

Fabrication and Characterization of a Polypyrrole Coated Copper Nanowire Gas Sensor

A.B.Kashyout*, H. Shokry Hassan*, A. A. A. Nasser**, I. Morsy**, and H. Abuklill**

*Advanced Technology and New Materials Research Institute, City for Scientific Research and technology application, new Borg el Arab City, Alexandria

**Arab Academy for Science, Technology, and Maritime Transport

Abstract: *The paper presents a synthesis and experimental procedure for producing Nano elements such as Nano dots, Nano dashes, and Nano wires. The process is a temperature controlled reaction with certain temperature elevation and reduction profiles. The reactants are copper chloride, Sodium Hydroxide, and Polypyrrole. The resulting Nano element characterization is carried out using the scanning electron microscopy (SEM). This characterization determines the structure of the Nano element (dot, rod or wire). This is followed by the X-Ray Diffraction (XRD) characterization that indicates the purity and intensity of the Nano element within the structure. The electrical characteristic of the sensor is determined by measuring the two terminal sensor's resistance at different concentrations of the gas for different temperature ranges. An order of magnitude change in the resistance was found to occur in response to a 100% change in temperature for constant concentration. This is a good measure for pollution in industrial applications*

1. Introduction

Copper nano-wires could have great potential as sensory materials due to their intrinsic high chemical activity and unique open inter-connected network [1]. However, the main drawback for copper nano-wires also lies in the relative weak environmental stability originating from the high reactivity of the bulk copper [2]. Copper nanowires are very susceptible to oxidation in air with a rapid transformation of its surface lattice from single crystal Cu to Cu₂O [2]. Therefore, in order to achieve stable application properties on the copper nano-wires, it's necessary to protect them from the surrounding environment, especially from air and aqueous droplets, to avoid irreversible oxidation degradation of the lattice structure. Polypyrrole coating seems to be a promising route to accomplish this task, based on its high protecting performance, good stability, and ease of implementation [3]. It is speculated that when being coated with polypyrrole, the environmental stability of the copper nano-wire could be enhanced substantially; distinct chemical properties could also be expected from the interfacial charge transfer interaction between the conducting coating material and substrate. This paper is organized as follows: experimental steps are presented in section 2. section 3 is assigned for results. Finally section 3 presents the conclusion.

2. Experimental Steps

2.1. Preparation of a Polypyrrole Coated Copper Nano-powders [4]

In a typical synthesis process, 1.0 mL of 0.1M CuCl₂ was slowly added into 30 mL of 7M NaOH solution under magnetic stirring. 10 minutes stirring was allowed to obtain a homogeneous blue solution. Afterwards, 0.5 mL of pyrrole was injected into the solution in a slow manner, the color of the solution turned from deep blue to yellowish brown rapidly after the pyrrole injection. Then the mixture solution was allowed to incubate for 30 minutes

in order to achieve thorough interaction of the reactants within. At the same time the reaction temperature was risen to 60°C at the rate of 1.5/min. The mixture solution was then allowed to undergo the thermal reduction process for 1 hour at 60°C, and the color of the reaction solution was gradually transformed from dark brown to light yellow. The mixture solution was transferred to a centrifuge tube after reaction, which was then centrifuged at 15000 rpm for 10 minutes in order to separate the solid products from the solution. Afterwards, the obtained solid products were re dispersed into a 20 mL de-ionized water and centrifuged at 15000 rpm for 6 minutes. This centrifuge- re dispersed process could be repeated for several times in order to achieve thoroughly removal of the particle products. The obtained solid product could be stored in air-dried at ambient condition.

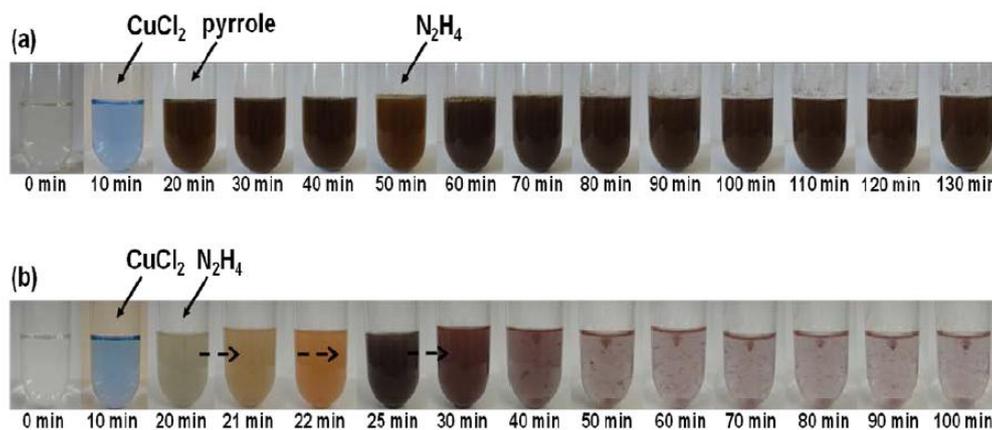


Figure 1 -Photographs of the reaction solution for the synthesis of polypyrrole coated copper nano-wire with (a) and without (b) the addition of pyrrole [4].

