Polyaniline Nanofibers for Security Printing Applications

Jeevan M. Meruga[*1], *Connor Holland*[2], *Jacob Petersen*[1], *William Cross*[1], *Jon Kellar*[1] *and Grant Crawford*[1]

[1]*South Dakota School of Mines & Technology/SPACT, Rapid City, SD, 57701.*

[2]*Southwestern Oklahoma State University, Weatherford, OK, 73096.*

E-mail: Jeevan.meruga@sdsmt.edu and jon.kellar@sdsmt.edu

Internet: http://spact-center.org/

Abstract

In this research we utilize polyaniline nanofibers in security printing applications. Polyaniline nanofibers were synthesized to allow an aqueous-based ink to be created. Inks with different weight percentages of polyaniline nanofibers were formulated, printed into desired patterns on a variety of substrates using digital fabrication and characterized for their conductive properties. The conductivity differences between the flash welded regions and non-flash welded regions were determined to help determine applicability for security-end products.

Introduction

Counterfeiting is a $600 billion problem and has grown over 10,000 percent in the past two decades [1]. The International Chamber of Commerce estimates that approximately 5-7% of the world trade is in counterfeit goods. In the United States alone, counterfeiting costs government and private industries about $200-$250 billion dollars and 750,000 American jobs annually [1]. Counterfeiting exists in virtually every area, including toys, automobile parts, currency, pharmaceuticals and much more [2]. The profits obtained from counterfeit goods have been linked to organized crime, drug trafficking and terrorist activity [1]. Some of the existing security applications have been breached or threatened by the skill and technology being used by the counterfeiters. Thus, there is a continuous need for new and innovative security applications in order to fight the growing problem of counterfeiting.

Polyaniline $([C_6H_4NH]_2)_n$ is considered to be one of the most useful conducting polymers because of its facile synthesis and environmental stability. Nanofibers of polyaniline have attracted a great deal of interest for the past few years because of their unique properties and performance [2]. Polyaniline nanofibers (PANI NFs) are already being used in memory devices, actuators, composites, sensors, etc. Some of the interesting features of these nanofibers include their conductivity and flash welding ability, and herein we explore PANI NFs-based inks for security printing. PANI NFs were synthesized using the methods of Huang et al. [3]. PANI inks were deposited into patterns using a HP® Thermal Inkjet Pipette System (TIPS) printer.

Experimental

To synthesize PANI NFs, interfacial polymerization was performed in an aqueous/organic biphasic system. Aniline (3.2 mmol) was dissolved in 10 mL of chloroform and stirred for 30 minutes. Ammonium peroxydisulfate (APS) (0.8 mmol) was dissolved in 10 mL of 1 M dopant hydrochloric acid (HCl) solution and stirred for 30 minutes. The aqueous solution was then carefully added to the organic phase in a separate beaker. The oxidation polymerization slowly started at the interface of the aqueous phase and the organic phase; and the PANI NFs start growing in the aqueous phase. This solution was left for about 24 hours to ensure the maximum yield of PANI NFs. The dark green colored aqueous phase was collected carefully and cleaned as per the below given procedure. Methanol was then added to the collected aqueous phase and vortexed for ~ 10 minutes at 3000 RPM. The vortexed solution was centrifuged at 6000 RPM for ~ 15 minutes and the methanol solution with all the byproducts was disposed. This cleaning process was repeated at least three times for all the batches of PANI NFs. The nanofibers were allowed to dry overnight before making inks with them.

From the above method, PANI NFs of diameters between 50 and 90 nm with lengths around 700 nm were obtained. Currently, optimization is under way, by altering the concentrations of acid and APS, to increase the yield and improve the stability of the nanofibers in the inks.

SEM Images of PANI NFs

Scanning Electron Microscopy (SEM) was conducted to confirm the size and shape of the PANI NFs. Figure 1 shows that the PANI NFs were successfully synthesized.

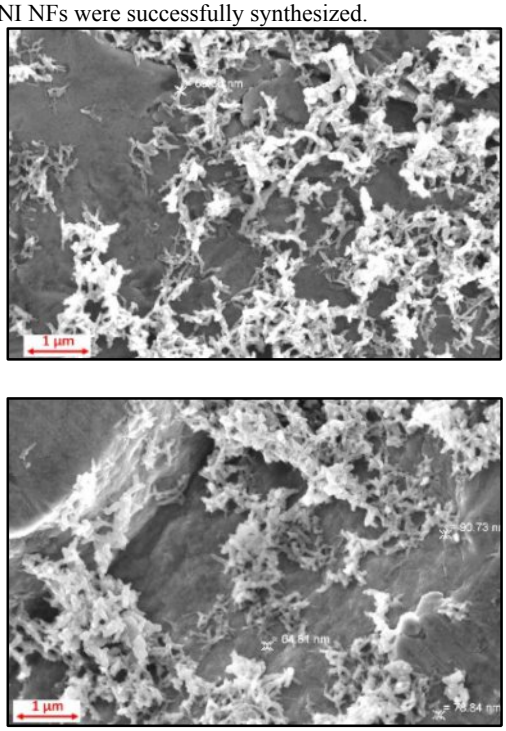

Figure 1. *SEM images of the synthesized PANI NFs.*

Ink Formulation

The PANI NFs disperse well in water and polar organic solvents including ethylene glycol and diethylene glycol [4]. Inks were formulated by adding 1 and 2 weight percent (wt%) of PANI NFs to de-ionized water and sonicated for ~3-4 hours for good dispersion. Our preliminary results showed that the PANI NFs made with a higher concentration of acid were more stable in the inks than the ones made with a lower concentration of acid as shown in the Figure 2.

