Chapter

Indium Oxide Based Nanomaterials: Fabrication Strategies, Properties, Applications, Challenges and Future Prospect

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Abstract

Nanostructured metal oxide semiconductors (MOS) in the form of thin film or bulk attract significant interest of materials researchers in both basic and applied sciences. Among these important MOSs, indium oxide (IO) is a valuable one due to its novel properties and wide range of applications in diversified fields. IO based nanostructured thin films possess excellent visible transparency, metal-like electrical conductivity and infrared reflectance properties. This chapter mainly highlights the synthesis strategies of IO based bulk nanomaterials with variable morphologies starting from spherical nanoparticles to nano-rods, nano-wires, nano-needles, nanopencils, nanopushpins etc. In addition, thin film deposition and periodic 1-dimensional (1D)/2-dimensional (2D) surface texturing techniques of IO based nanostructured thin films *vis-à-vis* their functional properties and applications have been discussed. The chapter covers a state-of-the-art survey on the fabrication strategies and recent advancement in the properties of IO based nanomaterials with their different areas of applications. Finally, the challenges and future prospect of IO based nanomaterials have been discussed briefly.

Keywords: metal oxide semiconductor, indium oxide based nanomaterials, fabrication strategies, periodic surface texturing, advanced applications

1. Introduction

It is no doubt that nanomaterials have attracted significant attention for both basic and applied sciences because these materials in nanodimension (1–100 nm) exhibit novel features including high surface area, excellent physical and chemical stability and lower material density compared to their bulk counterpart. In fact, these features of the nanomaterials help the researchers to design and fabricate novel functional nanomaterials/devices for practical use. Today, various forms of nanomaterials such as quantum dots, nanoparticles, nanoflakes, nanobelts, nanoribbons, nanosheets, nanofilms, nanotubes, nanofibers even nanocomposites have widely been used to improve the materials properties including thermal, electrical, mechanical, optoelectronics, corrosion resistant, self-cleaning, and sensing [1–3].

Over the past decades, nanostructured metal oxide semiconductors (MOSs) have drawn tremendous attention to materials researchers due to their widespread applications in various fields [4–6]. Among various MOSs, indium oxide (In_2O_3) has been investigated widely owing to its wide band gap, high electrical conductivity, stability and excellent optoelectronic properties [2, 7]. In_2O_3 (IO) is a wide band gap n-type semiconductor with direct band gap energy of 3.6 eV at room temperature [7, 8]. It is found that the band gap energy of IO thin film primarily depends on various factors such as annealing temperature and atmosphere as well as the nature of the substrate on which the film is to be deposited. The growth temperature also influences upon the morphological, structural, electrical and optical properties of IO based thin films. It is to be further noted that the thin films with enhanced functional properties like high electrical conductivity and visible transparency can be achieved by controlling the annealing temperature and atmosphere during the fabrication process [9]. It is noteworthy that these materials are suitable for different applications such as photovoltaic devices, liquid crystal displays, transparent conductive electrode in electronic devices, solar cells and flat panel displays, photodetectors, gas sensors, heat reflecting windows etc. [2, 8, 10]. On the other hand, different nanostructured IO based bulk nanomaterials such as nanosheets, nanowires, nanoparticles, quantum dots, single crystals are found to have potential applications [8, 11–13].

In the last decade, IO/IO based nanomaterials has been studied extensively. Around 54 years ago, Groth *et al.* [14] demonstrated that the small amount of Sn or Ti doping into IO can significantly enhance the electrical conductivity and infrared reflectivity without losing optical transparency in visible region. Based on this experimental observation, the Sn-doped In_2O_3, popularly known as indium tin oxide (ITO) creates an active area of research and development in the field of electrochromic and infrared reflective windows, light emitting diodes, transparent contacts for solar cells and flat panel displays and cladding layers for InGaN-based lasers [2]. Recently, the rapid increase in production of various electronic/optoelectronic devices with ITO results a sharp increase in price of indium. In order to minimize the cost without sacrificing the functional properties, indium oxide based thin films have been fabricated [15–17]. In this respect, the formation of heterostructure with band gap engineering of IO or IO based nanomaterials improve its functional properties for advanced applications especially in transparent electronic devices and sensors [18–20]. In this regard, Wang *et al.* [18] reported hierarchically structured ZnO decorated with IO nanoparticles synthesized by one-pot sol-gel process towards improvement in n-butanol sensing performance. Moreover, N-doped graphene quantum dots modified three-dimensional ordered macroporous IO based nanocomposites had been fabricated for NO_2 gas sensing application [10]. On the other hand, IO based nanomaterials are largely used for microelectronics and optoelectronic applications [2, 7, 19] and also found in significantly improved stability of solar cells without negotiating the performance of IO/ZnO electron transporting bilayer, synthesized by solution-process as reported by Kirmani *et al.* [20].

There are various methods now available to synthesize different types of IO/IO-based nanomaterials. The common techniques to deposit the thin films of IO based nanomaterials are sol-gel, spray pyrolysis, Ink-Jet printing, physical/chemical vapor deposition and atomic layer deposition [2, 4, 8, 21]. On the other hand, IO-based nanomaterials are generally synthesized by sol-gel, solvothermal/hydrothermal, co-precipitation, thermal evaporation and solid state reaction methods [22].

This chapter mainly highlights the synthesis strategies of IO based bulk nanomaterials with variable morphologies starting from spherical nanoparticles to nano-rods, nano-wires, nano-needles, nanopencils, nanopushpins etc. In addition, thin film deposition and periodic 1D/2D surface texturing techniques of IO based nanostructured thin films *vis-à-vis* their functional properties and applications have been discussed. Thus, the chapter covers a state-of-the-art survey on the fabrication strategies and recent advancement in properties of IO based nanomaterials with their different areas of applications. Finally, the challenges and future prospect of IO based nanomaterials have been briefly discussed.

