Gravure-printed ammonia sensor based on organic polyaniline colloids

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ABSTRACT

A chemoresistive ammonia sensor with sensitive polyaniline layer has been fabricated by gravure printing on flexible poly(ethylene terephthalate) substrate. Novel colloids of polyaniline hydrochloride, which were synthetized in xylene or chloroform in the presence of surfactant, were used as a printing formulation. The sensor characteristics of the colloid-based sensitive layers were compared with in-situ polymerized layers of polyaniline. The colloid-based sensors showed a good response to ammonia concentrations in the range from hundreds of ppb to tens of ppm. This provides an opportunity to use these sensors for both monitoring of maximum exposure limits for humans in workplaces as well as environmental air-pollution. Therefore, these fully printed, metal-free, low cost and flexible ammonia sensors based on organic materials can be used in detection systems for monitoring of hazardous gases.

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1. Introduction

Polyaniline (PANI) ranks among important conducting polymers with highly promising properties for gas sensors applications. The sensitivity of PANI to various vapors and gases is well known [1–20]. It is based on the conductivity or color changes associated with the conversion of conducting PANI salt to non-conducting PANI base [21]. Ammonia sensors based on different detection principles, which exhibit various sensing behavior and differ in detection range, have been described in the literature [22–32]. Many of these PANI-based sensors have been prepared by various techniques, which are usually well suited only for lab-scale fabrication. Regardless of the fabrication process, the sensor response can be generally detected by spectrophotometric or electrical measurements.

Arenas et al. [18] described spectrophotometric detection given by different absorption spectra of differently protonated/deprotonated form of PANI. An optical response of the polyaniline/poly(methyl methacrylate) composite for ammonia concentration below 10 ppm was described by Nicho et al. [19]. The same type of composite was used as a sensitive layer, integrated in an optical waveguide in order to modulate transmitted light power, depending on ammonia concentration [20]. Although spectrophotometric measurements seem to be a powerful tool for ammonia detection, these techniques are inconvenient for small, battery-powered sensor systems, such as smart labels, electronic noses and multi-detectors.

Chemoresistive gas sensors are more suitable for the above-mentioned applications in terms of sensor dimensions, power consumption and fabrication cost. The principle of gas detection is based on chemoresistive properties of differently protonated/deprotonated states of PANI, which can be easily measured as a resistance change [24,33–35].

Although many chemoresistive PANI-based ammonia sensors have been prepared by laboratory techniques, such as drop casting [3,36], spray [37,38] and spin-coating [27,39,40], these are not up-scalable for mass production of low-cost smart systems integrating chemoresistive ammonia sensors. For these applications, it seems to be the most viable way to use printing deposition techniques. In recent years, several research groups have focused on the preparation of printed PANI layers for chemical sensing by using

inkjet printing (IJP) [41–45], which was also used for fabrication of printed ammonia sensors based on various modifications of PANI [34,46–49]. The versatility of IJP was recently demonstrated by Danesh et al. [50] in a multilayered ammonia sensor with printed silver heater, dielectric layer, comb electrodes and in-situ PANI layer. Despite the high flexibility of IJP in pattern design without the need for physical printing form and relatively low ink consumption, there are substantial challenges in terms of low printing speed, pixelization and nozzle clogging which impede an effective usage of IJP for high-throughput mass production. Gravure and screen printing technique are usually much more convenient for roll-to-roll (R2R) manufacturing systems. Nevertheless, far too little attention has been paid to these technologies for printing of PANI-based ammonia sensors and so very few examples can be found in the literature [31].

The present study is focused on characterization of sensing behavior of fully printed, organic-based chemoresistive ammonia sensor prepared by using industrially up-scalable printing techniques: gravure and screen printing. The active layers were prepared from PANI colloids in organic solvents by gravure printing on poly(ethylene terephthalate) (PET) substrate. Such PANI colloids are novel and have not been used for the printing purposes before. This concept is suitable for future R2R printing and application in smart-labels for ammonia monitoring.

2. Materials and methods

2.1. Polyaniline layers

Polyaniline colloids in organic solvents, xylene or chloroform, were prepared by emulsion route by the oxidation of aniline hydrochloride with ammonium peroxydisulfate in 50 vol% water–organic solvent (chloroform or xylen) in the presence of sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) as a surfactant. The reaction mixture contained 0.1 M aniline hydrochloride, 0.125 M ammonium peroxydisulfate and 4 wt% AOT in aqueous phase. The aqueous solution of aniline hydrochloride and AOT (50 mL) was mixed with the solution of ammonium peroxydisulfate (50 mL) and organic solvent was added (100 mL). The mixture was vigorously agitated at room temperature for 1 h. After the polymerization, the system was left at rest to separate into two phases. The organic phase containing ≈1 wt% colloidal PANI was separated and used in the printing experiments. The prepared PANI colloids were characterized by UV–visible spectrometry using a Lambda 20 spectrometer (Perkin Elmer, UK).

