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Review Article

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Nanomaterials for sensing applications

Abstract

This review article is focus on the role of nanomaterials in gas sensing applications. Different kinds of nanomaterials have been widely used to detect toxic and pollutant gases. The gas sensing mechanism of nanomaterials is related to surface reaction, which is highly influenced by several factors like surface capping/ structure directing agents, modifying morphology, catalysis, working temperature.

Keywords: Nanomaterials, Nanostructure, Sol-gel, pH, Temperature, Stable oxygen anions, Ammonia gas, Hydrogen, Ethanol, Methane, Formaldehyde, Carbon monoxide, Poly pyrrole, Titanium dioxide, Tin oxide, Zinc Oxide, Benzene, Toluene, Xylene, Alcohol

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Abbreviations: LPG, Liquefied Petroleum Gas; CNTs, Carbon Nano Tubes; SWNTs, Single Walled Carbon Nanotubes; PANI, Poly Aniline; FTO, Fluorine Doped Tin Oxide; PVA, Poly Vinyl Alcohol; CTABr, Cetyl Trimethyl Ammonium Bromide; VOCs, Volatile Organic Compounds

Introduction

The nanoworld has been played a great role in the scientific and technological development in universe. The discovery of nanomaterials such as carbon fullerenes in 1985, carbon nanotubes in 1991 and ordered mesoporous materials in 1992 makes a revolution in the field of nanotechnology .[1-4] Nanomaterials can be differentiated into various categories on the bases of their dimensionality such as one dimensional (nanowire, nanotube), two dimensional (nanosheets), and three dimensional (nanoparticles) etc.

Nanomaterials are one of the most studied materials because at this level unique optical, magnetic, electrical and mechanical properties emerge. These emergent properties have attracted the attention of users in various applications such as catalyst, gas sensors, batteries, optoelectronic devices, biomedical and agricultural applications .[5-9] Among them, specific type of nanomaterials like pure and mixed oxides, organic based material are receiving a growing attention for gas sensing applications during last few years because they can enhance the sensitivity, selectivity and the response time remarkably. The nanomaterials of wide band gap have been proven to be excellent gas sensing materials with high response. The advantage of nanomaterials based gas sensors over bulk can be understood as nanosize grains are almost depleted of carriers (most carriers are trapped in surface state) and exhibit poor conductivity than bulk in ambient conditions. Hence when these are exposed to gas, exhibit greater conductance changes as more carriers are activated from their trapped states to the conduction band than with bulk sized grain. It is known that the morphologies, particle sizes and dimensionality of nanomaterials play a key role in observing their sensing characteristics .[10] Among these the crystallite size has an impact on the gas sensitivity i.e. maximum sensitivity is achieved only if the crystallite size within the film is comparable with its space charge layer thickness .[11-13]

The nanomaterials with different morphology like size confinement in two coordinates also offers better sensitivity to surface chemical reaction due to large surface to volume ratio and small diameter comparable with Debye length .[14-17] There are many methods for achieving the above. Generally pure nanomaterials divided into two parts namely n-type and p-type nanomaterials. Up to now several nanomaterials have been successfully used as sensing materials for detecting reducing and oxidising gases by conversion of information in terms of electrical signals when exposed to corresponding test gas .[18-24] Nanomaterials can be synthesised by following two different approaches like bottom up approach (chemical method, electrochemical method, sol-gel, Solvothermal etc.), in which material is build up from bottom i.e. atom by atom and top down (ball milling, laser ablation, lithography) in which material is synthesized from initially bulk materials .[25-32] According to literature survey many researchers have shown that the various kind of nanomaterials including different dopant, catalysis, adhesive, binders, surfactant all have been used to enhance the sensing characteristics of sensors made from these materials. In addition to the above, their film fabrication method also provides another variable for sensor design .[33-52] As a simple review of nanomaterials for sensing applications, this article will focus on the principle, film deposition method and use of a range of nanomaterials for gas sensors. This article will also focus on the various factors that have direct impact on sensitivity, selectivity, and response time of nanomaterials.

Synthesis of nanomaterials

Generally Nanomaterials have synthesized by approaching two different method bottom up and top down. Both the methods have received great attention because of their unique advantages like prepared nanostructures with less defects, more homogeneous chemical composition, and different range of ordering. Bottom up approach provides synthesis of material from atom by atom, molecule by molecule while top down provides preparation of nanomaterials from bulk materials (Figure 1).

