyr were reported 225 [2] and 275°C [1], respectively. The higher decomposition temperature shows the APC has more thermal stability than those of the previous reports. Figure 12 shows a gradually decreasing in the weight of APC sample 25 to 800 °C. In conductive polymers, this gradual weight loss is related to undoping of polymers.

3.6.3. Electrical conductivity

The electrical conductivity is one of the important parameters of charge/discharge ability of PAni and PPyr as positive materials of the rechargeable batteries. The electrical conductivities of the synthesized samples were measured by the direct two probes method. The results of electrical conductivities of the synthesized samples (according to Table 1) together with those of pure PAni [15] and pure PPyr [46] were summarized in Table 2.
Table 2. The results of electrical conductivity measurements in the APC samples (samples a, b, c and d according to Table 1) in comparing with the reported conductivities for PANi [41] and PPy [10].

<table>
<thead>
<tr>
<th>Sample</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>PPy</th>
<th>PANi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (mS cm⁻¹)</td>
<td>37</td>
<td>40</td>
<td>84</td>
<td>665</td>
<td>20</td>
<td>470</td>
</tr>
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</table>

As it can be seen in Table 2, the electrical conductivity of the sample d, is higher than other samples. According to Fig. 8, the hollow spheres particles were formed in sample d. These hollow spheres connected together. Thus, particles in sample d have a good connection with together and have more electrical conductivity than other samples. As it can be seen in Table 2, APC samples (a, b, c and d) have more electrical conductivity than PPy because the long conjugated π-bonds were formed with monomers of copolymers. Between four APC samples, sample a has a low conductivity. The sample a consisting uniform the smallest nanoparticles. The electrical contact between these nanoparticles are weaker than others.

4. CONCLUSIONS

APC nanoparticles can be prepared by using the pulsed current electrochemical method. In this method, pulse time, relaxation time, synthesis temperature are the most important factors affecting on the morphology and the size of particles in APC samples. The APC samples show the excellent reversibility in cyclic voltammetry so, they can act as a suitable cathodic material in the rechargeable batteries. The APC sample show higher thermal stability than PANi and PPy. The APC samples have higher electrical conductivities than PPy and lower than pure PANi.

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