REVIEW ARTICLE

A Review on Tungsten Oxide (WO_3) and their Derivatives for Sensor Applications

V. Hariharan[1]*, B. Gnanavel[2], R. Sathiyapriya[3,4], V. Aroulmoji[3]

[1]*PG & Research Department of Physics, Mahendra Arts and Science College, Kalipatti,*
Namakkal District – 637 501, Tamilnadu, India
[2]*PG & Research Department of Physics, Chikkaiah Naicker College, Erode – 638 004, Tamilnadu, India*
[3]*Center for Research and Development, Mahendra Engineering College, Mallasamudram,*
Namakkal District - 637 503, Tamilnadu, India
[4]*Department of Physics, Mahendra Engineering College, Mallasamudram,*
Namakkal District - 637 503, Tamilnadu, India

ABSTRACT: The nanostructured transition metal oxides (TMOs) have attracted considerable attention in the past decade because of their unique chemical and physical properties leading to numerous potential applications. Tungsten oxides ($WO_{3-\partial}$) represent a fascinating class of material used for flat panel devices, smart windows, anti glare mirrors, etc. because of its outstanding electro, photo and gas chromic properties. In particular, $W_{18}O_{49}$ has been explored for many applications such as gas sensors, photo catalysis, catalysis in electrochemical process, etc. Thus controlled production of WO_3 based nanostructures in the presence of surface modulators has become significant particularly due to their flexible processing chemistry. By bearing in mind the contributions of WO_3 nano dimensional materials for various applications, the present article focuses the review about the synthesis and properties of WO_3 nano dimensional materials for sensor applications.

KEYWORDS: Tungsten oxide, WO_3, Sensors, nanowire.

https://doi.org/10.29294/IJASE.5.4.2019.1163-1168

1. INTRODUCTION

Nanotechnology is becoming the most significant force towards the development of science and technology. It is getting the word hunger during the end, increase the speed of memory chips, modify the human body or become a devastating weapon. The term "nanotechnology" is derived from the Greek word "nanos" which means "dwarf". Nanotechnology combines cognitions and terms of many different kinds of sciences like physics, chemistry, biology and engineering which complement each other. Therefore nanotechnology has to be seen as one of the most important future technologies. It deals with atomic structures which are smaller than 100 nm. In future there is possibility of getting an injection of "smart" molecules that can seek out cancer cells and destroy them without harming any of the surrounding tissue. A simultaneous space launch via the shuttle of thousands of robotic probes, each no bigger than an insect, and each programmed to do a single task in concert with all of the others can be thought of in future. Nanotechnology will provide the capacity to create affordable products with dramatically improved performance.

Nanotechnology literally means any technology on a nanoscale that has applications in the real world. It is defined as fabrication of devices with atomic or molecular scale precision. Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. The nanoscale marks the nebulous boundary between the classical and quantum mechanical worlds; thus, realization of nanotechnology promises to bring revolutionary capabilities. Fabrication of nanomachines, nanoelectronics and other nanodevices will undoubtedly solve an enormous amount of the problems faced by mankind today [1]. Nanotechnology is likely to have a profound impact on our economy and society in the early 21st century, comparable to that of semiconductor technology, information technology, or cellular and molecular biology. Science and technology research in nanotechnology promises breakthroughs in areas such as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security. It is widely felt that nanotechnology will be the next Industrial Revolution.

Nanoscience and technology both together is considered in a very immature stage. However, we have the capability along with technology to reorganize matters in atomic scale and based on these there are

Corresponding Author:* ***vhariharan06@gmail.com*

Received: 21.04.2019 **Accepted:** 18.05.2019 **Published on**: 27.05.2019

already various products and sub products available as a direct result of our rapidly developing field such as nano science and technology that deals 1-100 nm.

On the other hand, Nanotechnology deals various types of structures made by nature and artificial techniques around nanometer scale (1-100 nm). For example, the size of a soccer ball (~ 30 cm) is reduced 10,000 times we reach the width of a thin human hair (~ 30 μ). Hence, if we try to reduce the size of the hair, it meets the width of a carbon nanotube (~3 nm). So, this nano science and technology is a remarkable one and exciting indeed.