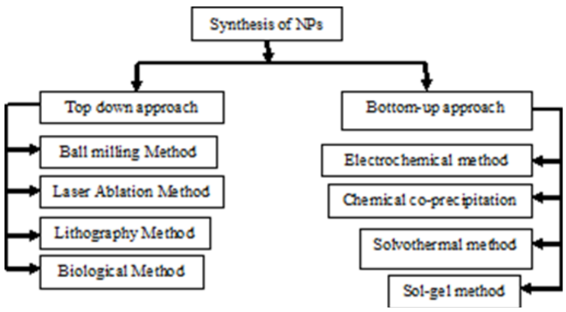

Figure 1 Schematic representation of synthesis of nanoparticles.

Mostly bottom up approach is preferred for synthesizing nanoparticles instead of top down. It provides uniform nanoparticles with controlled particle size with low cost and simplicity. There are several factors which also affects the synthesis of nanoparticles like precursor, solvent (water, polar/non-polar organic solvents), reducing agents (depends on the nature of precursors), capping agents/

stabilizing agents, heat treatment, pressure effect, and pH value of solution.

Working principle of gas sensors

Generally nanomaterials for gas sensing applications are characterised into two types of categories like n-type nanomaterials and p-type nanomaterials. The n-type nanomaterials have electrons as majority charge carriers while p-type nanomaterials have holes as a majority charge carriers. A range of nanomaterials from group III-VI called transition metal and their oxides with d^0-d^{10} electronic configurations are found to have lots of characteristics for sensing applications. The sensing behaviour of nanomaterials is based on electrochemical changes, catalytic combustion or resistance modulation of these materials. Metal oxide sensors are used based on the principle of gas adsorption on the surface that leads to a change in the electrical resistance or conductivity of these nanomaterials. The gas sensing mechanism of metal oxide nanomaterials gas sensors is complex and basically depends upon the adsorption/ desorption of test gases on their surfaces .[53-54]

Sensing mechanism

The gas sensing mechanism of nanomaterials for gas detection is quite complex to explain and is based on the resistance change due to the chemical and electronic interaction between the test gas and the nanoparticles. This complexity occurs due to the various influencing parameters like chemical composition, temperature, humidity and modified surface morphology. The sensing mechanism includes the adsorption ability, surface properties and catalytic effect. For sensor devices made up of n- type nanomaterials, when come into air environment, the oxygen will interact with such nanomaterials and capture the electrons from the conduction band of it to generate anionic species on the surface of sensor materials .[55-57] This will result in an electron depletion layer which enlarges electron transport barrier between nanoparticles. Thus, the anionic species adsorbed on the surface of nanomaterials sensor influences the resistance or conductance of nanomaterials based devices. During adsorption of Oxygen on the surface of nanomaterials, three types of stable oxygen anions namely O^{2-}, O^-, O^{2-} generates .[58-60] The whole reaction is given in steps as below:

$$O_2(gas) \leftrightarrow O_2(adsorbed)$$

$$O_2(\text{adsorbed}) + e^- \leftrightarrow O_2^-(ads)$$

$$O_2^-(\text{ads}) + e^- \leftrightarrow 2O^-(ads)$$

$$O^-(\text{ads}) + e \leftrightarrow O^{2-}(ads)$$

In the presence of test gas, the gas molecules will react with the adsorbed anionic species at the surface of nanomaterials and release the trapped electrons back to nanomaterials conduction band which leads to a reduced electron depletion barrier and contracted electron transport barrier .[61-64] The reverse is true for p-type nanomaterials.

Experimental set-up and fabrication of sensor devices

For gas sensing measurement, as synthesized nanomaterials are mixed with suitable organic solvent and deposited on a conducting substrate like Indium Tin Oxide coated glass plate, Alumina substrate with conducting electrodes and printed circuit board in the form of thin or thick film as shown below in Figure 2.

Such type of films are made via using spin coating method, screen printing method and electron beam deposition method. After being ready, the sensor device (thin or thick film) is placed in the test chamber of the measuring system and measure the resistivity or conductivity of the sensor device in the absence and presence of the test gas as shown in Figure 3.

Figure 2 Glass substrate with inter digitated electrodes for making gas sensor.