2. Nanostructured metal oxide semiconductors

Now-a-days, nanostructured MOSs draw special attention owing to their promising applications in various areas such as electronic, optoelectronic, energy storage and conversion, adsorption, catalysis and sensing for their fascinating characteristics including high surface-to-volume ratio, surface permeability, light harvesting capability, electrochemical and photochemical properties [4–6, 23]. Nanostructured materials can be classified as zero-dimensional (0-D, nanoparticles, core-shell nanoparticles), one-dimensional (1-D e.g. rods/wires), two-dimensional (2-D e.g. layered structures, composite nanowires), and equiaxed or three dimensional (3-D e.g. nanotubes/nanowires bundles). It is to be noted that hierarchical nanostructures can be formed by combining 0-D, 1-D, 2-D and 3-D nanostructures [24]. These nanoscale structures of MOSs are capable to exhibit an improvement in mechanical, optical, electronic, optoelectronic or magnetic properties [1, 24].

2.1 Indium oxide based nanomaterials

In the next sub-sections, a discussion has been made on IO based nanomaterials especially bulk nanomaterials and porous nanomaterials including nanostructured thin films.

2.1.1 Bulk nanomaterials

Development of functional nanomaterials in bulk form can fulfill the purpose of achieving some special properties which can not be possible in the form of thin film/coating. This is because the properties such as structural, optical, optoelectronic, microstructural, electrical etc. of a material in bulk form can greatly differ from its thin film counterpart. Thus, the fabrication of bulk nanomaterials is also highly essential for their widespread applications. In this respect, the method of their syntheses can determine the specific structural features related to grain size, interface boundaries, porosity, structural defects and so on [25–27]. In this regard, for the synthesis of some indium oxide based bulk nanomaterials few well-established methods and the applications of the products are listed in **Table 1**.

Nanomaterials with porous architecture are very much important in the field of nanoscience and nanotechnology because of the ability of the materials to interact with atoms, ions and molecules not only at their surface but also throughout the bulk region. Moreover, the surface area which is mainly dependent on the particle size, shape and volume of the void space present in a porous nanomaterial is directly related to the functional property [4–6]. Thus, to obtain superior functional properties, the textural properties should be tuned accordingly.

System	Synthesis method	Ref.
NiS-IO-GO	Ultrasonic/hydrothermal	[28]
WO_3-IO	Sol-gel	[29]
SnO_2-IO	Precipitation	[30]
Y_2O_3-IO	Co-precipitation/sol-gel	[27]
Mn(II) doped IO foam	Sol-gel	[31]
Organic–inorganic IO foam	Sol-gel	[32]
Colloidal IO nanoparticles	Laser ablation	[33]

Table 1.
Synthesis and application of IO based bulk nanocomposite materials.

2.1.2 Nanostructured thin films

Indium oxide based nanostructured thin films have great significance owing to their variable band gap energy (3.2–3.8 eV) with high visible transparency, substantial environmental and chemical stability as well as high electron mobility and metal-like electrical conductivity [34–45]. These nanostructured thin films have been fabricated (**Table 2**) with excellent optical and electrical properties towards various applications [34–45]. However, the thin films are mostly used as TCOs [34–45]. In this regard, ITO thin film is known to be one of the most extensively used TCO. In addition, after modification of thin film surface (**Figure 1**) by periodic texturing adopting soft lithography or breath figure process (BRF), the surface textured films can be used for light frequency modulation, photoelectrochemical application and photocatalysis [4].

Thin film system	Deposition method	Application	Ref.
Indium oxide	Spin coating	Buffer layer and transparent electrodes in solar cells	[34]
Indium-doped ZnO	Spin coating	High-performance thin film transistors (TFTs)	[35]
Indium-gallium-zinc oxide	Ink-jet printing	High performance printed TFTs	[36]
InGaZnO	Spin coating	White light illumination and TFT channel	[37]
Zinc indium oxide	Sol-gel and breath figure	Photoelectrochemical water splitting	[4]
Antimony doped indium oxide	Sol–gel	Heat absorbing window glass fenestration	[38]
$Cu(In,Ga)(S,Se)_2$ (CIGSSe)	Spray pyrolysis	Solar cell	[39]
Indium zinc oxide	Inkjet-printing	TFTs	[40]
ITO	PVD with glancing angle	TCO, gas-sensors, self-cleaning	[41]
ITO	Ultra-thin RF magnetron sputtering	Top electrode in photovoltaic devices	[42]
Indium-gallium-oxide	CVD process	Ultraviolet phototransistors	[43]
Indium oxide	Atomic-layer deposition	TFTs	[44]
ITO	Sputtering	Acetaldehyde sensing	[45]

Table 2.
Different methods of deposition and applications of selected IO based nanostructured thin films.

