

Preparation and characterization of Titanium oxide-composite polymers

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ABSTRACT

Two types of monomers polyindole and poly m-aminophenol were used to prepare conducting copolymer with use FeCl_3 as an initiator by using chemical polymerization. The prepared polymers were characterized using infrared spectroscopy, X-ray scattering, scanning electron microscope (SEM) and thermal analysis TGA. This study was included preparation of copolymers from both monomers in various ratios (1:1, 1:2, 2:1, 1:3, and 3:1) to study the effect of ratios on chemical and physical properties. Moreover, nano-metal oxide (TiO_2) (10%) of the weight of the monomers was added to copolymers to synthesis composite polymers. Results of FTIR, SEM and EDX were proved the prepared compounds. TGA findings were showed that composites have remarkably increased of thermal stability. Finally, nano-composite polymers have applied as electrochemical sensor for (NH_3) gas. Further, results display that the best sensitivity value is (24.12%) by using copolymer (1mA:3In) (without nano) with response time (7 seconds) and recovery time (3 seconds). Furthermore, results show that prepared nanocomposites have highly sensitive features with fast responses time even within a low concentration of ammonia gas at 25°C . The highest sensitivity value (79.14%), response time (3 seconds) and recovery time (3 seconds) was recorded when used nanocomposite titanium oxide (TiO_2) at the ratio (1mA:3In).

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1. Introduction

During the last few decades, conducting polymers have great interest in academia and industry society because of electrical and physical properties of these polymers with the traditional features of conventional polymers such as easy and low cost preparation and fabrication. Nowadays, most of the studies about conducting polymers are focused on Polyaniline (PANI), Polypyrrole (PPY), Polythiophene (PTh) and Poly (3,4-ethylenedioxythiophene) (PEDOT) due to they possess high conductivity and stabilities. The conductivity of such polymers is the result of several processes. Conducting polymers have become a successful alternative to many materials used in chemical sensors [1], corrosion inhibitors [2], electronics and batteries [3], motors and in the field of medical engineering [4]. Conductive polymers have recently enabled a revolution in

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important areas of industrial and scientific applications, as there has been an increasing interest in modifying and improving the properties of these polymers to be applicable in various scientific fields.

Conducting polymers are attractive materials for chemical sensors due to their conductivity and electrochemical. The inherent specificity for these polymers based electrochemical sensors stem from the chemical changings which can lead to a large conductance change which can be stimulated through further modification of the polymer. Conducting polymers have undergone from rapid modifications of their structure and shown considerable potential by application them in chemical gas sensors, where their electrical conductivity can be altered when exposure to gas molecules at room temperature. Upon interaction polymer chains with gas molecules, they behave as an electron donor or an electron acceptor, which can result in the increase or decrease of carrier concentration, which leads to the change in electrical conductivity or resistance of the sensing polymers.

Some disadvantages of electroactive polymers such as low stability, mid conductivity, and electrochemical activity can be modified by using nanomaterials. Due to remarkable electronic and mechanical properties of nano-materials, especially metal oxides, huge efforts have achieved over the past decade to fabricate conducting polymer with metal oxides composites for combining the features of each components.

Scientists are making great efforts to develop polymeric composite materials based on nano-metal oxides. Several materials have been used in this field, such as carbon, graphene, metals and metal oxides. [6] These new modified materials have been applied in many medical and industrial fields and considered as promising materials for future technical applications. [7] In this paper, conductive polymers were prepared with the addition of titanium nanooxides to improve the stability and electrical properties of polymers and their application as ammonia gas sensors was studied. These materials have found their use in many electronic and nanoelctronic devices.

Experimental

Indole (2mmol,0.218g) was dissolved in (15ml) acetonitrile was added to a solution of meta-aminophenol (2mmol,0.218g) was dissolved in (15ml) acetonitrile, then solution was mixed by magnetic stirrer for some minutes, then (6 mmol,0.96) of iron(III) chloride was added to the mixture as initiator. The mixture was continuously stirred using a magnetic stirrer for 24 hours at room temperature, it was observed that a dark brown precipitate was formed. The product was washed with ethanol and dried using oven and the resulting weight = 1.073g and the yield of the product was (76% m.p > 300) Fig.1 shows the chemical structure of the resulting copolymer.

