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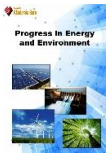

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Original Article

Formation of Polyaniline (PANI) multilayer film using humic acid as the bridging agent: Screening on the fabrication technique

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Abstract

The application of polyaniline (PANI) in flexible electronic devices has received increased attention due to its environmental stability, electrical conducting properties, and ease of production. While the electrical conductivity of a PANI film can be altered by modifying the number of PANI layers, this study aims to compare two techniques, namely ex-situ and in-situ, for the fabrication of PANI multilayer film. For the ex-situ technique, PANI was formed separately before being drop-casted on a filter paper; on the other hand, for the in-situ technique, polymerization of aniline into PANI and attachment of PANI on a filter paper was allowed to occur simultaneously. In both techniques, humic acid was used as the bridging agent. Results showed that the in-situ direct growth technique produced PANI multilayer film with good uniformity, lesser cracking, and detachment. On the other hand, the ex-situ drop-casting technique resulted in PANI film with very poor uniformity, irregular thickness, and severe detachment.

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1 Introduction

Nanotechnology has been a well-known field of interest for researchers over the past decades as the unique properties of nanoparticles enable a wide range of applications in biomedical [1], chemical processes [2], wastewater treatment [3-6], food industries [7], sensor industries [8,9], and many more. Polyaniline (also denoted as PANI), which possesses both attractive properties of conventional polymers and unique electronic properties of metals or semiconductors [10], is one of the many nanoparticles which received increased attention lately due to its good environmental stability, ability in conducting electricity, and high-temperature resistance [11]. PANI is commonly synthesized through chemical oxidative polymerization [12] or electrochemical polymerization [13] method. For either way, PANI in the form of emeraldine, pernigraniline, or leucoemeraldine (which was categorized based on their oxidation state) can be produced. The emeraldine, pernigraniline, and leucoemeraldine form of PANI are half-oxidized, fully oxidized, and fully reduced, respectively [14].

While researchers are outsourcing for the alternative in replacing metals, carbon, and metal oxide supercapacitors, PANI was then found to be one of the promising candidates due to its high theoretical capacitive characteristics, electrical conductive properties, and low cost [10,15]. In

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addition, PANI has been coated onto various flexible substrates for gas sensing [16,17] and pollutant adsorption applications [18]. In most of these applications, the conductivity of the PANI-coated substrate is one of the key properties to be studied. In this regard, it was recently found that the formation of multilayer PANI film offers a considerable increase in electrical conductivity [19]. On the other hand, Su and coworkers fabricated a flexible multilayer nanosensor through layer-by-layer self-assembly of a Pt nanoparticles-polypyrrole thin film on a polyester substrate; the produced flexible sensor exhibited high linearity towards H2 gas detection between 200 ppm and 5000 ppm, high reproducibility, as well as good long-term stability [20,21]. It is important to remark that the layer-by-layer assembly approach can incorporate various chemicals into a single entity and thus, optimize the properties of the sensing multilayer films [22]. Despite the promising results, there are limited studies available in investigating a suitable technique for fabricating such multilayer film.

Extending from this, the current work aimed to investigate various techniques in fabricating multilayer film of PANI with the aid of humic acid as a bridging agent. Here, the fabrication of PANI multilayer film was done through two techniques, namely (i) ex-situ: the drop-casting, and (ii) in-situ: the direct growth technique. Humic acid, which is a negatively charged natural organic compound, was used as the bridging agent as it possesses an opposite charge to the cationic PANI. It was envisaged that multilayer films of PANIs can be formed in a systematic manner (i.e. layer-by-layer) by alternating exposures of the substrate to PANI and the bridging agent. In this preliminary study, comparison was conducted through visual observation – qualitative analysis.

2 Experimental materials and methods

PANI was synthesized via oxidation polymerization by using ammonium persulfate as the oxidizing agent and hydrochloric acid as the acid medium. Three techniques were used in producing PANI multilayer film, namely the drop-casting, the alternate immersion, and the direct growth method. The substrate used in this study was Whatman #3 filter paper (6 µm pore size).

