Chapter

Indium Chalcogenide Nanomaterials in the Forefront of Recent Technological Advancements

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Abstract

In the last decade, there has been an increasing trend in the exploitation of indium chalcogenides in various applications which range from water splitting reactions in renewable energy to degradation of dyes in environmental rehabilitation. This trend is attributed to the interesting and unique properties of indium chalcogenide nanomaterials which can be easily tuned through a common approach: particle size, shape and morphology engineering. In this chapter, we outline the preferred attributes of indium chalcogenide nanomaterials which are deemed suitable for recent applications. Furthermore, we explore recent reaction protocols which have been reported to yield good quality indium chalcogenide nanomaterials of multinary configurations, e.g. binary and ternary compounds, among others.

Keywords: sulfide, selenide, telluride, multinary, applications

1. Introduction

Over the years, there has been an increasing demand on state-of-art solutions to solve real world problems such as the energy crises and efficient early-detection protocols in biomedical services. The current systems in place suffer from a range of issues, e.g. an increase in the depletion rate of fossil fuel and petroleum reserves as precursors in the electrical power generation plants [1]. Although, in the context of electricity generation, there exists alternatives such as nuclear power, unwavering challenges such as toxicity of nuclear waste still persist [2]. Another good example is the use of conventional dyes for the detection of tumors (typically having issues with stability and sensitivity) and drug delivery systems, which both generally lack selectivity i.e. in crucial need of smart, guide-assisted delivery to an affected target area [3]. As a response to these issues, among many that exist, scientists and engineers have presented a range of nanotechnology-based solutions through successes in the development and pioneering work on functional nanomaterials and related devices. There are, however, reservations in trusting these technologies in the general public domains, attributed to insufficient knowledge and/or lack of educational strategies [4]. Thus, progress in introducing these systems for general use still remains a challenge, with few successes such as QLED televisions [5] already available to the general public consumers for everyday use.

The core fundamental principle to grasp on nanotechnology and nanomaterials is that when the particle size dimensions of a bulk material decrease to the nanometer scale, improved and/or novel properties emerge. Thus, properties of a material can be tuned to desired standards best suited for specific applications, by simply manipulating particle size and shape. Indium chalcogenide nanomaterials are among many functional materials which boast rich literature in the aforementioned context, hence, their technological importance continues to be showcased in widespread applications to date.

The surge in the interest of indium chalcogenide nanomaterials has mainly been fueled by their recognition as alternative candidates against giants in the field of photovoltaics and sustainable energy solutions, such as cadmium chalcogenides which are known for their toxicity issues albeit achieving high performance and efficiency in metal chalcogenide-based semiconductor solar cells and other optoelectronic applications [6]. There are other less-to-non-toxic candidates which have been identified, such as antimony [7] and tin [8] chalcogenides, among others. However, indium chalcogenides contain a broad spectrum of crystallographic phases/species which exhibit unique properties attributed to different atomic compositions and crystal lattice orientation (polymorphism), contrary to antimony and tin chalcogenides. An example of this can be seen in the indium sulfide series, where InS, In_3S_4, In_6S_7 and In_2S_3 (α-In_2S_3, β-In_2S_3 and γ-In_2S_3 [9]) phases have been obtained experimentally [10]. This, in addition to manipulating particle size and shape, as well as employing other enhancement techniques such as doping and composite fabrications, present endless opportunities to harness tailor-made properties.

The most common and easy route to tune the properties of nanomaterials is by tweaking reaction parameters during synthesis. Therefore, the choice of synthetic methods best suited for specific precursors is of crucial importance [11]. Over the years, there has been an intensive research invested on precursor design necessary to produce high quality nanomaterials [12]. Hence, metalorganic compounds gained unprecedented attention as molecular precursors compatible with a range of fabrication protocols. These molecular precursors have made it possible to access various classes of nanomaterials, although the overall nanomaterial fabrication protocols were initially a hit-or-miss process. As a result of this approach, useful data has been obtained which has formed an integral part of theoretical models used to predict novel nanomaterials and their corresponding properties. As much as molecular precursors have demonstrated their preference and superiority over conventional salt-based precursors in the context of nanomaterial fabrication, the latter is however currently ideal for the development of devices which are sensitive to impurities, among other factors. Hence, recent technological advances (from late 2019 to date of this book chapter) of indium chalcogenide nanomaterials presented in the next sections are predominantly obtained through conventional salt-based precursor routes. Interesting literature on molecular precursors for indium chalcogenide nanomaterials is available elsewhere [13, 14].

