Room Temperature NH_3 Sensing by Polyaminophenol-Cobalt Oxide Nano Composite Sensor

Rashmi H S[1], Vishnumurthy K A[1], Raviraj Kusanur[1*]

[1]Department of Chemistry, RV College of Engineering, Bengaluru -59

Abstract

Conjugated polymer nanocomposite was prepared by simple one step oxidative polymerization method and was employed for sensing NH_3 gas in the environment. The thin film sensor showed good selectivity with reversible repeatability for the target gas at ambient temperature. The sensor with 5% nanoparticle showed fast response time of 6 sec and good recovery time of 103 sec. The small size of the Co_3O_4 as evidenced by SEM provided the large surface area required for the sensing. The consolidation of cobalt oxide nanoparticle showed increased response towards the analyte with shortened response and recovery time. Hence the nanocomposite can be a budding material for sensing NH_3.

Keywords**:** *Conjugated polymers, Cobalt oxide, Repeatability, Ammonia sensor.*

1.0 Introduction

Increasing population and increased demand for energy is affecting the human health with a number of environmental issues. Ammonia (NH_3) is a highly volatile chemical having irritating odour with vast industrial applications. It is a highly toxic gas which causes skin, eye or respiratory injuries when exposed to higher concentrations. Hence a safe and efficient detector to trace level of NH_3 is in urgent need [1].

Deployment of conducting polymers for sensing poisonous gases is an active area of research. Conjugated polymers have occupied prominent position in applications like solar cells [2], rechargeable batteries [3], memory cells [4], supercapacitors [5] and sensors [6]. The modifiable electric and optical properties of these polymers help easy identification of the target material. The electrical conductivity of conjugated polymer changes on exposure to oxidizing or reducing gases at room temperature. Many conjugated polymers which show excellent sensing of target gases such as NO_2, H_2S, SO_2, NH_3, etc. are reported. Polymers like polyaniline, polypyrrole, polythiophene, etc., have proved as promising materials for

**Mail address: Raviraj Kusanur, Associate Professor, Department of Chemistry, RV College of Engineering, Bengaluru – 59*
Email: ravirajak@rvce.edu.in, Ph: 9448823443

gas sensing. Apart from their good semiconducting nature, high specificity for moisture and other volatile organic compounds hinder their practical applications [7].

In recent days, inorganic metal oxides such as ZnO [8], Fe_2O_3 [9] and NiO are widely used as sensing materials. The metal oxides show excellent stability, ease of fabrication, high response etc., towards the gaseous analytes. The higher operating temperature and the low sensitivity of metal oxides limit their use. Considering these disadvantages, the hybrid materials containing both conjugated polymers and the semiconducting metal oxides emerged. These composites show combined effect of both the counter parts present.

Jung et al. prepared carbon nanotube/cobalt oxide nanocomposite for hydrogen gas sensing at room temperature. The nanocomposite exhibited good response for H_2 gas [10]. Conducting polymer/reduced graphene oxide nanocomposite thin film NH_3 sensor showed excellent sensing of target gas. The sensor exhibited higher reproducibility and LOD of 0.2 ppm [11]. Authors [12] reported NH_3 gas sensing using polyaniline mesh. The PANI mesh sensor showed good response with good reproducibility for the analyte gas [12]. Poly (o-aminophenol) fabricated by copper catalyzed air oxidation method was used as a biosensor for glucose. The biosensor showed good specificity and response for the target molecule [13]. NH_3 sensor for diagnostic purpose was fabricated by using PANI and Ppy with rGO. The rGO synthesized using pyrrole with PANI showed superior response for ammonia [14].

With this perspective, this research was aimed at design and synthesis of poly(o-aminophenol)/Cobalt oxide nanocomposite. The polymer nanocomposites were assembled on glass substrate with the help of spin coater and was exposed to NH_3 vapors at room temperature. The sensing results indicated that the thin film sensor can be a prospective candidate for NH_3 sensing.

