SELECTIVE CO SENSING USING NANOSTRUCTURED TiO_2 GAS SENSORS: A REVIEW

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Abstract- Fabricating a sensor for a toxic gas like carbon monoxide (CO) has been a constant need in many domestic and industrial applications. Although many sensors are commercially available, research is focused on developing a selective CO sensor with higher sensitivity, selectivity and low operating temperature. This paper reviews the fabrication, comparison and evaluation of different nanostructured titanium dioxide (TiO_2) sensors used in CO detection. After a brief description of the structural properties of TiO_2, the article presents sensing mechanism in semiconductor metal oxide sensors. For a reducing agent like CO, the surface reactions result in the reduction of sensor resistance. The parameters associated with sensor performance are discussed. The article presents a summary of main research findings in this field. Nanostructured morphologies offer better sensing performance and selectivity. The improved performance due to nanostructured TiO_2 is highlighted. The review clarifies the specific role of TiO_2 for the future research.

Index terms*:* Carbon monoxide (CO); metal oxide semiconductors; nanomaterials; sensitivity; titanium dioxide(TiO_2).

I. INTRODUCTION

Carbon monoxide (CO) has been considered one of the six principal air pollutants that is harmful to public health and environment by the United States Environmental Protection Agency (USEPA) [1]. As is well known, CO is a colorless, odorless gas generated during the incomplete combustion of fossil fuels, whose toxicity has been very well documented [2]. With the advance in industrialization, emissions from automobiles, domestic fuel burning appliances and sewage leaks have greatly contributed to the increase in the concentration of CO. Therefore, monitoring its levels in the ambient environment, in order to maintain air quality standards has assumed increased significance.

Among the various materials used for gas sensing, tin oxide (SnO_2) based sensors have been commercially popular and are extensively studied. Market analyses show that 35% of the research efforts are concentrated on tin oxide based sensors, while, mixed oxide based sensors are at 13%, zinc oxides at 10% followed by tungsten and titanium oxides at 7% each [3]. Conventionally, for a strong reducing agent like CO, SnO_2 based sensors have been thoroughly investigated. Nevertheless, other metal oxide sensors are explored as SnO_2 is sensitive to many other toxic gases, susceptible to humidity and generally consumes large power [4]. Whereas cross sensitivity and humidity sometimes raise false alarms, high power consumption practically renders impossible the design of portable gas monitors. Ideally, it is expected that a sensor must selectively respond to CO at low concentrations at reduced operating temperatures close to room temperature, unaffected by humidity and other environmental factors.

Titanium dioxide (TiO_2) has shown great technological potential due to its stability in wide temperature changes and sensitivity towards oxygen at different operating temperatures. Specifically, nanostructured TiO_2 with various morphologies, due to their large surface-to volume ratio, porosity, small diameter and the reactions between the oxygen species O^{2-}, O^{-} and O_2^{-} on the surface and samples have received much attention as gas sensors [5].

The present review deals with the performance of TiO_2 as gas sensor, in particular for CO. An effort is made to review its structure, transduction principle, sensing performance, gas sensitivity

and future prospects. Although the review focuses on nanostructured TiO_2, thick film sensors of TiO_2 have been mentioned for comparison.

II. STRUCTURAL PROPERTIES OF TiO_2 NANOMATERIALS

TiO_2 belongs to the family of transition metal oxides. Three main polymorphs of TiO_2 are found in nature: anatase, rutile and brookite. Whereas anatase and rutile types have tetragonal crystal structure, brookite has an orthorhombic crystalline structure. Rutile is the only stable phase. Anatase and brookite are metastable at all temperatures transforming to rutile when heated [6]. In rutile, the TiO_6 octahedron shows a slight orthorhombic distortion. In anatase, the TiO_6 octahedron shows a significant distortion so that its symmetry is lower than orthorhombic. In rutile, each octahedron is in contact with ten neibhbour octahedrons-two sharing edge oxygen pairs and eight sharing corner oxygen atoms, while in the anatase, each octahedron is in contact with eight neighbours-four sharing an edge and four sharing a corner. In both structures, each Ti atom is coordinated to six O atoms and each O atom is coordinated to three Ti atoms. These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 [7].

The as-prepared TiO_2 appears to be amorphous. Heat treatment plays a vital role in phase transformation, for example, by increasing the annealing temperature to $300-500℃$, amorphous structure can be changed to anatase and when the temperature further rises to $600-700℃$, anatase can be transformed to rutile [8]. The bandgap of anatase, rutile and brookite is 3.2eV, 3eV and 2.96eV respectively.