2. Indium sulfide series

Research on indium chalcogenide nanomaterials predominantly focuses on the indium sulfide series, attributed to readily available, abundant, cheap and stable precursors. This series finds applications in various applications, typically in optoelectronics. Among recent advancements is the selective NO_2 gas sensing abilities of β-In_2S_3 thin films prepared by spray pyrolysis; this preliminary study introduces β-In_2S_3 thin films as less toxic and cheaper alternatives to highly selective and sensitive cadmium sulfide-based NO_2 gas sensors [15]. In other work, In_2S_3

thin films prepared by ultrasonic spray pyrolysis was evaluated, for the first time, as photoelectrodes (**Figure 1**) for all-vanadium photoelectrochemical batteries [16]. The efficiency was linked to the degree of optical and photoelectrochemical behavior associated with the thickness of the In_2S_3 thin films. In both works, it becomes apparent that the physical alterations of the films are necessary to improve selectivity, sensitivity and efficiency. There are two notable recent reports which have provided preliminary solutions as per above: (i) band gap (1.9–2.3 eV) and electrical resistivity (5.5 x 10^0–6.0 x 10^3 Ωm) control through thermal treatment of as-prepared In_2S_3 thin films at different temperatures in the presence/absence of sulfur powder [17], and (ii) tunable morphological (root mean square roughness) and optical properties (transmittance and photoluminescence) of the In_2S_3 thin films by varying the S/In molar ratio in spray pyrolysis deposition experiments [18].

Similar to the research objectives in Ref [15], indium sulfide is yet again demonstrated as a promising alternative to the cadmium sulfide, in this case as a buffer layer in the Cu(In,Ga)Se_2 solar cell [19]. It was found that the indium sulfide-based solar cell achieved 15.3% efficiency compared to 17.1% recorded for the cadmium sulfide counterpart. The authors report that the observed efficiency is attributed to substrate temperature optimization during the sputtering method-based experiments. According to the study, the increase in substrate temperature tempers with the In_xS_y and Cu(In,Ga)Se_2 compositions; an increase in temperature resulted to a sulfur-rich In_xS_y buffer layer, as well as copper depletion observed in the Cu(In,Ga)Se_2 absorber layer, as seen in **Figure 2**. Furthermore, sodium doping was observed in both the In_xS_y layer and in the In_xS_y and Cu(In,Ga)Se_2 interface. Thus, it is these features which were identified to play a major role in the increase of the solar efficiency.

Other efforts to improve attractive properties of In_2S_3 thin films have been reported, such as silver doping as means of improving electrical transport [20], as well as plasma treatment which consequently results to the self-formation of metallic indium arrays at the surface thus presenting opportunities in fabricating

