PRINTING CONDUCTIVE POLYMER NANOWIRE NETWORK AND ITS APPLICATION IN CHEMICAL SENSING
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ABSTRACT
This work reports a printing technique for patterning a conducting polymer nanowire network on a flexible film for applications in chemical sensing. The novelty of this work is in the patterning capability of polymer nanowires to form a conducting path. Polyaniline nanowires were chemically synthesized in an aqueous solution and a surfactant was added to lower the surface tension which enabled the printing of the nanowires using a commercial inkjet printer. The printed device was tested as a chemiresistive sensor to detect pH and hydrogen peroxide concentration.

KEYWORDS: Inkjet printing, Polyaniline, Nanowire, Chemiresistive sensing

INTRODUCTION
Fabrication of disposable sensors using printing techniques has many advantages especially in chemical and biological sensors due to their low cost, mass producibility, and portability. Among the various printing techniques, an inkjet printing method can provide a quick, simple, and automated solution to developing disposable sensors [1]. Due to the many benefits that the nanomaterials offer especially in chemical and biological sensing, there have been numerous reports demonstrating the feasibility in inkjet printing of nanomaterials such as nanoparticles, nanotubes, and even graphene on a flexible substrate [2,3]. Inkjet printing of conducting polymer nanomaterials is also becoming a topic of great interest due to the unique properties of the conducting polymers that can be utilized in sensors and electronic devices. Inkjet printing of conducting polymer nanoparticles and nanograins have been previously reported [4], however the printing of the nanowires to form an interconnected network of polymer nanowires have not been demonstrated so far. Nanowire network morphology is ideal for producing highly conductive patterns and is also good as a sensing material due to the large surface area and porosity leading to enhanced sensitivity and faster response time.

Here, we present a method to pattern polyaniline nanowire network to form a conductive path utilizing an inkjet printer as illustrated in Figure 1.

![Figure 1: Schematic illustration of the inkjet-printed polyaniline nanowire-based chemical sensors: (a) printing of polyaniline nanowire network; (b) printing of a chemiresistive pH sensor; (c) a chemiresistive H₂O₂ sensor based on printed polyaniline nanowire network, and (d) the images of the actual printed chemical sensors (top: pH sensor, bottom: H₂O₂ sensor, scale bar: 5 mm).](image-url)
This technique was used to develop chemiresistive sensors to demonstrate its feasibility. Two types of sensors were developed: a polyaniline-based chemiresistive pH sensor and a polyaniline network functionalized with silver nanoparticles for selective hydrogen peroxide sensing [5].

EXPERIMENTAL

First, as described in Figure 1, a printable ink consisting of a well-dispersed polyaniline nanowires is prepared and loaded into the ink cartridge. Then, after designing a pattern from a drawing software, the pattern is printed on a flexible transparency film. The sensing area of the device is printed in polyaniline and the remaining electrodes are printed in multi-walled carbon nanotube (MWCNT) ink [2] as shown in Figure 1(b). Since the conductivity of polyaniline is pH-sensitive, the printed device in Figure 1(b) can be used as a chemiresistive pH sensor. For other chemical sensing, catalytic nanoparticles can be deposited on the surfaces of the polyaniline to selectively detect a specific chemical (Figure 1(c)). In this work, silver nanoparticles were used for the detection of hydrogen peroxide [5]. Figure 1(d) shows the actual images of the printed sensors.

The chemical synthesis of polyaniline nanowires was based on the reported procedure [6]. Briefly, 10 ml of 0.08 M Aniline (73.5 µl) in 1 M HCl, and 10 ml of 0.02 M ammonium peroxydisulfate (APS, 45 mg) in 1 M HCl were prepared in two separate vials. The two solutions were rapidly mixed together and left undisturbed overnight. The synthesized nanowires were rinsed by centrifuging the product at high RPM followed by replacing the aqueous liquid with a fresh deionized water. For lowering the surface tension of the ink, 10 mg/ml of sodium dodecylsulfate (SDS) was added to the nanowire dispersion and gently stirred until SDS was completely dissolved. The prepared ink was loaded into the inkjet printer cartridge (HP Deskjet 5600) and the patterns were printed with a maximum resolution setting onto a printable transparency film. For hydrogen peroxide sensors, a 5 µl droplet of a liquid dispersed silver nanoparticles (1 mg/ml, particle size: <100 nm) was dropped on the surface of the printed polyaniline area and dried.

RESULTS AND DISCUSSION

For sheet resistance characterization, a rectangular area with a dimension of 6 mm x 30 mm (as shown in Figure 2(a)) was printed from 1 to 25 times, and the sheet resistance of each rectangular strip was recorded. Figure 2(b) shows the measured sheet resistance as a function of the number of prints. After printing 25 times, the lowest sheet resistance of 3.5 kΩ/□ was obtained.

(a) (b) (c) (d)

Figure 2: Inkjet-printed polyaniline nanowires on a transparency film: (a) image of the printed patterns with 10, 15, 20, and 25 prints (from left to right, scale bar: 5 mm); (b) the measured sheet resistance vs. the number of prints; (c) scanning electron microscope (SEM) image of the as synthesized polyaniline nanowires (scale bar: 3 µm), and (d) the SEM image after inkjet printing on a transparency film (5 prints, scale bar: 3 µm).

To confirm the nanowire network morphology, the scanning electron microscopy (SEM) images of the synthesized polyaniline nanowires before (Figure 2(c)) and after inkjet printing (Figure 2(d)) on a substrate were compared. The two SEM images indicate that the nanowire morphology is preserved during the printing process and that the shape of the individual nanowires were maintained. The pH sensing results of
the printed device is shown in Figure 3(a), where the conductivity of the polyaniline nanowire network varies as a function of the pH and the measureable pH range is from 1 to 6. For $\text{H}_2\text{O}_2$ sensing result shown in Figure 3(b), the rate of the conductivity drop of the polyaniline-printed area increases as the concentration of the injected $\text{H}_2\text{O}_2$ increases.

![Sample injection point](image1)

(a) Sample injection point

![Sample injection point](image2)

(b) Sample injection point

Figure 3: Chemiresistive sensing results: (a) the inkjet-printed polyaniline nanowire-based pH sensor and (b) the polyaniline nanowire sensor functionalized with silver nanoparticles for $\text{H}_2\text{O}_2$ detection. In both graphs, $I$ is the sensing current value through the printed polyaniline layer and $I_0$ is the initial current value.

CONCLUSION
A low sheet resistance polyaniline nanowire network was printed using a commercial inkjet printer and the results show promising results in chemical sensing capability. The demonstrated technology has potential applications in disposable chemical and biological sensors which can easily be printed on-demand for various sensing and diagnostics.

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REFERENCES