



APPLICATIONS OF METAL OXIDE NANOMATERIALS- A REVIEW

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Abstract

The growing interest in renewable energy of recent decades has rapidly accelerated research into photovoltaic technology. Crystalline silicon, one of the most heavily researched photovoltaic materials and the current market leader, has yielded power conversion efficiencies of over 20%. For large scale power production, however, the energy required to process crystalline silicon makes these devices too costly to compete with inexpensive fossil fuel-based electricity. Various organic and polymer photovoltaic's have been regarded as one of the generation power sources. These low cost, lightweight, and mechanically flexible devices offer unique advantages and opportunities currently unavailable with crystalline silicon technology. Organic hybrid photovoltaic materials consisting of a conjugated polymer as an electron donor and a nanocrystalline metal oxide as the electron acceptor. Transition metal oxides are another attractive class of semiconducting materials. Owing to the wide range of properties that these offer both optically and electronically, transition metal oxides can play many different roles within a 'hybrid' organic photovoltaic device and applications of metal oxide- organic photovoltaic devices.

Keywords:- Metal Oxide , Nanomaterials, Applications.

1. Introduction

The continuous increase of the world's population, together with the substantial development of industry has brought about imperious demand for larger energy

consumption. At present, most of the energy production is made from the combustion of fuels, such as oil, natural gas, and coal. However, the depletion of fossil resources, the commensurate increase in noxious gas emissions, and the other associated environmental pollutions have put forward an urgent demand for developing sustainable energy technologies. Among all of the renewable energy technologies, including hydro, solar, wind, geothermal heat, and biomass, photovoltaic (PV) technology which converts solar energy into electricity is expected to be the most promising strategy for sustainable energy supply [1].

Organic-based photovoltaic's (PV) have attracted increasing attention in recent years and efficiencies exceeding 8% have recently been confirmed. These low cost, lightweight and mechanically flexible devices offer unique advantages and opportunities currently unavailable with crystalline silicon technology. Progress in the field of organic PV has been achieved in part due to the incorporation of transition metal oxides. These offer a wide range of optical and electronic properties, making them applicable in organic-based PV in many capacities. Transparent electrodes can be made from doped metal oxides. The high intrinsic charge carrier mobility of many undoped metal oxides makes them attractive as active materials and charge collectors. Metal oxides can increase the charge selectivity of the electrodes due to the energetic positioning of their valence and conduction bands [2]. A promising and rapidly developing low-cost PV system is based on organic semiconducting polymers. These can be dissolved and coated onto many different surfaces via low temperature techniques such as roll-to-roll processing semiconducting materials [3]. These have excellent charge transport properties and can be tuned in various ways through the introduction of dopants, the generation of nanostructures, or modification of their surfaces. Owing to the wide range of properties that these offer both optically and electronically, transition metal oxides can play many different roles within a 'hybrid' organic/ inorganic PV device. Organic molecular and polymeric semiconductors can form films with complex morphologies and varying degrees of order and packing modes through the interplay of a variety of non-covalent interactions. Their molecular structure consistently presents a backbone along which the carbon (or nitrogen, oxygen, sulphur) atoms are sp^2 -hybridized and thus possess a p-atomic orbital. The conjugation (overlap) of these p-orbitals along the backbone results in the formation of delocalized p-molecular orbital's, which define the frontier (HOMO and LUMO) electronic levels and determine the optical and electrical properties of the (macro) molecules [4]. Tremendous progress has been made in the field of OPV materials over the last 20 years [5]. These improvements are the result of both a better understanding of the working principles of OPV devices and the development of new,

more suitable organic materials. Since BHJ is a mixture of donor (designed to transfer holes) and acceptor (designed to transfer electrons) materials (**Figure 1**), interdigitation allows an efficient separation of excitons into free charges. Commonly, BHJ consist of polymeric, oligomeric, or defined small molecules, pi-conjugated donors and fullerene acceptors [6-7].