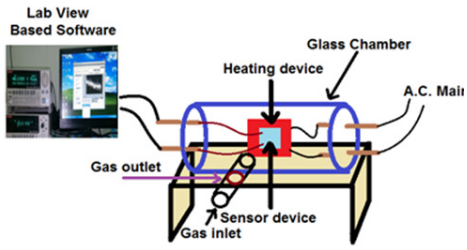

Figure 3 Schematic representation of gas sensing setup.

The measuring system consists of a gas sensing chamber, test gas or their mixtures, power supply, heater and the keithley source measure unit. The gas sensing chamber has two valve inlet and outlet valves. The inlet valve is connected to gas and the outlet valve is connected to an air pump to exit the test gas away.

Applications in gas sensing devices

During last few decades, the use of several kinds of gases in different areas like domestic, industries, food packaging, laboratories are creating a severe scene for us due to excess of these. So it is necessary to develop a device which is useful in detection of toxic and harmful gases. Many efforts have been done for developing such devices. But nanomaterials are playing a great role in developing these devices due to its potential applications. The sensing mechanism is based on changes in electrical resistance or conductance of nanomaterials due to chemical interaction in between the gaseous species and the nanomaterials. The charge transfer process induced by chemical interactions determines the resistance of the nanomaterials. If the nanomaterials are n-type the resistance decreases in presence of reducing gases such as Methane, Liquefied Petroleum gas (LPG), Ammonia gas (NH_3) while that of increases for p-type nanomaterials.

Different nanomaterials with various morphologies produced by using various synthesis processes were tested for reducing gases .[65] Zinc Oxide nanorods produced by hydrothermal method were tested as LPG sensors .[65] It was found that ZnO nanorods provide a good response to LPG and enhancing the response of those using zinc stannate micro cubes. The sensor response was found to be temperature dependent and exhibited maximum at 250°C

The role of ZnO nanomaterials and their nanocomposites have been investigated for gas sensing application. Different ZnO nanostructures like nanowires, nanobelts and tetrapod have been prepared and used for analysing sensitivity to H_2S and NO gases. The effect of different nanostructures on response of n-type semiconductor ZnO to both shows that the response to H_2S arises due to changes in grain boundary resistance while the response to NO arises due to changes in both intragrain and grain boundary resistances. The response of these structures to 4 ppm of H_2S shows that tetrapod have maximum while polycrystalline material has minimum sensitivity to H_2S. The films made up of tetrapod were found to be sensitive to 1 ppm due to oxygen vacancies and defects in lattice which create adsorption sites for oxygen .[54] Several literatures reported that the use of catalyst or promoters because of good dispersion to the nanomaterials is the most effective way to enhance the sensitivity of nanomaterials .[66-67] Ag NP embedded ZnO nanorods developed by photochemical method were investigated for ethanol sensing .[66] Ag–ZnO nanorods exhibited enhance response to ethanol at 10 ppm than pure-ZnO nanorods. The Ag-ZnO nanorods were also found to be highly selective for ethanol in between the mixture of Ethanol (C_2H_5OH), hydrogen (H_2), methane (CH_4), ammonia (NH_3), methanol (CH_3OH), formaldehyde (HCHO), carbon monoxide (CO) and acetone (CH_3COCH_3) (the concentration of all these gases was 50 ppm).

One dimensional nanomaterials are very promising sensors, and some of their results have shown that the devices based on one-dimensional nanostructures have great potential in overcoming the fundamental limitations of traditional nanomaterials based on sintered particles or thick-films such as low sensitivity, poor stability and high working temperature .[68-71] Aligned zinc oxide nanorods synthesized via a two-step solution approach on an Al_2O_3 tube were exhibited responses of 18.29 and 10.41 to 100 ppm ethanol and hydrogen, respectively, which occurs due to larger effective surface area of the aligned nanorods .[72]

Tin oxide based nanomaterials have received a great attention in the fabrication of gas sensors devices. Pure tin oxide and their composites have been used for reducing gas sensors .[73-74] Pure SnO_2 by sol-gel method and their mixture with CuO, Ag_2O, Al_2O_3, and La_2O_3 by hydrothermal route with average particle size of 6 nm were prepared to study the characteristics of LPG gas. The CuO 2 wt% doped SnO_2 5 wt% exhibited better gas sensing properties with good response time (15s) and recovery time (30s) in comparison to pure as well as other doped composites of it .[73] The SnO2 NWS were grown at 980°C on Si substrates deposited with Au catalyst while hierarchical SnO_2 nanostructures were produced at 800°C with Sn powder as the source. Hierarchical SnO_2 nanostructures have enhanced sensing performance to LPG and NH_3 gases in comparison with SnO_2 NWs .[74] This is due to high porosity, more active sites and addition of core-outer junctions to the materials.

