

# Metal oxide nanostructure for sensor applications

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**Abstract** — Over the years, metal oxide semiconductors are widely used in several sensor applications. Crystalline structure of various nanostructure materials is been employed. Various dimensions of the nanometric scale and their small crystalline size in a sensor performance. These nano-sensors are widely used because they are eco-friendly, low cost with good stability and with fast response and recovery time. Depending upon the recent development the nanostructure semiconductors metal oxides and they have various sensing properties in gas sensor, humidity sensors also ultraviolet sensor and biosensor. These sensors are based on various metal oxides such as zinc oxide, tin oxide, tungsten oxide, copper oxide etc and they have various properties correlated with each other such as their size, shape, and their doping mechanism. For fabrication various methods and techniques are addressed with their functionality with the sensor.

**Keywords:** metal oxide semiconductor, nanostructure material, crystalline size, sensors.

## I. INTRODUCTION

### 1.1 Nanostructure

Nanostructures and nanomaterials are the age of the future and the nanoscience, nanotechnology or nanostructure which is a foundation of usual science such a physics, chemistry, material science or biology. Nanotechnology consists of various novel technologies which is used to producing, designing of nano particles. In few metal oxides they have wide various morphologies such as nanobelts, nanowires, nanobelts and nanorings [1]. Production of new nanodevices are emerging in electronics, photonics and life science [2].

### 1.2 Structure

The nanostructure material is divided based on their dimensions of the structured material. Classification of those structured nanomaterials are 0-D (zero dimension), 1-D (one dimension), 2-D (two dimension) and 3-D (three dimension). The 0-D are onto larger than 100nm in a nanoscale, it is commonly used nanoparticles and they exhibit various form and shapes. The 1-D is completely outside the nanometric scale, these are needle shaped nanomaterials shaped as nanotubes, nanowires and nanorods. The 2-D nanomaterials have unique shape characteristics, they are nanofilms, nanocoating's, nano prism and nanolayers. Widely used insensor nanocontainers, reactors etc [3] [4]

They are made up of various chemical components and deposited in their substrate. The 0-D, 1-D and 2-D nanoparticles could be crystalline or polycrystalline also ceramic or metallic. The 3D nanomaterials are three times greater than 100nm and 3-D is an importance material as they are most widely used in the area of catalysis, magnetic materials etc.[4] They are nanocrystalline

structure and they involve the structure of nanoscale with multiple arrangement of multiple nanosize crystals in different orientations, 3D nanomaterials can contain dispersion of nanoparticles, bundle of nanowires and nanotubes in multi nanolayers [3].

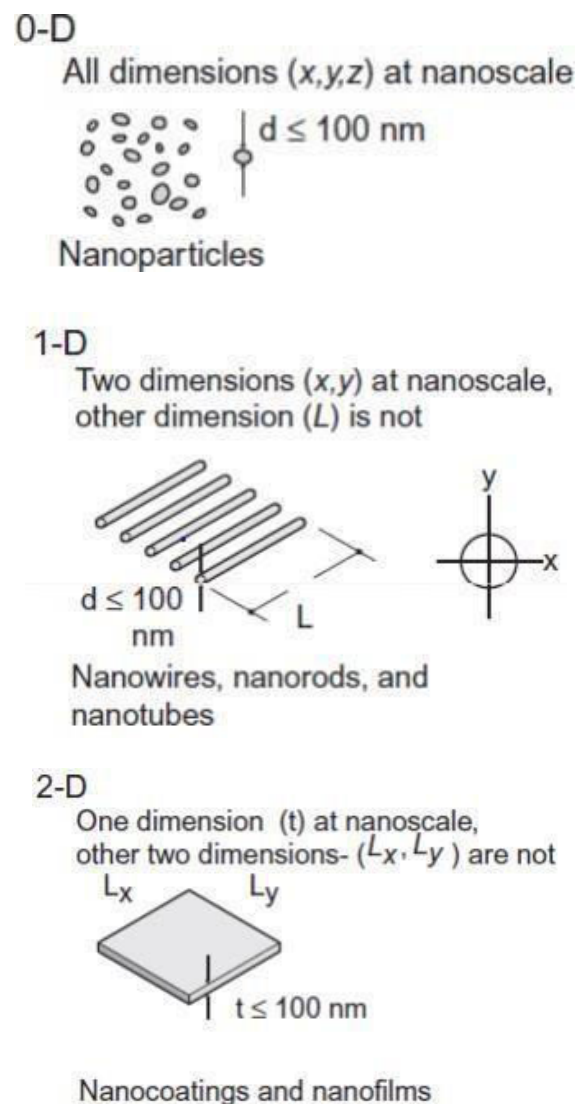


Fig.1 Different dimension of nanostructures material [3]

The three-dimension space showing the relationship among 0-D, 1-D, 2-D and 3-D structures nanomaterials. For 0-D the nanomaterials are fully confined, in 1-D and 2-D they are delocalization and confinement 3-D nanostructures are fully delocalized all these are potentially made inside the walls.[3]

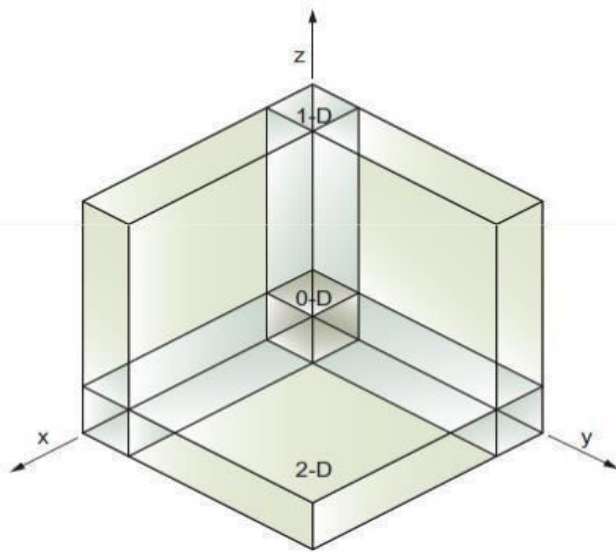


Fig. 2 Three-dimension spacing [3]

### 1.3 Synthesizing in Nanostructured materials

Various techniques have been used for synthesizing and fabricating of 0-D, 1-D, 2-D and 3-D nanosized material either by physical and chemical processes. Physical processes such as evaporation technique, it is used for thin film deposition, the evaporated atoms have collisions with the gas atoms or molecules and undergo condensation to form atom clusters for cold powder collection surface, the formed clusters should be removed from the region of deposition. [4]

Sputtering technique is used for ejecting the atoms or clusters of designated materials by subjecting them to an accelerated and inert gas such as helium. [4]

Lithography is a convertible process for different substrates, they are used for surface preparation in which a particular design is transferred from a photomask or reticle onto a substrate and multiple patterns are made of one exposure. [4]

Hot and cold plasma, here the hot refers to fully ionized ions, they are powdered type substances consisting of an arc melting chamber and collecting system. They are remelted twice or thrice melting a piece of bulk substrate in a mixing gas atmosphere [4]. Few other physical processes are spray pyrolysis, inert gas phase condensation technique, pulsed laser ablation and sono-chemical reduction.

The various chemical processes are lyotropic liquid crystal templates they are of various nanometric size. The shape and size can be controlled using this method. Widely used in drug delivery, catalysis etc.

In electrochemical deposition they use electrical current to deposit the layers of nanostructured material. [4] Consequently there are various other chemical techniques also.

The nanosized materials have various physical, chemical and mechanical properties, metal oxides components have positive and negative ions having numerous characteristics. Semiconductor metal oxides can be classified as p-type or n-type. The physical, electronic, mechanical and chemical properties of a nanomaterial depend upon their shape, size and composition by doping. Electronic structure range of a nanostructure material is classified in two categories: transition and non-transition metal oxides. To improve the performance of a metal oxide effective doping done

species, the technique for doped metal oxide is high purity and quality is not good. It is because of lack of sustainability for mass production.

