

## Fabrication of 1, 1-Dimethylhydrazine Gas sensor Based on Nano Structure Conducting Polyaniline

S. Pirsar,\* A. Afshar Asl, A. Khani, and A. Allahverdi Pur

*Department of science, Faculty of Engineering, Islamic Azad University Miyaneh Branch, Miyaneh, Islamic republic of Iran*

Received: 15 July 2013 / Revised: 8 October 2013 / Accepted: 22 October 2013

### Abstract

Determination of 1, 1-dimethylhydrazine (DMH) in air is carried out by spectrophotometry, GC or HPLC analysis, but in this study DMH was analyzed by a gas sensor based on nanostructure conducting polyaniline. Determination of DMH has been done very simply and quickly in recent work. Electrically conductive fibers have been prepared by polymerization of aniline on surfaces of commercial polymer fibers in the presence of an oxidizing agent. The resistance of poly aniline (PANI) coated fiber sensor (PANI-FS) was investigated and related to coating conditions, which was controlled by adjusting the reactant concentrations. The morphology of the conducting film on the surface of the fibers was examined by scanning electron microscope (SEM). The sensing behavior of PANI in the presence of some volatile organic compounds (VOCs) is studied experimentally. The PANI sensor had demonstrated to have good sensitivity for DMH and good reproducibility when reused.

**Keywords:** Poly aniline; Gas sensor, 1, 1-dimethylhydrazine, Nanostructure

### Introduction

Polyaniline (PANI) and polypyrrole (PPY) have been widely investigated in the field of conducting polymers with a variety of end applications [1–6]. Pyrrole (PY) is one of the most easily oxidizable specialty monomers, and a variety of oxidizing agents is available for the oxidative polymerization of PY. These include halogens, FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>2</sub>, Fe(BF<sub>4</sub>)<sub>3</sub>, Fe(ClO<sub>4</sub>)<sub>3</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, FeOCl [2,3], dichloro-5,6-dicyano-p-benzoquinone, ammonium perdisulfate (PDS), CuCl<sub>2</sub>, and Cu(ClO<sub>4</sub>) in bulk, aqueous, and nonaqueous media [7]. As with PY, various oxidant systems, such as PDS, FeCl<sub>3</sub>, FeOCl, CuCl<sub>2</sub>,

Cu(BF<sub>4</sub>)<sub>2</sub>, Cu(ClO<sub>4</sub>)<sub>2</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> [7] have been investigated for the oxidative polymerization of aniline (ANI). Among the transition metal ions, vanadium salts have been used in several systems. Biswas et al. and Kanatzidis et al. [8-10] reported that V<sub>2</sub>O<sub>5</sub> is an efficient heterogeneous catalyst for the polymerization of N-vinylcarbazole in bulk and in a toluene solvent. A great deal of attention was paid to the deposition of a thin layer of conducting PANI on various surfaces [11–13]. Mac Diarmid and Epstein [11] have reported that PANI may be deposited by in situ adsorption polymerization as a strong adhering film on a variety of substrates such as fibers, textiles, glass, gold, etc. [14,15]. This is by immersing the substrate in a

\* Corresponding author, Tel: +989145454914, Fax: +984232237040, E-mail: pirsar7@gmail.com

freshly mixed acidic aqueous solution of aniline and an oxidizing agent such as ammonium persulphate. Under this condition a radical cation of aniline in the form of the pernigraniline oxidation state [15] is first formed and adsorbed which subsequently polymerizes leading to the growing polymer chains [16]. The structure and properties of the PANI formation have been studied and some important results have been obtained [15–17]. Application of conducting polymers including PANI towards sensors for chemicals and biological is of considerable interest. In this aspect, PANI remains to be distinct from others by possessing unique structural characteristics and the consequent redox behavior, interlinked with the degree of doping and protonation [18]. Many studies have so far been conducted and devoted to the development of chemical sensors [19–23]. Currently, the focus is on the development of sensors for various organic pollutant vapors/gaseous molecules. Some remarkable findings of such studies are: sensor based on NMP-induced “tight coil” to “expanded coil” conformational change of nondoped polyaniline [24].

