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Synthesis and uses of copper indium selenide ($CuInSe_2$) nanoparticles: A short review

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Abstract:
Copper indium selenide nanoparticles ($CuInSe_2$ NPs), a class of ternary chalcogenide semiconductors, have emerged as promising materials in the field of optoelectronics due to their unique physicochemical properties. Characterized by a direct and tunable bandgap, high absorption coefficient, and intrinsic p-type conductivity arising from copper vacancies, $CuInSe_2$ is especially effective in harvesting solar energy. This review presents a concise overview of the synthesis strategies employed for the preparation of $CuInSe_2$ NPs, highlighting how various synthesis parameters influence their different characteristics. The nanoparticles have found significant applications in advanced technologies such as thin-film solar cells, photodetectors, and infrared optoelectronic devices. Particular emphasis is given to their role in high-efficiency photovoltaic devices, including Cu (In, Ga) Se_2 solar cells. Despite their advantages, challenges related to large-scale production, surface stability, and passivation remain key barriers. This review aims to summarize recent synthesis methods and uses of $CuInSe_2$ NPs for future research and practical implementation.

Keywords: $CuInSe_2$, nanoparticles, semiconductor, optoelectronics, solar cells, thin films.

1. INTRODUCTION

In the era of globalization, the demand for sustainable, efficient, and decentralized energy solutions has become increasingly urgent due to the growing global population, rapid industrialization, and escalating environmental concerns. Photovoltaic (PV) or solar-based devices have emerged as one of the most promising technologies to meet these demands by harnessing the abundant and renewable energy of the sun. Unlike conventional fossil fuels, solar energy is clean, inexhaustible, and widely available across geographical regions, making it particularly advantageous for developing countries and remote areas lacking access to centralized power grids [1]. The integration of PV systems plays a pivotal role in reducing greenhouse gas emissions and mitigating climate change, which is now recognized as one of the greatest global challenges of our time. The International Energy Agency (IEA) projects that by 2050, solar energy could account for up to one-third of the world's electricity demand, significantly reducing the reliance on fossil fuels [2]. The widespread adoption of solar energy supports the goals of energy security and economic diversification. It reduces the geopolitical dependencies associated with oil and gas markets and enables nations to pursue energy independence. Technological advancements in materials science, such as the development of thin-film solar cells, quantum dots, and nanostructured semiconductors like Copper indium selenide ($CuInSe_2$/CIS) and perovskites, have further enhanced the efficiency and affordability of solar devices, making them more accessible to a global market [3]. The declining cost of solar modules falling by more than 80% over the past decade has significantly accelerated global deployment, especially in emerging economies [4]. Solar technologies are now being integrated into a variety of applications beyond large-scale power plants, including rooftops, wearable electronics, transportation, and rural electrification projects. In essence, solar-based devices are not just a technological innovation but a socio-economic necessity in a globalized world striving for equitable development, environmental preservation, and resilient energy infrastructure. Their role in supporting the United Nations Sustainable Development Goals (particularly Goal 7: Affordable and Clean Energy) underscores their importance in shaping a more inclusive and sustainable future [5].

CIS is a ternary chalcogenide semiconductor material that has garnered substantial interest over the past few decades, primarily due to its exceptional optoelectronic properties and potential for application in thin-film solar cell technologies. Belonging to the I-III-VI$_2$ group of semiconductors, CIS possesses a direct bandgap (approximately 1.04 eV in its bulk form), strong absorption in the visible and near-infrared regions, and high absorption coefficients ($>10^5$ cm^{-1}), making it a highly efficient light-harvesting material [6-8]. These characteristics are critical in achieving high conversion efficiencies in photovoltaic devices and make CuInSe$_2$ an attractive alternative to traditional silicon-based solar technologies. The physical, electrical, and chemical properties of CuInSe$_2$ are reveal in Table 1.

