Study of polyaniline – iron oxides composites using for gas detection

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Polyaniline – Fe_2O_3 and polyaniline – $MgFe_2O_4$ composites were prepared by in – situ polymerization of aniline in the presence of oxides particles. The resulted composites were characterized by Fourier transform infrared spectra, scanning electron microscopy, particle sise distribution, and thermal analysis and sensing measurements. It has been found that the introduction of conducting polyaniline not only improved the conductivity of iron oxides particles, but also improved the dispersibility of ferrites. Polyaniline iron oxides composites are the most sensitive to acetone vapors and can be used as gas sensor. The higher value of specific surface of composites and a strong interaction between the polyaniline and ferrites particles can explain the sensitivity values obtained for composites samples.

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1. Introduction

Interest in the development of the new inorganic-organic nanocomposites has grown in recent years due to a wide range of potential applications of these materials [1, 2]. These hybrids constitute a class of advanced composite materials with unusual properties, which can be used in many fields such as optic, electronics or mechanics. One important class of hybrid materials Is that in which the organic fraction is composed of conducting polymers, such as polyaniline, polypyrole or polythiophene [3, 4].

Polyaniline (PANi) is known as one of the most promising conducting polymers due to of preparation, excellent environmental stability, better electronic properties, electrochemical properties and its applications in electrochromic display, electrocatalysis, rechargeable batteries, sensors and biosensors [5-8]. Polyaniline has a variety of oxidation states and three different states of them are usually referred to in the literature: leucoemeraldine base, emeraldine base (EB) and pemigraniline base. Emeraldine base is the most attractive one because it can be doped with protonic acid to become emeraldine salt (ES) and the conductivity of the ES is increased. However, conducting PANi is difficult to be processed through traditional methods as the most conducting polymers. Incorporation of PANi in different inorganic matrix is one of the techniques used to solve the problem of polymer processability. In recent years, composites containing PANi and different metal oxides exhibiting different nanostructures, such as nano-tubes, nano-rods, nano-fibres or core-shell nanostructures have been intensely investigated. Multi-component conducting polymer systems with nanoparticles of metal oxides can be tailored to obtain desired mechanical besides novel electrical, magnetic or optical properties.

Metal oxides exhibit electrical behavior that can vary from electrically insulating (MgO and Al_2O_3), wide-band semiconductor (TiO_2, SnO_2, ZnO, Ti_2O_3), to metal-like (V_2O_3, ReO_3, RuO_2) behavior. Some oxides have several stable oxidation states that are very important in surface chemistry. The sensitivity of any device is enhanced due to the increased number of interaction sites associated with the three-dimensional structure. The chemical and physical properties of nanostructurated materials can be much different than those observed for the bulk materials.

Among metal oxide nanoparticles, iron oxides have attracted technological importance due to their magnetic, catalytic and biological properties. The applications of iron oxedes nanoparticles can be found in the field of medicine, biology and catalysis such as magnetic storage devices, ferrofluids, magnetic refrigeration system, immunoassays, ultrahigh-density recording magnetic carrier, catalysis and other uses [9,10].

In this work, we synthesized conducting PANi-Fe_2O_4 particles respectively, using a simple synthesis process, in comparasion with other methods, *via in situ* polymerization of aniline in presence of ferrite particles. Then we examined their morphology, crystal structure, thermal stability and sensing properties to reducing gases like acetone, ethyl alcohol and liquefied petroleum gas (LPG).

2. Experimental

Aniline was purchased from Fluka and was used after double distillation. Spinel ferrites of composition Fe_2O_3, $MgFe_2O_4$ were prepared by sol-gel self combustion [11]. The powders of $Fe(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 3H_2O$, were weighed in the desired proportions and dissolved in small amounts of distilled water. Alcohol polyvinyl was added to make a colloidal solution. By adding NH_4OH solution, the pH was adjusted to about 8 and a sol of metal hydroxides an ammonium nitrate was resulted. After

heating at 120°C, for 12 hours, the dried gel was ignited in a corner. The combustion wave spontaneously propagates and converts the gel into a loose powder containing very fine crystallites. All residual organic compounds were eliminates by heating the power at 500°C for one hour and 1000°C for 3 hours to facilitate solid state sintering, followed by furnace cooling of the samples. Then, the combusted powder was compacted into pellets (cylindrical discs), of about 3.5 mm thickness and 14 mm diameter, at a pressure of 5×10 N/m^2.