The arc discharge method is used to produce several metal oxide nanostructures such as titanium dioxide, collected metal oxides are from the discharge chamber that have critical advantages in their sensor application from various differences such as diameter, grain size and length. They are easy and flexible method to dope.

with trace level

### 1.4 Various sensor application

Sensor is an electronic device that detects and responds to physical parameters to output. Sensors are used everywhere such as in houses, factories, stores, malls or in building premises. Using metal oxides, sensors are used to detect the quality of water, monitoring air such as the speed of the wind. The gas sensor is rapidly used in metal oxides as per literature study [5-6]. Portable and flexible metal oxides based are used in gas sensors. The gas sensors are classified in different types such as optical, electrochemical, capacitance based, calorimetric, acoustic based, and metal oxide-based gas sensor. They are classified based on their sensing method and are categorized in two: based on electrical properties and few variations on other properties. Comparison between various types of gas sensors is shown below. [7]

Parameters	Types of Gas Sensors				
	SMO Gas Sensors	Catalytic Combustion Gas Sensors	Electro Chemical Gas Sensors	Thermal Conductivity Gas Sensors	Infrared Absorption Gas Sensors
Sensitivity	E	G	G	P	E
Accuracy	G	G	G	G	E
Selectivity	F	P	G	P	E
Response Time	E	G	F	G	F
Stability	G	G	P	G	G
Durability	G	G	F	G	E
Maintenance	E	E	G	G	F
Cost	E	E	G	G	F
Suitability to portable instruments	E	G	F	G	P

E: excellent, G: good, F: Fair, P: Poor.

Table 1: Comparison between different gas sensors [7]

The gas sensors can be analyzed in various categories such as their response time, sensitivity, recovery time etc. The response time is the time when the gas concentration reaches a specific value that a sensor generates a corresponding signal. Recovery time is the time that is required for a sensor signal to return to its initial value after a step concentration. [7] The metal oxide semiconductor based gas sensors have prioritized applications, they are used for human breath as medical diagnosis and also as gas detection. [8] The sensor maintains the structure stability in the fabrication process. Gas sensors are most widely used in automotive industries.

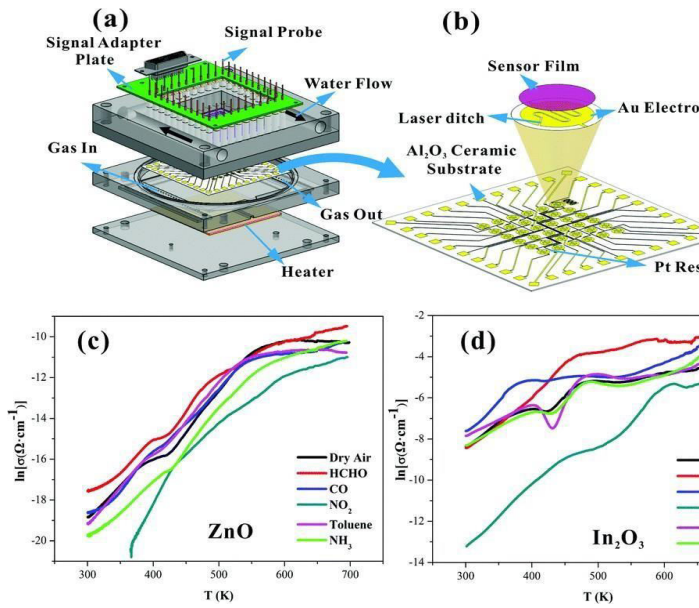


Fig 3 Metal oxide gas sensor (Royal society of chemistry) [8]

The humidity gas sensor consists of a ring-shaped oscillator circuit on a chip, they consist of sensitive film and integrated electrodes onto them. Sensitive films are made of zinc oxide and they are prepared using the sol-gel method.[8] Humidity sensors are widely used in medical, industrial and another domestic environment. These devices are employed in automobile and microelectronics industry [10]. In Fig 4b the capacitance of a humidity sensor is different temperature is shown with their variation in Fig 4c the output frequency of different temperature in the form of graph. The humidity sensors are showcased based on their properties such as morphology, surface area, pore size, sensing material etc.[10]

The gas sensor and the humidity sensor have similar features such as high sensitivity, constant response time, high stability, operating range etc.[12] A humidity sensor chip consist of a humidity sensor of capacitive type. [12] The UV sensors and the photodetectors are also used widely in medical, environmental safety, flame detection and few others. They detect the light in the UV wave form range.

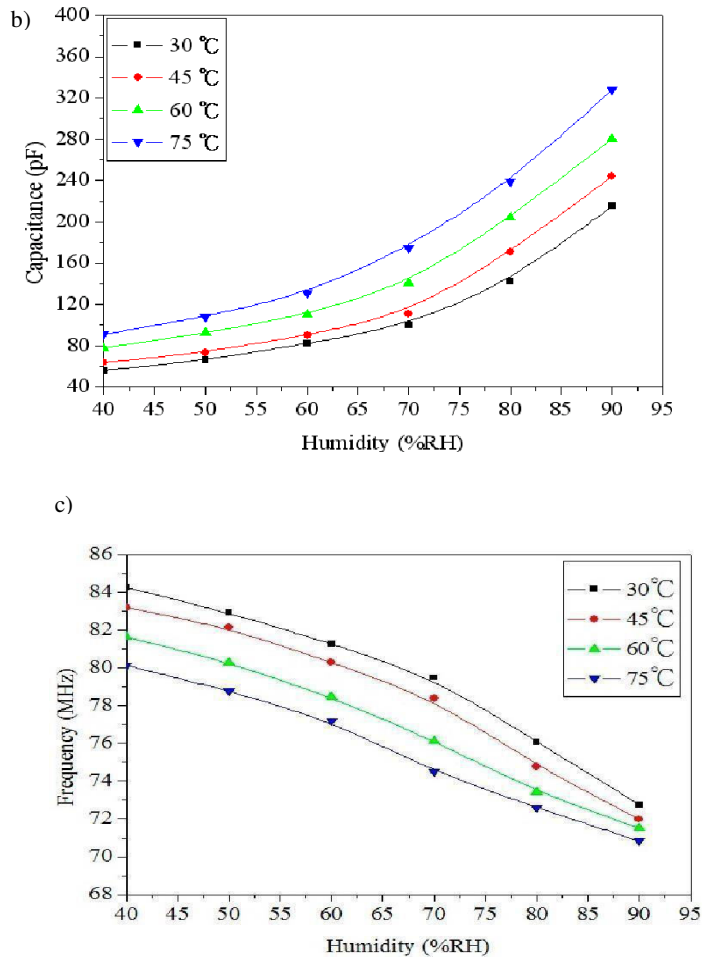


Fig 4 a) Humidity sensor b) capacitance of humidity sensor at different temperature c) output frequency [9][10]

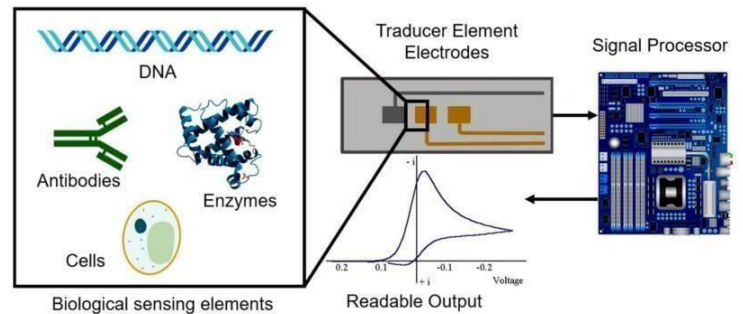
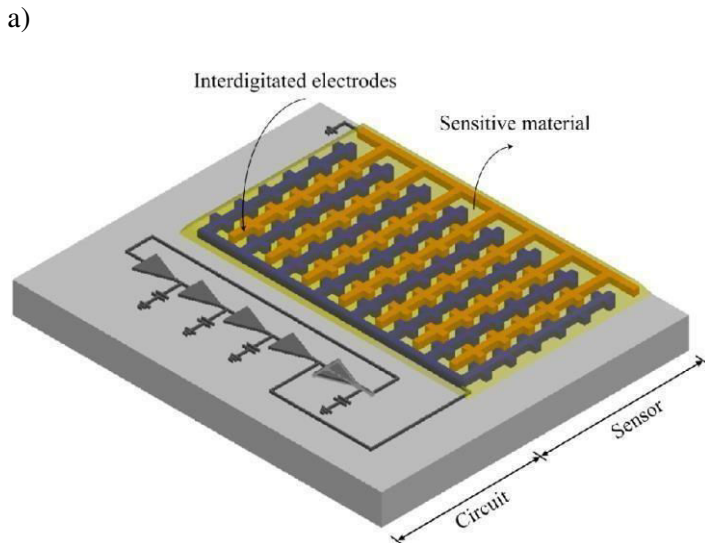