Table 1: Physical, Electrical, and Chemical Properties of CuInSe$_2$

Property Category	Property	Typical Value	Unit / Notes
Physical Properties	Crystal Structure	Chalcopyrite	Tetragonal
	Lattice Constants	a = 5.78, c = 11.62	Å (angstroms)
	Density	~5.77	g/cm^3
	Melting Point	~1045	°C
	Band Gap Energy	~1.04 (bulk), tunable to ~1.5	eV (direct band gap)
	Optical Absorption Coefficient	$>10^5$	cm^{-1}
	Color	Black to dark red	–
Electrical Properties	Conductivity Type	p-type	Due to Cu vacancies
	Electrical Resistivity	~10^{-1} to 10^4	Ω·cm (depends on stoichiometry & doping)
	Carrier Concentration	~10^{15} to 10^{18}	cm^{-3} (hole concentration)
	Hall Mobility	1–100	cm^2/V·s
	Dielectric Constant (static)	~13	–
Chemical Properties	Elemental Composition	Cu:In:Se = 1:1:2	Stoichiometric ratio
	Thermal Stability	Stable up to ~600 °C	In inert/controlled atmosphere
	Oxidation Sensitivity	Moderate	Surface oxidizes in air

	Solubility	Insoluble	In water and common solvents
	Toxicity	Low to moderate	Handle with care in nanoparticulate form

1.1 Historical Perspective and Development:

The origins of $CuInSe_2$ research trace back to the 1950s, when Hahn and his colleagues first reported the synthesis of chalcopyrite-type I-III-VI_2 compounds, including $CuInSe_2$ [9]. However, the material remained relatively underexplored until the 1970s, when it was rediscovered during the quest for alternative photovoltaic materials that could match or exceed the performance of crystalline silicon but be more suitable for thin-film deposition. In the 1980s, researchers began to demonstrate the feasibility of using $CuInSe_2$ as an absorber layer in thin-film solar cells. By 1981, the first $CuInSe_2$-based photovoltaic device exceeded 10% efficiency, marking a significant milestone [10]. The addition of gallium to form $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) was later found to further tune the bandgap and improve efficiency, resulting in devices with certified power conversion efficiencies exceeding 22%, among the highest for any thin-film photovoltaic material [11]. This innovation also drove interest in nanoscale $CuInSe_2$ materials, aiming to replicate and expand these benefits in nanostructured devices for a wide range of optoelectronic applications.

1.2 Structural and Electronic Properties

$CuInSe_2$ crystallizes in a tetragonal chalcopyrite structure, derived from the cubic zinc-blende lattice by ordering the cations (Cu^+ and In^{3+}) on alternating sites. The unit cell contains eight atoms arranged such that each anion (Se^{2-}) is tetrahedrally coordinated by two Cu and two In atoms [11, 12]. This ordered structure leads to its direct bandgap nature, which allows efficient electron-hole pair generation and separation upon light absorption without the need for phonon assistance. Intrinsic p-type conductivity in $CuInSe_2$ arises mainly due to copper vacancies (V_Cu), which act as acceptors. This property is particularly beneficial in photovoltaic applications, as it enhances charge carrier mobility and reduces recombination losses. The bandgap of CIS can be modified by substituting indium with gallium or selenium with sulfur to fine-tune its optical properties for specific applications [12, 13].

2. SYNTHESIS METHODS OF $CuInSe_2$ NANOPARTICLES:

The synthesis of $CuInSe_2$ NPs has evolved significantly, with various methods developed to control particle size, crystallinity, stoichiometry, and surface chemistry. These include hot-injection methods, solvothermal and hydrothermal synthesis, microwave-assisted synthesis, and single-source precursor decomposition. Each technique offers distinct advantages in terms of size control, morphology, and phase purity, which directly impact the performance of CIS in practical applications [14, 15]. Nanostructuring CIS introduces several additional advantages over bulk materials. Firstly, it offers the possibility of quantum confinement, which can modulate the bandgap and enhance light-matter interactions. Secondly, nanoparticles exhibit a large surface area-to-volume ratio, beneficial for catalytic, sensing, and light absorption processes. Thirdly, nanoparticles can be synthesized at relatively low temperatures using solution-based methods, which are scalable and compatible with flexible substrates [16, 17]. The different synthesis methods of CIS NPs are shown in Fig. 1.