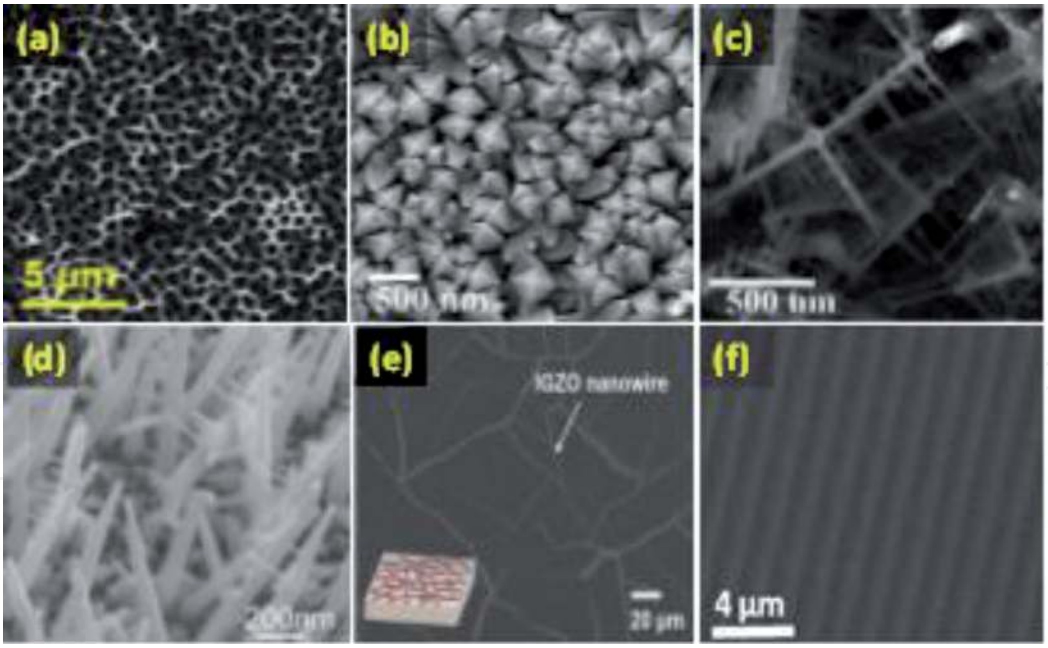

Figure 1.
FESEM images of IO based nanostructured thin films: (a) zinc indium oxide, (b-d) ITO, (e) indium gallium zinc oxide and (f) 1D surface patterned zinc indium oxide [4, 46–49]. (Copyright reserved to the American Chemical Society (2017), AIP Publishing (2015), Springer Nature (2018) and AIP Publishing (2014) for references [4, 46, 48, 49], respectively).

3. Fabrication strategies of indium oxide based nanomaterials

3.1 Indium oxide based thin films

Indium oxide based nanomaterials including nanostructured thin films and bulk nanomaterials are found to be a highly exploration area in the nano domain [34–45]. For deposition of nanostructured IO based thin films, several techniques including sol-gel, sputtering, physical vapor deposition (PVD), chemical vapor deposition (CVD), ink-jet printing, spray pyrolysis, atomic layer deposition (ALD) are available [34–45]. These are discussed in the next sub-sections.

3.1.1 Sol-gel coating technique

Sol-gel coating technique such as dip coating, spin coating or sometimes drain coating (especially for large size and heavy weight substrate) is also a very much useful for development/fabrication of various functional nanostructured thin films that are suitable for the use especially in the field of microelectronics and optoelectronics [4, 34–38]. The coating technique can fulfill to obtain desired physical and optical properties of the nanomaterials [34–38]. In this respect, sol-gel coating technique as a facile fabrication strategy has already been established as cost effective one for deposition of nanostructured IO based thin films [34–38]. Among other thin film fabrication techniques such as sputtering, CVD, ALD, PVD, spray pyrolysis and ink-jet printing, sol-gel technique is become a convenient one where high chemical and environmental stabilities of the nanomaterials can be obtained [34–38]. Sol-gel coating techniques can be applicable to deposit a huge numbers of high-performance nanostructured IO based thin films including ITO, IZO, IZGO, ZIO, IAO, Sb-doped IO, Cd-ITO, Cr-ITO for various applications [34–45]. A schematic diagram as shown in **Figure 2** where IO based thin films by sol-gel coating technique is described. In addition, some sol-gel based nanostructured IO thin films with their area of applications are highlighted in **Table 2**.

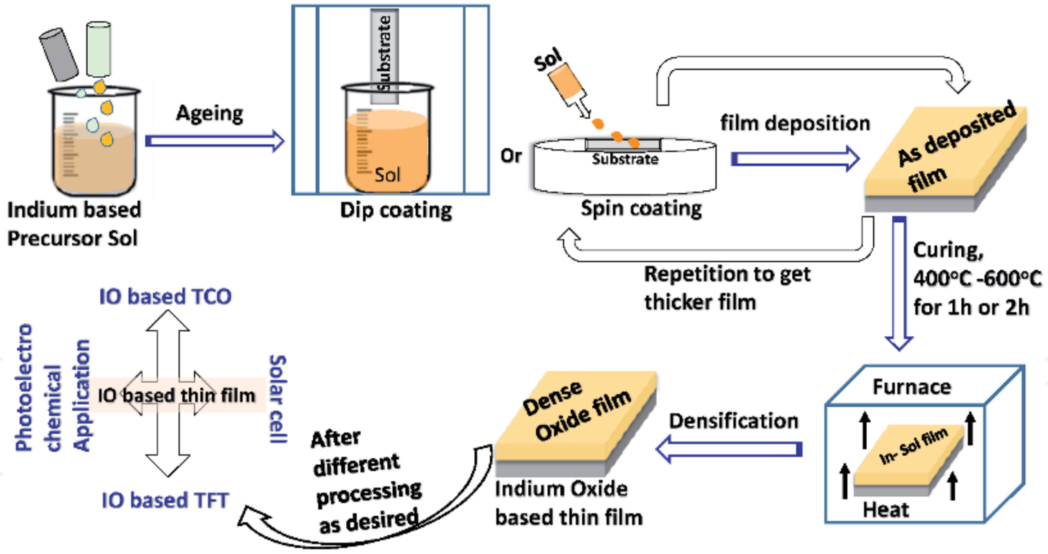

Figure 2.
Schematic presentation for the fabrication of IO based thin films by sol-gel coating technique.

3.1.2 Spray pyrolysis

In spray pyrolysis technique for IO based thin-film deposition includes spraying of suitable metal salt solution onto a heated substrate [39]. In this technique, the main steps are precursor solution atomization, transportation of resultant aerosol and decomposition of precursor onto a substrate [39]. Another important factor of this technique is to select an appropriate type of atomizer for desired application. Important parameters that have to be controlled are atomization, solute concentration, temperature gradient and carrier gas [39]. Adopting this technique, the fabrication of different IO based nanostructured thin films have been reported [2, 39]. Some of the potential nanostructured thin films and their applications are given in **Table 2**.