Alternatively, polyaniline film was directly in-situ polymerized on the PET substrate [51] by immersion into the aqueous reaction mixture used for the preparation of PANI in the absence of surfactant or organic solvent. Such aqueous mixture contained 0.2 M aniline hydrochloride and 0.25 M ammonium peroxydisulfate. The polymerization took place at room temperature and was completed in ≈10 min. The PET substrate was removed from reaction mixture, green PANI film was rinsed with acetone to remove adhering PANI precipitate, and left to dry in air. In-situ polymerized PANI layer was used as a reference layer because they are generally known to have well-ordered structure with high homogeneity, where its sensing properties are described in literature.

2.2. Sensor fabrication

The sensor platform was based on flexible PET foil (Melinex ST504, Dupont, thickness 175 μm), sensitive PANI layer and interdigital electrodes (IDE) (Fig. 1). In the first case, the sensitive PANI layer was in-situ polymerized. In the second approach, the sensitive layer from PANI colloids was deposited by gravure printing
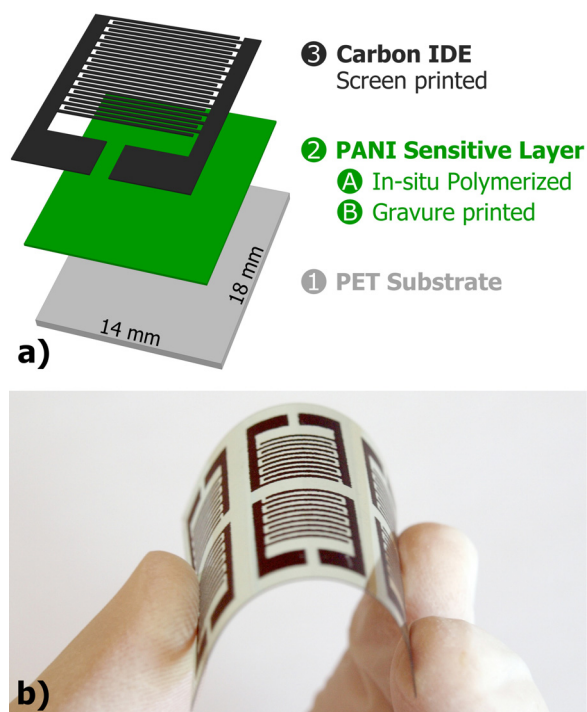

Fig. 1. (a) Sensor structure with layers ordering (the PANI layer was either in-situ polymerized or printed), and (b) a sheet of fully printed ammonia gas sensors.
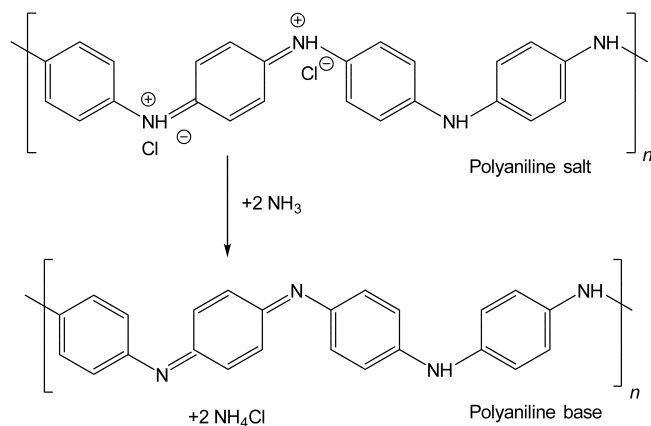

Fig. 2. Conducting polyaniline hydrochloride reacts with ammonia to a nonconducting PANI base.

(Norbert Schläfli Labratester, Switzerland), where the lineature of the printing form, within the printing area was 175 LPI, and the volume of the cells was 6 cm^3 m^{-2}. Subsequently, carbon-based (modified Gwent Group, C10903P14) IDE structure was printed onto the active PANI layer by using screen-printing (EKRA E1, Germany). The IDE structure was composed of 200 μm wide electrode fingers and gaps. Drying of printed layers was performed in air at 80 °C for 10 min (hot-air oven Memert UFP400). The dimensions of the chemoresistive sensor was approximately 14 × 18 mm^2.

2.3. Sensor testing

The apparatus for sensor testing included two gas tanks (reference gas mixture, synthetic air), five mass-flow controllers (Sierra Instruments), a test chamber, and a precision LCR meter (Agilent E4980A) connected to a computer. The reference gas mixture (1000 ppm ammonia in synthetic air) was mixed with humidified synthetic air to obtain required ammonia concentrations. Analyte