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Inkjet printing of conductive polymer nanowire network on flexible substrates and its application in chemical sensing

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ABSTRACT

This work reports an inkjet 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 commercially available inkjet printer. The nanowire network-based patterns were printed on a flexible transparency film, and its morphology characterization, patterning ability as well as the electrical properties were investigated. Finally, as a proof-of-concept, a fully-printed chemical sensors were developed by using the proposed printing technique on flexible films. Two types of sensors were fabricated: a pH sensor and a hydrogen peroxide sensor. The results demonstrate that the developed sensors can be utilized as a low cost, disposable, and easily printable chemical sensors. The proposed technology may find applications in the development of a simple print-and-use biochemical sensing kit for potential use in point-of-care diagnostics.

1. Introduction

Fabrication of a single-use and disposable sensor using various printing techniques has many advantages especially in chemo- and bio-sensors due to their low cost, mass producibility, and portability. Moreover, printed electronic materials are generally thin and flexible and therefore have potential applications in wearable and implantable electronics. 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 of inkjet printing of various nanomaterials including metal and oxide nanoparticles, carbon nanotubes [2], and even graphene sheets on a flexible substrate [3]. Inkjet printing of conducting polymer materials 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 [4,5]. However inkjet printing of conducting polymer nanowires to form highly interconnected network of 1-dimensional nanostructures have not been demonstrated so far. Nanowire network morphology is ideal for producing highly conductive patterns and is also desirable as a sensing material due to its large surface area and porosity leading to enhanced sensitivity and faster response time [6,7].

Polyaniline is one of the most widely studied conducting polymer and has found many applications as a sensing material for chemical and biological species. Polyaniline is a very interesting polymer due to its many unique properties. First, it is an intrinsically conducting polymer with a relatively high electrical conductivity (on the order of a few S/m) for a polymer material. Due to its ability to conduct electricity, it can be used for electronic sensor applications. Secondly, the conductivity of polyaniline is highly influenced by the pH of the environment to which it is exposed. Polyaniline exhibits maximum conductivity under a strongly acidic environment (low pH) and loses its conductivity at neutral or basic environment (pH 7 or higher). Therefore chemiresistive polyaniline-based pH sensors have been extensively studied and documented [8–10].

Inkjet printing of polyaniline nanoparticles and nanograins have been previously reported and the development of an ammonia sensor was demonstrated [4,11]. However, in order to form a well-conducting path for electron transport, an interweaved nanowire network is the desired solution for applications in resistive sensing. In this work, we demonstrate the capability of printing

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polyaniline nanowire network patterns on a transparency film to be used as chemical sensors. The novelties of this work are in the inkjet printing of conducting polymer nanowires and the development of fully-printable chemiresistive sensors.

2. Working principle

Fig. 1 illustrates the basic concept of the use of inkjet printing technique for the development of a printable chemical sensors. First, a nanowire dispersed liquid is loaded into the printer cartridge to be printed on a substrate. Due to the nanowire morphology of the polyaniline material, the printed patterns will contain a randomly oriented network of conducting polymer nanowires which forms electrically conducting patterns as shown in Fig. 1(a) and (b).

Since the conductivity of polyaniline is pH-dependent, a pH sensor can be developed by measuring the resistance across the polyaniline layer deposited between the two electrodes. This type of chemiresistive pH sensor can be implemented by the inkjet printing technique as illustrated in Fig. 1(b). A similar approach can be taken to develop a hydrogen peroxide sensor by including catalytic (silver) nanoparticles to the polyaniline nanowire network [12]. Fig. 1(c) depicts the configuration of the chemiresistive hydrogen peroxide sensor where the nanoparticles are evenly distributed throughout the network. When the catalytic reaction occurs between the nanoparticles and hydrogen peroxide, hydroxide ions (OH^-) are produced as the byproduct of the reaction which increases the local pH near polyaniline. Therefore, the resulting change in conductivity of polyaniline can be measured to determine the hydrogen peroxide concentration.

