



Review

The future of semiconductors nanoparticles: Synthesis, properties and applications



Augustine D. Terna^a, Elias E. Elemike^{b,*}, Justina I. Mbonu^b, Omosedo E. Osafule^c, Rachael O. Ezeani^b

^a Department of Chemistry, Federal University of Technology Owerri, Nigeria

^b Department of Chemistry, Federal University of Petroleum Resources Effurun, Nigeria

^c Department of Physics, Federal University of Petroleum Resources Effurun, Nigeria

ARTICLE INFO

Keywords:
Semiconductors
Nanomaterials
Synthesis
Applications
Band gap

ABSTRACT

In this review, synthesis, properties and applications of semiconductors nanomaterials was discussed. Semiconductors have become an all-important inorganic materials and their processing into nanoparticles or quantum dots has shown advanced and novel ways of applications. Different categories of binary, ternary and multinary semiconductors were highlighted. Semiconductor nanocomposites, on the other hand, have emerged from the combination of semiconductor nanoparticles with other materials such as metals, polymers, cellulose using different synthetic methods. Among all the methods, green techniques seem to be the interesting protocols for nanoparticles to be applied in biomedical fields since they involve non-toxic substrates and reaction media. Sonochemical method, solvothermal approach and microwave synthesis are among the facile methods which are being exploited and holds great future for large scale nanomaterials. The nanomaterials however are widely applied in photocatalysis, energy, sensing, water purification, biomedicine, electronics with further material engineering for other future applications.

1. Introduction

Semiconductors are solid substances which are neither good conductors (metals) or insulators (glass) but have crystalline structure and contain very few free electrons at room temperature. They have resistivities and energy gaps which lies between the conductors and insulators. Their conductivity is more than that of the dielectrics but less than that of conductors [1]. Fig. 1 explains the energy band gap of insulators, semiconductors and conductors (metals). Semiconductors behave like an insulator at room temperature but their electrical conductivity increases with increasing temperature contrary to the behaviour of a metal [1]. If suitable impurities are added to the semiconductors, the conductivity can be controlled. Some examples of semiconductors are silicon, germanium, carbon etc. Semiconductors are the basic building block of modern electronics, including transistors, solar cells, light-emitting diodes (LEDs), and digital and analog integrated circuits. The modern understanding of the properties of semiconductors lies on quantum physics which explains the movement of electrons and holes inside a crystal structure and also in a lattice. An

increased knowledge of semiconductor materials and fabrication processes has made possible continuing advancement in the complexity and speed of microprocessors.

Semiconductor devices can display a range of useful properties such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Since the electrical properties of semiconductor materials can be modified by controlled addition of impurities or by the application of electrical fields or light, devices made from semiconductors can be used for amplification, switching, and energy conversion. Current conduction in a semiconductor occurs through the movement of free electrons and “holes”, collectively known as charge carriers. Adding impurity atoms to a semiconducting material, known as “doping”, greatly increases the number of charge carriers within it. When a doped semiconductor contains mostly free holes it is called “p-type”, and when it contains mostly free electrons it is known as “n-type”. The semiconductor materials used in electronic devices are doped under precise conditions to control the location and concentration of p- and n-type dopants. A single semiconductor crystal can have many p-and n-type regions; the p-n

* Corresponding author.

E-mail address: elemike.elias@fupre.edu.ng (E.E. Elemike).

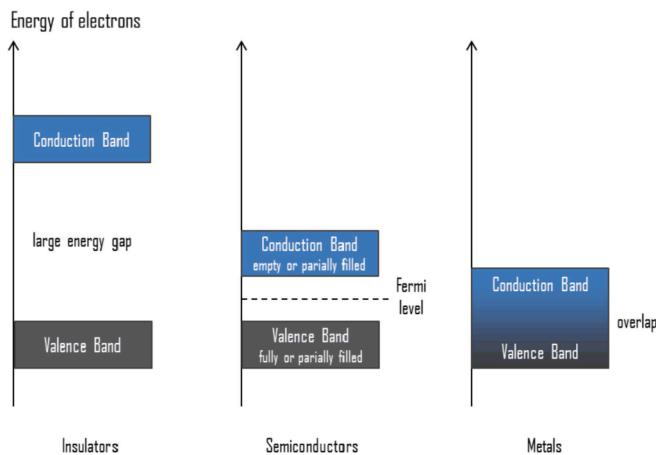


Fig. 1. Band gaps of different solid materials [1].

junctions between these regions are responsible for the useful electronic behavior. Although, some pure elements and many compounds display semiconductor properties; silicon, germanium, and compounds of gallium are the most widely used in electronic devices. A large number of elements and compounds that have semiconducting properties, include certain pure elements of group IV or 14 [2]. They have 4 valence electrons in their outermost shell which gives them the ability to gain or lose electrons equally at the same time; others are binary compounds, particularly between elements in groups III and V (such as gallium, arsenide), groups II and VI, groups IV and VI, and between different group IV elements (e.g. silicon carbide), certain ternary compounds, oxides and alloys. There are also organic semiconductors which are made of organic compounds majorly carbon materials. Most common semiconducting materials are crystalline solids but amorphous and liquid semiconductors are also known. Hydrogenated amorphous silicon and mixtures of arsenic, selenium and tellurium in a variety of proportions are among the known amorphous semiconductors. These compounds share with better known semiconductors, the properties of intermediate conductivity and a rapid variation of conductivity with temperature, as well as occasional negative resistance. Such disordered materials lack the rigid crystalline structure of conventional semiconductors. They are generally used in thin film structures, which do not require materials of higher electronic quality, being relatively insensitive to impurities and radiation damage. Nowadays semiconductor materials are used in every sector of modern technology. For technical applications, the high temperature materials are used widely.

1.1. Classification of semiconductors

Semiconductors may be classified broadly into intrinsic semiconductor and extrinsic semiconductor. Intrinsic semiconductors can also be referred to as pure or undoped elements (Si, Ge) whereas the

extrinsic semiconductors are doped with other materials otherwise referred to as impurities and they can be n-type or p-type... the iii

1.1.1. Intrinsic semiconductor

An intrinsic semiconductor can be seen as a very pure semiconductor material or a material in which the number of holes is equal to the number of electrons in the conduction band as shown in Fig. 2. The forbidden energy gap in such semiconductors is very minute and even the energy available at room temperature is sufficient for the valence electrons to jump across to the conduction band. Another characteristic feature of an intrinsic semiconductor is that the Fermi level of such materials lies somewhere in between the valence band and the conduction band. If a potential difference is applied across an intrinsic semiconductor, electrons will move towards positive terminal while holes will drift towards negative terminal. The total current inside the semiconductor is the sum of the current due to free electrons and holes. If the temperature of the semiconductor increases, the number of hole-electron pairs increases and current through the semiconductor increases. If temperature falls, the reverse happens [1]. In other words, it is temperature dependent.

1.1.2. Extrinsic semiconductor

These are semiconductors in which the pure state of the semiconductor material is deliberately diluted by adding very minute quantities of impurities. By so doing, their conductivity and properties are improved as compared to the intrinsic semiconductors. The impurities are known as dopants or doping agents. When materials with 3 (trivalent) or 5 (pentavalent) electrons in their valence band are used as dopants on a tetravalent base material (e.g Ge), p-type or n-type semiconductors are formed respectively. The trivalent atom such as B donates just three electrons to the tetravalent atom, leaving out one hole to be filled with an electron. This results to more holes than electrons and is referred to as p-type semiconductor. Holes therefore are majority charge carriers in p-type semiconductors whereas electrons are minority carriers. On the otherhand where pentavalent dopant such as antimony donates an extra electron in the crystal structure which is not required for covalent bonding purposes, the electron is shifted to the conduction band. This electron does not give rise to a corresponding hole in the valence band because it is already excess, therefore upon doping with such a material, the base material contains more electrons than holes, hence the nomenclature, n-type extrinsic semiconductors. Electrons are the majority carriers (of current) in n-type while holes are minority carriers. In all, the Fermi level is somewhere midway between the valence band and the conduction band, while it shifts upwards in case of n-type and drifts downward in case of p-type.

2. Semiconductor nanomaterials and quantum dots

Nanomaterials differ from micro sized and bulk materials not only in the scale of their characteristic dimensions, but also in the fact that they may possess new physical properties and offer new possibilities for

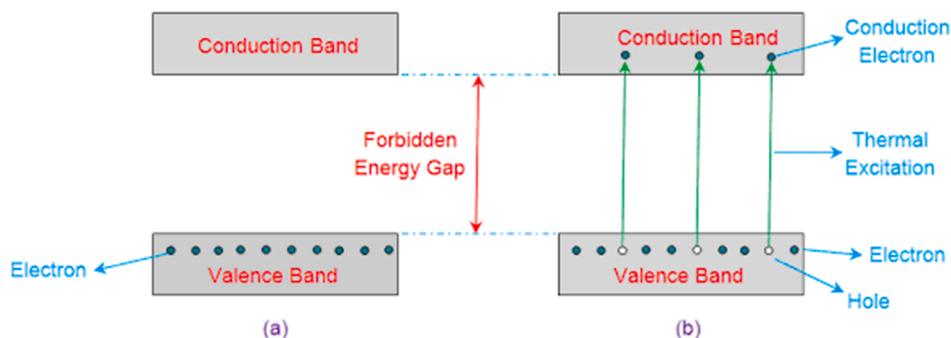


Fig. 2. Energy Band Diagram of intrinsic Semiconductor at (a) ok (b) Temperature > ok.

various technical applications. Semiconductor nanomaterials play critical roles in the recent advancement of some key technologies.

Over the past two decades, there have been extensive experimental and theoretical studies of optical responses of semiconductor nanoparticles, because they have a wealth of quantum phenomena and show unique size dependent materials properties. Semiconductors with widely tunable energy band gap are considered to be the materials for next generation flat panel displays, photovoltaic, optoelectronic devices, laser, sensors, photonic band gap devices, etc. Artificially obtained semiconductor structures with reduced dimensions present a large variety of new interesting properties in comparison to the bulk material and open new ways in the engineering of semiconductors. By simple combination of two semiconductor materials of different band gap energies, a spatial confinement of carrier motion in the direction of the growth axis is obtained. Further, the decrease of dimensions to one-dimensional and quasi-zero dimensional structures leads to large enhancement in their optical properties. Confinement of carriers in all three spatial directions consequently involves a redistribution of the energy in well-like energy levels.

A quantum dot is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (pair of conduction band electrons and valence band holes) in all three spatial directions. The confinement can be due to electrostatic potentials generated by external electrodes, doping strain, impurities, due to presence of an interface between different semiconductor materials and the semiconductor surface. Semiconductor quantum dots are prepared to exhibit quantum mechanical properties. Specifically, their excitons are confined in all three spatial dimensions. A quantum dot has discrete quantized energy spectrum. The corresponding wave functions are spatially localized within the quantum dot but extend over many periods of the crystal lattice. A quantum dot contains a small finite number of the order of 1–100 of conduction band electrons, valence band holes, or excitons, i.e., a finite number of elementary electric charges. Small quantum dots, such as colloidal semiconductor nanocrystals, can be as small as 2 to 10 nm, corresponding to 10 to 50 atoms in diameter and a total of 100 to 100,000 atoms within the quantum dot volume. Self-assembled quantum dots are typically between 10 and 50 nm in size. Quantum dots containing electrons can also be compared to atoms: both have a discrete energy spectrum and a small number of electrons. Quantum dots are sometimes called ‘artificial atoms’. In contrast to atoms, the energy spectrum of a quantum dot can be engineered by controlling the geometrical size, shape and the strength of the confinement potential. In quantum dots, the interband absorption edge is blue shifted due to the confinement compared to the bulk material. As a result, quantum dots of the same material, but with different sizes, can emit light of different colours [3]. The electronic properties of these materials are intermediate between those of bulk semiconductors and of discrete molecules [4–6]. Electronic characteristics of quantum dots are closely related to their size and shape. For example, the band gap in a quantum dot which determines the frequency range of emitted light is inversely related to its size. In fluorescent dye applications, the frequency of emitted light increases as the size of the quantum dot decreases. Consequently, the color of emitted light shifts from red to blue when the size of the quantum dot is made smaller [6].

Quantum dots are particularly significant for optical applications due to their high extinction coefficient. In electronic applications, they have been proven to operate like a single electron transistor and show the Coulomb blockade effect. Quantum dots have also been suggested as implementations of qubits for quantum information processing [7].

The ability to tune the size of quantum dots is advantageous for many applications. For instance, larger quantum dots have a greater spectrum-shift towards red compared to smaller dots and exhibit less pronounced quantum properties. Conversely, the smaller particles allow one to take advantage of improved quantum effects. iiiii

Being zero-dimensional, quantum dots have a sharper density of states than higher-dimensional structures. As a result, they have superior

transport and optical properties for use in diode lasers, amplifiers and biological sensors. High-quality quantum dots are well suited for optical encoding and multiplexing applications due to their broad excitation profiles and narrow/ symmetric emission spectra [7].

3. Types of semiconductor nanoparticles

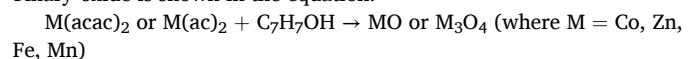
Figs. 3 and 4 are typical explanation of types of semiconductors. In Fig. 3, the part of the figure in red ink represents the wide band gap semiconductor nanoparticles whereas Fig. 4 further highlights the two dimensional semiconductor materials. Due to the size dependent nature, material tenability and tailorability of the semiconductor nanoparticles, they are attracting so much interest in sensing, electronics and light harvesting devices. [8]

3.1. Binary nanoparticles

This set of semiconductor nanoparticles contains a metal and non metal. The metals are majorly the d-block elements, groups III, lower members of groups IV and V whereas the non metals are mainly elements from earlier members of groups IV and V and elements of group VI. They include and not limited to cadmium selenide (CdSe), cadmium teluride (CdTe), zinc sulfide (ZnS), PbS, zinc oxide (ZnO), maghemite (γ -Fe₂O₃), magnetite (Fe₂O₃), GaN, TiO₂, SnS, Bi₂Se₃ and mercuric selenide (HgSe), among others.

3.1.1. Binary metal oxides

Metal oxide nanoparticles are important binary nanoparticles with applications in almost all fields of technology. These oxides mostly exist in combining powers of 2 and 4 and they include ZnO, NiO, SnO₂, CeO₂, TiO₂, Fe₂O₃, MoO nanoparticles etc. Their preparation requires time and energy but in recent times, microwave assisted method has been applied for timely, efficient and homogenous synthesis. There are other synthetic methods for these nanoparticles which also aim at controlling the crystallite size, morphology and patterns of nanoparticles assembly. The oxides can be prepared from metal precursors such as acetates, acetylacetone in the presence of solvents such as benzyl alcohol under microwave or autoclave heating. Example of microwave synthesis of binary oxide is shown in the equation:



The choice of method and precursor type plays an important role in determining the size and shape of the nanoparticles. The precursors can be changed to obtain nanorods, nanospheres, nanoflowers, nanohusks, nanocubes, distorted cubes, following simple, economical and sustainable synthetic protocols [11]. Other methods that have been applied include the laser ablation techniques, biological synthesis of reducing the metal precursors and so on.

