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REVIEW PAPER

Nanotechnology Applications for Chemical and Biological Sensors

M.K. Patra, K. Manzoor, M. Manoth, S.C. Negi, S.R. Vadera, and N. Kumar

Defence Laboratory, Jodhpur-342 011

ABSTRACT

Recent discoveries indicate that when the materials are brought down to sizes in the range 1–100 nm, these exhibit unique electrical, optical, magnetic, chemical, and mechanical properties. Methods have now been established to obtain the monodisperse nanocrystals of various metallic and semiconducting materials, single-walled and multi-walled nanotubes of carbon and other metallic and non-metallic materials together with organic nanomaterials such as supra-molecular nanostructures, dendrimers, hybrid composites with tailored functionalities. The high surface-to-volume ratio with an added element of porosity makes these highly potential candidates for chemical and biological sensor applications with higher degree of sensitivity and selectivity as compared to their bulk counterparts. The paper reviews the recent developments and applications of chemical and biological sensors based on nanomaterials of various structural forms.

Keywords: Nanotechnology, chemical sensors, biological sensors, nanocrystals, bio-sensing techniques, nanoparticle sensors, nanowire-based sensors, nanotube-based sensors, nanobelt-based sensors

1. INTRODUCTION

As our civilisation is becoming more technologically advanced, demand for information in every aspect of day-to-day life has grown tremendously. Sensors and sensing technology play a crucial role in the process of information gathering. The need for high throughput label-free multiplexed sensors for chemical and biological sensing has increased in the last decade in the newer application areas, viz., healthcare–genetics, diagnostics, and drug discovery; environmental and industrial monitoring; quality control, etc[1].

Chemical sensors are defined as the analytical devices that convert the chemical potential energy of targeted analyte into a proportionate measurable signal. The general concept of a chemical sensor is illustrated in Fig. 1. Based on the energy transduced in the sensor, these can be divided into four classes as illustrated in Fig. 2. In most of the chemical sensors, although sensitivity has increased significantly in recent years, however, not much improvement has been seen in terms of their selectivity. The selectivity of a chemical sensor is limited by the properties of the sensor materials that are used in a specific technology. The biological sensors can be considered as a subset of chemical sensors that employ biologically active molecules in the recognition functions associated with transduction. Further, biosensing techniques can be broadly classified into label-free and label-based techniques. Label-based techniques rely on the specific properties of labels like fluorescence[2], chemiluminescence[3], etc. for detecting a particular target and are much more sensitive compared to label-free technique because of their ability to select and tune the label for specific sensing applications. Similarly, there are other biosensors which are based on label-free techniques, viz., surface plasmon resonance (SPR), mass spectrometry, surface acoustic wave (SAW) sensors, surface stress sensors (microcantilevers),[4-6] etc.

The field of nanoscience and nanotechnology has been the most identifiable activity in modern era of materials science. There are two main attributes of nanomaterials, i.e., reduced size and high surface area which make these highly useful for molecular-recognition properties. Further, similarity of size scale between nanomaterials and biomolecules make nanostructures particularly attractive for intercellular tagging and ideal for bioconjugation, such as antibody targeting of a contrast agent. Recently, biologists have begun to use nanotools for a variety of applications, ranging from diagnosis of diseases to gene therapies, through integration of biomaterials (e.g., proteins, peptides or DNA) with semiconducting quantum dots and metal nanoparticles[7,8]. In view of these developments,

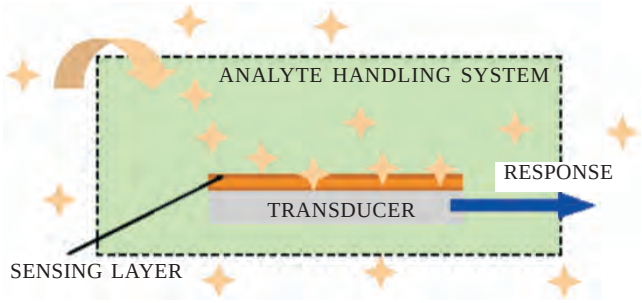

Figure 1. Concept of chemical sensor-reaction of the analyte with the sensing layer generate a signal that is converted by the transducer into a measurable response.

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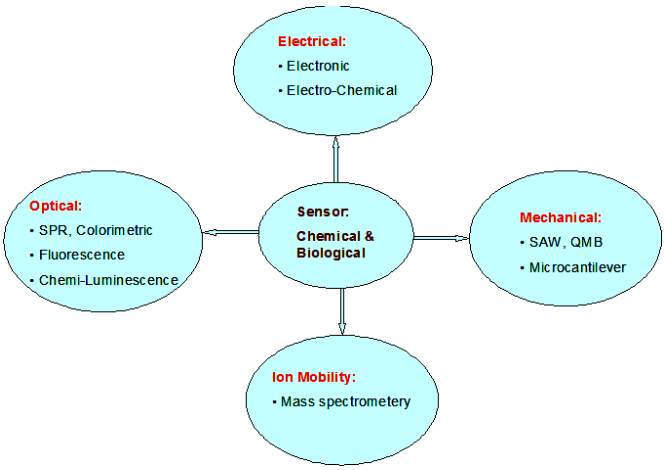


Figure 2. Classification of sensor technologies based on their energy transduction.

the nanomaterials have acquired great potential for sensing of chemical and biological species.

2. NANOTECHNOLOGY-BASED CHEMICAL AND BIOLOGICAL SENSORS

There is not a single sensing class or technology that can effectively detect everything of interest in every possible environment. Rather, selecting the optimum sensing approach from a group of materials or technologies may be the best method to address the sensing needs. Many new sensors are built by microfabrication techniques using advanced materials including Schottky diodes, metal-oxide semiconductors[1] (MOS) in micro- and nano-size forms, conducting polymers[9], electrochemical cells,[10] etc. Sensors developed using microfabrication techniques provide a host of advantages including low power consumptions, small, lightweight, etc. Moreover, such technologies can be used to produce a range of different basic microsensor platforms. Nowadays, the ability to control the particle size and morphology of nanoparticles is of crucial importance from the fundamental and industrial points of view, considering the tremendous amount of high-tech applications, as promised by nanomaterials of different categories (metal oxide, -chalcogenides, metals, self-assembled structures, carbon nanotubes, etc.). Characteristically high surface-to-volume ratio of nanostructured materials leads to increased reactivity and catalytic properties which are particularly very attractive for their chemical and biosensor applications. Current R&D trends thus suggest that nanoscience and nanotechnology is expected to make tremendous impact on the development of highly sensitive, small sized, and low-cost chemical and biological sensor devices.

Recently, nanomaterials in different structured forms such as nanowires, nanorods, nanobelts, nanorings, and nanocrystals, as they provide remarkable high surface area and interfacial properties compared to their counterpart at macroscopic size scale, are increasingly attractive for different types of sensing devices. Nanomaterial-based sensors may be used in the form of thin or thick films or porous pellets. The microstructure, namely high ratio of surface area-to-volume, very small grain and pore sizes, and shape of metal/metal oxide particles, are important for sensing properties, which gives better sensitivity and reproducibility due to activeness of all adsorbed species in producing a surface-depletion layer. It has been demonstrated that when the particle radius becomes comparable to the depth of the space charge layer, the space charge region can develop throughout the crystallites, thus leading to drastic resistance changes. In addition, the high surface-to-bulk ratio of nanoparticles allows a large density of molecules to get adsorbed on the surface, thus leading to a big effect on the electrical conductivity. Further, additives such as *Ag*, *Au*, *Pd*, *Pt*, etc. influence the microstructure of metal oxides and are beneficially used in generating specificity and enhancement of sensitivity at reduced temperature. Similarly, the diameter of nanostructured materials are comparable to the size of chemical and biological species, which sense and intuitively represent excellent primary transducers for producing signals that ultimately interface with macroscopic instrument. Inorganic nanostructured materials and nanocrystals exhibit unique electrical and optical properties that can be exploited for sensing. The size-tunable colours of semiconductor nanocrystals[11,12], together with their highly robust emission properties, are opening up new opportunities for labeling and optical-based detection of biological species that offer advantages when compared with conventional organic molecular dyes widely used these days. These characteristics of the nanostructured materials and nanocrystals suggest that devices based on these could revolutionise many aspects of sensing and detection of biological and chemical species. Some of the sensors based on different classes of nanostructured materials are discussed.