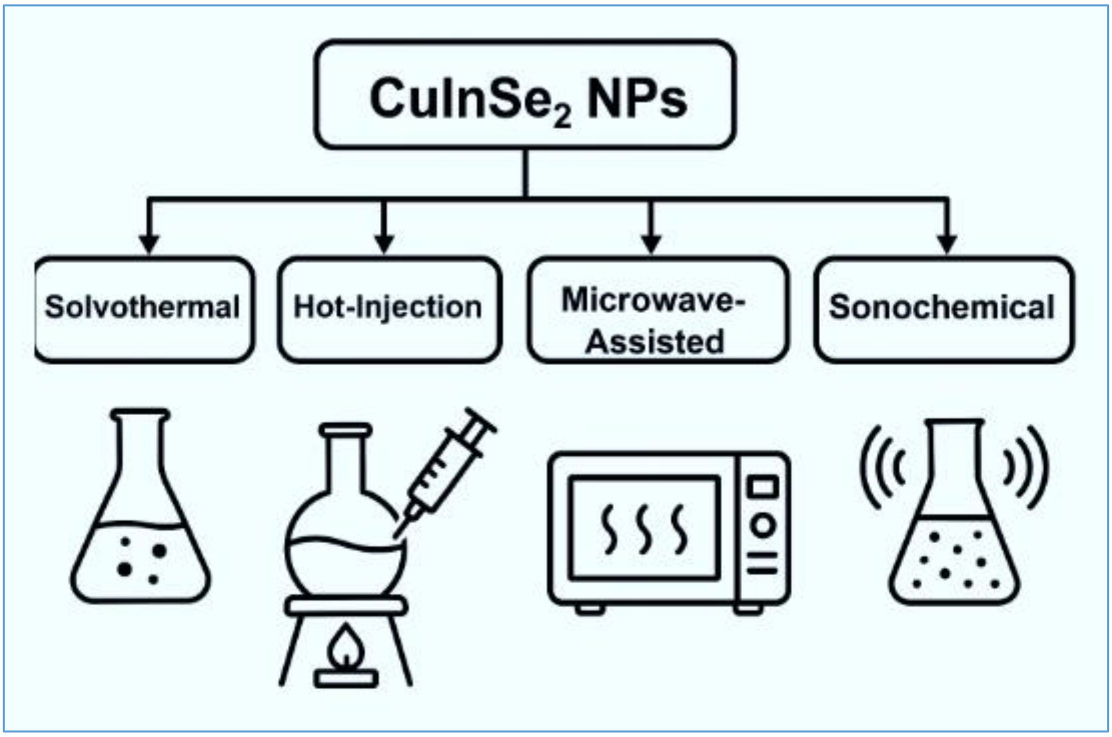

Figure. 1: Different synthesis methods of $CuInSe_2$ NPs

The synthesis of $CuInSe_2$ NPs has been extensively studied and developed using a variety of chemical and physical methods. These methods aim to control particle size, composition, crystallinity, and morphology parameters that disparagingly influence their optical and electronic properties. Below is a detailed explanation of the most prominent synthesis techniques for $CuInSe_2$ NPs.

a. Hot-Injection method

The hot-injection technique is one of the most widely used colloidal synthesis methods for producing high-quality, monodisperse $CuInSe_2$ NPs. In this method, organometallic precursors of copper, indium, and selenium (such as copper acetylacetonate, indium chloride, and trioctylphosphine selenide) are rapidly injected into a hot coordinating solvent like oleylamine or trioctylphosphine (TOP) at elevated temperatures (~180–280 °C) under inert atmosphere. This method allows precise control over nucleation and growth, resulting in uniform size and shape of the nanocrystals. It also enables the tuning of the bandgap via quantum confinement by controlling particle size [18, 19]. The requirement of high-temperature, inert gas, and expensive ligands may limit large-scale production.

b. Solvothermal and Hydrothermal methods

The solvothermal and hydrothermal methods involve the reaction of metal salts in a sealed autoclave at moderate to high temperatures (typically 150–250 °C) in either organic solvents or water, respectively. These methods are more environmentally friendly and scalable compared to hot-injection, and can produce crystalline $CuInSe_2$ NPs with various morphologies such as nanospheres, rods, and flower-like structures [20]. For instance, Xie et al. synthesized $CuInSe_2$ nanocrystals via a hydrothermal route using copper sulfate, indium nitrate, and selenium powder in ethylenediamine, achieving uniform morphology and high crystallinity [21]. The solvothermal method allows better control over phase purity and stoichiometry but may require longer reaction times.

c. Microwave-Assisted method

Microwave-assisted synthesis is an emerging method offering rapid and uniform heating, reduced reaction time, and enhanced reaction kinetics. In this approach, metal precursors are exposed to microwave irradiation in the presence of surfactants or stabilizers to yield $CuInSe_2$ NPs within minutes. This method reduces energy consumption and offers potential for scale-up. Duan et al. reported the successful synthesis of $CuInSe_2$ NPs within 10 minutes using microwave irradiation, achieving uniform crystallinity and good optical properties [22]. Despite its advantages, controlling the reaction mechanism during microwave exposure requires careful optimization.