Moreover, Nanotechnology has the impact on developing various materials that to be utilized by the society. It is already in use in cosmetics and sunscreens, in textiles, in coatings, in some food and energy technologies, along with some clinical products and medicines. Moreover, nanotechnology can take a part in environmental pollution.

Simultaneously, engineered nanostructures are having very interesting physical and chemical properties when compare to that of bulk materials, which may lead to new development in materials science. Indeed, the defense mechanism in normal human body may not be able to give adequate response to these tuned nano particles which may have the various physical and chemical characteristics which could never encountered before. In addition, nanoparticles may also spread and persist in the environment, and therefore have an impact on the environment. Hence it is considered to be a highly multidisciplinary field, drawing from fields such as applied physics, materials science, interface and colloid science, device physics, supramolecular chemistry (which refers to the area of chemistry that focuses on the non-covalent bonding interactions of molecules), self-replicating machines and robotics, chemical engineering, mechanical engineering, biological engineering, and electrical engineering.

Tungsten (VI) oxide, also known as tungsten trioxide or tungsten anhydride, WO_3, is a chemical compound containing oxygen and the transition metal tungsten. It is obtained as an intermediate in the recovery of tungsten from its minerals [9]. For the preparation of tungsten, tungsten ores are treated with various alkalis and their other raw contents to produce anhydrous WO_3 through various processes. Further this tungsten trioxide is reduced using carbon and hydrogen to get pure metallic tungsten. WO_3 is an intrinsically n-type bulk semiconductor; the stoichiometric behavior is arising due to excess of metal being oxygen vacancies. In the case of n-type metal oxides, the electros come from ionized donors via the conduction band (forms band gap), the charge carrier density at the interface is thereby reduced and a potential barrier to charge transport is developed in order to reduce the band gap energy for various applications.

Tungsten (VI) oxide naturally occurs in form of hydrates, the list of minerals which include tungsten is given below: tungstite $WO_3·H_2O$, meymacite $WO_3·2H_2O$ and hydrotungstite (of same composition as meymacite, however sometimes written as H_2WO_4). These minerals are rare to very rare secondary tungsten minerals. Hence with the continuation of the above introduction the present article gives the detailed reviews about WO_3 nano dimensional materials for sensor applications.

2. REVIEWS ON WO_3

Abraham Wolcott et al [1] reported the synthesis of ultrathin WO_3 nanodisks using a wet chemical route with polyethylene glycol (PEG) as a surface modulator. They reported nanodisk structure was based on the interaction of the non ionic 10000 g/mol PEG molecules with tungsten oxoanion precursors. The large flat surface area and high aspect ratio of the WO_3 nanodisks were potentially useful in PEC cells. It was reported that using PEG-10000 as a surface modulator that adsorbs preferentially to the (010) crystal face and thereby inhibits crystal growth and the nanodisk formation is critically influenced by the interaction between PEG and the $WO_3.2H_2O$ precursors as compared to other studies resulting in spherical nanoparticles.

Taylor et al [2] synthesized half-micron-thick tungsten oxide films by the sol-gel method onto indium tin oxide (ITO) coated soda lime silicate substrates. The samples were fired with carbon di oxide laser which increased the electro chromic response with increased firing temperature up to the point where crystallization of the tungsten oxide retarded electro chromic response. Thus they concluded that electro chromic windows with good properties were made by laser firing sol-gel-derived tungsten oxide films.

The fabrication and characterization of tungsten oxide nanofibers using the electro spinning technique and sol-gel chemistry was successfully demonstrated by Guan Wang et al. [3]. They insisted the potential applications of the electrospun tungsten oxide nanofibers as a sensor material for gas detection. Ultrafine tungsten and tungsten oxide powders with controllable particle size and structure had been synthesized by a reverse micro emulsion-mediated synthesis method by Liufeng Xiong et al [4]. The interesting applications in various fields such as catalysis, electronics, illumination, gas sensors were illustrated.

A facile and inexpensive method to produce thin films of nanostructured tungsten oxide was described by Erika Widenkvist et al [5]. They reported that the potential of this inexpensive synthesis method to produce large-area coatings of nanostructured tungsten oxide as well as patterned films makes it interesting for several different applications, such as batteries, gas sensors, and photocatalysts. Electrochromic tungsten oxide film was fabricated by a new soft chemistry route for electrochromic systems by Jin-Ho Choy et al. [6]. They found that depending on the concentration of PAA coating solution (1.0-3.0wt %), the thickness and tungsten oxide content of the film were found to vary, therefore, the electrode property of the PAA/WO_3 layer could easily be controlled.

