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Review

Recent Advances in the Study of Bulk Crystals: Copper Chalcogenides

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Abstract

Solid crystalline materials play a crucial role in a range of technological applications, from photovoltaics to thermoelectrics. Increasing the performance of these materials is important in terms of application efficiency. This review provides an overview of recent developments in the field, with a focus on photovoltaic materials, defect chemistry, and thermoelectric properties. Copper sulfide and selenides have advantages such as environmental friendliness, low cost and improved thermoelectric efficiency that set them apart from the competition. Special emphasis is placed on copper sulfides (Cu_2S) and selenides (Cu_2Se) due to their unique structural and electronic properties, making them promising candidates for sustainable energy applications. The manifestation of these copper chalcogens occurs within a variety of crystal structures, contingent on the liquid-like motion of the Cu^+ ion within the crystal. In this review, the defective, deficiency and regular structures identified in recent years were also discussed.

1. Introduction

Today, the use of fossil fuels to meet energy demands leads to severe environmental issues such as global warming, air pollution, and ecosystem degradation. Despite this, 81% of global energy consumption still relies on fossil fuels [1]. With the increasing world population and improving living standards, energy demand continues to rise rapidly. This trend exacerbates carbon emissions and intensifies environmental challenges worldwide. It is an undeniable fact that fossil fuels are not a sustainable energy source [2]. In this context, renewable energy sources are essential for meeting future energy needs and minimizing environmental impacts. Thermal energy is the most prominent kind of renewable energy resources due to abundance and not limited by geographical or temporal constraints [3]. Thermoelectric (TE) energy conversion technology has emerged as a promising alternative due to its ability to directly convert heat into electricity. TE conversion technology offers diverse applications, including power generation from waste heat, thermal management and cooling for electronics, integration with renewable energy systems, and even powering wearable devices through body heat [4]. It can also enhance automotive fuel efficiency by recovering waste heat from exhausts and is used in space exploration for reliable power generation [5]. Additionally, TE technology proves valuable in military and remote areas where conventional power sources are scarce [6]. With its ability to convert heat into electricity and provide sustainable energy solutions, TE technology holds significant potential across various industries.

TE energy conversion technology relies on materials that can efficiently convert heat into electricity through the Seebeck effect [7]. Common materials used in TE applications include semiconductors such as bismuth telluride (Bi_2Te_3), lead telluride (PbTe), and silicon-germanium (SiGe) alloys [8]. These materials are essential due to their ability to exhibit high thermoelectric efficiency, characterized by a high figure of merit (ZT), which determines the effectiveness of heat-to-electricity conversion. Bismuth telluride is widely used for applications at low to moderate temperatures, such as cooling devices and power generation from waste heat [9]. Lead telluride is more effective at higher temperatures and is used in industrial heat recovery and automotive systems [10]. Silicon-germanium alloys are often employed in high-temperature applications, including space exploration and energy recovery in engines [11]. The importance of these materials lies in their ability to enable sustainable energy solutions, improve energy efficiency, and reduce carbon emissions. However, current TE materials often suffer from limitations such as low efficiency and high cost, which hinder their widespread adoption [12]. Therefore, recent studies have led to the discovery of numerous new high-performance TE materials and significant improvements in the zT values of traditional TE materials. Copper sulfide (Cu_2S) and copper selenide (Cu_2Se)

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are interesting materials for energy conversion systems and technologies requiring high efficiency due to their superionic conductivity at high temperatures, high *zT* value, and low lattice thermal conductivity [13-15].

Recent advances in materials science and energy storage technologies offer promising solutions. Advances in materials science, such as improving electron and phonon transport properties, and the discovery of new materials with increased efficiency and sustainability, such as next-generation semiconductors and advanced thermoelectric materials, have shown great potential to meet growing global energy demands. These innovations can make TE technology more applicable for large-scale applications, contributing to cleaner energy production and thermal management solutions in various industries [16]. With their ability to utilize and convert renewable energy sources, these materials not only provide significant environmental benefits, but also offer new opportunities for energy security. This review aims to provide a comprehensive analysis of Cu_2S and Cu_2Se solid crystalline materials, focusing on their structural, defect, and functional properties, and discussing the future directions for their development and implementation in real-world applications.

