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TiO_2 AND ZnO BASED AMMONIA SENSORS

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ABSTRACT:

In this review article, importance of the two semiconducting metal oxides TiO_2 and ZnO as ammonia sensors has been elaborated in well detail. Ammonia is one of the major industrially important gas used in the manufacture of nitrogenous fertilizers and amination processes in synthetic chemistry. However, its large concentration in atmosphere may cause a great hazard to the living organisms. Thus, the detection of ammonia concentration in the atmosphere by using cost effective, abundant, environmentally benign and non-toxic TiO_2 and ZnO metal oxide based materials is of important trust area in research.

***KEYWORDS*:** Ammonia sensors, TiO_2, ZnO, Metal oxides.

INTRODUCTION:

Entry of ammonia in environment:

The amount of ammonia in the atmosphere is relatively low (1-2 ppb). Growth and development of living organisms on the earth is one of the major reasons of significant increase in the percentage of ammonia in atmosphere [1]. With increasing human activities, increase in ammonia in the atmosphere has been observed by the researchers [2]. The nitrogenous animal and vegetable matter is one of the major sources of ammonia. Ammonia and ammonium salts are coming out with rainwater, volcanic eruptions also emits some ammonical salts like ammonium chloride (sal ammoniac), and ammonium sulfate. Deposites of ammonium bicarbonate mineral are also very common in some regions like Patagonian. The ammonia is secreted by kidneys in order to neutralize excess acid formed during metabolic activities.Ammonium salts are found distributed through fertile soil and in seawater.Ammonia can be produced in our environment through various sources like animal manure, agricultural sources, industrial refrigeration, refining, nitrogenous fertilizers and automobile emissions as shown in following figure [3-5].

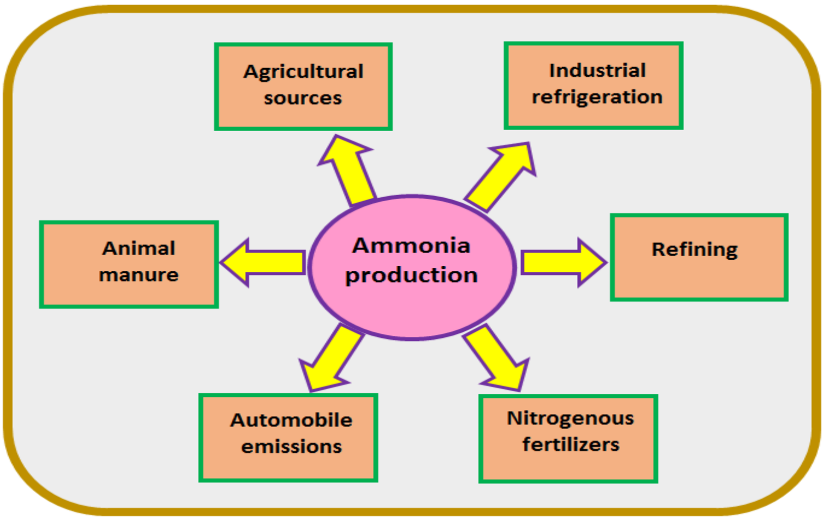

Figure 1. Various sources of ammonia production

Consequences of ammonia on environment:

Ammonia gas has a sharp, irritating, pungent smell, which is indicative sign for its hazardous nature for living organisms. However, the lower concentration of it never harm health of human and other mammals in any way. But, high concentrations of gaseous ammonia exposure can result in lung damage and death [6].Due to the existence of the specific mechanism in the bloodstream of the mammals ammonia is safely excreted out of the body through urine. Such mechanism is lacking in fish and amphibians. Thus, those organisms remove excessive ammonia through direct excretion. The mechanism of direct excretion is not so convenient for aquatic animals and thus it is considered as dangerous for the environment.Along with natural sources of ammonia in the environment through animal and plants metabolic activities, some artificial sources of ammonia like chemical industries for the production of fertilizers and the industries utilizing refrigeration systems also responsible for the pollution of environment.

So, as per the environmental point of view, ammonia detection is an important issue for the safety of living organisms.Here, in this review some important semiconducting metal oxides used in ammonia sensing devises have widely discussed.

Metal oxide ammonia sensors:

Majority of ammonia gas sensors are based metal oxide systems, most particularly utilizing metal oxides like SnO_2, TiO_2, ZnO, WO_3 etc. [7-10]. Various models were proposed by different workers to elaborate functionality and working mechanism of these gas sensors. Metal oxide films have a large number of grains, contacting at their boundaries. The formation of double Schottky potential barriers due to the charge trapping at the interface of adjacent grains influence the electrical behavior. The conductance depends upon height of this barrier. When the reducing gas like ammonia comes in contact with such films,the interface between the gas and the oxygen result in oxidation of the gas at the surface.

