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REVIEW ON METALLIC OXIDE NANOPARTICLES AND THEIR APPLICATION IN OPTOELECTRONIC DEVICES

Abstract

Among the large family of metallic oxides, there is a considerable group possessing excellent semiconducting properties. What follows, they are promising materials for applications in the field of optoelectronics and photonics. Thanks to the development of nanotechnology in the last few decades, it is now possible to manufacture a great variety of different nanostructures. By controlling their size, shape, composition and crystallinity, one can influence such properties as band gap, absorption properties, surface to volume ratio, conductivity, and, as a consequence, tune the material for the chosen application. The following article reviews the research conducted in the field of application of the metallic oxide nanoparticles, especially ZnO, TiO_2 and ITO (Indium-Tin Oxide), in such branches of optoelectronics as solid-state lightning, photodetectors, solar-cells and transparent conducting layers.

Key words

Metallic oxides, nanoparticles, ZnO, TiO_2, ITO, solar cells,

Introduction regarding metallic oxides in general

Metallic oxides (MOs) are among the most promising functional materials for several practical applications. The combination of positive metallic and negative oxygen ions, due to the high electronegativity of oxygen, results in the long-term stability of these compounds. The presence of oxygen atoms combined with metal atoms in the crystal lattice results in the formation of the bandgap in the range of 1 ÷10 eV [1], which allows the classification of these materials as semiconductors or insulators. These values may differ with the crystallographic form of the particular oxide. Exemplary MOs with their band gap at 300 K are included in Fig. **1**.

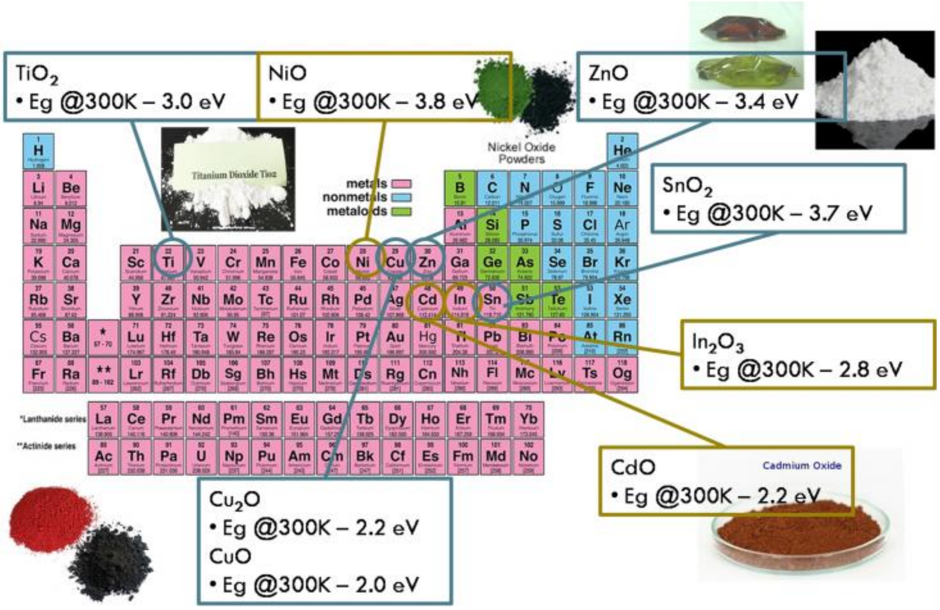

Fig. 1. Some metallic oxides which have found or may find applications in optoelectronics
Source: Authors, based on Ref. [1]

Last, but not least, with the abundant mineral resources, the majority of them are not very costly and can be an environmentally-friendly alternative to a lot of toxic or rare materials. Compared to organic substance, s they are more reliable and resistant to degradation due to humidity or harsh climatic conditions.

Taking into account all those advantages, it is not surprising that MOs already fulfil an important role in our everyday life, also being a common subject of research being lead in many different scientific fields.

Currently, a common application of MOs is to use them in the form of pigments in the chemical and food industry. They can be met in the form of powders of high opacity. TiO_2 and ZnO particularly are widely employed as a “perfect white” in paints, cosmetics and as a food colorant. Due to their band gap which corresponds to UV light, they are also used to form a UV-shielding layer, e. g in sun-protective creams, optical filters and anticorrosive coatings [2]. Due to the high thermal conductivity of ZnO, which depends also on its form [3][4], it is a common additive to rubber which enhance the heat dissipation rate [5]. The most popular industrial application in optoelectronics is Indium Tin Oxide (ITO), used in touch screens, LCDs, solar cells etc. [6].