Fig 5 Biosensor coupled with electrodes [11]

A silicon-based photodetector for ultraviolet light and spectral dependence occurs due to its absorption coefficient  $A_g$ . The  $A_g$  acts as gate electrode and the  $A_g$  photodetector has maximum responsivity when compared to PIN structured photodetector.[13] Ellipsometer is used to measure the thickness of oxide, a thin metal is stacked via evaporation with a

background pressure. The Ag metal is deposited for its band selection and they are evaporated on the bottom of its substrate. It is also a mechanism of tunneling process.[13]

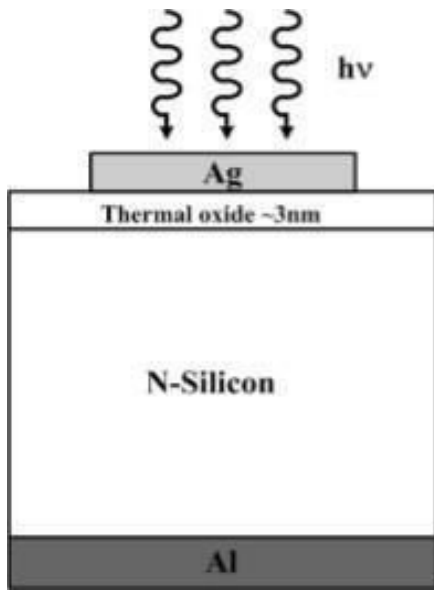


Fig 6 Structure of metal oxide semiconductor using UV sensor

In biosensor the metal oxide nanostructures are widely used as sensing devices that includes a transducer as shown in Fig 5 with few specific components. Such as bioreceptor.[10] The analysis of proteins, DNA, glucose, [11] bacteria and many others. Biosensors are powerful analysis tools in medical diagnostics for detecting of diseases and virus for food quality and safety. There are various type of biosensors and they are classified as bioreceptors and transducers. The most powerful biosensor is the glucose biosensor which is used to monitor the blood glucose level of patients.[10]

Recently, the metal oxide materials have been implemented in electron-transfer kinetics and strong absorption capability and this improves the biosensing properties and depend upon biomolecules with chemical binding and physical absorption [10]

## II. Metal Oxide Nanostructure

The metal oxide nanostructures are widely used in optical electronics and electronics that consists of transducer, capacitors, transistors. Mostly used for sensing and gases and vapors They are of p-type and n-type semiconductors. In n-type semiconductor titanium dioxide, zinc oxide, tin dioxide, tungsten dioxide and p-type semiconductors copper oxide and tin mono-oxide[10]. and these semiconductors are implemented in few sensors such as gas, humidity, biological and UV sensor and are exhibited in various terminals [10]. They are showcase in various nanoscale, nanowires, nanospheres and nanosheets [10][6].

### A. Tungstendioxide

The Tungsten diode ( $WO_3$ ) is a n-type semiconductor material with a wide energy band gap.  $WO_3$  have various crystalline structure such as tetragonal, triclinic, hexagonal, cubic and few other [10]. Tungsten is one of the best sensing materials for detecting the toxic gases in solid semiconductors [14]. They are of surface-controlled type.

As per study earlier gas sensor was coated with tungsten oxide nanostructure on the alumina substrate which is attached to electrodes[14] and the  $WO_3$  has high sensitivity gas-sensing materials which were used to detect the hazardous gases. The tungsten diode nanostructure is synthesized in different concentration as shown in Fig 7.

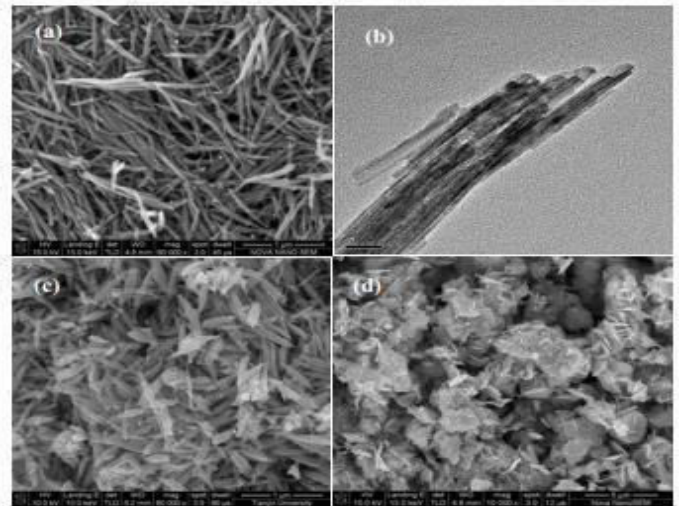


Fig 7 a) c) d) SEM images of  $WO_3$  concentration of 0.01M, 0.013M and 0.015M, b) TEM image [14]

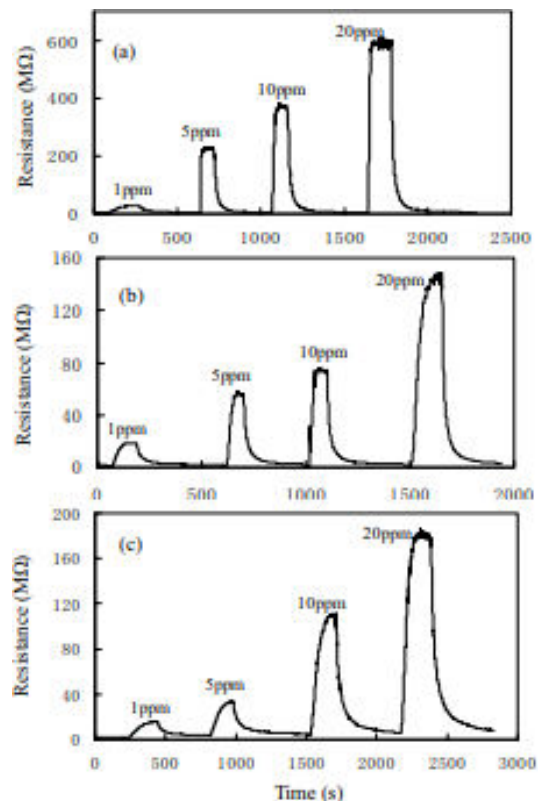


Fig 8 Dynamic response of  $WO_3$  various concentration a) 0.01M, b) 0.013M, c) 0.015M

In Fig 8 the dynamic response of the sensor is shown in various concentration, the nanowires bundle became shorter and thicker as the concentration increased and the longer and thinner nanowire had quicker response as per the study in [14] as it has highest sensitivity to various concentration. Tungsten oxide and zinc oxide pure are composed and prepared in various concentration[5].

B. Zinc oxide

Zinc oxide is a type of semiconductor that is used to optoelectronic devices, piezoelectric and pyroelectric. They are very potential and used in various fields such as LED (light emitting diode), solar cells, photo detectors and laser cells and few other more [16]. ZnO films have transparent properties. In Fig 9 the tetrahedral coordinates of  $Zn^{2+}$  and  $O^{2-}$ . The Zinc oxide are known to be unique because they inherit dual semiconductor and piezoelectric properties.[15]

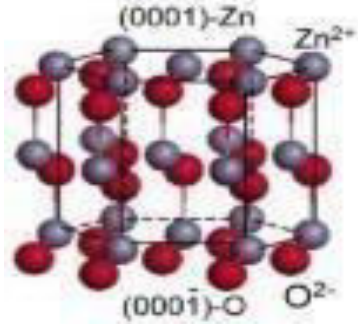


Fig 9 Tetrahedral coordinates of  $Zn^{2+}$  and  $O^{2-}$  [16]

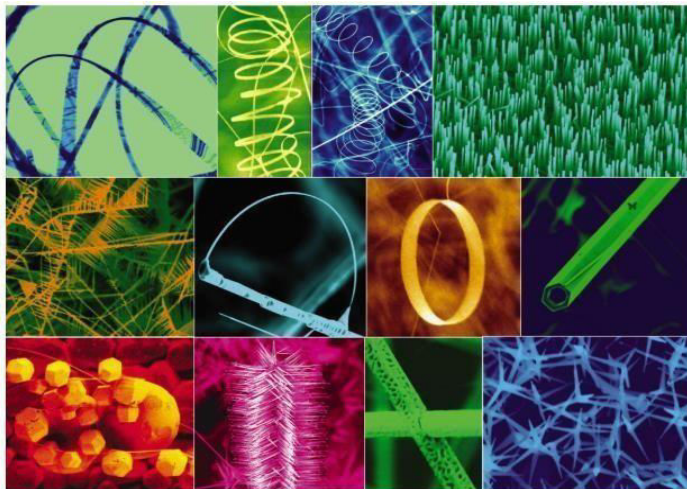


Fig 10 Collection of ZnO nanostructures in different formations [16]

ZnO have diverse structures and in [15] the formation of nano helices, nano bows, nanowires, nano propellers and nanocages of ZnO. They are also used in gas sensors to detect few gases. The Zinc oxide are crystalline in shape and have the formation of hexagonal, tetrahedral or cubical shape. In tetrahedral semiconductors the ZnO have higher piezoelectric properties. Basically zinc, have higher refractive index[16]. One among the popular method for improving the performance of ZnO is by doping, alike as gas sensor. There are many authors who have made a study on ZnO metal oxides performance and characteristics such as in [14-16].