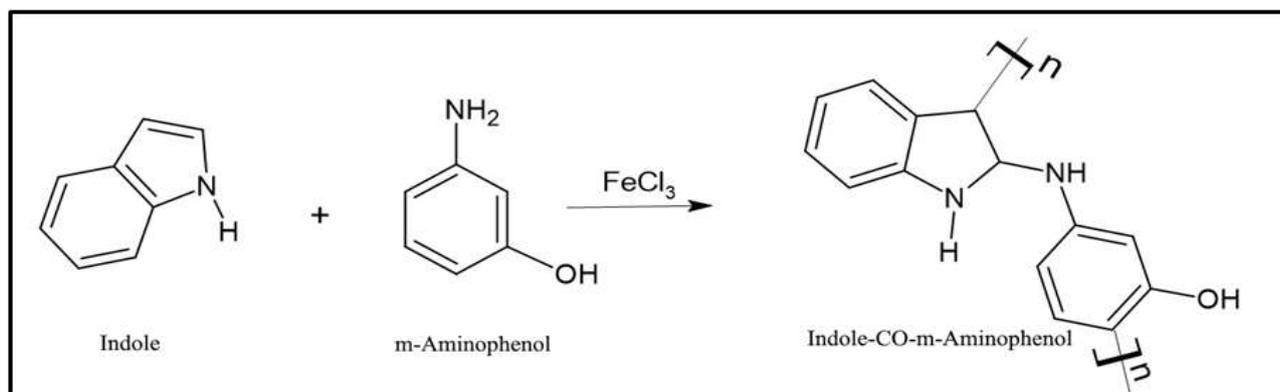


Fig.1 shows the chemical polymerization reaction to prepare the copolymer

Table 1 shows the mixing ratios of the copolymers

Number Experience	PAPH-CO- PIN (g)	FeCl ₃ (g)	PAPH (g)	PIN (g)	blending ratio	yield %
1	1.073	0.96	0.218	0.234	1mA:1In	76
2	2.650	1.44	0.42	0.234	2mA:1In	79
3	3.272	1.44	0.218	0.46	1mA:2In	75
4	1.425	0.192	0.218	0.702	1mA :3In	78
5	1.285	0.192	0.654	0.234	3mA:1In	84

2-1 - Preparation of polymeric composites using nanoparticles

Nanoparticle (TiO₂) with a size of (20nm) was also dissolved in acetone with a percentage (10%) of the weights of the copolymers and its different percentages by using ultrasound devices at room temperature for one hour. The solution of nanoparticle was gradually added to the monomer solution during the polymerization process, where the addition was achieved inside the ultrasound device for a maximum period of 30 min. Experiments were conducted according to the proportions shown in Table 2.

Table. 2 shows the addition of nanoparticle TiO₂ to different ratios of copolymers

Number Experience	TiO ₂ (g)	yield %		blending ratio
		mA	In	
1	0.0753	%50	%50	1Am :1In
2	0.1116	%66.6	%33.3	mA:1In2
3	0.1143	%33.3	%66.6	1mA:2In
4	0.1481	%25	%75	1mA :3In
5	0.1533	%50	%25	mA:1In3

2-2 Gas sensor system installation

The system consists of a glass flask (250 ml) placed on a hot plate. Ammonia chloride is placed with an equivalent amount of sodium hydroxide, and the temperature was gradually raised until ammonia vapour rises. Controlling of the gas flow can be done by a valve that connects between the flask and the chamber that contains the electrodes. Chamber contains a base for fixing the sample with the availability of two copper clamps for the purpose of connecting the sample electrodes to the electrical measurement circuit. The gas sensor system works after placing the sample in its designated place and connecting the electrodes of the sample to the electrical properties measurement circuit, which consists of a Famell Instruments type power supply, a voltmeter to measure the potential difference on both ends of the sample (Ley Bold) and an ammeter to measure current (Philips PM 2421).

Then the gas valve is closed to prevent the passage of ammonia vapor, which is the product of the reaction of aluminium chloride placed in the flask. The amount of current in the measuring circuit is measured after a certain voltage (60-10 μ A) is applied before the valve is opened and the current in the sample (before the gas

