Synthetic Metals 245 (2018) 237–244

Contents lists available at ScienceDirect

Synthetic Metals

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

Synthesis and spectroscopic characterization of polypyrrole PPy coating on flax fibers and its behaviour toward trimethylamine vapor

A. El Jaouhari[a], S. Ben Jadi[a], A. El Guerraf[b], M. Bouabdallaoui[b], Z. Aouzal[b], E.A. Bazzaoui[b], J.I. Martins[c], M. Bazzaoui[a,c,*]

[a] Laboratoire des Matériaux et Environnement, Faculté des Sciences, Département de Chimie, Université Ibn Zohr, B.P. 8106, Agadir, Morocco
[b] Faculté des Sciences, Département de Chimie, Université Mohammed Ier, 60000 Oujda, Morocco
[c] Faculdade de Engenharia, Departamento de Engenharia Química, Universidade do Porto, Rua Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

Keywords:
Sensors
Polypyrrole
Flax
Trimethylamine

ABSTRACT

This work aims to elaborate PPy-flax composite via chemical in-situ polymerization of pyrrole on flax fiber in aqueous medium. The flax-PPy gas sensor was examined for trimethylamine gases. It was found that the electrical resistance of PPy coating increases in the presence of organic vapors while it decreases in clean air. The results of this study show the high efficiency of flax-PPy sensor toward toxic vapors. The influence of input parameters such as gas concentration has also been investigated. The synthesized sensor was characterized by different techniques such as X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

1. Introduction

In the last few years, the development of toxic vapors sensors has received much interest due to their hazardous effect either to the environment and human health [1,2].Trimethylamine (TMA) is the substance chiefly responsible of the fishy odor related to rotten fish. Trimethylamine can induce to many health complications such as nausea, ocular, and respiratory system irritation with 15 ppm of TMA [3,4]. Several materials have been used astrimethylamine sensor based on semiconductor either with metal oxide or conductive polymers due to their attractive optical and electrical properties [5–9]. In particular, WO_3 hollow sphere [10], Th–SnO_2 [11], α-Fe_2O_3/TiO_2 [12], Pt–TiO_2 [13], and Cr_2O_3-decorated ZnO [14] have been investigated as sensors for detecting trimethylamine. However, metal oxide sensors require high temperature operation and high energy consumption in order to ensure good sensitivity [15]. Conductive polymer has attracted much attention due to their high conductivity which depends mainly on the doping level, low ionization potential, and high electron sensitivity. Furthermore, the oxidation level of conductive polymers is highly affected by the chemical or electrochemical mechanisms of doping/dedoping (oxidation/reduction), inducing to high sensitivity and quick response [16,17] toward a variety of chemicals gases. The overall properties give to these polymeric materials an important and effective contribution to the field of gas detection [18]. Among the conductive polymers, polypyrrole (PPy) is of particular interest owing to many advantageous properties such as good stability, high electrical conductivity, as well as it's environmentally friendly synthesis process [19]. Indeed, PPy has been widely used as gas sensors for hazardous gases including ammonia [20–23]. The main objective of this work is to improve the performance of polypyrrole-based sensors. These performances include low response time, good stability, sensitivity, selectivity, and reproducibility. In order to achieve these objectives, researchers were oriented to improve polymer properties in terms of morphology, doping rate, nature of the counter-ions, and conductivity. In this context, Zheng et al. [24], have synthetized polyaniline-TiO_2 nano-composite by QCM method and studied its behavior towards trimethylamine vapor. However, the sensitivity of composite still not good enough as well as its response time Otherwise, sensors based on polypyrrole are also used to detect other derivative amines vapors. In particular, trimethylamine (TMA). This organic volatile compound is widely used as an organic solvent, polymerization catalyst, preservatives, and synthetic dyes [25]. Although, the trimethylamine has a deleterious effect on the environment and human health. In this respect, many research studies have been investigated for the detection of trimethylamine vapors using polypyrrole [26,27]. Jamalabadi et al. [26], have developed aliphatic amines sensor based on hybrid nanocomposite (PPy-ZnO). The sensor exhibited good sensitivity to the vapor with time response less than 50 s and a detection limit of 100 ng at 100 °C. Sun

* Corresponding author at: Laboratoire des Matériaux et Environnement, Faculté des Sciences, Département de Chimie, Université Ibn Zohr, B.P. 8106, Agadir, Morocco.
E-mail address: m.bazzaoui@uiz.ac.ma (M. Bazzaoui).

https://doi.org/10.1016/j.synthmet.2018.09.014
Received 12 July 2018; Received in revised form 21 September 2018; Accepted 24 September 2018

et al. [27], have evaluated the properties of hybrid composite sensor based on polypyrrole/ WO3 toward trimethylamine. The PPy/WO_3 sensor shows a response of 680 to 100 ppm at room temperature. The improvement of the detection performance is mainly related to the formation of a p-n junction at the interface between the inorganic WO_3 and the organic polypyrrole.

Flax fibers composites are broadly used in several industrial fields such as automotive and aerospace. The flax fibers are classified as a bio-composites which present several advantages as structural materials due to their, reduced cost, eco-friendliness, as well as their acoustic, thermal insulation properties, and good mechanical properties [28,29]. In contrast, several recent research studies are intended for the study of the properties of these materials [8,30,31]. All of these works have shown that the fibers structure offers good properties which guarantee good mechanical and thermal stability for application in different fields [8,30,31]. These specific properties make flax fiber as the material of choice in this work. For this, flax fiber was used as polypyrrole support to improve the mechanical and thermal performance of the sensors.