ZnO is a n-type semiconductor merged with various crystal surface for increasing its conductivity. Electronics transfer from ZnO n-type electrode to NiO p-type electrode and that would lead to hole depletion into the surface of the electrodes. When a zinc oxide is used it is absorbed at the sensors surface and has low hysteresis, with high sensitivity and recovery time[10].

The Zinc oxide nanoparticles have different morphologies, shape, size and various types of parameters, for

synthesizing.[17] For synthesizing the sol-gel method most widely used in ZnO and after collision the solid particles turns into liquid [9]. There is various technique for morphology of zinc oxide as shown in Table 2.

Method	Materials	Size (nm)	Shape
Hydrothermal	Zinc acetate dihydrate, polyvinylpyrrolidone (PVP)	L: 5000, D: 50-200	Nanorods
	Zinc acetate dihydrate, zinc chloride, sodium hydroxide	60	Nanorods
Microwave decomposition	1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [bmim][NTf2], zinc acetate dehydrate	37-47	Sphere
Co-precipitation	Zinc acetate, double distilled water	D: 30-60, L: 80	Nanorods
	Tetrahydrated zinc nitrate, ammonium hydroxide	20-40	Crystals
Micro-emulsion	Zinc acetate dihydrate, ethylbenzene acid sodium salt (EBS), xylene, dodecylbenzene sulfonic acid sodium salt (DBS), ethanol and hydrazine	$D_{DBS}$ : 300 $D_{EBS}$ : 80	Nanorods
	$Zn(AOT)_2$ , heptane, diethyl oxalate, chloroform, methanol	10-20	Quasispherical
Solvothermal	Zinc acetate dihydrate, polyethylene glycol, absolute ethanol	10-20	Quasispherical
	Triethanolamine, zinc acetylacetonate monohydrate, 1-octanol, and absolute ethanol	$L_{rod}$ ~100 $D_{sphere}$ ~20	Rods (ethanol without triethanolamine—TEA) spherical (ethanol with TEA)
Sol-gel	Oxalic acid dihydrate, zinc acetate dihydrate, hydrochloric acid, ammonia, and absolute ethanol	20	Spherical
Sonochemical	Potassium hydroxide, zinc nitrate hexahydrate, and cetyltrimethylammonium bromide	200-400 wide, a few nm thick	Flakes
Chemical vapor deposition	Zinc acetate dihydrate, ethanol	Average D: 90 and L: 564	Nanorods
Electrochemical	Oxalic acid dihydrate purified, Zn electrode, potassium chloride, nitric acid, and sodium hydroxide	$D_{spherical}$ : 50-100 $L_{cylindrical}$ : 150-200	Spherical and cylindrical particles

Table 2: Morphology of zinc oxide (ZnO)[17]

The hydrothermal method is synthesized by ZnO and they vary upon temperature and concentration. The crystal growth includes the ability to create crystalline phases from solid to melting point. They grow material at higher vapor pressure when closer to melting point. The disadvantage of this method is that they are expensive. Sonochemical technology are used in wide materials of material science. Few researchers have used this method to defined different / new shapes of zinc oxide nano-crystalline structures[19].

Microemulsion method is used to define its isotropy they are numerously applied in chemical and biological fields. In the first picture below shown in Fig 11 the microemulsion method where energy triggering and one micro emulsion method is used, when energy is triggered the reaction is initialized with a triggering agent [20]. In microemulsion plus reactant they direct react to pure reactant which are in liquid or gaseous state and so they are first dissolved.

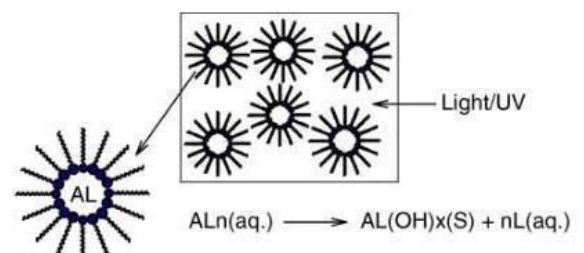


Fig 11 Microemulsion: Energy triggering method [20]

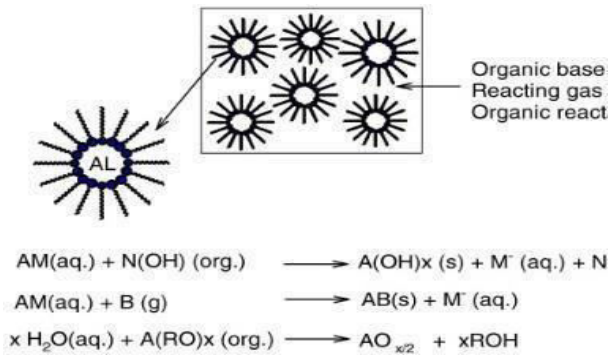


Fig 12 Microemulsion: plus, reactant method[20]

The solvothermal method is similar to hydrothermal method and they prepare a wide range of materials such as polymers, semiconductors, ceramics and metals.[18]The presence of solvents in a materials changes at its higher temperature such as their boilingpoint. They prepare both crystalline oxide and non-oxide materials. Solvothermal can exhibits in various quantum dot effects.

The deposition of solid film on a heated surface by a chemical reaction in a gas or vaporstate this method is knownas chemical vapor deposition (CVD), types of CVDs are photo-laser CVD, laser CVD, plasma CVD, and few others[21]. The Microfabrication technique is most widely used for deposit monocrySTALLINEMATERIALS [21].

Co-precipitation method have inorganic zinc and alkalis. In this method to achieve nanoparticles, calcination is done [17].In Fig 13(a) pure ZnO nanoparticles are shown in Fig 15(b) the co doped ZnO particles are shown and the co doped ZnO nanoparticles are reduced in size when compared to pure ZnO .This reduction is due to distortion.

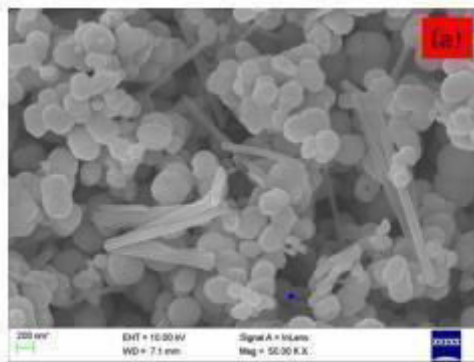


Fig 13 (a) Field emission scanning electron microscopic analyzes(a) Pure ZnO [22]

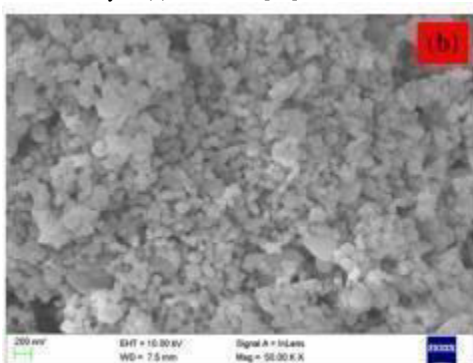


Fig 13 (b) Field emission scanning electron microscopic analyzes (b) Co doped ZnO nanoparticles [22]

The microwave assisted method is simple and doesn't cause thermal gradient effects and they are used to produce hydroxide, oxide and few other nanoparticles[17].

