Effect of silver nanoparticles on the ammonia gas sensing behavior in diphenylamine based conjugated polymer

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Abstract

In this paper, ammonia sensor operating at room temperature based on diphenylamine conjugated polymer has been designed and developed. The structure of the polymer was established by UV-Visible, FT-IR and NMR characterization techniques. The polymer was doped with silver nanoparticles by ex-situ method in 0.6 wt%, 1.2wt% and 1.8wt% to form silver nano-composites. The thin films of the polymer and its composites were cast by spin coating on the glass plate. The response of the polymer and its composite with silver nanoparticles has been studied for gas sensor applications. The polymer showed selectivity towards ammonia gas, whereas the polymer composite with silver nanoparticles exhibited selectivity towards ammonia gas and also to ethanol vapors. The response towards ammonia gas was found to increase with the increase in loading of silver nanoparticles. Reproducibility of the polymer and its composite is studied and is found to improve with the loading of silver nanoparticles. Copyright © 2019 VBRI Press.

Keywords: Conjugated polymers, diphenyl amine, ammonia sensors, electrical properties, silver nanoparticles.

Introduction

Ammonia is a toxic gas and its detection at lower concentration has become very crucial to prevent leakages and accidents in many industries [1]. Metal oxide sensors are widely used for their detection. But difficulty of fabrication and higher operating temperature limits its use [2, 3]. Conjugated polymers have replaced metal oxide sensors for their advantages of room temperature operation, low cost, ease of fabrication, better selectivity, sensitivity, good responserecovery times and reproducibility for many numbers of cycles [4, 5].

Among all conjugated polymers, Polyaniline and polypyrrole and its composites have been widely studied and extensively reported for their ability to sense toxic gases like NO₂ [6-8], ammonia [9, 10], and also nontoxic and volatile gases like alcohol [11-15]. The mechanism for their detection is also well explored. Inclusion of metallic nanoparticles in the organic polymer matrix gives materials having interesting properties of both [16-18]. These metal nanoparticles incorporated in the polymer form organic- inorganic hybrids and possess properties of both [4, 18]. Introduction of metal nanoparticles have been reported to improve the gas sensing properties like selectivity, sensitivity and reproducibility of the sensors [19-21].

Taking this into account, in the present study we have designed and synthesized a new conjugated polymer and incorporated silver nanoparticles in to it to form organic-inorganic hybrids. We have studied the response, selectivity, sensitivity and reproducibility of the polymer and compared to its silver loaded composites on exposure to various gases.

Experimental

Materials and methods

All the chemicals used in this work were procured from sigma Aldrich. All the solvents used were of analytical grade and used without any further purification.

Instrumentation

Infrared spectra of monomer and polymers were recorded on a Thermofisher Scientific Nicolet 6700 FT-IR, UV–visible spectra were recorded on a Specord S600 - 212C205. ¹HNMR spectra were obtained on a Bruker 400 MHz FT-NMR spectrometer using the TMS/solvent signal as an internal reference.

Synthetic plan

The design of the monomers was done as reported in our earlier work. The synthesis of the polymer P was carried out as shown in **Scheme 1**.

Synthesis of polymer by co-polymerization of Noctyldiphenylamine dialdehyde with 4,4'oxydianiline

Condensation polymerization of Octyldiphenylamine Dialdehyde with 4,4'oxydianiline was carried out in presence of anhydrous methanol. 1 equivalent of dialdehyde (0.00297 mole) was mixed with 1 equivalent of diaminodiphenylether (0.00297 mole) of in methanol. Addition of 2 drops of concentrated sulfuric acid immediately resulted in red colored precipitate. The polymerization reaction was carried for 4 hours. Polymerization was terminated by pouring in ice cold water. Then it is filtered through Buchner funnel. Nonpolar and polar impurities were removed by stirring the polymer in hexane and ethyl acetate respectively and decanting. The obtained precipitate was dried under ambient conditions. IR (KBr, cm⁻¹): 2926 (aromatic =C-H), 1592, 1514 (C=C), 1366 (=C-N-), 1128 (C-N), 823(p- disubstituted benzene out of plane C-H bending). ¹H NMR (400 Mhz, CDCl₃),d(ppm) 7.7-7.97(m, Aromatic-H), 7.1-7.3(m, Aromatic-H), 8.4-8.5 (m -CHO), 6.7(s, -CH=N), 6.9 (s, -N=CH), 3.8 (t, N-CH₂), 1.74(m,-CH₂), 1.2(m, -CH₂), 1.2(m, -CH₂), 0.9(t, -CH₃).