Iron oxide nanoparticles are unique in their nature due to extra advantage of magnetic properties and ability to be recovered and recycled. They possess larger surface area and improved hollow surface microspheres compared to other metal oxide semiconductors. They have higher load efficiency and can allow other molecules to be loaded on them which enhances their biocompatibility, stability, solubility and potential applications [12]. Manganese oxide is another metal oxide with outstanding properties compared to others in terms of redox behaviour, surface nano-architectures and crystal structure [13]. They perform excellently in the catalytic oxidation of organic contaminants for efficient water purification being stable at various pH of the medium. Their diverse oxidation states, layered structure and ion-exchange abilities have also enabled their applications as molecular sieves, electrode materials in lithium ion batteries, photocatalysts, magnetic materials, energy storage and conversion.

TiO₂ is an important semiconductor nanoparticle with good catalytic ability, long-term stability, inexpensive and non-toxic [14]. Among other applications, they are used as photocatalysts in water purification

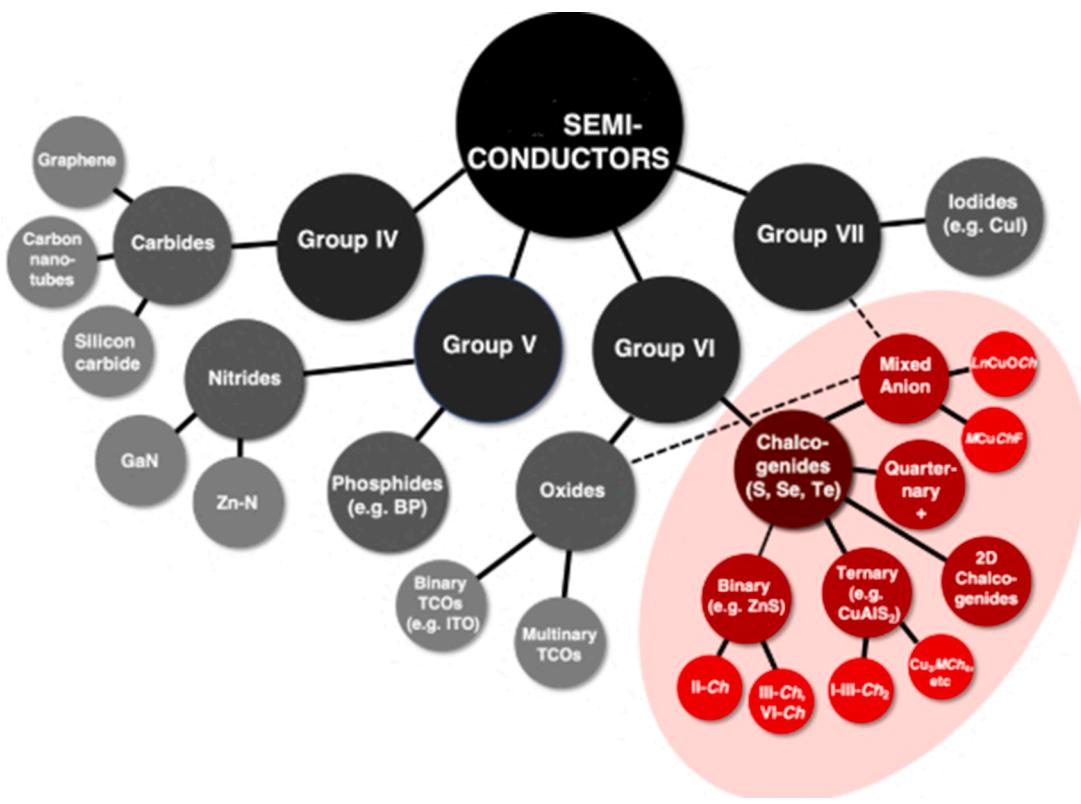


Fig. 3. Different types of semiconductor nanoparticles [9].

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂	Semiconducting dichalcogenides: MoTe _x , WTe _x , ZrS _x , ZrSe _x , and so on	Metallic dichalcogenides: NbSe ₂ , NbS ₂ , TaS ₂ , TiS ₂ , NS ₂ , and so on	Layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃ and so on	
2D oxides	Micas, BSCCO	MoO ₃ , WO ₃	Perovskite-type: LaNb ₂ O ₆ , (Ca,Sr) ₂ Nb ₂ O ₁₀ , Bi ₄ Ti ₃ O ₁₂ , Ca ₂ Ta ₂ TiO ₁₀ and so on	Hydroxides: Ni(OH) ₂ , Eu(OH) ₃ and so on	Others

Fig. 4. Some 2D semiconductors materials [10].

but this activity is hampered by their wide band gap and fast charge recombination rate. On illumination by light which have energy greater than the band gap of the semiconductor, there is electron-hole recombination process which interacts with the solution to determine the catalytic process and production of redox species. However, the semiconductors could be made to reduce the band gap energy and lower the recombination processes through introduction of materials that can trap electrons and holes.

ZnO is a multifunctional semiconductor material with wide band gap of 3.37 eV and high exciton energy of 60 meV. Just like TiO₂, its photocatalytic activity is promising due to large surface area, biocompatibility, easy synthesis and ecofriendliness though they also posses wide band gap. There are other various applications of ZnO nanoparticles such as in solar cells, UV lasers, light-emitting diodes, fuel cells, varistors, photo-detectors, phosphors, transparent conducting electrodes, surface acoustic wave devices, various sensors, piezoelectric transducers and optical and electrical device [15,16]. In solar cells application, ZnO functions to reduce electron recombination process due to their high room temperature charge carrier mobility ($115\text{--}155\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), which grossly improves the performance of solar cells [17,18].

In fuel cells, the zinc oxide and their composites have found attractive application as electrolyte membranes for low temperature-solid

oxide fuel cells [19]. This category of fuel cells exhibits high energy conversion efficiency, emit low greenhouse gases and posses good fuel flexibility [20].

3.1.2. Chalcogenides nanoparticles

This group of semiconductor nanoparticles comprises majorly the group IIIA, lower members of IVA and VA or the transition metals as the cations and group VIA non metals as the anions (except the oxides). There can be monochalcogenides (ZnS, ZnSe, CdSe, PbTe, PbSe, CdS, MoSe, CdSe, MnS, NiS, PdS, Cu₂S, NiS, ZnS, CdS, PbS, SnS), dichalcogenides (MoS₂, NiS₂, FeS₂, SnS₂) or trichalcogenides M₂S₃ (M = Bi, Sb, Ga, As). They show excellent optoelectronic behavior, strong edge effect and quantum confinement effect (due to their quantum dot-like nature), indirect band gaps and excellent stability.

Apart from the oxides, the cadmium chalcogenides are the most studied semiconductor nanoparticles and they are majorly obtained by thermal decomposition of the organometallic precursors in solvent containing the chalcogenide and capping or stabilizing ligand. Fig. 5 (a) explains the chalco-gel formation of hexagonal CdS nanoparticles from the metal complex, DMSO solvent and organochalcogen compound.

Hot injection method as shown in Fig. 5(b) is a procedure which has been used and currently trending for the preparation of monodispersed semiconductor nanoparticles. The reactants are immediately nucleated once introduced into the coordinating solvent at increasing reaction temperature [21]. The reaction follows a controlled growth and annealing system in a similar Ostwald ripening kinetics manner.

The dichalcogenides on the other hand posses band gaps within the region of 1–2 eV and outstanding charge carrier mobilities ($>100\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) suitable for high-performance optoelectronic devices [22]. The chalcogenides in general exist as 2D layered hexagonal structure which can be applied to flexible, ultra-thin or curved electronic devices.

Other interesting applications of the chalcogenides are in energy storage and conversion especially in solar cells, lithium-ion batteries, hydrogen evolution reactions and photocatalysis [23]. The metal

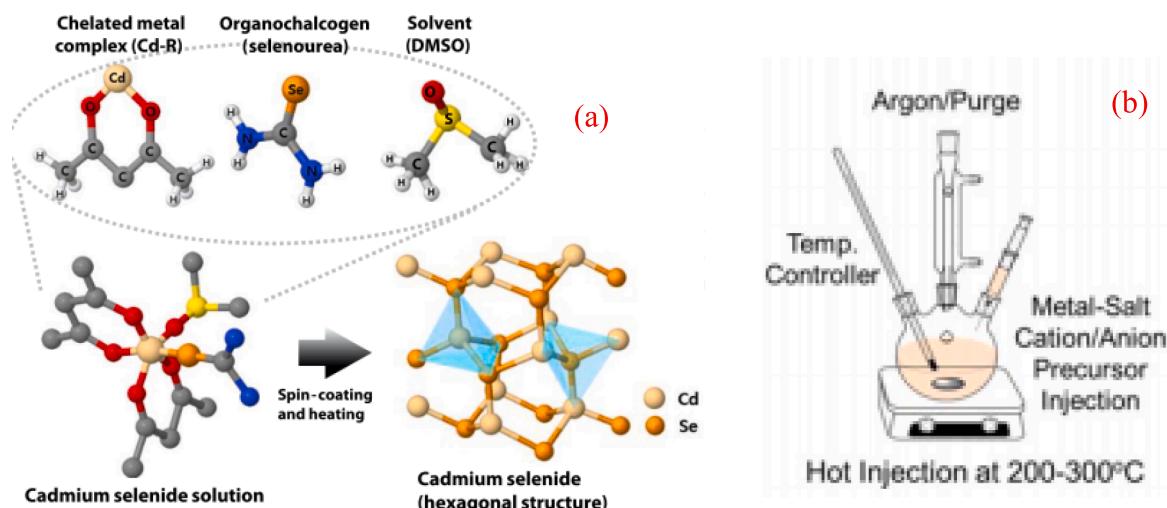


Fig. 5. (a) Synthetic illustration of formation of CdS nanoparticles (b) hot-injection procedure [22,28,32].

chalcogenide nanoparticles are sometimes more accessible for further applications as they tend to correct most of the anomalies seen in their oxide counterparts [24].

The photoresponsive nature of the semiconductors in the near infrared spectral region have enabled further applications in light emitting diodes (LEDs), cell labelling, photodetectors, lasers, cell tracking, DNA detection, in vivo imaging, biosensors, telecommunication, and so on [25,26].

Hydrothermally synthesized FeS_2 , CuS , and NiS_2 , have been applied in the photocatalytic hydrogen evolution reaction and dye degradation [27]. FeS_2 showed better activity among them which may be attributed to their improved electronic and optical properties, larger crystallite size, lower electron-hole recombination rate and smaller particle size [23].

3.2. Ternary nanoparticles

In preparing some ternary nanostructures such as $\text{Pb}_x\text{Cd}_{1-x}\text{S}$, Pb is added into CdS and some ratio of Cd is replaced by larger Pb ion thereby extending the optical absorption range and lowering the band gap energy. The incorporation of the PbS on CdS to form the ternary $\text{Pb}_x\text{Cd}_{1-x}\text{S}$ is such a difficult reaction resulting from the thermodynamic instability of the Pb-Cd-S reaction solution, however, a two-stage sequential ionic layer adsorption reaction (SILAR) process is adopted [29]. In this process, PbS NPs is grown on TiO_2 electrode, a second layer of CdS was also grown on top of the PbS and annealed to convert the double layer to ternary alloyed $\text{Pb}_x\text{Cd}_{1-x}\text{S}$ NPs.

The Cd based ternary nanostructures are the most widely studied but Cu based materials are gaining attention in recent times and they have shown to possess tunable absorption and emission properties better than the Cd counterparts. Cd based materials are also toxic to health and environment, therefore Cu materials could serve as a better replacement for extended applications even in biomedicine.

Ternary CuInSe (CISE) and CuInS (CIS) are direct ternary semiconductors with band gap energies 1.05 and 1.53 eV respectively and could serve as good light absorbers with high absorption coefficients of 10^5 cm^{-1} [30]. At room temperature, they appear in the chalcopyrite crystal phase whereas at high temperature, they exhibit the zinc blende and wurtzite crystal structures. CuSnSe (CTSe) and CuSnS (CTS) are another group of interesting direct semiconductors which can crystallize in many forms including the cubic sphalerite-like phase, metastable wurtzite structure, orthorhombic phase among others.

3.3. Quarternary nanoparticles/thin films

This group of nanomaterials involves more than two metal precursors and solvent with the capping or stabilizing agent. They are majorly prepared by hot injection method in one pot synthesis in a heating up approach to produce 0D or 1D nanorods.

Quaternary $\text{CuIn}_{1-x}\text{Ga}_x\text{S}$ (CIGS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) comprise earth abundant and non toxic elements with tunable band gaps which can be obtained by varying the cations and anions ratio to enable light absorption within the region of operation of most photovoltaic devices and high photoluminescence properties [30]. Due to their complex crystal configurations, they exhibit intrinsic lower thermal conductivities and good thermoelectric properties [31].

Thin film kesterite $\text{Cu}_2\text{ZnSnS}_4$ were prepared using tin chloride (0.8 M), zinc acetate (1 M), copper acetate (1.6 M), and thiourea (6.4 M) in the presence of 2-methoxyethanol solvent [32,33]. It must be noted that the stoichiometric quantity of the metal precursors is a key parameter in determining the nature and properties of the quartenary nanoparticles. Crystallinity was seen to increase with the thickness of the film. However, a secondary phase Sn_2 was also observed when the annealing pressure was increased.

It is rare to prepare 2D nanoplates or nanosheets of this group of multinary chalcogenides (ternary and quartenary) by hot injection due to their non-layered crystal structures which lacks the ability for 2D anisotropic growth. Cation exchange (CE) methods have emerged as an

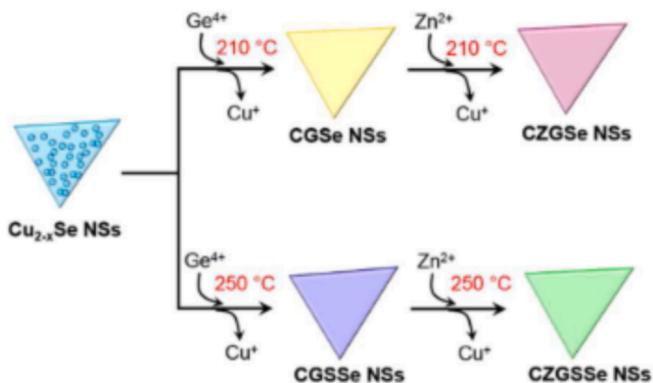


Fig. 6. Cation exchange methods for synthesis of multinary semiconductor nanomaterials [31].

alternative method which can produce nanomaterials with various morphologies as shown in Fig. 6.

The binary Cu_{2-x}Se nanostructures is firstly prepared by dissolving CuI in oleylamine and oleic acid followed by injection into a three necked flask, containing a solution of ultrasonicated selenium powder in oleylamine and 1-dodecanethiol in a heat-up approach [31]. The Cu⁺ is then partially replaced with Ge⁴⁺ at 210 °C to give the ternary Cu₂GeSe₃ nanostructures and further replacement with Zn²⁺ gives Cu₂ZnGeSe₄ quartenary nanostructures. Moreover, sulfur can be introduced into the CGSe nanostructures (NSs) and Cu cation partially replaced with Ge⁴⁺ and Zn²⁺ at 250 °C to form Cu₂GeS_xSe_{3-x} (CGSSe) and Cu₂ZnGeS_xSe_{4-x} (CZGSSe) NSs respectively. Apart from the Cu-based multinary nanostructures, the Germanium –Copper based Cu₂ZnGeSe₄ (CZGSe) is another interesting quartenary p-type semiconductor with band gap energy of 1.63 eV which should be given attention.