2.1 Synthesize of PANI via oxidation polymerization.

In the synthesis of PANI, ammonium persulfate and aniline were used as the oxidant and monomer, respectively [23]. The synthesis process was carried out in a 4:1 monomer/oxidant molar ratio. In a 250 mL flask, 20 mL of the aniline was dissolved in 40 mL of 1 mol/L hydrochloric acid aqueous solution. The flask was then kept inside a vessel containing ice at a temperature of approximately -10°C during the dissolution process. 12g of ammonium persulfate was dissolved in a separate 250 mL flask containing 160 mL of 1 mol/L aqueous solution of hydrochloric acid. The acid solution of ammonium persulfate was added slowly and carefully into the other flask containing aniline acid solution under constant stirring. The entire stirring process was ongoing for 2 hours while keeping the solution temperature at approximately -10°C. The reacted solution was then centrifuged thrice at 3500 rpm for 12 minutes and washed with distilled water in between. The supernatant was discarded and the product formed was PANI.

2.2 Synthesize of PANI multilayer film via ex-situ: drop-casting technique

A 2 × 4 cm clean filter paper was placed in a petri dish and a layer of PANI was coated onto it with the aid of a dropper. The PANI was left to attach to the filter paper for 15 minutes. Upon completion, the filter paper was rinsed with distilled water to remove any excess (unbounded) PANI from the filter paper. Next, the filter paper was alternately dipped into the second petri dish containing 20 mL of 300 mg/L humic acid for 15 minutes to create a thin multilayer film. The filter paper became bilayer consist of a layer of cationic PANI and a layer of anionic humic acid attached to it. The immersion process was repeated to synthesize PANI films from 2 layers to 5 layers during the fabrication process. Note that after the filter paper was dipped into humic acid, it was rinsed with distilled water before it was attached with PANI again.

2.3 Synthesize of PANI multilayer film via in-situ: direct growth technique

Unlike the drop-casting technique, the synthesis of PANI and attachment of PANI onto the filter paper were done simultaneously for this direct growth technique. To begin, a 2 × 4 cm clean filter paper was dipped into a petri dish containing well-mixed 13.333 mL of 1 mol/L hydrochloric acid and

6.6667 mL of aniline. The filter paper was left in the solution for 15 minutes to allow the adsorption process (Fig. 1a). After that, the filter paper was dipped into the second petri dish containing well-mixed 20 mL of 1mol/L hydrochloric acid and 1.5 g of ammonium persulfate (APS) (Fig. 1b). The filter paper was then left in the solution for another 15 minutes for the growth of PANI. Next, the filter paper was rinsed thoroughly with distilled water before it was placed in the third petri dish containing 20 mL of 300 mg/L humic acid. The filter paper was again rinsed with distilled water before it was dipped into the first petri dish containing well-mixed hydrochloric acid and aniline to produce multilayer films. The process was repeated until PANI films with 2 to 5 layers were formed.

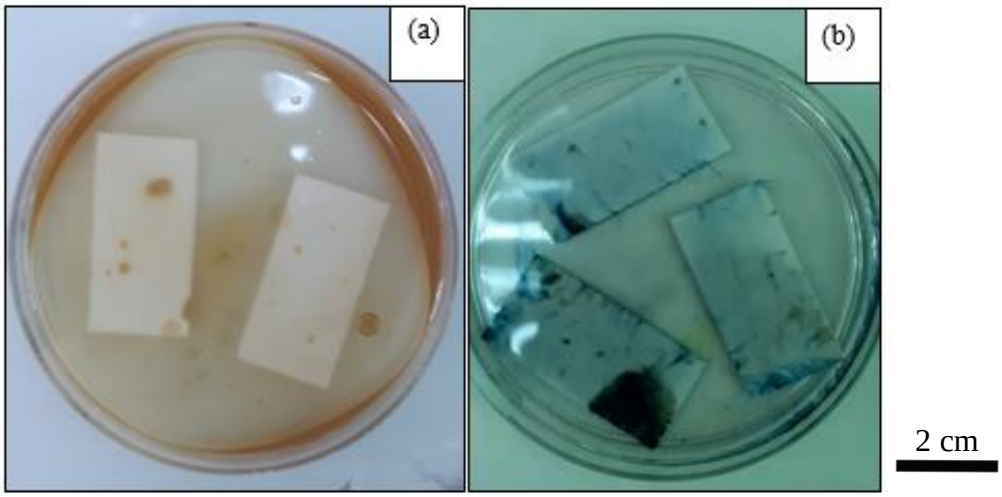

Fig. 1 Dipping on filter paper in (a) aniline and HCl solution, and later on in (b) APS and HCl solution.