The range of applications under research is also very wide. As in the group of MOs, one can find those which can be either intrinsically, or by doping, p-type or n-type semiconductors, they are used in the formation of various complex architectures in electronics. A lot of the oxides have been used in the construction of thin-film transistors [7] as well as in the form of charge-injecting layers [8] and charge-transporting layers [9]. Using MOs in bulk form or in thin films, light emitting diodes [10], laser diodes, photodetectors [11] and solar cells [12] - [14] are being constructed.

Apart from being semiconductors, MOs possess other interesting, exotic properties. Just to name a few: ZnO is characterized by a high piezoelectric constant [5] It also exhibits strong luminescence in the visible light [15], and therefore it can be used as a phosphor. ZnO and TiO_2 exhibit strong sensitivity of surface conductivity to the presence of adsorbed molecules. They can be used as gas sensors [16]. ZnO exhibits a non-linear optical response [5] and can be used in frequency converters. CuO and Cu_2O are known to be high-temperature superconductors [17]. TiO_2 and CuO/Cu_2O exhibit photocatalytic properties [18]. MnO_2, HgO, Ag_2O, PbO_2 are used in energy storing devices like batteries and super capacitors [19]. A lot of different applications are reviewed in [18][20][21].

A few words about nanoparticles (NPs)

Additional opportunities for engineering the properties of the above-mentioned materials are related to their miniaturisation up to the nanoscale. The advanced technology enables us to provoke a controlled growth to form such structures as thin planar films, where the movement of charge carriers is possible only in 2 directions (2-dimensional nanostructures), nanowires and nanotubes (1-dimensional nanostructures) and nanoparticles (0-dimensional structures), which, in the case when they are only several nanometers in diameter, are called quantum dots (QDs).

The miniaturisation results in t optical, electronic, thermal and chemical properties which may be quite distinct from the bulk counterpart of the nanostructure. When the size of the particle becomes of the order of several nm, its energy structure becomes similar to an atom, which can be excited only to discrete energy levels. These possible energy levels differ with the size and shape of the particle. Thus the effective band gap of NPs increases in comparison to the bulk material, which is reflected in the blueshift of the absorption and emission spectra. This effect is known as quantum confinement and, to some extent, allows the engineering of different features of NP.

Among all types of nanostructures, there are NPs which possess the highest density of states and therefore can exhibit high luminescence efficiency of 50% or more [22]. They also possess a very narrow emission spectra, which is a desirable property in the construction of light emitting devices and also allows us to construct a sensitive detector.

NPs are characterised by a high surface area in comparison to their volume, which signifies the increasing importance of the surface atoms and the modification of the properties of the particle itself as well as when it comes into interaction with the environment. This feature makes them very attractive for the applications where surface atoms play an important role, e.g. in gas sensors [16], super capacitors [20]. Fig. **2** schematically depicts a NP.

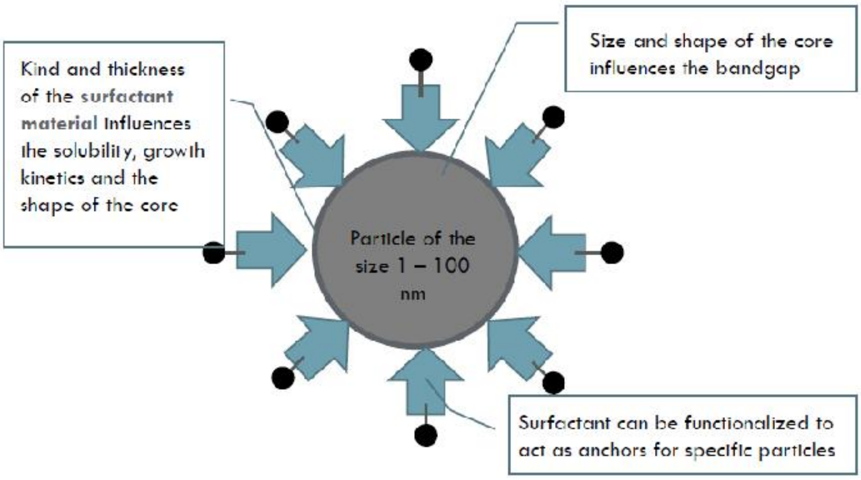

Fig. 2. Schematical view of the nanoparticle with a surfactant.
Source: Authors based on Ref. [20]

Synthesis of metallic oxide nanoparticles
There is a great variety of methods applied in order to synthesise nanoparticles. Three main subgroups can be distinguished: chemical methods, physical methods and mechanical processes such as milling. In case of MO NPs the most widely applied methods are listed below.