3.4. Graphene semiconductors

The discovery of two-dimensional semiconductor graphene is one of the greatest invention in the 21st century due to their interesting properties of mechanical flexibility and high charge mobility. They have found applications in electronics but failed in optoelectronics due to their zero band gap energy [34]. However, transition metal chalcogenides serve to replace graphene in that aspect. On the otherhand, their band gap energy can be tuned by formation of composites with metal based semiconductors.

3.5. Perovskite semiconductors

Perovskite materials which is a hybrid of organic and inorganic materials is currently an emerging semiconductor materials due to their wide applications in photovoltaics, electronics, thin-film transistors, optoelectronics and light emitting diodes. [35,36].

They have higher absorption coefficients, ability to tune optical band-gaps, longrange electron and hole transport. They are dielectric, ferroelectric, thermoelectric, electro-optic, superconducting, semiconducting and magnetoresistive [37].

Their general formula is MBX₃ where M represents methylammonium, B could be Pb²⁺ or Sn²⁺ and X is the halogens especially the low electronegative ones (eg CH₃NH₃PbBr₃). However, the organic chain length could also be modified (C_nH_{2n+1}NH₃)₂PbI₄ with an increase in the chain length leading to blue shift in optical transitions [38,39]. From the structural framework, intermolecular hydrogen bonds exist between the amino and halide ions, whereas Vander Waals forces occur among the organic ions. The lower members of the group IVA confer good optoelectronic properties and assist in fabrication of low-temperature devices whereas the low electronegative halogens, I and Br, enhances photo absorption in order to achieve wide band gap energy. On the other hand, Pb and Sn are toxic, therefore Bi³⁺ which is isoelectronic to Pb²⁺ is a cation of interest to replace them due to its low toxicity profile. Ge has not been widely explored but may not serve as an alternative because it is lighter and the + 2 oxidation state is unstable due to the lone pair effect.

The nature and properties of the perovskite can be improved by doping with group 1 elements such as Cs, Rb to form FA_(1-x)Cs_xPbBr₃ perovskites (where FA stands for formamidinium) [40].

Double perovskite halides bearing the formular A₂BBiX₆, (A = larger monovalent cation, B = smaller monovalent cation, X = halide ion eg Cs₂AgBiBr₆) can act as an alternative to the lead perovskite semiconductors. They are promising and have indirect band gap of about 1.95–3 eV but can degrade within a short while when under ambient air. To circumvent the problem, double perovskites materials of the type A' A''B'BiO₆ eg KBaTeBiO₆ have been synthesized with band gap of about 1.88 eV, high dispersed valence and conduction bands and excellent stability which can enable it last over a year under ambient conditions [41].

3.6. Organic semiconductors (OSCs)

Organic semiconductors mainly contain carbon, hydrogen, and oxygen and they have prospects of dual combination of electronic properties of semiconducting substrates and the chemical influence of the organic compounds [42]. Wet chemistry methods aid in the modifications of physical, chemical and electronic properties of the organic compounds to make them suitable as semiconductor materials.

The π-conjugated network of carbon chemical structures in the organic semiconductors offer delocalization of electrons necessary for the electrical conductivity of the materials. In contrast to the inorganic semiconductors, there is aggregation or conjugation of π-electron systems, overlap of molecular orbitals of adjacent molecules in order to achieve charge carrier mobility expected of semiconductor materials [43]. The OSCs are made by solution processing techniques due to their high solubility in organic solvents and they can also be produced in high yield at low cost.

Examples of organic semiconductors include 6, 13-bis(triisopropylsilyl)ethynyl pentacene (TIPS pentacene), conjugated thiophenes, poly(1,7)-carbazole derivates, Phenyl-C61-butrylic acid methyl ester (PCBM) and many more.

The n-type OSCs must be engineered in such a way that there is rigidity in the molecular framework, planarity of structure, consistency of overlaps and ability to avoid oxidation. As a result, active electron-withdrawing groups including cyano, imide, and halogen groups are introduced into the organic semiconductor frameworks. The n-type OSCs include 3,4,9,10-benzo[de]isoquinolino[1,8-gh] quinolinetetracarboxylic diimide (BQQDI). The electronegative atom in the structure improves structural and chemical robustness, core-to-core interactions, intermolecular charge transport [43]. The precursor compound 3,4,9,10-benzo[de]isoquinolino[1,8-gh] quinolinetetracarboxylic dianhydride (BQQ-TCD) can further be modified to obtain linear alkyl- and phenylalkyl-substituted BQQDIs which are more impressive semiconductors with high electron mobility as shown in Fig. 7. these OSCs find great applications in organic light-emitting diodes (OLEDs), field-effect transistors (OFETs) and solar cells

3.7. Semiconductor nanocomposites

Transition metal oxides and transition metal dichalcogenides based nanocomposites are among the commonly developed nanocomposites using various methods and have exhibited superior properties [44]. Consequently, developing nanocomposites may well be an answer to regulate the properties of individual nanomaterials appropriately. Particularly within the field of semiconductor materials, nanocomposites composed of two or more materials are widely engineered to alter their electronic and optical properties [45–49].

These nanocomposites can be prepared by integrating nanoparticles into other functional materials either by surface decoration or intercalation of the nanoparticles into the materials. Surface decoration of the nanoparticles is a big challenge since the known synthetic methods may not be able to apportion the nanoparticles to the expected locations. Some indirect procedures of applying the solution-based nanoparticles on the surface of the material while allowing the solvent to evaporate,

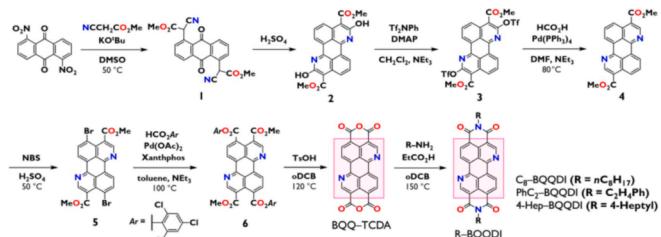


Fig. 7. Synthetic pathway of organic semiconductors [43].

layer to layer electrostatic assembly and biological template-directed assembly have been used [50–53].

Different semiconductor nanocomposites include noble metal–metal oxides, carbon materials–metal oxides, polymer–metal oxides etc.

The addition of two different materials to form the nanocomposites is an interesting way of tuning the band gap energy of semiconductors. ZnO/CuO mixed semiconductor nanocomposites comprising the ZnO, a wide band gap n-type semiconductor and CuO, a narrow band gap p-type semiconductor is prepared to give superior electrical, optoelectronic, photovoltaic, piezoelectric and catalytic properties [54]. The general methods of synthesis of nanoparticles are also applied in nanocomposites. However, the photo-deposition method is among the simplest methods used in synthesizing noble metal/semiconductor nanocomposites by utilizing the band gap of the semiconductor. Compared with most other methods that require extreme temperature, a further redox agent, potential drop, or multi step processing, the photo-induced reduction method requires only the irradiation of a light weight source. Furthermore, with the photo deposition of noble nanoparticles over 2-dimensional substrates, it's easy to manage the dimensions of metallic element nanoparticles by adjusting the concentration of the metal precursor, irradiation time and power. Also, this method enables material selectivity, whereby metallic element nanoparticles are only deposited on the semiconductor templates [55,56].

Some conductive polymers such as PAni can form composites with the semiconductor nanoparticles leading to an improvement in the radiative electron hole recombination for better applications in optoelectronics [57].

4. Synthetic methods of semiconductor nanoparticles

In general, synthesis of nanomaterials can be categorized into bottom-up approach and top-down approach. The bottom-up approach involves the reduction of materials units with further self-assembly process resulting in the formation of nanostructures [58]. During self-assembly, the physical forces operating at nano scale acts to combine units in order to obtain larger and stable structures. The bottom-up approach includes some of the chemical methods and all biological synthetic methods. Top-down approach involves the disintegration of initial larger structures into nanostructures using external forces. All physical methods and some chemical synthetic methods are classified under top-down approach e.g ball milling, laser ablation techniques, plastic deformation. [59]. On the other hand, the synthetic methods can be grouped into solid-phase approach, liquid-phase approach, vapour-phase approach, and the two-phase approach depending on the reaction medium [60].

Furthermore, the liquid-phase approach can be categorized into aqueous or water-based, organic or solvent based and the aqueous–organic approaches. The aqueous approach involves the hydrothermal treatment and chemical precipitation methods. They are ecofriendly and biocompatible but could hardly offer control over the sizes and morphologies of the nanoparticles. The solvent based or solvothermal approach however could make use of any high boiling solvents and therefore could control the synthesis of the nanoparticles. There could also be introduction of organic ligands which modifies the surface characteristics and properties of the nanoparticles. Hot-injection method and non-injection method could be used in this solvent approach. Nanoparticles made through this method could be slightly toxic due to the influence of the organic solvents. The aqueous–organic approach or rather interface-mediated means involves the dissolution of the reactants in the different media with formation of the nanocrystals at the interface. Spherical or common shape nanoparticles are produced from this method with no control over their shapes.

In all, the ability to control the size or obtain quantum dots in which the nanoparticle diameter is smaller than the exciton Bohr radius is of great interest in semiconductor nanomaterials.

The liquid phase approach in general is so far the most interesting

method of obtaining well dispersed colloidal semiconductor nanocrystals. In solution forms, they are very stable and can be applied for solution-based techniques including inkjet printing, spin-coating and roll-to-roll casting. The other vapour and solid-phase approaches may not give suitable nanocrystals due to limitations of the instruments and precursors.

depending

4.1. Physical methods

4.1.1. Pulse laser ablation

This method requires a high-power pulsed ray of light which is concentrated inside a chamber to strike a target within the material and plasma is formed, which is then converted into a colloid of nanoparticles. Mostly Second Harmonic Generation (ND: YAG) type laser is being employed to organize the nanoparticles. Fig. 8 shows the synthesis of nanoparticles using pulse laser ablation method. There are many factors that affect the ultimate product like the sort of laser, number of pulses, pulsing time and sort of solvent. ii

4.1.2. Mechanical/High ball milling method

Milling could be a solid state processing technique for the synthesis of nanoparticles. Within the milling process, material of micron size is fed to undergo several degree of changes. Different types of mechanical mills are available which are commonly used for the synthesis of nanoparticles. These mills are categorized based on their capacities and applications. Because of mechanical limitations, it's very difficult to supply ultra-fine particles using these techniques and it takes a very long time. However, simple operation, low cost of production of nanoparticles and therefore the possibility to scale it to supply large quantities are the main advantages of mechanical milling. The important factors affecting the standard of the ultimate product are the sort of mill, milling speed, container, time, temperature, weather conditions, size and size distribution of the grinding medium, process control agent, weight ratio of ball to powder and extent of filling the vial. A ball milling technique is shown in Fig. 9.

4.1.3. Mechanical chemical synthesis

During this process, reaction is induced by energy. The chemical fore runners are mostly a combination of chlorides, oxides and/or metals that react during milling or subsequent heat treatment to supply a composite powder during which ultrafine particles in a stable salt matrix are dispersed. These ultrafine particles are recovered by washing with suitable solvent from selective removal of the matrix [58]. A ball milling system which describes mechanochemical synthetic procedure is shown in Fig. 10.

4.1.4. Pulsed wire discharge method

Pulsed wire discharge (PWD) could be a physical technique to organize nanoparticles. Compared to any or all the previously mentioned methods, metal nanoparticles synthesized by the PWD technique follows a totally different mechanism. In PWD as shown in



Fig. 8. A schematic diagram of Pulse laser ablation [61].

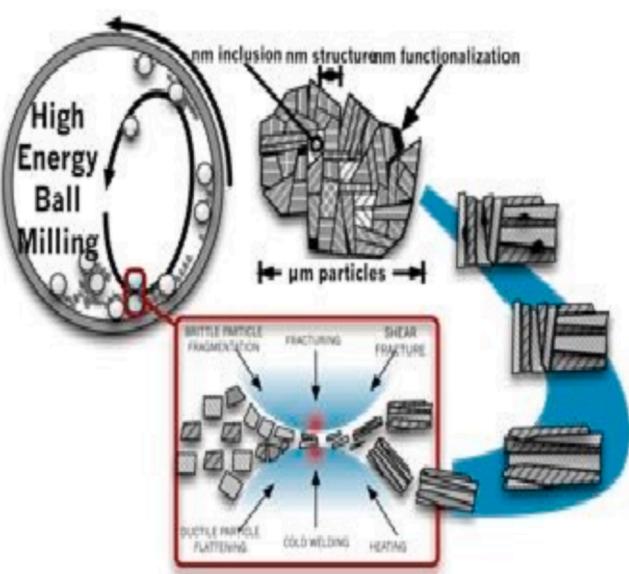


Fig. 9. A schematic high ball milling method [61].

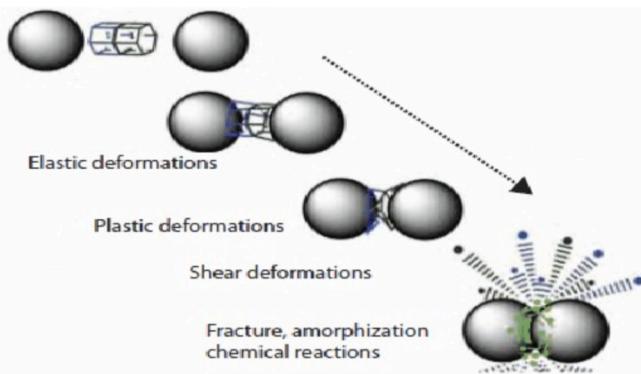


Fig. 10. Deformations within the material trapped between two colliding balls during ball milling [61].

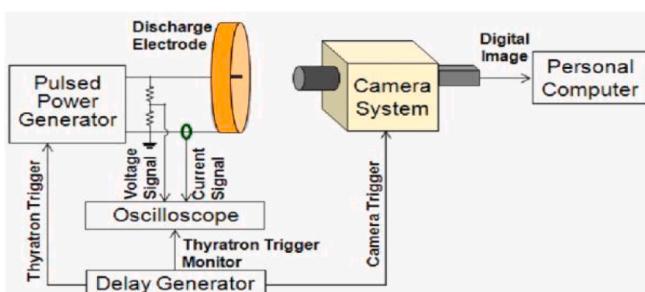


Fig. 11. A schematic diagram of Pulsed wire discharge [61].

Fig. 11, a metal wire is evaporated by a pulsed current to supply a vapor, which is then cooled by an ambient gas to make nanoparticles. Preparations of metal, metal oxide and nitride nanoparticles by PWD have been reported, and this method has the potential of a high production rate and high energy efficiency. This process is not used conventionally for common industrial purposes because it is not only very expensive but also impossible to use explicitly for various metals. It is mainly useful for those metals of high electrical conductivity that are easily available within the thin wire form [62].

4.1.5. Chemical vapour deposition (CVD)

This CVD method is greatly applied in semiconductor processing and it is particularly used to deposit thin films of different materials. CVD process makes use of low temperature and gives high purity crystalline nanomaterials in large scale. Volatile or gaseous precursors are decomposed on the surface of the substrate (eg SiO₂, Si, Si₃N₄) which forms the required deposit. There are different types of chemical vapour deposition which includes: Plasma CVD (PCVD), thermal chemical vapour deposition (TCVD), atmospheric pressure CVD (APCVD), modified metal-organic CVD (MOCVD), low-pressure CVD (LPCVD), Photo-initiated chemical vapor deposition (PICVD) and salt assisted CVD (SACVD) [63–68].