2.4 Characterization of PANI

The shape and size of PANI were determined through Transmission Electron Microscopy (TEM) analysis. The average size of PANI was determined by finding the average size of 20 randomly selected PANI from the TEM image produced. The polydispersity index of the PANI was calculated as the square of the standard deviation divided by the mean particle diameter [24].

3. Results and Discussion

3.1 Characterization of PANI

Fig. 2 shows the image of PANI obtained from TEM analysis. It was observed that the synthesized PANI particles were slightly agglomerated. The average particle size obtained is 356.94 nm ± 118.46 nm. Since the average size of the PANI synthesized here is mainly greater than 100 nm, thus, it does not fall in the nano-range. The polydispersity index of this synthesized PANI is 0.1101, which indicates that the sample is a polydispersed suspension.

3.2 Surface properties of PANI multilayer firm formed via ex-situ: the drop-casting technique

Fig. 3 shows the surface structure of several PANI multilayer films prepared via the drop-casting method. It was clearly seen that the attachment of PANI on the filter paper was not uniform. Cracking of the PANI layer has occurred for all of the PANI films. Such cracking was due to the detachment of the PANI particles from the filter paper upon being subjected to a 24 hours-room temperature drying process. In addition, it was noticeable that the cracking phenomenon became severe with the increase in the number of layers formed; similarly, the film thickness is irregular for all of the formed samples. The lack of adequate control over the film thickness is a common drawback of the drop-casting technique [25,26]. Such a phenomenon could be due to variation in evaporation rates across the paper substrate and/or PANI concentration fluctuations.

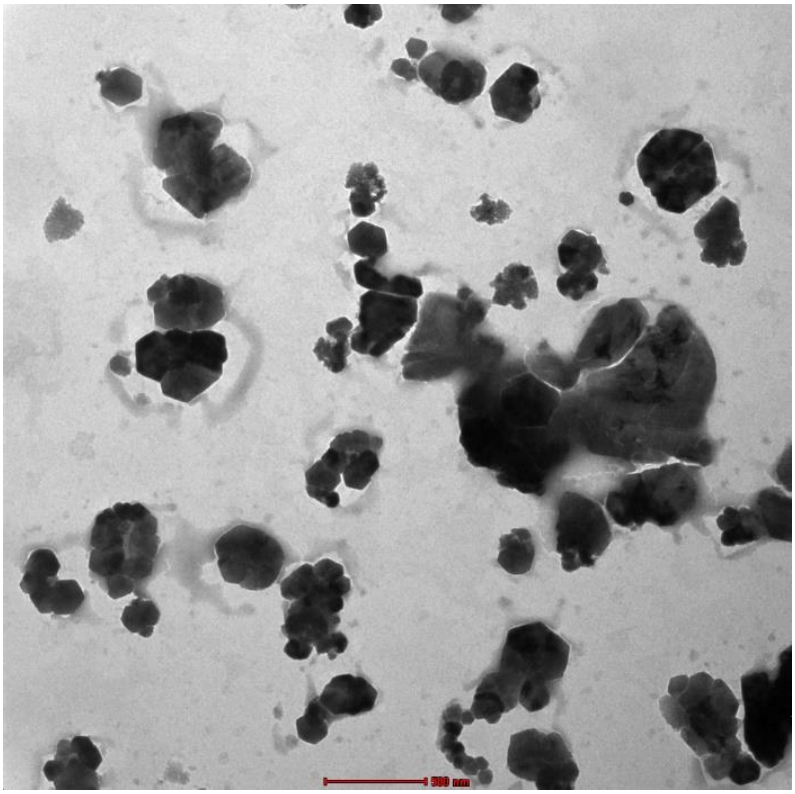

Fig. 2 TEM image of PANI.