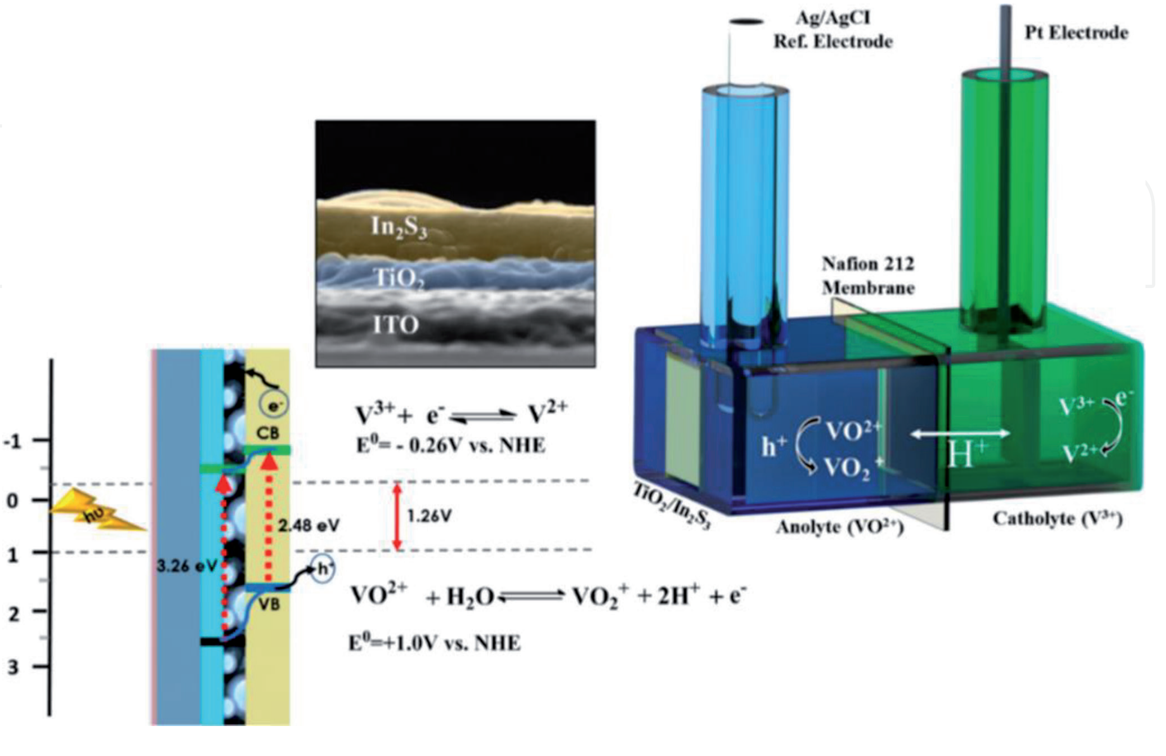


Figure 1.
Schematic representation of the photoelectrochemical VR-flow cell based on the In_2S_3-type photoelectrode. Reprinted with permission from Ref. [16]. Copyright 2020 American Chemical Society.

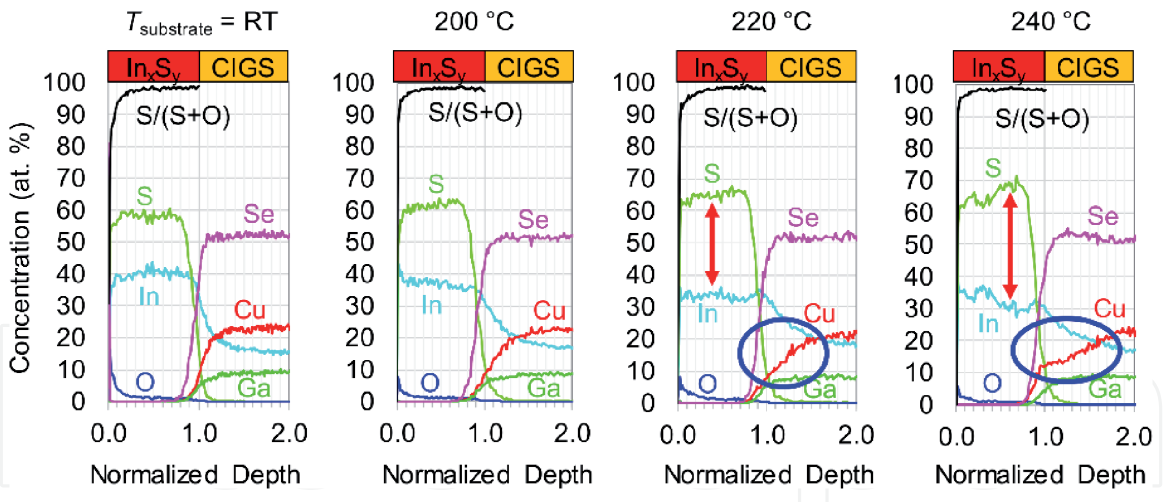
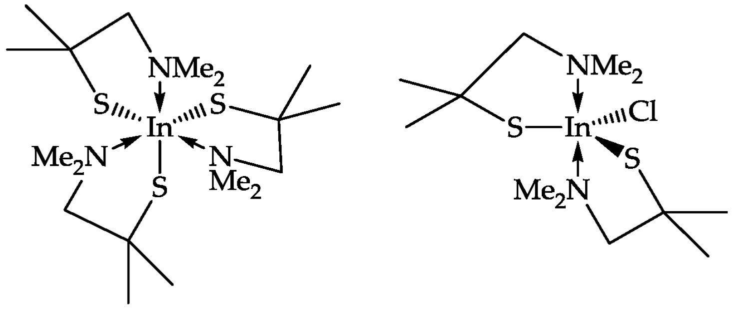


Figure 2.
Elemental composition of In_xS_y and $Cu(In,Ga)Se_2$ layers deposited at different substrate temperatures. Reprinted with permission from Ref. [19]. Copyright 2020 MDPI.

heterostructures for potential use optoelectronics [21]. Bilayer and trilayer InS triangular nanoflakes have also been prepared by chemical vapor deposition [22], potential applications envisaged as heterojunctions in nanoelectronic devices.

The films outlined above are predominantly obtained from existing technologies such as spray pyrolysis, thermal evaporation and chemical vapor deposition, where the films are directly prepared on a substrate. A new, solution-based synthesis of suspended 2D ultrathin sheets was developed [23]. This novel strategy, optimized through the synthesis of In_2S_3 sheets, exploits a self-assembling anisotropic growth mechanism templated by a combination of amine ligand with a geometrically-matched alkane. The obtained In_2S_3 sheets exhibited high photoelectric activities best suited for photoelectrochemical applications. Preliminary experiments displayed versatility of the method, attributed to the successful preparation of other 2D nanostructures such as Co_9S_8, MnS, SnS_2, Al_2S_3 and MoS_2. Thus, this presents an alternative route to easily prepare functional thin films which could ultimately be transferred to desired substrate post preparation and manipulation processes.