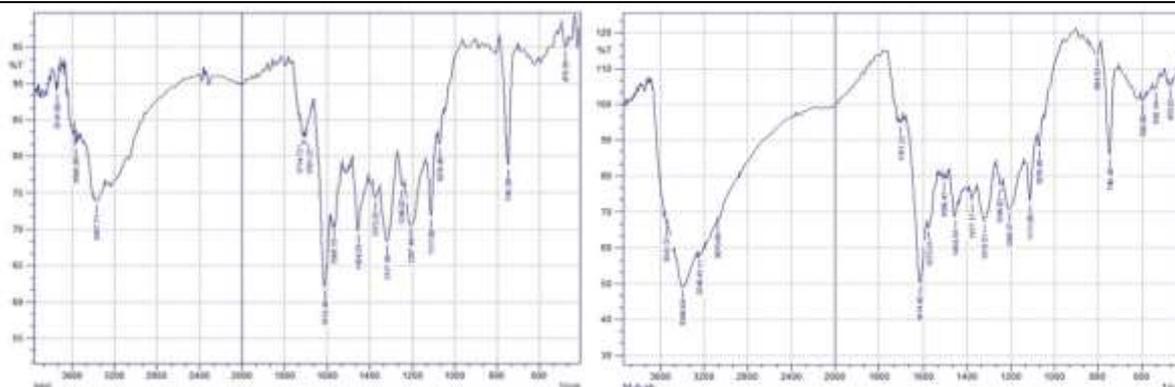
is passed) is recorded. Then the valve is opened for the purpose of allowing the ammonia gas to pass into the chamber containing the sample and to record the current passing through the sample (after exposure to the gas).

3. Results and discussion

FT-IR spectra Fig. 2 were used to determine the functional groups of copolymers. Fig. 2A shows the FTIR spectrum of copolymer Indole-co-m-aminophenol at 1:1. The spectrum consists of main peaks at 1596, 1495, 1320, 1215, and 1030 cm^{-1} . Copolymer Indole-co-m-aminophenol at 1:3 was characterized by infrared spectroscopy Fig. 2 B . Where the spectrum was showed a broad band within the range (3408.22-3363.86) cm^{-1} due to phenolic (OH) and the cyclic N-H group because of a hydrogen bond to the copolymer, as one of the phenolic (OH) groups forms an implicit hydrogen bond, and thus the band is wide and there is an overlap in the phenolic (OH) groups. A medium beam appears at a frequency of (1288.45) cm^{-1} that goes back to the amplitude of the phenolic (C-O) group, and a beam of low intensity appears at (1153.43) cm^{-1} that belongs to the C-N group. Table 3 show the main peaks of the prepared copolymers.

Table 3 Main peaks of the prepared copolymers

A	Mixing ratio	$\nu(\text{OH})$	$\nu(\text{N-H})$	B	$\nu(\text{C=C})$	$\nu(\text{C-O})$	$\nu(\text{C-N})$
				$\nu(\text{N-H})$ Bending			
	Indole	--	3367.71	1612.49	1568.13 _s	---	1317.38
			b	s			m
	m-Amino phenol	3396.64	--	1614.42	1573.91 _s	1209.37	1319.31 _s
		b		s		m	
	3mA:1I	3408.22	--	1612.49	1558.48 _s	1348.24 _w	1284.59
		b		s	1521.84 _s		m
		3393.86					
		b					
	1mA:3I	3408.22	--	1614.42	1519.91	1288.45	1153.43
		b		s	m		m
		3363.86			1510.26		
		b			m		