Nanostructures can be described as zero, one, two and three dimensional nanomaterials. All of these nanostructures can be amorphous or nanocrystalline. TiO_2 morphologies include nanotubes, nanowires, nanorods, thin films, composite materials and mesoporous structures. Nanostructured TiO_2 materials differ substantially in their properties from their bulk materials enabling them beneficial in a number of applications. Nanostructured TiO_2 is preferred in sensing applications due to their larger surface area (which provides more surface area for physical and chemical interactions) and better electron transition. A variety of synthesis methods have been used in the preparation of TiO_2 nanostructures like hydrothermal method, solvothermal method, sol-gel method, direct oxidation method, chemical vapor deposition, electrodeposition,

sonochemical method, microwave method [9]. The resultant thin films may have similar composition but will have different morphologies. The properties of the nanostructured TiO_2 thin films depend upon the preparation method and the annealing temperature. TiO_2 nanoparticles prepared from basic sol were found to have more surface states than those prepared from acidic sol as observed from the surface photovoltage spectra (SPS) measurements [10]. The density functional based tight binding (DFTB) method, employed to assess the structural stability of TiO_2 layer modifications, confirms that the anatase nanotubes are the most stable modifications in a comparison of singlewalled nanotubes, nanostrips and nanorolls. Their stability increased as their radii increased. The energies of anatase nanotubes relative to the infinite monolayer follow a $\frac{1}{R^2}$ curve. The anatase nanostructures are semiconductors with the wide direct band gap [11], in which surface properties get modified while interacting with the reducing or oxidizing gases. Therefore, the nanostructured anatase phase is preferred over rutile in gas sensing.

The addition of dopants to metal oxide semiconductors enables to control the selectivity and sensitivity in gas sensing mechanisms as this affects the electrical resistance of the intrinsic metal oxides. Specifically, the metal (titanium) or the non-metal (oxygen) component can be replaced in order to alter its properties. It is easier to substitute the Ti^{4+}cation with other transition metals than to replace the O^{2-}anion with other anions due to the differences in charge states and ionic radii [7]. Various metal ions like $Ag, Ni, Co, Au, Cu, Cr, Ce$ or metal oxides such as ZnO and SnO_2 doped onto TiO_2 have been found to influence the band gap, surface area, particle size, conductivity, thermal properties and thereby enhancing the sensing performance [12,13]. Doping can be performed by employing various chemical synthesis methods [12].

III. SENSING PRINCIPLE AND TRANSDUCTION MECHANISM IN METAL OXIDE SEMICONDUCTORS

Normally, a metal oxide semiconductor operates in air, in the presence of humidity and residual gases. In such conditions, at temperatures between $100°C$ and $500°C$, at the surface of the metal oxide, various oxygen, water and carbon-dioxide related species are present. Interaction with atmospheric oxygen below 150 ℃ leads to its ionosorption as molecular (O_2^-) species and above 150 ℃ leads to its ionosorption as atomic (O^-,O^{2-}) species. Before getting ionized, the oxygen

has to be adsorbed and dissociated at the surface of the metal. This process can be described by these following equations [14]:

$$O_{2(ads)} + e^- \rightleftharpoons O^-_{2(ads)} \quad (1)$$

$$O_{2(gas)} \rightleftharpoons O_{2(ads)} \quad (2)$$

$$O_{2(ads)} \rightleftharpoons 2O_{(ads)} \quad (3)$$

$$O_{(ads)} + e^- \rightleftharpoons O^-_{(ads)} \quad (4)$$

The ionosorbed species act as electron acceptors due to their relative energetic position with respect to their Fermi level E_F as shown in Figure 1. When O_2 molecules are adsorbed on the surface of metal oxides, they extract electrons form the conduction band E_C, trapping the electrons at the surface in the form of ions, leading to a negatively charged surface. This results in an electron-depleted region Λ_{air}, also called a space-charge layer. The thickness of the space-charge layer gives the length of band bending region as can be seen in the figure. The presence of negative surface charge and the consequent band bending generates a surface potential barrier $eV_{surface}$.The height ($eV_{surface}$) and the depth (Λ_{air}) of band-bending depend on surface charge which is determined by the amount and type of adsorbed oxygen.