1. Chemical synthesis is based on precipitation of solid phase (NPs) due to the supersaturation achieved in the liquid medium composed of various reactants. The supersaturation can be achieved either by rapid cooling of a previously-heated solution or by adding the necessary reactants. Chemical synthesis can be conducted with different surfactants (which is included in Fig. **2**). Surfactants enable the controlling of the structural form and size of the particle by modifying its surface tension. They also prevent particles from aggregation.

   - Sol-gel method is probably the most frequent method of MO NPs synthesis. The term "sol" stands for the solution, which is composed of MO dispersed in an organic solvent. Depending on the fact if the solvent is water, the method can be specified to be aqueous or non-aqueous. The sol-gel transformation consists of reactions of hydrolysis, condensation and polymerisation. As the hydroxide polymerises, a dense porous three-dimensional gel is obtained. Subjecting it to subsequent drying and heating, the final form of the oxide can be controlled which could be coatings, solid foam, fibres, nanoparticles etc. as depicted in the Fig. **3**.

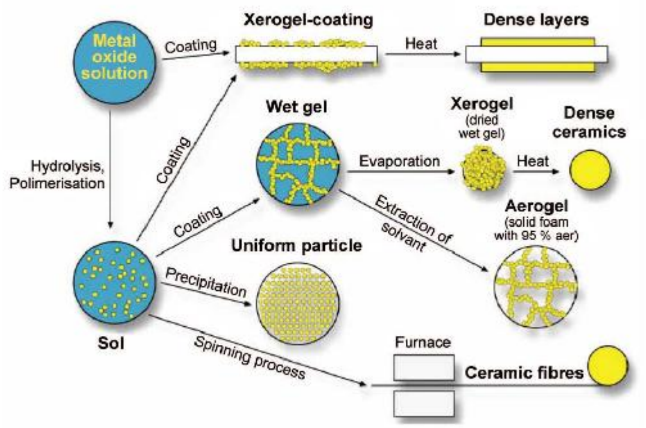

Fig. 3. Diagram of the sol-gel process.
Source: Universität Ulm, Anorganische Chemie

The pictures taken with the transmission electron-microscope (TEM) of different types of metal oxide nanoparticles synthesized by non-aqueous sol-gel method are depicted in the Fig. **4**.

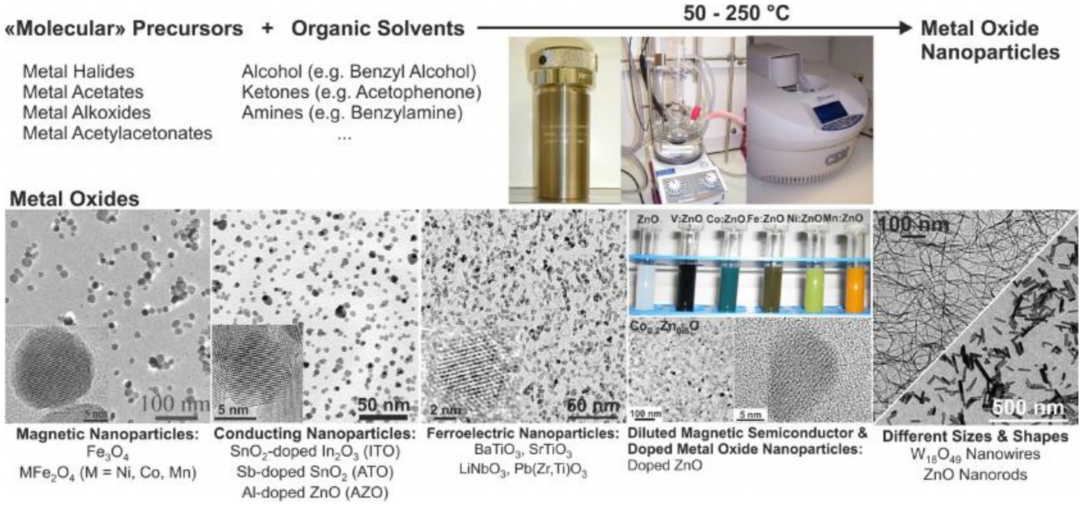

Fig. 4. Upper part: schematic of the non-aqueous and surfactant-free liquid-phase synthesis approach to MO NPs using autoclave, oil bath or microwave heating. Lower part: TEM images of selected MO NPs synthesized by the non-aqueous sol-gel approach.
Source: [24]