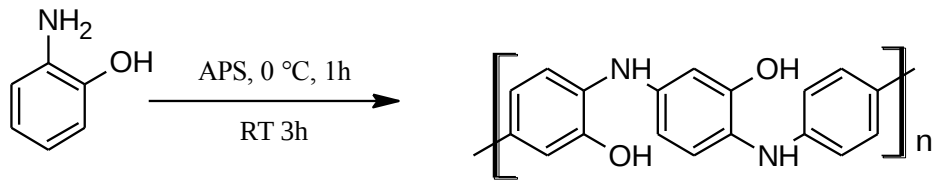
2.0 Materials and Methods

The chemicals used in this research were directly procured from Sigma Aldrich and used as received. The solvents were distilled before conducting the experiments. Thin films were fabricated by spin coating at room temperature.

2.1 Synthesis of Poly (o-aminophenol)

8g of o-Aminophenol (73.3mmol, 1eq) was added to 50 ml of Conc. HCl in a beaker with stirring at 0^oC. 66.9 g (293.1 mmol, 4eq) of Ammonium

per sulfate (APS) dissolved in cold distilled water was added dropwise to the above solution with stirring. The reaction mixture was stirred at 0^oC for an hour and brought to room temperature, 3h (Scheme 1). Dark blue-black coloured solid precipitate obtained was vacuum filtered. The obtained product was washed with distilled water and methanol to remove the impurity. Finally, the solid was dried in vacuum to get the pure polymer.



Scheme 1 Synthesis of poly (o-aminophenol) by oxidative polymerization method

2.2 Synthesis of Cobalt Oxide nanoparticle

2.5g of $CoCl_2$.$6H_2O$ was dissolved in 200 ml distilled water. Then 50ml of 2M NaOH solution was added dropwise with stirring. Complete addition of NaOH results in the formation of precipitate. Stirring was continued for another two hours. The precipitate was filtered, washed with water and ethanol repeatedly and dried. The powder obtained was calcined at 500^oC for two hours.

2.3 Characterization

The structure of the polymer was confirmed by Fourier Transmission Infrared Spectroscopy (Nicolet Avatar 5700 FTIR (Thermo Electron Corporation)). UV spectra was recorded using PerkinElmer UV-Visible spectrometer. UV spectra was recorded using DMSO as a solvent. Gas sensing measurements were performed using home-built gas sensing set up connected to Keithley sourcemeter. Cobalt oxide nanoparticles were characterized using X-ray Diffraction spectroscopy and scanning electron microscopy for phase purity and morphology.

2.4 Gas sensing studies

The poly (o-aminophenol)/Co_3O_4 nanocomposites were fabricated on glass substrates using Poly vinylidene difluoride (PVDF, 2%) as binder. Different weight ratios of Co_3O_4 nanoparticles were mixed with the polymer to obtain 5%, 10% and 15 wt. % nanocomposites. The as fabricated thin films were dried under vacuum. Gas sensing measurements were made based on change in resistance of the sensor in the presence of gas and in air respectively. The sensor response was calculated according to the equation S = (Rg - Ra)/Ra*100, where Rg is

the resistance of the sensor in gaseous environment and Ra is the resistance of sensor in air. All the sensing measurements were performed at ambient temperature in a controlled environment.

3.0 Results and Discussion

3.1 FTIR, NMR, XRD and SEM

FTIR spectroscopy was performed to confirm the structure and functional groups in the polymer. From the FTIR spectrum (Fig. 1) it is noticeable that, peaks at 1603 cm^{-1} and 1570 cm^{-1} corresponds to the benzenoid and quinonoid C=C stretching vibrations. The band at 1113 cm^{-1} is attributed to the C-O stretching vibrations and a peak at 1374 cm^{-1} is due to C-N stretching vibrations. Absorption peak at 3270 cm^{-1} is attributed to the -NH stretching in the polymer chain which may be due to another secondary amine group. The obtained data is in good agreement with the reported literature [16]. Peak at 760 cm^{-1} is assigned to the -C-H bending vibrations of o-substituted aromatic rings. Strong bands located at 1183 cm^{-1} and 3270 cm^{-1} indicates the -O-H stretching vibrations. Quinonoid and benzenoid C-N stretching vibrations are observed at 1460 cm^{-1} and 1501 cm^{-1}.