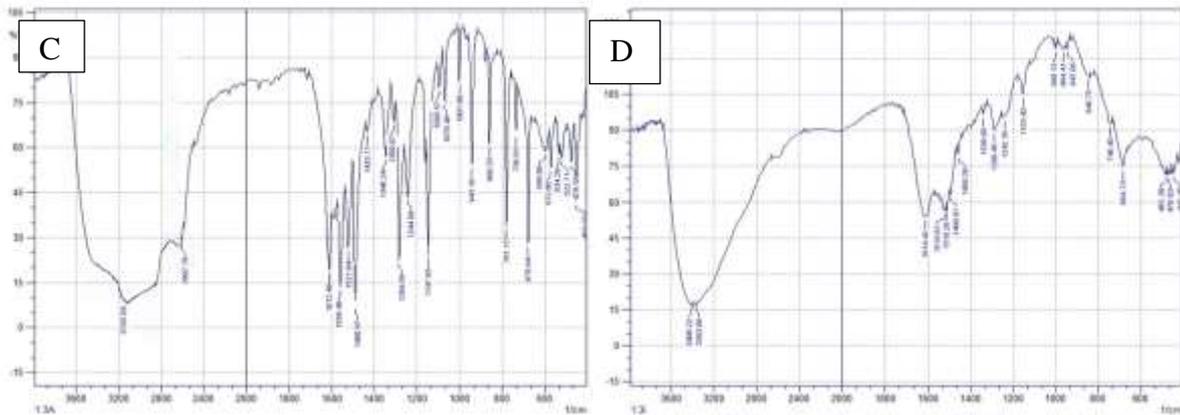
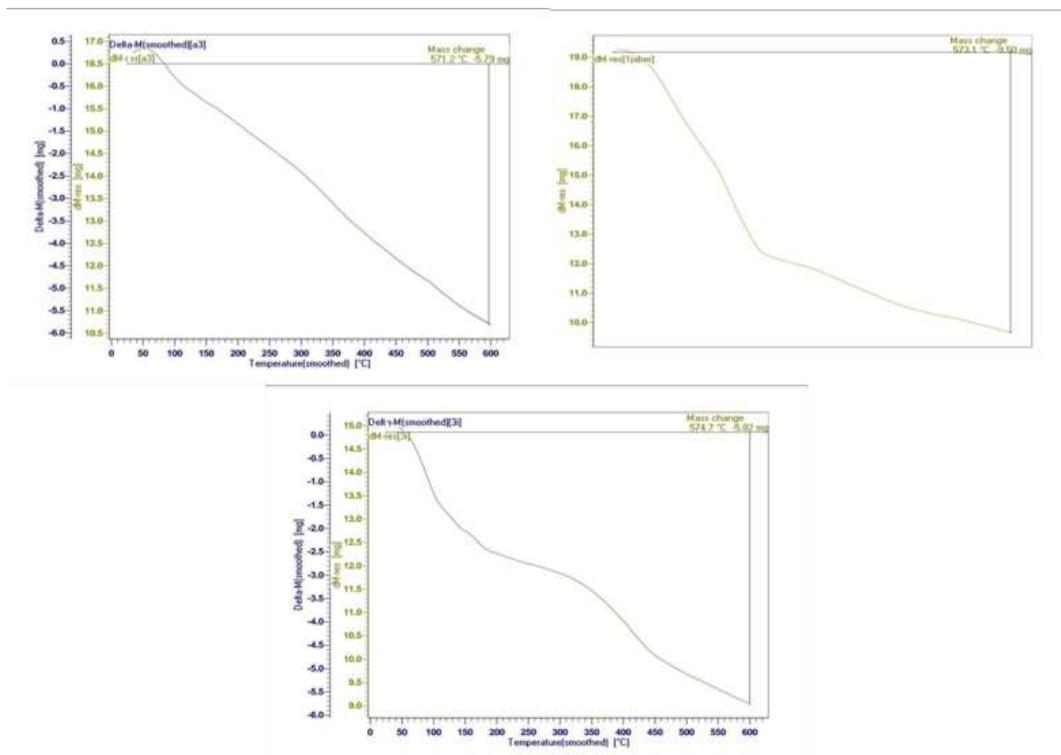


Fig. 2 shows IR spectra of copolymers

3.1 Thermogravimetric analysis of the prepared copolymers

Thermal gravimetric analyses (TGA) measurements were taken for the copolymers in the presence of nitrogen gas at a heating rate of (10) °C/min, a flow rate of (50) ml/min and a temperature range of (25-600) °C [8]. Thermogravimetric analyses for the prepared copolymers are shown in Fig. 3. It is clearly noted from the curve that there are two major stages of weight loss for copolymers; where in the first stage the weight losses are 12 % at temperatures (25-100) °C. Furthermore, the second stage is 48% at temperatures (100-600) °C. The TGA profiles of the polymer nanocomposites are shown in Fig. 3. The TGA profile of TiO₂ nanocomposites reveals a total weight loss of 14% at about 25-100 °C, attributed to the removal of moisture content. This is accompanied by a rapid weight loss of 24% at (25-100) °C. At > 600°C, the residue of TiO₂ composites is about 48 % this confirms that the presence of TiO₂ nanoparticles in the polymer nanocomposite improves its thermal stability.