- Solvothermal synthesis employs dispersing the starting material in the solvent (if the solvent is water the name of the method becomes "hydrothermal synthesis") and subjecting it to high temperature and pressure, which results in supersaturation followed by the nucleation growth of particles. The particle size and shape can be controlled by the chemical parameters of the reaction - kind and ratio of the reactants, and thermodynamic parameters – temperature, pressure, time [23].

2. Physical methods of synthesis essentially incorporate a decomposition of a solid precursor into molecules or even single atoms, which are than deposited in the desirable form of a nanostructure. Usually these types of methods are the costliest as they require expensive vacuum techniques and the deposited layer area is strictly limited by the chamber dimensions. There is a great variety of physical deposition methods, among which those successfully applied in the generation of MO NPs are:

    - Physical Vapour Synthesis (PVS) involves a plasma arc applied to a solid target in order to generate vapour and trigger reactions leading to supersaturation. Mixing the resultant atoms with the reactive gas and cooling down results in the formation of molecular clusters which then aggregate in the form of particles [26]. In this method, the parameters of the particles are controlled by the type of the reactant gas and cooling rate [27]. A form of this method when the supersaturated gas additionally is subjected to the supersonic adiabatic expansion is called low energy cluster beam deposition (LECBD) and is applied in the formation of e.g. ZnO NPs [28].

    - Pulsed laser ablation method uses a high-power laser beam to vaporise the atoms from the solid target. The process can be conducted in ultrahigh vacuum (in this case the target is a bulk metal oxide) or in the presence of a background gas like oxygen. In the latter case the target can be made out of pure metal and its oxidation happens during the deposition

3. Mechanical methods are the top-down approach in the production of nanostructures. Those based on milling of bulk MOs are often used in pigment manufacturing and the ink industry in order to achieve a fine grinding and uniform dispersion of particles in the pigment. The dimensions of particles achieved are of no smaller than 200 - 300 nm [20]. Although there is a mechanical method successfully applied in the creation of MO NPs of smaller sizes, namely mechanochemical processing.

    - Mechanochemical processing (MCP) is a synthesis method which combines a reduction of physical size in a ball-mill and chemical reaction, activated at the nanoscale during grinding [26]. The precursors collide in the ball mill in the presence of the proper diluent and an exchange reaction takes place. Often a heat treatment is applied for the further decomposition of the compound which comes into being (e.g. ZnCO3 obtained during synthesis decomposes to ZnO when heated). With this method, NPs of the size in the range 18÷40 nm have been produced, depending on the milling time and the temperature at which the heat treatment takes place [29]. This method can be applied for the generation of MO NPs of those oxides for which the suitable precursors can be found.

Table 1: Summary of the revised fabrication method with the type of synthesized MO and the NPs size.

	Method	Type of MO synthesized	NPS size
Chemical	Sol-gel	TiO_2, ZnO, MgO, CuO, ZrO_2 [23], SnO_2 and many others	>20 nm [30]
	Solvothermal Synthesis	MgO, TiO_2, Fe_3O_4, WO_x [25], and many others	Ultra small, single nm [25]
Mechanical	Mechanochemical processing	ZnO [29]	18÷40 nm [29].
	Milling	all	Larger than 200 - 300 nm [20]
Physical	Physical Vapour Synthesis	ZnO [28]	Av. size - 8 to 75 nm [27].
	Pulsed Laser Ablation	V_2O_5, WO_3, ZnO, SnO_2 [31], NiO, ZrO_2, Cu/Cu_2O [23] and many others	Av. Size – 20 nm [31]

Source: Authors'

A great advantage of NPs is the fact that they can be dispersed in a chosen matrix – e.g. polymer. They can be used to form inks, pastes and gels which can be easily deposited with non-costly techniques suitable for both small scale deposition laboratory techniques like spin coating and dip coating, as well as large scale thin film deposition methods like spray-coating, roll-to-roll printing or doctor-blading [32]. This feature opens a great variety of applications in thin film and flexible electronics [21].