It has been observed that the recent advances in indium sulfide nanomaterials outlined above predominantly use the multiple precursor route. Although progress has been made in the past few years, the search for novel metalorganic single-source precursors for indium sulfide continues. New indium complexes with aminothiolate ligands have been synthesized and characterized fully [24], their structures are provided in **Figure 3**. Preliminary evaluations as potential single-source precursors showed that complex **1** is able produce β-In_2S_3 nanoparticles, complexes **2** and **3**



1 **2** **3**

Figure 3.
Chemical structures of novel indium (III) aminothiolate complexes prepared by Ref. [24].

however need extensive work, as the diffraction studies for phase identification were inconclusive. However, microelemental analyses suggest that the nanomaterial exhibit general formulae In_2S_3 and In_2Se_2S from complexes **2** and **3**, respectively.

2.1 Indium sulfide-based ternary and quaternary nanomaterials

The main interest on indium sulfide-based ternary and quaternary nanomaterials is their optical properties, predominantly exploited in emission/photoluminescence applications. Recent studies in this field has focused on the chalcopyrite-type materials, copper indium sulfide ($CuInS_2$) and silver indium sulfide ($AgInS_2$) in particular. A recent, concise review on the synthesis and applications of $CuInS_2$ is available in Ref [25]. However, there are interesting literature reports which emerged subsequent to the publication of the review. For example, there is a study which has evaluated the influence of halide ions on the optical properties of $CuInS_2$ quantum dots [26]. Similar to our work where we evaluated the influence of halide ligands in the single-source precursors on the morphological and optical properties of cadmium sulfide [27, 28] and lead sulfide [29] nanoparticles, the authors in this case follow a multiple-source precursor route (through the solvothermal synthetic protocols) using CuX (where X = I, Cl and Br) salts. The optical properties show unique behavior with respect to the metal salt used, attributed to the physicochemical properties resulting from the growth processes which consequently promote accumulation of the halide ions in the crystal lattices of the quantum dots. In another report, the importance of controlling the Cu:In ratio