There are some shortcomings associated with some of the CVD techniques. For instance, PCVD and TCVD consume higher energy, and are preferably used for heat sensitive substrates and cannot be easily used for scale up production.

The use of salt can either act as an additive to the reactants or as a template for transition metal chalcogenides nanogrowth. Metal oxides such as MoO₃ and sulphur powder precursors can react in a vapour phase CVD technique to produce MoS₂.

Marimuthu *et al.*, have carried out the chemical vapour deposition of β-HgS nanoparticles from bis(cinnamylpiperazinedithiocarbamato) mercury(II) precursor [69]. The precursor was dissolved in toluene and deposited on glass substrates using argon carrier gas. The glass substrates which were inside reactor tube were heated prior to deposition. The carrier gas transported the aerosol droplets of the precursor into the hot wall of the reactor onto the glass substrates.

4.2. Chemical methods

There are numerous advantages of using chemical methods. In some cases, nanomaterials are obtained as colloidal particles in solutions, which might be filtered and dried to get powder or as thin films or nanoporous materials obtained through various chemical means. Chemical methods are simple inexpensive techniques that involves less instrumentation compared to several physical methods and of low synthesis temperature (<350 °C) there are different types of chemical synthetic procedures which includes polyol method, solgel, reduction methods, solvothermal, heating up, injection methods and so on.

4.2.1. Chemical reduction method

The chemical reduction method is one of the most common, easiest, simplest and facile method of synthesizing semiconductor nanoparticles.

Reducing agents such as NaBH₄, ascorbic acid, polyols, hydroquinones, hydroxylamine hydrochloride, saccharides, hydrazine, urea is introduced into the metal precursor compounds in the presence of solvent media. While some of the reducing agents are ecofriendly, the others may be hazardous. The reducing agent reduces the metal salts which leads to formation of nuclei and particle growth. There are also some of the reducing agents that are weak and their action can be improved by increasing the temperature of the reaction.

There are some materials like surfactants, polymers or biomolecules which can also be used in the reaction which include sodium bis(2-ethylhexyl) sulfo-succinate (AOT), cetyl trimethyl ammonium bromide (CTAB) and triton X-100, polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), polyacrylates, polyacrylamides, poly (ethylene glycol) (PEG), starch [70,71]. They are regarded as capping agents or stabilizing agents but also involve in the reduction process.

4.2.2. Polyol synthesis

This method is one of the good techniques employed for semiconductor nanoparticles especially the oxides. Polyol solvents such as ethylene glycol (EG), diethylene glycol (DEG), glycerol, butanediol, propanediol etc are used on the precursor metal salts (including the acetates, halides, nitrates, and alcoholates) which leads to particle nucleation. The polyols can coordinate to the nuclei or rather stabilizes

the formed nuclei which controls the particle size and removes agglomeration. Moreover, higher molecular weight polyols have higher boiling points and therefore allows the reaction to be carried out at higher temperature of about 200–320 °C which yields high quality crystalline nanomaterials [72]. As a result, the additional use of autoclave, high pressure system or post-sintering may no longer be necessary in the polyol process. The type of polyol used determines the suitability of the prepared nanoparticles. Ethylene glycol and diethylene glycol are the most suitable for metal oxide nanoparticles since they can be prepared at lower temperatures of about 100–180 °C. Metal nanoparticles require higher temperature and when the low temperature solvents (EG, DEG) are used, there is an incomplete nucleation or formation of nanoparticles, and after heating, the reduced nanoparticles may be re-oxidized again.

However, there are some disadvantages involved in using the polyol process which includes

the limitation in their reducing power and inadequate stabilization of the non-polar metal surfaces.

4.2.3. Hot injection method

This method is efficient in the preparation of epitaxial heterostructures of different shapes which involves heterogenous nucleation reaction. The preparation, kinetics and thermodynamic reaction process of the epitaxial heterostructures differs greatly from that of single phase nanocrystals [73]. Solvent plays an important role in all chemical methods. Some solvents (eg trioctylphosphine oxide (TOPO) makes available oxygen which can interact with methyl radicals from the organometallic precursors to form ether [25,74]. The ether may in turn react with the unreacted metals thereby changing the reaction yield and affecting the entire reaction procedure and conditions.

The introduction of the precursor into the hot solution in the reaction vessel is an art which has to be mastered and carried out carefully in order to limit the self nucleation and growth of the nanoparticles to be formed. The type of precursor compounds, manner of injection (either slow or fast) and injection temperature are other huge factors that must be considered during the reaction. This method enables the complex synthesis of core-shell or multishell or epitaxial heterostructures in one pot. Lee *et al.*, have prepared CdTe-CdSe tetrapod heterostructures by injecting trioctylphosphine telluride (TOP-Te) into Cd-oleate solution which leads to the formation of CdTe seeds. Afterwards, tri-octylphosphine-selenide (TOP-Se) solution was injected into the same pot in order to grow CdSe on the surface of CdTe to form CdTe-CdSe tetrapods [75]. In the synthesis of cadmium chalcogenides nanocrystals, CdO which is less toxic can be used as the precursor instead of the toxic organocadmium compounds [76]. This therefore highlights the importance of the precursor compounds in the synthesis.

4.2.4. Non-injection method or heating-up approach

The precursors are added in the reaction vessel and gradually heated which leads to nucleation and subsequent nanocrystal growth as shown in Fig. 12. A mixture of cadmium myristate, selenium powder, and 1-octadecene (ODE) have produced CdSe nanocrystals through a heat up method [77]. It was observed that the selenium powder which was initially insoluble at low temperature became soluble when the reaction temperature was raised to 220 °C. Polynary nanoparticles such as ternary CuInS has been prepared by mixing CuI, In(OAc)₃, and dodecanethiol(DDT) in an ODE solvent, with the addition of oleylamine as the organic capping agent and heated up to 200 °C at varying times [78]. The capping agent complexes with the precursor compounds and stabilizes the surface of the formed nanocrystals therefore determining their size and size distribution.

4.2.5. Sol-gel synthesis

The sol-gel method involves procedural steps which include hydrolysis, polycondensation, aging, drying and thermal decomposition. It has interesting control over the surface properties of the nanomaterials. In

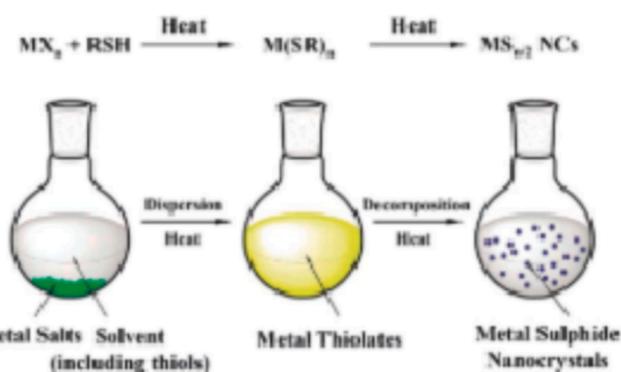


Fig. 12. Heat up approach of synthesizing semiconductor nanoparticles [60,79].

the hydrolysis stage, if water is used as the medium, it is aqueous sol-gel but when alcohol is used it is called a non-aqueous sol-gel synthesis [80]. The precursor compounds are dissolved in the solvent medium to form solution (sol).

Polycondensation involves removal of water or alcohol molecule in order to form either metal hydroxyl-metal (olation) or metal-oxide-metal linkages (oxolation) which is gel-like and therefore improves the thickness or density as shown in Fig. 13. During aging process, there are changes in properties and structures.

Drying process takes different forms since there are both water and organic components in the gel which needs to be removed to have porous nanoparticles. There could be atmospheric/thermal drying, freeze-drying and supercritical drying. Thermal heating involves high temperature giving rise to low surface area and pore volume xerogel. Supercritical drying gives rise to aerogels with high porosity and large surface area whereas freeze drying forms cryogel with lower structure/gel shrinkage than in thermal drying. Thermal decomposition or calcination or annealing gives the oxide nanoparticles and removes the residual constituents or water molecules. The calcination temperature determines the pore size of the nanoparticles.

4.2.6. Solvothermal decomposition

This process is well adapted in the synthesis of metal chalcogenides with great control over structural behavior for desired properties and could also be referred to sol-gel process in some cases. Within the solvothermal processes, the reaction takes place in a sealed vessel like bomb or autoclave, where solvents are dropped at temperatures well above their boiling points. When water is employed as solvent, it is called a hydrothermal process. There are many advantages in using supercritical conditions like, simplicity, very low grain size, presence of one phase and synthesis of high purity nanocrystals with high crystallinity and eco friendly nature. [81]

In the solvothermal synthesis of CdTe nanoparticles, CdCl₂ and KTe were dissolved in different organic solvents (ethylenediamine, ethanolamine, triethylenetetramine) and stirred which were transferred into a Teflon-coated stainless-steel autoclave [82]. The solution was heated up for long hours and later cooled to obtain the nanoparticles by centrifugation and washing. The different solvents used gave rise to different morphologies of the CdTe.

Ibrahim *et al.* [83,84] have reported the hydrothermal synthesis of PbTe at different sodium dodecyl sulfate concentrations and doping with Sm at different stoichiometric ratios for novel electrical and thermo-power properties.

Wang *et al.*, have reported the solvothermal synthesis of graphene oxide-CdS/ ZnS nanocomposites with high level of dispersion and coverage of the metal sulphides on the graphene oxide (GO) [85]. Metal (Cd, Zn) acetate salts, ethylene glycol (EG) and thiourea were used as precursors, solvent and sulfur source respectively. The choice of EG was

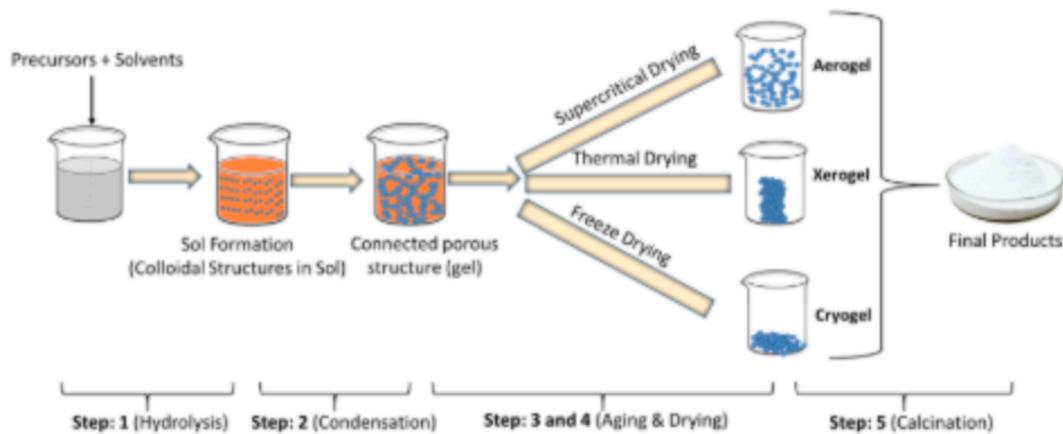


Fig. 13. Step-wise sol-gel synthetic method [80].

because it has the ability to dissolve both the graphene oxide and the metal salts to ensure homogeneity. The metal sulphides nanoparticles interact with the carboxylic functional groups of the GO for efficient nanocomposite formation. However, the carboxylic functional groups in the graphene oxide are located at the edges which means that there may not be enough for the interaction. Polyacrylic acid may be added in this case to provide more functional groups for improved synthesis.

TiO₂ nanoparticles have also been synthesized in a base fluid eutectic thermal oil mixture of biphenyl and diphenyl oxide, in the presence of benzylic alcohol reagent and the precursor compound, titanium isopropoxide added dropwise [86]. All the reaction was carried out in the autoclave, heated up and the nanoparticles centrifuged after cooling.

4.2.7. Micro emulsion/colloidal method

Micro-emulsion could be a technique for the synthesis of nanoparticles during which two immiscible fluids like water in oil (W/O) or oil in water (O/W) or water in supercritical carbon(IV)oxide (W/Sc.CO₂) become a thermodynamically stable dispersion with the help of a surfactant. A typical emulsion could be a single phase of three components, water, oil and a surfactant. Normally, oil and water are immiscible but with the addition of a surfactant, the oil and water become miscible because the surfactant is ready to bridge the surface tension between the two fluids. Micro emulsion consists of surfactant aggregates that are within the ranges of 1–100 nm. The situation of water, oil and surfactant phases affects the geometry of aggregate. The micro-emulsion is alleged to be oil in water (O/W), if water is the bulkier fluid and oil is in less quantity, with small amounts of surfactant. Similarly, the system is alleged to be water in oil (W/O), if oil is the bulkier fluid than water. The mechanism of oil in water and surfactant (O/W) is termed micelles. The water in oil micro emulsion carries oil or organic solvent in bulk making the system to be thermodynamically stable and called reverse micelles [87].

4.2.8. Sonochemical method

This process utilizes powerful ultrasound radiations (20 kHz to 10 MHz) on molecules to produce nanoparticles. Sound waves of fixed frequency are passed through a slurry or solution of carefully selected metal complex precursors which produces the nanoparticles. The important advantages of the sonochemical method include their simplicity, operating conditions (ambient conditions) and easy control of the dimensions of nanoparticles using precursors at different concentrations. Ultrasound power affects the entire chemical process due to the cavitation phenomena which involves the formation, growth and collapse of bubbles in liquid. The sonochemical reaction conditions such as use of a solvent with vapour pressure of a specific threshold, alternating waves of expansion and compression results in growth and implosion of cavities. Geng *et al.*, have prepared PbWO₄ nanostructures

using sonochemical method [88]. In the procedure, a homogenous solution of Pb(CH₃COO)₂·3H₂O in ethylene glycol–water was made and subjected to ultrasound irradiation. Na₂WO₄ in ethylene glycol–water solution was also added and the entire solution sonicated to form PbWO₄ nanostructures. The reaction systems, solvent ratio were varied to obtain different nanoparticles sizes. In another sonochemical reaction, Pd nanoparticles were prepared by reducing (NH₄)₂PdCl₄ precursor with ascorbic acid using PVP as capping agent. The Pd nanoparticles was deposited on TiO₂ nanospheres to form Pd-TiO₂ nanocomposites using ultrasonic probe irradiation [89]. Further ultrasonication can be carried out to obtain more nanocomposites by adding more of the palladium precursor.

Sonochemical synthesis employs both electrolytes and ultrasonic pulses for the assembly of nanoparticles [90].

4.2.9. Electrochemical method

Electrochemical synthesis is achieved by passing an electrical current between two electrodes separated by an electrolyte. The synthesis thus takes place at the electrode–electrolyte interface. The advantages of electrochemical techniques include avoidance of vacuum systems as utilized in physical techniques, low costs, simple operation, high flexibility, easy availability of apparatus and instruments, less contamination (pure product) and environment-friendly process. Much research work has been done on the electrochemical technique in advancing the essential understanding and industrial applications, but still many aspects of this method are under study [91].

Succinic acid solution has been applied as the electrolyte whereas copper and zinc served as anode and zinc alone used as cathode in the electrochemical synthesis of ZnO/CuO nanocomposite [54]. The synthetic procedure was shown in Fig. 14, where voltage was passed across the solution and samples produced was centrifuged, washed, dried and calcined.

4.2.10. Microwave synthesis

Microwave synthetic method is a simple, pollution free and time saving procedure. The precursor metal salt mixed with solvents (eg ethylene glycol) is introduced into microwave tubes and irradiated by the microwave oven under specified temperature, pressure and time of reaction.