Beside this, the main drawback of such metal oxide based gas sensors is they are unable to detect specific gas in the presence of other gases.

Therefore different attempts were made by the researchers to develop the specific gas sensor systems. Some important metal oxide ammonia gas sensors have been discussed in this article in detail.

TiO_2 based ammonia sensors:

Being cost effective and chemically stable, the nanostructured TiO_2 materials are promising candidates for ammonia gas sensors. A high activation energy required for interaction with adsorbed gases, the TiO_2 based sensors generally work at a high temperatures (< 350 ^oC). However, this disadvantage of high working temperature can be astounded by improving the adsorption-desorption rate of analyte gas molecules via formation of p–n heterojunction at the interface [11].

Biskupski et al [12] were prepared highly redispersibleanatase nanoparticles by a novel sol–gel based hydrothermal process for gas sensing applications. Thin titania films composed of nanoparticles were deposited on Au interdigital electrodes by dip-coating, annealed and tested in a gas test bench at 350°C. These films showed a very high sensitivity towards ammonia and no cross interference by other gases like CO_2, O_2 and C_3H_8.

Lee et al [13] developed a nanoassembled thin film approach for the sensitive detection of amine odors. The TiO_2/ Poly(acrylic acid) (PAA) inorganic-organic hybrid ultrathin films prepared using the gasphase surface sol-gel process enabled the rapid penetration of amine gases into the entire film. The concentration of the ammonia gas adsorbed on the surface of TiO_2/PAA film was 1370 times higher as compared with the ambient exposure concentration. Nanoassembled PAA layers incorporated into TiO_2 ultrathin layers leads to the improvement in intrinsicproperties of TiO_2 sensor. The utilization of the different functional organic polymers and the gas-phase surface sol-gel process are found effective in modification of present TiO_2 sensors for different gases.

Metal-organic precursor solution for coating glass substrates was synthesized by some workers [14] using a Ti alkoxide derivative, amino acid, platinum salt and methanol as a solvent. The prepared film showed high selectivity to trimethylamine TMA and NH_3. The selection of an appropriate starting metal-organic precursor and addition of titania sol were very effective in forming the desired microstructure with improved gas sensing properties. Perovskite-structure materials having suitable characteristics for oxygen monitoring and a mixed chromium-titanium oxide that responds selectively to the presence of ammonia in air were prepared by Moseley et al [15]. These materials proved effective in sensing applications.

Pawar et al [16] fabricated nanostructured PANi-TiO (0%–50%) thin-films by spin coating technique on glass substrate operating at room temperature. It is observed that PANi-TiO film has a very porous structure, interconnected network of fibers, and high surface area which contributes to a rapid diffusion of dopants into the film. FTIR and UV analysis revealed that insertion of TiO nanoparticles into polyaniline matrix. The response behavior observed of the PANi-TiOnanocomposite thin film reveled higher sensitivity values, faster response and recover rates to ammonia than those of pure PANi and TiO.

PbS quantum dots/TiO_2 nanotube arrays (NTARs)showed a good response towards ammonia gas at roomtemperature [17]. It has been revealed that PbS QDs/TiO_2 NTARs have anexcellent selectivity towards ammonia compared with ethanol, methanol, acetone and toluene at room temperature. Here, the PbS QDs in

PbS QDs/TiO_2 NTARs may provide more sites to absorb the ammonia molecules and increase the depletion layer, the well-combined interface may favor for the effective transportation of the electrons as well as the direct transportation of the electrons along the TiO_2 NTARs axis. The overall result is improvement in the sensing performance of TiO_2 NTARs.Cui et al [18] prepared an extra sensitive quartz crystal microbalance (QCM) gas sensor coated with thin PPy/TiO_2nanocomposite film by using layer by layer self-assembly (SA) technology. It showed a good ability on shelf-life evaluation of foodstuffs (mango, egg and fish). The resulting QCM based gas sensor coated with PPy/TiO_2nanocomposite via Layer by Layer self-assembly presented a promising capability to detect trace irritant gasesupto 10 ppm concentration like ammonia and food quality evaluation.