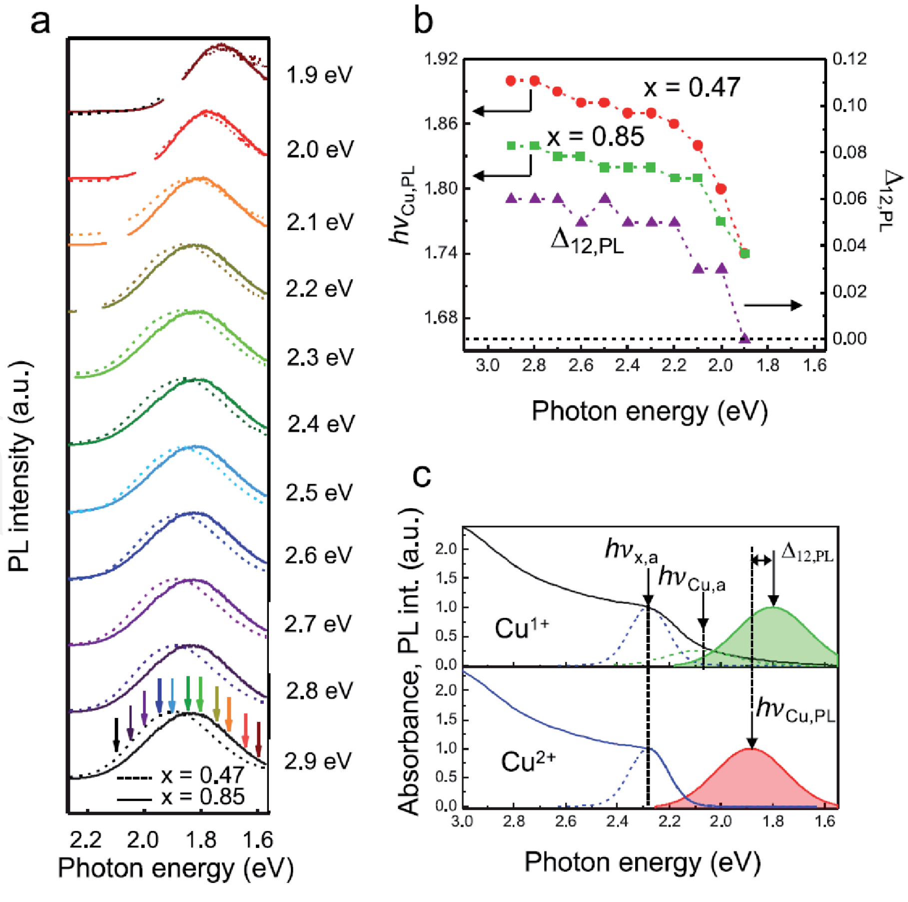


Figure 4.
(a) Resonant photoluminescence (PL) measurements of Cu_xInS_2 quantum dots where x = 0.47 (dashed lines) and x = 0.85 (solid lines), at different excitation energies. (b) the PL peak energies extracted from (a). (c) Simulated absorption (lines) and corresponding PL (shaded peaks) spectra of Cu_xInS_2 quantum dots with respect to Cu^{1+} and Cu^{2+} defects. Reprinted with permission from Ref. [30]. Copyright 2020 American Chemical Society.

in $CuInS_2$ quantum dots to harness different properties for various applications is discussed [30]. The report suggests that the change in the Cu:In ratio induces defects attributed to what the authors refer to as Cu^{1+} *vs* Cu^{2+} concentration defects, resulting in different optical emission behaviors as observed in **Figure 4**.

Although $CuInS_2$ is a reputably known non-toxic material displaying attractive properties which are already exploited intensively in biomedical-based applications, there are however recent reports which have shown compelling experimental evidence contradicting this non-toxic behavior. A recent research study has observed the instability of zinc sulfide (ZnS) shell-free $CuInS_2$ quantum dots relative to the shelled counterparts in the *in vitro* studies [31], degradation was demonstrated by rapid dissolution in simulated biological fluid (SBF) and artificial lysosomal fluid (ALS) through absorption spectroscopy measurements shown in **Figure 5**. Furthermore, it was demonstrated that shell-free $CuInS_2$ induces severe toxicity in the *in vivo* studies compared to the infamous, toxic cadmium selenide. In another report, $CuInS_2$ nanocrystals were exposed in environment-like conditions (including alkaline and acidic settings) thereby promoting weathering [32]. It was observed that when the environmental pathogenic bacteria *Staphylococcus aureus* CMCC 26003 strain is exposed to weathered $CuInS_2$ nanocrystals, it develops increased tolerance to certain antibiotics such as penicillin G, tetracycline and ciprofloxacin. Thus, these two studies are a constant reminder with regards to creating awareness that alternative "green" approaches require concise evaluations and any possible adverse effects towards disruption of natural and crucial processes.