2. Structural and Defect Chemistry

Structural and defect chemistry in crystalline solid materials plays a crucial role in determining their physical, chemical, and electronic properties. The structural framework of a crystal is defined by its unit cell, which consists of a repeating arrangement of atoms, ions, or molecules in a specific geometric pattern [17]. Crystal structures are classified according to their atomic lattice or structure [18]. However, real crystals are never perfectly ordered and contain defects that significantly influence their behavior [19]. In pure compound crystals, native defects are atoms missing from lattice sites where the crystal structure predicts atoms should be (vacancies), atoms present in sites where atoms should not be (interstitials), and atoms occupying sites normally occupied by other atoms (misplaced atoms) [20]. These defects can be classified as point defects, such as vacancies, interstitials, and substitutional atoms, which affect electrical conductivity and diffusion; line defects, like dislocations, which impact mechanical strength and plasticity; and planar defects, such as grain boundaries and stacking faults, which influence material stability and hardness [21]. Additionally, volume defects, including voids and precipitates, can alter thermal and optical properties. In this context, the structural and defect chemistry of Cu_2S and Cu_2Se semiconductor materials is of paramount importance to their electrical, thermal, and optical properties, rendering them highly relevant for energy and electronic applications [22]. Cu_2S exhibits polymorphism, transitioning between low temperature monoclinic, intermediate hexagonal and high temperature cubic phases [23, 24]. The cubic phase exhibits superionic conductivity due to mobile Cu^+ ions [25].The material is inherently nonstoichiometric, with copper vacancies being the prevailing defects, resulting in intrinsic p-type conductivity. These vacancies enable hole transport, thereby rendering Cu_2S an efficient semiconductor for photovoltaics and thermoelectrics. Furthermore, interstitial Cu atoms and anion vacancies affect charge carrier concentration and ionic conductivity [26]. The defect chemistry of Cu_2S is therefore crucial in optimising its performance in solar cells, batteries, and catalysis, where controlled defect engineering can enhance charge transport and stability [27]. Cu_2Se exhibits temperature-dependent polymorphism, transitioning from a low-temperature monoclinic or orthorhombic phase to a high-temperature cubic phase (Fm-3m) above ~400°C, where it becomes a superionic conductor due to the high mobility of Cu+ ions within a rigid Se sublattice [28]. The material exhibits inherent non-stoichiometry, with copper vacancies serving as the primary intrinsic defects. These defects induce p-type conductivity and facilitate efficient hole transport, a property that is further enhanced by the presence of Cu interstitials and Se vacancies [29]. These defects influence the charge carrier concentration and ionic diffusion, thereby significantly impacting the material's thermoelectric performance. The presence of dynamic disorder in the Cu sublattice also contributes to the ultra-low thermal conductivity, making Cu_2Se a promising material for energy conversion applications such as solar cells and thermoelectric devices [30, 31].

3. Thermoelectric Properties

Thermoelectric (TE) technology enables the direct conversion of heat into electrical energy through thermoelectric effects, while also allowing electricity to be used for cooling or heating applications [32]. Thermoelectric devices used for power generation are called "thermoelectric generators," whereas those used for heating or cooling are called "thermoelectric coolers" [33]. These devices accomplish these tasks only through the movement of electrons and vacancies in the solid state, which are material properties of the semiconductor thermoelectric materials of which they are composed. Due to their advantages such as silent operation, compact and lightweight design, maintenance-free use, and the absence of moving parts or working fluids, they are increasingly utilized in space technology, military applications, medical fields, industrial processes, and scientific research [34, 35]. However, current thermoelectric materials have lower efficiency and higher production costs compared to other systems with similar purposes [34-37]. The performance of these materials is measured by a dimensionless parameter known as the thermoelectric figure of merit (*zT*).

$$zT = \frac{S^2}{pk}T \tag{1}$$

Here, S, ρ, k and T are defined as the Seebeck coefficient (V/K), electrical resistivity (Ω.m), thermal conductivity (W/m.K) and average mean temperature (K), respectively. Improving the performance of a thermoelectric (TE) material has been associated with increasing both the Seebeck coefficient (S) and electrical conductivity (σ) while decreasing the thermal conductivity (κ) [38]. Current thermoelectric materials struggle to simultaneously achieve high S, high σ, and low κ due to the strong interdependence of these parameters [39]. Recent advancements in materials science, nanostructuring, and interface engineering indicate that reducing the thermal conductivity (κ) is essential to improve the performance of these materials. Figure 1 shows the thermoelectric value (*zT*) performance of the main materials used in solid-state thermoelectric (TE) technology [32].