2.2. Preparation of Solid State Semiconductor Gas Sensors and Films Fabrication:

The glass substrates were ultrasonically cleaned in acetone for 15 minutes, then rinsed several times with de-ionized water [5]. The glass substrates were put in the solution as the same time of the starting of the experimental steps. Then the film was allowed to dry in air.

2.3. Characterization of a Polypyrrole Coated Copper Nano-particle:

X-ray diffraction patterns of the Nano-powders were obtained using Shimadzu 7000 Diffractometer operating with Cu K α radiation ($\lambda = 0.15406$ nm) generated at 30 Kv and 30mA with scan rate of 2°min^{-1} for 2θ values between 10 and 100 degrees [6]. Nano-powders were then imaged by scanning electron microscopy.

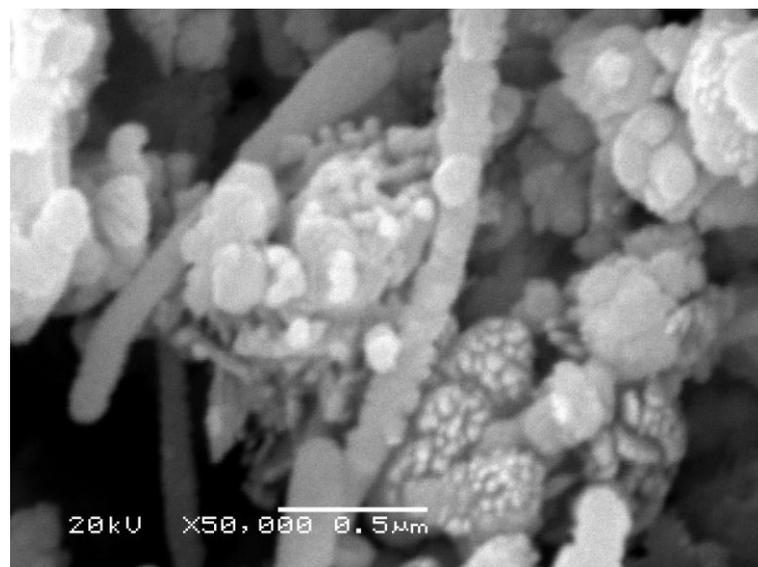
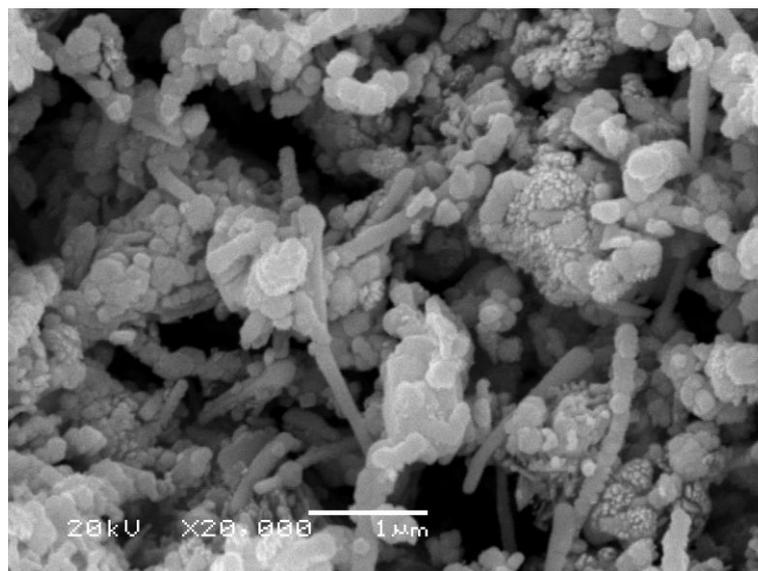
2.4. Electrical Properties of the Gas Sensors:

The resistivity of gas sensors were measured versus temperature utilizing O₂ gas. The measurements were carried out in the temperature range 20–200°C with O₂, which reflects the real fire conditions. The effect of Polypyrrole Coated Copper on the sensitivity of gas sensor was also studied. All of these measurements have been carried out using gas chamber able to work at high temperatures [7].