Generally pure oxide nanomaterials based gas sensors need to be operated at relatively high temperatures rendering their practical application difficult. To overcome this problem among all the surface-reacting materials, carbon nanotubes (CNTs) having unique geometry and amazing structural features appear as a potential candidate for gas sensors .[75] For enhancing the response and lowering the working temperature of nanomaterials, many efforts have been made. Since Last few years, carbon nanotubes (CNTs) have been used due to its unique geometry and amazing structural features appear as a potential candidate for gas sensors .[75-76] Nguyen Duc Hoa et al. [75] reported simple method to fabricate an ammonia gas sensor with a nanocomposite of single-walled carbon nanotubes (SWNTs) and SnO_2 with fast response time of ~100 s and quick recovery behaviour. The composite sensor can detect the concentration of NH_3 down to the 10 ppm level at room temperature and atmospheric pressure.

Tungsten trioxide nanomaterials have also received great attention for gas sensing applications. Pure WO_3 nanomaterials and their composites with modified morphology have been used for the detection of reducing gases. Xiang Q et al. [78] reported a special method for uniformly attaching monodispersed Au NPs onto the surface of WO3 nanorods for H_2 gas sensing. These sensors show highest response to 50ppm H_2 at 290°C in a mixture of several kinds of reducing gases (H_2, CO, C_2H_5OH, CH_3OH, HCHO, NH_3) with good response (8 s) and recovery time (10 s) to which confirms a high selectivity and response sensitivity of H_2 on the Au NP @WO_3 NR composite .[75] In addition stability is also a measure factor which must be considered and verified as being acceptable to be used for practical application. These exhibited high long term stability in their response and selectivity for detecting H_2 gas.

WO3 thick films prepared by screen printing method were investigated at different operating temperatures and gas concentrations. These thick films exhibit excellent LPG sensing properties with maximum sensitivity □133% at 400°C with fast response and recovery time and can be reliably used to monitor the concentration of LPG over the range (25–100 ppm) .[76]

SnO_2 activated Cr_2O_3 thick film is also investigated to sense Ethanol and LPG gas.[77] Instead of pure sensor the sensing response to ethanol is found to be two times for SnO_2 activated Cr_2O_3 thick film sensors. The addition of tin chloride solution on the sensor surface brought maximum reduction in activation energy of base materials and hence enhancing the sensing response to ethanol. The ethanol gas sensing reaction occurs under two different ways i.e. either dehydration or dehydrogenation process due to acidic nature or basic nature of sensor material respectively.[78,79] Organic materials, such as poly pyrrole (PPy), poly aniline (PANI), and metaphthalocyanines, have been used for enhancing the gas sensing characteristics for a long time.[80-83] These materials provide long response time due to the orderly structure hinders. Organic materials doped nanomaterials like Poly Aniline (PANI), Poly Aniline/Titanium dioxide (PANI/TiO_2), Poly Aniline/Tin Oxide (PANI/SnO_2) and Poly Aniline/thin films developed by in-situ self assembly method were also investigated for NH_3 gas sensing application .[84] PANI/TiO_2 nanocomposite thin film sensor showed optimum NH_3 gas-sensing characteristics rather than pure organic material based thin film sensor and their other composites. PANI doped nanocomposite thin film sensors have shown faster response/recovery rate, higher sensitivity, better reproducibility and long-term stability. Such characteristics reveal that PANI nanocomposite thin film sensors are highly potential candidates for NH3 detection, and perspective for electronic nose application.