2.1 Nanoparticle Sensors

2.1.1 Chemical Sensors

Semiconductor metal oxide (SMO) materials such as SnO_2, ZnO, TiO_2, WO_3, etc. are considered to be better materials for chemical sensors as compared to other gas-sensing materials/techniques such as conducting polymers, oscillators (QMB, BAW, and SAW), electrochemical cell and optical fibres. SMO gas sensors have certain specific advantages such as higher robustness, up to 10 years of life, less sensitive to environmental moisture and temperature, simple interface electronics, faster response and recovery time, etc.. The sensing properties of SMOs are highly influenced by a number of parameters including phase composition, structure, type of dopants, morphology, grain size, etc. Further, the reduction in grain size has remarkable effects on gas-sensing properties of the materials. When particle size is reduced to nanometers, especially because of the fact that the dimension of the crystallite is of the order of the thickness of the charge-depletion layer; energy band bending is no longer restricted to the surface region but extends into the bulk of the grains. In other words, the properties of the whole grain, not just the surface, may change completely due to solid-gas interactions. Accordingly, nanostructure is expected to have a dramatic influence on sensor performance.

Amongst the different categories of nanostructures, viz., nanoparticles, nanowires, nanotubes, nanobelts, etc., the nanoparticles are the most studied materials due to certain specific advantages such as ease of preparation, high surface-to-volume ratio, scope of developing large variety of materials with very good control on the particle size, availability of greater number of active centres. Examples of some such sensors are discussed below. Among the large number of nanocrystalline SMOs, SnO_2, in its pure and doped states, is the most widely studied materials for gas-sensing applications.

Zhang[13], *et al*. have reported the effects of composition, microstructure, and defect chemistry on the sensing performance of gas sensors based on *CuO*-doped SnO_2. It has been reported that SnO_2 (*CuO*) is more sensitive to *NO* as compared to pure SnO_2. When exposed to 1000 ppm of *NO* in *Ar*, the resistance of SnO_2 (*CuO*) changed by a factor of 4.3 as compared to a value of 2.9 for pure SnO_2 and showed shorter response time at a much lower temperature of 200 °C as compared to 300 °C for pure SnO_2. The authors have also studied the effect of particle size on the sensitivity of *CuO*-doped SnO_2 and found it to increase with decrease in the particle size. The sensor response to CO_2 and oxygen have also been reported.

Sarala Devi[14], *et al*. have done comparative studies on the electrical response of micron-sized SnO_2 particles

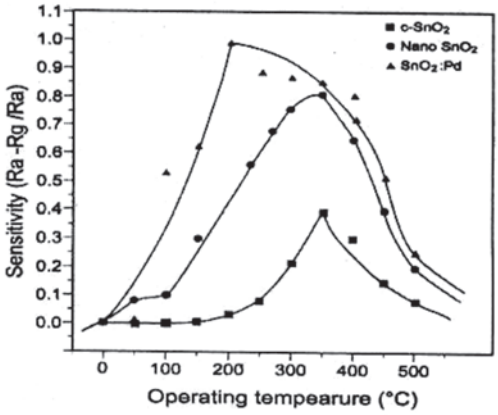


Figure 3. Temperature dependence of the sensitivity of SnO_2 thick films at different operating temperatures.

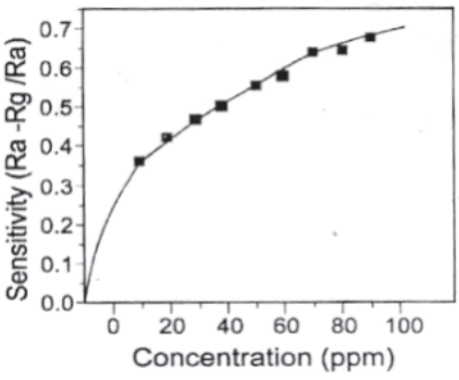


Figure 4. Sensitivity as a function of different concentrations of LPG gas at 200 °C.

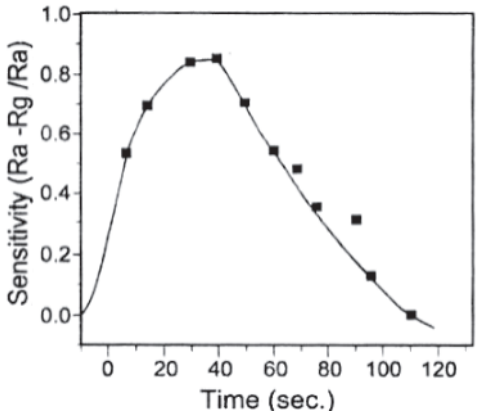


Figure 5. Response of the SnO_2:*Pd* thick film to 200 ppm LPG at 200 °C.

with that of nanocrystalline SnO_2 and SnO_2:*Pd* to LPG. The results show (Fig. 3) a drastic increase in the sensitivity of the sensor fabricated using nanosized SnO_2 than the conventional SnO_2 powder at an operating temperature of 350 °C. Further, the addition of small amount of noble metal Pd (0.1 per cent) resulted not only in the increase of sensitivity but also brought down the operating temperature from 350 °C to 200 °C. The detectability of LPG by the sensor was observed at as low as 10 ppm concentration level which has been attributed to the smaller size (7–10 nm) of particles (Fig. 4). The enhancement of sensitivity due to addition of *Pd* was attributed to the increase in adsorption sites for the sensing as well as to the change in oxidation state of *Pd*. The sensor was reported to show a quick response and recovery times of 50 s and 60 s, respectively (Fig. 5).

Sarla Devi[15], *et al*. have also reported the sensing properties of nanocrystalline *ZnO*-based thick films for NH_3. From the temperature-dependence of sensitivity studies the authors have reported that the nano-*ZnO* sensors show higher sensitivity as compared to the one prepared by using commercial *ZnO* (*C-ZnO*) powder (Fig. 6). The transient response characteristics of the sensors obtained at 300°C (Fig. 7) show that the nano-*ZnO* sensor exhibits relatively fast response and recovery time (35 s) whereas the response and recovery time for *C-ZnO* was 50 s. The authors have also reported the studies on the effect of *Pd* impregnation in nano-*ZnO* on gas-sensing properties for NH_3, N_2, LPG and H_2. At an optimum operating temperature of 300 °C, the sensor showed high sensitivity to NH_3 gas (S = 0.68) and was less sensitive to N_2 (0.1), LPG (0.25) and H_2 (0.32), thereby, suggesting that the sensor can be used for selective detection of NH_3.

Baruwati[16], *et al*. reported the gas-sensing properties of highly crystalline nanoparticles of *ZnO* prepared by hydrothermal route. The sensor response versus operating temperature for, as synthesised, *ZnO* nanoparticles towards reducing gases, viz. LPG and *EtOH* is shown in Fig. 8. The nanoparticles show typical *n*-type conductivity behaviour, as observed by a drop in voltage across the sensor element, indicating decrease in electrical resistance when exposed to both the reducing gases. Although the response of the

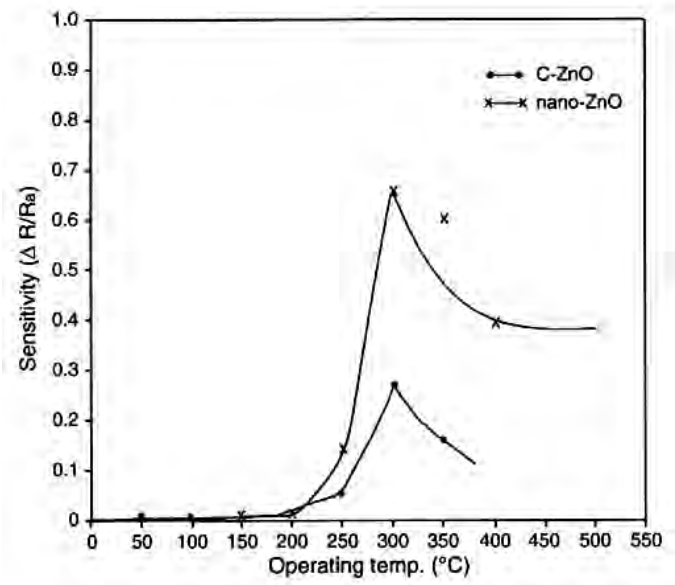


Figure 6. Sensitivity as a function of operating temperature of: (a) nano-*ZnO* and (b) *C-ZnO* exposed to 100 ppm NH_3 gas at 300 °C.