3.1.3 Ink-Jet printing

Ink-Jet printing technique (IJP) can mainly be divided into nozzle based digital inkjet printing and non-digital screen, offset, flexography and gravure printing [40]. In this technique with appropriate ink solvents, a widespread range of flexible thin-film devices can be fabricated such as transistors, light-emitting devices, sensors and energy harvesting and storage devices [40]. Although, gravure printing results high-throughput with high resolution and noble pattern fidelity but due to the characteristic contact nature of gravure printing along with the use of high-viscosity ink with binders, the contamination/residue related issues and degradation of printing materials may occur [40]. Few reports with respect to IO based nanostructured thin films are listed in **Table 2**.

3.1.4 Sputtering physical vapor deposition

A commonly used method for IO based thin film deposition is PVD in which the coating generates onto a substrate through atom by atom [41]. The PVD involves the atomization or vaporization of material from a solid source called target [41]. In this technique, the substrate majorly influences the properties of thin film. It is worthy to note that the deposition method must be performed under vacuum, plasma, gaseous or electrolytic environment. In this technique, the stresses generated into a thin film during cooling process or melting of substrate (mostly for an organic polymer) can limit the deposition process [41, 45]. Transparent conducting ITO thin films over silicon wafer can be fabricated by PVD techniques such as magnetron sputtering, vacuum evaporation, ion-plating [41, 45] towards gas-sensors, SERS, electrochromism and self-cleaning applications [41, 45].

3.1.5 Chemical vapor deposition

The IO based nanostructured thin films can also be fabricated by CVD [43]. In this process, the combination of gases react with substrate surface at comparatively high temperature that leads to decay of a particular constituent of gas combination. Hence, the fabrication of a metal or composite solid film can be deposited onto a substrate. This process can either be a pyrolysis of vapors of single organometallic compounds or a second reactant as an intermediate in vapor phase [43]. In this regard, some reports are available (**Table 2**) on single-phase metastable rhombohedral ITO epitaxial thin films with high transparency and electrical conductivity. The films had been deposited on Al_2O_3 substrate by CVD [43]. Also, indium gallium oxide thin film had been developed by co-sputtering using Ga_2O_3 and In_2O_3 as targets at room temperature [43].

3.1.6 Atomic layer deposition

ALD is also a technique for deposition of nano structured IO based thin films [44]. This technique mainly based on sequential pulsing principle of precursor chemicals in vapor state where each pulse is almost one atomic layer thin. The excess reactants as by-products can purge or evacuate with an inert carrier gas (e.g. N_2/Ar) [44]. The precursor used in this technique is pulsed into a chamber under vacuum (<1 Torr) condition for a certain period of time during each half-reaction. The process is cycled afterwards until a suitable film thickness reached. By applying this technique, a layer of very high aspect ratio of ITO crystals with nanoporous architecture can be fabricated. These materials can be used in photovoltaic or spectroelectrochemical applications [44]. On the other hand, In_2O_3 TFTs with ALD Al_2O_3 gate dielectrics had already been developed with significantly good electrical performance (e.g. field effect mobility, 7.8 $cm^2\,V^{-1}\,s^{-1}$ and on/off current ratio, 10^7) [44].

3.2 Periodic surface texturing of thin films

Periodic texturing also called patterning on thin film surfaces is a potential technique for the fabrication of photonic nanostructures for various optical applications [50]. It is worthy to note that the improved solar light absorption with high surface to volume ratio and enhanced light harvesting efficiency of the MOS thin films can be enhanced by periodic nanostructuring [6, 50]. There are several surface texturing techniques like conventional photolithography, nano-imprint lithography, electron-beam lithography, laser patterning, dip-pen lithography, reactive ion etching etc. available in the literatures [6] but these techniques are very costly, complicated, time consuming and also have several limitations owing to the nature of the component materials [6, 12]. Hence, versatile, simple and cost effective unconventional soft lithography is used now-days as an alternative to these conventional lithography techniques. This technique is largely used to generate periodic structures on metal oxide/mixed metal oxide including polymer based thin film surfaces [6, 12, 13]. In the next sub-sections, a special emphasis is given on sol-gel based soft lithography technique to perform periodic surface texturing on mixed metal oxide thin films.

3.2.1 Importance of periodic surface texturing

It is no-doubt that periodic surface texturing (pattering) is used to improve the functional properties of metal oxide thin films. The main objective of surface texturing is to effectively manage the incident light into thin film matrix. Thin films with different periodic surface structures are capable to enhance light absorption *via* light scattering and anti-reflective effects [50]. Improved light absorption ability of nanostructure thin films can enhance the performance of optoelectronic devices [6, 50]. Generally, light management in the nanostructure device based on two simple strategies- (a) anti-reflection and (b) enhancement in light absorption [50]. The enhanced light absorption occurs in surface textured thin films through multi-internal reflection which increases the light propagation length into the absorbing layer. Theoretically, it is possible to improve the light absorption up to an enhancement factor of $4n^2$ (Lambertian limit) where 'n' is denoted as refractive index of the material [50]. It is found that ordered three-dimensional nanostructured materials reach or exceed the Lambertian limit. Thus, it is established that the light absorption not only depends on the materials properties but also on the geometry of materials [50].