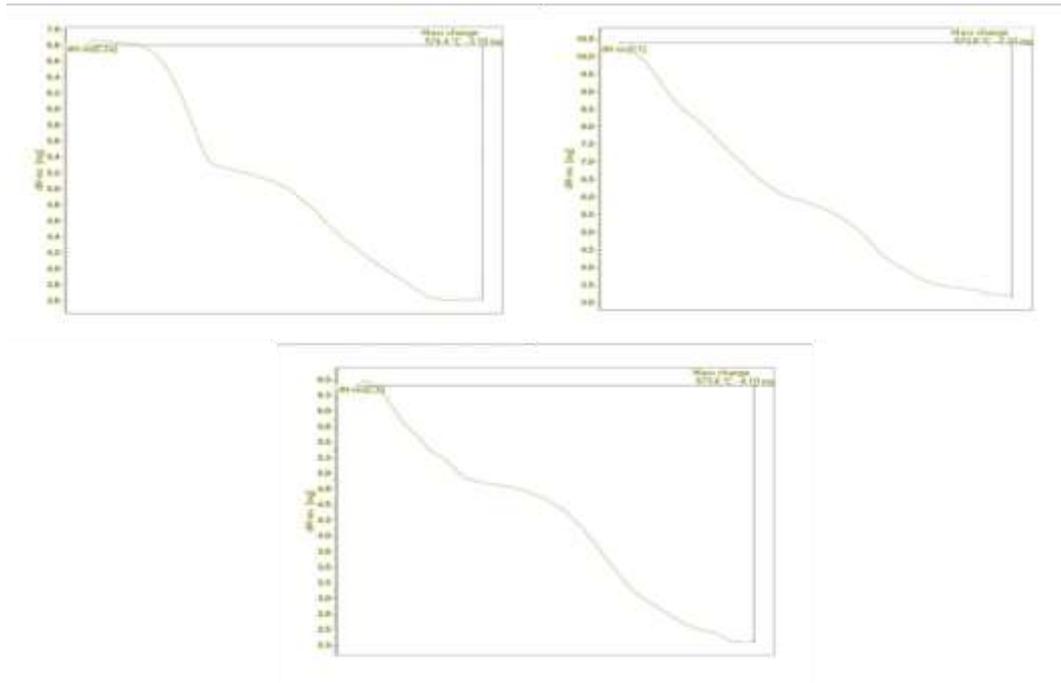


Fig.3 Thermal analysis of TiO_2 (IV) nanoparticles doped copolymers (1mA:1In),(3mA:1In) ,(1mA:3In) .

3.3 SEM analysis

SEM micrographs of copolymer of PmA-co-PIn which synthesis using chemically polymerization process of varying concentration of the copolymer by using oxidizing reagent FeCl_3 are shows in Fig. 4. It can be seen that the surface morphology spherical granules appear on surface. The SEM images clearly revealed that the PmA-co-PIn with TiO_2 composite has uniform surface with porous structures. The surface was agglomerated with a uniform structure with a high degree of spherical arrangement, it was observed that the copolymer particles aggregated to form groups in which TiO_2 nanoparticles were distributed within the polymeric chains in the prepared proportions. This could be attributed to the impact of TiO_2 during polymerization of PmA-co-PIn. It is palpable that such porous structure exhibited higher specific surface area of PTh-co-PANi-Ti copolymer composites, which may facilitate the diffusion of TiO_2 particle in materials.