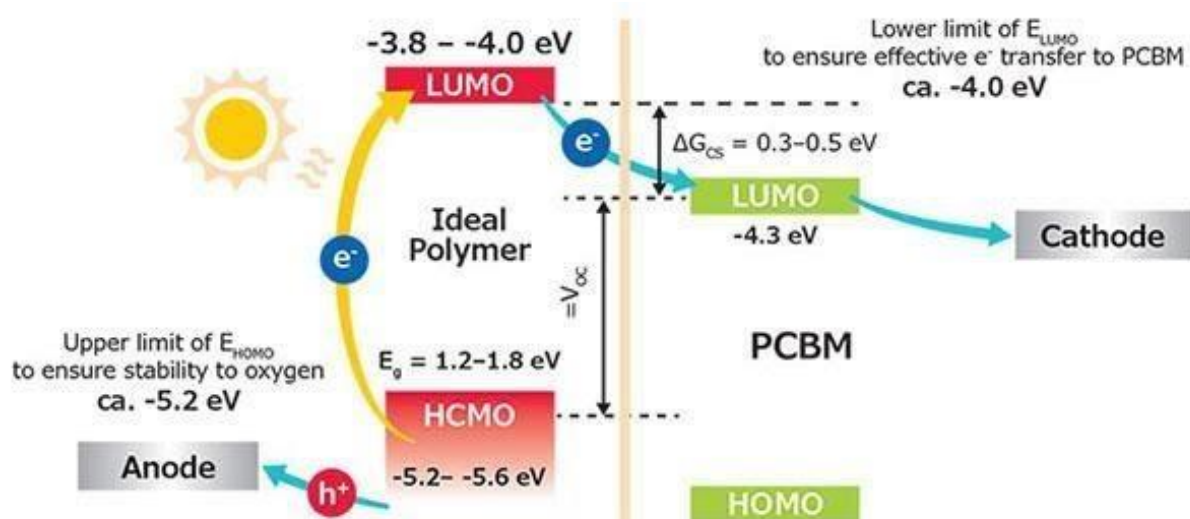


Figure 1. Working principle of OPV using the concept of the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) creating the band-gap for a donor polymer (same applies to oligomers and small molecules)

Trap states and localized electronic states in the forbidden gap of semiconductors caused by material imperfections are some of the main limiting factors to high-performance optoelectronic devices [8-10], such as solar cells, ultrafast photo detectors, field-effect transistors, and light-emitting diodes, among others. Thus, suppressing these traps states through a simple and efficient approach is critical to the enhancement of optoelectronic device performance. Metal oxides, as a typical class of transparent ionic semiconductors, have been widely used for efficient photovoltaic applications as selective contacts, such as WO_x , V_2O_x , TiO_x , SnO_x , and ZnO .

A lot of researches have been conducted on the investigation of photovoltaic technologies, with the aim to converse the energy from solar light to electricity. However, comparing with the traditional energy sources, the high costs of photovoltaic devices still limit their wide applications. The great elevation of the photo-generated carrier transport can be achieved by the interface engineering with insertion of the intermediate layer. The interface engineering has been demonstrated by the improved device efficiency. For example, metal oxides (Cu_2O , NiO , V_2O_5 , MoO_3) [11-12].

Various metal oxide-based nanomaterials and their polymer nanocomposites have been reported over the decades. Due to their outstanding properties, such as electrical, magnetic, mechanical, optical, catalytic, etc., metal-oxide based nanomaterials are playing an important role in a wide range of applications including gas sensors, fuel cells, advanced ceramics, chemical sensors, biosensors, batteries, solar cells, pyroelectric, super capacitors, catalysts, anticorrosion coatings, etc. [13-14]. A series of metal oxide nanoparticles have been synthesized including TiO_2 , SiO_2 , iron oxide, zinc oxide (ZnO), gallium oxide (Ga_2O_3), nickel oxide (NiO), copper oxide (CuO) etc. They have different morphologies such as spherical, triangular, star, nanowires, nanotubes, nanorods, etc. Due to a high density and limited size, metal oxide nanoparticles showed exciting results in terms of physical and chemical properties; therefore, it is highly desirable to understand their various aspects in terms of synthesis, properties, and applications. In order to prepare polymer-metal oxide nanocomposites with a nanophase-separated structure, the homogeneous dispersion of metal oxide nanoparticles including a reduction in the size of the polymer-metal oxide interface is very important as it essentially alters the physical property of the nanocomposites. Metal oxide nanostructures have attracted substantial research interest, mainly because of their unique characteristics at nano dimensions compared to those of bulk or single-particle species. Generally, the distinctive electronic structure defines the specific metallic, semiconductor, or insulator characteristics of metal oxide nanomaterial's [15]. The semiconducting materials at nanoscale are widely used for the manufacturing of various electronic, electrical and photovoltaic devices owing to their unique band structure, optical properties, good charge mobility and ability to absorb photons from light. Among various photovoltaic devices, a regenerative photoelectrochemical solar cell called DSSC is a promising photovoltaic device for achieving reasonably high conversion efficiency as compared to the conventional silicon solar cells. Various metal oxide semiconducting nanomaterials such as ZnO , TiO_2 , SnO_2 , Nb_2O_5 and CeO_2 -based thin film electrodes and their nanocomposites have also shown comparably good conversion efficiency of DSSC due to their good optical and electronic properties.

The different sizes and shapes of metal oxide semiconductors like nanorods (NRs), nanowires (NWs) and nanotubes (NTs) are anticipated to improve the photovoltaic properties and increase the electron transfer during the operation of DSSCs. On the other hand, the pure metal oxides such as zinc oxide (ZnO) [16], MnO_2 [17], TiO_2 [18] and ZrO_2 [19]. In this chapter, we have briefly discussed several metal oxides in terms of their processing, functionality and applications, especially in photovoltaic application. In addition, recent literature has been reviewed on the basis of the morphology, structure

and physiochemical properties of metal oxide nanostructure semiconductors, with a brief description from recent literature of their photovoltaic applications.