Many reports are focused on nanomaterials hetero junctions i.e. two layer type nanomaterials development to sense different gases .[85-89] The amorphous/porous nature of the silicon deposited by the plasma enhanced chemical vapor deposition technique was used under bias condition to enhance the sensitivity towards ethanol and water vapors .[85] A higher temperature sensor was reported by Ling and Leach towards humidity and NO_2 using a SnO_2/WO_3 hetero junction in pellet form .[86] Transparent oxides p–n hetero junction diodes based on $SrCu_2O_2$–ZnO were fabricated with post-annealing treatment at 923K and the effect of H_2 and CO gas introduction on the current–voltage characteristic was studied by Nakamura et al. [87] Recently, a few reports have emerged for room temperature LPG sensors based on electrochemically deposited p-poly aniline with n-CdTe deposited by the electrochemical method .[88] Ladhe RD et al. [89] was used room temperature soft chemical route for producing n-Bi_2S_3 films followed by p-CuSCN films onto Fluorine doped Tin Oxide (FTO) coated glass substrates for LPG gas sensor at room temperature. The device exhibited more than 70% response at 1370 ppm of LPG because upper porous structure allowed enough room for the gas species to adsorb and de-adsorb easily at the interface .[89] The nanocomposites of ZnO with CdO synthesized by sol-gel pyrolysis method based on polymeric network of polyvinyl Alcohol (PVA) of nanograin's diameter varying from 70 to 90 nm were used for CO gas detection. Such nanocomposite exhibits good ability to detect CO gas .[90]

One-dimensional (1D) nanostructures (nanowires, nanotubes, nanorods) have received considerable attention due to their unique properties and novel applications and can be developed including VLS (Vapor-Liquid-Solid), SLS (Solution-Liquid-Solid), template-based synthetic approaches and laser ablation .[91-94] Dang Thi Thanh Le et al. [95] reported preparation of TiO_2 nanowires by a hydrothermal process in KOH solution for LPG gas sensing analysis. The obtained nanowires diameter of ca. 10-20 nm and length of ca. 700-800 nm exhibited good response to LPG concentrations of 500, 1000, 2000, 4000 and 8000 ppm at operating temperature of 400°C .[95]

Detection of volatile organic compounds is important since these are used in many fields like chemical industries, laboratories which are very harmful for living species. Many researchers have also focused on developing to sense these harmful organic compounds at low concentrations. Al-doped ZnO thin films prepared by chemical spray pyrolysis were used as methanol sensors. Al- doped ZnO thin films show high sensitivity to methanol vapor in compare to undoped ZnO film at 275 C to 500 ppm with fast response and recovery time .[96] A novel ZnO porous nanosolid with a very uniform pore size fabricated by hydrothermal hot-press method were also used for analysing sensing applications towards several organic vapors .[97]

Wang HC et al. [98] reported the method of fabrication of SnO_2 thin film gas sensors towards methyl alcohol vapors operating at room temperature. The sensors exhibit ultra-fast and reversible electrical response (t90% □5 s for response and □1 s for recovery) at room temperature. . The particle size of the hydrolyzed SnCl4 affects the sensitivity of the sensors, but does not have much effect on their response time. The responses of sensors prepared from the precursor solutions with the colloid particle size of 6.0, 30.3, 49.2 and 319.9 nm were found to be 241, 318, 363 and 326, respectively. These sensors show fast electrical response and were highly reversible for both the sensing and the recovery process irrespective of the particle size .[98] Thorsten Wagner et al. [99] synthesized the ordered mesoporous SnO2 powders with large specific surface area by using Cetyl Trimethyl Ammonium Bromide (CTABr) as a structure-directing and used for the preparation of gas sensors by application to commercial sensor supports. Such a materials show a fast and intense response to low concentrations of CO as well as a remarkably strong insensitivity against humidity.

Babita Baruwati et al. [100] reported Highly crystalline zinc oxide (ZnO) nanoparticles prepared via hydrothermal route at 120°C over a range of different time period .[100] were used for sensing of reducing gases like Liquefied Petroleum Gas (LPG), Ammonia, Hydrogen, Ethanol (EOH), etc. These nanoparticles show high sensitivity to LPG and Ethanol at relatively low operating temperatures. Palladium is known to have a catalytic effect due to its excellent oxidation capability to convert hydrocarbons at lower temperatures .[101] making the sensor selective to hydrocarbons. In Pb-ZnO nanoparticles barrier is formed at the interface that is fully characterized by the electron affinity. Pd incorporation with ZnO results in a decrease in operating temperature by more than 100°C, and improves the sensing characteristics in terms of response and recovery times.