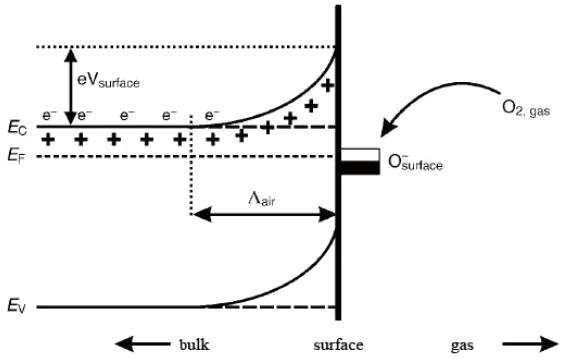

Figure 1. Simplified model illustrating band bending in a wide bandgap semiconductor (Adapted from Ref. [15]).

The space-charge layer Λ_{air} is an area of high resistance. It depends on the Debye length L_D which is a characteristic of the material of the semiconductor for the particular donor concentration and is determined by:

$$L_D = (\varepsilon_0 \epsilon k_B T / e^2 n_d)^{1/2} \quad (5)$$

where k_B is Boltzmann's constant, ε is the dielectric constant, ε_0 permittivity of free space, T is the operating temperature, e is the electron charge and n_d donor concentration assuming full ionization. It can be seen that, at steady operating temperature, the Debye length depends only on the donor concentration. This situation assumes that humidity is not involved in the surface reactions. However, any actual system under ambient conditions is influenced by the water forming hydroxyl groups that affect the sensor performance.

In polycrystalline sensors, the conductivity occurs when the electrons move from one grain to the next after crossing the insulating barrier $eV_{surface}$ of the adjacent grains. $eV_{surface}$ represents the Schottky barrier, which increases as the concentration of O^- increases. The density of electrons with sufficient energy to cross this barrier is n_s which could be obtained from the Boltzmann equation:

$$n_s = n_d \exp|eV_{surface}/k_B T| \quad (6)$$

where n_d is donor concentration. The conductance of the sensing material is proportional to n_s. Reducing gases such as CO, react with the ionosorbed oxygen species through the reactions:

$$CO + O^-_{(ads)} \rightarrow CO_2 + e^- \quad (7)$$

and

$$2CO + O^-_{2(ads)} \rightarrow 2CO_2 + e^- \quad (8)$$

desorbing finally as CO_2. The electrons trapped by the oxygen adsorbate return to the metal oxide film, causing a decrease in the space-charge layer height and thereby increasing conductivity [16].

TiO_2 is a n-type semiconductor having donor like oxygen vacancies. In titanium dioxide, there is excess of titanium, and because of the excess of the metal, electrons are present in the conduction band of the material. When the gas absorbs onto the TiO_2 surface, it releases electrons into TiO_2. Oxygen vacancies act as donors increasing the surface conductivity. The adsorbed oxygen ions act as acceptors, binding electrons and thereby decreasing surface conductivity [16]. The conductivity of TiO_2 can be enhanced by metal element doping. By controlling the doping pattern, dopant concentration and thermal treatment, the n-type TiO_2 could be transformed to p-type TiO_2. The n-type TiO_2 shows a decrease in resistance while interacting with the target gases, whereas the p-type TiO_2 shows an increase in resistance [17].

IV. SENSOR PARAMETERS

The performance of sensor is characterized by these parameters:

1. Sensitivity: Sensitivity measures the degree of influence of a certain target gas on the resistance of a sensor. It is generally defined as the ratio of the resistance of the sensing element in the target gas to that in air for a particular concentration. A sensor would have high sensitivity if exposure to low concentration of a gas resulted in large change in resistance of the sensor material. Depending on the type of the target gas, sensitivity is defined in various ways:

i) Mathematically, sensitivity(S), can be represented as [18]:

$$S = \Delta R/R_a = |R_a - R_g|/R_a \quad (9)$$

where $\Delta R = R_a - R_g$ = change of resistance in test gas

R_a = alue of resistance in air

R_g = value of resistance in of the sensor in the presence of test gas.

ii) The sensitivity is also defined by

$$S = (R_O - R_{gs})/R_{gs} \quad (10)$$

where R_0 is the resistance of the sensor before passing gas and R_{gs} is after passing gas and reaching a saturation value.

iii) Sensitivity could also be defined as, normalized conductance,

$$S = R_a/R_g \quad (11)$$

where R_a and R_g represent the resistance of the sensor in air and in target gas.

iv) Empirically, the sensitivity of the semiconducting oxide gas- sensitive sensor can usually be represented as

$$S_g = Ap_g^{\beta} \quad (12)$$

where p_g is the target pas partial pressure which in direct proportion to its concentration and the sensitivity is characterized by prefactor A and exponent β. The exponent β takes the value normally 1 or $1/2$ depending on the charge of the surface species and the stoichiometry of the elementary reactions on the surface. The sensitivity is dependent on the film porosity, film thickness, operating temperature, the presence of dopants and grain size.