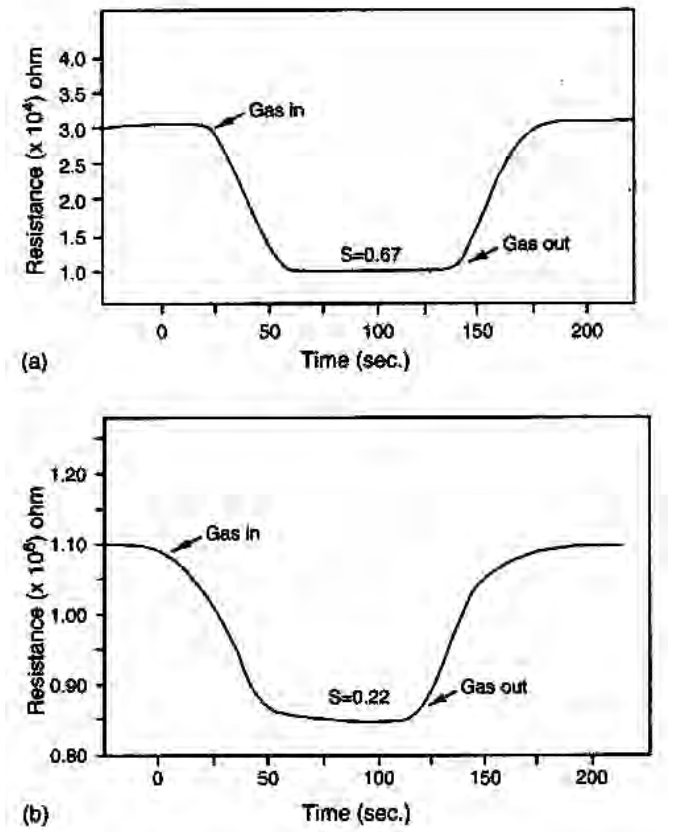


Figure 7. Transient response characteristics of *ZnO* exposed to 100 ppm NH_3 gas at 300 °C for: (a) nano-*ZnO* and (b) C-*ZnO*.

sensor is slightly better for *EtOH* at the same operating temperature (around 250 °C), its response to other interfering gases like H_2, NH_3, etc was very low as compared LPG and *EtOH*. Further studies on *ZnO* nanoparticles, incorporating 0.1 per cent *Pd*, showed a reduction in operating temperature by > 100 °C.

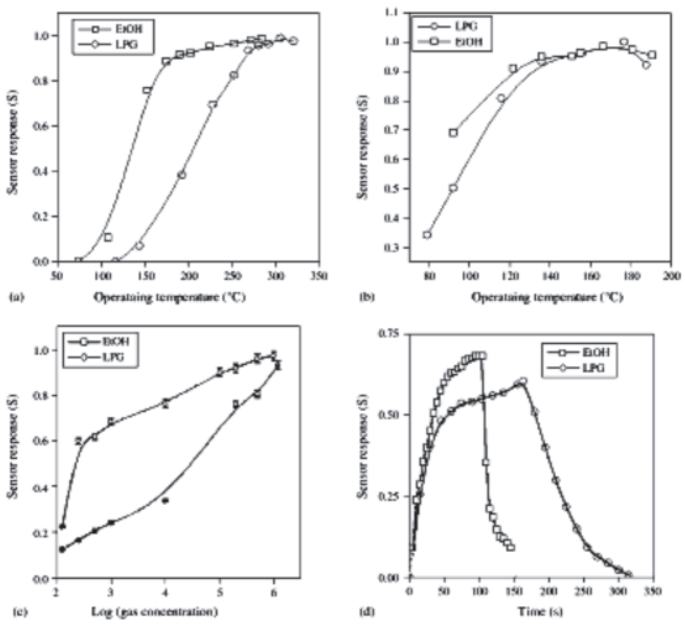


Figure 8. (a) Sensor response(S) versus opertaing temperature plot of *ZnO* nanoparticles towards 10 per cent LPG and Et-*OH*, (b) sensor response(S) versus operating temperatures plot of the *ZnO* nanoparticles towards 10 per cent LPG and Et-*OH* after 0.1 per cent *Pd* incorporation. (c) sensor response(S) versus logarithimic gas concentration plot of the *Pd*-incorporated *ZnO* nanoparticles at 170 °C. Error bar indicates the standard deviation, and (d) response characteristics of the *Pd*-incorporated *ZnO* nanoparticles to 200 ppm LPG and Et-*OH* at 170 °C. (Reproduced with permission from[16].© 2006 Elsevier Science)

Recently, several reports have appeared on the synthesis of nanocrystalline TiO_2 (NC TiO_2) and studies on their gas-sensing properties. Akbar[17], *et al.* have reported comparative studies on H_2 sensing properties of TiO_2 and mixed samples of SnO_2 and TiO_2 wherein it was observed that samples with higher surface areas were more sensitive to H_2 in the presence of oxygen. Ruiz[18], *et al.* reported the effects of various metal additives, viz., *Au*, *Ag*, *Pt*, *Pd*, *Cu*, *Co*, *Nb*, and *V*, on the gas-sensing performances of TiO_2 nanocrystals. Among different additives tested, *Au* was found to be the most attractive promoter for the *CO* sensing properties. Huo[19], *et al.* have reported studies on gas-sensing properties of nanosized titania thin films towards various alcohol gases.

Although extensive studies have been reported on gas-sensing properties of nanoparticles of different materials, there are only few reports on the gas sensors based on nanocomposite materials. In DL, Jodhpur, Kumar[20-22], *et al.* reported a novel method for room temperature synthesis of nanocomposites of metals and mixed metal oxides in a copolymer matrix of aniline-formaldehyde. The thin and thick films of pure and aluminum-doped ã-Fe_2O_3 have been reported to show high sensitivity, at ppm level, towards polar toxic gases such as NH_3, *CO*, *HCl*, *HCN*, oxides of sulphur and nitrogen[23,24]. The current versus *CO* concentration curve (Fig. 9) shows linear response of the sensor material

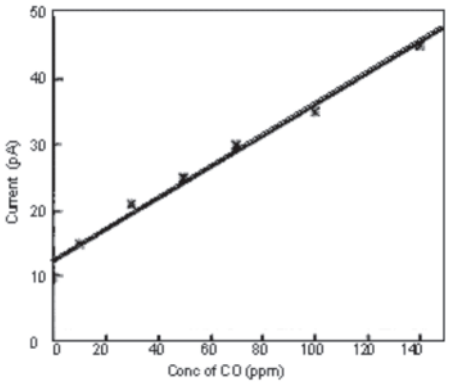


Figure 9. Plot of concentration of *CO* versus current for the sensor based on nanocomposite of aluminum doped iron oxide in a copolymer matrix of aniline-formaldehyde.

up to concentration level of 140 ppm. The sensors based on these materials have been found to show fast response and excellent reversibility. Gas-sensing studies on nanocomposites of TiO_2 and SnO_2 in conducting polymer matrix have been reported by Ram[25], *et al*. Kotsikau[26], *et al*. have reported the synthesis of Fe_2O_3-SnO_2 nanocomposites by sol-gel technology and influence of phase composition, structural peculiarities and grain size of particles on the gas-sensing properties towards NO_2 and C_2H_5OH.