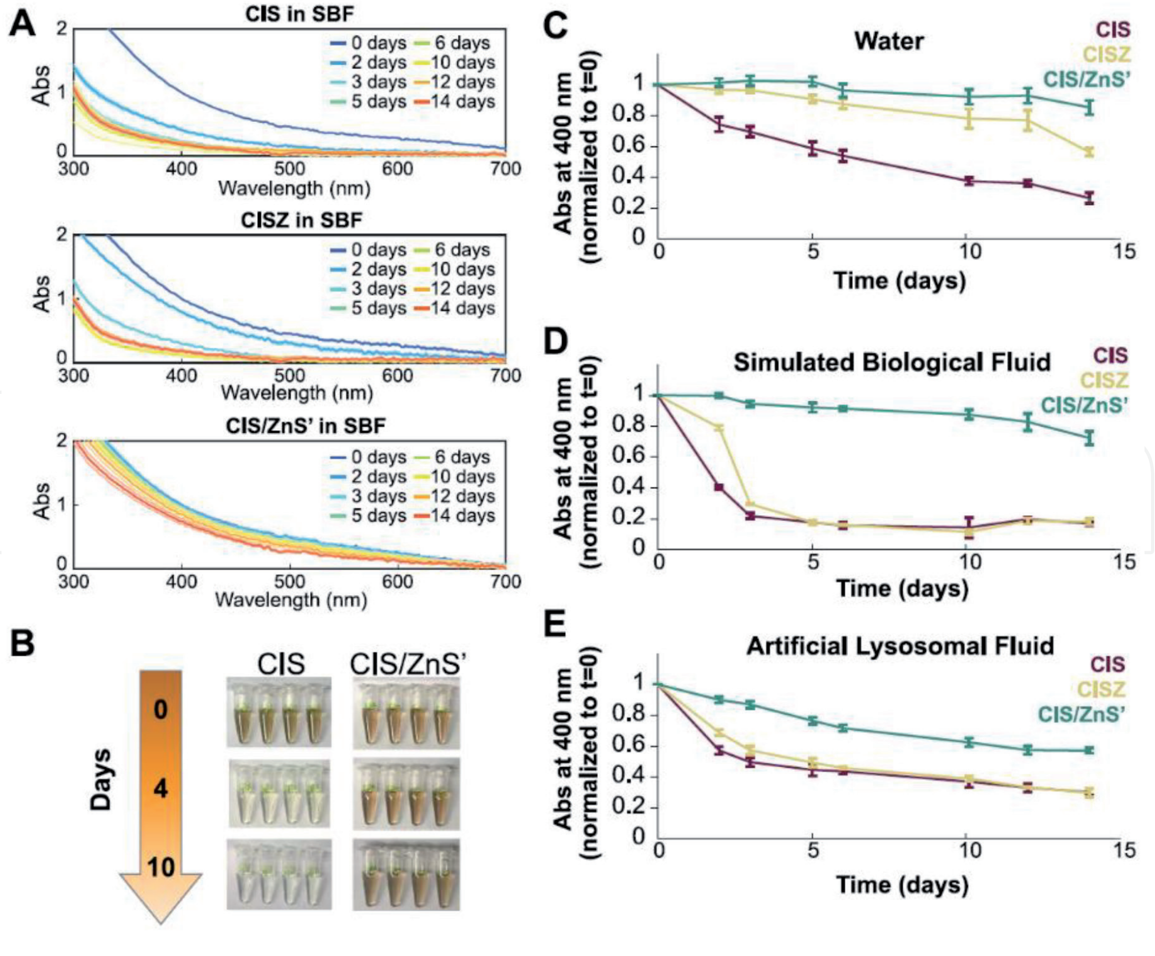


Figure 5.
(A) Comparative study on the dissolution of CIS ($CuInS_2$), CISZ (zinc-alloyed $CuInS_2$) and CIS/ZnS' ($CuInS_2$/ZnS core/shell) quantum dots by absorption spectroscopy measurements. (B) Visual evidence of dissolution in SBF. (C-E) dissolution studies in various media. Reprinted with permission from Ref. [31]. Copyright 2020 American Chemical Society.

This should however not deter attempts in developing similar technologies such as $AgInS_2$ quantum dots which have recently shown ultralong PL decay time attributed to the coordinating ligands which bear electron rich groups capable of passivating surface trap centers and achieving strong emissions [33].

Apart from the chalcopyrite series, other indium sulfide-incorporated multinary nanomaterials have made significant technological progress. Recently, $CdIn_2S_4$ and $ZnIn_2S_4$ nanostructures have been prepared by solvent-free green reaction protocols at moderately low temperatures [34]; the nanostructures displayed good photocatalytic activities in hydrogen evolution reactions through the splitting of hydrogen sulfide and water under visible light conditions. The activities were however lower than those of other $CdIn_2S_4$ and $ZnIn_2S_4$ nanostructures reported elsewhere [35, 36], attributed to synthetic the method limitations particularly on poor control of physical features such as particle size and shape. The quaternary system which has been recently reported is the $Zn_{2x}Cu_{1-x}In_{1-x}S_2$ [37] and $Zn_{2x}Ag_{1-x}In_{1-x}S_2$ [38] nanomaterials which display unique optical properties with varying composition and an active component potential in the light harvesting inorganic–organic hybrid nanomaterial, respectively.

3. Indium selenide series

The indium selenide series exhibits similar characteristics to the indium sulfide series, such as multiple crystallographic phases and polymorphic materials which have unique properties already found use in various applications. The chemistry, synthesis and application of the indium selenide series is already disseminated in comprehensive literature reviews available elsewhere [39, 40].

Among recent developments in the synthesis of indium selenide, is a novel reaction protocol which has been designed to growing ultrathin films of stoichiometric indium selenide (InSe) by precipitation of the thermally evaporated InSe crystal on a chemically neutral oil [41]. In another study, the thermal evaporation technique was used albeit to synthesize InSe nanowires on silicon and quartz silica substrates through an edge-epitaxial growth mechanism [42], this work presents a solution on challenges associated with growing nanowires on these substrates as a result of the lattice mismatch. This provides easy access to investigate the efficiency of nanowires on fabricated electronic and optoelectronic devices. The epitaxial growth approach has also been employed in the fabrication of few-layer β-In_2Se_3 thin films on c-plane sapphire and silicon substrates through the metalorganic chemical vapor deposition method [43], the synthetic protocols have potential scale up capabilities while retaining good quality uniform film. Obtaining defect-free nanomaterials from bulk counterparts through exfoliation mediated processes still remains an economically ideal route, however, the most common issue is low yields. Recent efforts towards this direction is the development of ultrafast electrochemical-assisted delamination of bulk In_2Se_3 through intercalation by tetrahexylammonium ions in a typical setup provided in **Figure 6(d)** [44], the authors demonstrated that the results are reproducible and the obtained yields of up to 83% flakes which have large micron-scale lateral sizes suitable for fabricating various nanodevices.