d. Single source Precursor Decomposition method

Single-source precursor (SSP) methods involve using a pre-synthesized organometallic complex that contains all necessary elements (Cu, In, and Se) in a single molecular structure. Upon thermal decomposition, the precursor breaks down to form $CuInSe_2$ NPs. This method ensures atomic-level homogeneity and stoichiometric control. Kwon and Jeong demonstrated this technique using a mixed-metal selenolate complex, resulting in phase-pure $CuInSe_2$ NPs [23]. The SSP route is especially beneficial in avoiding unwanted secondary phases but may involve complex precursor synthesis and purification steps.

e. Co-Precipitation method

The co-precipitation method is a simple and low-cost approach that involves mixing aqueous solutions of copper and indium salts with a selenium source (often NaHSe or selenourea) under controlled pH and temperature. A precipitate forms, which upon annealing or sintering transforms into $CuInSe_2$ NPs. Although this method is less sophisticated in controlling morphology or crystallinity compared to colloidal techniques, it is attractive for large-scale and industrial synthesis [24]. It is also compatible with eco-friendly solvents and ambient conditions.

f. Mechanochemical method

In mechanochemical synthesis, $CuInSe_2$ NPs are synthesized by mechanically milling the elemental powders or binary compounds (such as Cu_2Se and In_2Se_3) using a high-energy ball mill. This solid-state method avoids solvents and enables direct synthesis at room temperature. However, post-synthesis annealing is often required to improve crystallinity. This method is scalable and solvent-free but offers limited control over particle size and morphology [25].

3. USES OF $CuInSe_2$:

Although solar energy conversion remains the most prominent application of $CuInSe_2$, recent research has explored its utility in a broader range of optoelectronic devices. For instance, $CuInSe_2$ NPs have shown potential in photodetectors, light-emitting diodes (LEDs), infrared detectors, and photocatalytic systems for hydrogen generation and pollutant degradation [26-28]. Their ability to absorb a broad spectrum of light, coupled with tunable electrical properties, makes them suitable for next-generation electronic and energy storage devices. The compatibility of $CuInSe_2$ with flexible and wearable electronics devices to its growing relevance in the development of smart, portable, and sustainable technologies. Recent advances in colloidal $CuInSe_2$ quantum dots and hybrid nanocomposites have opened new possibilities in biomedical imaging, sensing, and energy harvesting [29-31]. The major uses of $CuInSe_2$ NPs are illustrate in Fig. 2.