2. Selectivity: Selectivity is the ability of a sensor to detect a particular target gas in a mixture of interfering gases. Generally, a unique signature of the target gas is detected by the sensor.

Selectivity depends largely on the operating temperature of the sensor and could be improved by the addition of catalysts.

3. Stability: Stability is the consistence in the response of the sensor under continuous use. The performance of the sensor should be repeatable over large number of cycles for extended periods, without undergoing degradation.

4. Operating temperature: The operating temperature of the sensor is a function of the semiconductor oxide composition and the gas which is to be detected. With respect to a single gas, the sensor reaches its maximum sensitivity at the operating temperature. It is desirable to keep the operating temperature low so as to reduce cost and improve stability.

5. Response and recovery time: Response time is generally defined as the time it takes for the sensor to reach a 90% of full scale reading after being exposed to a full scale concentration of the given gas. The response time is dependent on grain size, additives, electrode geometry, electrode position and diffusion rate. A small response time is indicative of a good sensor. Since response time decreases with decreasing particle size, nanosized particles are preferred for sensor applications [18] . Similarly, the recovery time is the time interval during which the sensor resistance reduces to 10% of the saturation value when the sensor is exposed to full scale concentration of the target gas and then placed in clean air. The small value of recovery time indicates that the sensor could be used repeatedly.

V. SENSOR FABRICATION

A sensor element normally consists of a sensitive layer deposited over a substrate provided with electrodes for measuring electrical characteristics. The device is usually heated by its own heater which is separated from the sensing layer and electrodes by an electrical insulating layer [19]. Synthesized TiO_2 nanomaterials are assembled into a sensing electrode and fixed in a sealed chamber, where the resistance of the TiO_2 film could vary when exposed to CO. Two electrical contacts are provided on TiO_2 film to measure conductance. The substrate types of electrode can be Transparent Conductive Oxide (TCO) glass, alumina, metal, S_i wafer, plastic etc [8].

One-dimensional (1D) nanofibers, due to their unique morphology and geometry, have been used in gas sensing applications. Nanofibers form a highly porous mesh and their large surface-to-

volume ratio makes it attractive in sensor fabrication. Among the most prominent methods of producing nanofibers is the electrospinning method. Although the process is predominantly used to make polymeric nanofibers, metal nanofibers can be constructed indirectly through electrospinning of their precursor material. Electrospun fibers can be deposited on surfaces such as metal, glass or microfibrous mat with relative ease.

Park, Jin-Ah, et al. fabricated TiO_2 nanofibers by electrospinning a hybrid mixture of TiO_2 sol precursor, polymer and solvent [20]. The nanofibers of 400-500 nm in diameter were deposited on the substrate in a multilayered random network structure. The nanofibers were mainly composed of anatase phase with grain size of about 15 nm. The nanofiber fabricated sensor showed a highest response of 4.4 at a working temperature of $200℃$ to a CO concentration of 25 ppm. It was found that the response of the sensor was proportional to the CO concentration. For CO concentrations of 1 ppm, 3ppm, 8ppm and 15ppm, the responses were 1.1, 1.2, 1.5, and 2.6 respectively. The response time and recovery time were in the range of 32-86s and 84-109s respectively. Although the sensor detects the presence of target gas, the sensitivity and the response/recovery time are low.

Nanocomposites are materials in which one or more phases with nanoscale dimension are embedded in a metal, ceramic or polymer matrix. Surface related factors, important in gas sensing such as optical, electronic, catalytic, mechanical and chemical properties can be obtained by nanocomposites synthesized from various materials. It should be noted that most of the chemireistor sensors are devices based on metal oxide and metal, metal oxide or noble metal nanocomposites. Nanoclusters of metals like Ni, Co, Cu, Cr, Ce or metal oxides like $Fe_2O_3, La_2O_3, Cr_2O_3$ etc or noble metals like $Pd, Pt, Au, Rh,$ or Ag incorporated in the TiO_2 matrix improve sensor performance.