2.0 Metal oxide nanomaterials

Metal oxides because of their electronic structure differences, exhibit metallic, semiconductor or insulator character. Preparation of these materials through the novel synthesis procedures can be described as physical and chemical methods. In general, two approaches have been used for the synthesis of these metal oxide nanostructures, top-down and bottom-up fabrication techniques. These approaches involve liquid–solid or gas–solid transformations [20-21]. Metal oxide nanostructures among the most versatile groups of semiconductor nanostructures stand out as one of the most common, most diverse and most probably richest class of materials due to their extensive structural, physical and chemical properties and functionalities. In recent times metal oxides have been at the heart of many dramatic advances in the materials science. These materials display most fascinating and widest range of properties. Due to the unique and tuneable properties of these metal oxides such as optical, optoelectronic, magnetic, electrical, mechanical, thermal, catalytic, photochemical etc. made themselves excellent candidates for various high level technological applications. For instance, fuel cells, secondary battery materials, ceramics, chemical sensors, gas sensors and biosensor, solar cells, alkaline and lithium ion batteries, pyroelectric, piezoelectric, ferroelectric, magnetic, actuator, super capacitors, optical devices, lasers, waveguides, infrared(IR) and solar absorbers, gate dielectric, dielectrics in dynamics random access memories, High TC superconductivity, decoupling capacitors, magneto- resistance and so on. Hence metal oxide nanostructure materials have been actively studied in a broader perspective by the researchers. Therefore it is essential to explore its understanding in great details in terms of their synthesis, properties and applications.

3.0 Synthesis techniques of metal oxide nanomaterial's

Synthesis of nanomaterials with desired morphology and composition is the most challenging task in the field of nanoscience and nanotechnology. In last several decades, the synthesis of metal oxides nanostructures has stimulated the great interest because of their novel properties which provide intense research efforts to fabricate the efficient miniaturized devices for the application in various nano electronics and photonics. So, a variety of fabrication techniques have been explored in the literature for the synthesis of these metal oxide nano-structures such as thermal evaporation [22] metal organic and

chemical vapour deposition [23], hydrothermal synthesis [24] template-based synthesis [25] etc. The synthesis methods can be classified into spontaneous as well as template-based synthesis category [26]. In the spontaneous synthesis, the crystal structures and surface properties grow along a particular direction, while as in the case of template based-synthesis, different templates are used to facilitate the growth of nanostructures. The spontaneous class of synthesis is further divided into three classes: dissolution-condensation growth, evaporation-condensation growth and vapour-liquid-solid (VLS) growth. In the dissolution-condensation process, the precursors are used to be first dissolved into a solvent or a solution and diffused latter on the surface resulting the formation of nanostructures, while as the evaporation-condensation growth process differs a little in the sense that one or more precursors used to be first evaporated to vapour at high temperature and then the resultant are condensed to solid at lower temperature. In the VLS classification, the materials used to go through three different phases; wherein some catalysts are usually needed to control the growth direction and growth area of nanostructures [27]. **Figure 2** represents general methods that can be used to synthesize metal oxide nanoparticles[28].

Nanoparticle research includes synthesis, characterization of the structural, chemical and physical properties, assembly into 1-, 2- and 3-dimensional architectures and application in various fields of technology. Various different synthesis techniques used for the fabrication of nanomaterials with a wide range of compositions and well-defined and uniform crystallite sizes. Two ways for the synthesis of nanomaterials are gas phase and the liquid phase. Although gas-phase processes are successfully employed for the low-cost production of large quantities of nanopowders [29]. A liquid-phase synthesis is flexible with regard to the controlled variation of structural, compositional, and morphological features of the final nanomaterials. The significance of nanoparticle synthesis is clear from the fact that many groundbreaking findings that can be regarded as milestones in the history of nanoscience are directly related to synthetic work, for example the discovery of carbon nanotubes [30], the synthesis of well-defined quantum dots [31] , or the shape control of CdSe nanocrystals (NC) [32]. The size- and shape-dependent physical and chemical properties of semiconductor nanoparticles [33] as well as the increased surface-to-volume ratio of nanoscale materials in general raised expectations for a better performance of nanomaterials compared to their bulk counterparts.

Two strategies are generally pursued to prepare nanostructures: the “top-down” approach, using physical methods such as photolithography and related techniques,

and the “bottom-up” employing physical and chemical approaches. For the miniaturization of electronic devices and the fabrication of complex 3D architectures, the bottom-up approach, making use of both specific and non-covalent interactions (e.g. hydrogen bonding, electrostatic and Van der Waals interactions) between molecules or colloidal particles to assemble discrete nanoscale structures, represents a valuable way [34]. The bottom-up approach for the assembly of nanoparticles seems to prove a solution to the technological challenges faced by the semiconductor industry [35].