Applications in optoelectronics

This section presents the state-of-the-art in the application of some of the MO NPs, whose properties and fabrication techniques has been previously considered (Figure 1, Table 1).

- Applications in light emitting devices
  As nanoparticles are prone to have high luminescence quantum yield they can be possibly applied in the light emitting devices. They should also possess a direct band gap to emit light in the limited and desired spectral range. The exemplary constructions of the devices based on nanoparticles are depicted in Fig. **5**.

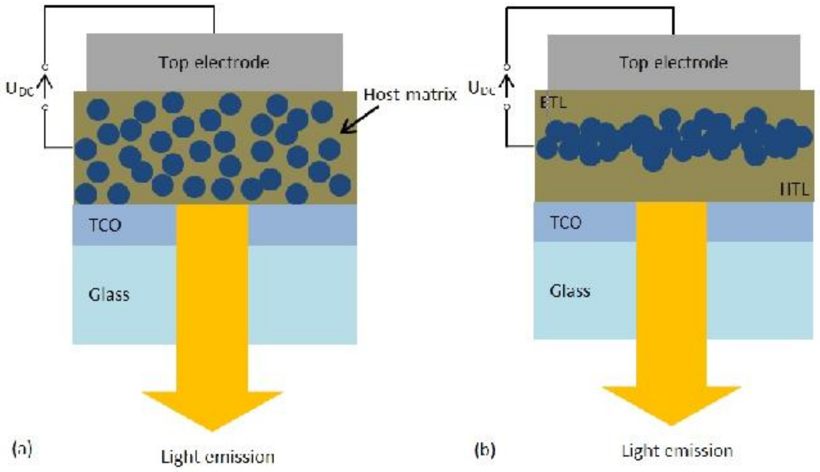

Fig. 5. Different concepts of NPs-based DC LEDs with transparent conducting oxide (TCO) as an anode and a metallic top electrode as a cathode, and a DC voltage applied across them. In the design a) the NPs are dispersed in an organic host matrix whereas in the design b) the light-emitting NPs are assembled in a tight layer neighbouring with hole- and electron transporting layer (HTL and ETL respectively).
Source: Authors based on Ref. [20]

The concept of LED depicted in Fig. **5**, a) was successfully realised for the first time in 1994 with CdSe QDs [33]. The efficiency of this device was low – 0.01%, but a lot of devices of similar structure, based on NPs have been developed since then.

Among the group of MOs it is ZnO that fulfils the condition for light emitting deivce (direct band gap), which is above 3 eV at room temperature [5]. Natural defects in ZnO particles, like oxygen vacancies or Zn interstitials, as well as doping with metal atoms, can result in additional energy states within the bandgap and the emission of different wavelengths in the visible range becomes possible [15]. In the case of defect-related emission, the emitted colour is not connected to the size of the particles. Thus crystals of the sizes larger than 100 nm can be used which decreases the manufacturing cost. A ZnO nanoparticle-based light-emitting diode has been constructed by Neshataeva et al. [34]. In this design the ZnO nanoparticles were sandwiched between transparent electrodes made of Fluorine doped Tin Oxide (FTO) and a layer of Al acting as a cathode (Fig. **6**a). The defect-related electroluminescence has been observed - Fig. **6**b, with the spectral range covering red and NIR wavelengths for lower bias values like 4V with a spectrum shifting towards the lower wavelengths when a larger bias – 10 V- has been applied. Such a spectrum resulted in the emission of white light.