PANI is a special conducting polymer since its doped state can be controlled by acid/base reactions. This is widely used to detect acidic and basic gases. When exposed in ammonia and some amines gas, PANI undergoes dedoping by deprotonation [25–27]. The protons on  $-NH-$  groups were transferred to  $NH_3$  molecules to form ammonium ions while PANI itself turned into its base form. This process is reversible, and in fact, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and proton. After reaction with acidic gases, such as HCl,  $H_2S$  and  $CO_2$  (in present of water) PANI will be doped [28, 29].

The primary routes of potential human exposure to DMH are inhalation, ingestion, and dermal contact [30]. The general population potentially could be exposed by ingestion of residues present on foods treated with DMH. DMH has been detected in tobacco products (at concentrations of up to 147 ng/g); therefore, people who chew tobacco may be exposed to small amounts of DMH [30, 31]. However, it has been detected in cigarette mainstream smoke [32]. The potential for exposure to DMH may be higher for people who live near military installations where the chemical is used as an aerospace propellant or for people who live near hazardous-waste sites contaminated with hydrazines. In the mid 1970s, DMH was measured in the air at levels of up to 1.7 ppm (4.1 mg/m<sup>3</sup>) (limit of detection = 0.001 ppm [0.002 mg/m<sup>3</sup>]) [33]. In 1997, DMH was identified as a contaminant at three hazardous-waste sites on EPA's National Priorities List [33].

Our experience showed that  $K_2Cr_2O_7$  (KDC) can be used as an oxidizing agent to polymerize aniline in acid medium. Polyester substrate coated by PANI and was used as a gas sensor the determination of DMH in air. A few interferences in air such as air humidity and  $CO_2$  did not have any significant interference in DMH determination in air.

## Materials and Methods

### Reagents

Aniline (Fluka, Switzerland) was distilled and stored in a refrigerator in dark prior to use. Potassium dichromate ( $K_2Cr_2O_7$ ) was used as oxidant from Aldrich. All organic compounds used for sensitivity tests were purchased from Merck.

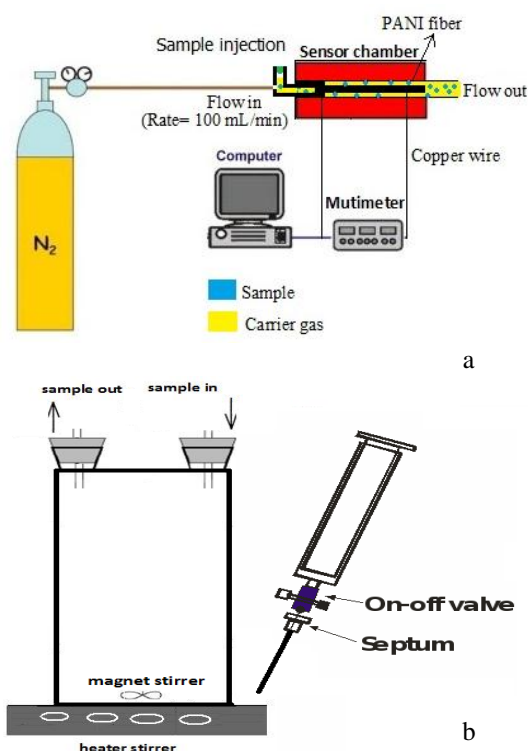
### Fabrication of PANI-F sensor

The PANI polymer was synthesized by chemical polymerization on the polyester at room temperature under atmospheric condition.