ZnONPs was prepared by microwave method through the irradiation of a mixture of Zn(NO₃)₂·6H₂O and p-hydroxybenzoic acid in the ratio of 1:2 which formed zinc(II) p-hydroxybenzoate complex [92]. The reaction occurred under 5 mins in the presence of 1 N NH₄OH and ethanol solvent (10 mL). The resulting complex was washed, dried in a vacuum and later calcined at 600 °C for 2 h to obtain the ZnO NPs.

Onwudiwe 2019, synthesized cube-like and rod-like PbS nanostructures using lead(II) bis(N-butyl-N-phenyldithiocarbamate) and

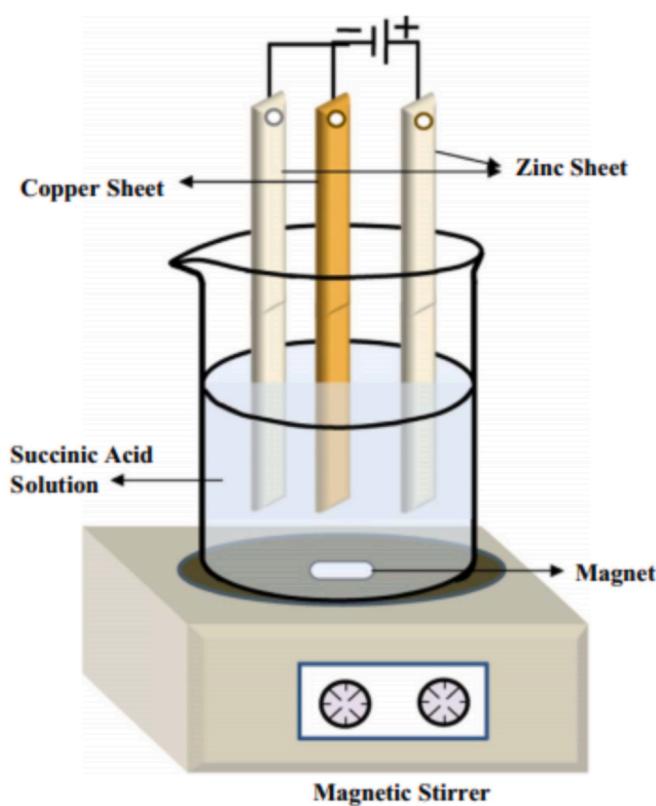


Fig. 14. Electrochemical synthesis of ZnO/CuO nanocomposites [54].

lead(II) bis(N-ethyl-N-phenyldithiocarbamate) single source precursors respectively [93]. The microwave method involves dispersion of the dithiocarbamates in ethylenediamine followed by sonication and further transferred into the Teflon tube in the microwave oven. The microwave reaction system was set at some reaction conditions and different conditions and precursors affect the shape, size and optoelectronic

properties of the nanostructures.

4.3. Biological/green synthesis

Nature is ready to synthesize a range of semiconductor nano-materials under ambient conditions [94]. This method of synthesis can be from plant parts, microorganisms or agricultural wastes. Nano-materials made from this way are ecofriendly, biocompatible and of low-cost which diversifies their usage especially in nanomedicine. In addition, biological synthesis involves lesser energy than their physico-chemical counterparts. Though, the biological method has been seen as a traditional way of synthesis, however, the plant-mediated technique is more widely explored with on-going extensive research than the microorganisms' technique which has proven to give more yield. Numerous noble metal nanoparticles have been prepared using this method but employed in few semiconductor nanoparticles as shown in Table 1.

Unlike the chemical and physical methods, the biological synthesis seldomly yield desired size and/or shape of nanoparticles together with an occasional yield. Some of their processes may take several hours and even some days to complete. Moreover, the decomposition of formed nanoparticles may occur after a specific period of time, because of their biocompatibility. Despite all, biological synthesis remains very attractive [95].

4.3.1. Plant-mediated method

Most plants contain both primary and secondary metabolites. The primary metabolites include the carbohydrates, lipids, nucleic acids, vitamins and proteins whereas the secondary metabolites are the poly-phenolics, alkaloids, terpenes, steroids, lignins, esters etc. These metabolites have reducing properties and can be extracted from the plants for facile, green and low-cost preparation of nanoparticles. They are safe, environmental friendly and economical. Fig. 15a shows the interaction of components of plant extracts with zinc precursors whereas Fig. 15b further illustrates the mechanistic reaction of a particular metabolite (carbohydrates) with zinc precursor compounds to form ZnO NPs. Among the semiconductors nanoparticles, the plant mediated

Table 1
Some semiconductors nanoparticles synthesized by biological methods (organisms and plants).

S/ No	Biological specie	Nanoparticles	Size (nm)	Morphology	Application	References
1	<i>Magnetospirillum magnetotacticum</i>	Iron oxide	47		Handle shape cluster	[101]
2	<i>E.coli</i>	CdS	2–5	Fluorescent labels	Wurtzite structures	[102]
3	<i>Aeromonas hydrophila</i>	ZnO	57–72	Crystalline	Treats Aspergillus flavus disease in maize	[103]
4	<i>Streptomyces</i> spp.	CuO	78–80	spherical	Treats Alternaria alternata, Fusarium oxysporum, Pythium ultimum, and Aspergillus niger in multiple crops	[104]
5	<i>Klebsiella aerogenes</i>	CdS	>20			[105]
6	<i>Shewanella oneidensis</i>	UO ₂	1–5			[106]
7	<i>Aspergillus terreus</i>	ZnO	8	spherical	Catalysis, biosensing, drug delivery, molecular diag-nostics, solar cell, optoelec-tronics, cell labeling, and imaging	[107]
8	<i>Aspergillus flavus</i> TFR7	TiO ₂	12–15	spherical	Plant nutrient fertilizer	[108]
9	<i>Aloe barbadensis</i> Miller (<i>Aloe vera</i>)	In ₂ O ₃	5–50	spherical	Solar cells, gas sensors	[109]
10	<i>Medicago sativa</i> (alfalfa)	Iron oxide	2–10	crystalline	Cancer hyperthermia, drug delivery	[110]
11	<i>Sedum alfredii</i> Hance	ZnO	53.7	Hexagonal wurtzite and pseudo-spherical	Nanoelectronics	[111]
12	<i>Rosmarinus officinalis</i> flower	MgO	<20	flower	Treatment of Xanthomonas oryzae pv. oryzae disease	[112]
13	<i>Matricaria chamomilla</i> flower	MnO ₂ and MgO	9–100	Disk shaped spherical	Treatment of Acidovorax oryzae	[113]
14	<i>Olea europaea</i> leaves	ZnO	>41	Crystalline	Treatment of Xanthomonas oryzae pv. oryzae disease	[114]
15	<i>Lycopersicon esculentum</i> fruits	ZnO	>66	crystalline	Treatment of Xanthomonas oryzae pv. oryzae disease	[114]
16	<i>Parthenium hysterophorus</i>	ZnO	28–84	Spherical and hexagonal	Treatment of Fusarium culmorum in Barley	[115]
17	Citrus lemon fruits	ZnO, TiO ₂	>20	polymorphic	Treatment of Dickeya dadantii in sweet potato	[116]
18	<i>Cassia fistula</i> and <i>Melia azadarach</i>	ZnO	2.72	Spherical	Antibacterial properties	[97]

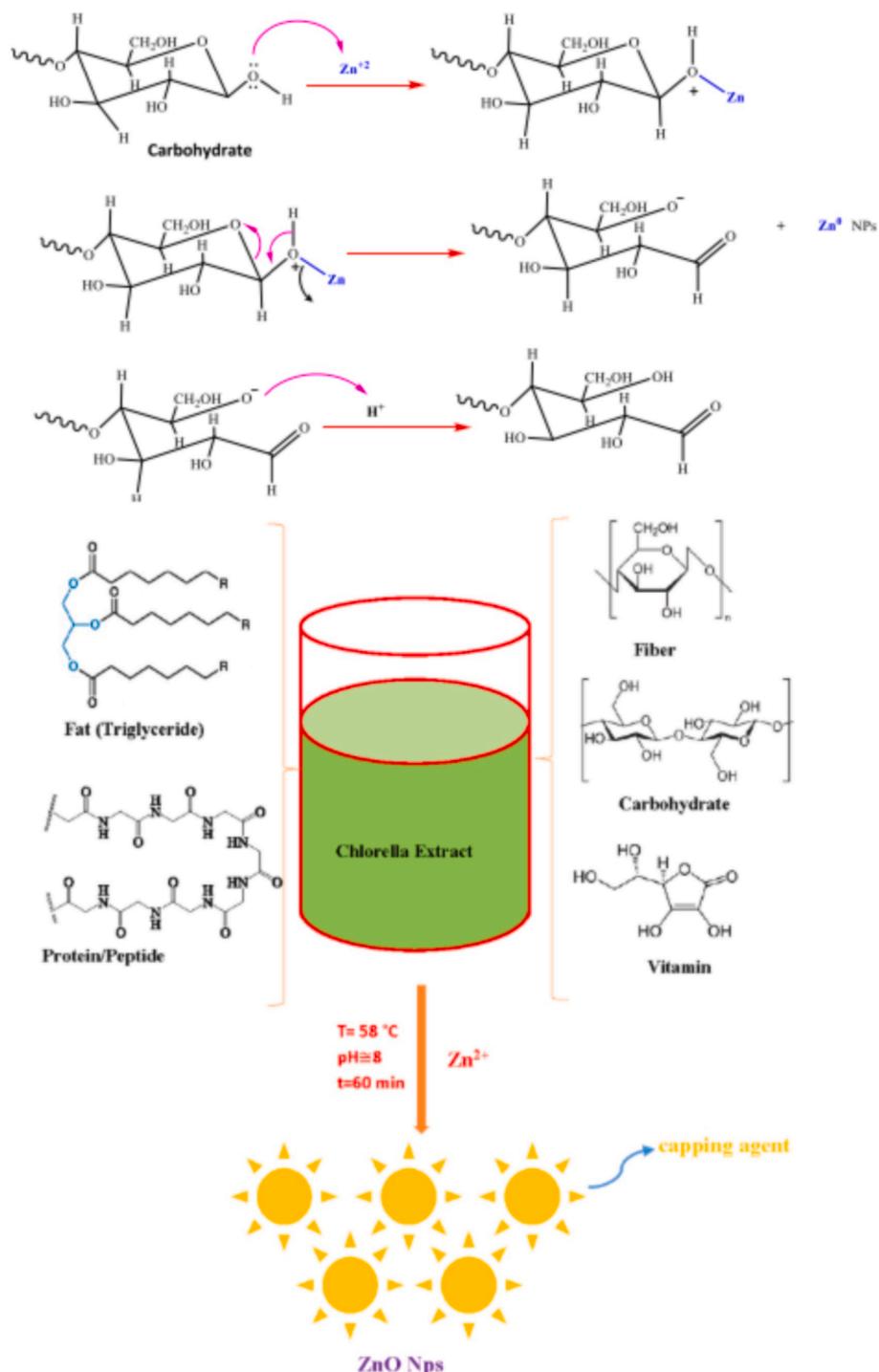


Fig. 15. Schematic illustration of (a) plant extract synthesis (b) the interaction between carbohydrates and zinc salts to form ZnO NPs [98].

method has been mostly applied to the synthesis of ZnO nanoparticles. Green tea leaves extract have been used as the bioreductant in the synthesis of ZnO NPs using the zinc acetate dihydrate as precursor compound [96]. In another work as reported by Naseer et al., *Cassia fistula* and *Melia azedarach* leaves extract have been used for the synthesis of ZnO nanoparticles with particle size of 2.72 nm and high antibacterial activities [97]. Table 1 shows some semiconductors synthesized by plant extracts and their possible applications.

4.3.2. Microbial synthesis

Microbial synthesis is a green method just like the plant mediated

synthesis because it is non-toxic, does not require energy, high temperature, pressure, toxic chemicals or solvents and stringent operational conditions. Bacteria, fungi and viruses are some of the organisms used for nanoparticle synthesis and could be referred to as green nanofactories. Fig. 16(a) and (b) describe the synthetic pathway and mechanism of production of semiconductor nanoparticles while Table 1 shows some microorganisms synthesized semiconductor nanoparticles.

This method is supported by the fact that the bulk of the bacteria inhabits ambient conditions of varying temperature, pH, and pressure. By varying parameters like microorganism type and strain, its growth phase, culture growth medium, pH, substrate concentrations,

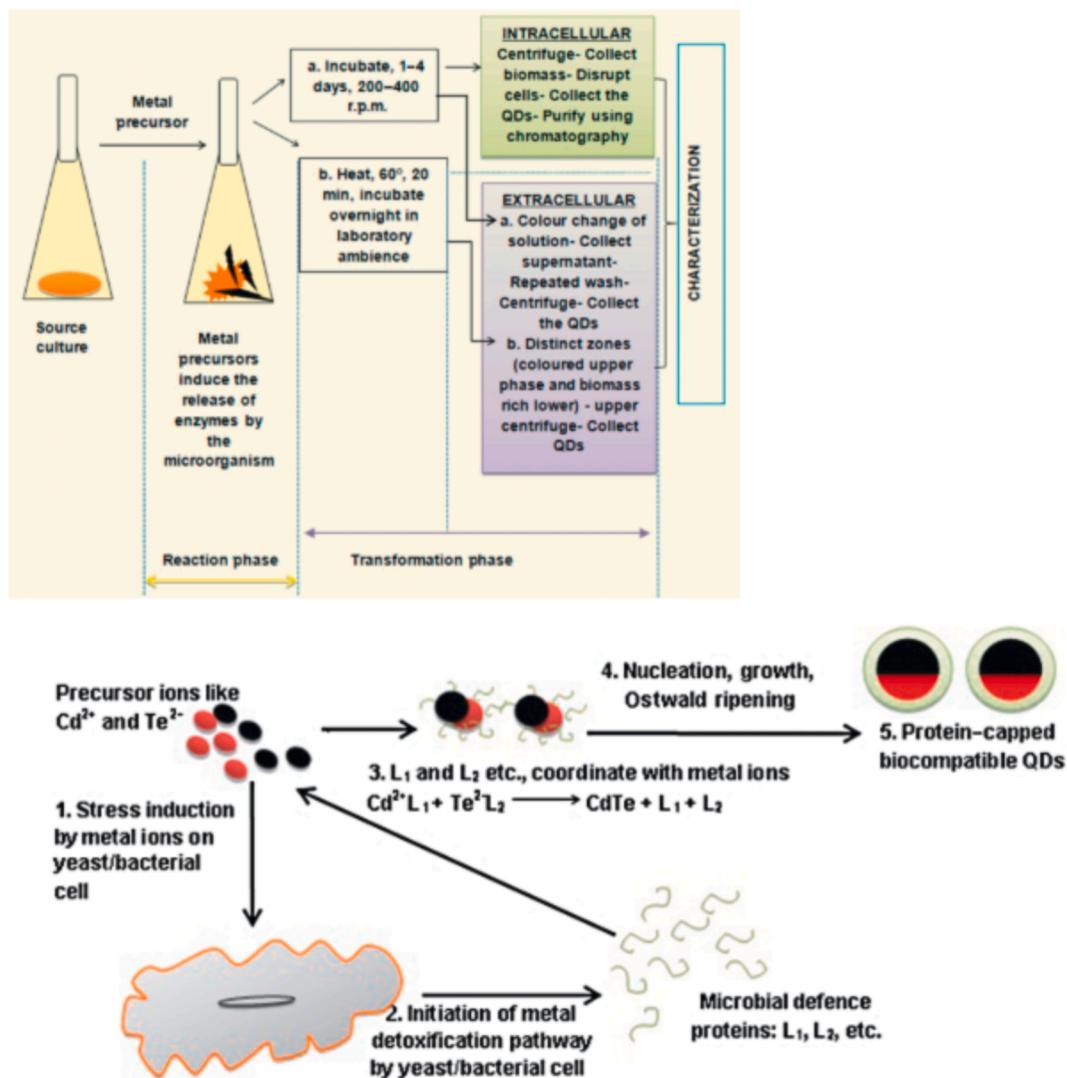


Fig. 16. (a) Microbial synthetic pathway (b) mechanism of production of quantum nanodots [25].

temperature, interval, addition of non target ions and a source compound of the wanted nanoparticles, it is possible to manage size of particle and their monodispersity [95].

