

Polypyrrole Based Love-Wave Gas Sensor Devices with Enhanced Properties to Ammonia [†]

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Abstract: Love-wave (LW) sensors based on gas sensitive polypyrrole (PPy) nanoparticles (NPs) and their modification with different gold (Au) loads are developed in this work. The research is focused on the fabrication process of the gas sensor devices and their sensing properties to ammonia (NH₃).

Keywords: gas sensors; Love-wave sensors; polypyrrole; ammonia

1. Introduction

NH₃ is a highly toxic gas with an unpleasant odor that can harm the human body, affecting the immune system or inhibiting the cell growth. High NH₃ concentrations (e.g., 300 ppm) may be dangerous to life, whereas very low concentrations (92–4240 ppb) in the exhaled breath may act as biomarkers of chronic kidney diseases. Hence, the interest in NH₃ sensors with remarkable performance and capable to reach low detection limits. In general, in the literature, NH₃ sensors have been fabricated based on semiconductor metal-oxides (MOX) and conductive polymers (CPs). However, MOX are contingent on very high working temperatures (100–400 °C), whereas CPs can operate at room temperature with less power consumption making it more competitive compared to NH₃ sensors based on MOX [1].

CPs such as PPy with various nanoscaled morphologies (e.g., particles, wires, ribbons) have been used in the past for NH₃ detection. These materials were mostly integrated with chemo-resistive transducing platforms and despite their great advances, some functional issues such as the low response magnitudes or the moderate limits of detection (LOD) have shown to be still a challenge to be solved [1]. The functionalization of CPs with diverse nanosized materials like noble metals, metal oxides and different types of carbon based materials was found to have a crucial effect on the final sensitivity. This resulted in dramatically enhanced sensor performance in comparison with non-modified CPs sensitive layers [1]. The advantages of gravimetric sensors, for instance, surface acoustic waves (SAW), include relatively low cost, easy fabrication, and mainly high sensitivity which result from changes in the mechanical, electrical, and elastic properties of the sensitive layers. Recent reports have demonstrated that the use of mass-sensitive transducing platforms based on LW propagations provided enhanced sensitivity and response time in NH₃ sensing application [2,3].

Therefore, this work focusses on the fabrication of LW sensors based on PPy NPs and PPy NPs modified with gold (AuPPy NPs) and their validation to NH_3 detection.

2. Materials and Methods

PPy NPs were obtained via oxidative chemical polymerisation of pyrrole monomer. This reaction is based on the formation of complex between water-soluble polymer, poly(vinyl) alcohol, acting as a stabilizer and ferric cations from iron (III) chloride acting as oxidizing agent in aqueous solution, as described previously [1]. The synthesis of colloid Au NPs was performed according to Turkevich method, i.e., via chemical reaction between gold(III)chloride hydrate and sodium citrate dihydrate.

PPy and AuPPy NPs with two different Au loads (1:10 and 1:2) were used to develop LW sensors. The LW sensor platforms were based on quartz piezoelectric substrates with Al interdigitated electrodes and a SiO_2 layer deposited on substrate via plasma-enhanced chemical vapour deposition. The layer of SiO_2 works as an electrical isolating layer and acts as the first guiding layer of the multi-guiding layer sensor. PPy or AuPPy NPs layer serves as the second guiding layer and sensitive layer at the same time. The multi-guiding layer structure contributes to enhance the mass sensitivity of SAW sensors with appropriate attenuation of the wave [4]. In order to optimize the Insertion Loss properties of the LW sensors, we tuned the thickness of the second guiding layer (PPy or AuPPy films) deposited via spin-coating technique on the SiO_2 layer. Different speeds (2000, 2500, 3000, 3500 and 4000 RPM) were tested. The optimal Insertion Loss for the sensors was found the second guiding layer deposited at 4000 RPM.

The analysis of the sensitive layer was performed using transmission electron microscope (TEM; JEOL 1011) and DualBeam microscope (Helios G4 FX DualBeam), respectively. The optical properties of Au NPs were studied with UV-Vis-NIR spectrophotometer (Cary 5000). Additionally, the LW devices were characterized before and after the integration of PPy NPs using RF transmission parameter S_{21} . This analysis was performed using a 360B Automatic Network Analyzer (Wiltron). Tests of PPy and AuPPy NPs LW gas sensors were carried out via monitoring of frequency changes towards various concentrations of NH_3 . The exposure time of the sensors to each concentration was 2 min and afterwards the system was purged with synthetic dry air for 30 min. All measurements were performed at room temperature, and each test condition was repeated four times with the first measurement being discarded.

