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Biocompatible and degradable gelatin dielectric based low-operating voltage organic transistors for ultra-high sensitivity NH$_3$ detection

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We developed an ultra-high sensitive ammonia (NH$_3$) gas sensor that incorporates a biocompatible/degradable gelatin dielectric layer in a top-contact organic thin-film transistor. The sensitivity study of the gas sensor involves detecting the saturation current change with analyte concentrations, exhibiting a saturation current changing from 17.6% to 45.1% for the concentration of NH$_3$ from 500 ppb to 30 ppm. Importantly, this type of sensing platform shows an excellent detecting limit of 174.0 ppb with a low operating voltage of 4 V. To understand the mechanism of this phenomenon, we fabricated another group of devices that incorporates an additional thin layer of polystyrene covered on top of the gelatin layer. The response sensitivity of this type of sensor is only 5.1% for the NH$_3$ concentration of 30 ppm. Systematic studies including morphology analysis of the organic films and electrical properties of the sensors were performed. The results indicate that the functional groups on the gelatin dielectric surface groups have ability to adsorb NH$_3$ analyte, thereby leading to a superior sensing performance. This work demonstrates that the biocompatible/degradable gelatin with unique functional groups is applicable for readily manufacturable low-operating voltage and high-performance thin-film transistor-based gas sensors. Published by AIP Publishing. https://doi.org/10.1063/1.5054026

With the advent of the Internet of Things (IoT) era, more and more emphasis is placed on the humanization and portability of electronic products. Meanwhile, in order to protect the nature environment and human race, developing low-cost, efficient, and low-loss gas sensing devices for monitoring pollutant gases, especially the harmful and toxic gases, becomes an urgent topic.1–3 Among various gas-sensing devices, organic thin-film transistor (OTFT)-based sensors have attracted intriguing attention due to their advantages of lightweight, flexibility, and low material/process costs.4–6 Moreover, by virtue of the field effect tuned multiple electrical parameters, OTFTs can function as both signal transducers and amplifiers. Therefore, OTFTs are widely adopted as the unit component of high performance sensors.7–11

Toxic gas ammonia is one of the major industrial chemical products, which is detrimental to human health and environmental issues. Long-time ambient NH$_3$ exposure, even very low NH$_3$ concentration (ppb level), can cause asthma, severe respiratory inflammations, and lung diseases.12,13 Therefore, developing low cost and high sensitivity NH$_3$ gas sensors becomes a significant topic, and a lot of research efforts has been devoted to enhancing the NH$_3$ sensing property of OTFT-based sensors.14–16 For example, Khim et al. demonstrated flexible, highly sensitive NH$_3$ gas sensors with ultrathin donor-acceptor (D-A)-type semiconducting conjugated polymers.17 Introducing a tris(pentafluorophenyl)borane (TPFB) compound in a semiconducting layer as the receptor of NH$_3$ is another route for detecting low concentration NH$_3$.18 Besides the development of semiconducting materials, high-performance OTFT-based gas sensors can also be realized by introducing an additional function layer.19 However, most reported OTFT-based NH$_3$ sensors mainly focus on developing semiconductor engineering but neglects the problem of high driven voltages.20,21 Developing and engineering dielectric layers in OTFT-based sensors is the most straightforward route to lower power consumption. Due to the fact that charge carrier transportation in OTFT mainly occurs at the interface between a semiconductor and a dielectric layer, a proper dielectric layer may also determine the sensing property.7,22

On the other hand, with the rapid development of biodegradable and wearable electronics, bio-compatible materials show immense potential in next-generation electronics.23,24 Some naturally existing biological materials, such as silk fibroin, chicken albumen, DNA, and RNA, have attracted intriguing attention owing to their advantages of biodegradability, biocompatibility, environmental friendliness, and abundance.25,26 Among them, Gelatin, obtained from bones and skins of the animals, a kind of natural protein, has been widely used for biological detections in recent years.27–29 A large number of studies verified that gelatin not only contains plenty of chemical groups but also exhibits excellent dielectric properties.30 The application of gelatin as the dielectric layer in high performance OTFTs was also reported.31 Consequently, gelatin shows enormous potential of


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application in biocompatible/biodegradable OTFT-based sensors. Nevertheless, reports on gelatin-based gas sensors are rarely seen.