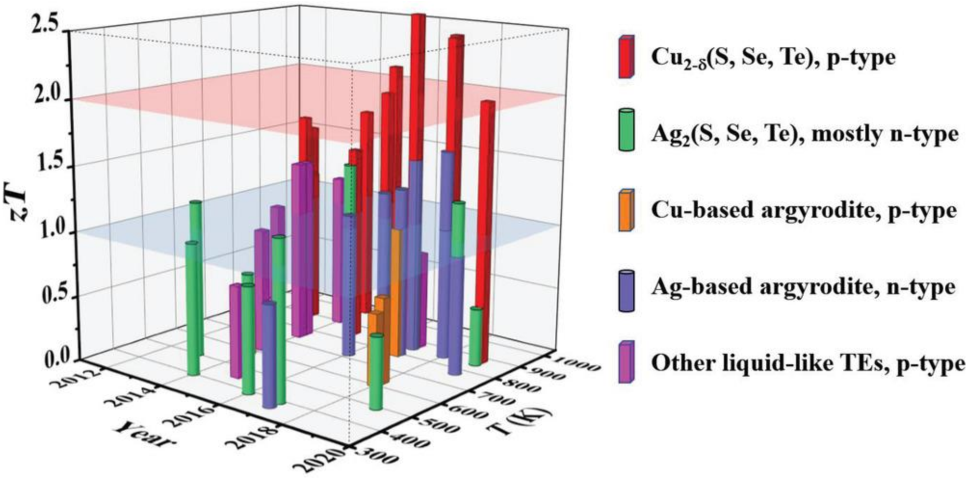

Figure 1. Comparison of (figure of merit) zT values of thermoelectric materials [32].

Cu_2S (Copper Sulfide) and Cu_2Se (Copper Selenide) are materials studied for thermoelectric applications due to their ability to convert heat into electricity and vice versa. Cu_2S is a superionic semiconductor with very low thermal conductivity, resulting in high values of the thermoelectric figure of merit (ZT) [40, 41]. Moreover, high values of the thermoelectric figure of merit (ZT) are important in tailoring the electronic and thermal properties of the material [42]. For example, Cu_2S has a *zT* of 1.7 at 1000 K [43]. Similarly, the *zT* value for Cu_2Se was found to be 1.9 at 1000 K [44]. Alloying Cu_2S and Cu_2Se can increase the electrical conductivity but may form a mosaic nanostructure that suppresses the enhancement. Studies indicate that doping Cu_2S with Sn or O enhances its thermoelectric efficiency, while graphene incorporation in Cu_2Se significantly boosts its figure of merit (*zT*) to values as high as 2.44 at 870 K [45]. Cu_2Se (copper selenide) is a promising thermoelectric material with its unique combination of high electrical conductivity and low thermal conductivity, achieving *zT* values in the range of 1.5–2.5 at ~1000 K [46, 47]. Cu_2Se exhibits a Seebeck coefficient typically in the range of 100–300 μV/K depending on temperature and doping [47]. As a p-type semiconductor, its electrical transport is governed primarily by hole carriers. The Seebeck coefficient tends to increase with temperature, driven by enhanced carrier excitation and thermally activated transport mechanisms. Cu_2Se has a high electrical conductivity (~10^4–10^5 S/m), attributed to its intrinsically high carrier concentration (10^{18}–10^{20} cm^{-3}). The material undergoes a phase transition near 400–450 K, where its superionic state enhances electrical transport. Cu_2Se has an extremely low lattice thermal conductivity (~0.3–0.5 W/m·K at high temperatures) due to phonon scattering from Cu ion diffusion in its superionic phase [48]. Studies on doping Cu_2Se with elements such as Ag, Te or Br to optimize the carrier concentration to improve the thermoelectric performance are also attracting attention [49]. In summary, Cu_2S (Copper Sulfide) and Cu_2Se (Copper Selenide) are a highly promising thermoelectric materials due to their unique superionic phase transition, high electrical conductivity, and ultra-low lattice thermal conductivity. Cu_2S and Cu_2Se, which have the ability to reach *zT* values exceeding 1.7 at high temperatures, have strong potential against state-of-the-art thermoelectric materials such as Bi_2Te_3 and PbTe.