2.1.2 Biosensors

There has been significant interest in metal nanoparticles due to their applications as sensor in biological and medical fields. These particles also have remarkable recognition capabilities of biomolecules, which lead to miniature biological electronics and optical devices including probes and sensors. Such devices may exhibit advantages over existing technology, not only in size but also in performance. For example, DNA sequence-specific detection is the most important topic nowadays because of its application in the diagnosis of pathogenic and genetic diseases. Mostly, gold metal nanoparticle-based nanoprobes and sensors have been employed for detection of DNA-specific sequence, DNA hybridisation, and polynucleotide detection. Recently, Sun[27], *et al*. have reported studies on DNA-based nanomaterials as biosensors for detection of DNA sequence and hybridisation. Similarly, Fritz[28], *et al*. have demonstrated DNA immobilisation and hybridization using microcantilever measured by optical deflection detection. To simplify the detection system, Marie[29], *et al*. developed cantilever systems using piezoresistive detection system instead of optical deflection method for sensing DNA hybridisation. In addition to metal nanoparticles, there are also a large number of studies on semiconducting quantum dots conjugated with biomolecules as novel probes. These dots provide important advantages of water solubility and biocompatibility when compared with organic dyes. Further, the emission wavelength of quantum dot nanocrystals changes with different crystal sizes and a single light source can be used for simultaneous excitation of all different-sized dots. These novel optical properties render quantum dots ideal flurophores for ultrasensitive, multicolour, and multiplexing applications in molecular biotechnology and bioengineering.

2.2 Nanowire-based Sensors

2.2.1 Chemical Sensors

The unique and fascinating properties of nanostructured materials have triggered tremendous motivation among researchers to explore the possibilities of using these in various shapes and sizes for sensing applications. Amongst various nanostructures, inorganic quasi one-dimensional (Q1D) systems show promising sensing capabilities for gas molecules and biological species. Mostly, semiconducting Q1D systems are natural candidates for chemical-sensing applications due to their large surface-to-volume ratio and finite charge carrier concentration, which can be significantly influenced by the chemical surroundings. It has been well accepted that the electrical property change is the consequence of charge transfer between Q1D systems and chemisorbed species. Based on the mechanism of detection, various Q1D systems have been configured as chemical sensors

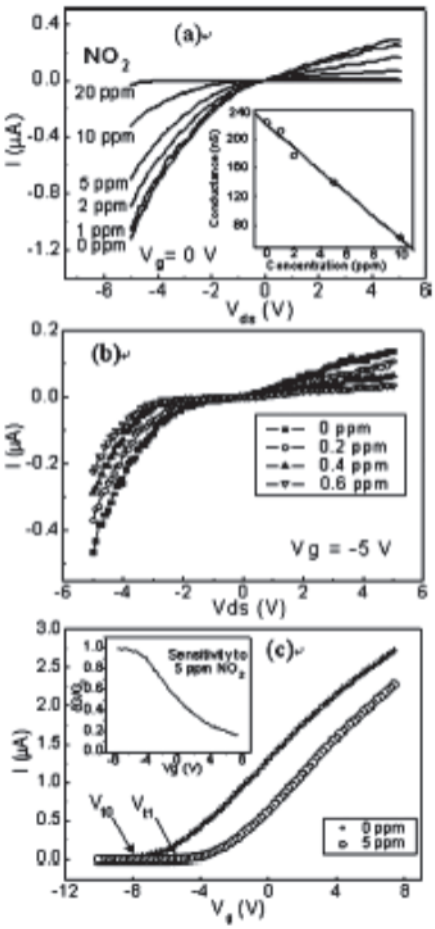


Figure 10. (a) *ZnO* NW I–V curves obtained in different NO_2 concentrations at $Vg = 0$ V and $Vg = -5$ V (b) Inset: NW conductance versus NO_2 concentration at $Vds = -5$ V (c) NW FET *I–Vg* curves obtained in pure *Ar* (0 ppm), 5 ppm and 10 ppm NO_2. Inset: detection sensitivity as a function of gate voltage. (Reproduced[30] with permission from American Institute of Physics, 2005).

for detection of toxic and flammable gases such as NO_2, CO, NH_3, ethanol, etc. For example, Fan[30], *et al.* demonstrated *ZnO* nanowire field effect chemical sensor for detection of NO_2 and NH_3 at room temperature (Fig. 10). It was observed that the detection sensitivity can be tuned by the back gate potential and large negative gating could significantly expedite the desorption process at room temperature. Further, the ammonia-sensing behaviour of nanowires was observed to switch from oxidizing to reducing when temperature was increased from 300K to 500K.

Similarly, Rao[31] *et al.* prepared *ZnO* nanowires by electrochemical deposition in alumina membranes as well as *ZnO* nanotubes and their sensing characteristics were investigated for H_2 and ethanol vapour. The sensing properties of these nanostructures were also investigated after impregnating these with 1 per cent *Pt*. They observed that nanowires after impregnation with *Pt* show excellent sensitivity to H_2 and low concentration of ethanol vapour at relatively low temperatures (=150 °C).

Further, Xiangfeng[32], *et al.* fabricated gas sensors from In_2O_3 nanowires and investigated their gas-sensing properties. Sensors based on In_2O_3 nanowires exhibited excellent performance, characterised by high response, good selectivity, very short response time to dilute C_2H_5OH and proved to be practical detectors for dilute ethanol.

For O_2 gas detection, nanostructured titania pad arrays were fabricated by Zuruzi[33], *et al.* wherein, anatase titania was formed in sponge-like structure consisting of interconnected nanoscale wires and walls. The variation of hundreds of oxygen molecules over a 20 µm nanostructure titania square pad sensing element were detected at 250 °C. These sensors operate at lower temperature, show fast response time and superior sensitivity relative to oxygen sensors based on porous undoped titania.

Another class of metal oxide nanofibres also show high sensitivity and selectivity for amines. Rible[34], *et al.* fabricated chemiresistor-type gas sensor by the deposition of V_2O_5 nanofibres from aqueous suspension onto silicon substrate. Due to high conductivity of these fibres, sensors could be operated at room temperature. The researchers observed that these sensors were extremely sensitive for 1-butyalamine (limit of detection below 30 ppb) and moderate sensitivity for ammonia. The response transients ($\Delta R/R_{ini}$) of the V_2O_5 chemiresistors are shown in Fig.11.

Recently, Sawicka[35], *et al.* synthesised composite nanostrucrures consisting of polymer (PVP) and metal-oxide nanofibres/nanowires of MoO_3/WO_3 using electrospinning technique. They observed that WO_3 nanofibres can be used as NO_2 gas-sensing elements and the results were superior in terms of sensitivity (Fig. 12), faster response and lower gas detection limits compared to sol-gel processed films of the same materials. Recently, Dobrokhotov[36], *et al.* fabricated chemical sensors of GaN nanowires decorated by gold nanoparticles and their electrical properties as a function of exposure to *Ar*, N_2, and methane gas. It was observed that gold nanoparticle-decorated nanowires exhibit chemically selective responses. These sensors exhibited a nominal response to *Ar* and slightly greater response to N_2 (Fig. 13).

In addition to metal-oxide nanowires, metal/semimetal nanowires are also attractive for sensing applications.The method of fabrication of different metal nanowires on various substrates and their sensing properties were studied. For example, Atsbar[37], *et al.* fabricated arrays of *Pd* nanowire on to the top step edges of highly oriented pyrolytic graphite

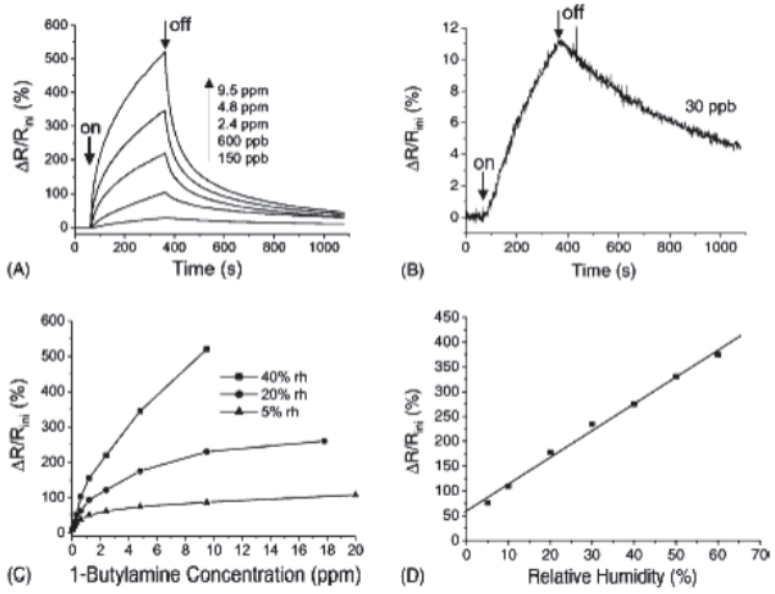


Figure 11. Response transients (R/R_{ini}) of the V_2O_5 chemiresistor at 40 per cent R*H* to 1-butylamine: (a) between 150 ppb and 9.5 ppm, (b) at 30 ppb, (c) shows the response amplitudes measured after 300 s analyte exposure as a function of the1-butylamine concentration, at 5 per cent R*H*, 20 per cent R*H*, and 40 per cent R*H*. (d) shows how the response amplitude to 1.2 ppm 1-butylamine vapour increases linearly by 5.4 per cent with increasing humidity by 1 per cent. All measurements were performed at room temperature. (Reproduced[34] with permission from Elsevier Science, 2005).