Green synthesis is very energy-efficient,low cost and eco-friendly [17].It is used as an alternative method for chemical and physical method instead of biological method. They exhibit in various shape and size. Reducing the metal ions could reduce the stability of the nanoparticles that are risked. Here nanoparticles with biocompatibilityare produces and agents are natural present producing biological organisms [23].

### C. Titanium Dioxide

The titanium Dioxides are photocatalysis, they are used as creams and coatings that absorb UV without any coating. Titanium Dioxide are molecules of one atom of titanium with two oxygen atoms. They are nanotubes and molecules are bonded in cylindrical shapes, which result in cylindrical lattice with oxygen and twotitanium.

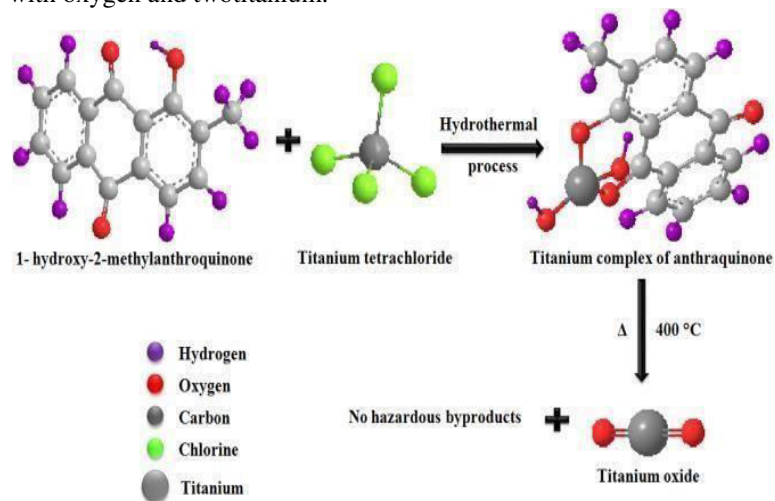


Fig14 MechanismofTiO<sub>2</sub>nanoparticles[24]

TiO<sub>2</sub> nanoparticles are characterized by X-ray diffraction.In fig 1 the mechanism of titanium oxide nanoparticles is synthesized. TiO<sub>2</sub> is a n-type semiconductor and have wide energy band gap and they can engage by adding more nanostructures to it or structural defects or by doping nonmetal elementals and these have higher refractive index with high dielectric current passing throughthem [10][24].

TiO<sub>2</sub> can be produced in various methods such as solvothermal synthesis, thermal evaporation, sputtering, and various other technique. This nanomaterial is exhibit in various form not only in nanotubes such as in nanowire, nanosphere, nanorods etc. and these are non-toxic and eco-friendly [24]. These are high quality sensor and have good sensitivity with short response, recovery time, and longer life cycle.

In the graph below the X-ray diffraction for Titanium oxide nanoparticles with its comparative pattern of synthesized and standard nanoparticles. TiO<sub>2</sub> are photoactive layer of gas sensor when doping is done between small metal clusters then point defects occur. Combining several oxides have limitation onto them.

In humidity sensor, TiO<sub>2</sub> have superior sensitivity as a result of low surface-to-volume ratio. When compared to UV photodetector the TiO<sub>2</sub> films have various difference in structural characteristics . TiO<sub>2</sub> nanoparticles are used a composite with graphene oxidenanosheets.

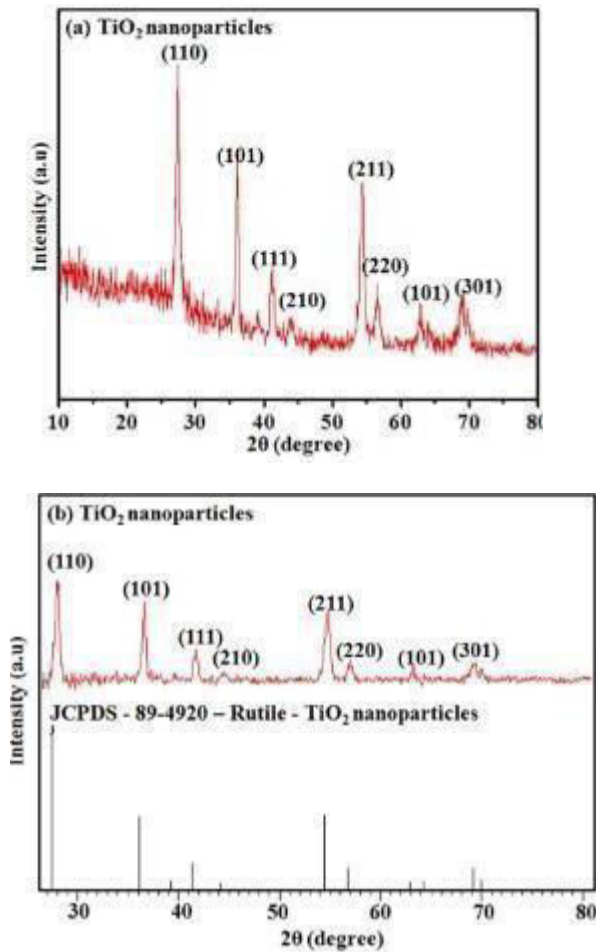


Fig 15 (a) Synthesized TiO<sub>2</sub> nanoparticles (b) Synthesized and standard TiO<sub>2</sub> nanoparticles [24]

The different types of titanium nanoparticles are shown in Table 2. There are three different forms namely anatase, rutile and brookite, when heating anatase and brookite convert to rutile which always stable. The Properties of anatase and rutile phase is shown below

Property	Anatase	Rutile
Molecular weight (g/mol)	79.88	79.88
Melting point (°C)	1825	1825
Boiling point (°C)	2500–3000	2500–3000
Specific gravity	3.9	4.0
Light absorption (nm)	$\lambda \leq 385$ nm	$\lambda \leq 415$ nm
Mohr's hardness	5.5	6.5 to 7
Refractive index	2.55	2.75
Dielectric constant	31	114
Crystal structure	Tetragonal	Tetragonal
Lattice constants (Å)	$a = 3.784$ $c = 9.515$	$a = 4.5936$ $c = 2.9587$
Density (g/cm <sup>3</sup> )	3.79	4.13
Ti–O bond length (Å)	1.937 (4) 1.965 (2)	1.949 (4) 1.980 (2)

Table 3 Properties of anatase and rutile of TiO<sub>2</sub>[25]

In TiO<sub>2</sub>, the photocatalysis very efficient and have high activity in the photodegradation for organic and inorganic materials. In various research it is told that TiO<sub>2</sub> have certain properties such as they have particular shape, size etc. They are good photovoltaic materials. With different quality [25].

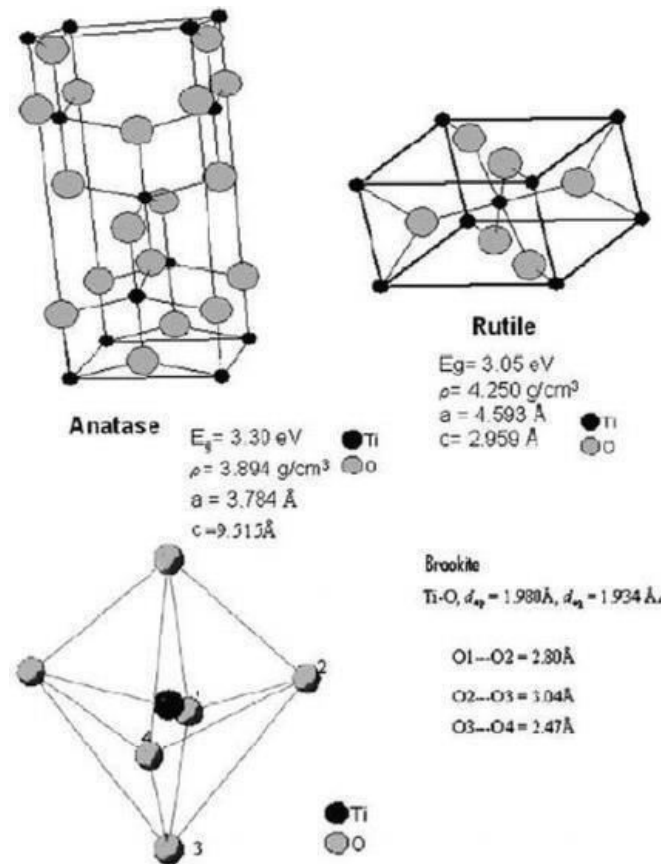


Fig 16 Different forms of TiO<sub>2</sub>[25]

#### D. Copper oxide

Nanomaterials such as nano shuttles, nano disks and nanoparticles are exhibited by hydrothermal and wet chemical method. CuO is a p-type semiconductor with a narrow bandgap [26]. They are categorized based on their thermal conductivity, photovoltaic properties, high stability, and few others [27].