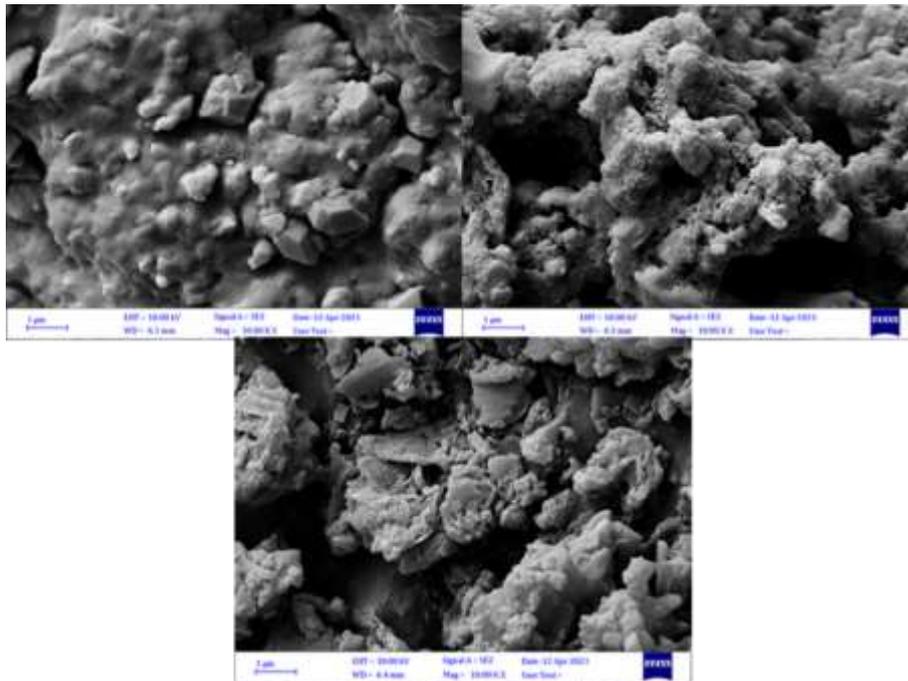
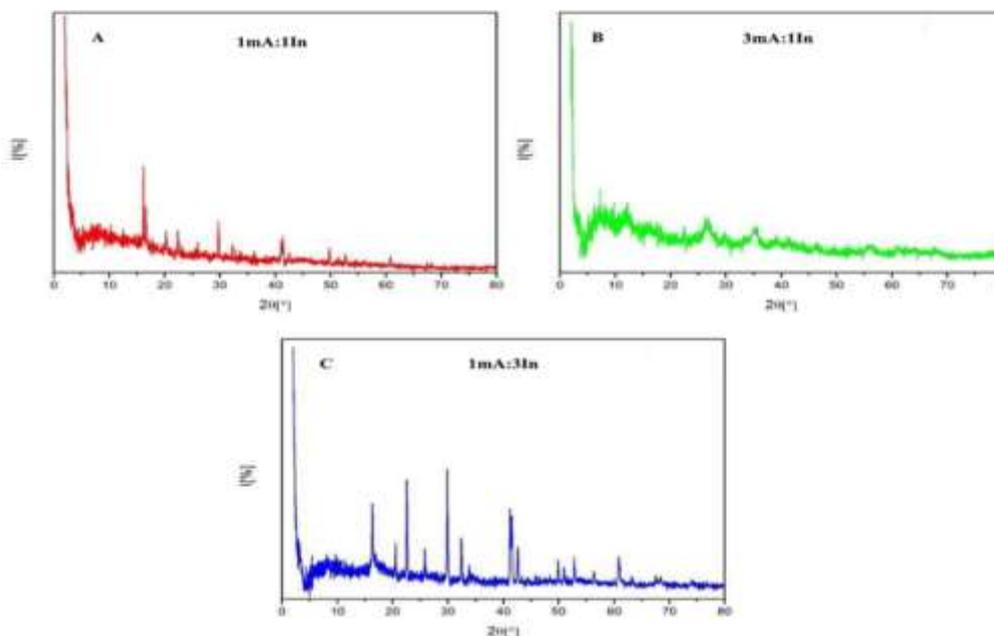


Fig.4 SEM of as-prepared copolymers doped with titanium oxide TiO_2 at magnification strength of 10000KX.

3.4. XRD analysis

Figure 5 exhibited the XRD patterns for evaluated the amorphous of that materials of as-synthesize PmA-co-PIn copolymer. While the copolymer PmA-co-PIn with TiO_2 copolymer composite has crystallinity sites. We can see that in Fig. 5 all copolymer system of PmA-co-PIn shows some sharp peaks and noisy in the range of 19–23. Which are reflecting feature of semi crystalline compounds, it is indication of the relatively small range order. However, most sharp peaks appear at around 22–30, they reflect the presence of Ti cluster in PmA-co-PIn copolymer. They attributed the crystallinity as-prepared sample but wide broad peak change into the corresponding polymers. From the observation of XRD patterns some noisy peak appear at in the range 22–32 reflects that crystalline nature but broad peak at 20–33 indicates the presence of an amorphous phase.