Fungi could easily result to scaling up production due to fermentation mode of operation and efficient secretion of extracellular enzymes [25]. It is therefore preferable to use fungi for synthesis because it is easier to handle them and the procedure is more economical. CdSe quantum dots have been synthesized by intracellular incubation of yeast cells with Na₂SeO₃ and CdCl₂ [99].

Raliya and Tarafdar [100], have synthesized ZnO, MgO and TiO₂ nanoparticles by using fungi. In the synthesis, an enzymatic reaction replaces the chemical process which eliminates the assembly of toxic wastes and is more eco-benign. The particles generated by the process have higher catalytic reactivity, if not coated with a lipid layer [100]. In some cases, nanoparticles produced in microorganisms are purified and coated with protein which makes their physiological solubility and stability critical for biomedical applications.

4.4. Choice of synthesis method

A broad form of techniques for fabrication of nanostructured semiconductor materials exists and have been enumerated. The explanation of the methods stems mostly from their vast technological applications. Except biological means, all described methods can provide

nanocrystals of top quality, with precisely defined particles size or shape. However, for many of the above mentioned techniques, it is uphill to ascertain control over all the involved characteristics simultaneously, more so when synthesizing polymetallic oxide nanoparticles. During this perspective, the foremost efficient is chemical vapor synthesis that gives additionally a really high crystal purity similar to other vapor based techniques. Another exceptional advantage of chemical vapor synthesis is, however, the stabilization of otherwise unstable crystal phase. Nanoparticles agglomeration, that plays a big role in determining some functions of the nanoparticles is another issue that determines the choice of synthetic method. The tendency for the agglomeration is favored by electrostatic forces between particles itself, even when they are not dissolved. A number of solution-based fabrication techniques use surfactants which additionally affect the particles size and tend to decrease the agglomeration degree between particles [117]. In such cases, however, the presence of foreign, mostly organic groups attached to the surface of primary metal oxide nanoparticles leads to the formation of nanocomposites instead of pure mono or multi oxides or sulphides. Moreover, solution based techniques struggle with the matter of contaminations present during a resulting metal oxide product. Indeed, nanoparticles remain frequently contaminated with anions present within the precursor salts despite multiple and obligatory washing cycles. Another issue that needs constant investigations is the toxicity profiles of the semiconductors for various applications. It is

therefore pertinent to adopt strategies and protocols that can produce high quality nanoparticles at low cost, ecofriendly, high yield and no or low harmful effects. Chemical and physical methods are definitely superior in producing larger quantities of nanoparticles but their main advantage over biological is the ability to manage the dimensions and shape. [118]

5. Properties of semiconductor nanoparticles

5.1. Optical and luminescence properties

Bulk metal samples absorb radiation while thin films of metals may partially transmit, simply because there's insufficient material to soak up the radiation. There are important phenomena other than 'insufficient material' effects, which play significant roles in optical properties of nanomaterials. They include the dominance of surface plasmons, quantum confinement effects and surface states or effects. There is a blue shift in optical absorption and emission or increase in energy with decrease in the sizes of the quantum dots. The reduction in dimension leads to stronger quantum confinement effects which is more prominent within the case of semiconductors as compared to metals.

In photoluminescence, there is excitation by electromagnetic radiation, followed by relaxation to state by emission of photons. When the semiconductor relaxes to the bottom state by recombination of electron and hole, a photon is emitted. If the photon energy lies within the range 1.8–3.1 eV, the radiations are within the visible range luminescence. By changing the dimensions of the nanoparticles, the frequency of emission is affected. The luminescent properties are a characteristic of the material or nanoparticle core whereas the shell contributes towards enhancement of the luminescent properties of the core. In nanocomposites, when materials of larger band gap energy than the core of the semiconductor are deposited on them, they simply act as 'luminescence enhancement' arising from the suppression of radiation and less recombination mediated by surface states. Some of the examples include CdS coated with MoS₄, ZnS coated with CdSe, CdSe coated with CdS with bandgap tunable within the near-IR, which might be useful as IR biological luminescent markers [119].

The II-VI (eg ZnS) and III-V (GaP) type semiconductors exhibit lower exciton Bohr radii and prevents migration into the strong quantum confinement regime unlike the IV-VI semiconductors (eg PbSe). The electron and hole masses are reduced and almost the same in the IV-VI semiconductors leading to large Bohr radii, strong confinement in large structures and reduced surface effects since the surface-volume ratio is low [120]. The IV-VI type semiconductors are large quantum dots with lesser atoms at the surface, low influence of surface defects and traps leading to non-degenerate conduction and valence bands and simple energy spectra. Interesting vibrational modes with weak electro-n-phonon coupling, negligible exchange and coulomb energies, temperature independent band gap are some of the resulting key properties which leads to greater applications in infrared transition devices, optoelectronics and fluorescence microscopy [25].

The values of the absorption spectra of the semiconductor nanoparticles can be used to estimate their energy band gap. The band gap energy (Eg) is the energy required for an electron to move from the valence band (VB) to the conduction band (CB) and most semiconductor nanoparticles have band gap within 0 < Eg < 4 eV [57]. There are other wide band gap semiconductors that can record band gap energy of over 4 eV as Alqahtani et al have reported that Al₂O₃ can have E_g up to 6.2 eV [121]. Any material with band gap of above 6.2 eV can be regarded as an insulator [122]. The energy gap may be direct or indirect. The optical energy band gap (Eg) of the semiconductors can be obtained using the relation [123]:

$$(\alpha h\nu) = A (h\nu - E_g)^n$$

where α (absorption coefficient) = $\ln(\frac{1}{T}) / d$ where T = transmittance, d

= thickness) and hν is photon energy.

n = 1/2 for direct band gap energy (eg ZnO has a direct band structure) and n = 2 for indirect band gap (eg GaP)

when n= ½, the plot of (αhν)² against hν gives a curve with the tangential drawn to the horizontal axis of the hν giving the value of E_g.

Since the band gap energy can also be obtained from UV-vis-NIR spectra data, it can also give a clue to the crystalline sizes of the nanoparticles without further instrumental analysis such as the powder x-ray diffraction studies and the transmission electron microscopy. In order to obtain the nanocrystalline diameter size(nm) from the band gap energy value, the following relation can be used [123,124]:

$$D(E_g) = \frac{0.32 - 2.9(E_g - 3.49)^{1/2}}{3.50 - E_g}$$

5.2. Biological properties

The properties of the nanoparticles have great influence when they interact with biological organisms. Morphological properties like shape and size, surface properties and presence/absence of targeting ligands can influence NPs circulation and targeting within the body [125–128]. These properties are accountable for variations in the degradation rate of NPs and drug release kinetics [129]. The form and size of nanoparticles are accountable for specific cell signaling [130]. It is difficult to apportion some properties of the nanoparticles for a particular function or a specific biological effect, however, variations in any of the properties can, potentiate enormous changes within the material performance. NPs diameter also play a fundamental role in drug delivery applications, if the drug release relies on NPs matrix degradation. As an example, poly (lactic-co-glycolic acid) (PLGA) NPs was used to assess the kinetics of degradation and release of loaded proteins [131]. At initial time, smaller particles presented faster degradation and protein release rates than larger particles [131]. NPs surface electrical potential, otherwise referred to as zeta potential, is the potential of a particle or molecule due to its charge in a certain medium. These particles in the medium have the tendency to aggregate thereby changing in sizes [132]. While some of the particles are charged, there are neutral particles as well, therefore, electrostatic interactions occur which is a complex reaction and greatly affect the behavior of the particles inside the organisms. Charged nanoparticles are more nonspecifically internalized than neutral nanoparticles [133]. For charge-dependent reactions, the tendency for internalization is additionally cell-dependent [134].

After administration, it is desired that nanoparticles, contrary to other alternative therapies, should have the flexibility to focus on a particular anatomical site, so as to eliminate side effects on healthy tissues. To attain this goal, targeting approaches, either passive or active, are possible with nanomaterials unlike other procedures. Within the passive targeting, it's exploited by the physicochemical/structural characteristics of the target site [135]. For instance, the sizes of nanoparticles are reduced during the improved permeation and retention mechanism that occurs in tumor cells, resulting from their characteristic leaky vasculatures [136]. During active targeting, molecules such as ligands, monoclonal antibodies, engineered antibody fragments, proteins, peptides, carbohydrates and other nutrients are linked to the surface of the nanoparticles for efficient interaction [135]. The active targeting mechanism takes advantages of the highly specific interactions between the molecule present in specific tissues, cells or organelles within the body and a molecule linked at the surface of the nanoparticles [137].

5.3. Dielectric properties

The dielectric properties, electrical transport and Hall effect for nanostructured materials differ from those of micron sized materials because of increased interfacial atoms/ions and sinking of huge amount of defects at/or near the grain boundaries. Each interface acts as a capacitor thus changing the dielectric value of the materials. This

transformation is extremely pronounced in ceramics and composites. The electrical conductivity of the polycrystalline material is due to the charge carrier within the grains and along/across the grain boundaries.

Dielectric properties of ceramics and composites are important considering their application in electronics. The dielectric property of nanostructures gets modified because of defects, grain size, matrix of the composite, density distribution of the solute within the insulating matrix etc. The electrical resistivity on the otherhand depends on the sort of solids, metal, insulator or composite, grain size, defects and doped impurities [138].

6. Applications of semiconductors

Semiconductor nanomaterials have interesting physical and chemical properties and useful functionalities, when compared to their conventional bulk counterparts and molecular materials. Narrow and intensive emission spectra, continuous absorption bands, high chemical and photobleaching stability, processability, and surface functionalities are among the most attractive properties of these materials. The development of “nanochemistry” is reflected in an immense number of publications on the synthesis of semiconductor nanoparticles [139]. For instance, the spatial quantum confinement effect results in significant change in optical properties of semiconductor nanomaterials. The very high dispersity (high surface-to-volume ratio), with both physical and chemical properties of the semiconductor has a major influence on their optical and surface properties. As a result, semiconductor nanomaterials have been the focus of research for about 20 years and have attracted significant interesting research and applications in diverse disciplines such as solid state physics, inorganic chemistry, physical chemistry, colloid chemistry, materials science, and recently biological sciences, medical sciences, engineering, and inter disciplinary fields. Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor nanomaterials is primarily governed by the well-known quantum confinement, and the transport properties related to phonons and photons are largely affected by the size and geometry of the materials [140–143]. The specific surface area and surface-to-volume ratio increase drastically as the size of the material decreases [143,144]. Parameters such as size, shape, and surface characteristics can be varied to control their properties for different applications of interest [145]. These novel properties of semiconductor nanomaterials have attracted significant attention in research and applications in emerging technologies such as nanoelectronics, nanophotonics, energy conversion, non-linear optics, miniaturized sensors, imaging devices, solar cells, catalysis, detectors, photography and biomedicine.

6.1. Applications of semiconductors in energy

Nanomaterials offer many advantages in energy conversion and storage applications. Energy conversion and storage involve physical interaction and/or chemical reaction at the surface or interface. The specific surface area, surface energy, and surface chemistry therefore play a very important role in energy. The surface effects also affect the kinetics and thermodynamics of heterogeneous reactions occurring at the interface, the nucleation reaction and subsequent growth when phase transitions are involved. The smaller dimensions of nanomaterials may also offer more favorable mass, heat, and charge transfer, as well as accommodate dimensional changes associated with some chemical reactions and phase transitions. Nanomaterials also introduce new challenges in the application of energy conversion and storage. For example, large specific surface area offers more sites for charge recombination in photovoltaics [146,147] and smaller pores may limit the penetration of electrolyte ions in supercapacitors. [148,149]. Nanostructured inorganic materials for photovoltaic applications such as dye-sensitized solar cells and quantum dot sensitized solar cells are typically required to have a large specific surface area so that sufficient dye molecules and quantum dots can be adsorbed onto the inorganic materials, serving as

an antenna for optical absorption. The surface chemistry must be such that the dyes or quantum dots can be adsorbed favorably to form closely packed conformal monolayers, not only for maximizing photon capture, but also for minimizing the interfacial charge recombination.

The nanostructured inorganic framework must possess excellent charge mobility and long lifetime, and possibly possess some light scattering or photon trapping capability. Since perfect crystallinity and minimal surface and bulk defects are desired, the grain boundaries connecting individual nanostructures should be controlled to be as low as possible. Nanostructured materials as electrodes for lithium ion batteries should offer a set of properties or characteristics including large specific surface area for fast interfacial Faradaic reaction, small distance for mass and charge transport, and small dimensions to accommodate the volume change accompanied with lithium ion insertion and extraction. However, in order to achieve high energy and power density as well as long cyclic life, nanostructured electrodes should possess more open space to accommodate more guest ions and allow the ions to diffuse effectively. For a given chemical composition, an amorphous material may be better-suited than its crystalline counterpart, and electrodes with perfect crystallinity may be less desirable than poor crystallinity. High energy facets and surface defects may promote and catalyze the interfacial reactions and phase transitions. Bulk defects may enlarge the lattice constants and enhance the electrical conductivity. Nano-carbon coating may not only enhance the electrical conductivity of the electrode, but also introduce surface defects that promote the interfacial Faradaic reactions and phase transitions. The most outstanding advantage of nanostructures is their ability to create architectures with significantly larger internal surface area in view of their nano-scaled size. This feature of nanostructures enables them to be suitable for use in devices such as dye-sensitized solar cells, lithium ion batteries, supercapacitors, and hydrogen storage systems. All of these applications involve a chemical reaction that takes place at either a solid-liquid interface or a solid gas interface. Therefore, a larger interface results in an active material with a stronger ability to induce the reaction. Besides providing large surface area, it will be shown that nanostructures have other specific merits when used for energy-related devices. For example, one-dimensional nanostructures, including nanowires/ nanorods and nanotubes, have demonstrated the ability to serve as anti-reflection layers in solar cells and give rise to highly efficient electron transport, especially in dye sensitized solar cells and polymer solar cells. Metal nanoparticles may generate surface plasmon resonance, and thus enhance the optical absorption of all types of solar cells. Quantum dots are a promising type of nanostructure that may potentially lead to solar cells with internal conversion efficiencies of approx. 100% owing to the multiple exciton effect. In regard to lithium ion batteries, it will be shown that recently developed micro/ nanostructures and hollow structures exhibit enhanced lithium ion intercalation capability and surface permeability. In view of their distinct geometrical characteristics, they facilitate electrolyte diffusion and electron/ ion transport while offering a large surface area. Mesocrystals, which are relatively new structure consists of crystallographically oriented nanoparticles, show great promise in creating high performance lithium ion batteries because of their more prevalent and uniform pores, compared to traditional nanoparticles films, that can ease lithium ion intercalation by decreasing the diffusion distance. Surface modification and the utilization of defects, are fairly new concepts to lithium ion batteries and still require further understanding. These strategies controllably create nucleation sites at the electrode-electrolyte interface so as to promote phase transitions between the redox and charge/ mass transfer processes, thereby enhancing the efficiency and cycling performance of lithium ion batteries.