Applications of binary indium selenide nanomaterials are provided in **Table 1**. As observed, the choice of synthetic method is crucial since it produces nanomaterials suitable for specific applications. Recent interests are towards synthesizing good quality nanosheets and thin films, attributed to the development of novel next-generation devices for use in various fields. It is apparent that the sought-after features of binary indium selenide nanomaterials are optical properties-related, hence exploitation predominantly observed in optoelectronic applications.

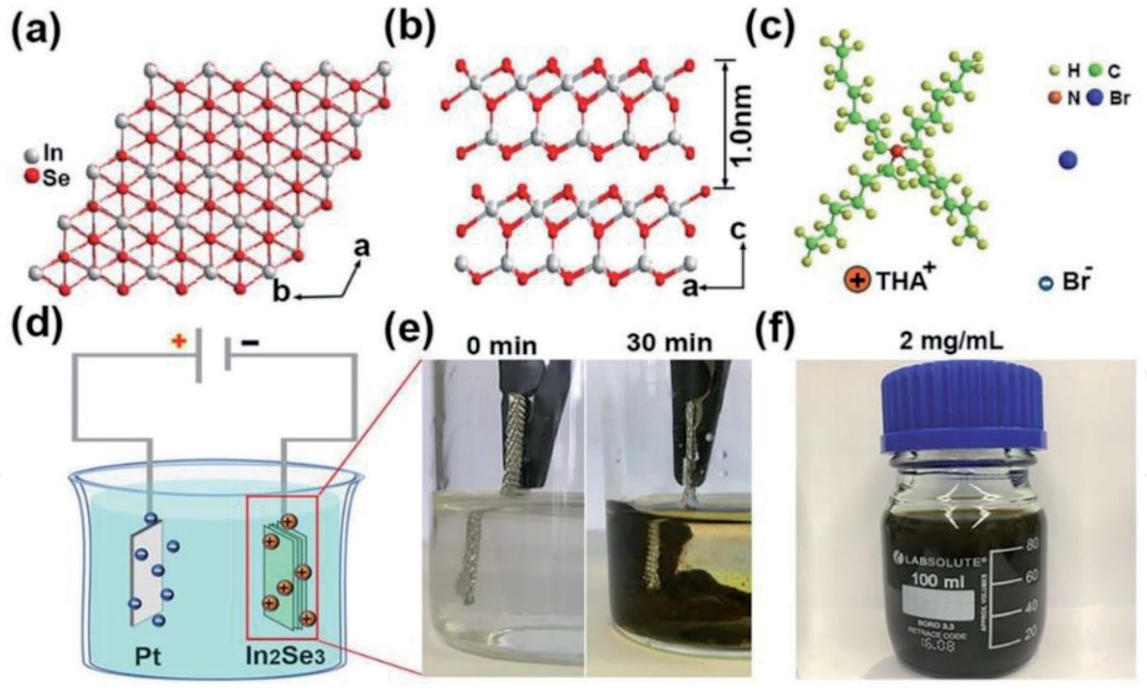


Figure 6.
(a) Top and (b) side view of the layered crystal structure In_2Se_3; (c) the chemical structure of the tetrahexylammonium-based intercalant; (d) experimental setup; (e) images showing the beginning and completion of the experiment; (f) dispersion of delaminated In_2Se_3 nanosheets in dimethylformamide. Reprinted with permission from Ref. [44]. Copyright 2020 WILEY-VCH.

Material	Synthetic method	Application	Material type	Reference
InSe	Mechanical exfoliation (Scotch tape)	Saturable absorber for mid-infrared pulsed laser	Thin films	[45]
Sn-doped InSe		Photoluminescent sensor for sulfur vapors	Nanosheets	[46]
InSe		Field-effect transistor		[47–49]
		Field-effect transistor for pressure sensors		[50]
	Edge-epitaxial growth	Photodetector	Nanowires	[42]
	Liquid phase exfoliation	All-optical diodes and switching	Nanosheets	[51]
α-In_2Se_3		Potential use in Ultrafast photonic devices		[52]
γ-In_2Se_3	Electrosynthesis	Electrocatalyst for carbon dioxide electroreduction to Syngas	Nanoparticles	[53]
α-In_2Se_3	Mechanical exfoliation (Scotch tape)	Photodetector	Nanosheets	[54]
In_2Se_3	Electrochemical-based exfoliation			[44]
In_3S_4	Electron-beam deposition	Potential applications in electrical and thermoelectrical devices	Thin films	[55]

Table 1.
Recent advances in the application of binary indium selenide nanomaterials.