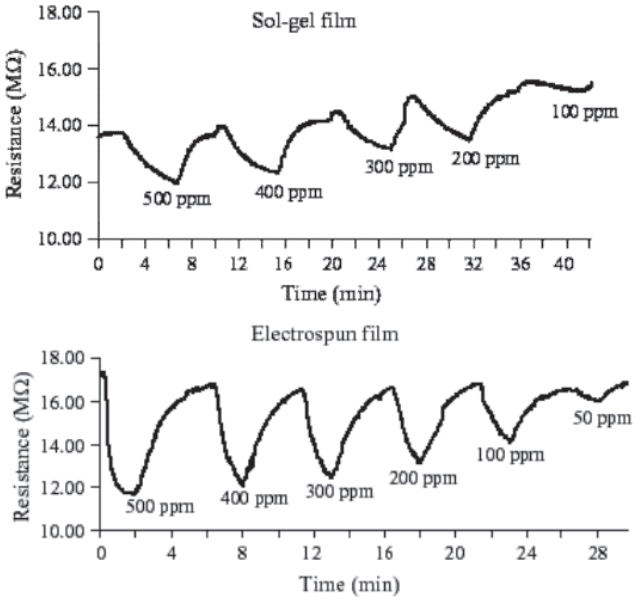


Figure 12. (a) Sensing data for the sol-gel-based WO_3 thin film's response to NO_2 and (b) Sensing data for the nano-fibre-based WO_3 film response to NO_2. (Reproduced[35] with permission from Elsevier Science, 2005).

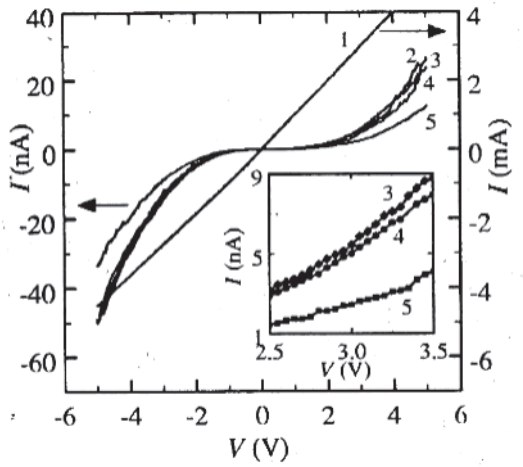


Figure 13. V-I curves of bare GaN nanowires sensor (1) (right hand vertical axis) and a sensor constructed from material of gold nanoparticle-decorated GaN nanowires (curves2-5) (left-hand scale) for in vacuum(2), and atmospheres of *Ar*(3), N_2(4), and methane (5). The inset is an expanded view of the I-V data in the first quadrant (♦: vacuum, •: N_2, ■ :methane). (Reproduced[36] with permission from American Institute of Physics, 2006).

using electrodeposition technique. Later on, these nanowires were transferred on to nonconducting polymer surfaces to study the gas-sensing properties. It has been observed that the sensor response to H_2 gas was fast and resembled a switch with two orders of magnitude change in conductance. Recently, Shao[38], *et al.* reported that the *Si* nanowire film modified with can be used as a sensor for glucose detection in aqueous solution. These sensors also show wide linear range (0–10 mM glucose), high sensitivity (172 nA/m mol^{-1}), good reproducibility and long term stability. Further, nanowire films of *Si* modified with *Mg* are shown to perform as sensors for detecting H_2O_2 in aqueous solution. Recently, Kamins[39], *et al.* have grown metal-catalysed silicon nanowires in between silicon electrodes and their sensing properties were studied by exposing to vapours containing *HCl* or NH_3 at reduced pressure. These nanowires showed increase in conductance while exposed to *HCl* vapour and decrease in conductance to NH_3 vapour.

2.2.2 Biosensors

Since the nanowire diameter can be comparable with the size of biomolecules, these materials could be exploited for detection of biological species. Cui[40], *et al.* demonstrated sensitive biochemical sensor using biotin-modified (*B*-doped) *Si* nanowires to detect streptavidin down to pico molar concentration. They also showed that antigen-functionised

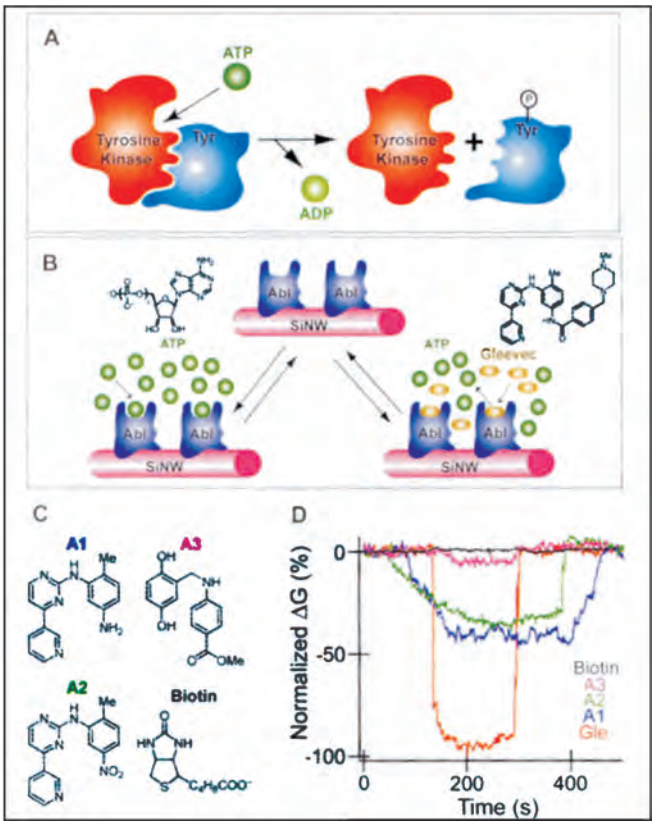
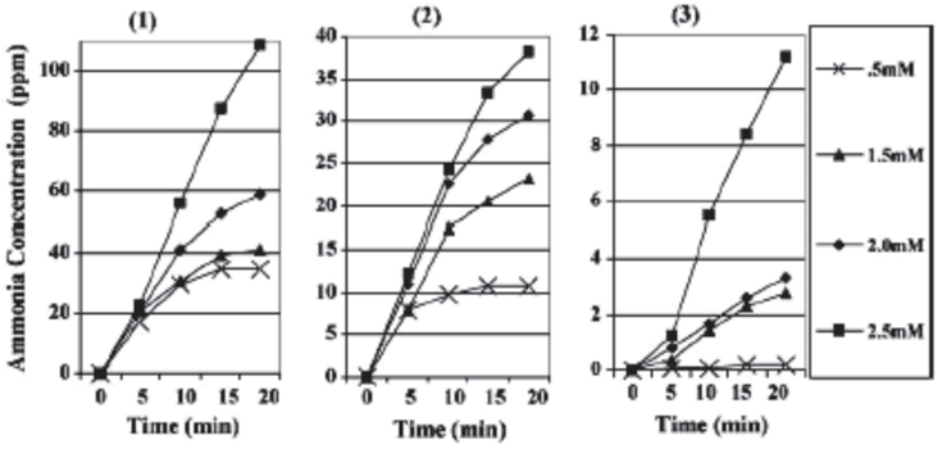


Figure 14. Nanowire sensors for drug discovery (A) ATP (adenonsine triphosphate) binds to the kinage active site and than phosphate is transferred to a tyrosine (Tyr) residue of the substrate protein, (B) detection of ATP binding and a small-molecule inhibition using Si nanowire sensor device functionalised with the tyrosine kinase Abl, (C) structures of small molecules investigated for the inhibition of ATP binding to Abl, and (D) normalised conductance versus time data recorded from Abl-modified *Si* nanowire devices using solutions containing 100 nMATP and 50 nM small molecule Gleevec (red), A1 (blue), A2 (green), A3 (pink), and biotin (black). (Reproduced[41] with permission from National Academy of Science,USA, 2005).