4. High-Pressure Behavior

The high-pressure behavior of thermoelectric materials is crucial for understanding and enhancing their structural, electronic, and transport properties. Pressure serves as a powerful tool to tune band structures, optimize carrier transport, and enhance thermoelectric performance by modifying key parameters such as electrical conductivity, Seebeck coefficient, and thermal conductivity. Cu_2S undergoes significant structural changes when subjected to high pressures [50]. Research suggests that it undergoes two major phase transitions at approximately 3.2 GPa and 7.4 GPa [51]. Initially, Cu_2S exists in a $P2_1/c$ phase, which transforms into two distinct monoclinic structures as the pressure increases. The bulk modulus of Cu_2S has been reported to range from 72 to 113 GPa, reflecting its varying compressibility under different conditions [52]. Similarly, Cu_2Se exhibits a series of phase transitions under pressure. The low-pressure phase (C2/c) transitions to a second phase at around 3.2 GPa, followed by a semimetallic phase, and ultimately a bulk metallic phase ($Pca2_1$) at approximately 7.4 GPa [53]. These transitions are associated with changes in the material's electronic states, suggesting a close link between its structural modifications and electronic properties. Both Cu_2S and Cu_2Se demonstrate complex high-pressure behaviors, including multiple phase transitions and significant changes in their elastic properties. Notably, their high-pressure phases may adopt similar monoclinic structures, indicating potential commonalities in their crystal chemistry. Understanding these transitions is crucial for thermoelectric applications, where structural stability under varying pressure conditions influences performance [54]. High-pressure techniques are effective for synthesizing thermoelectric materials and tuning their transport properties. Experimental methods for studying the high-pressure behavior of Cu_2S and Cu_2Se often involve a combination of high-pressure techniques and analytical methods such as X-ray diffraction (XRD). Synchrotron-based single-crystal XRD is frequently employed to analyze phase transformations and elastic properties at high pressures. Diamond Anvil Cells (DACs) are used to compress the materials, and in situ high-pressure single-crystal XRD experiments are conducted using a monochromatic X-ray beam [55]. This allows researchers to study phase transformations and elastic properties by analyzing diffraction patterns to determine crystal structures and lattice parameters under pressure [55, 56].

To summarize, the high-pressure phases of Cu_2S and Cu_2Se can exhibit improved thermoelectric properties due to structural modifications that affect electronic transport and thermal conductivity. For instance, the phase transitions in Cu_2Se lead to a semimetallic phase that can enhance thermoelectric performance by optimizing the Seebeck coefficient and electrical conductivity while minimizing thermal conductivity [54]. These transitions, occurring in the gigapascal range, are accompanied by metallization as the band gap closes, leading to enhanced electrical conductivity. Additionally, their superionic behavior, characterized by high Cu-ion mobility at lower pressures, diminishes as compression stabilizes the structure and suppresses ionic transport. Overall, Cu_2S and Cu_2Se transform from semiconducting, superionic conductors to metallic phases with potential superconducting properties under high pressure [55].

