Ammonia detection of one-dimensional nano-structured polypyrrole/metal oxide nanocomposites sensors

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ABSTRACT

The nanocomposites based on polypyrrole (PPy) nanostructures containing tin dioxide (SnO_2) or zinc oxide (ZnO) nanoparticles were prepared and studied via different methods such as Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), ultraviolet-visible (UV–vis) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The ammonia sensing performances of one-dimensional (1-D) nano-structured polypyrrole and its nanocomposites with metal oxides were investigated and the effect of nanofiller type on the sensors behaviour was studied. The PPy and its nanocomposites with metal oxides exhibited high selectivity for ammonia with respect to methanol and ethanol vapors. The response of the sensor based on PPy/ZnO nanocomposite was found to be much pronounced and more retainable than that of PPy and PPy/SnO_2 when exposed to ammonia. The cyclability and linearity of the response for this sensor in presence of ammonia vapor has been investigated as well, suggesting a great potential in detection of ammonia for the prepared sensor.

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1. Introduction

The sensitive detection of ammonia is of great importance in different industrial processes, including fertilizer production and food technology industry. The ammonia detection is also used in environmental pollution monitoring because of the high toxicity of this gas [1,2]. Additionally, elevated breath ammonia is potentially a marker of a number of adverse clinical conditions and hence, is important in medical diagnoses [3].

Several materials have been utilized so far for manufacturing the ammonia gas sensors. Intrinsically conductive polymers (ICPs) and metal oxides are two main material categories that have been proved to be rather efficient for this purpose. ICPs possess notable features, such as controllable electrical conductivity, low ionization potential, and high electron affinity, which make them suitable candidates for sensing applications [4]. These materials however suffer from poor selectivity [5]. Metal oxides such as tin dioxide (SnO_2) and zinc oxide (ZnO) have shown significant advantages for commercialized gas sensing; however they need high power consumption and high temperature condition for indicating reasonable sensitivity [6]. Considerable attention has been devoted in recent years to develop suitable conducting composite materials based on ICPs/metal oxides for the possible

applications in gas sensors [7–10]. It is thought that organic/inorganic hybrid nanocomposites could overcome the short-comings of conventional pristine ICPs and metal oxide sensors [11].

Recently, it is found that the one-dimensional (1-D) nano-structures (nanotubes and nanofibers) in gas sensors show better sensing response as compared to other nano-size structures due to further enhanced surface to volume ratio [12,13]. Polypyrrole (PPy) is a relatively air-stable ICP with high electrical conductivity, good environmental, chemical and electrical stability and easy synthesis [14]. Though PPy has been widely used in gas sensors for detection of a variety of gases including ammonia [15–18], there are few reports however, focusing on the ammonia detection capability of 1-D nano-structured PPy-based systems containing SnO_2 and ZnO. Wang et al. [19], investigated the ammonia sensing performance of the ZnO/TiO_2 nanofibrous mat coated with polypyrrole. Khorami et al. [4], prepared (SnO_2–ZnO)/PPy coaxial nanocables by polymerization of PPy on the surface of SnO_2–ZnO nanofibers and studied the sensing response of the prepared nanocomposite when exposed to ammonia environment. Both these two studies focused however on the polymerization of PPy on the surface of metal oxide nanofibers which requires additional process such as electrospinning step for preparation of the nanofibrillar structures. Accordingly, investigation on the ammonia sensing of PPy/metal oxide nanocomposites prepared via direct synthesis of 1-D hollow polypyrrole nanostructures without requirement of any further treatment can be considered as a novel and interesting research topic.

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In this work, one-dimensional nano-structured PPy/metal oxides nanocomposites were prepared via a template-based approach using methyl orange (MO). To the best of our knowledge, this method has not been used before for synthesis of PPy/ZnO or PPy/SnO$_2$ nanocomposites. The effect of nanofillers on the ammonia sensibility of the polypyrrole-based sensors has been studied. The morphology of the synthesized samples has been characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The chemical structure, semi-crystalline structure, and electronic transport properties of nanocomposites were studied via Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and Ultraviolet–visible (UV–vis) spectroscopy, respectively.

2. Experimental

2.1. Materials

The pyrrole monomer, methanol, ethanol, ammonia solution (25%), and anhydrous iron (*III*) chloride (FeCl$_3$) were all purchased from Merck (Darmstadt, Germany). Methyl orange ((CH$_3$)$_2$NC$_6$H$_4$N = NC$_6$H$_4$SO$_3$Na) was supplied by Azoshimi (Tehran, Iran). All materials were used as received. Zinc oxide nanopowder with the average particle size of 10–30 nm (specific surface area = 20–60 m^2/g) was purchased from US Research Nano-materials, Inc. (Houston, USA). Tin dioxide nanopowder with the average particle size of 50–70 nm (specific surface area = 10–20 m^2/g) was supplied from NaBond Technologies Co. (Hong Kong, China).