ZnO based ammonia sensors:

Rawal [19]prepared ZnO nanoparticles by surfactant mediated facial hydrothermalprocess. The prepared ZnO nanoparticles have wurztile phase confirmed from XRD measurements. HRTEM study suggests the formation of hexagonal shaped nanoparticles ofZnO with particle size ~ 20 nm. The gas sensing response of the prepared nanoparticles has been recorded in ammonia environment. The sensing responses of the ZnO nanoparticles was 3.96% at 46 ppm of ammonia at 100^{o}C. the decrease in width of depletion layer in ammonia environment leads to the decrease in electrical resistance of the prepared nanoparticles.The FTIR and Raman spectroscopic measurements in the presence of ammonia environment revealed the interaction of ammonia molecules with the oxygen molecules at the grain boundaries, which causes the formation of localized water molecules. This will tune the width of depletion layer and hence, responsible for gas sensing behavior of the nanoparticles.

Self-assembled ZnO nanowires prepared by solution method [20]. The positive temperaturecoefficient for resistance was observed with ZnO nanowires in the high temperature range (>250◦C), due to the strong surface effects. The response to ammonia (NH_3) was evaluated in isothermal and temperature-pulsed operation mode;the relative higher response observed in the latter case demonstrates that the use of this methodologyis a good strategy to improve the performance of metal oxide sensors based on nanomaterials. Cross-linked ZnOnanorods (NRs)based ammonia gas sensors have been fabricated and investigated by some workers [21]. The effect of electrode spacing d and working temperature on ammonia sensing performance wasstudied. It was observed that when the electrode spacing d is reduced, the ammonia sensor responseS increased due to the configuration transformation of ZnO NRs. The optimal working temperature is about 300^{o} C due to the temperature dependence on reactions of oxygen species. The studiedsensor with an electrode spacing d of 2 m showed a maximum ammonia sensor response S of 81.6 percent to a 1000 ppm NH3/air gas at 300^{o} C. Finally, the studied sensor exhibitsgood gas sensing response and repeatability toward NH_3gas. Thus, the studied sensor with a cross-linkedconfiguration as efficient high-performance ammonia sensing material.

ZnO/ Surface acoustic wave (SAW) sensor was showed good response towards liquor ammonia [22]. To study the completemechanism, ZnO thin films (40 nm) were deposited using radiofrequency sputtering in different reactive gas composition of argon and oxygen. The increase in oxygen content (30–100%) during film growth leads todecrease in the value of stress and bond energy. The individual contribution of different SAW sensingmechanisms such as mass loading, elastic effects and acousto-electric interaction, was evaluated andanalyzed to understand the distinct response for liquor ammonia. It was found that mass loading seemsto get affected by the presence of stress whereas elastic loading was affected by the crystallite size and bond energy (ZnO) in ZnO thin films. Another SAW ammonia gas sensors based on

ZnO/SiO_2bi-layer nanofilms on ST-cut quartzsurface acoustic wave devices were fabricated and characterized. The ZnO and SiO_2layers were coatedonto SAW resonators by combining a sol–gel process and a spin-coating technique. The gas sensing results showed thatthe sensitivity of sensors was dependent on the value of sheet conductivity of the sensing films. As a result, the bi-layer nanofilms were much more sensitive than the single layer films due to their appropriate sheetconductivity, and the absolute response value was dependent on the thickness of the top ZnO layer. Thesensor based on the bi-layer nanofilm with 60 nm top ZnO layer showed the best gas sensing property.It exhibited a frequency shift of 2000 Hz in 30 ppm ammonia gas with good repeatability and stability [23].

A novel route for the synthesis of polyanilinenanofibers in the presence of varying amounts of zinc oxidewas reported [24]. The homogeneous PANI nanofibers were prepared through templateapproach, in which the ZnO nanoparticles were used as template. Opto-electronic properties of synthesized nanofiberswere analysed using various sophisticated physical techniques. The thick films of the synthesized polyaniline powder were deposited on aluminasubstrate and their sensing response to ammonia gas was investigated. Optimum sensing response wasachieved with PANI nanofibers synthesized in the presence of 30 wt% ZnO powder. The sensing response offabricated sensor was proportional to the ammonia gas concentration and exhibited excellent selectivitytoward ammonia gas.

An optical-fiber based evanescent ammonia vapor sensor was constructed with surface-passivatedgrowth of zinc oxide (ZnO) nanostructures, which was achieved through a three-step wet chemicalprocess[25]. At the first ZnO nanostructures were synthesized using a wet-chemical method andsubsequently surface-passivated with materials like cadmium sulphide(CdS) and cadmium selenide (CdSe) nanoparticles individually using a citric acid assisted chemicalsynthesis technique. The nano-sized

CdS particles decorated on thesurface of ZnOshowed a high vapor sensing behavior nearly3 times larger than the core–shell like ZnO/CdSe nanostructures.This is due to the formation of tunable hetero-junction interfaces.