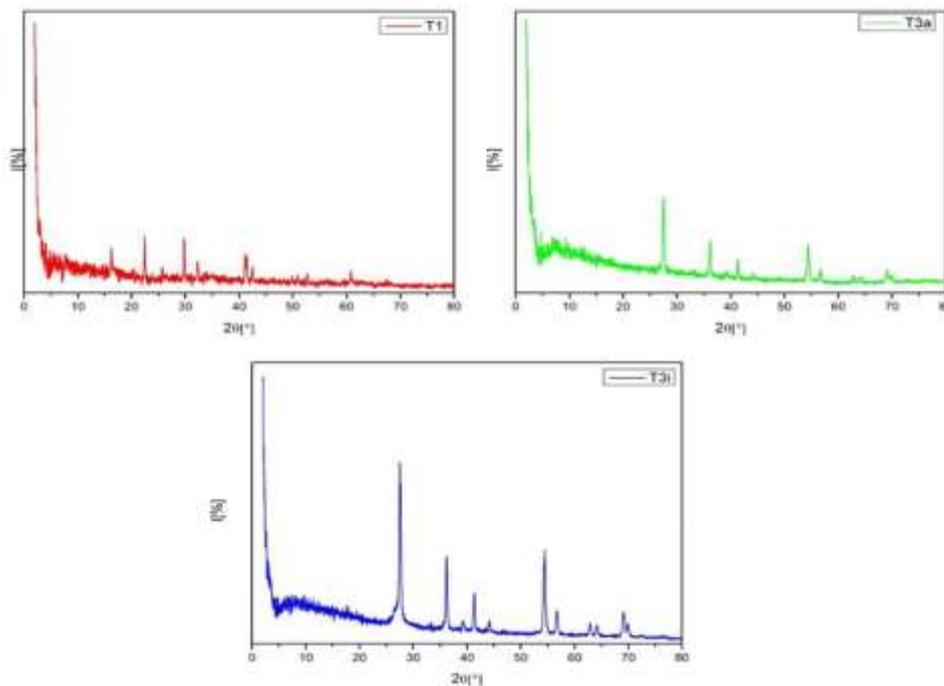


Fig. 5 X-ray spectroscopy of titanium oxide doped nanopore's copolymers TiO_2 . (1mA:1In), (3mA:1In), (1mA :3In)

4- Electrical conductivity

Measurements of the electrical properties of the copolymer:

The electrical conductivity of the polymer models (grafted and non-expanded in nanoparticles) was measured using a bipolar cell by measuring the current passing through the models when a continuous electric field is applied that can be controlled through a voltmeter. The results of ohmic behaviour (model resistance to current) between current I and voltage V and over a specific range of voltage (5-50 volts) for all samples, as the slope (Slope) was calculated in the conductive region of metals, through which the conductivity (σ) is calculated according to the equation next: As in the numbered equation 1,2

$$\sigma = \frac{IL}{VA} \text{ ----1}$$

$$\sigma = -[\text{Slope}] \frac{L}{A} \text{ ----2}$$

In order to measure the phenomenon of electrical conductivity in polymers in a practical way, we used in our research this ungrafted copolymer with different proportions as shown in Table(4)

Then these polymers were grafted with nanoparticles at a percentage of (10%-5%) and the electrical conductivity was measured before and after grafting[9].

The conductivity values showed that it decreases as the proportion of meta-aminophenol in the copolymer increases, and the reason is that it occupies more than one substitution site on the indole, which makes it difficult to transfer electrons through the hydrogen bonds between the molecules of the copolymer, as shown

in Table 4 as The increase in conductivity can be seen from the diagram (3-45) based on the increase in the indole ratio.

Table.4 Conductivity measurements of prepared and doped copolymers with titanium oxide nanoparticles.

Conductivity s.cm ⁻¹ x10 ⁵				
mA	In	1mA:1In	3mA:1In	1mA:3In
0.014	0.04	0.024	0.012	0.12

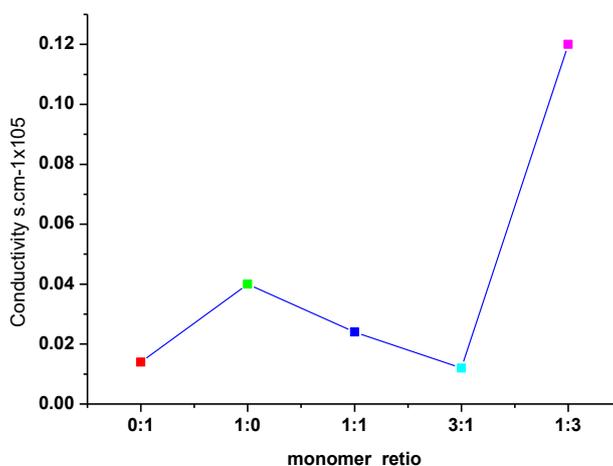


Fig. 6 The effect of nanoparticles on increasing the conductivity with the increase in the proportion of monomers

5- Calculation of the sensitivity of the prepared copolymers:

Conductivity measurement is most commonly used for gas sensors based on a typical conductive gas sensor consisting of a polymer substrate, electrodes and selective layer. A constant voltage is applied between these electrodes and the change in current is monitored by an electrometer[10]. Therefore, it is possible to calculate the sensitivity (%S) of the prepared polymeric films doped with nanoparticles towards NH₃ gas at a concentration of ppm (1000) according to equation No. (2

$$S\% = \frac{Ra - Rg}{Ra} \times 100 \dots\dots\dots (3)$$

This means that (prepared copolymers) the sensitized membrane before being grafted with nanometals operates at a low temperature with a high sensitivity value (24.12%) and a short response time (7 seconds) and a recovery of 3 seconds, it can be observed that the change in sensitivity values with time is caused by a change in the value of Surface pH, which affects the surface morphology, particle size and thickness of these films as shown by SEM assays, sensitivity is a function of the particle size and surface roughness, the decrease in the particle size leads to an increase in the surface area and this leads to an increase in the adsorption process for gases.[11]

Table 5 shows the values of sensitivity (%S), response time (tres) and recovery time (trec) at room temperature.