Scheme 1. Synthesis of Polymer P.

Synthesis of silver nanoparticles

Silver nanoparticles were synthesized by using Polyvinyl Pyrrolidone (PVP) as a protecting agent as well as reducing agent as reported in the literature [22, 23]. For this, silver nitrate and PVP (1:1) was mixed and dissolved in ethanol. Within 10 minutes there was formation of yellow colloidal sol which remained stable.

Characterization of silver nanoparticles

UV-Visible characterization:

UV Characterization showed characteristic Plasmon absorption peak at 426.05 nm as shown in **Fig. 1** which confirmed the formation of silver nanoparticles.



Fig. 1. UV-Visible Characterization of silver nanoparticles.



Fig. 2. XRD Characterization of silver nanoparticles.

XRD characterization

XRD of silver nanoparticles shows characteristic peaks of 20 values at 38, 44, 64 and 77 respectively and is shown in **Fig. 2**. This confirms the formation of silver nanoparticles. The nanoparticles were spherical in shape with average size in the range from 20 to 60 nm.

SEM characterization

Morphological Characterization of silver nanoparticles is as depicted in the **Fig. 3**. It shows silver nanoparticles having average size of 30-50 nm. Silver nanoparticles also exists as aggregates.



Fig. 3. SEM Characterization of silver nanoparticles.

Preparation of polymer composites

The polymer was dissolved in chlorobenzene and thin films were casted on a glass plate by spin coating. Also the polymer were mixed with silver nanoparticles by ex situ method in 0.6wt % (Poly P1), 1.2wt% (Poly P2) and 1.8wt % (Poly P3) respectively to form silver nanocomposites and thin films of these polymer composites were caste on a glass plate and dried in air.

Results and discussion

UV-Visible characterization of polymer nanocomposite

Polymer and its composite were characterized by UV-VIS spectroscopy and are shown in **Fig. 4**. With the addition of silver nanoparticles there was no change observed in the maximum wavelength absorption band which was 434 nm for polymer and its composites. The band gap of the polymer and its composite was determined by absorption edge [**26**] and it was found to be 2.65 eV for polymer P and P1 whereas 2.62 eV for poly P2 and P3. The decrease in the band gap of the polymer P2 and P3 is mainly attributed to the incorporation of silver nanoparticles. And hence the UV absorption band of the polymer shifted slightly towards red along with a slight decrease in the band gap of the polymers P2 and P3.



Fig. 4. UV-Visible Absorption spectra for Polymer P and its composites.

SEM characterization

Fig. 5 depicts the SEM characterization of the polymer composites. Silver nanoparticles are seen to be incorporated in the polymer matrix.

Gas sensor studies

Thin films of Polymer were used for gas sensor studies. Silver paste was used to make the electrodes for the electrical measurements and the resistance of the polymer films was measured using two probe method and Kiethley 6517A which serves as both voltage source and current meter. The gas sensor studies were carried out at room temperature at constant humidity using a home built air tight chamber. Solutions of different ppm concentrations were prepared and the saturated gas vapors in the headspace were used for the measurements. The gas was pumped to the air tight chamber after drying with calcium oxide. The response of the sensor was calculated using the relation.

Response % = Ra - Rg/Ra*100

where, Ra- Resistance of the film in air Rg- Resistance of the film on exposure to analyte gas.



Fig. 5. SEM Characterization of polymer composites. (a) Polymer P (b) Poly P1 (c) & (d) Poly P3.

Selectivity

The polymer P was exposed to different gases like C_2H_5OH , $CH_3COOC_2H_5$, THF, CH_3COOH , HNO_3 , HCl and NH_3 gas of 1000ppm concentration operating at room temperature. The polymer was found to be highly selective for ammonia gas (53%) as well as Hydrochloric acid gas (49%) depicted in **Table 1** and **Fig. 6**. But, its selectivity towards HCl gas was found to decrease with decrease in the concentration of gas. It was observed that when the concentration of gas is lowered from1000 ppm to 500 ppm the response of the sensor film was very poor with HCl gas (4%) while with ammonia gas, the response was found to be good (23%) as shown in **Table 2** and **Fig. 7**. Therefore, the response of the polymer P was measured by taking ammonia gas of different concentrations.