Copper oxide are widely used as gas sensors, active catalyst, metal conductivity as they have good selectivity in nanomaterials. Compared to other nanostructures CuO has unique magnetic and superhydrophobic characteristics, they have various morphologies such as their shape, size and various dimensions depend on physical and chemical properties[27]. Water is a pure solvent and are of low cost and safest so CuO utilizes waster as solvent. In fig 17 the crystalline structure of CuO is shown.

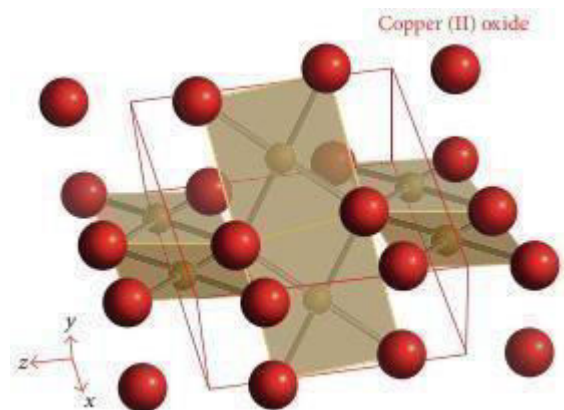


Fig 17 Crystalline structure of CuO [27]

Morphology	Size	Solvent
Hierarchical superstructure	Diameter: 200 nm; length: 600 nm SEM	Distilled water
Cubic	230 nm	Water
Sphere	40 nm, 90 nm, and 140 nm (as the concentration of salt increases)	Ethylene glycol
Nanoparticle	50 nm XRD	Water
Nanoparticle	5-8 nm TEM and XRD	Ethanol
Nanoparticle	44 nm (XRD) 80 nm (TEM)	Deionized (D)
Nanorod	Diameter: 50-100 nm Length: microns	2-Propanol
Nanosheet	Width: 1-2 mm; thickness: 20 nm	Ethanol
Nanoparticle	22 nm	Deionized wa
	10 nm	Ethylene glycol
Flower-like	400-600 nm	Deionized W;
Nanoparticle	3-9 nm (XRD) 11 nm (TEM)	Alcohol
Nanoplatelet	Lengths: 4-5 μm; thickness: 65-80 nm (SEM)	1-Butyl-3-met imidazolium [BMIM]BF <sub>4</sub>
Nanoneedle	Length ~100 nm Diameter 10-20 nm (TEM)	Water
Nanobelt	Length: 2.5-5 μm Width: 150-200 nm	Distilled water
Nanoparticle	100 nm (SEM)	Ethylene glycol

Starting materials	Surfactant	Method
Cu(CH <sub>3</sub> COO) <sub>2</sub> NaOH	Ethylene diamine-tera-acetic acid disodium	Sonochemical
Cu(CH <sub>3</sub> COO) <sub>2</sub> NaOH	Without surfactant	Microwave
	PVP, CTAB	
CuCl <sub>2</sub> , NH <sub>4</sub> OH	Thiourea	Chemical and annealing
Cu(CH <sub>3</sub> COO) <sub>2</sub> NaOH, methanol, and NH <sub>4</sub> OH	No	Alcothermal
Cu(NO <sub>3</sub> ) <sub>2</sub>	Citric Acid; ethylene glycol	Sol-gel
Cu(NO <sub>3</sub> ) <sub>2</sub>	No	Solvothermal
CuSO <sub>4</sub>	Ascorbic acid NaBH <sub>4</sub> PVP	Chemical reduction
Cu(CH <sub>3</sub> COO) <sub>2</sub>	No	Hydrolyzing method
Cu(CH <sub>3</sub> COO) <sub>2</sub>	No	Alcohol thermal
Cu(NO <sub>3</sub> ) <sub>2</sub> NaOH	[(BMIM)BF <sub>4</sub> ]. It serves both as solvent and as surfactant.	Hydrothermal
Cu(NO <sub>3</sub> ) <sub>2</sub> NaOH	Oleic acid Sodium oleate	Coprecipitation
CuSO <sub>4</sub> NaOH	H <sub>2</sub> O <sub>2</sub>	Hydrothermal
Cu(CH <sub>3</sub> COO) <sub>2</sub> urea	No	Microwave

Table 4: Different Morphology of CuO nanomaterials [27]

Unlike, other nanomaterials, CuO also imposes various method such as solvothermal, sol-gel, sono-chemical method and few others, for preparation the nanoparticle [27]. At high temperature solvothermal process is used and they take longer time as high pressure is invoked, On the other side sol-gel method is difficult and there are various parameters to be measured and controlled [27]. Because of the high temperature the form a homogenous gradient and reduce the reaction time and they form into small particles of uniform size and shape.

As shown in Fig 17, CuO have monoclinic structure and of square planar configuration of 110. Compared to other properties such as field emission, electrical conductivity or optical property have less conductivity [27]. Also, the band gap depends upon their quantum size in different CuO nanostructures. Consequently, CuO is different from antiferromagnetic transition metal monooxides.

CuO nanostructures are widely used in material science and engineering, as have unique properties and understand the synthesis process and fundamental properties, they are transition metal oxides, enhancing super thermal conductivity, high stability and few other properties.

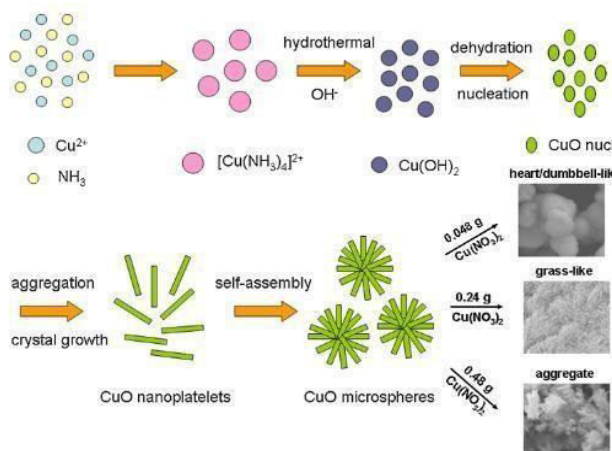


Fig 18 Formation of different CuO nanostructures [26]

In Table 4 different formation of CuO nanostructures with their solvents and surfactant and morphology are shown. By hydrothermal reaction the crystal growth increases and ion size depending upon their room temperature and they grow to 1D nanostructures where nanoparticles are aggregated nanoparticles and rearrange themselves because of their intrinsic anisotropic property. [26] The nanoparticles combine with each other to form dumbbell like structure and they grow grass like structure with well-arranged nano leaves that are the nanoplatelets as shown in fig 18.

In Fig 19, the SEM images of different CuO nanostructures in different concentration is shown where a and d are Dumbbell shaped CuO, b and e are grass shaped CuO and c and f are aggregated CuO [26].

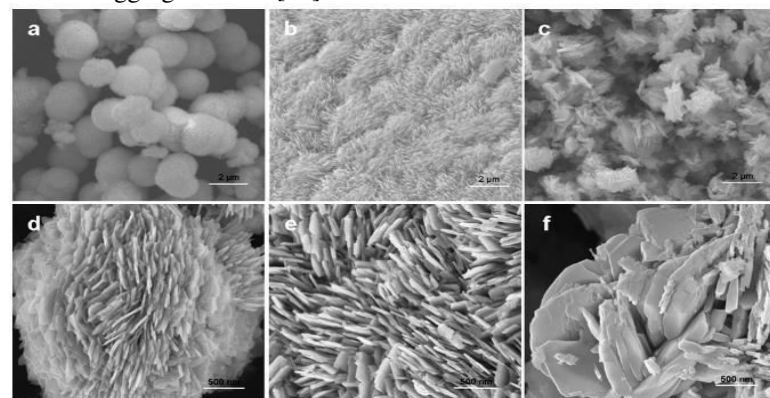


Fig 19 SEM image of different CuO nanostructures in different concentration [26]

### E. Tin Oxide

They represent the important class of crystalline semiconducting nanomaterials with wide band gap. Tin oxide are n-type semiconductor and these materials are used as catalysts, sensors and few other [28]. To control their band gap modification can be done. They exhibit low electric resistance and have good electrical conductivity for gas sensing based on the nanostructures size. SnO<sub>2</sub> have few parameters depending upon their crystal size of nanocrystalline and have good crystalline that is defined by hydrothermalsynthesis.