In supercapacitors, these nanostructures give rise to easy access for electrolyte to the active material and short diffusion distance, leading to improved energy storage. Hydrogen storage systems benefit from the use of nanostructured materials as a result of the reduced gravimetric and volumetric storage densities and additional binding sites provided by

the nanostructures on the surface and within pores [150].

6.1.1. Applications in solar cells

Semiconductor nanoparticles based solar cells can replace Si-based cells due to their low cost, tunable band gap, multiple electron-hole pair generation, optical absorption coefficient and quantum size effect. Most binary metal chalcogenides including PbS, PbSe, CdS, CdSe and Ag₂S have been used in solar cells because they have the ability to absorb within band gap of 1.1–1.4 eV [29]. However, their light harvesting and power conversion efficiency is very low which requires material modification for improved efficiency. Combination of the semiconductors with different band gap materials such as CdS/ZnO, PbSe/TiO₂ etc may reduce the charge carrier recombination leading to higher light absorption and conversion. Ternary nanoparticles such as Ag₂S₂, AgInS₂, CuSbS₂, CuBiS₂, and Pb₅Sb₈S₁₇ are also being considered for good optical absorption especially with non-stoichiometric component ratios. CdS was incorporated into Sb₂S₃ to form Cd_xSb_{2-y}S_{3-x} nanocrystals which have improved photovoltaic ability. There may also be variation of the material composition (cation, anion and cation-anion composition) and doping of the nanoparticles which affects the particle size and the band gap energy.

In ternary semiconductor nanoparticles with the formula A_nB_{1-n}Y e.g. Cd_nPb_{1-n}S, the variation in the composition of the cations Cd and Pb can increase the absorption wavelength thereby tuning the band gap. On the other hand, when the anionic components are varied eg SnSe_nS_{1-n}, larger absorption is also experienced leading to greater efficiency [29].

6.1.2. Applications in hydrogen evolution reactions (HER)

Photocatalytic splitting of water gives hydrogen which is an environmentally safe and alternative energy that can replace the ill effects of fossil fuels. Photocatalysts are applied in the hydrogen production and this technique is emerging because, the energy source is water which is ubiquitous and solar energy activates the catalysts which produces eco-friendly by-products. Photocatalysts used for such energy generation should be chemically stable, resistant to corrosion and could also absorb radiation within the visible region [151].

Transition metal dichalcogenides (TMDCs) including MoS₂, WS₂ have been applied as electrocatalysts for hydrogen evolution reaction (HER) but their performances are hindered by limited active reaction sites and relatively low electrical conductivity [152,153]. Metallic TMDCs (PtSe₂) with high electrical conductivity seems to have improved activity but they are affected by ambient conditions which further intensifies the search for efficient electrocatalyst for HER [153].

Some metal oxides can be doped with nitrogen to form metal oxy-nitrides which can absorb radiation in the visible region, possess lower band gap energy and have efficient photoelectrochemical water splitting applications. Abd El-Rahman and Mohamed [154], have reported the preparation of TiO₂/TiO_xN_y bilayer film which transformed from hydrophobic to hydrophilic character and also possesses improved photoelectrochemical properties. As they become more hydrophilic, then tend to adsorb more of hydroxyl radical than oxygen which enhances the production of hydrogen. Similarly, TiN was added on TiO_xN_y to form TiN/TiO_xN_y nanocrystallites which has great wettability and improved photoelectrochemical performance arising from the synergy between the two materials [155].

6.2. Applications of semiconductors in electronics

The electrical conductivity of the solids is determined by its electronic structure or band structure. A crystalline solid is called a metal if the uppermost energy band is partly filled or the uppermost filled band and the next unoccupied band overlap in energy. In the case of semiconductors, the completely filled valence band and the empty conduction band are separated by an energy gap (*Eg*) which is small (<3eV). The electrons can be excited from the valence band to conduction band using light or heat, which results in partial conductivity. In insulator, the

Eg is high and the electrical conductivity is restricted. The conducting nature of the solids can be affected by various factors like, temperature and particle size. When the particle size is reduced to nanometer range, the *Eg* increases and hence the conductivity is reduced. In the case of metal nanoparticles, the density of states in the conduction and valence bands are reduced and electronic properties changed drastically i.e., the quasi-continuous density of states is replaced by quantized levels with a size dependent spacing. In this situation, the metal does not exhibit bulk metallic or semiconducting behaviour. Semiconductors serve both as an insulator and conductor. They are easy to regulate and their properties made them very useful in the field of electronics. Semiconductor devices are all around us. They can be found in many commercial products ranging from the family car to the pocket calculator. Today semiconductor devices are used in a wide range of industries, including computers, communications, aerospace, manufacturing, agriculture, and healthcare. Semiconductors have made electronic devices – such as MP3 players, HDTVs /TVs, CD players, computers, and cell phones – smaller, cheaper, faster, and more reliable. Science and industry also depend heavily on semiconductor devices. Research laboratories use these devices in all sorts of electronic instruments to perform tests, measurements, and numerous other experimental tasks. Industrial control systems (such as those used to manufacture automobiles) and automatic telephone exchanges also use semiconductors. Even today heavy-duty versions of the solid-state rectifier diode are being used to convert large amounts of power for electric railroads. In general, the solid-state devices, space systems, computers, and data processing equipment are most of the devices that deploy semiconducting techniques.

6.3. Applications of semiconductors photocatalysis and water purification

A photocatalyst harnesses UV radiation from sunlight or artificial light and uses the energy to break down different substances including organic materials, dyes, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses) and chlorine resistant organisms, inorganic molecules (eg. nitrous oxides (NO_x) and, in combination with precipitation or filtration, also removes metals such as mercury [146–148]. Due to this universal applicability, photocatalysts are used in reduction of air pollution, in building materials, for self-cleaning surfaces, and water purification.

There are a lot of contaminants including dyes (methylene blue (MB), methyl orange (MO), Rhodamine B (RhB), Rhodamine 6G (Rh6G)), organic chemicals (toluene, phenol, polyaromatic hydrocarbons (PAH) and heavy metals (Ni²⁺, Cr³⁺, Hg²⁺, Pb²⁺, Cu²⁺, Cd²⁺, Co²⁺ and As³⁺) which cause serious damages to the water bodies.

Techniques ranging from adsorption, ion exchange, membrane-based filtration, reverse osmosis photodegradation, chemical precipitation, evaporation, solvent extraction have been applied to in order to make the water clean for human use but some of the procedures are either expensive or pose difficulties in releasing the sludge after treatment. The application of semiconductor nanomaterials in water treatment for removal of dyes, heavy metals and toxic organic substances is an interesting option due to efficient large surface area of the materials for adsorption, their low cost, photocatalytic behavior, wide band gap and ecofriendly nature.

Fe₃O₄, TiO₂, ZnO and their nanocomposites are among the semiconductor nanomaterials that have been applied in purification of surface water, industrial effluents, groundwater, and drinking water [156]. The surfaces of the nanoparticles can be functionalized with groups such as carboxyl, amines, thiols etc to enable efficient adsorption and photocatalytic degradation of the pollutants.

Titanium dioxide (TiO₂) is the most common photocatalyst and comparably little research has been conducted on zinc oxide, ZnO, which could be an available alternative. Semiconductor photocatalysis with a primary focus on TiO₂ as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to

water and air purification. To avoid free nanoparticles in water, TiO_2 nanoparticles are usually immobilized on a substrate [149] or integrated into thin-films and other materials. The anatase TiO_2 however has higher photocatalytic behavior than the rutile form [157,158]. For the activation of TiO_2 , UV irradiation from sunlight or artificial light is needed. To allow activation by visible light, TiO_2 can be modified with other materials to form composites capable of absorbing in the visible region. In spite of the extensive efforts to dope TiO_2 with C, N, S and transition metal ions such as Ag, Au, Fe, Ru, photocatalytic activity of TiO_2 in the visible region has remained quite low, an issue that has been addressed in recent times highlighting issues and challenges associated with the application of photocatalysis. Mohamed et al have doped TiO_2 with Fe which exhibited enhanced photocatalytic reaction since the Fe works to trap electrons and/or holes on the surface of the TiO_2 thereby generating charge carriers [158].

Generally, two or more phases are involved in a photocatalytic reaction – a light source and a semiconductor material are used to initiate the photo-reaction. The catalyst system can simultaneously carry out oxidation and reduction reactions using long wavelength, UV light as well as sunlight as a method for contaminant control in water and air. Heterogeneous photocatalysis using semiconductors such as titanium dioxide is more efficient than conventional methods. This is because as the photocatalytic process gradually breaks down the contaminant molecules, no residue of the original material remains and therefore no

sludge requiring disposal to land fill is produced. The catalyst itself is unchanged during the process and no consumable chemicals are required leading to considerable savings and a simpler operation of the equipment involved. [150].

Ag decorated on the surfaces of ZnO nanostructures have been used for the degradation of dye pollutants in water through photo activation [159]. Since there is an electron-hole recombination effect associated with the semiconductors alone, the introduction of the noble metal Ag to form the nanocomposites assists in interfacial charge transfer kinetics. The Fermi level of the Ag is lower than the energy level of the conduction band which prompts electron flow from the conduction band of the ZnO nanoparticles into the Ag. The Ag therefore acts as a sink for photogenerated electrons and prevents electron-hole recombination. While the holes react with water, the electrons react with O_2 forming OH^\bullet and O_2^\bullet radical respectively which strongly oxidizes the dye components in water.

Mohamed [160] has reported that ZnS-Cu nanofilm exhibited better photocatalytic degradation of methylene blue than undoped ZnS. However, decomposition efficiency was higher with low Cu content than when Cu is high.

6.4. Biomedical applications of semiconductor nanoparticles

The size, morphology, crystal orientation, concentration in growth

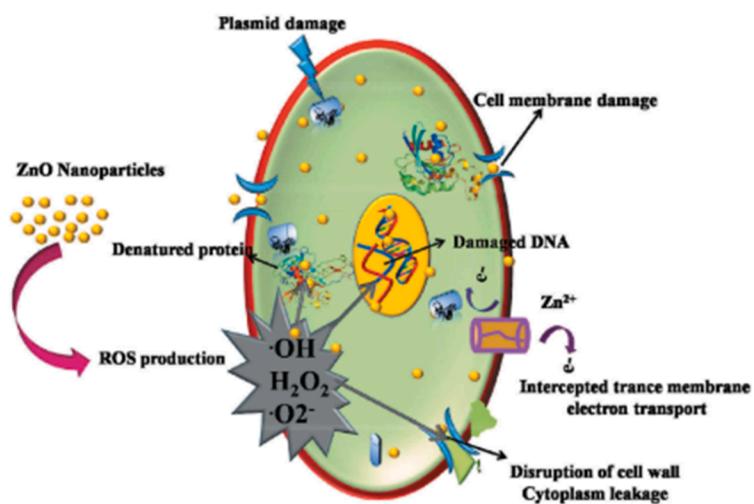
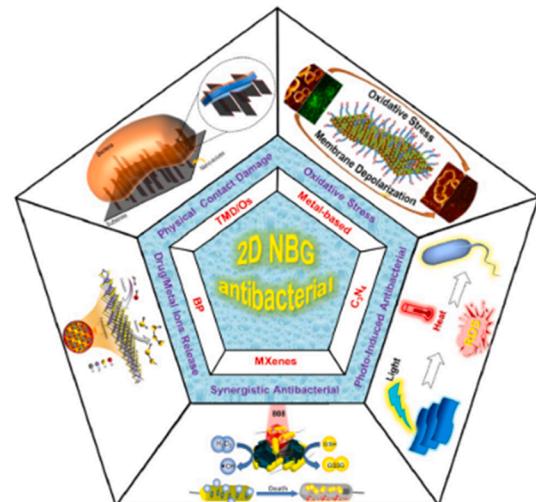
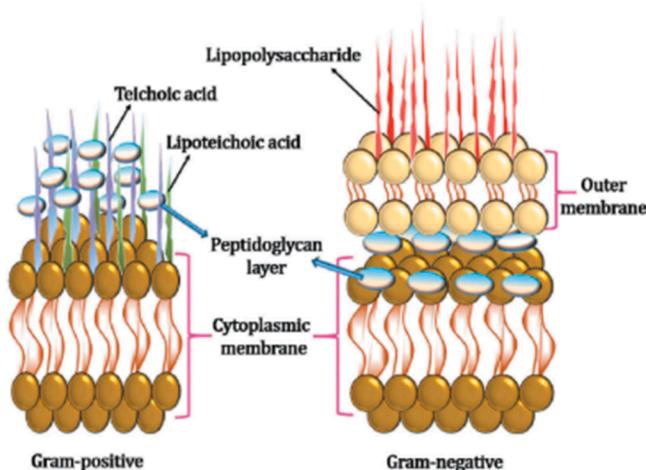


Fig. 17. (a) Structure of the cell membrane of bacteria (b) different antibacterial mechanism (c) oxidative damage mechanism [161,166].

medium, stability and surface functionalization of the nanomaterials play key role in their antimicrobial, anticancer, antiviral and other major biomedical applications. The two-dimensional nanomaterials beyond graphene (2D NBG) that comprises 2D layered transition metal dichalcogenides (TMDCs), graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), transition metal oxides (TMOs), black phosphorus (BP), layered double hydroxides (LDHs), transition metal carbides and nitrides (MXenes) have exhibited excellent antibacterial activities [161,162]. There are several ways through which antibacterial action can be performed by the semiconductor nanoparticles or 2D NBG which include physical contact damage, oxidative stress, drug-metal ion release, photo-induced and synergistic antibacterial action as shown in Fig. 17(a-c). Physical contact destruction of the bacterial cell membrane is one of the interesting mechanism that has been observed for antibacterial action of the nanoparticles. Bi_2Se_3 nanodiscs have been reported to damage the bacterial cell membrane by binding with lipoteichoic acid component of the Gram + bacteria [163]. Structural study of WS_2 has shown that the sharp edges of the nanosheets have the capacity of destroying the structural integrity of the bacteria cell wall [164]. The edges of MoS_2 , MoO_3 , RuO_2 and MnO_2 have also shown similar destruction of the bacterial cell wall.

Oxidative stress mechanism of antibacterial action involves both dependent and independent release of reactive oxygen species which leads to the destruction of the cellular make-up and DNA of the bacteria. While the ROS dependent oxidative stress destroys the bacteria through generation of species such as peroxides, hydroxyl radicals, superoxides etc, the ROS-independent oxidative stress destroys by nanomaterials induced direct oxidation.

The photoinduced antibacterial mechanistic procedure is a non-invasiveness and a targeted selective treatment method with low or no side effects. The photoresponsive semiconductors are triggered when light energy falls on them which excites fluorophores that are converted to heat or ROS thereby attacking the bacteria organisms. In this regard, MoS_2 nanosheets possess near infra-red photothermal efficiency and therefore could be regarded as an excellent photothermal antibacterial agents [161]. ZnO and TiO_2 nanoparticles have also been activated by ultraviolet radiation to destroy pathogenic bacteria [165]. Both of them have also been considered as safe multifunctional antimicrobial agents and have been applied not only in drugs or pharmaceuticals but also in cosmetics, food packaging, wound healing due to their biocompatible nature [166].