Mesoporous semiconducting films consisting of preferentially orientated monoclinic-phase nanocrystals of tungsten trioxide had been prepared using a novel version of the sol-gel method by Clara Santato et al [7]. They illustrated that the shape and size of WO_3 nanoparticles, the porosity, and the properties of the films depend critically on preparation parameters, such as the tungstic acid/PEG ratio, the PEG chain length, and the annealing conditions. Well-crystallized WO_3 films combine excellent photo response to the blue region of the solar spectrum, up to 500 nm, with good transparency at wavelengths larger than 550 nm. They suggested the particular applications of these nanocrystalline WO_3 films include photo electrochemical and Electrochromic devices.

Jinmin Wang et al [8] reported the synthesis of uniform crystalline WO_3 nanorods and their assembly without any surfactants. WO_3 nanorods had been synthesized by using a facile hydrothermal process without employing lithium ions and sulphates. The resulting WO_3 nanorod film exhibits high electrochromic stability and comparable color display, contrast, and coloration/bleaching response was reported.

Photo luminescent behaviour of $BaWO_4$ powders processed in microwave-hydrothermal was observed by L.S. Cavalcantea et al [9]. Photoluminescence (PL) at room temperature was observed in $BaWO_4$ powders processed in microwave hydrothermal at 140 °C for different times. PL behavior was attributed to the existence of distortions on the $[WO_4]$ tetrahedron groups caused by microwave radiation. XRD studies of thermally stable mesoporous tungsten oxide synthesized by a templated sol–gel process from tungstic acid precursor had been done by Wei Wang et al [10]. This work opens a new pathway for the preparation of mesoporous tungsten oxide films using tungstic acid precursor with many advantages including reduced cost, easy handling, and insensitivity to moisture.

One-dimensional (1D) self-assembled single-crystalline hexagonal tungsten oxide (h-WO_3) nanostructures were synthesized by hydrothermal method at180^{0}C using sodium tungstate, ethylene diamine tetra acetic (EDTA) salts of sodium or ammonium, and sodium sulphate by Jang-Hoon Ha et al [11]. The synthesis of 1D self-assembled h-WO_3 nanowires bundles and urchin-like structures was differentiated by means of Na^+- and NH_4^+- based EDTA salt solutions. Deepa et al [12] pointed out that by electrochemically controlling the structure of the surface aggregates; the grain microstructure has been optimized to yield mesoporous thin films of tungsten oxide (WO_3) at the electrode–electrolyte interface in a peroxotungstate sol in the presence of a structure-directing agent (Triton) at room temperature.

Fusong Jiang [13] prepared tungsten oxide and iridium oxide porous films and their electro chromic properties were analysed. Sol–gel preparation of porous tungsten oxide and iridium oxide films by using polystyrene template was described. Cyclic voltammograms showed that the electro chromic properties of the porous films were 1–2 orders better than those of relative non-porous films. The porous films are expected to be used to buildup a new ECD with better electro chromic properties than normal ECD Composed by corresponding non-porous films.

Deepa et al. [14] studied the influence of polyethylene glycol template on microstructure and electro chromic properties of tungsten oxide. Electro chemical synthesis of tungsten oxide (WO_3) thin film nano structures by potentiostatically controlling the surface aggregates formed at the electrode–electrolyte interface, in the presence of a polymeric template (polyethyleneglycol400) from a plating sol of peroxo tungstic acid (PTA) is presented. This film also exhibits fast switching between the clear and blue states. These are repercussions of the mesopore structure and the interconnected nanocrystallite phase.

A comparison of electrochromic properties of sol–gel derived amorphous and nano crystalline tungsten oxide films was done by Deepa et al [15]. A pristine acetylated peroxotungstate sol with and without 4wt% of oxalic acid dehydrate (OAD) yielded nanocrystalline and amorphous tungsten oxide (WO_3) films respectively by dip coating technique. Band gap widening upon lithium insertion observed for both films, is a repercussion of Burstein–Moss effect and structural changes that occur upon coloration was also reported.