5. Photovoltaic properties

There are three main methods of generating electricity from solar energy: Photovoltaic (PV), Concentrated Solar Power (CSP), and Concentrated Photovoltaic (CPV) [57]. Photovoltaic (PV) electricity generation from solar energy involves the direct conversion of sunlight into electricity using semiconductor materials, typically silicon-based solar cells. When sunlight strikes these cells, it excites electrons, creating an electric current. This method is widely used in residential, commercial, and utility-scale solar power systems due to its efficiency, scalability, and ability to generate clean, renewable energy [58, 59]. Concentrated Solar Power (CSP) is a technology that generates electricity by using mirrors or lenses to focus sunlight onto a small area, typically a receiver. This concentrated solar energy heats a fluid, such as molten salt or oil, which then produces steam to drive a turbine connected to a generator [60]. Concentrated Photovoltaic (CPV) is a solar power technology that uses lenses or mirrors to focus sunlight onto high-efficiency photovoltaic (PV) cells. Unlike standard PV panels, which use flat solar cells to absorb sunlight directly, CPV systems concentrate sunlight to intensify its power and improve energy conversion efficiency [61]. Figure 2 schematically illustrates the photovoltaic electricity generation process [62].

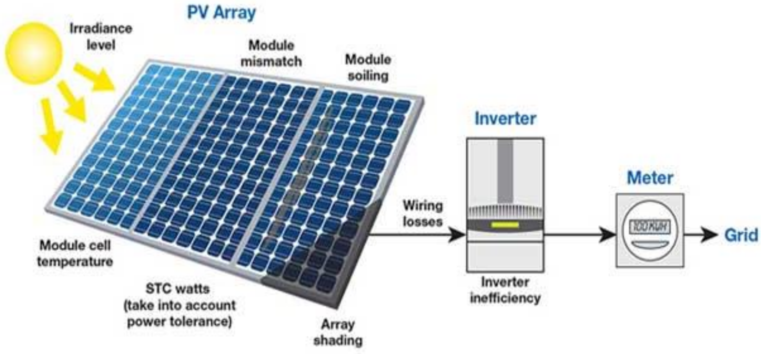

Figure 2. schematically illustrates the photovoltaic electricity generation process [62].

Copper-based chalcogenides, such as Copper Sulfide (Cu_2S) and Copper Selenide (Cu_2Se), have gained attention as promising semiconductor materials for photovoltaic (PV) energy production due to their abundance, low toxicity, tunable optical properties, and cost-effectiveness [63, 64]. These materials are widely explored for use in thin-film solar cells, nanocrystal-based solar cells, and hybrid photovoltaic devices [65]. Cu_2S is an indirect gap semiconductor with a bulk band gap of 1.21 eV [66]. Copper sulfide (Cu_2S) nanocrystals have been synthesized for application in photovoltaic devices such as dye sensitized solar cells, all-inorganic nanoparticle solar cells, and hybrid nanocrystal-polymer composite solar cells. These materials offer advantages in terms of processing, scalability, and cost-effectiveness compared to conventional single-crystal and thin-film solar cells. In one study, Cu_2S nanocrystals integrated into photovoltaic devices achieved a power conversion efficiency exceeding 1.6% [67]. A device incorporating Cu_2S with CdS nanorods exhibited an open-circuit voltage of 0.6 V and a short-circuit current density of 5.63 mA/cm², leading to an overall power conversion efficiency of 1.6% [68]. Cu_2S can also be combined with other non-toxic and abundantly available semiconductors to create new photovoltaic material sets. The addition of different dopants such as tin (Sn) or zinc (Zn) has been studied to improve the electrical properties of Cu_2S [69]. These dopants can alter the carrier concentration and enhance the conductivity of Cu_2S, enabling more efficient charge collection and potentially leading to higher efficiency in photovoltaic devices. Cu_2Se is another promising p-type semiconductor with similar properties to Cu_2S but with enhanced stability and tunability. Photovoltaic studies on chemically deposited copper selenide thin films show potential for converting solar energy to electrical energy [70]. Studies of power output characteristics have resulted in an open circuit voltage of 290 mV, a short circuit current of 20 μA, and a fill factor of 49.36%, with a lighted ideality factor of 2.59. Cu_2Se-based photovoltaic devices have demonstrated efficiencies exceeding 2%, with ongoing research aimed at further improving performance through material optimization and interface engineering [71]. Despite the promising results, there are several challenges that need to be addressed to make Cu_2S-based solar cells more efficient and commercially viable such as, stability and efficiency limitations [72]. For example, although Cu_2S-based solar cells have achieved PCEs of around 1.6%, they still lag behind established technologies such as silicon-based and cadmium telluride (CdTe) solar cells, which routinely achieve efficiencies above 20% [68]. While Cu_2S performs well under controlled laboratory conditions, its long-term stability in outdoor environments still requires further investigation. Degradation due to exposure to moisture and oxygen is a concern, and studies are exploring methods to passivate the Cu_2S surface to improve its environmental stability. Recent advances in computational modeling suggest that surface passivation techniques can significantly improve Cu_2Se's stability and efficiency. Consequently, both Cu_2S and Cu_2Se hold significant potential for next-generation photovoltaic technologies due to their low-cost production, high absorption properties, and compatibility with various solar cell architectures. While Cu_2S has been widely studied in thin-film and nanoparticle-based solar cells, Cu_2Se offers enhanced stability and electrical properties, making it a strong candidate for high-performance PV devices. Ongoing research in material engineering, nanostructuring, and interface optimization is expected to further boost the efficiency of Cu_2S- and Cu_2Se-based solar cells, making them viable alternatives to traditional silicon and CdTe technologies. Table 1 shows the performance indicators of Cu_2S and Cu_2Se in PV Energy Production [68, 71, 73-76].