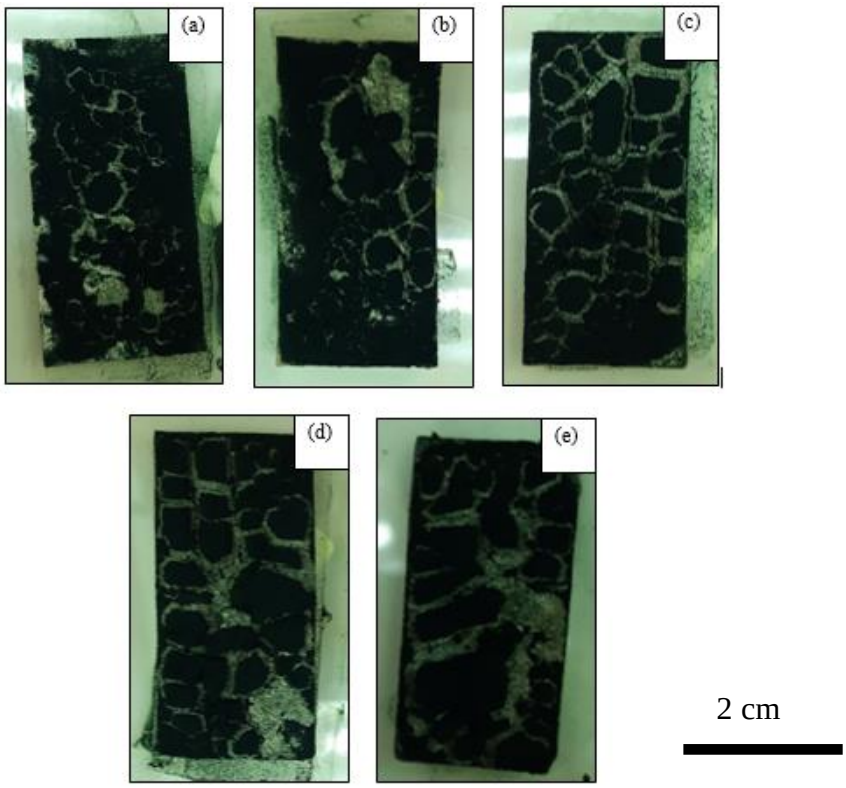

Fig. 3 (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers, and (e) 5 layers PANI film synthesized from ex-situ drop-casting method.

3.3 Surface properties of PANI multilayer firm formed via in-situ: direct growth technique

Here, the immersion of filter paper in the precursor solution allows PANI polymerization, and growth directly occurs on the substrate surface. Fig. 4 shows the surface structure of several PANI multilayer films produced through the direct growth method. Interestingly, it was observed that PANI is more uniformly attached on filter paper by using this technique as compared to PANI film synthesized from the drop-casting technique. Via the direct growth method, lesser cracks are observed although there are some moldy spots on the film.

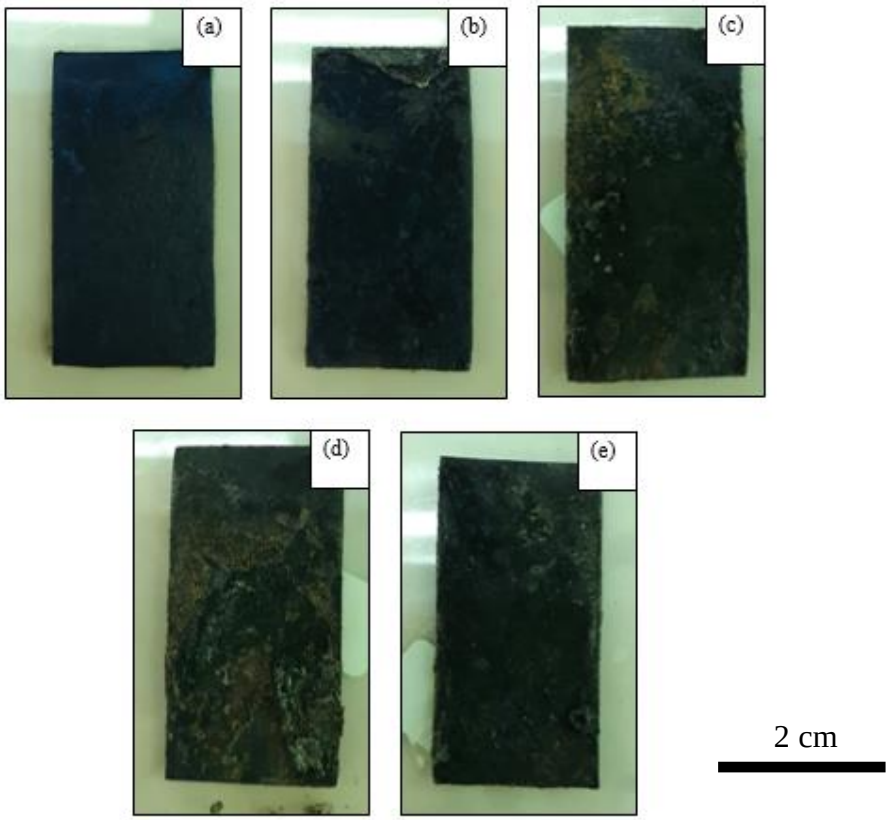

Fig. 4 (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers, and (e) 5 layers PANI film synthesized from in-situ direct growth method.