Wang, et al. synthesized Cu doped TiO_2 nanofibers through an electrospinning method and studied its sensing performance [13]. A paste of as-synthesized TiO_2 and deionized water was coated on a ceramic tube on which a pair of Au electrodes was previously printed. Platinum-lead wires attached to these electrodes provided the electrical contacts. After the ceramic tube was sintered at $300℃$ for 2 hours, a small $Ni-Cr$ alloy wire was placed through the tube as a heater that provided the operating temperature. It was observed that the sensitivity rose linearly in low concentrations (5-500 ppm) and saturated above 1000 ppm. At the optimum operating temperature of $300℃$, the sensitivity was about 21 to 100 ppm. The response time and recovery

time were about 4 and 8 s, respectively. The selective response to CO was very high in a mixture of gases.

Comini, E., et al. prepared a nanostructured Ti/Fe mixed oxide thin films using radio frequency magnetron sputtering assisted annealing [21]. The composite film was dense and compacted with 20-30 nm TiO_2 grains. The grains were made only of TiO_2 while the Fe_2O_3 phase was present only at grain boundaries. The sensor performance was affected by the number of Fe insets, i.e, the larger the abundance of Fe, the higher the response. The response was quite high: 310% for the film with eight insets of Fe and 60% for the film with only two insets to 15 ppm of CO at a working temperature of 300℃. Above 250℃ of working temperature, the response time and recovery time were always found to be within 30s and 90s respectively. The sensitivity varied from 2.8 to 15 in the range of 10-1000 ppm. The higher performance is ascribed to the nanosized structure of the film. In a similar study, $ZnO-TiO_2$ nanocomposites, synthesized by chemical vapour deposition technique, also showed a sensitivity of 6.5 to 500 ppm CO in a temperature range of 200℃-400℃ [22,23].

Noble metal particles such as Pt, Pd, Au and Ag show catalytic properties that modify gas-metal oxide chemical interactions and enhance sensing process. These metallic nanoparticles doped on the surface of metal oxide, activate or dissociate the detected gas, making it easy for the activated products to react with the adsorbed oxygen species resulting in a change of the resistance.

Tan, Joy, et al. fabricated Au doped TiO_2 thin films on a langasite(LGS) substrate using radio frequency magnetron sputtering [24]. The performance of this sensor was compared with pure TiO_2 thin films on a LGS substrate. It was found that $Au-TiO_2$ sensor showed superior sensitivity to CO than pure TiO_2 thin films at low concentrations. The $Au-TiO_2$ sensor response was three to five times larger than the pure TiO_2 thin film sensor while exhibiting good repeatability. The response and recovery time was less than 20s to 60 ppm and 125 ppm of CO at 318℃ respectively. A similar result was also achieved by Buso, Dario, et al. who fabricated Au nanoparticles with controlled morphology and homogenous dispersion inside a TiO_2 matrix using sol-gel method [25]. A sensitivity of 3.04 to 100 ppm CO was achieved [23].

Point contact based gas sensors operating on Yanson point contact spectroscopy have yielded high quality results at room temperature and at low concentrations. Point contact probes do not contain tunneling barriers and their sizes are smaller or close to the mean free path of the charge carriers. With the small sizes, one gas atom can be enough to react with the constriction area

material of the point contact and induce measurable changes in the conductivity of the contact [26]. Liu, Xu, et al. proposed a CO sensor based on the point contact between Pd decorated TiO_2 nanotube array [27]. Highly ordered TiO_2 nanotube array was fabricated on titanium wire by electrochemical anodic oxidation and Pd catalytic nanoparticles were modified by the micro-emulsion electrochemical deposition. Pd epitaxially grew on the tube walls and were distributed on the surface of the nanotubes. Current-Voltage (I-V) characteristics showed that a Schottky barrier was formed at the interface between TiO_2 and Pd that played a significant role in the sensing mechanism. The sensor exhibited a sensitivity of 1.25 to 100 ppm CO at 200℃ in less than 20 s. In this case, the sensitivity was dependent on the temperature.

It is proposed that nanomaterials with low density and high surface area make better gas sensors. Xerogels have a 3-dimensional network structure of connected nanosized pores in the entire volume of the material. Unlike aerogels, which have high porosity that results in high resistance and, therefore, cannot be used as gas sensors, xerogels have lower porosity, enormous surface area, very small pore size and a well distributed nanostructure. Lee, Jin-Seok, et al. prepared TiO_2 xerogel films for CO sensing by a solvothermal drying process [23]. The porosity of the prepared xerogel films varied from 15% to 62 %. When exposed to 50 ppm CO at 350℃, the sensor fabricated with the xerogel film of 62 % porosity with a surface area of 487 m^2/g showed a sensitivity of 6.8 with response time less than 18 s and a recovery time of 42 s. In this case, the gas sensitivity and the response time of xerogel thin films varied as a function of their porosity.

