Sensors and Actuators B 178 (2013) 140–143

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Ink-jet printed conducting polyaniline based flexible humidity sensor

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ARTICLE INFO

Article history:
Received 8 September 2012
Received in revised form
10 December 2012
Accepted 12 December 2012
Available online 22 December 2012

Keywords:
Conducting polyaniline
Chemical synthesis
Spectroscopy
Ink-jet printing
Flexible sensor

ABSTRACT

Ink-jet printed, intrinsically conducting polymer (ICP), polyaniline have been used for humidity sensing at room temperature. Polyaniline based, aqueous ink-jet printable ink has been synthesized by single step, chemical oxidative polymerization technique. Sulphonic acids were used as a dopant during the in situ polymerization process. This is a single step polymerization process for the direct synthesis of conducting emeraldine salt phase of the polymer as an ink formulation. The synthesized polyaniline ink was further characterized by spectroscopic (UV–visible and FT-IR) analysis which confirmed the presence of conducting emeraldine salt phase of the polymer. The viscosity of the ink was measured by using Brook-field viscometer. The successive trials were performed for the printing of IDT pattern on the flexible, untreated polymer substrate using HP ink-jet-printer. The printed sensor was subjected for the humidity sensing measurements. The change in the resistance with change in the %RH was observed. It is suggested that the increase in conductivity at high humidity may be related to a vapour-induced change in the transfer of charge carriers between the polymer chains. The synthesized polyaniline based ink can also be considered as a good candidate for variety of ink-jet printed low cost electronics devices.

1. Introduction

Manufacture of electric circuits on polymer substrates is broadly referred to as flexible electronics and has gained significant interest as a pathway to low-cost or large-area electronics [1,2]. Although conventional vacuum deposition and photolithographic patterning methods are well developed for inorganic microelectronics, they are not appropriate for this application. Flexible polymer substrates are chemically incompatible with resists, etchants, and developers used in conventional integrated circuit (IC) processing. In practice, the usual IC fabrication processes involve multiple steps and high processing temperatures and produce toxic waste, all of which add to their cost. Furthermore, the increasing size of electronic devices such as displays poses great difficulty in adapting standard micro fabrication techniques, including lithographic patterning. Devices based on organic semiconductors are considered to be very promising for these applications since they may potentially be fabricated entirely using printing technologies, eliminating the need for such major costs as in lithography, vacuum processing including physical vapour deposition, plasma etching, and chemical vapour deposition (CVD), while simultaneously allowing the use of reel-to-reel processing, resulting in reduced substrate handling and clean-room costs as well. Furthermore, since printing is inherently additive in nature, material and disposal costs are also expected to be reduced, resulting in an extremely low net system cost. To print electronics, conducting ink is a key factor for the proper performance of printed electronics. Conductive polymers are currently being developed for a range of different applications, such as chemical sensors, displays and 'plastic' transistors [3–5]. Inkjet printing is now an important technology for depositing layers of conductive polymers [6,7]. The method works by ejecting an ink through very fine nozzles. The nozzle diameters of recent thermal or piezoelectric inkjet printers decreased to 3 μm for better printing resolutions. Also, electrohydrodynamic inkjet printers can use a submicron size nozzle to print dots with diameters smaller than 1 μm [8–10]. The advantages of inkjet printing over other thin film techniques lie in its patterning capability, the efficient use of material, the high speed and low cost of the process, and in the fact that thin films can be printed on flexible substrates. For chemical sensing applications, the more 'open' morphology of inkjet printed films (i.e. a series of connected droplets) may allow rapid diffusion of the water vapour molecules into and out of the film, leading to fast response and recovery times.

Among organic conducting polymers, polyaniline (Pani) is regarded as one of the most technologically promising electrically conductive polymers due to its ease of synthesis, low cost, versatile processability and relatively stable electrical conductivity.

Industrial processes and human comfort, both, need to measure and control the humidity in the environment. In recent years, the need of humidity sensor has greatly increased because of its

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http://dx.doi.org/10.1016/j.snb.2012.12.046

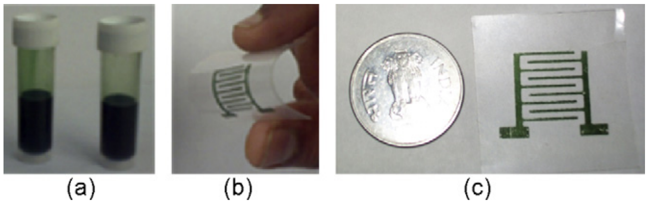

Fig. 1. Polyaniline ink (a) and ink jet printed IDT pattern on flexible polymer substrate (b and c). (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

applications; in control of air conditioning, quality control of food products in a wide range of industries, paper and textile industries, optimal functioning of modern solid state electronic equipment, civil engineering, etc. The operating conditions and requirements of humidity sensors depend on the field of application. Therefore, development of low cost humidity sensors with better specifications is required.

In this report, we would like to present the direct synthesis of inkjet printable conducting polyaniline based ink via a single-step, in situ polymerization process using sulphonic acids as a dopant. Also, herein we report the physico-chemical characterization of the developed ink, its successive printing of interdigitated (IDT) pattern on flexible, untreated polymeric substrates and its utilization as a flexible, printed humidity sensor.