Synthesis of nanomaterial with controlled morphology, size, chemical composition and crystal structure [29]. The different synthetic is processed using methods like vapor synthesis and solid-state synthesis. The crystalline structure of tin oxide is shown below.

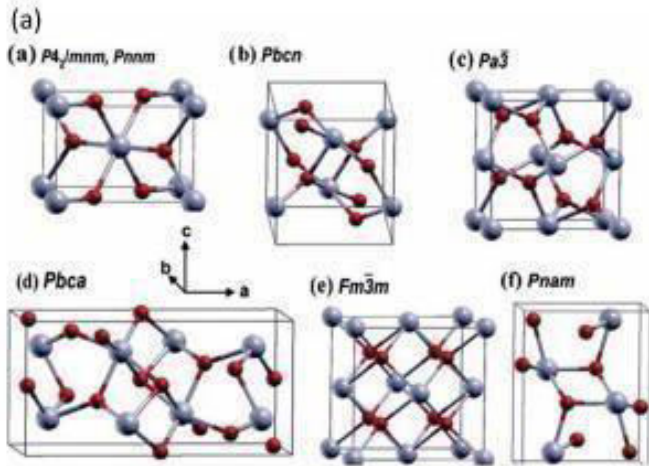


Fig 20) Crystalline structures of the SnO<sub>2</sub> p (a) Rutile and CaCl<sub>2</sub> (b) R-PbO<sub>2</sub>, (c) pyrite, (d) ZrO<sub>2</sub>, (e) fluorite, and (f) cotunnite [29]

Various chemical synthesis method is such as sol-fel method, hydrothermal method, precursor compound method and emulsion technique for the synthesis of metal oxide nanoparticles. The sol-gel method is a technique where the gelling of a solution containing the metal salts, they result in the formation of tin oxide nanoparticles with large surface area.[29]

They grow in the form of 1D nanostructure and form in tube, belts and road or wires.[30] They have high impact as these are used in novel structures in next generation sensor and nanodevices they have higher integration with low power consumption and also eco-friendly with low power cost [30]. The SnO<sub>2</sub> consist of two metal ions and four oxygen atoms each Tin oxide atom is placed in between six oxygen atoms which results in forming octahedron[29]. Oxygen atoms are covered by three Sn atoms and they for Sn-O-Sn in a triangle like structure.

SnO is formed when Sn is in oxidation and it is in metastable phase that converts to SnO<sub>2</sub> even in the absence of oxygen if exposed to a certain temperature [10]. SnO<sub>2</sub> are doped materials with electrical and optical properties. The electrical properties of SnO depends on oxygen stoichiometry[30].

SnO and SnO<sub>2</sub> are used in widely in Li-ion batteries, water splitting, transistors with thin films, photocatalysis [27-30]. Tin oxide are also used for detection of various gases such as H<sub>2</sub>, O<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub> and CO and these have fast response speed with high chemical stability and low cost [10].

In fig 21 of SnO<sub>2</sub> at different ammonia feed rate is shown and in table 5 synthesis of tin oxide nanoparticles using various methods is displayed.

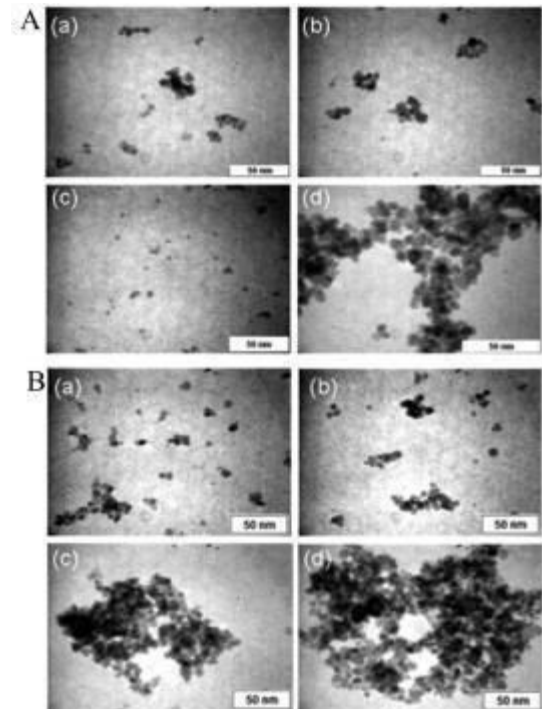


Fig 21 TEM micrographs of SnO<sub>2</sub> at different ammonia feed rate[29]

Methods	Solvents	Precursors/surfactants	Temperature	Morphology	Average crystallite size
<b>Solution processing method</b>					
Sol-gel	Water		200 °C	Spherical	2.5 nm
			400 °C	Spherical	3.5 nm
			800 °C	Spherical	18.2 nm
			450 °C	Spherical	20 nm
Solvothermal	Ethanol Ethylene glycol Water		195 °C	Spherical	20 nm
			200 °C	Spherical	5.5 nm
			600 °C	Spherical	10-30 nm
Precursor compound method		Organometallic Carboxylate precursor Polyacrylate precursor Poly(propyleneimine) Poly(amidoamine)	135 °C	Spherical	20 nm
			295 °C	Spherical	5.2 nm
			600 °C	Spherical	15 nm
				Flower like	2.5 nm
				Flower like	4-5 nm
Amino acid mediated synthesis	Water		200 °C	Nearly spherical	10-20 nm
Microemulsion method		SDS surfactant CTAB surfactant PEG surfactant		Floral petal	8 nm
				Florets of cauliflower	11 nm
				Sheets and rods	13 nm
Microwave irradiation	Acidified water		200 °C	Spheres irregular shape and size	6 nm
			400 °C		9 nm
			600 °C		21 nm
			800 °C		33 nm
Sonochemical	Water		80 °C	Irregular shape	3 nm
<b>Vapour phase synthesis</b>					
Laser ablation			900 °C	Nanowire	20 nm (diameter)
Arc plasma				Nearly spherical particles of irregular size	5 nm
Flame spray			200 °C	Nearly spherical particles of irregular size	20 nm
<b>Solid state synthesis</b>					
Mechanical pressing			25 °C	Nearly spherical	3-15 nm
Ball milling, 4 h, 600 rpm			600 °C	Nearly spherical	25-40 nm
Focused solar irradiation				Nearly spherical	20-60 nm
Bio-synthesis	Water	Plant/bacteria extract	150 °C	Spherical	~30 nm

Table 5 Tin oxide nanoparticles synthesized via various methods [29]

### III. Performance of metal oxidesensors

The comparison between different metal oxides and their sensing devices is discussed. As per study the metal oxides have been largely integrated in gas sensors with various concentration onto them. The temperature also varies for each metal oxide. The widely used metal oxide gas sensors are ZnO and TiO<sub>2</sub> as they have high chemical stability and are of low cost. Practically they are very fast at recovery and response rates. Deep investigation is being done for all metal oxide semiconductors and it is also noting that ZnO nano structures.

have fast response rare when doping is done.  $WO_3$  are eco-friendly and are safely monitored. Sensitivity of  $WO_3$  have limitation and the operation temperature is lower when compared to ZnO and  $TiO_2$ , as these two have fast recovery and response time.

Copper oxide-based gas sensors are formed by p-n hetero-junctions as per study and copper oxides have p-type characters and they are eco-friendly, nontoxic with wet-chemical synthesis.  $Cu_2O$  oxides are unstable and they can be easily converted to CuO.  $SnO_2$  is used for the detection of different gases, such as  $H_2$ ,  $O_2$ , CO,  $NO_2$  and  $NH_3$ , as they have fast response and recovery time and they are eco-friendly with low cost.

The nanostructured metal oxide-based humidity sensors are used to detect the humidity change and they have good detection range the only drawback of this sensor is that they have limited sensitivity improvement. In humidity sensor the tin and copper oxides are not widely used but they have good response, recovery and stability.