(a) (b) (c)

Figure 15. Ammonia concentration versus time when urea solutions reacted with (a) 0.2 ml of urease in PBS buffer, (b) 0.2 ml 30 per cent urease in buffer/70 per cent PVP in ethanol solution, and (c) 0.1 ml of urease/PVP nanofibre material. (Reproduced[44] with permission from Elsevier Science, 2005).

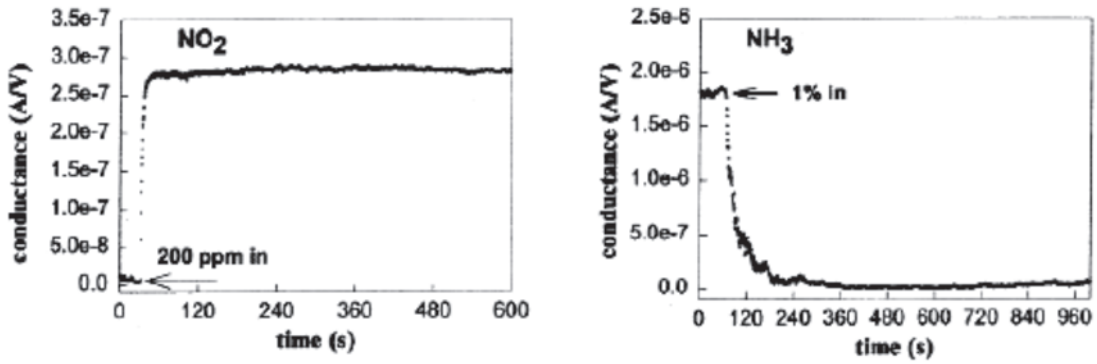
Si nanowires showed reversible antibody binding and concentration-dependent detection in real time.

Further, Patolsky and Liber[41] in their review have described the *Si* nanowire-based FET devices for protein, DNA, drug molecules and viruses down to single molecule detection (Fig. 14). Similarly, Curreli[42], *et al*. demonstrated selective functionalisation of an array of In_2O_3 nanowire-based devices by electrochemically activating their surfaces and then immobilising single-stand DNA. Recently, Kumar[43], *et al* reported that nanoscale *ZnO* structures can be effectively used for the identification of the biothreat agent like *Bacillus anthracis* by successfully discriminating its DNA sequence from other genetically related species. The authors have explored both covalent and non-covalent linking schemes to couple probe DNA strands to the *ZnO* nanostructures. They observed that the use of nanomaterials greatly enhancesd the fluorescence signal collected after carrying out duplex formation reaction. Further, they found that the presence of underlying *ZnO* nanomaterials were critical in achieving increased fluorescence detection of hybridised DNA and therefore accomplishing rapid and extremely sensitive identification of the biothreat agent. In addition, Sawicka[44], *et al*. prepared nanocomposite fibres of urease and PVP by the electrospining technique and the materials have proved to be good urea biosensors. These sensors may find their applications in the areas of medical diagnosis, environmental and bio-industrial analysis. (Fig. 15)

2.3 Nanotube-based Sensors

2.3.1 Chemical Sensors

Nanotubes of carbon and metal oxides have been attractive since last few years for their sensing properties for different analytes. Among these nanotubes, carbon nanotubes (CNTs) are mostly used as sensor devices. In 2000, Colin[45], *et al*. demonstrated that CNTs exhibit very good adsorption properties because of their high specific surface area and a nano-scale structure that provides a large number of sites where the gaseous molecules can react. The adsorption of gaseous molecules on to the surface of a CNT alters its electrical properties, enabling the CNT to act as a gas sensor. Such sensors operate at room temperature, since then, various sensing devices have been fabricated using different structural CNTs (single-walled and multi-walled) and their sensing characteristics have been studied by a number of researchers at room temperature. For example, Kong[46], *et al*. developed a gas sensor based on single-walled carbon nanotube (SWCNT),



(a) (b)

Figure 16. (a) Electrical conductance response of a semiconducting SWNT to 200 ppm NO_2 (b) Electrical conductance response of a semiconducting SWNT to 1 per cent NH_3. vapour. (Reproduced[46] with permission from Science Publishing Group, 2000).

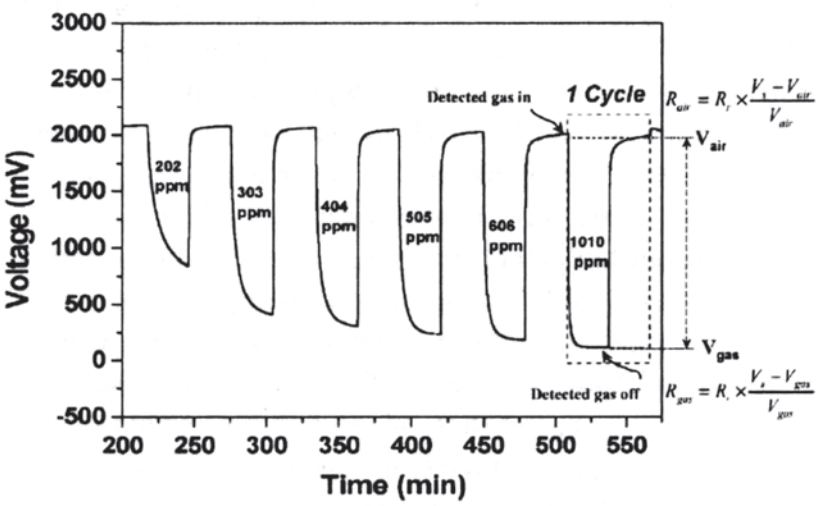


Figure 17. Response curve of hybrid SWCNTs/SnO_2 sensor to NO_2 in N_2 at room temperature. (Reproduced[48] with permission from Elsevier Science, 2004).

whose electrical conductance changes quickly on exposure to gaseous molecules such as NO_2 and NH_3 with very high sensitivity. They found that conductivity of the semiconducting SWCNT changed rapidly over several orders of magnitude upon exposure to NO_2 and NH_3 gases. In particular, an increase in the conductivity by up to three orders of magnitude was observed within 10 s after exposing the SWCNT to 200 ppm NO_2, while conductivity decreases by two orders of magnitude, within 2 min, upon exposure to 1 per cent NH_3 vapour (Fig. 16). Recently, Young[47], *et al*. achieved ultra high sensitivity detection of NO_2 gas using composite films of SWCNT mesh doped with alkanethiol monolayer-protected gold clusters (MPC). They observed that the detection limit of NO_2 gas was improved 9.6-fold to 4.6 ppb compared with pure SWCNT sensors.

In addition, Wei[48], *et al* have fabricated new hybrid SWCNTs/SnO_2 gas sensors by adding SWCNTs into SnO_2 substrate. Later on, these hybrid sensors were utilised for the detection of NO_2 in flowing air or N_2 and have shown much higher sensitivity and recovery property than a pure SnO_2 sensor. (Fig. 17).

For organic vapour detection at room temperature, Penza[49], *et al*. fabricated microacoustic sensors, wherein SWCNTs were embedded in cadmium arachidate (*CdA*) amphiphilic matrix. This microacoustic sensor was based on surface acoustic waves (SAWs) ST, X quartz 315 MHz and 433 MHz two-port resonator oscillator. The measured acoustic sensing characteristics indicated that the SAW sensitivity of the composites to polar and non-polar organic molecules (ethanol, ethyalacetate, and toluene) was up to two times higher than that of unembedded *CdA* devices. Recently, Consales[50], *et al*. fabricated multilayers of SWCNTs with different thicknesses and successfully transferred these directly on to the sensor surfaces and tested for detection of toluene and xylene at room temperature. The results obtained indicate that SWCNTs-based sensors showed high sensitivity, very low limit of VOC detection.