Other chemicals used were purchased from Fluka. All materials were used as provided without any further purification.

PANi – ferrite composites were prepared as follows: 4.5 ml aniline was injected into 70 ml of 2M HCl containing 1g Fe_2O_3 or $MgFe_2O_4$, respectively, under magnetic stirring. After 2h, 11.5 g $K_2S_2O_8$ (dissolved in de-ionized water) was dropped into solution with constant stirring. The polymerization was allowed to proceed for 6h al 25°C. The reaction mixture was filtered, washed with 2M HCl and de-ionized water, and then dried at 60°C overnight, under vacuum, to obtain the final product.

The FTIR spectra (KBr pettlets) of samples were recorded in the range 4000-400 cm^{-1}, using a Bruker Vertex 70 spectrometer. The SEM studies were performed on samples fixed by means of colloidal silver on copper supports. The samples were covered with a thin layer of gold, by sputtering (Emitech K550X). the coated surface was examined by Environmental Scanning Electron Microscope (ESEM) Quanta operating at 15kV with secondary electrons. Measurement of particle size was done with a Master size 2000 system (version 5.31) Malvern Instruments (England). The system is constituted of an optical bank which users laser light He-Ne 632nm/2mW, a dispersion unity of the sample Hydro 2000A type equipped with stirrer, recirculating pump, and ultrasonic device. The measurement domain is between 0.020-2000 μm.

Thermal gavimetric analysis (TGA) was performed by means of a Mettler Toledo TGA-SDTA 851e device, in air stream, a heating speed of 10 K/min (25-600°C range) and the sample weight of 4-6 mg. constant operating parameters were kept for all the samples in order to obtain comparable data.

The composites and iron oxides powders compacting in a disc shape (14 mm diameter and 3.5 mm thickness) were carried out in a stainless die by cold pressing at approximately 5×10^6 N/m. the sample porosity was calculated using the relation:

$$p = 1 - \frac{d}{d_x} \tag{1}$$

The bulk density d, was evaluated from the sample's weight and from its dimensions, d_x is the theoretical density.

The specific surface area (S_{spec}) was determined using the equation [10]:

$$S_{spec} = \frac{s}{v \times d} \tag{2}$$

where s and v are the particle surface and volume, respectively. It is assumed that he particles of a specimen have the same size and the same shape.

Electrical measurements were carried out using tow silver electrodes, applied on sample's surface like in Fig. 1.

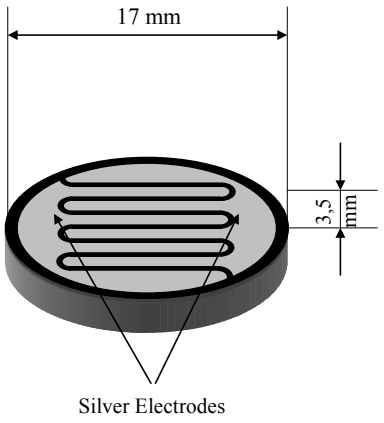

Fig. 1. The design of semiconductor polymer sensor with silver electrodes.

The sensor element (semiconducting polymer-iron oxide disc), for the gas sensing detection was provided with a heater, a fan and the all assemble was introduced in a glass chamber (volume 2 dm^3). The experimental arrangement is shown in Fig. 2.

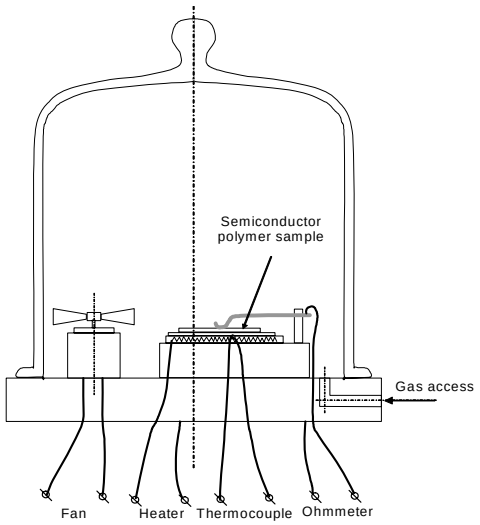

Fig. 2. Experimental setup for measurements of gas sensitivity.