3. Results and Discussion

TEM analysis confirmed the formation of uniformly distributed spherical PPy NPs with different sizes, generally between 30 and 50 nm (Figure 1a). UV-VIS analysis of the Au NPs displayed the characteristic plasmon peak at 523 nm, which indicates the synthesis of NPs with diameters between 15 and 20 nm (Figure 1b).

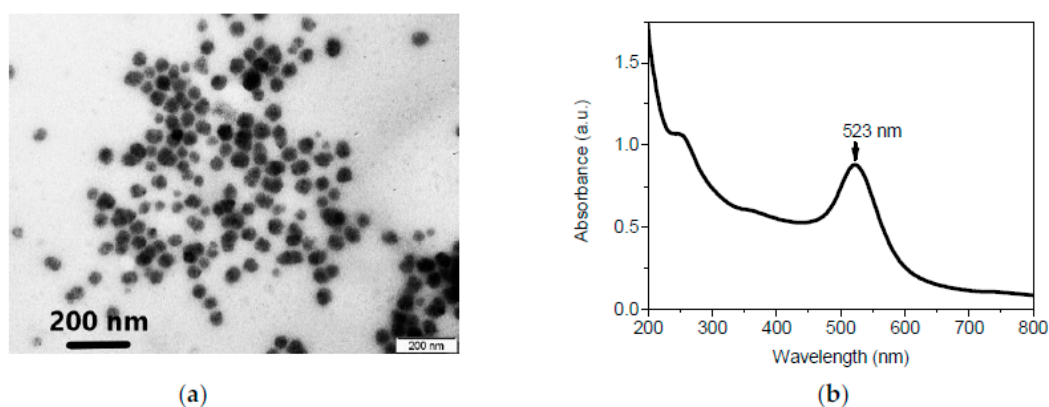


Figure 1. (a) TEM image of the PPy NPs; (b) UV-VIS analysis of the Au NPs.

After spin coating of the PPy and AuPPy NPs (i.e., the second guiding layer) on the LW transducing platforms, the films displayed a porous morphology as can be noticed in the cross-section shown in Figure 2a. Moreover, Figure 2b shows an example of the Insertion Loss (−21 dB) and frequency (162 MHz) measured in the LW sensors tested in this work.

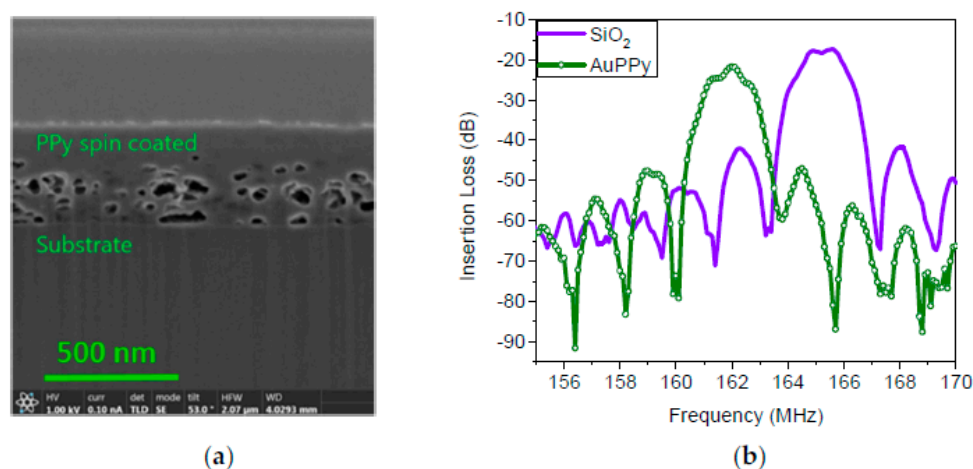


Figure 2. (a) Cross-sectional SEM image of the spin-coated PPy NPs; (b) Comparison of the amplitude of transmission parameter S_{21} of the LW sensors with the first guiding layer (SiO_2) and multiguiding layer (SiO_2 + AuPPy NPs).