 Table 1. Response of polymer P on exposure to different gases at 1000 ppm concentration.

	Initial	Final		
	Resistance	Resistance	Diff in	%
Gas	in M ohm	in M ohm	R Ohm	Response
Ethanol	342	328	14	4.1
Ethyl				
acetate	2750	2690	60	2.2
THF	310	270	40	12.9
Acetic				
Acid	343	298	45	13.1
HNO ₃	366	290	76	20.8
HC1	205	103	102	49.8
NH ₃	460	212	248	53.9





Table 2. Response of polymer P on exposure to different gases at 500 ppm concentration.

Gas	Initial	Final	Diff	%
	Resistance	Resistance	R	Response
	in M ohm	in M Ohm	Ohm	-
Ethanol	1.77	1.67	0.1	5.6
Ethyl	1.65	1.64	0.01	0.6
acetate				
THF	1.72	1.65	0.07	4.1
Acetic	1.7	1.62	0.08	4.7
Acid				
HNO ₃	1.75	1.67	0.08	4.6
HC1	1.66	1.6	0.06	3.6
NH ₃	1.72	1.32	0.4	23.3



Fig. 7. Response of polymer P on exposure to different gases at 500 ppm concentration.

Sensitivity

Ammonia solutions were prepared in ppm concentrations in the range from 50 to 500 ppm and the saturated gas from the headspace is and passed to home built airtight closed chamber after drying with calcium oxide. All the measurements were done at room temperature. The regeneration of the film was done by opening the lid of the chamber and exposed to dry air.

The response of the polymer film was studied in the concentration range of 50 to 500 ppm. It was observed that the response drastically increases in the concentration range from 100 to 200 ppm. After 300 ppm of concentration the response was seen to be almost constant up to 500 ppm. The results are summarized in **Table 3** and shown in **Fig. 8**.

Table 3. Response of polymer P for ammonia concentrations of50-500 ppm.

Concentra	Initial	Final	Diff	Respo	Recov	%
tion of	Resista	Resista	R	nse	ery	Respo
Ammonia	nce in	nce		Time	time in	nse
gas in	M Ohm	In M		in sec	sec	
ppm		ohm				
50	430	400	30	49	79	7.0
100	446	405	41	54	85	9.2
150	449	390	59	57	90	13.1
200	460	360	100	64	99	21.7
250	480	372	108	71	106	22.5
300	460	363	97	82	115	21.1
350	470	369	101	88	135	21.5
400	485	376	109	79	144	22.5
450	460	355	105	72	156	22.8
500	450	334	116	61	249	25.8



Fig. 8. Response of polymer P for ammonia concentrations of 50-500 ppm.

Response time, recovery time and reproducibility studies

The response and recovery time of the polymer were also studied. The response time of the polymer film was found to be within 90 sec for the concentrations between 50 to 500 ppm. Initially the response time increases with the increase in the concentration up to 350 ppm above this it decreases. The recovery time for the polymer films also increases with the increase in the concentration of the gas. The highest recovery time is for 500 ppm concentration i.e., 249 sec. The relation between the sensor response along with response time and recovery time for different concentrations of ammonia is summarized in the **Table 3**. The response and recovery graph is as shown in the **Fig. 9**.



Ammonia gas (ppm)

Fig. 9. Response and recovery graph for polymer P.



Fig. 10. Reproducibility studies of polymer P for three cycles.

The reproducibility of the film is also studied for three cycles by constantly exposing the film to ammonia gas of 500 ppm concentration and the results have been depicted in the **Fig. 10**. These observations revealed that the response of the sensor was satisfactory