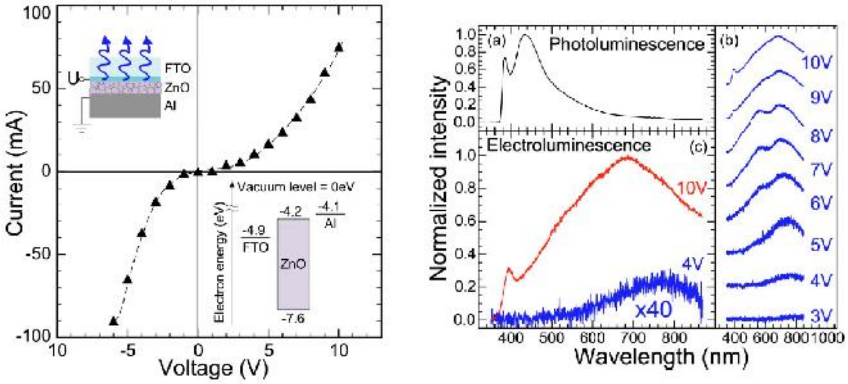

Fig. 6. a) Room temperature I-V characteristics of the light-emitting device based on ZnO nanoparticles and its b) 334.5 nm-excited PL spectrum and EL spectra of the device biased in the forward direction.
Source:[34]

Another approach in creating a white light emitting device is taking advantage of the photoluminescence effect of the ZnO nanoparticles. A stack of different phosphor layers emitting in red, green and blue excited by UV or blue light is one of the concepts for the creation of white LED [35].

ZnO as well is considered an alternative to GaN, as creating only blue or UV emitting diode from ZnO is theoretically possible, but has not been proved experimentally [20].

- MO NPs as Charge Transporting Layers
  MOs have been used both in the form of bulk and nanostructured materials for the formation of charge transporting layers (CTL) (they are included in the scheme depicted in Fig. **5**, b). This allows the formation of organic-free LED, which is highly desirable as organic substances tend to rapidly deteriorate when exposed to humidity or oxygen [34] and also enables the use of much higher current densities [21]. In literature, one can find the applications of CuO as the hole transporting layer (HTL) [36], nanoparticles of ZrO_2 as the electron transporting layer (ETL) [37], QD LED with MoO_3 used as an HTL and TiO_2 used as an ETL [38], ZnO as the ETL [1]. These layers have been used in the construction of light emitting devices, photodetectors and solar cells. Especially in organic dye sensitized solar cells (DSSC) a very important role is fulfilled by TiO_2, which serves as a charge transporting layer and the area of which is used for the absorption of dye. The mesoporous structure of titania, which can be achieved e.g. by sintering TiO_2 NPs, provides ~100-fold enhancement of the surface area per micrometer of thickness in comparison to the flat film [20]. A larger active area leads to high-density packed monolayer of the dye and the enhancement of the light harvesting properties of the solar cell.

- MO NPs as light-converting medium

  The photoluminescence effect of NPs can be also used to create a light converting layer. It may find application e.g. in photovoltaics as the conventional homojunction solar cells are not able to use the whole solar spectrum with UV and NIR being particularly problematic. ZnO NPs have been proposed as down-converting (DC) agents, which are able to absorb the UV light and then re-emit it in the visible range [39] - [41]. Doping or mixing them with rare earth elements (REE) [42] can prolong the luminescence time and efficiency. MO NPs have been also applied in the up-conversion (UC) process [43], in which low energy photons from near infrared are absorbed in order to obtain the emission of the photons from the visible range. For this application the MO NPS of e.g.. ZnO, ZrO_2, Y_2O_3, Lu_2O_3, $BaTiO_3$, TiO_2 [15] have been used as a host matrix for such REE as Er, Ho, Nd, Yb [44].

  The photoluminescence effect of NPs can be also used for the fabrication of luminescent converters [45], which is one of the forms of geometric concentration of sunlight reaching the photovoltaic cell. The operation principle is explained in the Fig. **7**.

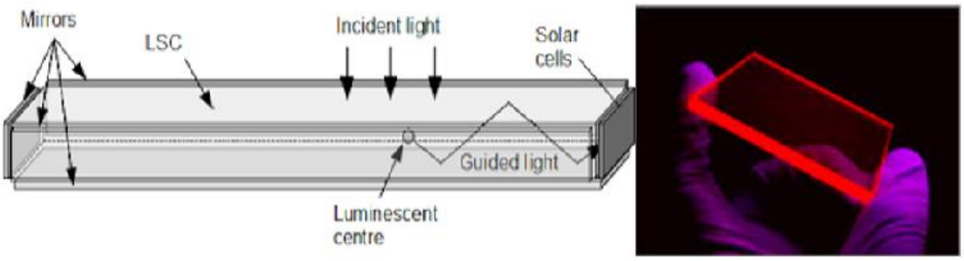

Fig. 7. Schematic picture of a luminescent concentrator. NPs act as luminescent centers, they absorb the incident light and emit the light in different frequency. Total internal reflection traps the emitted photons in the concentrator and guides the light towards the solar cells on the edges. Part of the light striking the internal surface at very steep angles manages to escape the structure through escape cone of total internal reflection.
Source: [46].