In general, the sensors based on the Au modified PPy demonstrated enhanced sensing properties towards NH_3 compared to the sensors based on non-modified PPy. We further observed that the sensors based on lower Au loadings (i.e., 1:10) provided better responses compared to those based on higher Au loadings (i.e., 1:2). Namely, AuPPy (1:10) sensors showed frequency shifts in kHz and an increase in the response of 20, 27 and 36% to 2, 5 and 10 ppm, respectively, as compared to PPy sensors. The response (frequency shift) of LW sensors based on AuPPy (1:10) to 2 ppm of NH_3 is shown in Figure 3a, whereas a comparison of the calibration curves of both sensors based on PPy and AuPPy (1:10) towards NH_3 is presented in Figure 3b. The response times for the sensors (i.e., based on PPy and AuPPy) were below 60 s.

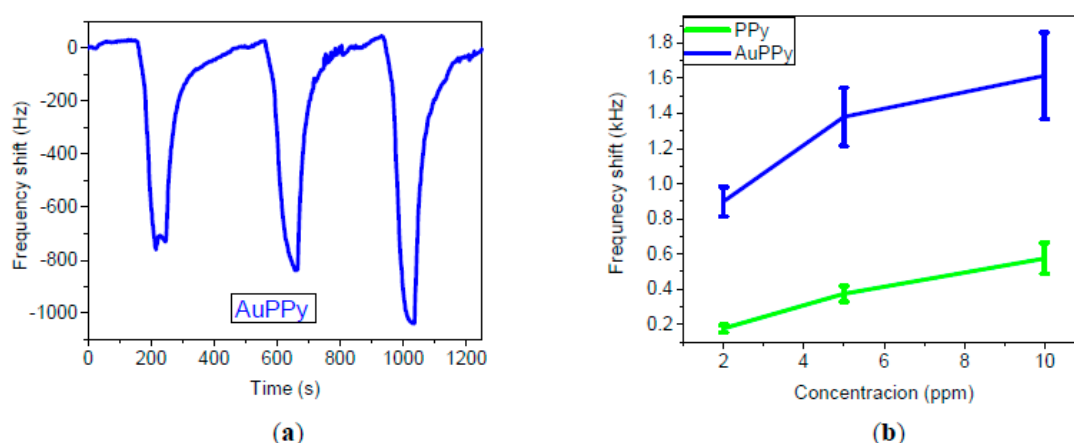


Figure 3. (a) Response of the AuPPy (1:10) based-LW sensor to 2 ppm of NH_3 ; (b) Calibration curves to NH_3 using the PPy and AuPPy (1:10) sensors.

The estimated LOD of AuPPy (1:10) sensors to NH_3 was determined to be about 133 ppb, considering that the minimum signal intensity is 3 times higher than noise. This value is significantly lower compared to PPy based sensors in other studies (see Table 1), which reported LODs of 5 ppm [1] and 10 ppm [5]. Also, we found that the LOD determined here is lower compared to $\text{Fe}_2\text{O}_3/\text{WO}_3$

based SAW sensors reported previously [2]. The enhanced sensing performance of our AuPPy LW sensors, make them promising for the detection of very low NH_3 concentrations and for potential medical applications, in which NH_3 needs to be detected at low concentrations as 92 ppb. [1]

Table 1. The limit of detection for various sensors towards NH_3 .

Type of Sensor	Limit of Detection (ppm)	Reference
AuPPy LW	0.133	Current work
PPy chemiresistive	5	[1]
PPy SAW	10	[5]
$\text{Fe}_2\text{O}_3/\text{WO}_3$ LW	1	[2]

4. Conclusions

LW sensors based on PPy and AuPPy NPs were fabricated and validated towards different NH_3 concentrations. Our results demonstrated enhanced sensing properties for the AuPPy (1:10) LW sensors as compared to the non-modified PPy sensors and PPy sensors modified with higher Au loadings (1:2). The estimated LOD for the AuPPy (1:10) LW sensors was notably lower compared to other PPy based sensors reported in the literature. The relatively easy technological fabrication steps and low cost of these sensors, as well as their enhanced sensing properties towards low NH_3 concentrations make them attractive for future studies and applications where traces of other gases and VOCs are involved.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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