3. Experimental methods

3.1. Chemical synthesis of the polyaniline nanowires

The method for the chemical synthesis of polyaniline nanowires is based on the technique developed by Kaner [13]. 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 and vigorously mixed together and left un-agitated overnight. The synthesized nanowires were rinsed by centrifuging the product at 13,000 RPM for 10 min followed by removing the aqueous liquid, adding the same volume of DI water, and gently agitating the centrifuge tube. This rinsing step was repeated twice to thoroughly remove the unreacted oxidants and acids from the liquid.

3.2. Printable ink preparation

In order to print the polyaniline nanowires through the ink cartridge, the surface tension of the ink must be sufficiently low so that the ink droplets can be discharged through the nozzle. For lowering the surface tension of the nanowire suspension, 10 mg/ml of sodium dodecylsulfate (SDS), which is a common surfactant, was added to the nanowire dispersion and gently stirred until SDS was completely dissolved.

3.3. Inkjet printing of conducting polymer patterns

The printing process was performed using a commercially available inkjet printer (HP DeskJet D1520) which was used as received without further modification. A letter sized printable transparency film was used as a printing substrate. The black ink cartridge was thoroughly rinsed with water to remove any previously filled ink. Afterward, the prepared nanowire suspended ink was loaded into the cartridge by soaking the sponge inside the cartridge with the nanowire ink using a syringe. Then, the print head nozzle on the bottom of the cartridge was gently treated with ultrasonication in order to prevent the clogging of the nozzles. The print patterns were drawn using a standard Windows software (e.g. Microsoft Word and PowerPoint). The highest resolution print setting was selected for optimum printing performance. To further increase the number of nanowires per unit area, multiple layers of the same patterns were printed on a single substrate.

4. Results and discussion

4.1. Morphology characterization of the polyaniline nanowire network

To verify the nanowire network morphology, the scanning electron microscopy images of the polyaniline nanowires immediately after chemical synthesis and after inkjet printing on a substrate were compared. Fig. 2(a) confirms the nanowire morphology of the chemically synthesized polyaniline using the rapid mixing technique. The dimensions of a typical nanowire are approximately 100–150 nm in diameter and a few micrometers in length. Fig. 2(b) shows the SEM image of the polyaniline nanowires on a transparency film deposited with inkjet printing technique and confirms that the nanowire network morphology of the polyaniline is preserved even after undergoing the printing process.

4.2. Electrical properties

As evidenced by the images in Fig. 2, the randomly interweaved nanowire network structure forms many conducting paths throughout the printed area resulting in a low sheet resistance.

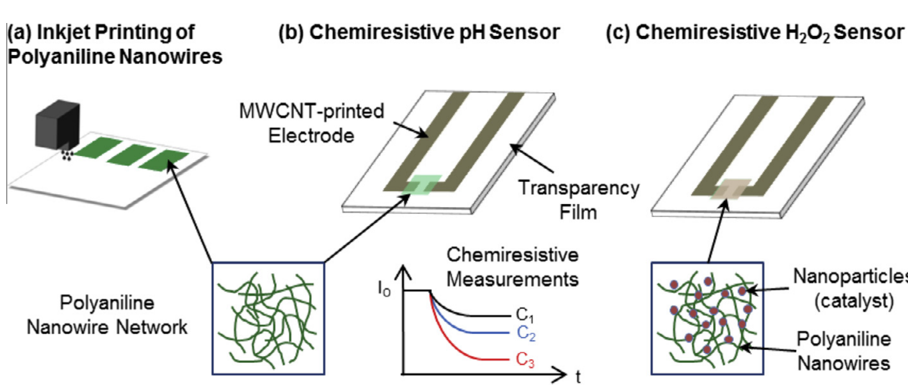

Fig. 1. Illustration of the processes for the inkjet printing of nanowires for the development of a fully-printed disposable chemical sensor.