In this work, we present a simple OTFT-based NH3 sensor platform with biocompatible/degradable gelatin as dielectric layers, which provides a low-power consumption route for ultra-sensitive detection of NH3 gas. As a comparison, OTFT gas sensors with conventional polyester dielectrics were also studied, and these devices show much poorer performance in NH3 sensing than those gelatin-based ones. The functional groups on the gelatin dielectric surface exhibit the ability of NH3 absorption, thus resulting in superior NH3 gas responsivity and selectivity of the gelatin-based devices. With the contribution of the high capacitance of the gelatin dielectric layer, the operating voltage of the OTFT-based NH3 sensor is as low as −4 V. The results establish considerations in design for low-cost, biocompatible/degradable sensors.

Figure 1(a) shows the schematic diagram of a top-contact (TC) OTFT-based NH3 sensor with biocompatible/degradable gelatin as the dielectric layer. Indium tin oxide (ITO)-coated glass used as the substrate and the gate electrode was cleaned in an ultrasonic bath with detergent, acetone, deionized water, and isopropanol for 15 min each. Gelatin (extracted from animal skin, Sigma-Aldrich) was dissolved in deionized water with a concentration of 50 mg/ml. Next, a 400 nm thick gelatin dielectric layer with a unit capacitance of 18.7 nF/cm2 (shown in Fig. S1, supplementary material) was spun-coated at 2000 rpm for 1 min and then baked on a hot plate at 80 °C for 15 min to remove the residual solvent. Then, a 30 nm thick pentacene semiconducting layer (purchased from Tokyo Chemical Industry Co., Ltd) was vacuum deposited on the gelatin dielectric layer under 2 × 10−4 Pa at a rate of 0.2 Å/s. Finally, 30 nm thick Au source and drain electrodes were thermally evaporated using a shadow mask at a rate of 0.2 Å/s under 3 × 10−3 Pa. The channel width/length ratio was 100 (W = 10 mm, L = 100 μm). The OTFT-based sensor was put in an airtight test chamber (approximately 2 ml) for sensing property testing. Dry air and 100 ppm standard NH3 gas (anhydrous, Sichuan Tianyi Science & Technology Co.) were mixed to form various concentrations ranging from 0 to 30 ppm and then introduced into the test chamber by a mass flow controller. Capacitance measurements of the gate gelatin and gelatin/PS dielectrics were performed by sweeping the capacitance-frequency properties from a metal-insulator-semiconductor (MIS) architecture, specifically, ITO/Gelatin/ Au and ITO/Gelatin/PS/Au, using an Agilent 4294A (Santa Clara, CA, USA). The gas sensing characteristic of these devices was measured using a Keithley 4200 sourcemeter at room temperature.

The transfer curves with a source-drain voltage (VDS) of −4 V were used for characterizing the sensing properties of the OTFT-based sensor. Figure 1(b) shows a set of transfer curves correlated with the sensor at various concentrations of NH3 exposure. For the I-V response to different concentrations of NH3, the device was exposed to each tested concentration of NH3 for 2 min before measurement. The transfer characteristics clearly demonstrate that gelatin-based OTFT exhibits an excellent NH3 response sensitivity. As another important index of sensing sensitivity, the field-effect mobility (μ) of the OTFTs will be discussed next. μ can be extracted in the saturation regime by using the following equation:

\[
I_D = \left(\frac{W}{2L}\right)\mu C(V_{GS} - V_T)^2
\]

where L and W are the channel length and width, respectively, C is the capacitance (per unit area) of the dielectric layer, and VGS is the gate voltage. To intuitively discern sensing properties, the variation of IL and μ, defined as Y = |(YNH3 − Y0)/Y0| × 100%, is presented in Fig. 1(c). In this work, over 100 devices were fabricated, and their transistor performance is very consistent. Due to the long duration data collection time, here we summarized an average value of five representative samples. Y of IL of the gelatin-based sensors exhibits a changing range of 41.9% to 58.2% for 30 ppm NH3. A similar trend of μ in these devices was also observed, with a changing range of 62.2% to 73.1% for 30 ppm NH3. The means of decrease in IL and μ of the gelatin-based OTFTs are 45.1% and 65.8% when exposed to 30 ppm NH3, respectively. Notably, the IL and μ values of these devices still show a decrease of 17.6% and 26.6% when exposed to 500 ppb NH3. Meanwhile, the response time and recovery time were also tested by real-time sensitivity testing, as shown in Fig. S2, supplementary material. The response time and the recovery time are 15.4 s and 42.2 s, respectively. Further tests were also performed on lower NH3 concentrations for the purpose of estimating the limit of detection (LOD) using the linear fitting method shown in the following equation:

\[
Y_{LOD} = -a + \frac{b + \sqrt{a^2 + b^2 - (b^2 - \eta^2 \times \Delta b^2)(a^2 - \eta^2 \times \Delta a^2)}}{b^2 - \eta^2 \times \Delta b^2}
\]

where η = 1.96 corresponds to the 95% confidence level; a, b, Δa, and Δb are the parameters extracted from the linear fit.
of Fig. S3, supplementary material. The estimated LOD of the sensor in this work is 174.0 ppb, indicating that the sensor can effectively monitor trace amounts of NH3 in the practical environment.

To understand the reason for superior gas-sensing properties, comparable and parallel studies were carried out by investigating the influence of different dielectrics on the performance of OTFT-based sensors. Here, we fabricated another group of OTFT devices with the same structure but covering the gelatin layer by a thin film of polystyrene (PS), as shown in Fig. 1(d). The fabrication process started with dissolving PS (average Mw ~ 290k, Sigma-Aldrich) in xylene (Tokyo Chemical Industry Co., Ltd.) with a concentration of 3 wt. %, spin-coated onto the gelatin layer at 5000 rpm for 1 min, and baked in an oven at 130 °C for 1 h. After covering the thin PS (100 nm thick) layer, the OTFT cannot embody a transistor feature under operating voltage of −4 V (VGS and VDS) due to the decrease in the capacitance of the dielectric layer. Instead, the operating voltage was increased up to −40 V. These OTFTs with the gelatin/PS dielectric layer were tested at various NH3 concentrations. As shown in Figs. 1(e) and 1(f), the variations of Ion and μ of the gelatin/PS devices are only 5.1% and 7.6% when exposed to 30 ppm NH3, respectively, while the Ion and μ values just exhibit slight changes of 0.8% and 1.1% for 500 ppb NH3, respectively.

The sub-threshold slope (SS) is another significant parameter to characterize the sensing properties in OTFT-based sensors since the SS reflects the charge trap density (N) at the interface between the dielectric and organic semiconductors. N can be extracted using the following equation:8

\[
SS = \frac{kT}{q} \ln 10(1 + qN/C),
\]

where \(q\) is the electronic charge, \(k\) is Boltzmann’s constant, \(T\) is the absolute temperature, and \(C\) is the areal capacitance of the dielectric. The SS of gelatin/PS-based OTFT shows a negligible change at different NH3 concentrations, which means that the NH3 analyte does not change the trap state at the interface between PS and pentacene. In contrast, the SS of gelatin-based OTFT has remarkable response with the introduction of NH3 analyte. Such a result implies that plenty of NH3 molecule is adsorbed at the interface and interacts with trapping charge carriers. Based on the above results, it can be seen that sensing performance of gelatin-based OTFT is much greater than that of the gelatin/PS-based OTFTs. Compared to gelatin/PS-based OTFT, a 21× greater response sensitivity in gelatin-based OTFT was observed. It is noteworthy that the operating voltage of the device with the gelatin dielectric layer is only −4 V.