3.2.2 Periodic surface texturing techniques

As already stated in the previous sub-sections, periodic surface texturing of thin films is generally performed by conventional photolithography. Beside photolithography technique, several other techniques like nano-imprint lithography, electron-beam lithography, laser patterning, dip-pen lithography, reactive ion etching etc. are also used for the surface texturing [6, 13]. In soft lithography, one of the nonconventional lithography techniques, a soft organic material is mostly used to produce patterned structures without using light or any other high energy particles [6]. The main feature of this technique is to use a surface patterned elastomeric stamp which is generally made of polydimethyl siloxane (PDMS). This PDMS stamp can be used either as a mold to impart the patterns through physical confinement of a liquid precursor that dries to build the patterned film or as a stamp to directly transfers the precursor material to the substrate [51]. This technique mainly consists of different types such as replica molding (REM), microcontact printing (μCP), micromolding in capillaries (MIMIC), microtransfer molding (μTM). By using soft lithography techniques, it is possible to fabricate periodic surface textured films with features, ≥30 nm [51].

3.2.3 Applications

Periodic surface textured metal oxide based thin films have diverse applications in various fields like self-cleaning, photovoltaics, catalysis, energy conversion and storage, electronic devices, sensor and solar water splitting [52]. Now-a-days, surface patterned metal oxide thin films are also largely used in photovoltaic cells as active layers, photocatalysis and photoanode in photoelectrochemical (PEC) cells [4–6, 52]. Nanostructuring on the thin film surface increases the active surface area as well as photon capturing ability which are beneficial for the enhancement of photocatalytic and PEC performances [6, 13]. Thus, the PEC performance of MOS thin films can be improved by periodic surface texturing. It is worthy to note that overall PEC performance for solar water splitting depends on three fundamental factors- (i) absorption efficiency (η_{abs}), (ii) charge separation efficiency (η_{sep}) and (iii) charge transfer efficiency (η_{trans}). The performance for solar water splitting is expressed as $\eta_{abs} \times \eta_{sep} \times \eta_{trans}$ [53]. It is very challenging to get high value of the product of η_{abs} and η_{sep} (i.e. $\eta_{abs} \times \eta_{sep}$) because these are coupled with each other [53]. By increasing the active layer thickness, it is possible to increase η_{abs} value but it reduces the η_{sep} value.

As a result, the product of η_{abs} and η_{sep} decreases. However, the nanostructuring on MOS metal oxide thin film surfaces can mitigate the problem. Several nanostructured mixed metal oxide thin films including IO based nanostructured thin films are reported for improving PEC performances [4, 6, 53].

3.3 Synthesis of indium oxide based bulk nanomaterials

Indium oxide/indium oxide based nanomaterials can be synthesized by various synthesis methods. Some of them are sol-gel, solvothermal/hydrothermal, co-precipitation, thermal evaporation and solid state reaction. These are discussed in the next sub-sections.

3.3.1 Sol-gel method

Sol-gel is a wet chemical method for synthesis of various nanomaterials from sols. Generally, this method involves controlled hydrolysis of metal alkoxides like zirconium propoxide or metal salts such as metal nitrates or chlorides in an aqueous or organic solvent medium. It is to be noted that at the initial step of this method the hydrolysis and polycondensation reactions occur that lead to the generation of polymeric/colloidal sol with particles of nano dimension [5, 18]. By increasing mass of the desired material into sol or other significant changes in sol like solvent substitution, pH variation, solvent evaporation, etc. results the formation of gel with three-dimensional network of porous nature. The solvent is enclosed inside the porous gel structure [5, 18]. Heat treatment of the gel structure produces dense ceramics. It is well-known that the extremely pure and homogeneous multicomponent oxide can be synthesized by this method. Metal ions doped indium oxide and indium oxide based nanomaterials in the form of thin films or bulk nanocomposites can be fabricated/synthesized by adopting the sol-gel method [4–6, 12, 13, 18].

3.3.2 Solvothermal/hydrothermal method

Solvothermal or hydrothermal synthesis method is termed depending upon the solvent used in the synthesis method. In the hydrothermal method, water is generally taken as solvent whereas organic solvent instead of water is used in solvothermal method. In these methods, aqueous solutions of metal nitrates, chlorides and acetates are generally used as precursor materials for the synthesis of metal oxides [8, 10]. In this method, the precursor materials and solvents are taken in a particular stoichiometric ratio and stirred for a particular time period to obtain a homogeneous solution. Then, the solution is transferred into a Teflon coated stainless steel autoclave and placed it in an oven at elevated temperature for a certain time. Finally, the autoclave is allowed to cool down at room temperature and the precipitates obtained is dried and cured at higher temperature. Different indium oxide based bulk nanomaterials have been synthesized by solvothermal/hydrothermal method. In this regard, Suzuki *et al.* [54] synthesized indium tin oxide nanoparticles *via* solvothermal method for sustainable coating application.

3.3.3 Co-precipitation and thermal evaporation

Co-precipitation is a simple classical method to synthesize metal oxide nanomaterials. This method is cost-effective, very fast process and useful for larger scale industrial applications [27, 30]. By this method, it is possible to synthesize highly pure nanomaterial through an eco-friendly route. In this typical method, metal salts in the form of nitrate, chloride, or oxychloride as precursor materials are generally dissolved in aqueous solution and precipitated these into their corresponding hydroxides by addition of a base like sodium hydroxide or ammonium hydroxide. Finally, the precipitates are washed and calcined at high temperature to get metal oxide nanomaterials. Several reports are available on synthesis of indium oxide based nanomaterials by this method [55, 56].

3.3.4 Solid state reaction

Solid-state reaction is a well-known method for the synthesis of polycrystalline material from solid precursor materials. Generally, the reaction occurs at very high temperature. The main advantage of this method is its simplicity and the ability of large scale industrial production. Synthesis of pure In_2O_3 nanoparticles had been performed via solid state reaction method for the fabrication of optoelectronic devices by Jothibas *et al.* [57]. Moreover, Bykova *et al.* [58] reported Co-In_2O_3 nanocomposites thin film by solid-state reaction method and investigated its structural and magnetic properties. Recently, Co-In_2O_3 nanocomposites and cobalt-doped In_2O_3 have attracted significant attention due to their applications in optoelectronic, spintronic devices and gas sensors [58].