Herein, the present work aims to deposit conductive polypyrrole on flax fiber by chemical polymerization of pyrrole using $FeCl_3$ as oxidant where the flax-PPy was used as trimethylamine sensor and the results have been compared with those of ammonia. The morphology and chemical composition of the flax-PPy sensor were studied by different spectroscopic and microscopic techniques. The main advantages of flax-PPy gas sensor involve its capability of operating at room temperature as well as its acceptable detection of low concentration of trimethylamine.

1.1. Reagents and solutions

Pyrrole monomer (Aldrich) was distilled under nitrogen, anhydrous iron chloride ($FeCl_3$), the analytical grade is used as received (Sigma-Aldrich). Trimethylamine solution (30%) and Ammonia solution (25%) was from Merck.

1.2. Preparation of the flax fiber coated polypyrrole

Under magnetic stirring, flax fiber was immersed in a solution of 775 µL of pyrrole and 37.5 mL of distilled water until total disappearance of pyrrole suspension. Then, the polymerization reaction starts by dropping the oxidant agent solution (0.2 M $FeCl_3$, $6H_2O$). The mixture was kept under regular magnetic stirring for two hours. Afterward, a black colored solution was obtained indicating the polymerization of pyrrole. The obtained flax-PPy was rinsed several times with distilled water and ethanol respectively, then dried at 60 °C for two hours.

1.3. Sensor fabrication and testing equipment

The synthesized flax-PPy composite was cut into small pieces of 0.5 cm of length and fixed between two copper wires in the gas chamber. The connections to sensor boards were established with (SPI) using conductive silver paste. The gas sensor was conducted at room temperature using two different methods. The first one, consists in placing a precise volume of ammonia or trimethylamine into a tube and placed in the chamber testing conducting to an equilibrium between the liquid and gas phase. The second method is established by fixing the flax-fiber in the gas chamber where known volumes of gas were injected by gas-tight syringe to the gas chamber equipped with circulating fan in order to obtain the desired uniform concentration of the vapor (Fig. 1). The change in DC resistance of sensors was monitored in the basis of the two-point technique using a digital multimeter (Protek 506 Digital multimeter with RS-232C interface) connected to the computer

The response curves of the flax/PPy sensor were recorded by measuring the resistance variation as a function of time during exposure to vapor (gas in) and clear air (gas out). The sensor response time is the

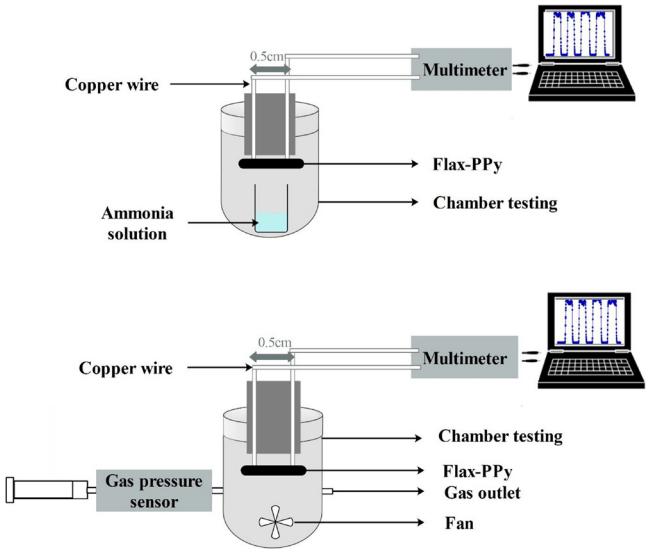

Fig. 1. Schematic illustration for the assembling and operation of the sensor.

time required for 90% of the total change in resistance (stabilization of resistance in a bearing) to exposure to gas and clear air, respectively. The sensor response was calculated using the following equation:

$$Reponse\% = \left(\frac{R_{gas} - R_{air}}{R_{gas}} \right) \times 100$$

Where R_{air} and R_{gas} are the resistors of the sensor in the air and the test gas respectively.

1.4. XPS and SEM analysis

Scanning electron microscopy (SEM) micrographs were obtained on a JOEL Ltd., JXA-8900 instrument. The microscope chamber was maintained at a pressure between 4 and 10 Pa. The specimen surface compositions were analyzed using X-ray photoelectron spectroscopy (XPS, Shimadzu Co: AXIS ULTRA). The X-ray source was Mg Ka operated at 15 kV, the anodic current was 10 mA, and the operating pressure in the vacuum chamber was lower than 5 10^{-7} Pa.

2. Results and discussion

2.1. Characterization of the polypyrrole coated flax fiber by XPS and SEM analysis

X-ray photoelectron spectroscopy (XPS) of flax fiber/PPy composite was performed to analyze the chemical state and elements of this composite. The X-ray photoelectron spectroscopy was also used to characterize the flax fiber before the deposition of polypyrrole as well as pure polypyrrole. The surface of cellulosic fibers is formed mainly of carbon and oxygen atoms, the XPS provides quantitative information about the chemical composition of the surface as well as for the bonds formed between individual components. In the present study, we recall that the sampling depth of XPS is estimated approximately at about 10 nm under the conditions used [32]. On the other hand, we know that fibrous materials once covered with a layer are called cuticle, characterized by a thickness of about 12 nm [33]. The cuticle is composed principally by non-cellulosic lipophilic such as waxes, sterol esters, and triglycerides where cellulose and pectin are less ordered in this composition [34]. The amount of lipids in the fibers is estimated at 1.8% [32]. The major constituents of lipids in the fibers are waxes composed of long saturated chains of n-fatty acids esterified with long chain fatty n-alcohols [32]. Thus, the O/C ratio has a significant importance in the characterization of this type of material. This ratio differentiates