Table 1. Comparison of Cu_2S and Cu_2Se in PV Energy Production

Property	**Copper Sulfide (Cu_2S)**	**Copper Selenide (Cu_2Se)**
Band gap	~1.2 - 1.5 eV	~1.4 - 1.7 eV
Absorption Coefficient	High	Very High
Stability	Moderate	Higher than Cu_2S
Efficiency (PCE)	~1.6%	~2%+
Charge Carrier Mobility	Moderate	High
Cost & Scalability	Low-cost, highly scalable	Slightly higher cost, scalable
Application	DSSCs, thin-film, heterojunction solar cells	Thin-film, quantum dot, tandem solar cells
Refs.	[68, 73, 74]	[71, 75, 76]

6. Copper Chalcogenides in Lithium-Ion Batteries

The use of fossil fuels as a source of energy poses two major problems for our planet. Firstly, fossil fuels are a limited resource and are not evenly distributed around the world, leading to various economic and political problems between countries. Additionally, the consumption of fossil fuels contributes to global warming, disrupting the balance of ecosystems [77]. Therefore, the transition to sustainable alternative energy sources is of great importance. Renewable energy sources such as wind, solar, and geothermal offer a significant solution; however, their biggest challenge lies in their seasonal and environmental variability. Thus, efficiently storing energy and making it available when needed is a crucial requirement for a sustainable energy future. To meet storage needs, battery technologies, especially lithium-ion battery technology, are at the forefront of energy storage systems today [78]. A battery is a device composed of one or more electrochemical cells (galvanic cells) that transform chemical energy into electrical energy through oxidation-reduction (redox) reactions [79]. The key components of an electrochemical cell include the anode (the negative electrode where oxidation occurs during discharge), the cathode (the positive electrode where reduction happens during discharge), the electrolyte (a conductive medium that enables ion movement between the anode and cathode), and the separator (a material that prevents internal short circuits by physically isolating the anode and cathode while permitting ion flow through the electrolyte) [80-82]. The schematic view of the battery is given in Figure 3 [83].

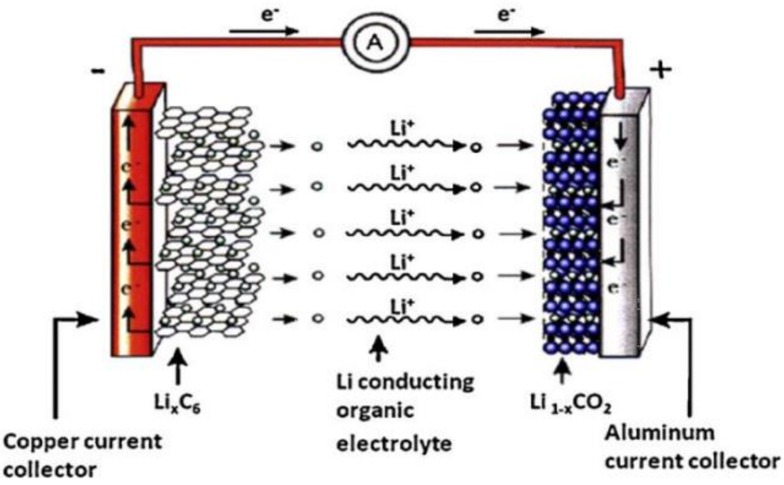

Figure 3. schematic view of the battery [83].