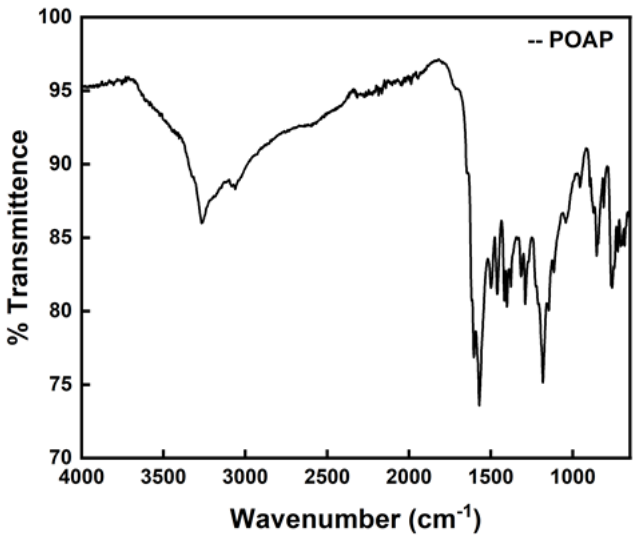


Fig. 1. FTIR spectra of pure poly (o-aminophenol) polymer.

Further nuclear magnetic spectra of the polymer were recorded in DMSO-d6 solvent at 400 MHz Bruker instrument. The spectra (Fig. 2) indicate the chemical shift of benzene ring protons in region δ 6-8ppm. A peak at δ 3.35 is due to the hydrogen atom attached to the carbon adjacent to the -OH group containing carbon in the ring. A multiplet

observed at δ 7.41 – 7.81 are due to aromatic protons. Peak at δ 7.793 corresponds to the -NH- present in the polymer backbone. Peaks at δ 2.49-2.52 are assigned to the -CH_3 protons of the DMSO solvent.

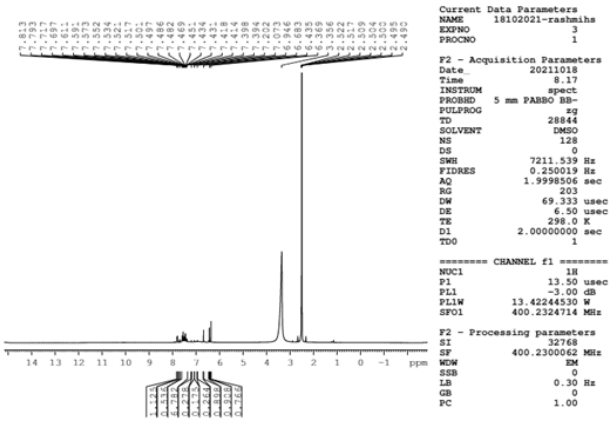


Fig. 2. NMR spectrum of the pure poly (o-aminophenol) polymer.

XRD spectra of the Co_3O_4 nanoparticles were recorded to examine the crystalline nature and phase purity of the sample (Fig. 3). The spectrum shows diffraction peaks 2θ at 31.4, 37, 45.1, 59.56 and 65.47 which corresponds to (220), (311), (400), (511) and (440) planes respectively. Highly intense, sharp and eminent peaks indicate the crystalline nature of the nanoparticle and also the cubic structure of Co_3O_4. The average crystallite size calculated by Debey-Scherrer relation was found to be 24 nm.