Carbon nanotubes (CNT) have been explored as potential sensors in the recent times [28]. Single-walled carbon nanotube (SWCNT) is a grapheme sheet rolled-up into a seamless cylinder and multi-walled carbon nanotube (MWCNT) is composed of several such cylinders nested concentrically. A carbon nanotube is entirely a surface material and its circumference is comparable to the size of many small molecules. Even a single molecule of the target gas that attaches on the surface of a carbon nanotube can significantly vary its conductivity. As such, carbon nanotubes are characterized by unique electrical properties, high surface area, fast heterogeneous electron transfer and electrochemical stability all which make them useful in the sensing devices. The addition of functionalized CNT's to the substrate would be an effective way to increase the surface area and improve conductivity.

Lee, Jin-Seok, et al. synthesized MWCNT doped TiO_2 xerogel composite thin films using solvothermal combined sol-gel method [29]. The sensor was evaluated at 300℃ to 50 ppm CO balanced with dry air. Comparing with the pure TiO_2 xerogel films mentioned in [23], the sensitivity showed a remarkable increase to 15.8(as against 6.8 of pureTiO_2 xerogel film). The response time and recovery time were 4s and 16s respectively. The improved performance is attributed to the increase in the specific surface area and the n-p junction structure of TiO_2 xerogel coated on MWCNTs. A similar study by Kim, Hyuncheol, et al. also confirmed the role of MWCNTs in the enhanced performance of gas sensors [30]. Upon the incorporation of MWCNTs into direct-patternable TiO_2 thin films prepared by photochemical solution deposition, it was observed that the surface area and the electron conductivity showed significant increase. With the doping of MWCNT, the sensitivity increased from 2.19 to 89.2 for 100 ppm CO at 400℃ with the response time and recovery time being 5.16s and 2.72s respectively. While the presence of MWCNTs did not significantly alter the crystallinity of the films, the surface morphology and roughness of the film was increased. The study showed that direct patterning of MWCNT-incorporated TiO_2 thin films could be performed without a conventional photoresist or etching process avoiding exposure to possible damage from dry etching and simplifying the micro-scale patterning procedure.

Porous networks with interconnected voids have properties advantageous in adsorption, mass and heat transport which are regarded as useful in many practical applications. Colloidal dispersions are used as a template to produce continuous porous networks used in sensing devices. The use of colloidal templates as self-assembled building blocks for the fabrication of quasi-ordered sub-micron structures of various materials has led to a new class of sensors. Sacrificial templates comprising close packed silica or polymer microspheres can be used to prepare macroporous layers comprising (quasi-)ordered arrays of metal oxide hollow hemispheres. In these porous materials the structure of the necks or links between individual micro or nanostructures plays critical role in gas sensing properties. A porous metal oxide material with long narrow necks has higher sensitivity than with the one having short, wide necks. These unique “egg shell” structures provide a high surface area while keeping the interface area with the substrate small-necessary conditions to achieve high sensitivity [31].

Moon, Hi Gyu., et al. fabricated a highly sensitive gas sensor based on a network of nanostructured TiO_2 hollow hemispheres (NTHH) [32]. Polystyrene microsphere was used as a

template material as it could be completely burned out during calcination at high temperatures. An O_2 plasma treatment on a closely packed monolayer colloid template of polystyrene microsphere formed ordered nanostructures in the colloid template. Using this template, a thin film composed of nanostructured TiO_2 hollow hemispheres is achieved by room-temperature sputtering and subsequent calcination at $550℃$. The performance of the NTHH sensor was compared with plain TiO_2 film based sensor and TiO_2 hollow hemispheres (THH)-based sensor (without O_2 plasma treatment). For 500 ppm of CO at $250℃$, the sensitivity was measured to be 2.95, 10.4 and 43.2 for the plain film, THH and NTHH sensors respectively. The NTHH sensor exhibits around 15 times higher sensitivity than the plain-film sensor. It is interesting to note that all the three sensors respond and recover within the time of ~ 10s indicating identical mechanisms for the adsorption and desorption of gas molecules on the TiO_2 surface. The NTHH sensors also showed higher thermal stability. The narrow necked morphology of NTHH facilitates electron transport and gives easy access to the CO molecules to the NTHH sensor. In a similar study, embossed TiO_2 thin film gas sensors were fabricated through highly ordered colloidal templating [33]. An O_2 plasma treatment created a hydrophilic surface on the substrates so that well distributed large area monolayer microspheres were obtained subsequent to colloid deposition. Colloid templated TiO_2 thin film gas sensors treated with O_2 plasma exhibited enhanced CO sensing properties as compared to colloid-templated TiO_2 thin film gas sensors that did not receive surface treatments prior to colloidal templating. The response of the sensor was 5.48 to 50 ppm CO at $250℃$. The study also shows that surface treatments do influence the surface wettability of substrates.