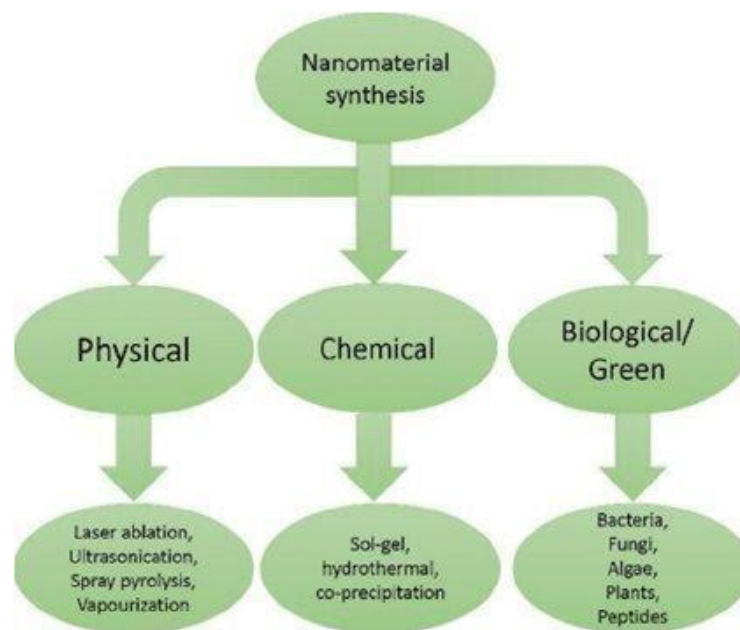


Fig-2 various methods for synthesis of nonmaterial's.

3.1.1) Vapour Phase growth Process

For the growth of a versatile group of nanostructures, the vapour phase deposition is the most versatile technique. In vapour-phase synthesis of nanoparticles, conditions are created where the vapour phase mixture is thermodynamically unstable relative to formation of the solid material to be prepared in nanoparticulate form. This includes the usual situation of a supersaturated vapour. It also includes a third process ‘chemical supersaturation’ in which it is thermodynamically favourable for the vapour phase molecules to react chemically to form a condensed phase [36].

3.1.2) Thermal Evaporation Process

Various materials nanostructures are grown up by thermal evaporation process. For this technique, there is a need of high temperature thermal furnace, used for vaporizing the source material and facilitates the deposition of the nanostructures at relatively low temperatures. Here in this process, the vapour species of source materials are generated first by physical or chemical methods, and subsequently are condensed under certain conditions such as temperature, pressure, on silicon substrate. Numerous

nanomaterial's have been grown by this method that range from elemental nanowires to a variety of semiconductor materials [37].

3.1.3) Pulsed Laser deposition Process (PLD)

The interaction of laser radiation with solid materials is primarily determined by the nature of the materials and the properties of the laser radiation. The use of a pulsed laser to induce the stoichiometric transfer of a material from a solid source to a substrate, simulating earlier i.e., 1965 flash evaporation methods was reported in the literature [38].

3.1.4) Sputtering Process

The ejection of atoms from the surface of a material (the target) by bombardment with energetic particles is called sputtering. Sputtering is a momentum transfer process in which atoms from a cathode/target are driven off by bombarding ions. Sputtered atoms travel until they strike a substrate, where they deposit to form the desired layer [39].

3.1.5) Metal- organic chemical vapour deposition (MOCVD) process

This technique (MOCVD) is also called as Metal-Organic Vapour Phase Epitaxy (MOVPE) and is widely used for preparing epitaxial structures by depositing atoms on a wafer substrate. For various thin film growths, this method has been extensively used. The operational principle is very simple. For the specific crystal growth, the desired atoms, which are bind with a particular complex organic gas molecules are passed over a hot semiconductor wafer. Due to heat, the complex organic molecules breakup and deposit the desired atoms layer by layer onto the substrate surface. The undesired remnants are removed or deposited on the walls of the reactor. By varying the composition of the gas, the crystal properties at almost atomic scale can be changed. Using this technique, layers of the precisely controlled thickness can be obtained, which is important for the fabrication of materials with specific optical and electrical properties. By MOCVD, it is possible to build a range of semiconductor photo detectors and lasers. Furthermore, recently scientists inclined to grow nanostructures with this technique too in addition to application of thin film growth. Varieties of semiconductor nanostructures have been synthesized by this technique as reported in the literature [40].

3.1.6) Cyclic feeding chemical vapour deposition (CFCVD) process

This technique was first developed by Umar et al in 2005 [41]. It differs from other chemical vapour deposition techniques in the way that it is based on cyclic feeding of reactant gases and precursor of the deposited materials. Therefore each precursor

required for the growth, is introduced into the reaction chamber only after a certain interval of time. This dosing sequence of precursors inhibits the gas phase reactions on the deposited material. This technique (CFCVD) yields the growth of low impurities content and is relative faster than the other conventional deposition techniques.

3.1.7) Spark discharge generation

Another means of vaporizing metals is to charge electrodes made of the metal to be vaporized in the presence of an inert background gas until the breakdown voltage is reached. The arc (spark) formed across the electrodes then vaporizes a small amount of metal. This produces very small amounts of nanoparticles, but does so relatively reproducibly. Weber et al. in 2001 used this method to prepare well-characterized nickel nanoparticles for studies of their catalytic activity in the absence of any support material [42].