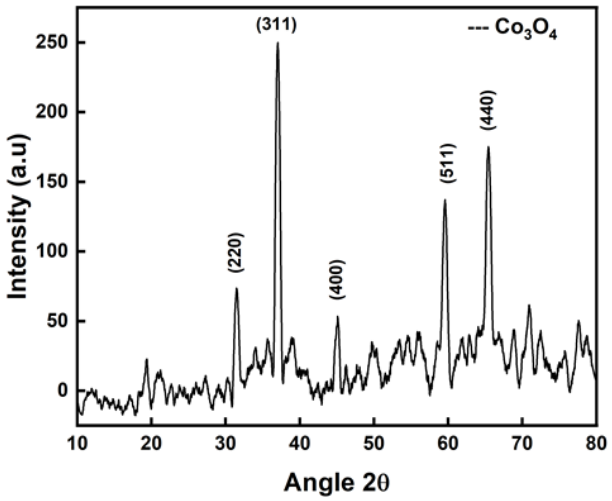
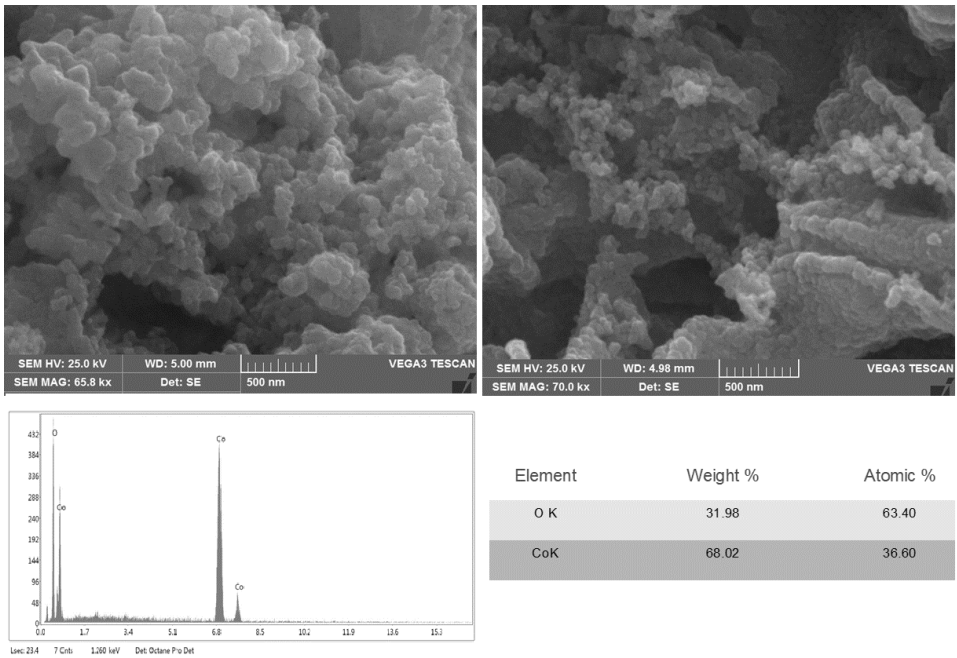


Fig. 3. XRD spectra of Cobalt oxide.



Element	Weight %	Atomic %
O K	31.98	63.40
CoK	68.02	36.60

Fig. 4. SEM micrographs of Co_3O_4 nanoparticles synthesized by co-precipitation method

Morphology of the synthesized Co_3O_4 nanoparticles was studied using SEM. The micrographs of Fig. 4 confirms the nano size of the material. The size calculated using the Image J software indicates the average size around 45 nm. The elemental analysis confirms the presence of oxygen and cobalt elements in proper ratio and hence confirms the formation of cobalt oxide nanoparticle. The small size of the nanoparticle enhances gas sensing capabilities of the sensor.

The polymer poly (o-aminophenol) showed two absorption bands at 320 nm and 695 nm in the UV-Visible spectrum. First peak at 320 nm corresponds to the π-π* transition of phenyl rings and second peak at 695 nm is due to n-π* transition of benzenoid rings in the molecule. The optical band gap calculated for the polymer in DMSO solution is found to be 2.64 eV. The data is in well agreement with the literature [15]. The polymer showed broad absorption well in the visible range of the electromagnetic spectrum indicating its use as light absorbing material.

3.2 Gas sensing

Conjugated polymers with their extended conjugation play a crucial role as toxic gas sensors. The poly(o-aminophenol) with its greater number of active sites responds well towards gaseous analytes like ammonia. Inclusion of Co_3O_4 nanoparticles in the polymer matrix enhances the response of thin film sensor for NH_3 gas.