Additionally, the increase of the film thickness and roughness with the increase of the number of coating layers is more visually observable for the PANI film synthesized by this direct growth technique (see Fig. 4). There was also less detachment of PANI from the films produced by this technique; as such, the direct growth of PANI on the film is a better alternative as it offers higher uniformity of attachment for a longer time. Similarly, a recent review by Ellis et al. [27] reported that the advantage of the in-situ over ex-situ synthesis technique is the adhesion strength of the coating layer on the substrate.

Other than that, few holes were seen on all the samples prepared via this direct growth method. This condition occurs in a similar study of multilayer film carried out by Jeon et al. [28]. It was pointed out that during the deposition of polyelectrolyte, which has an opposite charge to the nanoparticles that have already attached to the substrate, will form a complex resulting in the nucleation of small holes. Correlating to the current study, the holes on the samples protrude as the humic acid molecules pull the PANI particles towards it, leaving spots on the samples which are uncovered by the nanoparticles.

Fig. 5 delineates the synthesis and attachment of PANI on filter paper through this direct growth method. Note that PANI particles formed instantaneously upon immersing the filter paper that has been pre-soaked with the aniline-HCl solution into the APS-HCl solution.

4 Conclusion

This study compared two strategies to coat a multilayer of PANI particles on a paper substrate based on the surface structure of the formed PANI film. Here, humic acid was used as the bridging agent. Despite being simple, easy, and fast, the drop-casting technique formed PANI multilayer film with poor uniformity and severe detachment. Cracks were seen on the film layer. On the other hand, the direct growth technique was found to be a more feasible technique in producing PANI multilayer film as the samples produced have better uniformity, lesser to almost no cracking. In addition, it was noticeable that the PANI layers bound stronger on the paper substrate when the polymerization and particle growth occur directly on the substrate surface (in-situ).

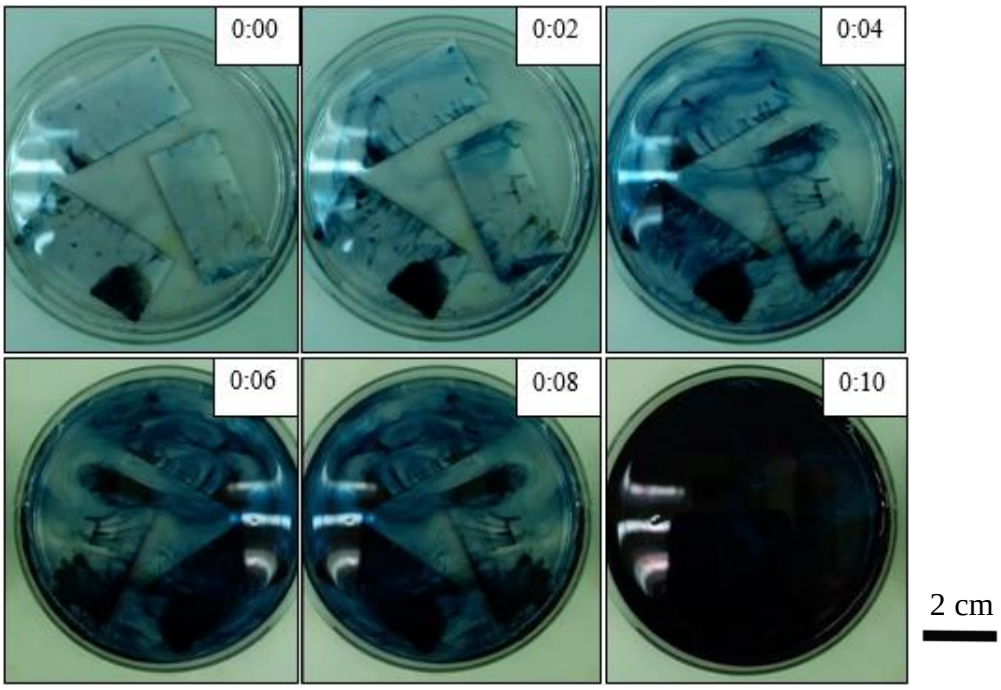

Fig. 5 Time-lapse images showing direct growth of PANI on filter paper.

Declaration of Conflict of Interest

The authors declared that there is no conflict of interest with any other party on the publication of the current work.

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