3.1.8) Electrochemical deposition process

This method has been widely used for the fabrication of metallic nanowires in the porous structures. This method is convenient for the fabrication of metal oxide nanostructures. This method, from dissolved precursors, especially in aqueous solution, is a low cost and a scalable technique, well suited for a large scale of semiconductor thin film production. Recently, the electrochemical method attracted much attention due to its short reaction times and low cost. Yang et al. in 2007 reported the synthesis of highly ordered ZnO ultrathin nanorod and hierarchical nanobelt arrays on zinc substrate with an electrochemical route in the mixed H_2O_2 and NaOH solution [43].

3.1.9) Surfactant and capping agent assisted process

This method is an effective way for the synthesis of nanostructures. For obtaining a desired product, careful selection of precursor and surfactant species as well as controlling other parameters such as pH, concentration and temperature of the reactants are needed. In this regard, the surfactant assisted method is a trial and error based procedure, and it requires endeavor to choose proper capping agents and reaction environment. The capping reagents are used to confine the lateral growth of the desired product. It serves as a soft template which can change the free energies of the various surfaces and thus alter their growth rates. Earlier this method was used to control the morphology of the nanoparticles and now it is extensively used to for the synthesis of nanomaterials. Variety of nanomaterials such as ZnO, SnO_2 , NiO, $PbCrO_4$, CeO_2 etc have been synthesised by this process and are reported in the literature [44].

3.1.10) Sonochemical method

Sonochemical processing has been proven as a useful technique for generating novel materials with unusual properties. Sonochemistry arises from acoustic cavitation phenomenon which involves the formation, growth, and collapse of many bubbles in the aqueous solution [45]. Under extreme reaction conditions, for instance extremely high temperatures more than 5000 K, pressures larger than 500 atm, and very high cooling rates higher than 10¹⁰ K/s attained during cavity collapse. It leads to many unique properties of the irradiated solution, results the formation of nanostructures via chemical reaction. A variety of nanostructures are already prepared and reported in the literature [46].

3.1.11) Chemical precipitation method

Chemistry has been taking the leading role in developing new materials with novel properties for technological applications. It is comparatively easy to design materials of varied morphology and composition with a better control through chemical synthesis routes. Since properties of a nanomaterial are very sensitive to the resulting shape, size, and composition of the material, synthesizing nanomaterials through chemical route is gaining popularity. The potential of large scale synthesis of nanomaterials by chemical routes, in a cost-effective manner, is also one of the reasons behind its popularity. Metal oxides are prepared using chemical precipitation route. Selection of proper reactants is the most important factor in any chemical synthesis process. For this purpose extensive knowledge on chemical reactivities of the reagents, and the reaction steps that reactants supposed to undergo is required. The morphology and the composition of a nanomaterial can be controlled in a better way if each reaction step is known and controlled. The chemical reaction can start just by mixing the reactants in a beaker or in a round-bottom flask. Concentration of reactants, time and order of addition of reactants to the solution, temperature, pH, viscosity, and surface tension of the solution are the parameters to control. When reaction products get supersaturated, spontaneous nucleation occurs. Subsequently, it goes through the growth mechanism. Nanomaterials with different morphology, can be prepared during this step if proper care is taken. The major difficulty in the chemical precipitation method is to get rid of the contamination, particularly due to the by-product generated in chemical reaction. The optimization procedure is really a tedious job. So many experiments at different parameters need to be carried out in order to get the desired result. For any chemical method other working conditions like stirring speed, vibration, exposure to light, cleanliness of glassware etc. can significantly affect the quality of nanomaterial formed. Hence, synthesis of

nanomaterials of desired morphology and composition through chemical methods is considered to be an art, to some extent [47].

3.1.12.) Sol-Gel Technique

The sol-gel method is considered effective to modify the surface of substrates. Obtaining of a high surface area and stable surfaces is the most important advantage of the sol-gel method. The chemical and physical properties of the materials obtained by the sol-gel method are related to the experimental conditions applied. The sol-gel method involves two main reactions: (1) hydrolysis of the precursor in the acidic or basic mediums and (2) polycondensation of the hydrolysed products. In this way a polymeric network is formed in which MNPs can be retained [48].

3.1.13) Hydrothermal Technique

The hydrothermal technique has been most admired, garnering attention from scientists and technologists from different disciplines. The term hydrothermal is solely geological in origin. It was first used by British geologist Roderick Murchison (1792–1871) to describe the action of water at elevated temperature and pressure in bringing about changes in the earth's crust leading to the creation of rocks and minerals. The hydrothermal synthesis has been successful for the preparation of important solids, such as micro porous crystals, superionic conductors, chemical sensing oxides, electronically conducting solids, complex oxide ceramic and fluorides, magnetic materials, and luminescence phosphors. It is also a route to unique condensed material, including nanometer particles, gels, thin films, distinguished helical and chiral structures, and particularly stacking-sequence materials. Hydrothermal synthesis refers to the synthesis by chemical reactions of substances in a sealed heated solution above the ambient temperature and pressure [49].