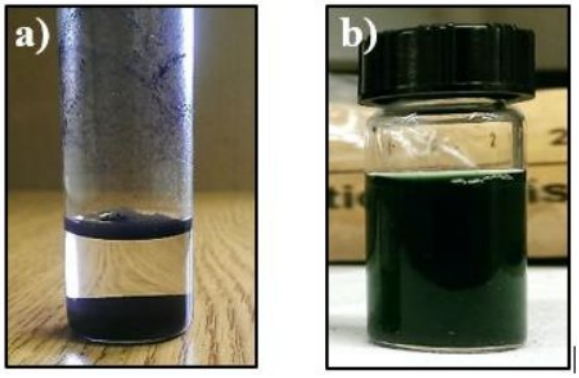

Figure 2. *Stability PANI NFs in the inks. a) PANI NFs settled in the ink after a day. b) PANI NFs dispered well and stable in the ink after a day.*

Results

The 1 wt% and 2 wt% PANI NF inks were printed on substrates including Kapton®, paper and glass using a HP® TIPS printer as shown in Figure 3. To the authors' knowledge this is the first time that PANI NF inks have been printed using a HP® TIPS printerRelevant printing parameters are shown in the Table 1.

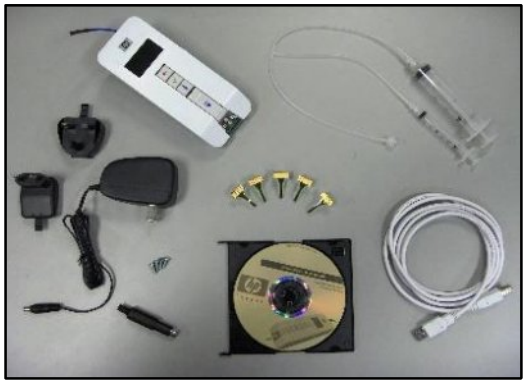

Figure 3. *HP® Thermal inkjet pipette system (TIPS).*

Table 1. Parameters used in HP TIPS printer to print antennas.

Dispenser design	Voltage (V)	Pulse width (µs)	Frequency (Hz)	Pulse (number of drops)
21 Design (10 nozzles)	29.2	3.7	500	1500

Simple antennae (1 mm × 10 mm) with different numbers of passes were printed on the above mentioned substrates using a stencil as shown in the Figure 4. Substrates were placed on a hot plate which was heated to 60 °C while printing. Heat was applied so that the water-based PANI ink would evaporate without spreading.

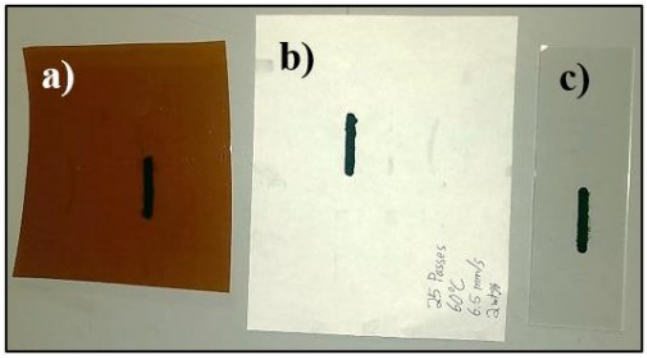

Figure 4. *Antennae printed with 2 wt% PANI ink using the HP® TIPS and a stencil (to study the conductivity). a) antenna printed on Kapton®. b) antenna printed on paper. c) antenna printed on glass slide.*

PANI Conductivity Measurements

Preliminary resistance measurements of the PANI antennas were obtained. Conductivity of these antennas can be calculated by measuring the thickness of the patterns and resistance value. Resistance of PANI antennas shown in the Figure 3 was measured using a two probe digital multimeter. The preliminary results on glass and Kapton® substrates were in the range of ~ 1-5 kΩ. And on paper, the resistance values varied from 50 to 150 kΩ, which is expected as the paper's surface is rough with uneven fibers that absorb a considerable amount of ink because of capillary forces. The conductivity of the PANI inks on different substrates will be evaluated further to determine how different wt% of PANI loading would change the print quality and the conductivity of the patterns.

Future Work

The resistance values show that the conductivity is not high like metallic nanoinks [5], but can be improved considerably by introducing conducting metal nanoparticles in the PANI NF's synthesis. The resistance of the PANI patterns can be increased significantly by flash welding the patterns and this could be useful in designing complex security antennae. In the future, more experiments will be conducted to understand and determine the maximum loading of the PANI NFs that can be loaded into the inks to make them conductive enough which would provide an economic alternative to the currently used QR code antennas based upon silver ink [6-8].

It should be noted that the printed antennas shown in Figure 4 did not adhere well and they come off easily on glass and Kapton® substrates. Thus, future research will be focused on how to make the printed patterns more permanent by formulating the inks with binding agents. Also, the ink formulation needs to be optimized for other digital printing platforms, which will allow a variety of complex patterns effectively without using a stencil or a mask.

Conclusion

PANI NFs were synthesized and characterized. Stable inks were formulated using the PANI NFs and antennae were printed using the HP® TIPS printer. Preliminary resistance measurements were obtained to determine the potential applications to design conductive antennas using PANI inks. From the above mentioned

preliminary results it appears that PANI NFs-based inks have great potential in security printing.

Acknowledgements

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Author Biography

Jeevan Meruga received his Ph.D. in Materials Engineering and Science from South Dakota School of Mines & Technology (SDSM&T) (2013). Since then he has been working as a Postdoctoral Researcher for the Center for Security Printing and Anti-Counterfeiting Technology (SPACT) in SDSM&T.