After the analysis of biosensor, it is also observed that ZnO and  $WO_3$  nanostructures are most used. The Zinc oxide and copper oxide are widely used for the detection of glucoses they have high sensitivity with low concentration and are also of low cost.  $TiO_2$  and  $SnO_2$  are also used in biosensing and have low detection limit. [10]

#### IV. Conclusion

In review summarization of various sensing technique on different sensors such as gas sensor, humidity sensor, UV sensor and biosensors. Different nanomaterial types were explained with example such as nanowires, nanotubes, nanofibers, nanosheets, nanosphere, nanocubes, and few other. Various sensing mechanism and properties of metal oxide is being discussed.

Limitation of various metal oxide material with their sensor are addressed with various approaches, the impact of doping exhibiting on semiconductors was addressed. Usage and application of each gas sensing technique with their properties are shown in a form of graph as a review. Different dimension of nanostructures is built and discussed, their properties, limitation and performance of each nanomaterials is focused.

#### V. REFERENCES

- [1] Lin-Hua Xu, Dnyaneshwar S. Patil, Jiazhi Yang, and Jingzhong Xiao, Metal Oxide Nanostructures: Synthesis, Properties, and Applications, Hindawi, 7-sept-2015
- [2] Giorgio Sberveglieri, Camilla Baratto, Elisabetta Comini, Guido Faglia, Matteo Ferroni, Alberto Vomiero, Single crystalline metal oxide nanowires/tubes: controlled growth for sensitive gas sensor devices, IEEE International Conference on Nano/Micro Engineered and Molecular Systems, 16-Jan-2007, Bangkok, Thailand
- [3] Po-Chiang Chen, Guozhen Shen, Chongwu Zhou, "Chemical Sensors and Electronic Noses Based on 1-D Metal Oxide Nanostructures", IEEE, 2008
- [4] F. Fanga, J. Kennedy, J. Futtera, A. Markwitz, E. Manikandanb, Transition metal doped metal oxide nanostructures synthesis by arc discharge method, 2013 International Conference on Manipulation, Manufacturing and Measurement on the Nanoscale, IEEE, 30-Aug-2013
- [5] Anupriya J.T. Naik\*, I.P. Parkin, Russell Binions†, "Gas Sensing studies of an n-n heterojunction Metal Oxide Semiconductor sensor array based on  $WO_3$  and ZnO composites", IEEE 2013
- [6] Awani Khodkumbhe, Mohd Nahid, Vikas Saini, Ajay Agarwal, Rahul Prajesh, "Metal Oxide Semiconductor-based gas sensor for Acetone sensing" IEEE Nanotechnology Symposium (ANTS) 2018
- [7] Ananya Dey, "Semiconductor metal oxide gas sensors: A review", Science Direct, March 2018
- [8] Jian Zhang, Ziyu Qin, Dawen Zeng and Changsheng Xie, "Metal oxide semiconductor based gas sensor: screening, preparation and integration", Royal Society of Chemistry, 24-Jan-2017.
- [9] Ming-Zhi Yang, Ching-Liang Dai, Chyan-Chyi Wu, "Sol-Gel Zinc Oxide Humidity Sensors Integrated with a Ring oscillator Circuit on-a-chip", Sensory 2014.
- [10] D Nunes, A Pimentel, A Gonçalves, S Pereira, R Branquinho, P Barquinha, E Fortunato and R Martins, "Metal oxide nanostructures for sensor applications", ScienceDirect, 11-March-2019
- [11] Gustavo Hernandez-Vargas, Juan Eduardo Sosa-Hernandez, Sara-Saldarriaga-Hernandez, Angel M. Villalba-Rodriguez, "Electrochemical Biosensors: A Review", Sensors 2014
- [12] Su P-G and Huang Humidity sensors based on  $TiO_2$  nanoparticles/polypyrrole composite thin films Sensors Actuators, 2007
- [13] W.S. Ho, C.-H. Lin, P.-S. Kuo, W. W. Hsu, C. W. Liu, T.-H. Cheng, and Y.-Y. Chen, "Metal Oxide Semiconductor UV Sensor", ResearchGate, October 2018
- [14] Yuxiang Qin, Ming Hu, and Jie Zhang, "Synthesis and  $NO_2$ -sensing Properties of One-dimensional Tungsten", Sensors 2014
- [15] Hongxia Li, Jiyang Wang, Hong Liu, Huaijin Zhang, Xia Li, "Zinc oxide films prepared by sol-gel method", Sensors 2014
- [16] Zhong Lin Wang, "Nanostructure of zinc oxide", ScienceDirect, June 2004
- [17] Mohsin Abbas, Mieke Buntinx, Wim deferme, Roos Peeters, "(Bio)Polymer/ZnO Nanocomposites for Packing Application: A review of Gas Barrier and Mechanical Properties, MDPI, 19-October-2019
- [18] Vincent Caldeira, Laurent Jouffret, Julien Thiel, François R. Lacoste, Saïd Obbade, Laetitia Dubau, Marian Chatenet, "Ultrafast Hydro-thermal synthesis of zinc oxide nanomaterials", Nanotechnol. 2012
- [19] Djuricic, A.B.; Chen, X.Y.; Leung, Y.H. Recent progress in hydrothermal synthesis of zinc oxide nanomaterials. Nanotechnol. 2012
- [20] Maqsood Ahmad Malik, Mohammad Younus Wani, Mohd Ali Hashim, "Microemulsion method: A novel route to synthesize organic and inorganic nanomaterials: 1st International Conference on Nanotechnology and Nanomaterials, 19-20 October 2019, Kuala Lumpur, Malaysia
- [21] A. B. Rosli, N. D. H. Abd Patah, M. A. Rosdan, M. A. Rosli, "Synthesis and Characterization of Zinc Oxide Nanoparticles by Sol-Gel Method", Journal of Materials Science: Materials Chemistry, 2019

- M. Marbie, M. H. Juhari, S. S. Shariffudin, S. H. Herman, and M. Rusop, "Influence of Metal Catalyst for Zinc Oxide Nanostructures Grown by TCVD Method for Extended-Gate FET Sensor Application", IEEE, 2013
- [22] P. Geetha Devi, A. Sakthi Velu, "Synthesis, structural and optical properties of pure ZnO and co doped ZnO nanoparticles prepared by the co-precipitation method," Journal of Theoretical and Applied Physics, Springer, 07-May-2016
- [23] Hayrunnisa Nadaroglu, Azizie Alayli, Selvi Ince, "Synthesis of nanoparticles by Green Synthesis Method", ResearchGate, December 2017
- [24] Sundrarajan M, Bama K, Bhavani M, Jegatheeswaran S, Ambika S, Sangili A, Nithya P, Sumathi R, "Obtaining titanium dioxide nanoparticles with spherical shape and antimicrobial properties using M. citrifolia leaves extract by hydro thermal method, Journal of Photochemistry and Biology B: Biology, ScienceDirect, June 2017
- [25] Pardon Nyamukamba, Omobola Okoh, Henry Mungondori, Raymond Taziwa, Simcelilev, "Synthetic Method for titanium Dioxide Nanoparticles : A Review, Open access peer-reviewed chapter, 05-Nov- 2018.
- [26] Peng Gao, Dawei Liu, "Facile synthesis of copper oxide nanostructures and their application in non-enzymatic hydrogen peroxide sensing", Sensors and Actuators: Chemical, ScienceDirect, 01-March-2015.
- [27] Thi Ha Tran, Viet Tuyen Nguyen, "Copper Oxide Nanomaterials Prepared by Solution Methods, Some Properties, and Potential Applications: A Brief Review", Hindawi, 17-Dec-2014.
- [28] Maisara A. M. Akhir, Khairudin Mohamed, Lee H.L., Sheikha A. Rezen, "Synthesis of tin oxide nanostructures using hydrothermal method and optimization of its crystal size by using statistical design of experiment", 5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015, ScienceDirect, 2016
- [29] Dipyaman Mohanta, M. Ahmaruzzaman, "Tin oxide nanostructured materials: an overview of recent developments in synthesis, modifications and potential applications", Royal Society of Chemistry, 15-November- 2016.
- [30] Anima Johari; Vikas Rana; M.C. Bhatnagar, "Synthesis and characterization of Tin Oxide nanostructures at atmospheric pressure, The 4th IEEE International NanoElectronics Conference, IEEE, 18th-August-2011.