3.1.14) Inert Gas Condensation

Inert gas condensation (IGC) is the most widely used method for the synthesis of metal nanoparticles. In IGC, metals are evaporated in an ultrahigh vacuum chamber filled with helium or argon gas at very high pressure. The evaporated metal atoms lose their kinetic energy by collisions with the gas, and condense into small particles. These particles then grow by Brownian coagulation and coalescence and finally form nanocrystals [50].

3.1.15) Microemulsion

The micro emulsion method is one of the ideal techniques for the preparation of inorganic nanoparticles, yet the mechanism of nanoparticle formation in the microemulsion has not yet been understood well. However, some researchers have suggested a mechanism for nanoparticle synthesis within microemulsions. When the microemulsion materials, including reactants, are mixed together, reactant exchange takes place during the collision of water droplets in the microemulsion. The reactant exchange is too fast and a precipitation reaction occurs in the nanodroplets, which is followed by nucleation growth and coagulation of primary particles, resulting in the final nanoparticles surrounded by water and/or stabilized by surfactants [51].

3.1.16) Microwave Assisted

Nanomaterials are the pillars of nanoscience and nanotechnology and to realize their full potential in various potential applications, synthetic methodologies/routes need to be established that are simple, fast and cost-effective. Wet-chemical approaches for nanomaterial synthesis have proven to be among the most versatile and effective routes to finely tailor nanocrystals with varying compositional and architectural complexity. Microwave-assisted solution route represents an efficient wet-chemical approach for the synthesis of nanomaterials that offers additional advantages, such as rapid volumetric heating, high reaction rates, size and shape control by tuning reaction parameters, and energy efficiency. In addition, the homogenous heating of the reactants in microwave synthesis minimizes thermal gradients and provides uniform nucleation and growth conditions that lead to the formation of nanomaterials with uniform size distribution [52].

3.1.17) Ultrasound

Ultrasound has become an important tool for the synthesis of nanoparticles. When liquids are irradiated with ultrasonic irradiation, ultrasonic cavitation will form. Ultrasonic cavitation produces a variety of physical and chemical effects, such as high temperature, pressure, and cooling rate, which provides a unique environment for chemical reactions under extreme conditions. Ultrasound is a fine method for the preparation of nanoparticles with controllable morphologies [53].

3.1.18) Chemical Vapour

Deposition Chemical vapour deposition is a chemical process used to produce high-quality, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical chemical vapour deposition,

the water (substrate) is exposed to one or more volatile precursors that react and/ or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber [54].

3.1.19) Physical Vapour

Deposition Physical vapour deposition describes a variety of vacuum deposition methods that can be used to produce thin films and coatings. Physical vapour deposition is characterized by a process in which the material goes from a condensed phase to a vapour phase and then back to a thin film condensed phase. The most common physical vapour deposition processes are sputtering and evaporation [55]. The procedure for physical vapour deposition is as follows: (i) sputtering/evaporation of different components to produce a vapour phase; (ii) super saturation of the vapour phase in an inert atmosphere to promote the condensation of metal nanoparticles; and (iii) consolidation of the nanocomposite by thermal treatment under inert atmosphere [56].

3.1.20) Colloidal Method

The colloidal method is a chemical process in which the chemical reduction of inorganic salts in a solution is used to synthesize metal particles; thereafter, consolidation of the dry material, followed by drying and thermal treatment of the resulting solid in a reducing atmosphere, such as hydrogen, in order to promote selective oxide reduction and generate the metal component [57].

4.0 Properties of nanomaterials

The nanoscience and nanotechnology has created various nanostructures in forms such as nanoparticles [58-59], nanowires [60-61], nanotubes [62-63], nanobelts [64-65], and assembling thereof like oxide aggregates [66-67]. A predominant feature of the nanostructures is that the size of their basic units is on nanometer scale (10^{-9} m). i.e., A nanostructure is any structure with one or more dimensions measuring in the nanometer range. A nanostructure should have characteristic dimension lying between 1nm and 100 nm. The structural, optical and electronic properties of intrinsic bulk semiconductors are not expected to change with mere changes in size or shape. i.e., In a bulk crystal, the properties of the material are size independent and are only chemical composition dependent. Nanostructured materials/films have received broad attention due to their distinguished performance in electronics, optics and photonics due to their peculiar size dependent properties. Novel properties are inherent to nanosized/nanostructured systems or films due to the reduction in dimensionality or