In air quality monitoring sensors, influence of humidity is an important factor that affects the sensitivity. Detecting CO in low concentrations, in the presence of humidity requires that the sensor is not affected by water content. Jun, Youn-Ki, et al. fabricated porous TiO_2 films by micro-arc oxidation of Ti plates and investigated the sensing properties for ambient air quality control [34]. Micro-arc oxidation (also called plasma electrolytic oxidation in its anodic branch) is an electrolyte based method that basically consists of sample immersion in an electrolyte with a relatively high applied potential. During this process, the surface of the sample is subjected to a continuous sparking and based on the electrolyte used and the applied mode of current, different nanostructured coatings such as oxides, carbides etc. can be produced. In the present paper, the Ti plates were micro-arc oxidized in an electrolytic solution containing $0.5M\ H_2SO_4$ at an applied

voltage of 200V for 10 min. A circular Pd electrode of 5 mm diameter was sputtered on both sides of the oxidized specimens and the effect of humidity was compared with that of SnO_2 sensor. At the optimum temperature of $350℃$, the sensor response to 10 ppm CO was 1.68. The TiO_2 sensor showed much better signal stability than the SnO_2 sensor in the presence of humidity. The sensor signal increased almost linearly with the CO concentration from 5 to 100 ppm.

For application in exhausts, potentiometric gas sensors based on ion conduction membranes of yttria stabilized zirconia (YSZ) are used as these sensors provide sufficient stability against harsh environments. For the detection of gases other than oxygen, a subcategory of potentiometric sensors known as "mixed potential" sensor is used. In this case, the sensor consists of two different electrodes and a solid electrolyte. Usually Au and Pt are used as electrodes and YSZ as the electrolyte. Both electrodes are exposed to the same gas. As electrodes are different, the redox reaction kinetics leads to different potentials in each electrode [35].

Park, Jun-Young, et al. developed a solid-state YSZ-based potentiometric sensor using n-type TiO_2(anatase) electrodes on one side and TiO_2-Y_2O_3 composite film doped with $5wt\ \%\ Pd$ (TYP) p-type electrodes on another side [36]. The potentiometric sensor was highly sensitive to CO over a relatively wide range up to 1000 ppm and could resolve a 10 ppm variation in gas concentration. The resistance of the TYP film increased with increasing CO concentration up to 500 ppm within the temperature of range of $500℃ - 700℃$. The sensitivity, calculated as $S = mV/\log[CO, ppm]$ was -41.84. The sensor responded in less than 2 minutes. The potentiometric sensor is suitable in high temperatures.

Recent efforts in sensor fabrication have focused on reducing operation temperatures down to room temperature. Realization of room temperature sensing simplifies sensor fabrication process, reduces production cost as no heating element is needed, reduces energy consumption and increases operational safety as elevated temperatures may trigger explosions. However, the intrinsic resistance of oxide semiconductors is too high at room temperatures and is beyond detection limit. Besides, the surface interaction between the chemisorbed oxygen species and target gas molecules is too slow at room temperatures to give an obvious resistance change and quick response. Su, Juan, et al. showed a self-doping strategy to overcome difficulties in high resistance and low reaction rate [37]. Using a porous amorphous TiO_2 and urea as the starting materials, a porous titania with heavily self-doped Ti^{3+}($Ti^{3+} - TiO_2$) was prepared. The Ti^{3+}

dopant in TiO_2 decreases the resistance of TiO_2 and enhances the surface reaction activity. The sensor shows high selective response only to CO at room temperature. The sensor showed a wide response range for CO from 100 to 10000 ppm. The best results were obtained when the sensor was exposed to 100 ppm CO, its resistance showed a rapid decrease and returned quickly to its original value when the sensor was exposed to air again. A higher CO concentration resulted in lower resistance change. The response time was less than 10s and the recovery time was less than 30 s. Self-doping, as the study suggests, should be explored more for better results.