Ammonia gas sensors based on organic field-effect transistor (OFET) using poly(methyl methacrylate) (PMMA) blending with zinc oxide (ZnO) nanoparticles as a gate dielectric layer were fabricated [26].The sensing properties of these devices usingZnO/PMMA hybrid as the gate dielectric layer were significantly improved than pure PMMA when exposedto various amounts of NH_3, and the response was nearly 10 times higher than thatusing pure PMMA under 75 ppm NH_3. By careful analysis of ZnO/PMMA hybrid formation of dielectric layer was confirmed and found responsible for the improvement in the sensing response.Also, the decreased grain size of pentacene was formed on the ZnO/PMMA hybrid dielectric, facilitating $NH_3$to diffuse into the conducting channel and then interact with the ZnO nanoparticles. Environmental stability of sensors was confirmed by keeping them under ambientatmosphere for 40 days.

Some workers reported the easy, economical and large scale preparation of a highly ordered luminescent ZnO nanowire array using a lowtemperature anodic aluminium oxide (AAO) template route [27]. The as-synthesized nanowires have diameters ranging from 60 to 70 nm and length∼11 μm. Furthermore, the ZnO nanowirearray-based gas sensor exhibits excellent sensitivity and fast response to NH_3 gas at room temperature and was fabricated by a simple micromechanical technique.Moreover, for 50 ppm NH_3 concentration, theobserved value of sensitivity is around 68%, while the response and recovery times are 28 and29 seconds, respectively.

CONCLUSION:

In the present article, polluting gas ammonia is well discussed with its sources and consequences on the environment. TiO2 and ZnO semiconducting metal oxides having good stability and less toxicity are excellent candidates for ammonia gas sensing applications. The different materials based on TiO2 and ZnO oxides are discussed here with respect to their preparation, characterization and mechanism of gas sensing.

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REFERENCES:

[1] Warneck, P. Chemistry of the Natural Atmosphere (1999): Academic Press Inc.

[2] Campbell, N. A., Reece, J. B., Biology (2002): Pearson Education Inc.

[3] Timmer, B., Olthuis, W., and Van Den Berg, A. (2005): Ammonia sensors and their applications—a review. Sensors and Actuators B: Chemical, 107(2), 666-677.

[4] Kannan, P. K., andSaraswathi, R. (2014): An impedimetric ammonia sensor based on nanostructured α-Fe_2O_3. Journal of Materials Chemistry A, 2(2), 394-401.

[5] Ashraf, P. M., Lalitha, K. V., and Edwin, L. (2015): Synthesis of polyaniline hybrid composite: A new and efficient sensor for the detection of total volatile basic nitrogen molecules. Sensors and Actuators B: Chemical, 208, 369-378.

[6] de la Hoz, R. E., Schlueter, D. P., and Rom, W. N. (1996): Chronic lung disease secondary to ammonia inhalation injury: a report on three cases. American journal of industrial medicine, 29(2), 209-214.

[7] Li, J., Tang, P., Zhang, J., Feng, Y., Luo, R., Chen, A., and Li, D. (2016): Facile

Synthesis and Acetone Sensing Performance of Hierarchical SnO_2 Hollow Microspheres with Controllable Size and Shell Thickness. Industrial & Engineering Chemistry Research, 55(12), 3588-3595.

[8] Sánchez, M., Rincón, M. E., andGuirado-López, R. A. (2009): Anomalous sensor response of TiO_2 films: electrochemical impedance spectroscopy and ab initio studies. The Journal of Physical Chemistry C, 113(52), 21635-21641.

[9] Katoch, A., Kim, J. H., Kwon, Y. J., Kim, H. W., and Kim, S. S. (2015):Bifunctional sensing mechanism of SnO_2–ZnO composite nanofibers for drastically enhancing the sensing behavior in H2 gas. ACS applied materials & interfaces, 7(21), 11351-11358.

[10] Kida, T., Nishiyama, A., Hua, Z., Suematsu, K., Yuasa, M., andShimanoe, K. (2014): WO_3nanolamella gas sensor: porosity control using SnO_2 nanoparticles for enhanced NO_2 sensing. Langmuir, 30(9), 2571-2579.

[11] Choi, S. W., Katoch, A., Sun, G. J., Kim, J. H., Kim, S. H., and Kim, S. S. (2014): Dual functional sensing mechanism in SnO_2–ZnO core–shell nanowires. ACS applied materials & interfaces, 6(11), 8281-8287.