4. Properties of indium oxide based nanomaterials

4.1 Indium oxide based nanostructured thin films

IO based nanostructured thin films are immensely important due to their excellent optical, electrical, and mechanical properties suitable for various applications like energy conversion, biological and chemical sensing, solar cells, thin film transistors etc. [34–45]. Structural, optical, magnetic and electrical properties of IO based nanostructured thin films are discussed in the next sub-sections.

It is well known that IO based nanostructured thin films can act as excellent n-type transparent conducting oxides (TCOs) [34–45]. In bcc-Sn doped In_2O_3 forming ITO, the low formation energy implies a greater abundance of both the neutral and the cationic states of Sn dopant [38]. The structures of the thin films as confirmed by X-ray diffraction study, indicate that the films are polycrystalline with bcc structure having a 100 intensity peak at (222) plane of the crystal lattice. It is observed that the mobility of atoms and clusters on the surface of a substrate is proportional to their energy that would increase with increasing curing temperature. This would lead to the growth of In_2O_3 crystallites along a crystal plane (100). Among the fabricated IO based thin films, ITO is the most widely used efficient TCO due to its low energy of defect formation towards enhancing greater electrical properties [34–45]. It is worthy to note that the optical properties of IO based thin films are primarily dependent upon post annealing temperature, film microstructure, film physical thickness, surface roughness, levels of impurities, defect (like oxygen vacancies) concentration and deposition parameters [16, 17, 34–45, 59]. Low absorption (0.04–1.10%) of incident light in visible region is a crucial factor for IO based TCOs. The optical band gap widening or narrowing of IO based films occurs also based on dopant concentration [34]. In this context, different values as obtained from the reported works on IO based thin films show a high optical transparency (82–93%) of the films [34–45]. On the other hand, it is very much important to achieve the magnetic properties of IO or IO based thin films and bulk nanomaterials. In order to obtain the magnetic properties of these nanomaterials different magnetic metal such as Cr, Mn, Fe, Co, etc. ions with variable oxidation states are generally doped into the metal oxide [59]. It is found that the magnetic property is induced in indium oxide due to the presence of oxygen vacancies. The property basically depends on the nature/concentration of external dopant [59, 60].

4.2 Indium oxide based bulk nanomaterials

Functional properties of bulk nanomaterials can sometimes be advantageous compare to nanostructured thin films and the properties such as structural, optical, optoelectronic, microstructural and electrical in bulk nanomaterials differ from their respective thin film counterpart. In this respect, the preparation methods that govern the generation of specific structural features, porosity and defects in the bulk nanomaterials. It is reported that ITO and nickel doped ITO nanomaterials exhibit X-ray diffraction peaks similar to that of pure In_2O_3 with cubic bixbyite structure [27–30]. To calculate the band gap energy (BGE), the optical reflectance spectrum of a bulk nanomaterial can be recorded and then converted into its absorption spectrum. The absorption coefficient (α) can be determined using Kubelka-Munk function relation, $\alpha = (1 - R)^2/2R$. The BGE (E_g) can be determined from the relation, $\alpha h\upsilon = A\ (E_g - h)^{1/2}$, where h, υ and A are Plank's constant, frequency of light, proportionality constant, respectively [57, 61]. The BGE value of a metal doped IO/IO based nanomaterial varies depending on the nature of dopant element [27–30]. On the other hand, magnetic properties of IO/IO based nanomaterials are of great interest for basic science. Pure In_2O_3 shows diamagnetic behavior while the ITO displays ferromagnetism at room temperature. Moreover, different transitional metal doped In_2O_3 nanomaterials exhibit ferromagnetism at room temperature due to presence of oxygen vacancies [59, 60].

5. Applications of indium oxide based nanomaterials

Because of high optical transmittance and excellent electrical conductivity, indium oxide/IO based nanomaterials have variety of applications especially for fabrication of optoelectronic and microelectronics devices [2, 16, 17]. These are discussed in the next sub-sections.

5.1 Transparent conducting oxide

Generally, transparent conducting oxides (TCOs) are the materials that possess two major properties of (a) high electrical conductivity and (b) excellent optical transparency. Indium oxide is an important MOS material that mainly uses as TCO [62]. The properties of In_2O_3 are improved by doping or coupling of other semiconductors with wide BEGs. Improved electrical and optical properties of In_2O_3 based nanomaterials can promote to fabricate a variety of potential modern devices such as touch screen displays, low emissivity windows, solar cells, and gas sensors [2, 62]. Till date, ITO is the most successful TCO in terms of optoelectronic properties used commercially. It is found that ITO demonstrates a very high electrical conductivity and carrier concentrations without losing visible light transparency [62, 63].

5.1.1 Transparent conductive electrode

Transparent conductive electrodes made with TCOs are hugely used in flat panel displays, touch panels, lamps and thin film solar cells [62, 63]. Among the various TCOs, IO and ITO are highly used to fabricate transparent conductive coatings. It is noted that various properties of TCO thin films can be tuned by selecting suitable dopant with its optimized concentration. Thus, impurity doped ZnO, In_2O_3, and SnO_2 thin films are the best materials for practical utilization as transparent conducting electrodes [62, 63]. Also, different indium oxide based materials have already been explored to fabricate transparent conductive electrode [62–64].

5.1.2 Antireflection coating

Antireflection coating (ARC) is an optical coating which reduces undesirable reflections from substrate surfaces and increases transmittance [65, 66]. It is extensively used in industrial applications such as solar cells and photovoltaics, electronic device displays, and also general purposes, like spectacle and photographic lenses [65–67]. In this regard, IO based nanomaterials especially ITO has gained a special attention and ARC can be applied on this TCO thin films for the applications [66, 67].