Sol–gel derived tungsten oxide films with pseudocubic triclinic nanorods and nanoparticles were synthesized by Srivastava et al [16]. Tungsten oxide films were deposited using acetylated peroxo tungstic acid as the precursor material adopting sol–gel dip coating route, followed by thermal treatment. The kinetic mechanisms responsible for the formation of nanorods have also been elucidated. It was reported that both the nanorods and the particles exhibited a pseudocubic triclinic crystal structure.

Jiun-ChanYang et al [17] adopted solution-based synthesis of efficient WO_3 sensing electrodes for high temperature potentiometric NOx sensors. Electrode nanostructures as well as species at electrode–electrolyte interfaces have substantial influence on the sensitivity, response and recovery times of electrochemical sensors. YSZ-based potentiometric NOx sensors with WO_3 sensing electrodes have shown considerable promise for enhanced sensitivity had been reported.

The Influence of annealing on electrochromic performance of template assisted, electro chemically grown, nanostructured assembly of tungsten oxide was studied by Deepa et al [18]. Nano structured tungsten oxide (WO_3) thin films have been electro chemically grown from a self-assembly of sodium dodecyl sulfate–tungsten oxide aggregates at the electrode–electrolyte interface. Poor color-bleach rates observed for the films annealed at 250 and 500°C are attributed to pore shrinkage, high density and crystallinity.

Deepa et al. [19] compared spin coated versus dip coated electrochromic tungsten oxide films and studied structure, morphology, optical and electrochemical properties. They revealed a superior performance for the cycled dip coated film in terms of higher transmission modulation and coloration efficiency in solar and photopic regions, faster switching speed, higher electrochemical activity as well as charge storage capacity. While the dip coated film could endure 2500 color–bleach cycles, the spin coated film could sustain only a 1000 cycles. The better cycling stability of the dip coated film which is a repercussion of a balance between optimal water content, porosity and grain size hints at its potential for Electrochromic window applications.

Effects of oxalic acid dehydrate on optical and electrochemical properties were studied by Deepa et al [20] of sol–gel derived amorphous Electrochromic WO_3 films. Tungsten oxide (WO_3) films have been prepared from an ethanolic acetylated peroxotungstic acid sol containing different amounts of an organic moiety, namely oxalic acid dehydrate (OAD) by sol–gel technique. Changing the precursor solution chemistry by varying the dopant proportion the microstructure of the films gets modified, which are otherwise amorphous to X-rays. Fast color–bleach kinetics, good coloration efficiency and anion storage capacity renders it to be suitable for smart window applications. Qingjun Sun et al [21] synthesised monodisperse $WO_3{\cdot}2H_2O$ nanospheres by microwave hydrothermal process with L (+) tartaric acid as a protective agent. The X-ray powder diffraction (XRD) pattern indicated that the product was in good agreement with the standard JCPDS data for $WO_3{\cdot}2H_2O$. They revealed the formation mechanism for L (+) tartaric acid-assisted MH synthesis of the $WO_3{\cdot}2H_2O$ nanospheres.

Ismael Jimenez et al. [22] studied the structural and gas-sensing properties of WO_3 nanocrystalline powders obtained by a sol-gel method from tungstic acid. They obtained WO_3 nanocrystalline powders from tungstic acid following a sol-gel process. Evolution of structural properties with annealing temperature was studied by X-ray diffraction and Raman spectroscopy. It was revealed that grain growth was controlled by annealing conditions. Sol-gel material appeared to be suitable for NO sensing. Similarly humidity affected NO detection by varying the chemisorptions sites. The sensor response corresponding to the thickness of the film was also revealed. Csaba Balazsi et al. [23] in his work, hexagonal tungsten oxide (hex-WO_3) nanopowders were prepared by acidic precipitation from a sodium tungstate solution. Novel hybrid composites were fabricated by embedding a low amount of carbon nanotubes into the hex-WO_3 matrix. Metallic nanoclusters (Ag, Au) were added to the carbon nanotubes for improving the gas sensing properties of the films. It was reported that the addition of MWCNTs lowered the temperature range of sensitivity of the hex-WO_3 nanocomposites to NO_2 hazardous gas.