3.1 Indium selenide-based ternary and quaternary nanomaterials

Multinary indium selenide-based nanomaterials, with the exception of the binary system, are rarely subjects of research interest compared to the sulfide counterparts, most probably due to synthetic challenges associated with limited economic precursors. Hence, recent technologies outlined in section 3 above rely mostly on pre-synthesized (at extreme reaction conditions) and commercial indium sulfide bulk material. Regardless of this, recent efforts on multinary indium selenide-based nanomaterials have been reported.

Silver indium sulfide nanocrystals of the $AgIn_5Se_8$ phase have been synthesized through an eco-friendly electrochemical method using L-glutathione as a stabilizing agent [56]. The photoluminescence spectra of the nanocrystals showed an increase in quantum yields with an increase in silver-to-indium ratio used during synthesis. Furthermore, the nanocrystals displayed good photothermal responses which are ideal for hyperthermia applications. Layered manganese indium sulfide nanosheets of the $MnIn_2Se_4$ phase prepared by mechanical exfoliation, have recently been demonstrated as a potential candidate for use in magnetic and optoelectronic devices due to their interesting magnetic and transport properties [57]. Computational studies using first-principle calculations have predicted properties of the layered indium selenide bromide (InSeBr) which have significantly been ignored [58]. The comprehensive Raman scattering measurements have predicted that InSeBr would be a good potential candidate for use in optoelectronic properties. Research interests on quaternary indium selenide-based nanomaterials have primarily focused on copper indium gallium selenide [$Cu(In,Ga)Se_2$] materials which are heavily invested in the fabrication of next-generation semiconductor solar cells; a recent, comprehensive review on the science, synthesis and application of $Cu(In,Ga)Se_2$ nanomaterials is available elsewhere [59].

4. Indium telluride series

Indium telluride and derived nanomaterials are rarely common, due to a limited application scope. The most common application of indium telluride nanomaterials is in thermoelectrics. There has been attempts in gas sensing applications showing unsatisfactory sensitivity, attributed to the low electrical resistance of the nanomaterial [60]. Other applications have been mentioned elsewhere with references therein [61]. In a recent report, the authors devised a method of preparing In_2Te_3 thin films composed of nanowire structures from bulk InTe using a chemical vapor deposition technique through a gold-catalyzed vapor-liquid–solid growth mechanism [62]. It was however observed that the low electrical resistivity and thermal conductivity cannot be improved by simply changing the morphology of the particles. A separate study has reported that these properties can be effectively improved by doping In_2Te_3 with aluminum and antimony [63]. The stoichiometric InTe phase is also used in thermoelectric applications; recent studies also identify that the thermoelectric performance is improved by doping with antimony [64].

4.1 Indium telluride-based ternary and quaternary nanomaterials

Ternary analogues of indium tellurides also find use in thermoelectric applications, such as copper indium telluride ($CuInTe_2$) and silver indium sulfide ($AgInTe_2$). The thermoelectric properties of the former have recently been reported to be enhanced by doping with manganese [65], while for the latter, adjusting only the silver concentration x (in $Ag_{1-x}InTe_2$) was sufficient [66]. The interesting properties of another ternary material potassium indium telluride ($KInTe_2$), for the first time, have been recently predicted and investigated through theoretical first-principle calculations [67]; preliminary studies suggest the material is a semiconductor with an indirect energy band gap.

5. Conclusions

For over a decade, indium chalcogenide nanomaterials continue to make significant contributions in the development of next-generation functional materials and devices, attributed to their unique properties which can be tuned easily using existing methods. As a result of their multiple crystallographic phases, in addition to the manipulation of the physical features such as morphology, indium chalcogenide nanomaterials remain of interest due to diversified opportunities which still need to be explored.

With the aid of computational modeling and related tools, it has become easier to identify application-specific objectives which guide the thought process when designing reaction protocols for nanomaterial fabrication. The current research-driven focus is on providing easy and efficient solutions to challenges associated with purity, quality and yield which affect the performance of the nanomaterial in desired applications. Hence, the recent literature reports provided in this book chapter have rather revisited classical methods of synthesis which are reputably known for producing high quality precursors, even though having received a lot of criticism over the years due to harsh and/or sensitive reaction protocols best executed by skilled personnel. Therefore, there is now and urgent need for the alternative routes such as the use of low-temperature decomposing single-source molecular precursors, which have been developed over the years, to be improved and incorporated in the fabrication of functional nanodevices.

In many literature reports, there continues to be an exacerbated use of 'non-toxic alternatives' and related terms whenever nanomaterials which do not contain heavy metals are presented. Novel and/or improved properties resulting from the physical changes of the material is a good indication that the nanomaterial could exhibit features and behavior different to the bulk counterpart, toxicity could be an example. Thus, an increasing trend on the interest of toxicity studies for nanomaterials is envisaged in the coming years.

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Conflict of interest

We declare no conflict of interest.

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