Gas sensing response for the polymer composite

Thin films of colloidal silver nanoparticles were also cast on glass plate by spin coating, dried and used for the gas sensor measurements. Silver nanoparticles and its composites are reported to be used in ammonia gas sensor [24, 25]. It has been well established that presence of silver nanoparticles in polyaniline has improved the selectivity, sensitivity and response-recovery times [11, 12]. In order to evaluate the effect of silver nanoparticles in the polymer and to study its effect on selectivity, sensitivity and response-recovery time, the AgNP synthesized and the polymer nanocomposites were exposed to different gases at 500 ppm concentration. The % response for all these has been as shown in the **Fig. 11**. AgNp thin films showed sensitivity towards ammonia and HCl vapors. The polymers composite films consisting 0.6wt % AgNP (Poly P1), 1.2wt% AgNP (Poly P2) and 1.8wt % AgNP (Poly P3) were also subjected to the gas sensor studies. All the composites with silver nanoparticles Poly P1, P2 and P3 showed selectivity not only towards ammonia gas but also towards ethanol vapors. This study revealed that the response of these composites towards both ammonia gas and ethanol vapors increased with the increase in the % of silver loading. The nanocomposite with 1.8 wt% of silver loading i.e. Poly P3 showed maximum response towards ammonia gas when compared with Poly P1and P2 in the concentration range from 50-500ppm. Therefore gas sensing studies of polymer composite with 1.8% silver loading (Poly P3) was selected for further studies.



Fig. 11. Response of polymer composites and silver nanoparticles on exposure to different gas.

Poly P3 nanocomposite was exposed to different concentrations of ammonia gas and its % response was measured. The results are summarized in the **Table 4** and the graph is shown in **Fig. 12**. It was observed that for the nanocomposite P3 the % response increased from 23% to 52% while the detection limit for ammonia gas lowered from 50 ppm to as low as 4 ppm concentration. The response-recovery studies shown in **Fig. 13** revealed that both response time and recovery time for the polymer composite P3 was very quick i.e. within 80 sec and 100 sec respectively.

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Table 4. Response of Poly P3 on exposure to ammonia gas at different concentrations.

Concentra tion of Ammonia gas in ppm	Initial Resista nce in M Ohm	Final Resista nce	Respo nse Time in sec	Recov ery time in sec	Diff R	% Respo nse
2	645	575	45	25	70	10.9
4	724	613	48	27	111	15.3
6	798	639	54	33	159	19.9
8	802	534	62	91	268	33.4
10	838	552	71	102	286	34.1
20	928	594	77	98	334	36.0
30	980	600	81	103	380	38.8
40	1100	670	65	107	430	39.1
50	1200	691	60	77	509	42.4
100	1060	660	64	98	400	37.7
200	161.5	78	97	66	83.5	51.7
500	113	58	133	70	55	48.7
1000	117	49	106	60	68	58.1



Fig. 12. Response of Poly P3 on exposure to ammonia gas at different concentrations



Fig. 13. Response-recovery studies of Poly P3 on exposure to ammonia gas.



Fig. 14. Reproducibility studies of Poly P3 on exposure to ammonia gas.

The polymer nanocomposite was also studied for reproducibility and the graph is as shown in the Fig. 14. The reproducibility of the polymer nanocomposite was found to be improved when compared to the reproducibility of the polymer alone. This can be clearly visualized from the figure. This improvement in the reproducibility can be attributed to the presence of silver nanoparticles.

Conclusion

A new conjugated polymer based on diphenylamine was designed and synthesized. The obtained polymer was blended with synthesized silver nanoparticles in 0.6 wt % (Poly P1), 1.2 wt% (Poly P2) and 1.8 wt % (PolyP3) respectively. The polymer and its nanocomposites were subjected to gas sensor studies. The studies revealed good response of the polymer towards ammonia vapors. The polymer composites exhibited improvement in the response towards ammonia gas with increase in the silver loading. It was found that both sensitivity and selectivity for the polymer composites containing 1.8 wt% of AgNP (PolyP3) towards ammonia gas was the highest. When compared to the polymer, the % response of the nanocomposite P3 increased from 23% to 52% while the detection limit for ammonia gas was lowered from 50 ppm to 4 ppm. It was also noted that the response time for both was within 80 sec, but the recovery time for the nanocomposite decreased from 250 sec to 100 sec. These results indicate that inclusion of silver nanoparticles not only increased response and selectivity towards ammonia gas but also improved its reproducibility.

Thus the developed conjugated polymers offer a better alternative to commercially available metal oxide gas sensors and have low cost and can be operated at room temperature. They have shorter response and recovery times and have good reproducibility. However, there are many challenges associated with them like environmental stability, selectivity to more than one analyte, moisture instability etc. Thus developing a novel sensor remains a challenge in the field of sensor technology.

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Author's contributions

Vishnumurthy K.A and K Natarajan Conceived the plan:Pallavi S.G Performed the experiments and Wrote the paper: Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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