Undoped and Sb-doped needle-shaped ZnO nanoparticles produced by vapor condensation method were investigated for Volatile Organic Compounds (VOCs), benzene, toluene, xylene, acetone and alcohol, as a function of temperature. The doping of Sb to ZnO nanoparticles modified the morphology of the doped materials from needle shape to polygon which is found to be greatly useful in improving the gas sensitivity .[102]

ZnO thin films prepared by sol–gel dip coating method were also used for investigating gas-sensing properties of the multi-layers for alcohols with different chain lengths (Methanol, Ethanol and Propyl Alcohol vapor) .[103] The film of these nanomaterials was sensible to Methanol, Ethanol and Propyl Alcohol vapor as low concentration as 1, 10 and 0.5 ppm, respectively. This film shows with good sensitivity to the test gases with quick response–recovery characteristics, i.e., the sensitivity of the film to 10 ppm gases is 2.1, 5.1 and 18.1 to Ethanol, Methanol, and Propyl Alcohol vapor.

Komilla Suri et al. .[104] reported that magnetic nanomaterials and their nanocomposites were also play a great role in gas sensing applications .[28] Nanocomposites of iron oxide and poly pyrrole fabricated by simultaneous gelation and polymerisation process were analysed for humidity gas sensing application. These nanocomposites were showing the increment in response with increasing poly pyrrole concentration. These sensors were also investigating for CO_2, N_2, and CH_4 with varying pressure. According to the above these were highly sensitive according to the following order $CO_{2\ N2CH4}$. This happened due to variation in kinetic diameter of the gas molecules having the order $CO_2<N_2<CH_4$.[104]

Weber IT et al. [105] reported a pechini method for preparing SnO_2. Nb_2O_5 powder in nano range for an Ethanol vapor sensor. The use of Nb_2O_5 inhibits the particle growth and also to increase the conductivity of SnO_2 and hence improved the sensing performance.[105] Ji Haeng Yu et al.[106] reported the ZnO-SnO_2 composites for CO gas sensing.[106] He explained that SnO_2-rich samples as well as ZnO rich samples are more sensitive to CO gas than pure materials. This is happened due to more porous microstructures. He also reported that CuO and ZnO doped SnO_2 nanocomposites for CO gas detection. CuO and ZnO doped SnO_2 gas sensor were prepared by ball milling method to detect CO and H_2 gases .[107] The CuO added SnO_2 sensor show good sensitivity to 200 ppm CO with varying concentration of CuO. Pure SnO_2 exhibits maximum sensitivity at 350°C while addition of CuO to it reduces the operating temperature 150-200°C. The addition of ZnO into the CuO doped SnO_2 slightly shifted the H_2 gas sensing curve to a higher temperature while detect the CO relatively at low temperature. ZnO and Sb doped ZnO nanoparticles produced by sol-gel method investigated for O_2 and CO_2 gas sensing were reported by Kashyout AB, et al. [108] The gas sensitivity was higher for O_2 gas than CO_2, and the sensitivity improved to Sb doping with maximum enhancement at Zn:Sb (93:7) .[108] Hence there are various types of nanomaterials which play a role in gas sensing.

Conclusion

In this review, we discuss the synthesis of nanomaterials, importance of nanomaterials in gas sensor devices, working principle and their sensing mechanism. Several kinds of nanomaterials have been used to detect a range of toxic, hazardous gases. Both nanomaterials and their nanocomposites are responding to both types of gases (reducing and oxidising gases). Composite nanomaterials show better sensitivity to the target gas than the pure nanomaterials at optimum working temperature. Many efforts have been done to enhance the sensitivity like by using good catalyst, surface capping/ structure directing agents, modifying morphology etc. Porous nanostructures with high surface to volume ratio of nanomaterials seem to be useful for gas sensing. These nanostructures have lots of active sites with pores among them.

Since the gas sensitivity also depends upon the nano particle size. It is also showed that the sensitivity is enhanced by reducing the grain size. Working temperature is also a major issue in gas sensing analysis. Pure nanomaterials are sensible to target gases at high temperature (150-450°C). So, it is necessary to reduce the working temperature and enhance the sensitivity of nanomaterials. Usually carbon nanotubes/graphenes are used to keep a balance in between lowering the working temperature and enhancing the sensitivity. Besides these, Humidity also affects the gas sensitivity of nanomaterials which is removed by heating the sensor device at optimum temperature.

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