The anode, acting as a reducing agent, should have a high coulomb capacity (Ah/g), good electrical conductivity, stability, and low cost. The cathode, functioning as an oxidizing agent, should possess a suitable operating voltage and remain chemically stable when in contact with the electrolyte. The electrolyte, serving as an ionic conductor, should not react with the electrodes, exhibit minimal changes in properties with varying temperatures, be safe to use, and be cost-effective [84, 85]. Nanostructured Cu_2S and Cu_2Se materials, particularly nanorod-like morphologies, have demonstrated excellent performance as anodes in lithium-ion batteries (LIBs). These materials exhibit high theoretical capacity, stable lithium-ion insertion/extraction, and superior rate performance [86, 87]. Cu_2Se-based LIBs show high electronic conductivity and capacity retention at elevated temperatures [88]. The electrical conductivity of these materials can have positive effect on their electrochemical behavior for battery applications. Cu_2S and Cu_2Se have high theoretical capacities of 335 mAh/g and 326.8 mAh/g respectively [89, 90]. The high and flat charge/discharge voltage plateaus are approximately 1.7 V for Cu_2S and 1.7 V for Cu_2Se [89, 90]. As a result, the energy density (calculated as capacity × potential) is 569.5 Wh/kg for Cu_2S and 555.56 Wh/kg for Cu_2Se, which is comparable to or even higher than that of conventional $LiCoO_2$ (545.96 Wh/kg) cathodes [91]. These characteristics indicate that Cu_2S and Cu_2Se are a promising candidates as an alternative cathode materials. However, these materials may experience capacity degradation in carbonate-based electrolytes, limiting their commercial use in high-voltage cathodes. Therefore, using ether-based electrolytes and forming Cu_2S/C composites may help suppress the failure mechanisms of Cu_2S in carbonate-based electrolytes [89]. Recent findings highlight that heterostructuring Cu_2Se with carbon-based materials can significantly improve charge-discharge cycling stability [92].

7. Photo-Induced Enhancement

Photocatalysis is inspired by natural photosynthesis. It has been established that photosynthetic green plants are capable of capturing sunlight and converting it into chemical energy. The energy is then stored in various molecules, with examples of this type of molecule including carbohydrates. In the field of photocatalysis, a semiconductor material, known as a photocatalyst, absorbs light energy and subsequently generates electron-hole pairs. The ability of these carriers to drive redox reactions on the photocatalyst's surface has been well documented [93]. The band structure of semiconductors exhibits a separation between the conduction and valence bands by means of a band gap. In the event of a semiconductor being irradiated with light energy equal to or greater than its bandgap, it is possible for electrons to be excited from the valence band to the conduction band, with the result that positively charged holes are left in the valence band [94]. The photogenerated carriers can undergo either non-radiative or radiative recombination, resulting in the release of energy as heat or photons, respectively. Alternatively, when electrons and holes reach the semiconductor surface, they have the capacity to promote reduction and oxidation reactions of the adsorbed species. In this context, the employment of thin films or nanoparticle layers of solid crystalline materials is advantageous because it reduces the distance that charge carriers must travel to reach the surface. However, it should be noted that redox reactions can only occur if the positions of the valence and conduction bands of the photocatalyst are correctly matched to the redox potentials of the desired reaction (see Figure 4 for a schematic representation of the photocatalytic process [93]).