Two solutions are needed to polymerization of PANI, solution number one contained 10 mL of 0.1 mol L<sup>-1</sup> Aniline as monomer and solution number two include 10 mL 0.2 mol L<sup>-1</sup>  $K_2Cr_2O_7$  as oxidant as well as HCl of 1 mol L<sup>-1</sup>. Solution number two was added to solution number one (20 cm of polyester fiber has been submerged to solution number one) for the purpose of initiation of polymerization. This solution was maintained for 3 h at room temperature. PPy layer was prepared on the polyester substrate by using the dip coating method. After the polymerization and coating, the substrate was taken from the reaction solution and abundantly washed with deionized water for 10 min, and finally dried for 1 h at 70 °C in oven. Polyaniline fiber (PANI-F) was prepared for the gas sensor fabrication.

### Apparatus

The PANI-F sensor consisting of a fiber of 15 mm length having a diameter of ca. 0.5 mm was put in a copper tube of 4 mm inner diameter. The gas sensors were tested with different gases using a system including a sensor chamber, carrier gas and injection port Fig. 1a. The detected materials, having the gas phase at atmospheric pressure, were vaporized by heated closed system. Fig. 1a and fig. 1b depict the experimental setup of a PANI-FS detection system with an assembled computer interface (RS232) for data processing and signal acquisition, which were automatically performed on a microcomputer.



**Figure 1.** Diagrams of the PANI-F sensor (a) and Gas sample preparation (b).

A sensor was directly connected to the outlet of the injection port, and the whole part was placed in a copper tube. The copper tube is surrounded with a silicone

rubber. Sensor temperature is regulated by a thermistor and temperature control circuit. The carrier gas was N<sub>2</sub> with flow rate of 100 mL min<sup>-1</sup>. After the injection of gases to the sensor system, the samples pass from sensor surface and the resistance change of sensor was measured. The resistance was monitored every 0.5 s with Escort 3145 Multimeter. The scanning electron micrographs (SEM) of the fiber surface were obtained using a Philips XL30 scanning electron microscopy (Holland).