The working temperature was measured with a Cromel-Alumel thermocouple located in the close proximity of the sensors element. The electric resistance of the sensor was recorded at fixed temperatures, both in air

and in the presence of the test gas, using a digital LCR meter at 100 Hz. The sensitivity, S, was calculated using the relation:

$$S = \frac{\Delta R}{R_a} = \frac{R_a - R_g}{R_a}, \quad (3)$$

where R_a is the polymer resistance in air and R_g is the polymer resistance after the exposure to the test gas, recorded at a given temperature. Taking into account the thermal inertia of polymers, all measurements were carried out under the thermal stabilization conditions. All data were collected at least 30 minutes after gas exposure. After each change of the test gas, the sensor element was activated by submitting it to heat treatment for 5 minutes in order to form the initial structure and to be thermodynamically stabilized. Heat cleaning of the samples was found to be necessary for better and reproducible sensitivity.

3. Results and discussion

The SEM micrographs of iron oxides and polyaniline-Fe_2O_3 composites are shown in Fig.3, in which is indicates that agglomerated clusters of iron oxides are reduced by polymerization on aniline on it's surface. This aspect is also revealed by measurements on particle size distribution, Fig. 4, which show a leveling of particle size in composites due to the presence of polyaniline.

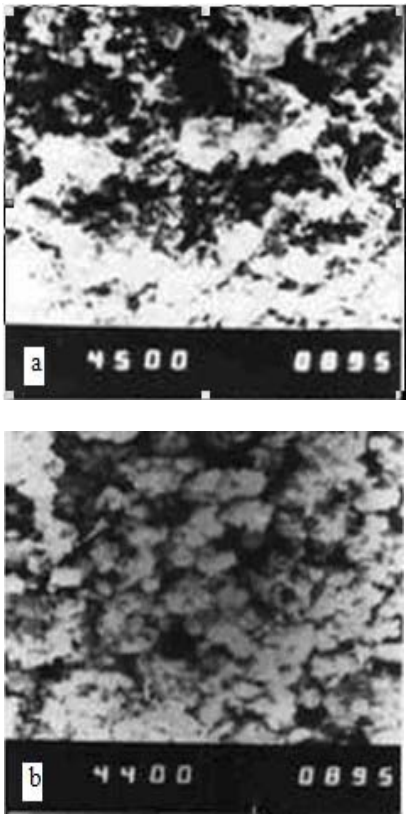

Fig. 3. SEM images of: a) Fe_2O_3; b) PANi- Fe_2O_3.

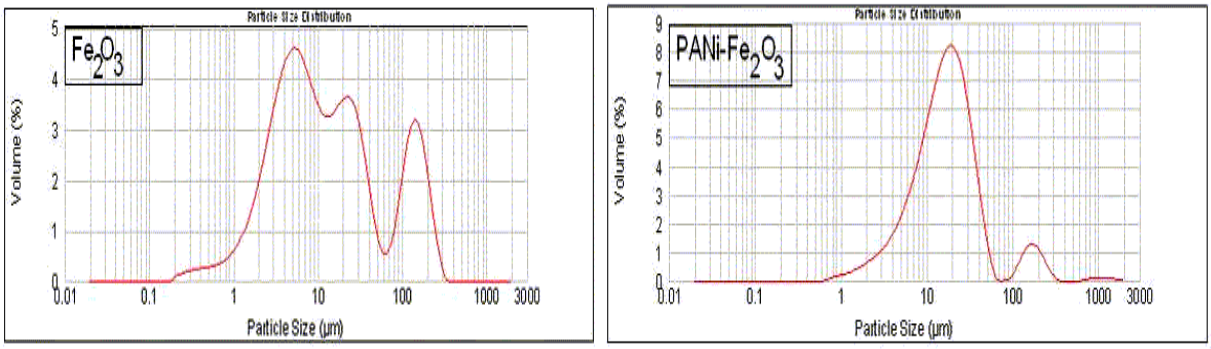

Fig. 4. Particle size distribution.

Fig. 5 shows the FTIR spectra for PANi-Fe_2O_3 and PANi-$MgFe_2O_4$ composites. The FTIR spectrum confirms the bonding of PANi to ferrite particles by the presence in the composite spectrum of peaks characteristics to both components: iron oxides particles. The peaks at 1572 and 1490 cm^{-1} can be attributed to C=N and C=C stretching mode for the quinoid and benzenoid rings; peaks at around 1300 cm^{-1} and 1140 cm^{-1} correspond to C-N stretching (-N-benzenoid-N) and C=N stretching (N=quinoid=N).