2.2. Synthesis of PPy and PPy/metal oxide nanocomposites

PPy and PPy-based nanocomposites were prepared via a template-based method by the oxidation of pyrrole with FeCl$_3$ in presence of methyl orange. 1.5 mmol of anhydrous FeCl$_3$ was added into the 30 mL of 5 mM methyl orange/deionized water solution. The resulted MO–FeCl$_3$ aggregate was then precipitated immediately as the soft template. Then, specified amount of SnO$_2$ or ZnO nanoparticles (10 wt.% based on the monomer content) was added to the mixture. After complete stirring and sonication, 1.5 mmol of pyrrole monomer was added dropwise and the mixture was stirred at room temperature for 24 h. The formed PPy nanocomposite precipitate was washed with ethanol and deionized water several times until the filtrate became colorless. The polypyrrole is not soluble in conventional solvents. This is because of the rigidity of its molecular chains of π-conjugated structure [20]. Therefore for preparing the polymer films, PPy nanocomposites were dispersed in water (via magnetic stirring and ultra-sonication) and then drop-casted onto the glass substrate and left to dry for one day according to the method applied in other studies for the similar systems [21–25]. A same procedure was applied in the preparation of pristine polypyrrole without adding any filler. The thickness of the polymer films were around 150–170 μm, measured using a digital *caliper* (*Shoka gulf*; Spain). In addition, the surface topography of the polymer films has been studied by atomic force microscopy in our previous work [26]. The mean surface roughness value of the polymer films was found to be 250 nm suggesting a quiet rough sensing element.

2.3. Characterization and property measurements

2.3.1. XRD characterization

X-ray diffraction analysis was carried out on a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) using CuKα radiation (40 kV, 40 mA, and λ = 1.54 Å). Samples were scanned at 2°/min in the range of 2θ = 5–80°.

2.3.2. FT-IR spectroscopy

The FT-IR spectroscopy was used to characterize the chemical structure of the samples. For this purpose, a JASCO FT-IR-6300 spectrometer (Japan) with a resolution of 4 cm^{-1} was used in the range of 400–4000 cm^{-1}.
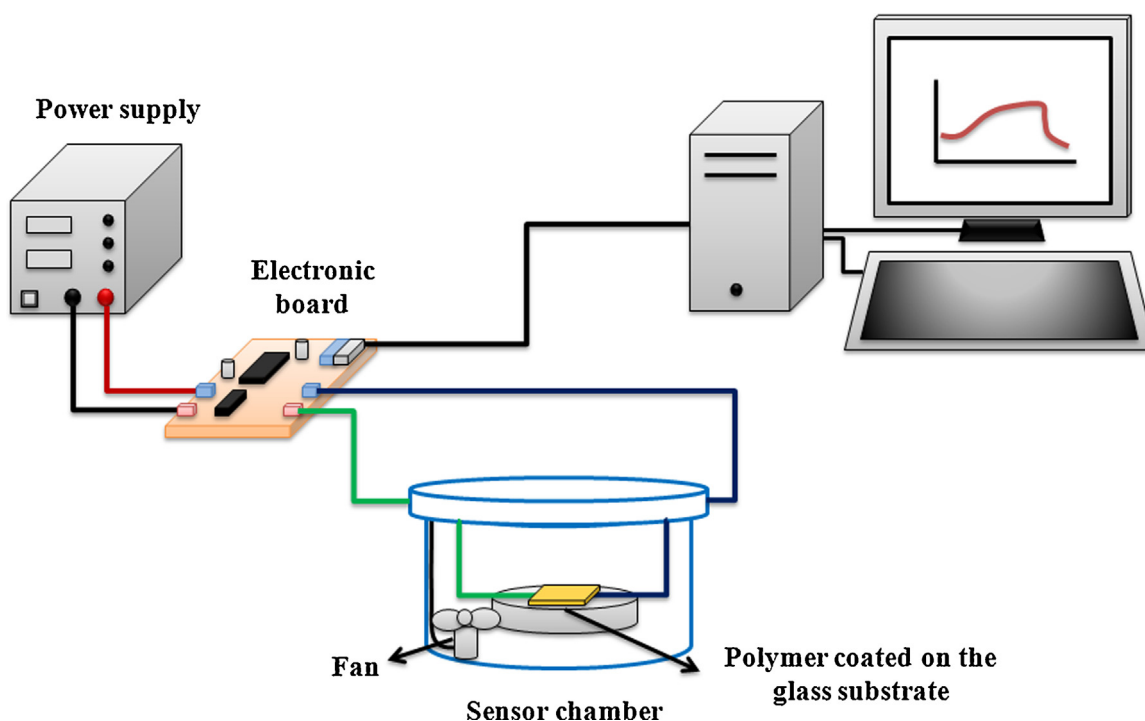

Fig. 1. The schematic of the experimental setup used for sensing measurements.