Apart from the SWCNTs, MWCNTs-based gas sensors have been developed by various authors. For example,

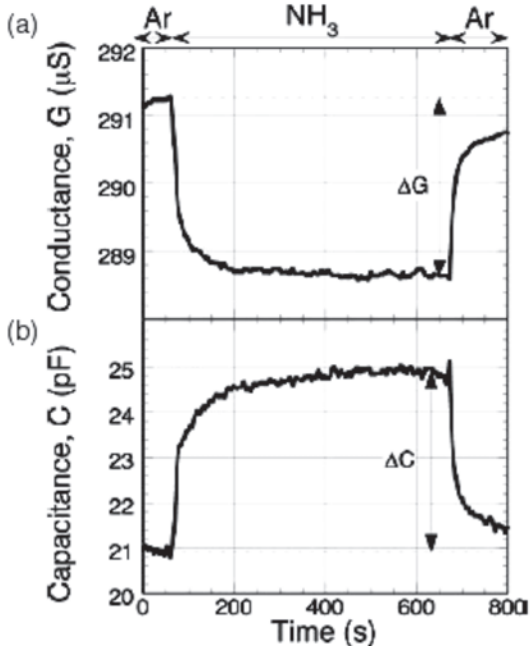


Figure18. Impedance response of the MWCNT gas sensor to ammonia gas (10 ppm). The sensor was obtained after a 3 h DEP trapping process.The amplitude and frequency of the electrode energising potential were 8 V (peak-to-peak) and 100 kHz, respectively. (*a*) conductance response, (*b*) capacitance response. (Reproduced[51] with permission from Institute of Physics, UK, 2003).

Suehiro[51], *et al*. successfully fabricated MWCNTs-based gas sensors by positive dielectrophoresis (DEP) on a microelectrode array. In this sensor, MWCNTs were trapped and enriched in an interdigitated microelectrode gap under the action of DEP force. Finally, microelectrode-retaining MWCNTs was exposed to NH_3 gas while electrode impedance was monitored. It was found that electrode impedance was altered on its exposure to NH_3 at ppm level at room temperature. The impedance response of the MWCNT sensor to ammonia gas (10 ppm) is shown in Fig. 18 and conductance change as a function of NH_3 gas concentration is shown in Fig. 19.

The metal oxide nanotube-based gas sensors have

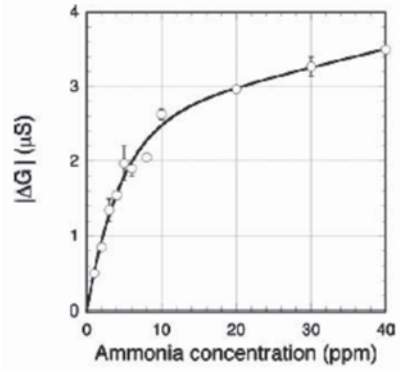


Figure 19. Conductance change of the MWCNTs gas sensor as a function of ammonia. (Reproduced[51] with permission from Institute of Physics, UK, 2003).

also been reported by many researchers. Recently, Chen[52], *et al*. synthesised MCo_2O_4 (*M = Ni, Cu, Zn*) nanotubes by a porous alumina-template method. These nanotubes show excellent selectivity and high sensitivity to various gases such as ethanol and SO_2 due to their one-dimensional electronic conductivity. Similarly, Hamaguchi[53], *et al*. fabricated SnO_2 nanohole arrays by liquid phase deposition method. These nanohole arrays, later on covered by noble metal electrodes (*Au*, *Pt*, and *Pd*) and their sensing properties were studied under exposure to H_2 gas. These sensors exhibited reversible response to H_2 in air and their temperature-dependent gas responses were studied by varying the electrode positions. The authors reported that H_2 response was much higher in the sensor coated with a pair of electrodes at both the surfaces as compared to sensor equipped with inter-digitated electrodes on one side only.

2.3.2 Biosensors

Carbon nanotube is an equally attractive material for the development of biosensors because of its capability to provide strong electrocatalytic activity and to minimize surface fouling of the sensors. A disposable biosensor based on acetyl cholinesterase–functionalised acid purified MWCNTs-modified thick filmstrip electrode for organophosphorus (OP) insecticides has been developed by Sotiropoulou and Chaniotakis[54]. The degree of inhibition of the enzyme acetylcholinesterase (AChE) by OP compounds was determined by measuring the electrooxidation current of the thiocholine generated by the AChE catalysed hydrolysis of acetylthiocholine (ATCh). This biosensor detected as low as 0.5 nM (0.145 ppb) of the model organophosphate nerve agent paraoxon with good precision, electrode–to–electrode reproducibility and stability.

Similarly, glucose biosensor has been fabricated based on immobilising glucose oxidase (GO_x) on the negatively charged CNT surface by alternatively assembling a cationic polydiallldimethylammonium chloride (PDDA) layer and a GO_x layer[55]. The unique sandwich-like layer structure (PDDA/GO_x/PDDA/CNT) formed by self-assembling provides a favorable microenvironment to keep the bioactivity of GO_x and to prevent enzyme molecule leakage. The excellent electrocatalytic activity towards H_2O_2 of the fabricated PDDA/GO_x/PDDA/CNT electrode indicated that the polyelectrolyte –protein multilayer does not affect the electrocatalytic properties of CNT, enabling sensitive determination of glucose. The detector has a wide linear response range of 15 μM to 6 mM and detection limit of 7 μM. This biosensor has shown excellent properties for the sensitive determination of glucose with good reproducibility, remarkable stability, and freedom of interference from other coexisting electroactive species.

Another amperometric biosensors based on functionalised MWCNTs grown on *PT* substrate for detecting glucose has been developed by Anthony[56], *et al*. The opening and functionalisation by oxidation of the nanotube array allows for the efficient immobilisation of the model enzyme, glucose oxidase. The carboxylated open-ends of nanotubes were used for the immobilisation of the enzymes, while the *Pt* substrate provided the direct transduction platform for signal monitoring. This sensor showed linear response from 0.25 to 2.5 mM of glucose and sensitivity of 93.9 ± 0.4 μAmM^{-1} cm^{-2}.

Further, CNTs have been used for DNA detection[57]. The high surface area of SWCNTs provides additional advantages in DNA detection.To date, there are several reports on electrochemical detection hybridisation using MWCNTs electrodes. Whereas electrochemical methods rely on electrochemical behaviours of labels, measurement of direct electron transfer between SWNTs and DNA molecules paves the way for label-free DNA detection. SWNT-based field-effect transistors have been developed[57] and explored for highly sensitive electronic detection of biomlecules such as antibodies.

2.4 Nanobelt-based Sensors

Nanobelts of semiconducting oxide, with ribbon like morphology are very promising for sensor applications due to further enhancement in the surface-to-volume ratio. In the polycrystalline and the thick film devices only a small fraction of the species adsorbed near the grain boundaries is active in modifying the device, electrical transport properties. On the other hand, in the new sensors based on single crystalline nanobelts, almost all of the adsorbed species are active in producing a surface depletion layer. Although, many different oxides have been investigated for their gas-sensing properties, the most promising material for gas sensors in the form of thin or thick films or porous pellets is SnO_2. Therefore, intense research has been focused for the fabrication of SnO_2 nanobelts of different sizes and as a matter of interest, for their sensing properties. In addition, since the size of the depletion layer for SnO_2 due to oxygen ionosorption penetrates 50 nm or more through the bulk, the belts are probably almost depleted of carriers as a pinched-off FET because belt thickness is typically < 50 nm. The presence of poisoning species will switch the structures from a pinched-off to conducting channel with strong modification of electrical properties. Further, reduction of belt size could lead to the development of quantum