No.	Co-polymers	Sensitivity (S%)	Response Time (sec)	Recovery Time (sec)
1	1mA:1In	10.68	12	4
2	3mA:1In	10.20	12	5
3	1mA :3In	24.12	7	3

As shown in Table 6 the sensitivity (%S) and the response and retrieval time for all models after inoculation with nanoparticles, it appears that the films at room temperature (25 C°) are sensitive to NH₃ gas at the same concentration (1000ppm), where the highest sensitivity value was recorded (79.14).

Short response time (sec3) and recovery time (sec3) when doped with titanium oxide (TiO₂) at the ratio (1mA:3In) of the prepared copolymer[12].

Table 6 shows the values of sensitivity (%S), response time (tres) and recovery time (trec) at room temperature.

nano oxide	Co-polymers	Sensitivity (S%)	Response Time (sec)	Recovery Time (sec)
	1mA:1In	59.3	4	3
TiO ₂	3mA:1In	65.5	3	2
	1mA :3In	79.14	3	3

5.conclusions

In this paper, conducting copolymers were synthesised successfully from two monomer (polyindole and poly m-aminophenol) were used to synthesis conducting copolymer with use FeCl₃ as an initiator by using chemical polymerization. The prepared polymers were characterized using infrared spectroscopy, X-ray scattering, scanning electron microscope (SEM) and thermal analysis TGA. This study was included preparation of copolymers from both monomers in various ratios (1:1, 1:2, 2:1, 1:3, and 3:1) to study the effect of ratios on chemical and physical properties. Moreover, nano-metal oxide (TiO₂) (10%) of the weight of the monomers was added to copolymers to synthesis composite polymers. Nano-composite polymers have used as electrochemical sensor for ammonia gas. Further, results display that the best sensitivity value is (24.12%) by using copolymer (1mA:3In) (without nano) with response time (7 seconds) and recovery time (3 seconds). Furthermore, results show that prepared nanocomposites have highly sensitive features with fast responses time even within a low concentration of ammonia gas at 25° C. The highest sensitivity value (79.14%), response time (3 seconds) and recovery time (3 seconds) was recorded when used nanocomposite titanium oxide (TiO₂) at the ratio (1mA:3In).

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تحضير وتشخيص بوليمر متراكب مطعم باوكسيد التيتانيوم النانوي

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الملخص

معلومات البحث

تم استخدام نوعين من مونومرات بولي اندول وبولي امينوفينول لتحضير بوليمر مشترك موصل باستخدام $FeCl_3$ كبادئ باستخدام البلمرة الكيميائية. تم تشخيص البوليمرات المحضرة باستخدام التحليل الطيفي بالأشعة تحت الحمراء، تشتت الأشعة السينية EDX، المسح بالمجهر الإلكتروني (SEM) والتحليل الحراري الوزني TGA. اشتملت هذه الدراسة على تحضير بوليمرات مشتركة من كلا المونومرين بنسب مختلفة (1:1، 2:1، 1:2، 3:1، 1:3) لدراسة تأثير النسب على الخواص الكيميائية والفيزيائية. علاوة على ذلك، تمت إضافة أوكسيد النانو فلز (TiO_2) (10%) (من وزن المونومرات لتكوين البوليمرات المركبة. أثبتت نتائج FTIR و SEM و EDX صحة المركبات المحضرة. أظهرت نتائج التحليل الحراري الوزني (TGA) أن المركبات قد زادت بشكل ملحوظ من الاستقرار الحراري. أخيرًا، تم تطبيق البوليمرات النانوية المركبة كمستشعر كهروكيميائي لغاز الأمونيا (NH_3). علاوة على ذلك، تظهر النتائج أن أفضل قيمة حساسية هي (24.12%) باستخدام البوليمر المشترك (1 مللي أمبير: 3 بوصة) (بدون نانو) مع وقت استجابة (7 ثوان) ووقت استرداد (3 ثوان). علاوة على ذلك، أظهرت النتائج أن المركبات النانوية المحضرة لها سمات حساسة للغاية مع وقت استجابة سريع حتى في ظل تركيز منخفض من غاز الأمونيا عند 25 درجة مئوية، وأعلى قيمة حساسية (79.14%)، وزمن استجابة (3 ثوان) ووقت استرجاع (3 ثوان) تم تسجيله عند استخدام أكسيد التيتانيوم المركب النانوي (TiO_2) بنسبة (1mA: 3In).

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