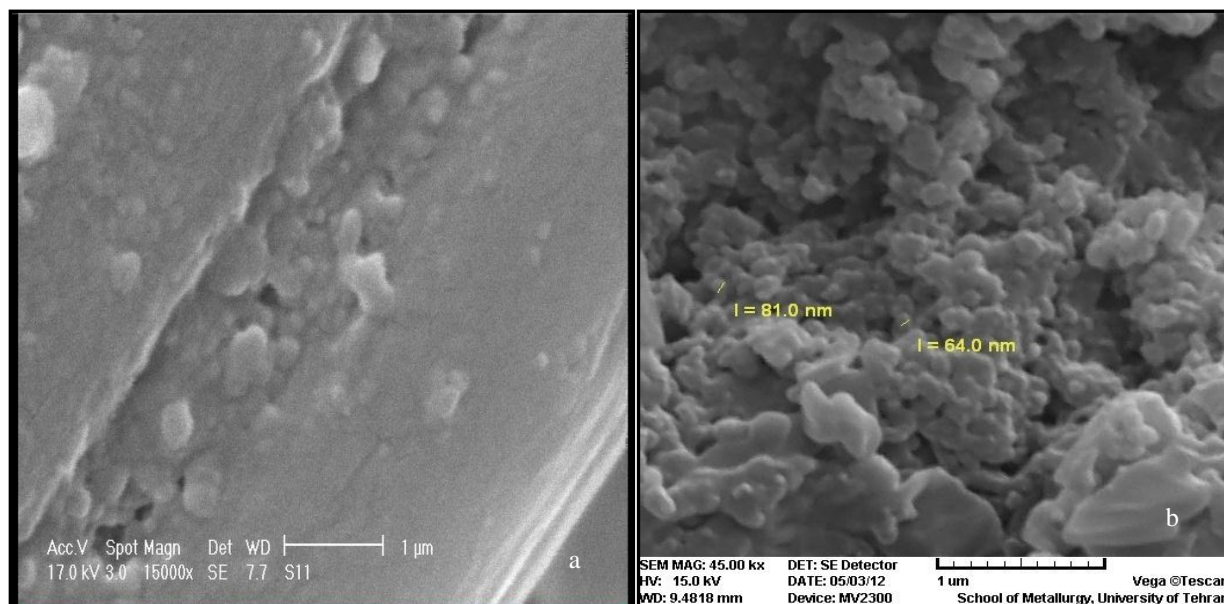
## Results and Discussion

### Morphology

Fig. 2a–b shows the SEM micrographs of the PANI-F sensor. It is clear that the fiber is chemically coated by the nanostructure polymers. The SEM image shows most of the particle with a cabbage shape having size with diameter of around  $80 \pm 5$  nm. The SEM figures of fibers have been shown before (Fig. 2a) and after (Fig. 2b) coating. Because of the perfect adhesion of polyaniline to polyester fiber, to form very stable film the conduction of PANI-F are stable even after running for more than 24 h continuously.

### Response behavior of PANI-F sensor toward VOCs

Usually, the signal resulting from a sensor–volatile compound interaction is quantified in terms of the relative electrical resistance difference (RRD) of the film used as sensor. The RRD was calculated by



**Figure 2.** SEM images before introduction of Polyaniline on the surfaces of the fiber (a) and PANI-F (b).

**Table 1.** Figure of merits of PANI-F sensor for some compounds at room temperature.

Sample	DL (ppm)	LR (ppm)	Sensitivity (1/mg L <sup>-1</sup> )	R <sup>2</sup>
DMH	0.5	1-70	3.6×10 <sup>-4</sup>	0.995
Methyl amine	5	10-70	2.1×10 <sup>-4</sup>	0.994
Ethyl amine	7	10-70	1.9×10 <sup>-4</sup>	0.992
DMSO	10	20-120	1.5×10 <sup>-4</sup>	0.991
Acetone	200	200-1000	1.4×10 <sup>-5</sup>	0.994
Benzene	-	-	-	-
CO <sub>2</sub>	-	-	-	-
H <sub>2</sub> O	60	100-1000	2.1×10 <sup>-5</sup>	0.993

(R-R<sub>0</sub>)/R<sub>0</sub>, where R<sub>0</sub> and R denote the initial resistance and real-time resistance (resistance of the sensor when it was exposed to analyte gas). We present the RRDs of the sensors used in this work measured after several second of exposure to each one of the VOCs (for three replicate injections). We have done our tests in two sensor temperatures (100 °C and room temperature) by exposing of 10 ppm of each sample to sensor. Fig. 3 shows the RRDs of PANI-F sensors to different volatile organic compounds. Results show that room temperature is suitable for detection and sensor has better relative response in room temperature to all tested gases than 100 °C, and PANI-FS have a selective behavior to DMH detection in air samples so PANI-FS is a suitable sensor to determination of DMH.

Table 1 gives the response behavior of PANI-F sensor, which was prepared from 0.1 mol L<sup>-1</sup> aniline, and 0.2 mol L<sup>-1</sup> aqueous K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 1 mol L<sup>-1</sup> HCl solutions by chemical polymerization method. The detection limit, linear ranges, calibration sensitivity, and correlation coefficients of PANI-F sensor are reported. Fig. 4 shows the typical response behavior of the PANI-F sensor to switching between N<sub>2</sub> and different organic compounds (DMSO and Acetone) in cycle tests at flow rate of 100 mL min<sup>-1</sup> and room temperature. It is seen that the response of the PANI-F sensor upon exposure to different gases could completely return to the original value in all the cycle and reversible in subsequent cycle tests. It can be seen that electrical resistance increased upon exposure to analyte gas, and recovered when flushed with nitrogen flow (no significant drift of the background resistance after several exposures). The PANI-FS exhibited excellent response reproducibility for different gases.