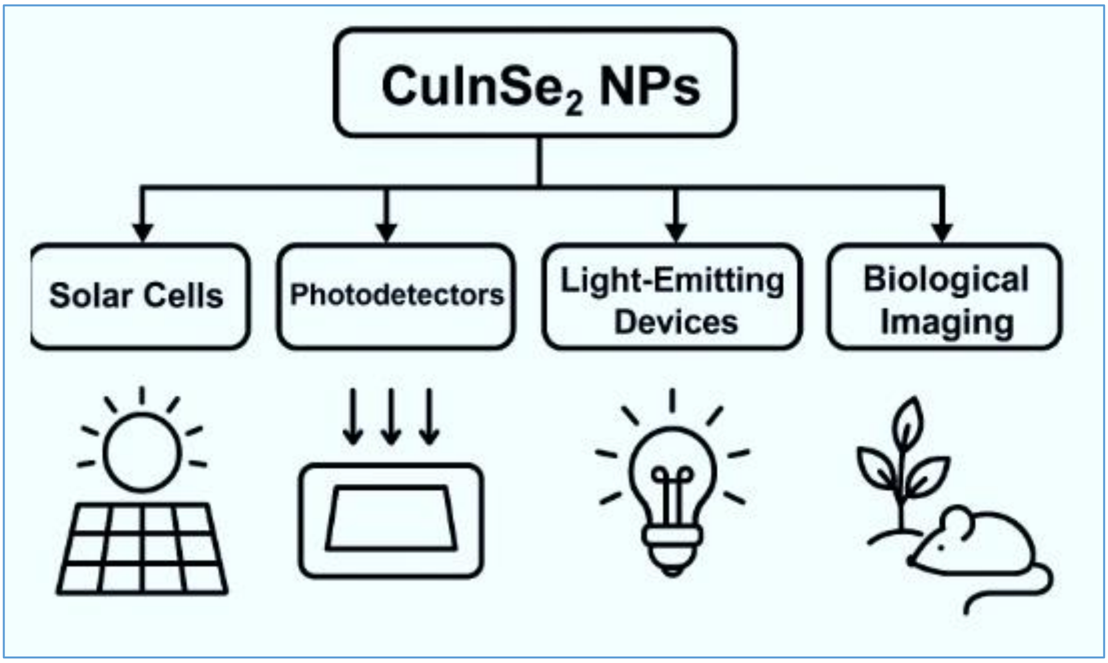

Figure. 2: Different uses of $CuInSe_2$ NPs

4. CHALLENGES AND RESEARCH DIRECTIONS

Despite the promising prospects, several challenges remain in the large-scale deployment of $CuInSe_2$ NPs. These include achieving high phase purity, uniform stoichiometry, and long-term chemical stability. The presence of secondary phases such as Cu_2Se or In_2Se_3 can significantly affect the electronic properties and device performance. Surface oxidation and recombination centers also reduce efficiency in photovoltaic and sensing devices. The environmentally benign and cost-effective synthesis routes must be developed to meet the demands of commercial scalability. Surface passivation strategies, core-shell structuring, and doping with other elements are currently being explored to overcome these challenges. Furthermore, in-depth studies on the correlation between synthesis conditions and the resultant physicochemical properties are essential to optimize their performance for specific applications.

5. LITERATURE SURVEY

Kim et al. (2013) developed monodisperse CIS nanocrystals using a phosphine-free hot-injection synthesis with elemental Se and metal acetates, showing that ligand choice played a critical role in particle stabilization and nucleation rate control [34]. Alternative hydrothermal and solvothermal approaches have gained popularity for their simplicity and scalability. He et al. (2012) reported a hydrothermal synthesis method using selenium powder with ethylenediamine as a coordinating solvent at moderate temperatures, yielding CIS nanoparticles with high crystallinity and minimal secondary phases [35]. Similarly, Fang et al. (2015) utilized a mixed-solvent solvothermal technique to control nanoparticle morphology by adjusting the precursor concentration and reaction time. Their work highlighted the effectiveness of using long-chain amines as stabilizing agents to achieve uniform size distribution [36]. Choi et al. (2018), microwave irradiation enabled the formation of CIS nanoparticles within 10 minutes, significantly reducing reaction time while maintaining desirable optical and structural properties [37]. The electrodeposition techniques, although more often associated with thin-film fabrication, have been adapted for the synthesis of CIS nanoparticles, offering better control over stoichiometry and electrochemical properties through voltage modulation and bath composition, as explored by Velumani et al. (2016) [38]. Bhattacharya et al. (2017) demonstrated CBD-based synthesis of CIS quantum dots with tunable sizes by varying bath temperature and ligand concentration, indicating the potential for low-cost device fabrication [39]. Solid-state mechanochemical synthesis, using high-energy ball milling, was investigated by Das and Mahapatra (2019), who achieved crystalline CIS nanoparticles through the dry milling of elemental powders, followed by controlled annealing [40]. Zhang et al. (2020) used XRD to confirm the formation of the chalcopyrite phase, noting that peak broadening provided insights into quantum confinement effects in particles below 10 nm [41]. Raman spectroscopy, with its sensitivity to crystallographic order, complements XRD by detecting characteristic A_1 and B_2 vibrational modes around 174 cm^{-1} and 210 cm^{-1} respectively, as described by Kong et al. (2015) [42]. Huang et al. (2017) revealed spherical and rod-shaped CIS nanoparticles with diameters ranging from 5 to 20 nm, depending on the synthesis method, while selected area electron diffraction (SAED) patterns confirmed their polycrystalline nature [43]. Li et al. (2016) conducted XPS studies and confirmed Cu^+, In^{3+}, and Se^{2-} species, indicating minimal oxidation and near-stoichiometric purity [44]. Liu et al. (2019) reported bandgap narrowing in Cu-rich CIS nanoparticles, attributing it to defect-induced states near the conduction band [45]. Yao et al. (2016) developed inkjet-printable CIS inks with optimized viscosity and particle dispersion, achieving film uniformity suitable for device integration [46]. Zhao et al. (2018) integrated CIS quantum dots onto TiO_2 nanorods, significantly improving visible-light-driven hydrogen generation through effective charge separation at the heterojunction interface [47]. Similarly, Wang et al. (2021) fabricated CIS-based photodetectors capable of detecting near-infrared light with high responsivity and low noise, attributing the performance to efficient carrier mobility and low recombination rates [48]. Sun et al. (2020) demonstrated that nanostructuring enhanced phonon scattering, improving thermoelectric figure of merit (ZT) values in CIS-based composites [49].