Santos et al. [24] revealed that the hydrothermally synthesized Tungsten oxide nanoparticles and were characterized diverse microscopic, spectroscopic and electrochemical methods. Their data indicate that the WO_3/ITO electrodes represent novel, compactable platforms for the study of protein electron transfer reactions using tungsten oxide nanocomposite materials. Further optimization of the electrodes by fabrication process is currently under development as per their suggestion and aiming at the improvement of the electroanalytical performance of the electrodes and their suitability for the construction of miniaturized, fully integrated and cost effective biosensing devices. The authors further identified that the exchange rate constant of WO_3/ITO electrodes with cytochrome increased one order of magnitude, while the analytical parameters of the CCNiR/WO_3/ITO electrodes response to nitrite (the Michaelis- Menten constant is 47 μM and sensitivity of 2143 mA M-1 cm^{-2}) are comparable to those reported for carbon based electrodes. Hence he suggested that these metal oxide nanoparticles are good alternative materials for electrochemical applications, such as non-mediated biosensors. Anitha et al. [26] found that the kinetic parameters like diffusion coefficient, electron transfer coefficient and heterogeneous electron transfer rate constant involved in the oxidation of 5-HT at the 100 kGy GI-WO_3/GCE indicate the suitability of the fabricated electrode for the detection of 5-HT. Further under the optimized conditions using microwave irradiation technique as their synthesis method.

Maduraiveeran et al. [27] addressed about to emphasize the recent development in the design of biosensors by choosing their platforms based on functional nanomaterials for biological and biomedical applications. Also they chosen high sensitivity and selectivity, fast response, and excellent durability in biological media are all critical aspects for further development in the fields of Bioelectronics and Biosensor. In order to understand clearly the role of tungsten oxide (WO_3) for sensor applications, various metal oxide based chemical and biosensors are tabulated when compare to that of the existing material is given in Table.1

Table.1. Metal Oxide based Chemical and Bio-Sensors

Metal oxide	Target species	Salient features	Reference
V_2O_5 nanofibres	1-Butylamine, toluene, propanol	Extremely high sensitivity was measured for 1-butylamine (below 30 ppb) and moderate sensitivity for ammonia. In contrast, only very little sensitivity was observed for toluene and 1-propanol vapours.	*Sens. Actuators B* 106 (2005) 730.
SnO_2 nanobelts	CO, NO_2, ethanol	Sensitivity at the level of a few ppb	*Appl. Phys. Lett.* 81 (2002) 1869.
In_2O_3 nanowires	NH_3, NO_2	The response times have been determined to be 5 s for 100-ppm NO_2 and 10 s for 1% NH_3, and the lowest detectable concentrations are 0.5 ppm for NO_2 and 0.02% for NH_3	*Appl. Phys. Lett.* 82 (2003) 1613.
ZnO nanowires	Ethanol	Sensitive to ethanol concentration is in the range of 1–100 ppm. Sensitivity increases sharply as the temperature is raised from 200 to 300 °C	*App. Phys. Lett.* 84 (2004) 3654.
MoO_3 nanorods	Ethanol and CO	The detection limit for ethanol and CO is lower than 30 ppm	*Chem. Phys. Lett.* 407 (2005) 368
Cd-doped ZnO nanowire	Relative humidity	Cd-doped ZnO nanowires show a clear positive temperature coefficient of resistance effect, which is quite abnormal as compared to pure ZnO nanowires	*App. Phys. Lett.* **84** (2004) 3085.
SnO_2	Dimethyl methylphosphonate (DMMP)	Sensitive to 53 ppb DMMP and can be improved via doping nanobelts with catalytic additives.	*App. Phys. Lett.* 86 (2005) 063101.

3. CONCLUSION

The present article successfully reviewed about the role of tungsten oxide nano dimensional materials and their derivatives for chemical and bio sensor applications. Also it provides brief ideas about various synthesis methods such as chemical precipitation method, sol gel, ball milling, microwave irradiation methods, etc., and various characterization techniques in order to know the suitability of the proposed material for sensor applications. Moreover, it covers the possible durability in biological media are all critical aspects for further development in the fields of Bioelectronics and Biosensor.

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