5.1.3 Infrared reflective and electrochromic coatings

In electrochromic devices, the optical properties such as absorption, transmission, reflection and/emission can be changed when an electrical potential is applied. These devices are ubiquitous in daily life and are used as antidazzle rearview mirrors in cars as well as state-of-charge indicator strips of batteries. Now-a-days, an aim of research in electrochromic devices is to develop smart windows. It is applied in buildings to save energy cost by controlling the incident sun light and heat radiation. In this regard, Llordes *et al.* [68] reported a nanocomposite capable of tunable visible light as well as near-infrared transmittance. It is found that the development of smart windows with various switchable states including transparent, dimmed, cold and hot is possible with the use of this material. In this nanocomposite, the heat radiation transmittance can be controlled by ITO nanocrystals that exhibit an extensively tunable localized surface plasmon resonance [69]. It is also reported that the infrared transmittance is electrochemically controlled by the carrier concentration of ITO nanocrystals [69].

5.2 Optoelectronic applications

5.2.1 Photovoltaic cells

In photovoltaic (PV) cells/solar cells sunlight is directly converted into electricity. Generally, a PV cell is fabricated by two or more thin layers of semiconducting material. On illumination of sun light, the PV cells generate electrical charges that are conducted away by metal contacts. The PV cells have minimal maintenance cost and have a long life. Another important advantage of PV cells is that they generate solar electricity without emitting greenhouse or any other environmentally hazardous gases. Single PV cells generally provide very small amount of current. In order to obtain a demandable current and voltage output, a number of PV cells are connected together in series and confined with a glass cover, called solar cover glass and plastic sheet to form a PV panel.

Basically, it is a p-n junction diode. Under the exposure of light into the p-n junction, number of electron-hole pairs are generated and separated to produce electricity [70]. Up to date, three types of photovoltaic cells are available such as the first generation, second generation, and third generation PV cells. Crystalline silicon wafers as p-n junction diodes are the first generation cells. It is noted that the silicon solar cells has better efficiency but these are very expensive. The second generation solar cells are based on thin films of crystalline or amorphous silicon and $CuInSe_2$-based cells. It is found that the third generation cells such as polymer-based solar cells, nanocrystals based solar cells, dye-sensitized solar cells, quantum dot sensitized solar cells, perovskite solar cell and concentrated solar cells are very potential to harvest the solar energy (**Figure 3**) [70]. Recently, the inexpensive and flexible polymer thin films with stable inorganic nanostructures as fourth generation solar cells are developed to improve the efficiency [70]. In this regard, different indium oxide based nanomaterials are used for fabrication of advanced solar cells that can efficiently convert light energy into electricity [71, 72].

5.2.2 Photoelectrochemical cell

Photoelectrochemical (PEC) cell is a typical device where solar energy is converted into chemical energy in the form of fuel. Generally, it is made with photoactive semiconductor electrodes (photocathode and photoanode). The electrodes are immersed in a suitable electrolyte solution and the semiconductor-electrolyte junction is illuminated with a light source that has higher energy compared to the BGE of the semiconductor (**Figure 4**). As a result, the electrons and holes are

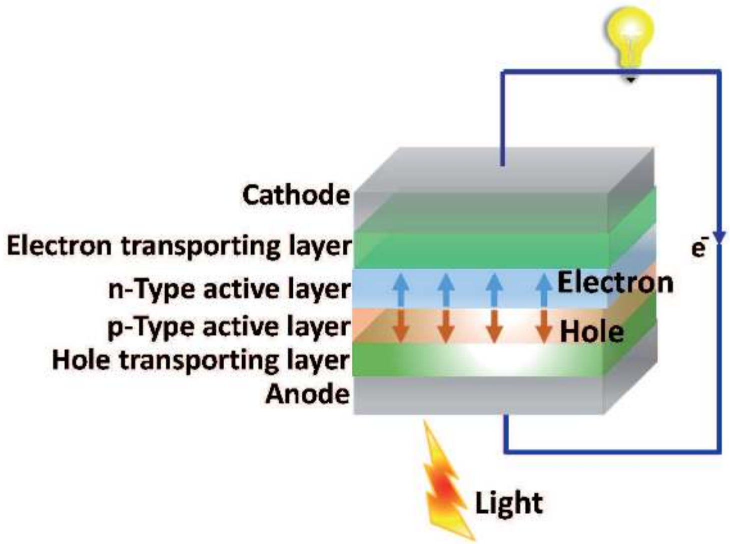

Figure 3.
Schematic presentation of a solar cell.

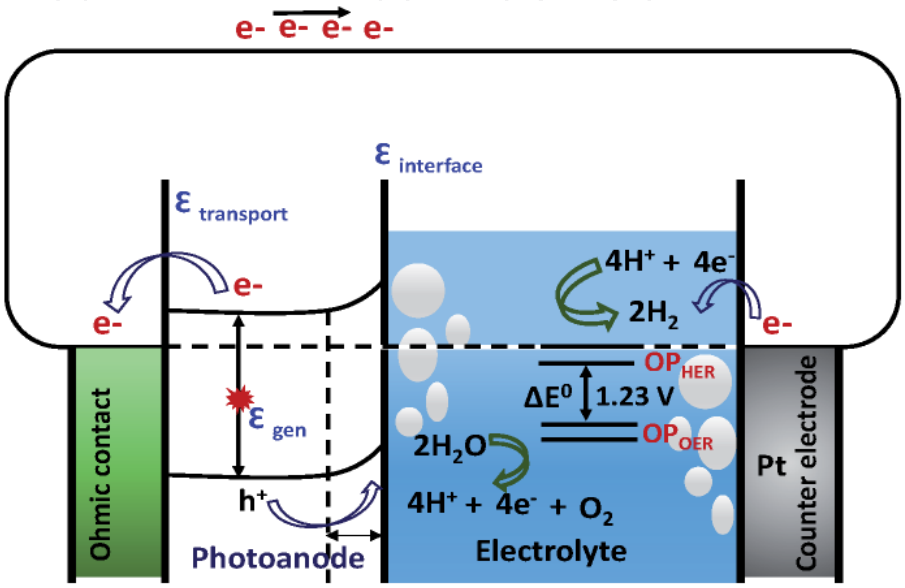

Figure 4.
Schematic diagram displaying the basic principle with key parameters of PEC water splitting.

