Printable ammonia sensor based on organic field effect transistor

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ABSTRACT

We report an organic field-effect transistor (OFET)-based sensor made from printable materials with an unusually high sensitivity of 0.5 ppm v/v for ammonia and with limit of detection on the order of 0.1 ppm v/v. The device developed has a polyethylene terephthalate (PET) substrate, bottom contacts, and poly (3,3‴-didodecylquaterthiophene) (PQT-12) cast from 4 mg/mL cholorobenzene solution as active semiconductor. The fabrication process is simplified by replacing the gate electrode and dielectric deposition steps with the introduction of static charges on the back surface of the PET substrate by corona charging, a procedure that is adaptable to roll-to-roll processing. Hydrophobic polymers applied to the back surface stabilize this charge, providing evidence for their activity at that location. In the proposed sensor, these static charges are used as a static gate, reducing the OFET architecture to a chemiresistor. The sensor is selective for ammonia over common organic solvent vapors, and the response is generally reversible. The device also demonstrates memory behavior required for dosimetric sensors when kept at low temperature (4 °C to −30 °C). A converse response from an n-channel semiconductor is also reported.

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1. Introduction

Ammonia sensing is of intense interest due to its potential association with chronic diseases like asthma, severe respiratory inflammations, and lung diseases arising from its presence as an environmental pollutant [1,2] (see also https://www.sciencemag.org/content/343/6168/238.full, accessed 21 January 2014). Currently the exposure limit for ammonia is effectively dictated by the ammonia sensing capabilities of available technologies rather than any detailed study on the effects of lower environmental ammonia concentrations that could be present.

Ammonia sensors with limits of detection ranging from as high as 200 ppm down to 0.35 ppm have been reported in the last decade, based on technologies such as metal-oxides, catalytic processes, organic polymer films, optical detection techniques and mass spectrometry coupled with gas chromatography (GC–MS) [3,2,4–8]. The detailed study required for designing personalized intervention strategies for the ammonia exposure in relation to human health and environmental monitoring calls for a highly sensitive sensing technique along with other attributes such as cost effectiveness, high selectivity, light weight, compactness and mass production. Organic polymer based field effect transistors (FETs) provide a highly suitable match for the proposed study as all the other mentioned techniques are either very expensive, bulky with high

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temperature requirements, lack high selectivity or have a limit of detection too high for non-occupational settings.

Over the past decade, organic field effect transistors (OFETs) have been established as vehicles for alternative electronic technologies such as wearable electronics and robotic skin due to their attributes like printability, low cost, and flexibility [9]. From the first thiophene-based OFET reported by Koezuka et al. in 1987 [10] to fully printable plastic based OFETs, several major milestones have been achieved, such as very high mobility, low hysteresis, and steadily improving stability [11]. An ultralight thin (2 μm, 3 g m^{-2}) OFET reported by Kaltenbrunner et al. with a foldable hybrid anodic aluminum oxide gate dielectric added a new level to robustness and stability of OFETs [12]. The better understanding of the physics behind OFETS [13] can enable tremendous improvement in OFET-based chemical sensors.

Recently, Yu et al. reported flexible ammonia sensors based on spray-coated TIPS-pentacene OFETs as active layer with a PMMA dielectric layer on glass and plastic substrates [6]. Though the reported device is very low cost and printable, the highest sensitivity of these devices is only 10 ppm; though the high reversibility and stability were advantageous. Huang et al. also reported a printable pentacene based OFET ammonia senor with poly (vinyl alcohol), poly(4-vinylphenol), poly(methyl methacrylate) and polystyrene dielectric layers which affected the grain size and dielectric-semiconductor interface of the pentacene; the reported limit of detection was 1 ppm [5]. Tiwari et al. developed a poly-3-hexylthiophene based OFET ammonia sensor with detection ranging between 0.1 and 25 ppm, the ppm definition used in that work was 1 mg ammonia/L, a thousand times more concentrated than 1 ppm v/v [8].