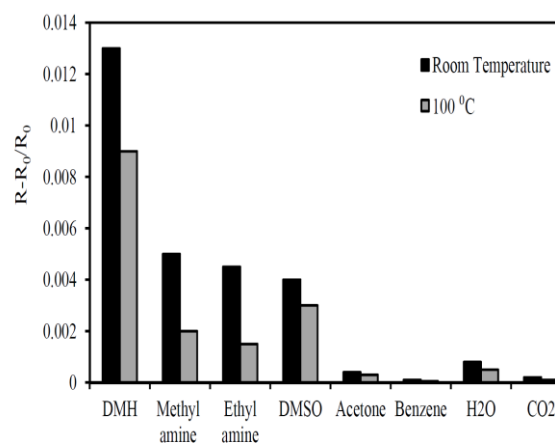
The detection limit of the PANI-FS sensor, which was calculated as the amount, gives a reading equal to three times the standard deviation of a series of the procedural blank or background signals (response of the

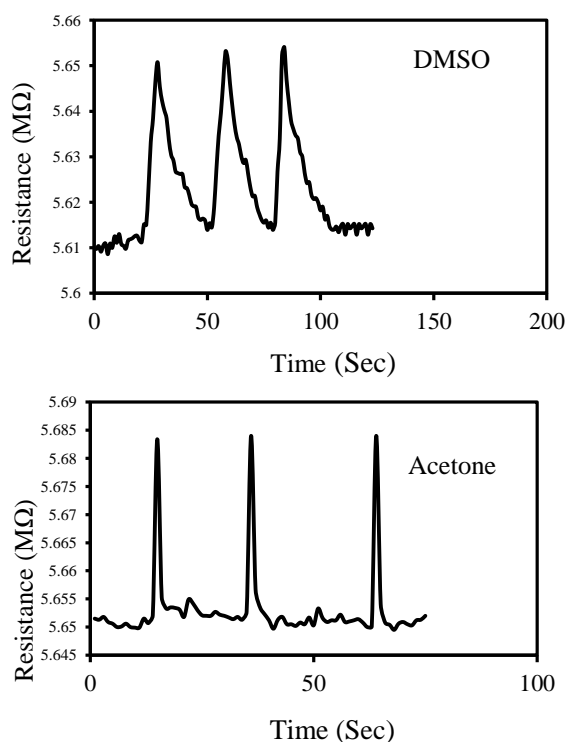
sensor, measured in the absence of compound) [34], can be estimated as follows:

$$DL = 3\sigma / (\text{calibration sensitivity}) \quad (1)$$

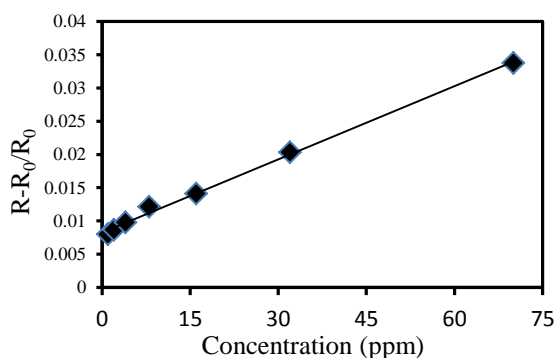
The detection limits of the PANI-FS for various organic compounds are listed in Table 1. It is obvious that the PANI-FS can detect various organic compounds with a good sensitivity within the detection limits of approximately 0.5–200 ppm. The highest response is observed for DMH (DL=0.5 ppm). A typical calibration curve relating the normalized electrical resistance vs. the concentration of DMH is shown in Fig. 5.

There are several theories to interpret the sensing mechanism of conducting polymer. Most of the conducting polymers are doped /undoped by redox reactions; therefore, their doping level can be altered by transferring electrons from or to the analysts. Electron transferring can cause the changes in resistance and work function of the sensing material. The work function of a conducting polymer is defined as the

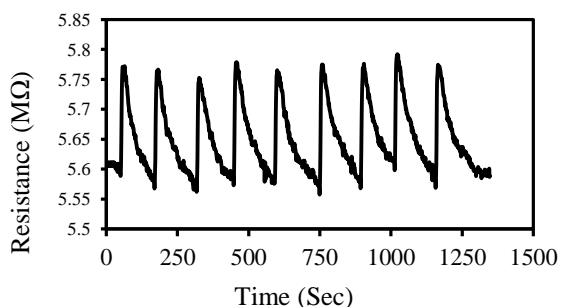
**Figure 3.** The response behavior of PANI-F sensor to 10 ppm of different gases.