The band at around 801 cm^{-1} is attributed to aromatic C-H bending out of the 1,4 – substituted aromatic rings. The 1160 cm^{-1} band of pure polyaniline has been refereed as the electronic like band is shifted to around 1137 cm^{-1} in the case of composites.

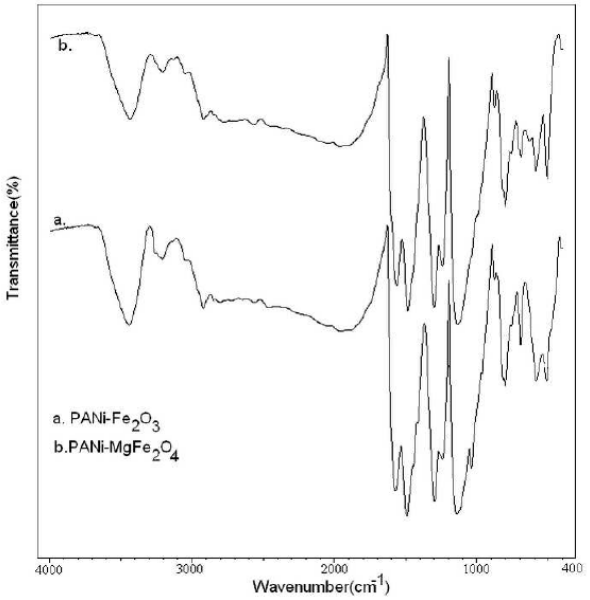

Fig. 5. FTIR spectrum of PANi-Fe_2O_3, PANi-$MgFe_2O_4$.

The sensing measurements were performed on both iron oxides: $MgFe_2O_4$, Fe_2O_3 and composite particles: PANi-$MgFe_2O_4$, PANi-Fe_2O_3, respectively. Fig. 6 shows the sensitivity diagram of sensor elements to reducing gases and Table 1 gives the structural characteristics of iron oxides and composites particles.

Table 1. Structural characteristics for the studied samples.

Sample	Bulk density d (g/cm^3)	Porosity p (%)	Specific surface area S_{spec} (m^2/g)	Sintering temperature ($^{\circ}C$)
Fe_2O_3	3,72	28,45	3,12	1000
$MgFe_2O_4$	2,48	31,27	2,96	1000
PANi-$MgFe_2O_4$	1,56	44,18	3,54	1000
PANi-Fe_2O_3	1,46	46,32	3,92	1000

We have tested the sensitivity of the four sensors to the presence of small quantities (150ppm) of three volatile organic compounds: acetone, ethyl alcohol and LPG. All sensors respond to the tested gases but they do it in varying extents. The gas sensitivities of iron oxides and composites samples are presented in Fig. 6 as a function of operating temperature, towards acetone, ethyl alcohol and LPG vapors. Each of the curves shows a maximum of sensitivity corresponding to an optimal temperature of the each sensor element. For the PANi-$MgFe_2O_4$ sensor element the maximum sensitivity appears at 200°C and for PANi-Fe_2O_3 it appears at 220°C.