3. Results and Discussion

3.1. The SEM measurements of the Polypyrrole coated copper material

The morphological and size information of the synthesized polypyrrole coated copper nano-wires could be easily obtained with the electron microscopy characterization methods [8]. The resulting morphologies of the synthesized polypyrrole coated copper nano-wires from SEM could be seen from Figure2. The surfaces of the obtained nano-wires are roughly coated with an unorganized layer, which could be reached back to the polypyrrole coating. The copper nano-wires are randomly interconnected with each other, forming an extensive open interconnected network with high nano-wire density.



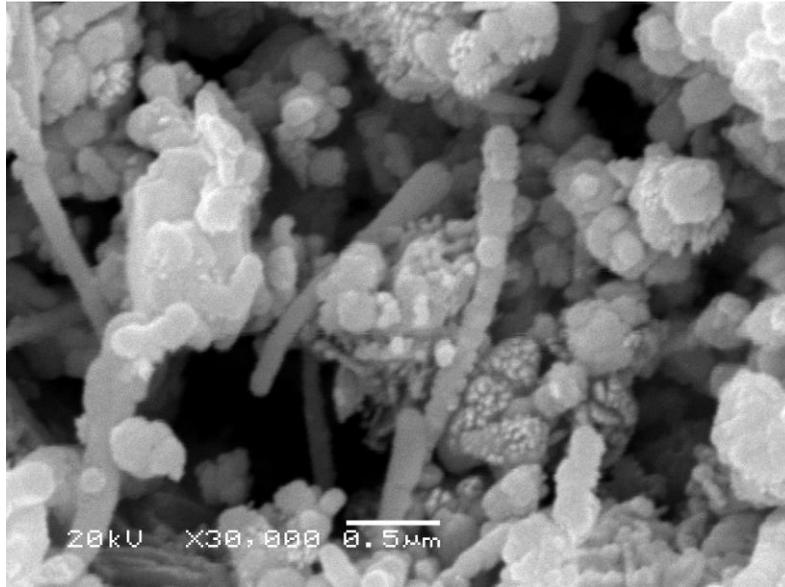


Figure 2- SEM image of the synthesized polypyrrole coated copper nano-wires

3.2. The XRD measurements of the polypyrrole coated copper material:

From the X-RD analysis of the polypyrrole coated copper nano-wires composite film, it can be seen that the film exhibited broad scattering peaks at 2θ value around 13° and 55° respectively, which suggests that the polypyrrole coated copper nano-wires composite films are virtually amorphous. Previous X-ray scattering studies of polypyrrole films have been reported to be highly disordered and non-crystalline. Figure shows the X-RD diffractogram of conducting polymer composite film. Three diffraction peaks at $2\theta=16,34,52$ could be observed clearly from the XRD pattern, which could be indexed to the diffraction of {111}, {200}, and {220} crystal planes of face-centered cubic (fcc) Cu, respectively [9].

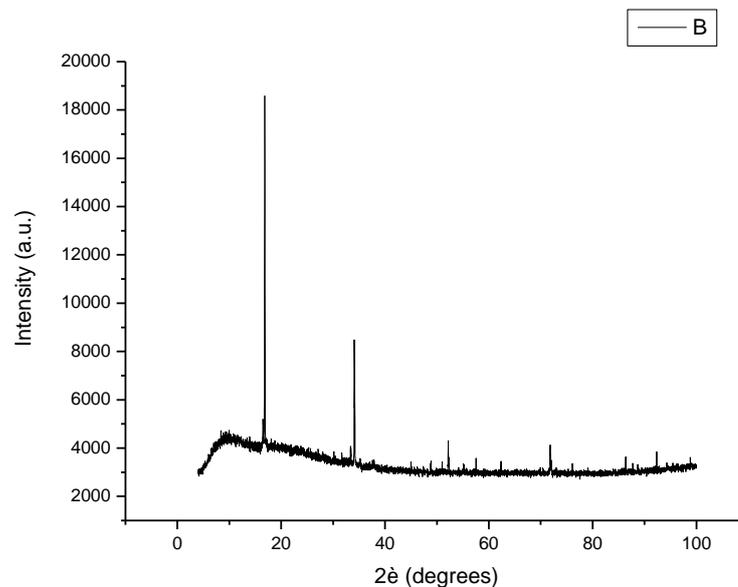


Figure 3- XRD pattern of the synthesized polypyrrole coated copper nanowire

3.3 Oxygen Gas Sensitivity of ppy coating copper Gas Sensors Devices

In order to study the temperature at which the oxygen sorption process is dominated for the gas sensor device, these device were heated from room temperature up to 200 °C at a constant heating rate and resistance measurements were carried out over this temperature range. Figure shows the oxygen gas sensitivity of the gas sensor device that was fabricated using ppy coating copper. It can be observed from the figure, that the sensor shows the highest sensitivity at 25-200 °C, and the sensitivity decreases as the working temperature increases. The gas sensitivity, S [10], is given by

$$S = R_a/R_g \quad (1)$$

Where R_a and R_g express the resistance of the sensor in air and in detecting gas respectively.