**Figure 4.** Resistance responses of the PANI-F sensor to switching between  $N_2$  and different organic compounds for 20 ppm DMSO and 20 ppm Acetone at flow rate of  $100 \text{ mL min}^{-1}$  and room temperature.



**Figure 5.** Normalized electrical resistance responses calibration curve for DMH.



**Figure 6.** Reproducibility of PANI-FS upon exposure to 50 ppm of DMH.

minimal energy needed to remove an electron from bulk to vacuum energy level. This process occurred when a conducting polymer such as PANI, PPy, PTh and some other conducting films exposed in electron donating (DMH,  $NH_3$ , DMSO and  $H_2S$ ) and electron accepting ( $NO_2$  and  $I_2$ ) gases [35–43]. DMH is an electron-donor (by two nitrogen atom) that has more electron donor ability than other tested compounds, according to this reason PANI-FS has the better resistance change response to DMH, when PANI is exposed with DMH, its electric conductance dwindles down sharply. However, after washing with carrier gas, the resistance of the sensing layer can be totally or partly recovered.

#### Reproducibility of the PANI-FS

The reproducibility of the PANI-FS was also investigated with a series of 9 repetitive injections of 10 ppm of DMH gas sample. As shown in Fig. 6, the response to DMH exhibited good reproducibility with a relative standard deviation (R.S.D.)  $<7\%$  and could be used repetitively.

#### Conclusion

Polyaniline was polymerized chemically by  $K_2Cr_2O_7$  as oxidant and was doped with HCl resulting in a conductive material, suitable for application in chemiresistor sensor. The sensors are easy to make, and the response was fast, reversible and reproducible. The gas-sensing abilities of the sensor, including the sensitivity and selectivity, of the sensor were dependent on the sensor temperature. The PANI-FS has a good selectivity for 1, 1-dimethylhydrazine gas. Determination of DMH in air can be done by PANI-FS in presence of air humidity and other interferences such as  $CO_2$  in ppm levels.

#### References

1. Bhadra S., Chattopadhyay S., Singha N. K., Khastgir D. Effect of different reaction parameters on the conductivity and dielectric properties of polyaniline synthesized electrochemically and modeling of conductivity against reaction parameters through regression analysis. *Polym. Sci. Polym. Phys.* **45**: 2046–2059 (2007).
2. Burgmayer P., Murray R. W. An ion gate membrane: electrochemical control of ion permeability through a membrane with an embedded electrode. *J. Am. Chem. Soc.* **104**: 6139–6146 (1982).
3. Sambhu B., Dipak K., Nikhil K., Joong L. Progress in preparation, processing and applications of Polyaniline. *Progress in Polymer Science.* **34**: 783–810 (2009).
4. Li Z-F., Blum F.D., Bertino M.F., Kim C. Amplified Response and Enhanced Selectivity of Metal-PANI Fiber