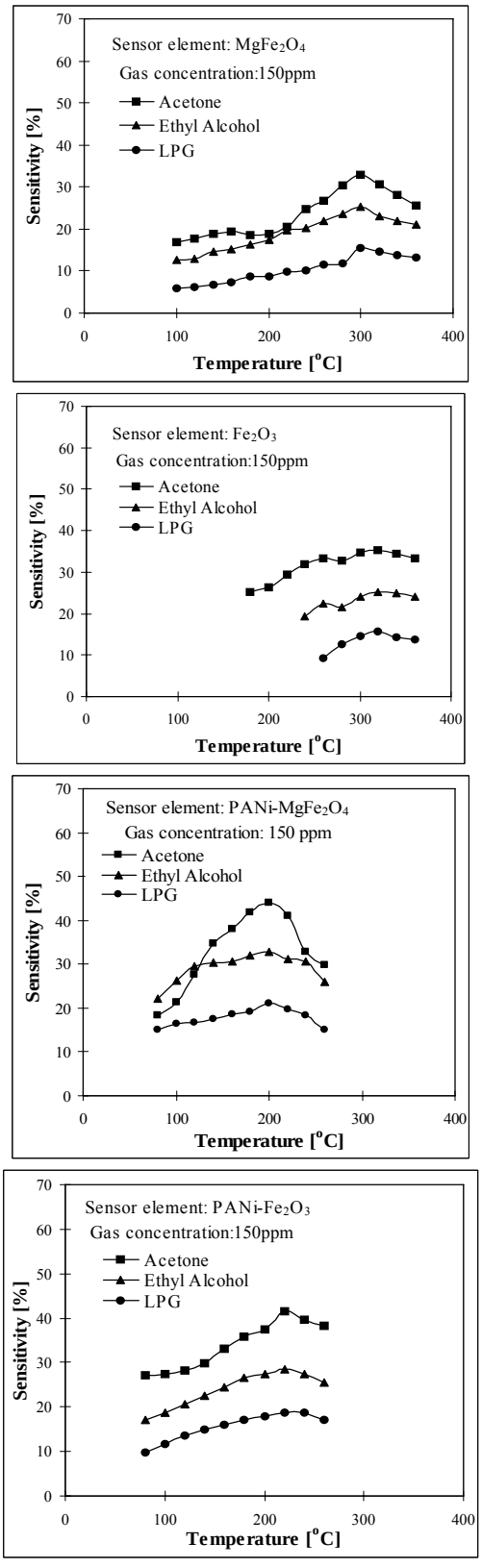

Fig. 6. Diagram for sensitivity of tested samples to reducing gases.

A decrease in bulk density of samples results in an increase in porosity, as it can see from dates presented in Table 1. PANi-Fe_2O_3 is characterized by the highest porosity 46.32%, which imply a much more active surface towards test gases. The sensitivities of tested samples towards the three reducing gases are compared and presented in Fig. 7. Here, the sensitivity value corresponds to the optimized working temperatures for each sensor element.

As it can see from Fig. 7, PANi-$MgFe_2O_4$ and PANi-Fe_2O_3 composites present better sensitivity to gas vapors, compared with iron oxides sample. The highest sensitivities it was obtained for acetone. This enhancement of electrical conductivity of composites can be attributed to a strong interaction between the polyaniline and iron oxides.

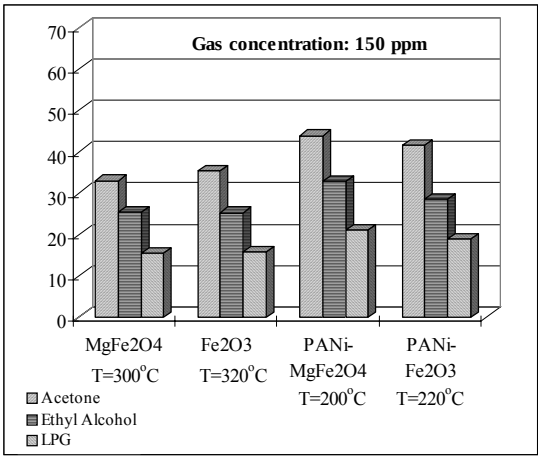

Fig. 7. Sensitivity of tested element sensor to reducing gases.

There are some attempts proposed to explain the change of electrical properties of semiconducting polymers in presence of gases. The first one is based by modification of electrical conductivity of conjugated polymers in presence of oxidizing or reducing agents that acts as dopants for the polymer chain. Another explanation is based on modification of physical properties of the polymers, i.e., morphology, crystallinity, etc in presence of gases and volatiles that could also explain the change of electrical conductivity through an increase in the interchain electron transfer.

In the present case, the action of vapors of ethanol, acetone and LPG on sensor active elements based on semiconducting polymer is based on their absorption on polymer surface followed by diffusion through the inner-domain spaces having as final effect a reducing of interchain distances. A doping process of the conjugated polymer by the volatiles tested to explain the lowering of electrical resistance is less probable.

4. Conclusions

New PANi-iron oxides composites were successfully obtained by in-situ polymerization of aniline in the presence of iron oxides particles. The synthesis method is a simple one and has a great potential for the commercial applications. Samples morphology is evident from SEM pictures. FTIR analysis confirms the interaction between PANi and Fe_2O_3 and $MgFe_2O_4$, respectively. The composites particles exhibit a better sensitivity to vapors compared with simple iron oxides. The highest sensitivities were recorded for acetone.

These results are preliminary and further studies, regarding the gas sensors fabrication by using conducting polymers, such as polyaniline are in progress.

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