6. FUTURE PERSPECTIVES OF $CuInSe_2$ NANOPARTICLES

The future perspectives of $CuInSe_2$ NPs are promising and multifaceted, driven by the material's outstanding optoelectronic properties, compositional flexibility, and compatibility with emerging nanotechnologies. As the global energy landscape shifts toward renewable sources, it is expected to play a central role in next-generation thin-film photovoltaic technologies, particularly in tandem or flexible solar cells. Unlike conventional silicon solar cells, CIS-based devices can be fabricated on lightweight and flexible substrates, paving the way for portable and wearable solar-powered electronics, building-integrated photovoltaics (BIPV), and aerospace applications. The bandgap of CIS can be tailored by incorporating gallium (in $Cu(In,Ga)Se_2$) or sulfur ($CuIn(S,Se)_2$), allowing spectral tuning and potential integration into multijunction solar cells with enhanced efficiency. Beyond photovoltaics, $CuInSe_2$ NPs are increasingly explored in photodetectors, infrared imaging systems, and thermoelectric devices, where their strong absorption in the near-infrared (NIR) region, low thermal conductivity, and direct bandgap are highly advantageous. Additionally, advances in colloidal quantum dot synthesis of CIS NPs have enabled solution-processable inks, allowing cost-effective fabrication of large-area optoelectronic devices using printing or spray-coating techniques. In the field of photoelectrochemical (PEC) water splitting and photocatalysis, CIS nanoparticles are under investigation as efficient light absorbers for solar-driven hydrogen production and pollutant degradation, with promising early results owing to their high surface-to-volume ratio and suitable conduction band alignment with water redox potentials. From a materials science standpoint, surface passivation, doping, and core-shell engineering of $CuInSe_2$ NPs represent key research directions to overcome current limitations such as surface traps, recombination centers, and oxidation sensitivity. Developing non-toxic, earth-abundant precursors and green synthesis routes will also be essential for the sustainable and large-scale deployment of CIS-based nanodevices. The integration of $CuInSe_2$ with other 2D materials (like graphene or MoS_2) and perovskites in hybrid heterostructures opens new frontiers for advanced photonic and electronic applications, including sensors, memory devices, and neuromorphic computing. With the continued progress in scalable synthesis, surface engineering, and device integration, $CuInSe_2$ NPs hold significant potential to become a cornerstone of future optoelectronic, energy conversion, and environmental remediation technologies. Interdisciplinary collaboration among material scientists, chemists, physicists, and engineers will be critical in transforming laboratory-scale innovations into commercially viable, sustainable solutions.

CONCLUSIONS:

Copper indium selenide nanoparticles have emerged as a highly promising class of materials in the field of optoelectronics and energy conversion, particularly for thin-film solar cell applications. Their intrinsic properties, such as a tunable direct bandgap (~1.04–1.5 eV), high optical absorption coefficient, and natural p-type conductivity, make them exceptionally efficient in absorbing sunlight and converting it into electrical energy. The ability to engineer their band structure through alloying or quantum size effects opens up further possibilities for optimizing device performance across a broad spectrum of applications. The $CuInSe_2$ NPs represent a fascinating and versatile class of materials that lie at the intersection of materials chemistry, nanotechnology, and renewable energy. Their tunable bandgap, high absorption capacity, and favorable charge transport characteristics make them suitable for a wide spectrum of high-performance devices. With continued advances in synthesis, characterization, and integration technologies. It is poised to play a key role in future generations of optoelectronic and energy-conversion systems. Numerous synthesis techniques including hot-injection, solvothermal, microwave-assisted, single-source precursor decomposition, co-precipitation, and mechanochemical methods have been developed to produce high-quality $CuInSe_2$ NPs with controlled size, morphology, and phase purity. Each method offers unique advantages and is suited for specific applications, highlighting the material's adaptability to various fabrication strategies. However, challenges such as controlling stoichiometry, minimizing surface defects, preventing oxidation, and achieving large-scale, environmentally friendly production remain areas of active research. The future developments in $CuInSe_2$ NPs research is rely heavily on advances in nanostructuring, surface passivation, and hybrid integration with other functional materials. The $CuInSe_2$ NPs represent a key material platform with the potential to drive innovation in sustainable energy, electronics, and environmental applications, contributing significantly to the global efforts toward clean and efficient technologies.

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Availability of data and materials

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Declaration of competing interest

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