- Composite Based Vapor Sensors. *Sens. Actuators B.* **161**: 390-395 (2012).
- Ding M., Tang Y., Gou P., Reber M. J., Star A. Chemical sensing with polyaniline coated single-walled carbon nanotubes. *Adv. Mater.* **23**: 536-540 (2011).
  - Li X., Wang Y., Yang X., Chen J., Fu H., Cheng T. Conducting polymers in environmental analysis. *Trend Anal. Chem.* **39**: 163-179 (2012).
  - Toshima N., Hara S. Direct Synthesis of Conducting Polymers from Simple Monomers. *Prog. Polym. Sci.* **20**: 155-161 (1995).
  - Biswas M., Gazi M. A., Bhagawan S. A cation exchange resin based on the condensation product of poly(iso-butyl vinyl ether) and furfural. *Makromol. Chem.* **179**: 1209-1212 (1978).
  - Kanatzidis M. G., Wu C. G., Marcy H. O., Kannewurf C. R. Conductive-polymer bronzes. Intercalated polyaniline in vanadium oxide xerogels. *J. Am. Chem. Soc.* **111**: 4139-4144 (1989).
  - Kanatzidis M. G., Tonge L. M., Marks T. J., Marcy H. C., Kannewurf R. In situ intercalative polymerization of pyrrole in FeOCl: a new class of layered, conducting polymer-inorganic hybrid materials. *J. Am. Chem. Soc.* **109**: 3797-3802 (1987).
  - MacDiarmid A. G., Epstein A. J. Polyanilines: a novel class of conducting polymers. *Faraday Discuss Chem. Soc.* **88**: 317-321 (1989).
  - Ryuji H., Tohru S., Masamitsu S. Selective formation of polyaniline on wool by chemical polymerization, using potassium iodate. *Synthetic Metals.* **146**: 73-77 (2004).
  - Sapurina I., Riede A., Stejskal J. In-situ polymerized polyaniline films: 3. Film formation. *Synth. Met.* **123**: 503-508 (2001).
  - Yoke Fo. Polymerization of aniline using mixed oxidizers. *Polymer.* **36**: 639-643 (1995).
  - Manohar S. K., MacDiarmid A. G., Epstein A. J. Polyanilines: a novel class of conducting polymers. *Bull Am Phys Soc.* **34**: 582-587 (1989).
  - Xugang J., Kecheng G. Diffusion-Deposition of Polyaniline onto Textiles with High Electric Conductivity and Improved Adhesion. *Journal of Industrial Textiles.* **26**: 36-44 (1996).
  - Manohar S. K., MacDiarmid A. G., Epstein A. J. Polyaniline: Pernigranile, an isolable intermediate in the conventional chemical synthesis of emeraldine. *Synth. Met.* **41**: 711-716 (1991).
  - Guliz C., Zuhail K., Savas K. Conductive copolymers of polyaniline, polypyrrole and poly(dimethylsiloxane). *Synth. Met.* **151**: 10-18 (2004).
  - Bartlett P. N., Ling-Chung S. K. Conducting polymer gas sensors Part III: Results for four different polymers and five different vapours. *Sens. Actuators.* **20**: 287-292 (1989).
  - Bidan G. Electroconducting conjugated polymers: New sensitive matrices to build up chemical or electrochemical sensors. *Sens. Actuators B.* **6**: 45-56 (1992).
  - Radhakrishnan S., Deshpande S.D. Conducting Polymers Functionalized with Phthalocyanine as Nitrogen Dioxide Sensors. *Sensors.* **2**: 185-194 (2002).
  - Chen J., Tsubokawa N. Novel gas sensor from polymer-grafted carbon black: Vapor response of electric resistance of conducting composites prepared from poly (ethylene-block-ethylene oxide)-grafted carbon black. *J. Appl. Polym. Sci.* **77**: 2437-2447 (2000).
  - Koul S., Chandran R., Dhawan S. K. Conducting polyaniline composite: a reusable sensor material for aqueous ammonia. *Sens. Actuators B.* **75**: 151-159 (2001).
  - Zheng W., Min Y., MacDiarmid A. G., Angelopoulos M., Liao Y. H., Epstein A. J. Effect of organic vapors on the molecular conformation of non-doped Polyaniline. *Synth. Met.* **84**: 63-64 (1997).
  - Jin Z., Su Y.X., Duan Y.X. Development of a polyaniline-based optical ammonia sensor. *Sens. Actuators B.* **72**: 75-79 (2001).
  - Nicho M.E., Trejo M., Garcia-Valenzuela A., Saniger J.M., Palacios J., Hu H. Polyaniline composite coatings interrogated by a nulling optical-transmittance bridge for sensing low concentrations of ammonia gas. *Sens. Actuators B.* **76**: 18-24 (2001).
  - Hu H., Trejo M., Nicho M.E., Saniger J.M., Garcia-Valenzuela A. Adsorption kinetics of optochemical NH<sub>3</sub> gas sensing with semiconductor polyaniline films. *Sens. Actuators B.* **82**: 14-23 (2002).
  - Agbor N.E., Petty M.C., Monkman A.P. Polyaniline thin films for gas sensing. *Sens. Actuators B.* **28**: 173-179 (1995).
  - Bai H., Shi G. Gas Sensors Based on Conducting Polymers. *Sensors.* **7**: 267-307 (2007).
  - Smith C. J., Perfetti T. A., Rumble M. A., Rodgman A. IARC Group 2A Carcinogens Reported in Cigarette Mainstream Smoke. *Food Chem. Toxicol.* **38**: 371-383 (2000).
  - Tamura T., Shibutani M., Toyoda K., Shoda T., Takada K., Uneyama C., Takahashi M. Tumor-promoting Activities of Hydroquinone and 1,1-dimethylhydrazine after Initiation of Newborn Mice with 1-methyl-1-nitrosourea. *Cancer Letters.* **143**: 71-80 (1999).
  - Simpson C.F., Barrow M. V. Toxicity of a Substituted Hydrazine for Turkeys. *Arch. Environ. Health.* **25**: 349-353 (1972).
  - Schemltz L., Abidi S., Hoffmann D. Turmogenic Agents in Unburned Processed Tobacco: N-Nitrosodiethanolamine and 1,1-Dimethylhydrazine. *Cancer Letters.* **2**: 125-132 (1977).
  - Pirsa S., Alizadeh N. Design and fabrication of gas sensor based on nanostructure conductive polypyrrole for determination of volatile organic solvents. *Sens. Actuators B.* **147**: 461-466 (2010).
  - Nguyen V.C., Potje-Kamloth K. Electrical and chemical sensing properties of doped polypyrrole/gold Schottky barrier diodes. *Thin Solid Films.* **338**: 142-148 (1999).
  - Van C.N., Potje-Kamloth K. Electrical and NO<sub>x</sub> gas sensing properties of metallophthalocyanine-doped polypyrrole/silicon heterojunctions. *Thin Solid Films.* **392**: 113-121 (2001).
  - Xie D., Jiang Y.D., Pan W. Li D., Wu Z.M., Li Y.R. Fabrication and characterization of polyaniline-based gas sensor by ultra-thin film technology. *Sens. Actuators B.* **81**: 158-164 (2002).
  - Mello S.V., Dynarowicz-Latka P., Dhanabalan A., Bianchi R.F., Onmori R., Janssen R.A.J., Oliveira O.N. Langmuir and Langmuir-Blodgett films from the N-hexyl-pyrrole-