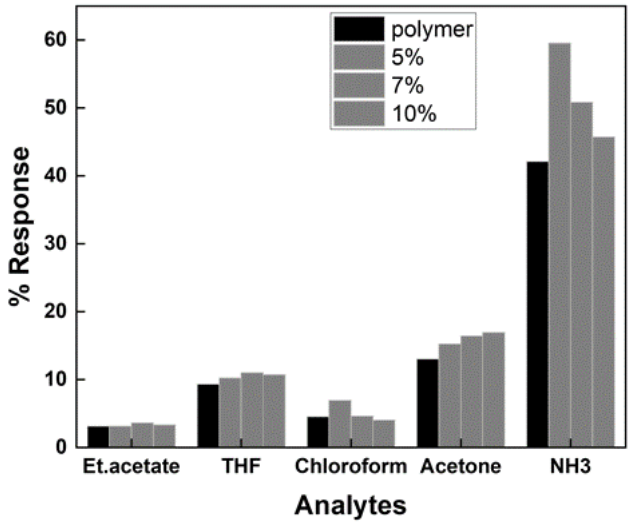


Fig. 5. Response of the poly (o-aminophenol)/Co_3O_4 nanocomposite for increasing ammonia concentration

Selectivity of the fabricated sensor for a particular analyte is the key factor for its applicability as sensor. Selectivity is the specificity of the thin film sensor for a particular target gas in the presence of other interfering gases. The selectivity of the poly (o-aminophenol)/Co_3O_4 nanocomposites and the pure polymer for ammonia gas was studied in the presence of gases, namely, ethyl acetate, tetrahydrofuran, chloroform and acetone. All the three nanocomposites and the pure polymer showed good specificity for ammonia gas. 5% Co_3O_4 doped nanocomposite showed highest response of 59.5 for the target gas as shown in Fig. 5. Increase in the response of sensor with increased concentration of Co_3O_4 was observed for the nanocomposites with 5% and 7% nanoparticles but for 10% nanocomposite the response decreased.

Sensitivity of the sensors can be explained with the relation **S = Rg / Ra,** Rg is the resistance of the sensor in gas and Ra is the resistance in air respectively. Sensitivity of the pure polymer and the three (5%, 7% and 10%) nanocomposites are calculated using this equation and highest sensitivity was achieved with 7% nanoparticle doping.

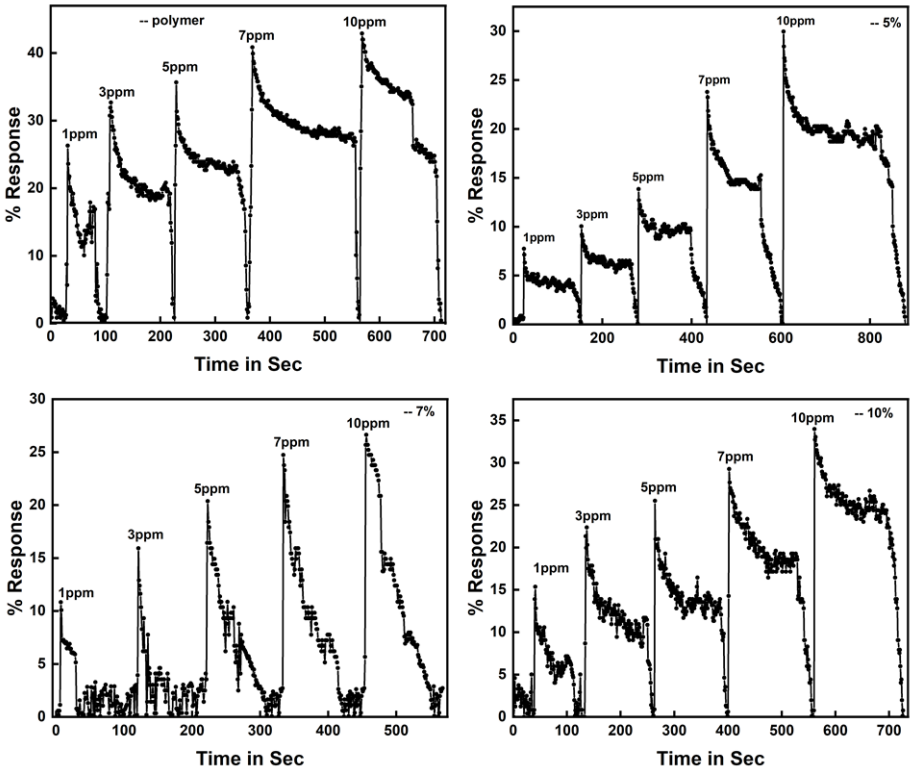


Fig. 6. Effect of gas concentration on response of sensor.