Along with sensitivity, selectivity is another crucial part of any sensor study, which can be a challenge for a device depending solely on morphological features, although this kind of dependence is very helpful for reversibility of the response. Li et al. developed a novel dendritic microstripe-based dialkyl tetrathiapentacene (DTBDT-C6) OFET ammonia sensor using a dip coating process to avoid the drawbacks of solution-processed films. The proposed device combined the two useful features of selectivity and reversibility, but was only reported to detect 10 ppm of ammonia [4].

In order to use flexible printable OFET devices for environmental and human health studies we need to achieve high selectivity along with sub-ppm v/v sensitivity. For these applications, reversibility might not play a very significant role if dosimetric sensing is required. Our group reported OFET-based ammonia sensors that could detect concentrations of 0.45 ppm v/v, with a limit of detection of 0.35 ppm, the highest sensitivity reported to date for semiconductor films [7]. These OFETs, however, were vapor-deposited, leading to long process time and high cost of production, making the sensor less feasible for mass-production.

To address some of these challenges, we report herein a printable OFET sensor with sensitivity of 0.5 ppm v/v for ammonia and a conservative limit of detection of 0.1 ppm, using much more time- and cost-efficient processes

than a vapor deposition. A key step is corona charging of a polyethylene terephthalate (PET) substrate. PET, with a dielectric constant of 3.2, is a widely used dielectric material for charge storage applications (e.g. film capacitors). Numerous studies have been published on the nature of the charges on the PET surface due to corona charging [14–22]. Inherent static charges present on PET surfaces could be easily tailored by this technique or similar techniques like oxygen plasma to manipulate OFET characteristics, e.g. threshold voltage [23]. Taking advantage of this technique, we have been able to use PET substrate as gate dielectric material and the static charges present on it as a static gate, thus significantly simplifying the OFET structure to that of a chemiresistor.

2. Experimental

2.1. Material

The schematic of the PET OFET fabrication process and the device structure are shown in Fig. 1. The modified OFET structure was developed on 12-μm thick PET sheets supplied by Mitsubishi polyester films. Poly (3,3′′′-didodecylquaterthiophene) (PQT-12) and 2,2′-[(2,5-dihexadecyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diylidene)dithiene-5,2-diylidene] dimalononitrile (DPP-CN) were synthesized in our laboratory. DPP-CN [24] was prepared according to modified literature procedures. For PQT-12 synthesis, 5,5′-bis(trimethylstannyl)-2,2′-bithiophene was purchased from Sigma–Aldrich and was further recrystallized for polymerization. Monomer 5,5′-Dibromo-4,4′-didodecyl-2,2′-bithiophene [25] was prepared from 5,5′-bis(trimethylstannyl)-2,2′-bithiophene which was purchased from Sigma–Aldrich and was further recrystallized for polymerization.

2.2. Synthesis of PQT-12 [26]

5,5′-Dibromo-4,4′-didodecyl-2,2′-bithiophene (0.5 mmol, 0.330 g), 5,5′-bis(trimethylstanny)-2,2′-bithiophene (0.5 mmol, 0.246 g), tris(dibenzylideneacetone)dipalladium(0) (0.02 mmol, 18.3 mg), and tri(o-tolyl)phosphine (0.08 mmol, 24.4 mg) were added to a reaction vial, which was then purged with argon for 15 min. Anhydrous chlorobenzene (15 mL) was added through a septum and the reaction mixture was then stirred at 115 °C for 72 h. The reaction mixture was poured into methanol (150 mL) and HCl (10 mL). The polymer was filtered and subjected to Soxhlet extraction with acetone (24 h), hexane (24 h), dichloromethane (24 h) and chlorobenzene (24 h). The chlorobenzene fraction was concentrated and precipitated into methanol. Following filtration, the purified polymer (0.3 g, 90%) was obtained as a brown solid GPC: M_n = 20.5 kg/mol; M_w = 24.3 kg/mol; PDI = 1.2.

2.3. Device preparation

The PET sheet was cut into 1 in. by 1-in. square samples that were cleaned in an ultrasonic isopropanol bath for 10 min and then rinsed with distilled water. Following