VI. FUTURE PROSPECTS

Table I gives a summary of the various gas sensors fabricated using nanostructured TiO_2. A gas sensor with high selectivity and high sensitivity coupled with low operating temperature drives the research in this field. As can be seen from table I, the sensitivity is significantly improved with nanostructured TiO_2 owing to its large surface-to-volume ratio and a grain size comparable to the depth of space-charge layer. Modification of the sensing surface of nanostructured TiO_2 with noble metals, metal oxides or polymers effectively improves interaction between surface and gas molecules, reduces operating temperature and enhances electron transfer.

Recent efforts are focused on improving selectivity using “electronic nose” or integrated sensor that combines several sensors or transducers in multielement modular sensor systems [38]. An integrated chip with various sensors, light emitting diodes and dye-sensitized solar cells can detect not only gases but also humidity and biomolecules. The specific advantage of using TiO_2 is that its excellent photocatalytic abilities would enable the integrated dye-sensitized solar cell to serve as a self-powering source, eliminating the need for external power source.

VII. COMPARISON OF NANOSTRUCTURED TiO_2 SENSORS FOR CO(ADAPTED FROM REF [8] AND [23])

Table 1: Comparison of nanostructured sensors for TiO_2 for CO

TiO_2 structure	**Fabrication method**	**Substrates**	**Detection range (ppm)**	**Operating temperature (℃)**	**Sensitivity***	**Response time**	**Recovery time**	**Concentration (ppm)**	**Ref**
Cu/TiO_2 Nanofiber	Electro spinning	Ceramic tube	5-500	300	42(A)	4s	8s	200	[13]
TiO_2 nanofiber	Electro spinning	Ceramic tube	From 1-	200	4.4(A)	32s	84s	25	[20]
TiO_2/Fe_2O_3	RF sputtering	alumina	----------	300	15(B)	~50s	----------	1000	[21]
ZnO/TiO_2	Chemical Vapor Deposition	Silicon/aluminum oxide	----------	$200-400$	6.5(C)	< 1 min	<1 min	500	[22, 23]
TiO_2 xerogel	Sol-gel	Silicon wafer		350	6.8(A)	< 10s	90s	50	[23]
Au/TiO_2	RF sputtering	Langasite	----------	230	----------	< 20s	< 20s	125	[24]
Au/TiO_2	Sol-gel	----------	5-300	300	3.4(A)	10s	15s	100	[25]
Point contact between $Pd-TiO_2$	Electrochemical anodic excitation	----------	10-100	200	1.25(A)	< 20s	----------	100	[27]
MWCNTs $/TiO_2$	Sol-gel	Silicon wafer	----------	350	15.8(A)	4s	16s	50	[29]
MWCNTs $/TiO_2$	Sol-gel	glass	----------	400	89.2(A)	5s	2s	100	[30]
TiO_2 hollow hemispheres	RF sputtering/ inverse opal	SiO_2/Si	1-500	250	43.2(A)	10s	10s	500	[32]
Colloid templated TiO_2 thin films	RF sputtering/ O_2 plasma treatment	SiO_2/Si	----------	250	5.48(A)	----------	----------	50	[33]
Porous TiO_2	Microarc oxidation	Ti plate	5-100	350	1.6(A)	200-400s	----------	10	[34]
TiO_2	powder	YSZ	10-1000	500	-41.84(D)	< 2 min		10-1000	[36]
Porous TiO_2	Self-doping	Alumina tube	100-10000	25 ± 3	----------	10s	30s	100	[37]

*Sensitivity is calculated as follows: A, $S = R_a/R_g$; B, $S = \Delta R/R_a$; C, $S = A[\text{gas concentration}]^{\beta}$; D, S=mV/(log[CO, ppm]

VIII. CONCLUSION

An attempt is made in this article to review the current status and future prospects of selective CO sensing using nanostructured TiO_2. Although, many metal oxide based chemical sensors are commercially available, yet detecting CO in low concentrations still remains a challenge. Various morphologies of the nanostructured TiO_2, due to their unique properties, offer a possibility that a selective CO sensor could be fabricated. The study explains the structural properties of TiO_2 useful in sensing applications. The basic sensing mechanism and transduction principle of reducing gases is explained. Various fabrication methods used in the preparation of sensors are discussed. The inherent advantage of nanosized TiO_2 is clarified. It is expected that sensor arrays based on nanosized TiO_2 would make promising candidates in sensing applications.

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