- thiophene (AB) semi-amphiphilic copolymer. *Colloids and Surfaces A Physicochemical Engineering Aspects*. **198**: 45–51 (2002).
39. Bhat N.V., Gadre A.P., Bambole V.A. Investigation of electropolymerized polypyrrole composite film: Characterization and application to gas sensors. *Journal of Applied Polymer Science*. **88**: 22–29 (2003).
  40. An K.H., Jeong S.Y., Hwang H.R., Lee Y.H. Enhanced Sensitivity of a Gas Sensor Incorporating Single-Walled Carbon Nanotube–Polypyrrole Nanocomposites. *Advanced Materials*. **16**: 1005–1009 (2004).
  41. Li G.F., Josowicz M., Janata J., Semancik S. Effect of thermal excitation on intermolecular charge transfer efficiency in conducting Polyaniline. *Applied Physics Letters*. **85**: 1187–1189 (2004).
  42. Elizalde J., Hu H.L., Garcia-Valenzuela A. NO<sub>2</sub> induced optical absorbance changes in semiconductor polyaniline thin film. *Sens.Actuators B*. **98**: 218–226 (2004).
  43. Ram M.K., Yavuz O., Aldissi M. NO<sub>2</sub> gas sensing based on ordered ultrathin films of conducting polymer and its nanocomposite. *Synthetic Metals*. **151**: 77–84 (2005).