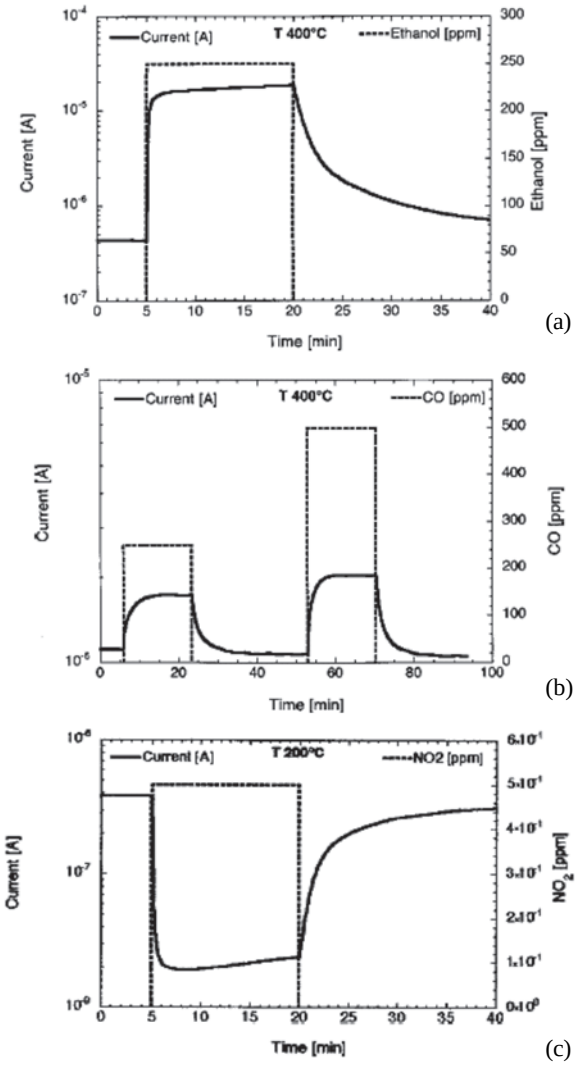


Figure 20. (a) Response of the SnO_2 nanobelts to ethanol at a working temperature of 400 °C and 30 % RH. (b) Response of the SnO_2 nanobelts to CO at a working temperature of 400 °C and 30 % RH. (c) Response of the SnO_2 nanobelts to NO_2 at a working temperature of 200 °C and 30 % RH. (Reproduced[58] with permission from American Institute of Physics, 2002).

confined structures and nanodevices. For example, Comini[58], *et al*. fabricated gas sensors using single crystalline SnO_2 nanobelts. These nanobelt sensors are shown to be very sensitive to polluting gaseous species like CO and NO_2 and are highly suitable for environmental applications. Further, these sensors also show sensitivity to ethanol vapours in breath analysers and food-control applications. Response current of the SnO_2 nanobelts to different gaseous environment (CO, NO_2 and ethanol) at 30 per cent RH (relative humidity at 20 °C) are shown in Fig. 20. The sensor response, defined as the relative variation of conductance due to the introduction of gas was found 4160 per cent for 250 ppm of ethanol and –1550 per cent for 0.5 ppm NO_2 at 400 °C and 200 °C, respectively. Very recently, Li[59], *et al*. has prepared V_2O_5 nanobelts coated with Fe_2O_3, TiO_2, and SnO_2 nanoparticles by mild hydrothermal reaction. The gas sensitivity of these coated nanobelts were investigated and compared to pure V_2O_5 nanobelts. The experimental results show that the nanobelts coated with nanosize metal oxide offered better sensitivity than uncoated nanobelts. The comparison of the gas-sensitivity properties of V_2O_5 nanobelts with different coating materials was also been demonstrated.

Apart from nanobelts of SnO_2 and V_2O_5, ZnO nanobelts also show gas-sensing properties. Sadek[60], *et al*. fabricated SAW gas sensor based on ZnO nanobelts. In these sensors, 36° YX $LiTaO_3$ and 64° YX $LiNbO_3$ substrates were used as transducing platforms for gas-sensing investigation. ZnO nanobelts layer was deposited on to the active area of SAW devices and sensing behaviour was investigated for H_2 and NO_2 gasses at different operating temperatures between 20 °C to 200 °C. It was observed that, the response of 64° $LiNbO_3$ SAW transducer towards 10 ppm NO_2 with 3.5 kHz frequency shift at 160 °C and 36° $LiTaO_3$ SAW transducer towards 1 per cent H_2 with 3 kHz frequency shift at 185 °C. The response curves of these sensors together with frequency shift wrt NO_2 and H_2 concentration are shown in Figs. 21 and 22. Further, fast response and recovery time were also observed from these sensors.

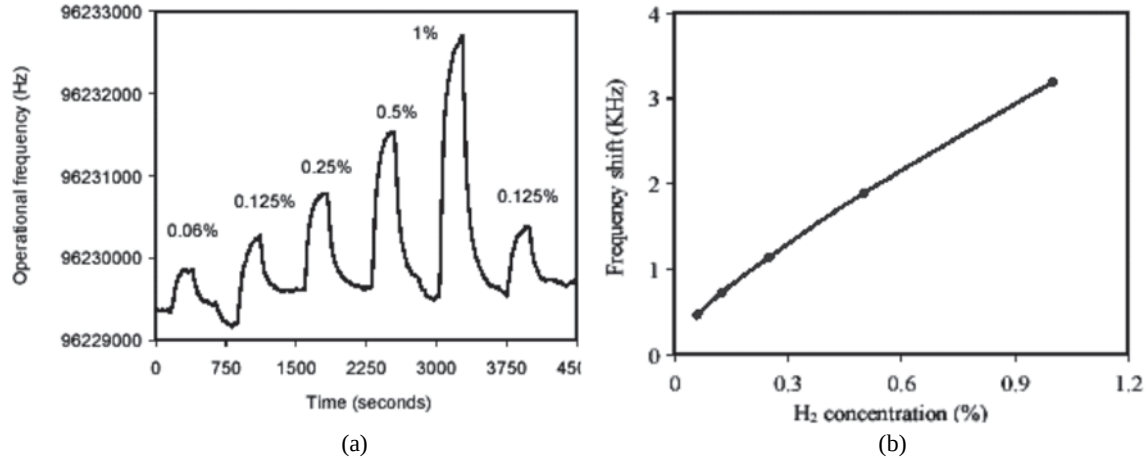


Figure 21. (a) Response of a 36° YX $LiTaO_3$ SAW-based sensor towards different concentrations of H_2 gas at 185 °C and (b) Frequency shifts versus H_2 concentrations (%). (Reprinted[60] with permission from IEEE, 2005).

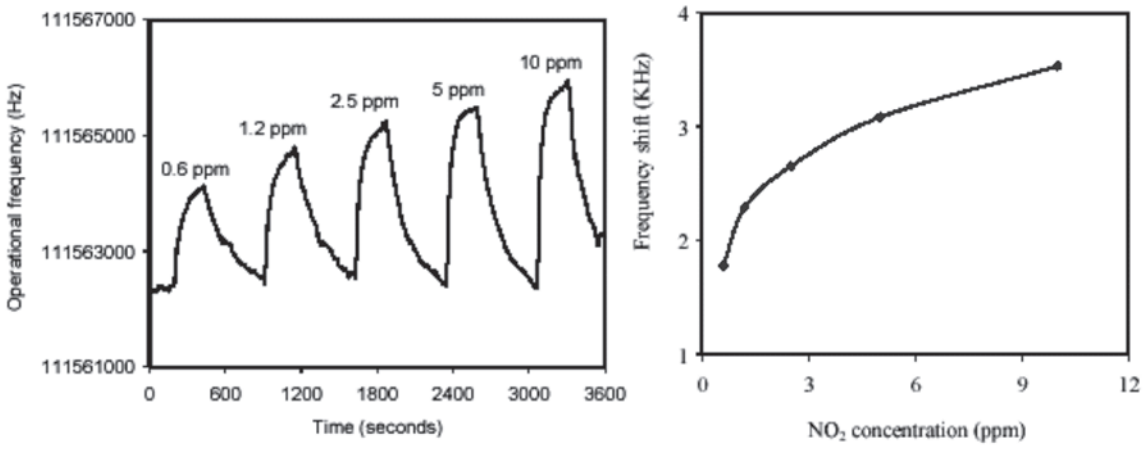


Figure 22. (a) Response of a 64° YX $LiNbO_3$ SAW-based sensor towards different concentrations of NO_2 gas at 160 °C. (b) Frequency shift versus NO_2 gas concentration (ppm). (Reprinted[60] with permission from IEEE, 2005).

3. CONCLUSIONS

The foregoing discussions indicate that the sensors based on nanomaterials in different structural forms, i.e., particles, wires/fibres, tubes, and belts are of great potential, both for detection of chemical and biological species with greater sensitivity and selectivity of analytes. It is expected that through expanded R&D on synthesis of new materials in different structural forms will lead to development of miniaturised devices and find their application in diverse areas such as healthcare, pollution control, and defence, etc.

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