generated and separated in the space charge region [4, 6, 11]. Now-a-days, various indium oxide based nanomaterials are used as both photoanode and photocathode materials for PEC water splitting application. Under light illumination, the photogenerated minority carriers (holes) in photoanode reach at the interface of electrolyte-semiconductor whereas majority carriers (electrons) accumulate at the interface of semiconductor-conducting substrate and transported with the help of a connecting wire to the counter electrode. These photogenerated charge carriers react with electrolyte solution to produce O_2 and H_2 [73]. In this regard, Cao *et al.* [11] fabricated a 3D hierarchically porous In_2O_3/In_2S_3 heterostructure array onto fluorine-doped tin oxide glass substrate *via* an ion exchange–induced synthesis and used the heterostructure film as photoanode in PEC cell with incident photon-to-current conversion efficiency of 76% at 400 nm.

5.2.3 Photodiodes

Photodiode is a lightweight sensor in which light energy is converted into electrical current or voltage. It is made of semiconducting materials and p-n junction is developed within it. Generally, it accepts light energy as input to produce an electric current as output. Different indium oxide based materials have been utilized as photodiode applications [74, 75].

5.3 Other applications

5.3.1 Photocatalysis

IO based photocatalysts are used for removal of volatile organic compounds, degradation of organic pollutants, hydrogen evolution and so on [76]. The photocatalytic activities of a single photocatalyst is usually limited due to their high recombination rate of photo-generated charge carriers and also their low utilization of visible light energy. In this respect, the fabrication of semiconductor nanocomposite based photocatalysts by imposing various novel strategies (such as doping impurity element into the metal oxide semiconductor or coupling with other semiconductor oxides, metals, and carbon) have been investigated as a feasible and promising strategy to overcome the shortcomings. Some IO based photocatalysts that are already studied by several researchers are displayed in **Table 1**.

5.3.2 Gas sensors

Gas sensors have widely been explored in recent years to monitor and rapidly detect flammable, explosive, and toxic gases in an environment. The most important factors in determining the gas-sensing performance of these sensors are sensitivity, working temperature, response/recovery time, and also the selectivity. Thus, significant research has been focused on exploring various methods to lower the working temperature, increase the sensitivity, shorten the response/recovery time, and also to improve the selectivity of metal oxide semiconductor based sensors. In the last decades, In_2O_3 [77] based gas sensors have been extensively studied because of the facile material synthesis and their high response to target gases. Among different metal oxide semiconductors, In_2O_3 is found to be an important and most promising gas-sensing material owing to its good electrical conductivity and high chemical stability. Till date, various nanostructures based on In_2O_3 for high-performance gas-sensing material in the form of thin films [78], nanowires [79], nanocrystals [80], and hollow microspheres have been developed [81].

5.3.3 Nonlinear optical properties

Nonlinear optics (NLO) is a wing of optics that explains the behaviour of light in nonlinear media, i.e. the media in which the polarization density, P responds nonlinearly to the electric field, E of the light. It is noted that nanocomposite materials showed large values of optical nonlinearities and fast response time. Thus, these materials can potentially be used in areas such as image processing, optical switching, optical modulation, optical information processing, and medical applications like cancer therapy [82]. Fellahi *et al.* [83] studied the nonlinear optical properties of fluorine doped and undoped In_2O_3 thin films using X-ray diffraction, electrical resistivity, transmission and third harmonic generation. The best value of nonlinear optical susceptibility $\chi^{(3)}$ is obtained from the doped films with low electrical resistivity of $6 \times 10^{-3}\ \Omega$ cm. This is because free carrier concentration in fluorine-doped In_2O_3 samples is higher than that in undoped In_2O_3 [83].

6. Challenges and future prospect

A variety of IO/IO based nanostructured materials ranging from nanodots to nanorods, nanoneedles, nanowires or nanoplates have been obtained for various applications that are already discussed in this chapter. In case of IO based materials particularly for TCO application, the efforts have already been focused on the enhancement of electrical conductivity by adopting suitable material fabrication techniques and tuning the chemical composition with doping level of impurities. Apart from the electrical and optical properties, some other properties such as thermal stability, chemical and mechanical durability, deposition temperature, toxicity and cost of the TCO materials have also to be taken into consideration for a specific application. These properties are influenced by diverse factors, some of which being controlled by the preparation method. The main challenges for the extreme improvements of TCO as well as optoelectronics performances rely on three major areas. Firstly, it is important to understand the mechanism of structure-properties relationships and carrier mobility of TCO materials for achieving low resistivity and high transparency over extended wavelength region. Secondly, it is very much important to develop the deposition methods of IO based materials as TCO on varieties of substrates especially on temperature sensitive substrates for more efficient use of these materials and reduce the overall manufacturing costs. Moreover, it is required to perform the manufacturing and recycling techniques that would be compliant with environmental protocols. Last but not the least, fabrication/deposition of nanostructured IO based materials with reproducible properties would definitely represent a long-term opportunity in TCO industry. It is expected that the development of multicomponent IO based nanomaterials would be highly beneficial to use in various applications starting from photovoltaics to lighting, TCO, electronic devices, smart windows, gas sensors and so on.

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Conflict of interest

The authors declare no conflict of interest.

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