when the size of nanoparticles decreases below intrinsic length scales such as the Fermi wavelength of electrons, the ferromagnetic exchange length, etc [68]. When the particle size of the film material decreases, the volume fraction of atoms at surfaces or in interfaces largely increases. Due to the enhanced surface-to-volume ratio in nanostructures, their properties may depend sensitively on their surface conditions and geometrical configurations. Structural and geometric factors play an important role in determining the various attributes of nanostructures and leads to a modification of the thermal, chemical, electrical, optical, magnetic properties, etc., compared to their coarse-grained counterparts. Specific physical and chemical properties of an structured materials include size, shape, surface area, surface porosity, roughness, morphology, crystalline, solubility, chemical composition, surface chemistry, reactivity etc. Nanostructures are of both basic and practical interest since their physico-chemical properties can be tailored by controlling their size and shape at the nanoscale, leading to improved and/or novel applications. Films constructed with nanostructures are highly porous. The films comprised of nanoparticles can give a high specific surface area. Nanostructured films with well-aligned nanorods or nanowires or nanotubes may exhibit much larger surface areas than films prepared from randomly oriented nanoparticles. These nanowires, nanorods and nanotubes can provide direct pathways for electron transport. Moreover, when these nanorods are packed very densely, they enable fast and effective transport of electrons. Three-dimensional nanostructures such as metal oxide aggregates assembled with nanoparticles or other nanomaterials possess highly porous structure and are able to generate effective scattering to light in the solar spectrum. Imperfections, size dispersion, shape dispersion, defects, residual stresses, impurities, etc., in the material are known to influence the properties of nanostructured materials. Chemical properties of nanostructured films are generally surfacedominated. The surface of nanostructured materials plays an important role in the fundamental properties. The surface atoms are chemically more active than that of the bulk crystal. This is because they usually have fewer adjacent coordinate atoms and unsaturated sites. For example, oxygen vacancies on metal-oxide surfaces are chemically and electrically active. These vacancies function as n-type donors; often significantly increase the conductivity of oxide. Upon adsorption of charge accepting molecules at the vacancy sites such as NO_2 and O_2 , electrons are

Effectively depleted from the conduction band leading to a reduced conductivity of the n-type oxide. On the other hand, molecules, such as CO and H_2 would react with surface adsorbed oxygen and consequently remove it, leading to an increase of conductivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum confinement effects. The electronic structure of the

material is altered from continuous electronic bands to discrete or quantized electronic levels. Accordingly, continuous optical transition between the electronic bands becomes discrete. Quantum confinement varies the optical properties of the materials. Quantum confinement effects in semiconducting nanomaterials increase the band gap energy relative to bulk materials [69]. For films associated with larger nanoparticles, the electron excitation across the band gap depends only on the energy difference between the valence and conduction band. The quantum confinement effect begins to influence the excitation energy across the band gap especially when the size is of the order of Bohr radius of the material [70-71].

5. Applications

5.1 Photovoltaic device applications of nanomaterials

Due to the increased energy demands and depleting fossil fuels, renewable energy approaches such as solar cells have become increasingly popular. Briefly, the solar cell is an electrical device that can convert the electromagnetic radiation into electric energy. This device contains semiconducting material and works based on photovoltaic effect. The classes of solar cells are organic photovoltaics (OPVs), dye-sensitized solar cells (DSSCs), quantum-dot solar cells (QDSCs), oxide-based solar cells (OSCs) and perovskite solar cells (PSC). Since many metal oxides contain excellent semiconducting properties, they have been used extensively in this field [72]. The typical all-oxide solar cell configurations are depicted in **Figure 3**. [73]

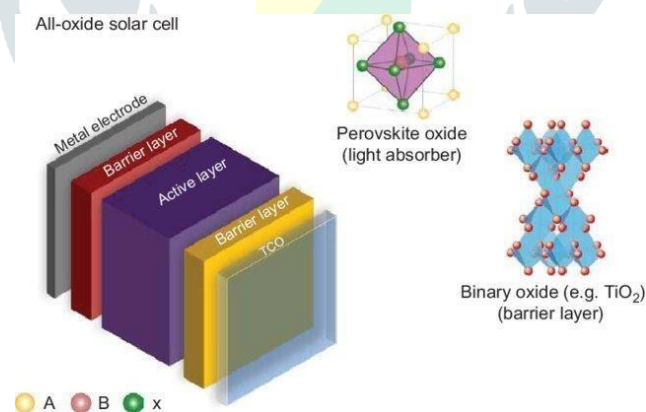


FIG.3 Schematic representation of an all-oxide solar cell.

5.1.1 Organic photovoltaic (OPVs):-

Organic photovoltaic (OPV) cells are currently attracting a great deal of scientific and economic interest and are playing a crucial role as one of the leading emergent photovoltaic technologies for low cost power production. Recent researches have unanimously proven the promise of this young photovoltaic technology in terms of their light weight, mechanical flexibility, ease of processing and low cost. In terms of performance, organic solar cells have witnessed a rapid increase in power conversion

efficiency driven primarily by materials development, physical understanding and device optimization. Although the highest reported power conversion efficiencies have not yet reached those of their inorganic counterparts, the perspective of cheap production as well as the perpetual improvements in device stability drives the development of organic solar cells further in a dynamic way [74].