2. Experimental details

All chemicals used were of analytical reagent (AR) grade and the solutions were prepared in doubly distilled water. The polymerization of the monomer, aniline (1 M) was initiated by the dropwise addition of the oxidizing agent, Ammonium persulphate (1 M) under constant stirring at low temperature between 0 and 5 °C in an acidified solution containing 1.33 M organic sulphonic acids. The monomer to oxidizing agent ratio was kept as 1:1. After dropwise addition of oxidizing agent, the reaction mixture slowly turned slightly pink and then converted to a dark green colour after complete addition of the oxidizing agent under constant stirring for 24 h. The dark green coloured aqueous suspension of the polymer was further subjected to physico-chemical characterization. UV–visible spectra of the polymer solution were recorded by using a Hitachi-U3210 spectrophotometer in the range of 300–900 nm. FT-IR spectra of the polymer were taken on a Perkin-Elmer Spectrum 2000 spectrophotometer between 400 and 4000 cm^{-1}.

A commercial Hewlett-Packard (HP) thermal printer (DeskJet 693C) with a resolution of 600 × 600 dots per inch was used in this paper. The only modification to the equipment was to replace the original ink with the polyaniline ink solution. The printer cartridges were emptied and thoroughly rinsed with pure water and acetone to ensure that, there was no ink left in the reservoir. The perfectly cleaned cartridge was then refilled with the developed polyaniline based aqueous ink and the IDT pattern was printed on untreated polymeric substrates, crystal clear polyester sheet (OHP transparency).

The humidity sensing measurements were performed at room temperature by subjecting the printed flexible sensor to dynamic humidity measurements; details about the humidity chamber and measurements have been published in our earlier paper [11].

3. Results and discussion

Fig. 1 shows the dark green polyaniline based aqueous ink (a) and printed IDT pattern on the flexible, untreated polymer substrate (b) and (c). In the present investigation we have used an untreated OHP transparency (crystal clear polyester sheet) for printing the IDT pattern. We also have performed a 'Scotch tape test' to check the adhesion of the ink to the substrate by applying the tape and peeling back by a rapid pull force applied approximately perpendicular (right angle) to the test area. The adhesion of the developed ink was found to be good on the polymer (transparency) sheet.

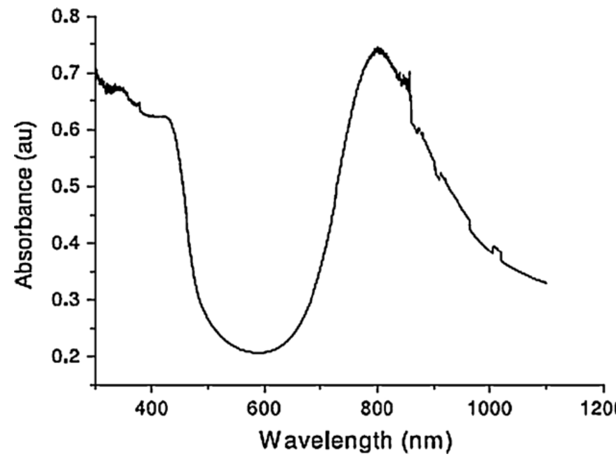

Fig. 2. UV–visible absorption spectrum of polyaniline ink.

The UV–visible absorption spectrum of the polyaniline based aqueous ink is presented as Fig. 2.

The optical absorption spectrum exhibits a peak at 320 nm together with a shoulder at 420 nm and a very sharp peak at 820 nm with an extended free carrier tail at higher wavelength. The peak at 320 nm corresponds to the π–π^* transition of the benzenoid rings, while a small peak at 420 nm can be attributed to the localized polarons which are the characteristics of the protonated polyaniline. The sharp peak at 820 nm characteristic of the extended coil conformations assigned to the conducting emeraldine salt phase of the polymer [12]. The spectral feature observed in Fig. 2 reveals efficient doping of the polymer by sulphonic acid and is further supported by FT-IR spectroscopic characterization.

Fig. 3 represents the FT-IR spectra of the polyaniline based aqueous ink.

The peak at 809.02 cm^{-1} is assigned to the para disubstituted aromatic rings indicating polymer formation. C—H out of plane and in plane bending vibration appears at ~601.53 and 1121.54 cm^{-1}

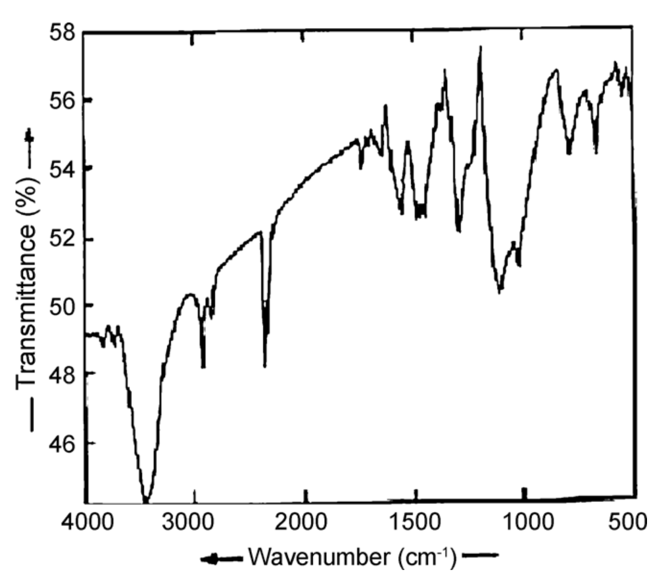

Fig. 3. FT-IR spectrum of polyaniline ink.