To disclose the origin of sensing performance enhancement, the surface topographies of the gelatin film, the gelatin/PS film, and pentacene films (on top of the dielectrics) were first probed by atomic force microscopy (AFM) (Agilent, AFM 5500). It is well known that the morphologies of both dielectric and organic films could significantly affect the sensitivity.8,22 As shown in Figs. 2(a) and 2(b), the gelatin film and the gelatin/PS film show similar morphologies, with the root mean square roughness (RMS) of 0.49 nm and 0.45 nm, respectively. Pentacene films deposited on top of dielectrics exhibit similar crystal growth as shown in Figs. 2(c) and 2(d). The grain size of pentacene deposited on the gelatin film is slightly larger than that on the gelatin/PS film. The results of the topographies indicate that film roughness and gaps in-between pentacene grains are not the dominating factors for sensitivity improvement.32,33 The analyte-caused capacitance change of the dielectric layer in OTFT-based sensors is also a well-known mechanism. Here, the capacitances of the gelatin are tested by the static testing method before and after NH3 (1 ppm) introduction to verify if any swelling occurred on gelatin, as shown in Fig. S4, supplementary material. The results show that the capacitances are almost unchanged.

Therefore, the surface properties of the gelatin are confirmed to be the main contribution to the sensitivity enhancement. X-ray photoelectron spectroscopy (XPS) (Micron ESCA Probe, Tokyo, Japan), a powerful surface characterization tool, was next utilized to analyze the surface chemical elements of the dielectrics. Three dominant peaks at ~286, ~400, and ~532 eV in the XPS survey spectrum depicted in Fig. 2(e) were related to C 1s, N 1s, and O 1s species, respectively. This result implies that the gelatin contains a lot of functional organic chemical groups. The gelatin film was next analyzed by Fourier transform infrared (FTIR) spectroscopy (Thermo Scientific, Nicole-10) to further identify these functional organic chemical groups. As shown in Fig. 2(f), clear vibrational peaks at ~1078, ~1334, ~1535, ~2927, and ~3285 cm⁻¹ can be observed, which correspond to C-O, C = C, C = O, -NH, and -OH, respectively.29,34 The combination of these polarization chemical bonds forms functional groups, which could interact with NH3 analyte. When the polar molecules NH3 diffuse into the interface of gelatin/pentacene, the functional group on the gelatin would trap more NH3 molecules, thus restraining charge carrier transport in the conducting channel. As a result, a large amount of free hole carriers will be fettered by electron donors.35,36 As shown in Figs. 3(a) and 3(b), compared to the PS film, the gelatin film will absorb more NH3 due to the existence of functional groups. In contrast, such interaction will not occur between NH3 and benzene rings.20 Therefore, the trapped NH3 at the interface of gelatin/pentacene effectively reduces the magnitude of the source-drain current and charge carrier mobility.
Considering practical applications, selectivity of gas sensors is an open matter for evaluating the possibility of commercialization. So, we investigate the response of gelatin-based OTFT to several representative coexisting air pollutants including NH₃, H₂S, CO, NO₂, and SO₂. As shown in Fig. 3(c), it is clear that the response of NH₃ is at least 2.5 times greater than all the other gases: the sensitivities to H₂S, CO, NO₂, and SO₂ under 30 ppm are 13.5%, 9.8%, 18.0%, and 12.9%, respectively. It is apparent that the current variations of NO₂ and SO₂ are opposite to those of NH₃, H₂S, and CO since NO₂ and SO₂ usually act as electron acceptors for pentacene. Furthermore, to explore the influence of moisture on the sensing properties, we put the device in the ambient (RH = ~50%) for 60 min and then we measure the sensing properties in the same environment. Compared to the results tested in the testing chamber, the variation of Iₜ₀ of these devices is a little lower, exhibiting a 12.5% change to 500 ppb NH₃. Moreover, the device shows deterioration of NH₃ sensing after long time testing in the moisture environment, as shown in Fig. S5, supplementary material, indicating that more efforts are needed to further improve this sensing platform.

In summary, an ultra-sensitive and low-operating voltage organic transistor-based NH₃ sensor was obtained by introducing a gelatin dielectric layer. The change in saturation current achieves 17.6% for the NH₃ concentration of 500 ppb, while the applied operating voltage is only −4.0 V. Combination of experimental and theoretical results, an excellent LOD of 174.0 ppb for this type of sensor, is demonstrated. Meanwhile, this sensor also presents outstanding selectivity to NH₃. We believe that OTFTs with the biocompatibility and degradation gelatin dielectric layers open an effective way to realize high-performance, low-cost, portable electronic noses.

See supplementary material for capacitance-frequency characteristics, real-time sensitivities, limit of detection, and typical transfer curves, including Figs. S1–S5.

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