- Applications as transparent conducting oxides (TCO)

  The general electro-optical requirements for the transparent conductor is the resistivity of the order of 10^{-3} Ω cm or less, and the average transmittance above 80% in the visible range. Therefore, a semiconductor material suitable for this application should have a carrier concentration at least 10^{20} cm^{-3} and an energy band gap above 3.0 eV [47]. An important group of MOs possesses these properties, the most popular studied materials and their dopants are gathered in Table 2.

Table 2: Most popular TCO materials and their dopants.

	Material	**Dopant or compound**
	SnO_2	Sb, F, As, Nb, Ta
	In_2O_3	Sn (ITO), Ge, Mo, F, Ti, Zr, Hf, Nb, Ta, W, Te
	ZnO	Defect-controlled doping, Al (AZO), Ga (GZO)
	CdO	In, Sn
	TiO_2	Ag, Nb
Binary oxides	ZnO – SnO_2	Zn_2SnO_4, $ZnSnO_3$
	ZnO – In_2O_3	$Zn_2In_2O_5$, $Zn_3In_2O_6$
	CdO – SnO_2	Cd_2SnO_4, $CdSnO_3$
	CdO – In_2O_3	$CdIn_2O_4$
	$MgIn_2O_4$	
	$GaInO_3$	
Ternary oxides	ZnO-In_2O_3-SnO_2	$Zn_2In_2O_5$ – $In_4Sn_3O_{12}$
	CdO-In_2O_3-SnO_2	$CdIn_2O_4$ – Cd_2SnO_4
Quarternary oxides	ZnO-CdO-In_2O_3-SnO_2	

Source: Authors', based on [46].

Currently, the most widely used transparent conductor is Indium-Tin Oxide (ITO). It has been found that the 90/10 atomic ratio of In_2O_3 to SnO_2 results in the optimal electro-optic properties [6]. However, this material possesses some disadvantages, namely its brittleness – it can fracture at relatively low strains of 2-3% which causes an increase in resistivity [48] [49], and scarcity of supply - indium is a fairly rare material and current demand for ITO consumes about ¾ of global indium consumption and is constantly rising [6].

Among other materials studied, especially interesting and environmentally friendly materials is ZnO and its Al and Ga-doped versions, commonly named AZO [50] and GZO respectively. Recent advances in the deposition methods of such thin films have allowed the achievement of comparable results in terms of resistivity as for ITO [47].

A solution for the inconveniences of the ITO bulk electrode is manufacturing a printing paste containing ITO NPs dispersed in a solvent and depositing it on the polymer flexible substrate [51].It has been proved that UV treatment and annealing under various atmospheres enables the achievement of a resistivity of 0.035 Ω cm with 89% optical total transmittance electro-optic properties [52] are sufficiently satisfying to apply the NP layer as a contact f. e. in organic photodiodes. What is more, such geometry of electrodes (conducting NPs dispersed in a non-conducting host matrix) results in a higher charge-transfer surface than a plain electrode and highly increases the electrode kinetics [54]. This concept has also been applied to different types of MOs – e.g. the ZnO NPs for the inter-electrode in tandem organic cell [55].

Summary and conclusions

In the frame of the following review, the general properties of MO and NPs have been described, as well as some applications of MO NPs in optoelectronics have been enumerated. It should be taken into account that they are only the tip of an iceberg already in the field of optoelectronics, not to mention other domains. In some fields MO NPs are already the leading solution like in the field of transparent electrodes. Some of the similar features are possessed by carbon nanostructures and advanced polymers [6], which achieve approximate, but still inferior, parameters. Although for the majority of optoelectronic applications the MO NPs are being extensively researched as an alternative material to some of the rare and costly semiconductors. An noticeable trend in electronics is the gradual shift from all-inorganic and Si-centered devices towards hybrid flexible and lightweight organic-inorganic devices. The MO NPs seem to be a suitable candidate, but there are still some obstacles before commercializing the practical application of them. Either an effort should be made in order to increase the effectiveness of the prototype devices or the stress should be put to lower the cost of the manufacturing and deposition techniques.

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