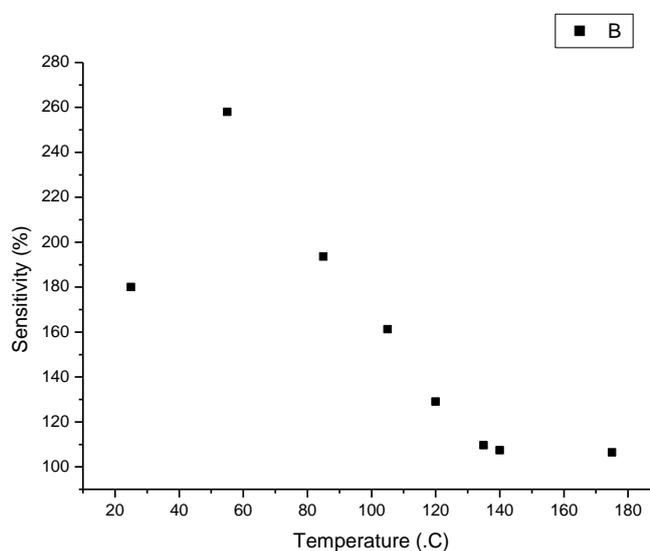


Figure 4-Sensitivity of gas sensors towards CO₂ measured in air as a function of temperature

4. Conclusions

High quality polypyrrole coated copper nano-wires were prepared by dipcoating chemical reaction. Temperature dependent electrical transport measurements showed the sample to be semiconducting with low degree of trouble. Single nano-wire-based sensors showed good limit of detection and sensitivity and excellent selectivity for oxygen gas.

5. References

- [1] Kevin, M.; Ong, W. L.; Lee, G. H.; Ho, G. W. Formation of Hybrid Structures: Copper Oxide Nanocrystals Templated on Ultralong Copper Nano-wires for Open Network Sensing at Room Temperature. *Nanotechnology* 2011, 22, 235701.

- [2] Mohl, M.; Puzsai, P.; Kukovec, A.; Konya, Z. Low-Temperature Large-Scale Synthesis and Electrical Testing of Ultralong Copper Nano-wires. *Langmuir* 2010, 26, 16496-16502.
- [3] Riaz, U.; Ashraf, S. M.; Ahmad, S. High Performance Corrosion Protective DGEBA/Polypyrrole Composite Coatings. *Prog. Org. Coat.* 2007, 59, 138-245.
- [4] Synthesis of Polypyrrole Coated Copper Nano-wire and Its Application as Hydrogen Peroxide Sensor by Yang Liu A thesis submitted to the Graduate Faculty of Auburn University in partial fulfillment of the requirements for the Degree of Master of Science Auburn, Alabama December 12, 2011.
- [5] Hindawi Publishing Corporation *Journal of Nano-materials* Volume 2010, Article ID 341841, 8 pages doi:10.1155/2010/341841.
- [6] Single Polypyrrole Nano-wire Ammonia Gas Sensor. April 24, 2007. DOI: 10.1002/elan.200703933.
- [7] R. Martins, E. Fortunato, P. Nunes et al., "Zinc oxide as an ozone sensor," *Journal of Applied Physics*, vol. 96, no. 3, pp.1398–1408, 2004.
- [8] Christopher, P.; Linic, S. Engineering Selectivity in Heterogeneous Catalysis: Ag Nano-wires as Selective Ethylene Epoxidation Catalysts. *J. Am. Chem. Soc.* 2008, 130, 11264-11265.
- [9] Liu, Z.; Yang, Y.; Liang, J.; Hu, Z.; Li, S.; Peng, S.; Qian, Y. Synthesis of Copper Nano-wires via a Complex-Surfactant-Assisted Hydrothermal Reduction Process. *J. Phys. Chem. B* 2003, 107, 12658-12661.
- [10] N. J. Dayan, S. R. Sainkar, R. N. Karekar, and R. C. Aiyer, "Formulation and characterization of ZnO:Sb thick-film gas sensors," *Thin Solid Films*, vol. 325, no. 1-2, pp. 254–258, 1998.