The response of the sensor for increasing gas concentration was studied with respect to time. From Fig. 6 it is clear that the gas concentration is directly proportional to the response of the sensor. As the concentration increased from 1 ppm to 10 ppm, the response increased. The pure polymer as well as three compositions showed similar trends in response to varying gas concentration.

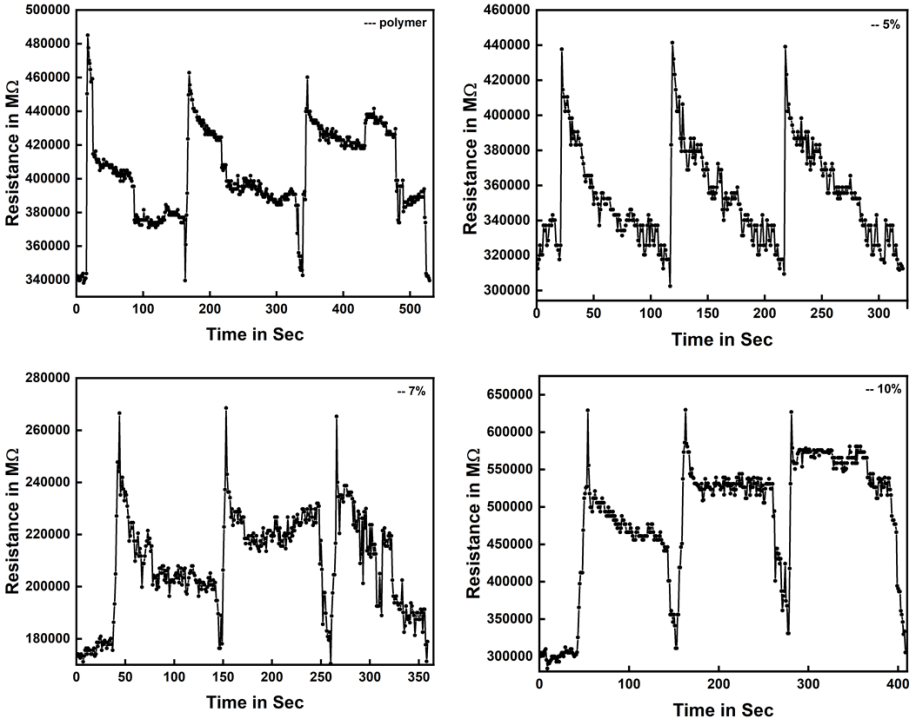


Fig. 7. Reproducibility of the sensor for 10 ppm of ammonia gas

Repeatability of the sensor is the persistence of sensor against itself and is the deciding factor of the practicality. The thin film sensor was studied for three cycles of repeatability by exposing them to 10 ppm of ammonia gas (Fig. 7). All three composites and the pure polymer showed superior reproducibility with reversibility for the target gas. The prepared thin film sensors can repeatedly be used for ammonia sensing. The sensor showed quick response (5 sec) and good recovery (103 sec) when exposed to ammonia vapours.

The mechanism of sensing can be understood with the help of adsorption theory of gases. At low temperatures (< 200), O^{2-} will be the dominant adsorbent species on the sensor surface. The adsorbed oxygen extracts electrons from Co_3O_4, when ammonia gas is passed, the electrons are released back to Co_3O_4 and oxygen species will accept electrons from NH_3, due to which the resistance of the sensor increases. The poly (o-aminophenol) present in the composite with its increased number of active sites provides good platform for the adherence of the target gas and thereby improved response.