There could also be photocatalytic disinfection mechanism by the nanoparticles which depend on large surface area, the photo-induced

charge-separated state and the production of ROS resulting from charge center interactions, neighboring oxygen and water molecules. In the case of the drug-metal ion release, the semiconductors act as nano-carriers which releases the antibacterial agent to the site of action when needed. The synergistic mechanism involves the combination of the other methods for a holistic bactericidal action. Graphene materials have also emerged as promising materials through inactivation of pathogens and photocatalytic disinfection for robust antimicrobial action [167].

MoS_2 polydopamine-Ag nanosheets have been developed as an efficient antibacterial nanoagent where the mechanism involves both realease of Ag ions, photoactivity which generates heat and ROS for further damage of the bacteria organisms [168].

On the other hand, the functionalization of semiconductor nanoparticles with other materials including polymers, organic ligands may lead to improvement in the antimicrobial properties. Khan *et al* have reported the enhanced antibacterial activities of glutamic acid functionalized ZrO_2 nanocomposites as shown in Fig. 18 [169].

In general, the gram negative bacteria are more negative than the gram positive strains and as a result will have more electrostatic interactions with the positive ion components of the nanoparticles or nanocomposites leading to greater efficiency in antibacterial activities.

6.4.1. Anticancer behaviour

Cancer chemotherapy is becoming challenging with the use of metal-based drugs due to the fact that during transportation into the cell membrane, there are some transformational or decompositional behaviours leading to non specificity of the drug action [170]. As a result, non-classical metallodrug-functionalized nanostructures are developed which exhibits different mechanistic ways of impairing the cell DNA and leading to the tumor cell deaths. Iron oxide nanoparticles (IONPs) is one of the most important semiconductor nanoparticles with multifunctional properties especially for cancer diagnosis and therapy due to their magnetic and non-toxic nature, biocompatibility, stability and low cost [171]. Other biomedical applications of IONPs include targeted drug delivery, magnetic resonance imaging (MRI), magnetic separation, magnetic fluid hyperthermia and thermoablation and biosensing [171,172] as shown in Fig. 19.

The magnetic and fluorescent behaviours of the IONPs can be improved when functionalized with some chalcogenides semiconductors therefore enhancing their biomedical activities. IONPs coated with silica and CdSe/ZnS have been seen to cause apoptosis in pancreatic cancer cells through radiofrequency radiative mechanism

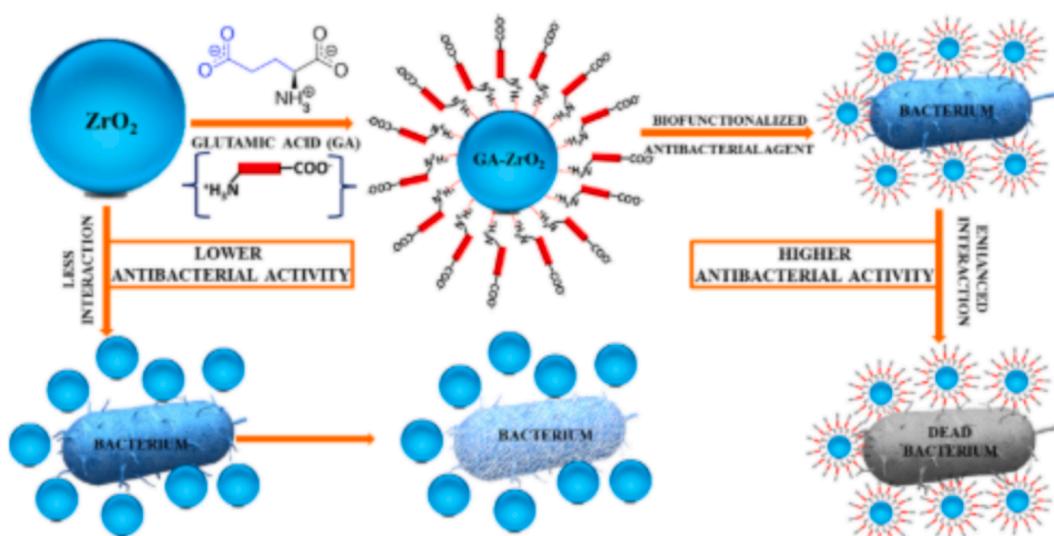


Fig. 18. Antibacterial effect of functionalization of semiconductor nanoparticles. [169]

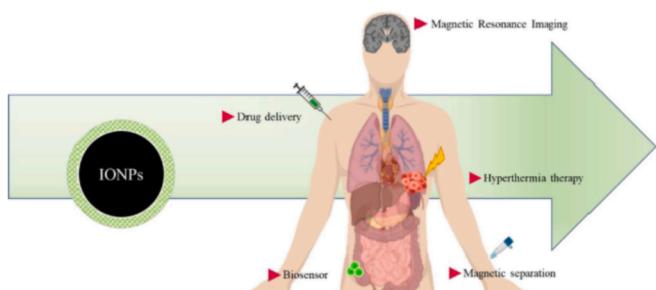


Fig. 19. Biomedical applications of IONPs [171].

[173].

Metal oxide semiconductors including CuO, SiO₂, Fe₂O₃, Fe₃O₄ and TiO₂ have been reported to be cytotoxic to human adenocarcinoma A549 cells through autophagy process with CuO showing the highest cytotoxicity [174]. The carcinoma cells proteins and organelles are surrounded by the nanoparticles in a double membrane technique and finally leads to their death [175].

The CuO nanoparticles releases Cu²⁺ which causes cell protein denaturation, interferes with the biological functions and gradually leads to cell death. The presence of capping agent such as polyethylene glycol which has chemopreventive properties would also enhance the cytotoxic behavior [176].

There is excitation of electron in TiO₂ nanoparticles when UV radiation with energy greater than their band gap energy (3.2 eV) falls on them which leads to creation of electron-hole pair. The TiO₂ therefore behaves as inorganic photosensitizers which generates reactive oxygen species (ROS) needed for destruction of microorganisms, degradation of organic substrates and photodynamic therapy (PDT) [177]. Other interesting applications of TiO₂ nanoparticles are in wound healing, tissue engineering, gene therapy, stem-cell therapy, etc.

TiO₂ loaded on graphene is another combinatorial nanoplatform of triggering improved anticancer behavior due to the contributory high electroconductivity of graphene. Due to the interesting electroconductive nature exhibited by graphene, when there is ultrasound irradiation on the graphene-TiO₂ nanosensitizers, separation of electron-hole pairs is facilitated leading to improved sonodynamic therapy efficiency on destruction of cancer cells [177].

6.5. Applications in sensing

Majority of natural and human activities including forest fires, explosives, petroleum and metal refining, mining waste, vehicle emissions, natural gas, plastic, coal, combustion of fossil fuels, food and industrial manufacturing, volcanoes generate a lot of pollutants which needs to be constantly monitored and curbed [178]. As a result of the environmental concerns, sensing has become an integral part of environmental studies in order to detect hazards around us. A sensor is simply a fabricated electronic device which shows changes on the surface when stimulated by chemical agents [179]. Chemical sensors can detect and monitor dangerous chemicals, gases, gas alarms, temperature, water and soil pollutants, human health and so on. The sensing material comprises the receptor which recognizes the polluting substances and the transducer which converts the substance into electrical signals. The electrical signals are observed due to the interaction of the polluting substance and the sensing materials.

Semiconductor nanomaterials are greatly used in gas sensing due to their high electron mobility, high surface-volume ratio, charge confinement ability, crystallinity, chemical and thermal stability. The high reactivity of the semiconductors or nanostructured metal oxides present electrical resistance to the target pollutant gas. On the contrary, they are not specific and selective in action and operates at high temperature which involves high energy and may not operate in all

environments.

On this note, the search for high performance semiconductor sensors with high level of sensitivity and selectivity is paramount and elicit great interests.

Colloidal quantum dots including ZnO, PbSe, SnO₂, WO₃, PbS etc have been used for selective detection of substances or gases such as NH₃, NO₂, LPG, CH₄, ethanol, H₂S etc at room temperature [180]. Nanogab sensors decorated with SnO₂ can be used for detection of drunk driving, food quality and safety systems [181].

SnO₂ incorporated into reduced graphene oxide (rGO) have been applied in the electrochemical detection of heavy metal ions in drinking water with high selectivity [182].

The non-toxic nature of TiO₂ and ZnO nanostructures has made them the sensing material of interest for medical and pharmaceutical systems. They are biocompatible and can easily bind with biological entities to act as biosensor in detecting the level of danger of some chronic diseases, zika virus in urine or even corona virus in fluid samples [183]. Due to their versatile morphologies, they show different behaviours and response to pollutants or molecules resulting from their structural or morphological influence on the electron transfer rate. Fig. 20 has shown the biosensing behavior of some metal oxides semiconductor nanoparticles, their crystalline nature, electron transfer band structure and interaction with the molecules. The p-type semiconducting NiO nanostructures has also shown efficient sensing of formaldehyde gas due to improved electrochemical activity in the electrode-electrolyte system brought about by large surface area of the semiconductor electrode material [184].

7. Toxicological behaviour of semiconductor nanoparticles

The toxicity of nanoparticles depends on their sizes, material concentration, charge, material composition and their stability [185]. The in vitro and in vivo toxicological assessment are carried out with emphasis on the histological changes, biodistribution, pharmacokinetic influence, biochemistry metabolism, and clearance. The in-vivo evaluation further focuses on analysis of nanoparticles impact on digestive, renal, respiratory, hepatic, hematological, cardiovascular, nervous and immune systems [186]. The mechanism of toxicity can be by cell proliferation, necrosis, apoptosis, DNA damage, and oxidative stress.

Human skin, lungs, and therefore the gastro-intestinal tract are in constant contact with the environment. While the skin is usually an efficient barrier to foreign substances, the lungs and gastro intestinal tract are more vulnerable. These three ways are the foremost likely entry points for natural or anthropogenic nanoparticles. Injections and implants methods are other possible routes of exposure, primarily limited to engineered materials. Because of their small size, nanoparticles can

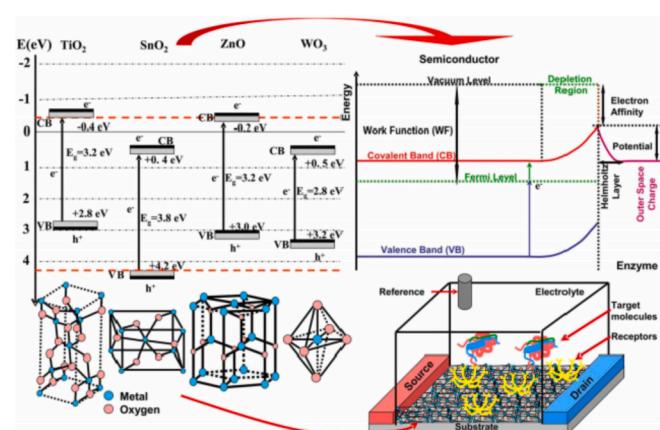


Fig. 20. Biosensing nature of some semiconductors, showing crystal structures, energy band structures and biosensing interactions with biomolecules [183].

move from these entry portals into the circulatory and lymphatic systems, and ultimately to body tissues and organs.

They can produce irreversible damage to cells by oxidative stress or/and organelle injury. It should be noted that, not all nanoparticles produce these adverse health effects; the toxicity of nanoparticles depends on various factors, including: size, aggregation, composition, crystallinity, surface functionalization, etc [187]. Additionally, the toxicity of nanoparticles to an organism is decided by the individual's genetic composition, which provides the biochemical toolbox by which it can adapt to and fight toxic substances. Diseases related to inhaled nanoparticles are asthma, bronchitis, emphysema, carcinoma, and neurodegenerative diseases, including Parkinson's and Alzheimer's diseases. Nanoparticles within the gastro-intestinal tract are linked to Crohn's disease and carcinoma cell growths. Nanoparticles that enter the cardiovascular system are associated with occurrence of arteriosclerosis, blood clots, arrhythmia, heart diseases, and ultimately cardiac death. Exposure to some nanoparticles is associated to the occurrence of auto immune diseases, such as: systemic lupus, scleroderma, and atrophic arthritis [187]. Basic cellular processes such as proliferation, metabolism, and death are also greatly influenced by nanoparticle sizes whereas most diseases are linked with dysfunction of these basic processes. For instance, cancer results from uncontrolled cell proliferation, while neurodegenerative diseases are caused partly by premature cell death [188]. Oxidative stress has been implicated in many diseases, including cardiovascular and nervous disorder, pancreatitis, and cancer [189]. Severe inflammation is assumed to be the initiating step [190] in the appearance of auto immune diseases (systemic lupus, scleroderma, and rheumatoid arthritis) which can be compared to exposure to some nanoparticles, like silica and asbestos [191,192].

Toxicity of the metal oxides nanoparticles in human cell lines has been verified and TiO_2 was reported to be less toxic than ZnO and CuO [193]. The toxicological verification of other oxides Cr, Mn, Fe, Co, Ni, Cu, and Zn shows that toxicity increases with atomic number except for Fe_2O_3 which is low in toxicity and CoO and V_2O_5 which are unusually high [194]. Other factors which affect the toxicity includes the synthetic methods, particle characteristics and nature of the cell lines. Moreover, cationic nanoparticles easily interact with the heparin sulfate proteoglycans on the surface of the cell membrane and therefore attacks the cell more than the anionic nanoparticles [195]. The adverse health effects of transition metals are usually diminished by metal chelators [196].

8. Future considerations

The study of semiconductor nanomaterials is a vast and interesting field which has endeared the interest of the science community. The chemical tailorability and size design or reduction into quantum dots are some of the features that are constantly explored for newer applications. There are various methods which have been applied in the preparation of the different semiconductor nanomaterials. Among all the methods, ultrasonication, microwave, and solvothermal techniques seem facile and may be adopted for novel semiconductor composite materials due to the fact that they give rise to well dispersed colloidal semiconductor nanocrystals. However, for the purpose of biomedical applications, biosynthetic methods are preferable because they are safer and use less-toxic or non-toxic reagents and solvents.

Different innovations in semiconductors nanomaterials are due to their large surface to volume ratio, chemical and thermal stability, high reactivity and conductivity. These properties have enabled the widespread applications of semiconductor nanomaterials in emerging technologies like energy conversion and storage, nanoelectronics, nanophotonics, solar cells, biomedicine detectors and sensors.

The wide band gap semiconductors are greatly applied in energy generation and conversion, wireless communications, radiofrequency devices and power electronics because of inherent advantages ranging from high breakdown voltage, performance in harsh environments and

conditions, volumetric efficiency, lower losses for higher efficiency, high switching frequency, high temperature control, increased bandwidth, larger power densities, reduced input and output capacitance, easier impedance matching. GaN, InGaN have advanced the development of lightning materials from filaments to devices utilizing light emitting diodes. Surface functionality of the semiconductor materials and easy of composite formation have also improved sensing applications ranging from pollution monitoring, heavy metal detection, biosensing to food safety and health monitoring.

The application of nanotechnology principles will lead to new inventions and great turn-around in semiconductor materials. More investigations are encouraged in order to apply the underutilized semiconductor materials for extensive applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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