[12] Biskupski, D., Herbig, B., Schottner, G., and Moos, R. (2011):Nanosizedtitania derived from a novel sol–gel process for ammonia gas sensor applications. Sensors and Actuators B: Chemical, 153(2), 329-334.

[13] Lee, S. W., Takahara, N., Korposh, S., Yang, D. H., Toko, K., andKunitake, T. (2010):Nanoassembled thin film gas sensors. III. Sensitive detection of amine odors using TiO_2/poly (acrylic acid) ultrathin film quartz crystal microbalance sensors. Analytical chemistry, 82(6), 2228-2236.

[14] Hayakawa, I., Iwamoto, Y., Kikuta, K., and Hirano, S. (2000): Gas sensing properties of platinum dispersed-TiO_2 thin film derived from precursor. Sensors and Actuators B: Chemical, 62(1), 55-60.

[15] Moseley, P. T., and Williams, D. E. (1989): Gas sensors based on oxides of early transition metals. Polyhedron, 8(13), 1615-1618.

[16] Pawar, S. G., Chougule, M. A., Patil, S. L., Raut, B. T., Godse, P. R., Sen, S., andPatil, V. B. (2011): Room Temperature Ammonia Gas Sensor Based on Polyaniline-TiONanocomposite. IEEE sensors journal, 11(12), 3417-3423.

[17] Liu, Y., Wang, L., Wang, H., Xiong, M., Yang, T., andZakharova, G. S. (2016): Highly sensitive and selective ammonia gas sensors based on PbS quantum dots/TiO_2 nanotube arrays at room temperature. Sensors and Actuators B: Chemical.

[18] Cui, S., Yang, L., Wang, J., and Wang, X. (2016): Fabrication of a sensitive gas sensor based on PPy/TiO_2nanocomposites films by layer-by-layer self-assembly and its application in food storage. Sensors and Actuators B: Chemical, 233, 337-346.

[19] Rawal, I. (2015): Facial synthesis of hexagonal metal oxide nanoparticles for low temperature ammonia gas sensing applications. RSC Advances, 5(6), 4135-4142.

[20] Shao, F., Fan, J. D., Hernández-Ramírez, F., Fàbrega, C., Andreu, T., Cabot, A., and Ali, S. Z. (2016): NH_3 sensing with self-assembled ZnO-nanowire μHP sensors in isothermal and temperature-pulsed mode. Sensors and Actuators B: Chemical, 226, 110-117.

[21] Chen, T. Y., Chen, H. I., Hsu, C. S., Huang, C. C., Wu, J. S., Chou, P. C., and Liu, W. C. (2015): Characteristics of ZnOnanorods-based ammonia gas sensors with a cross-linked configuration. Sensors and Actuators B: Chemical, 221, 491-498.

[22] Raj, V. B., Singh, H., Nimal, A. T., Sharma, M. U., Tomar, M., and Gupta, V. (2017): Distinct detection of liquor ammonia by ZnO/SAW sensor: Study of complete sensing mechanism. Sensors and Actuators B: Chemical, 238, 83-90.

[23] Tang, Y. L., Li, Z. J., Ma, J. Y., Guo, Y. J., Fu, Y. Q., andZu, X. T. (2014): Ammonia gas sensors based on ZnO/SiO 2 bi-layer nanofilms on ST-cut quartz surface acoustic wave devices. Sensors and Actuators B: Chemical, 201, 114-121.

[24] Talwar, V., Singh, O., and Singh, R. C. (2014):ZnO assisted polyanilinenanofibers and its application as ammonia gas sensor. Sensors and Actuators B: Chemical, 191, 276-282.

[25] Yogamalar, N. R., Sadhanandham, K., Bose, A. C., andJayavel, R. (2016): Band alignment and depletion zone at ZnO/CdS and ZnO/CdSe hetero-structures for temperature independent ammonia vapor sensing. Physical Chemistry Chemical Physics.

[26] Han, S., Huang, W., Shi, W., and Yu, J. (2014): Performance improvement of organic field-effect transistor ammonia gas sensor using ZnO/PMMA hybrid as dielectric layer. Sensors and Actuators B: Chemical, 203, 9-16.

[27] Kumar, N., Srivastava, A. K., Nath, R., Gupta, B. K., andVarma, G. D. (2014): Probing the highly efficient room temperature ammonia gas sensing properties of a luminescent ZnO nanowire array prepared via an AAO-assisted template route. Dalton Transactions, 43(15), 5713-5720.