4.0 Conclusion

The poly (o-aminophenol)/Co_3O_4 nanocomposite sensor was successfully fabricated using spin coating. The nanocomposite thin film sensor with 5% nanomaterial addition showed swift and enhanced response of 59.5 for ammonia gas. The FTIR and the H NMR spectra confirmed the polymerization of monomers. The average size of synthesized cobalt oxide nanoparticle as calculated from SEM and XRD, clearly indicated the increased surface to volume ratio. Smaller size of the nanoparticle has positive effect on the sensing response of the prepared sensor. The sensitivity of the nanocomposite containing 7% nanoparticle is superior to that of the others. The formation of heterostructures on the sensor surface helps in the detection of gas at room temperatures. Further the pol(o-aminophenol) polymer with its active sites (-NH and O) helps in faster and efficient detection. Hence the prepared thin film sensor can be a leading candidate for ammonia sensing.

References

1. A F Al-Hossainy, M S Zoromba, M H Abdel-Aziz, M Bassyouni, A Attar, M Zwawi, A A I Abd-Elmageed, H A Maddah, A B Slimane, Fabrication of heterojunction diode using doped-poly (ortho-aminophenol) for solar cells applications, *Physica B: Condensed Matter*, 566, 6–16, 2019
2. T C Bicak, S Soylemez, E Buber, L Toppare, Y Yagci, Poly(o-aminophenol) prepared by Cu(ii) catalyzed air oxidation and its use as a bio-sensing architecture, *Polym. Chem.*, 8, 3881–3888, 2017
3. J Cai, C Zhang, A Khan, C Liang, W D Li, Highly transparent and flexible polyaniline mesh sensor for chemiresistive sensing of ammonia gas, *RSC Adv.*, 8, 5312–5320, 2018
4. Y J Cheng, S H Yang, S C Hsu, Synthesis of Conjugated Polymers for Organic Solar Cell Applications, *Chem. Rev.*, 109, 5868–5923, 2009
5. M Faisal, S B Khan, M M Rahman, A Jamal, M M Abdullah, Fabrication of ZnO nanoparticles based sensitive methanol sensor and efficient photocatalyst, *Applied Surface Science*, 258, 7515–7522, 2012
6. M A Ghanem, Development of Conducting Poly(o-Aminophenol) Film and its Capacitance Behavior. *International Journal of Electrochemical Science*, 11, 9987–9997, 2016

7. D Jung, M Han, G S Lee, Room-temperature gas sensor using carbon nanotube with cobalt oxides, *Sensors and Actuators B: Chemical*, 204, 596–601, 2014

8. P Kar, N Pradhan, B Adhikari, Ammonia sensing by hydrochloric acid doped poly(m-aminophenol)–silver nanocomposites, *Journal of Materials Science*, 46, 2905–2913, 2011

9. S Liu, X Chen, G Liu, Conjugated polymers for information storage and neuromorphic computing, *Polymer International*, 70, 374–403, 2021

10. T N Ly, S Park, Highly sensitive ammonia sensor for diagnostic purpose using reduced graphene oxide and conductive polymer, *Scientific Reports*, 8, 18030, 2018a

11. T N Ly, S Park, Highly sensitive ammonia sensor for diagnostic purpose using reduced graphene oxide and conductive polymer, *Scientific Reports*, 8, 18030. 2018b

12. R K Sonker, B C Yadav, Low temperature study of nanostructured Fe2O3 thin films as NO2 sensor, *Materials Today: Proceedings*, 3, 2315–2320, 2016

13. T J alegaonkar, Y B Patil, D R Patil, Polyaniline-ZnO nanocomposites as ethanol gas sensors, *AIP Conference Proceedings*, 1953, 030258, 2018

14. J Xie, P Gu, Q Zhang, Nanostructured Conjugated Polymers: Toward High-Performance Organic Electrodes for Rechargeable Batteries, *ACS Energy Lett.*, 2, 1985–1996, 2017

15. Y C Wong, B C Ang, A S M A Haseeb, A A Baharuddin, Y H Wong, Review—Conducting Polymers as Chemiresistive Gas Sensing Materials: A Review, *Journal of The Electrochemical Society*, 167, 037503, 2020

16. M H Zoromba, M H Abdel-Aziz, Ecofriendly method to synthesize poly (o-aminophenol) based on solid state polymerization and fabrication of nanostructured semiconductor thin film, *Polymer*, 120, 20–29, 2017