OPV technology is still a relatively new type of thin film solar cells in the PV industry, in terms of performance, stability, and maturity. It involves photoactive organic layers, comprised of chains and bucky-balls of p-type and n-type semiconducting polymers and oligomer materials. In such polymeric OPV materials, the energy levels of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are analogous to the respective valence and conduction bands of conventional inorganic semiconductors. Organic semiconductors are thus selected, characterized, and tailored (through different chemical syntheses) based on the energy gaps between LUMO and HOMO levels. The representative examples of the commonly used organic donors (p-type polymers) include poly(p-phenylenevinylene) (PPV), poly(2-methoxy-5-(2-ethylhexyloxy)-1-4-phenylenevinylene) (MEH-PPV), and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)]-p-1-4-phenylenevinylene (MDMO-PPV). Others are poly(p-phenylene benzobisthiazole) (PBZT) and poly(3-hexylthiophene) (P3HT) [75].

5.2 Titanium Dioxide (TiO₂)

Organic Solar Cell (OSCs) with inverted structure have attracted much attention in recent years because of their improved device air stability due to the use of stable materials for electrodes and interface layers. TiO₂ is widely used in photovoltaic field like dye-sensitized solar cells, quantum dot-sensitized solar cells and so on because of its proper forbidden band width, good optical and chemical stability, nontoxicity, corrosion resistance and simple manufacturing process etc. Recently, inorganic-organic hybrid perovskite solar cell has attracted great attention as a new class of photovoltaic devices and its rapid development has led the power conversion efficiency up to 20%. TiO₂ nanomaterial appears to be a good candidate to be applied in it, which is usually used as compact layer or skeleton layer in perovskite solar cells. As an important part, its crystalline phase, particle size, morphology, preparation methods, film thickness and coverage have great influence on the performance of solar cells [76].

5.3 Zinc Oxide (ZnO)

The rapidly increasing demand for energy together with more and more concerns about the environment force us to seek sustainable energy resources and clean energy

technologies. As a result, photovoltaics have received increased interest in recent years. In order to further lower the cost of solar cells, organic solar cells based on fully organic semiconductors and hybrid solar cells based on a combination of organic and inorganic semiconductors have been intensively investigated as promising approaches to low-cost photovoltaics. Zinc oxide (ZnO) has received exceptional attention as a promising material for solar cell applications due to its nontoxicity, good stability, good electrical and optical properties, and low cost [77].

5.4 Molybdenum Oxide (MoO_3)

In polymer photovoltaic cells, a poly3,4-ethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) interlayer has been demonstrated to be effective to enhance both the short-circuit current as well as the open-circuit voltage [78]. In organic light emitting diodes OLEDs, the insertion of a poly9,9-dioctylfluorene-co-N-4-butylphenyl-diphenylamine TFB interlayer between a PEDOT:PSS and the light emitting polymer layer improves the device efficiency and stability [79]. Recently, molybdenum trioxide MoO_3 interlayer between the ITO anode and the hole transporting layer has been used for small molecule OLEDs and improved hole injection and operational stability have been reported [80]. More recently, transition metal oxide interlayer has also been used in organic photovoltaic cells [81].

5.5 Tin Oxide (SnO_2)

Tin oxide (SnO_2) is one of these oxides and last years, a growing interest has been devoted to tin oxide thin films. Due to its high chemical stability, as well as optical magnetic and electrical properties, SnO_2 has a wide range of applications such as films for electro chromic devices, organic light emitting diodes, n-p junction electrodes in dye sensitized solar cells. As shown recently SnO_2 appears to be one of the more promising anodic electro chromic materials [82].

5.6 Tungsten Oxide (WO_3)

Sang Bin Lee et al investigated the effect of tungsten oxide (WO_3) interlayer as a whole collection layer on the performance of organic photovoltaic cells according to the thickness and temperature of the interlayer. The characteristics of organic photovoltaic cells such as fill factor, current density, and open circuit voltage are continuously improved by increasing the temperature of the WO_3 interlayer. The surface of a treated WO_3 film promotes the crystallization of P3HT because a treated WO_3 film is more hydrophobic than a pristine WO_3 film. Furthermore, the energy barrier between P3HT and the WO_3 interlayer is minimized since the work function of the WO_3 film after

annealing progressively increases until a hole can be smoothly transferred. Therefore, organic photovoltaic cells using an interlayer of treated WO_3 film have higher hole mobility and better efficiency. [83] This study revealed that WO_3 based cells have significant shunt resistance which contributes to a high fill factor and open-circuit voltage. This demonstrates potential for using WO_3 in poly(styrenesulfonate) doped poly(3,4-ethylenedioxythiophene):(PEDOT:PSS)-free systems [84].

5.7 Vanadium Pentoxide (V_2O_5)

Vanadium pentoxide V_2O_5 films were fabricated by way of electrochemical deposition technique for application as hole transport buffer layer in organic solar cell. A thin and uniform V_2O_5 films were successfully deposited on indium tin oxide-coated glass substrate. The characterization of surface morphology and optical properties of the deposition suggest that the films are suitable for photovoltaic application. Organic solar cell fabricated using V_2O_5 as hole transport buffer layer showed better devices performance and environmental stability than those devices fabricated with PEDOT:PSS. In an ambient device preparation condition, the power conversion efficiency increases by nearly 80 % compared with PEDOT:PSS-based devices. The devices lifetime using V_2O_5 buffer layer has improved by a factor of 10 over those devices with PEDOT:PSS [85].

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