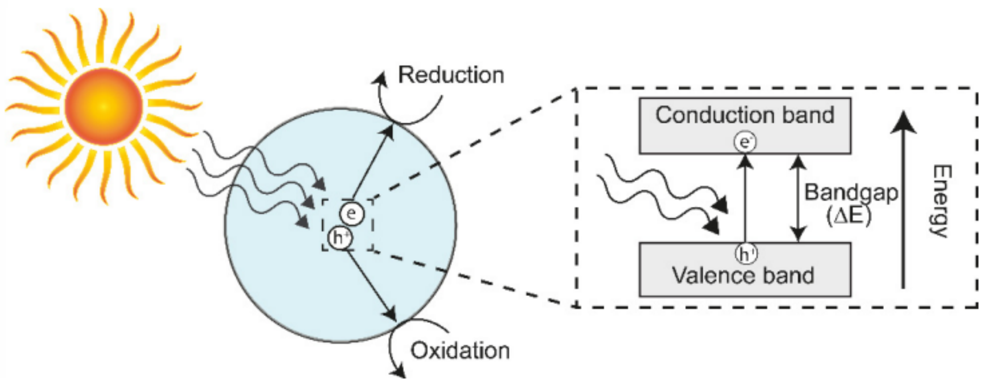

Figure 4. Schematically illustrates the photocatalysis process [93].

Element doping is one of the most commonly used methods to optimize carrier concentrations and has been widely applied to almost all thermoelectric materials. In addition to element doping, carrier concentration can also be externally adjusted using electric fields, magnetic fields, and light radiation [95]. These approaches have been reported to enhance thermoelectric performance. Among these three external fields, light radiation stands out as the simplest and most accessible method, offering a strong influence on the control of carrier concentration in semiconductors. The photo-Seebeck effect, an important factor in determining the performance of thermoelectric (TE) materials, refers to the modulation of the Seebeck coefficient (thermoelectric voltage) in a material due to photoexcitation [96]. It combines the photovoltaic and thermoelectric effects, where incident light alters the charge carrier concentration in a semiconductor or thermoelectric material, leading to changes in the thermoelectric properties. The photo-Seebeck effect has been observed not only in classic thermoelectric materials with narrow band gaps but also in various semiconductors with wide band gaps, such as Ge, Si, GaAs, ZnO, and PbO [97]. However, these photoinduced materials generally exhibit low thermoelectric performance. Recent research has shown that high-energy photons can activate charge carriers in Cu_2S and Cu_2Se, significantly enhancing their electrical conductivity and thermoelectric performance [96]. For example, the $Cu_{2-x}S$ compound is a suitable material for solar energy absorption due to its non-toxic nature, low cost, and ideal band gap range of 1.2–2.5 eV [99]. The concentrations (4.8 × 1018 cm^{-3}) and Seebeck coefficient (0.1 μ V/K) of $Cu_{2-x}S$ at 298 K are considerably lower compared to classical thermoelectric materials [43]. A relatively large band gap and low carrier concentration are required to achieve a large photoinduced effect. Therefore, Cu_2S can be used in the development of low-cost, renewable and environmentally friendly technologies to obtain energy from renewable sources in terms of its thermoelectric performance. Moreover, optical studies indicate that Cu_2Se exhibits strong photoluminescence properties, making it a potential candidate for optoelectronic applications [100].

8. Future Directions and Challenges

Future research on Cu_2S and Cu_2Se is focused on optimizing their thermoelectric, photovoltaic, and electronic properties for energy conversion and storage applications. Researchers are exploring novel synthesis techniques, such as high-throughput computational screening and machine learning-driven material discovery, to accelerate the identification of new crystal structures with desirable properties. Advances in synthesis techniques, such as nanoscale engineering and doping strategies, aim to enhance their electrical conductivity and thermal stability while maintaining their inherently low thermal conductivity key factors for improving thermoelectric efficiency. Additionally, exploring their defect chemistry and phase stability is crucial for mitigating issues related to structural degradation and performance fluctuations over time. However, significant challenges remain, including the need for precise control over crystallization processes, scalability of production methods, and stability under extreme conditions. The scalability of advanced synthesis methods like 3D printing for fabricating thermoelectric devices poses practical challenges. Ensuring uniformity and reproducibility in large-scale production while maintaining material properties is critical for commercial applications.Addressing these challenges requires a multidisciplinary approach, combining experimental characterization with computational modeling to tailor material properties for next-generation energy technologies.

9. Conclusion

Advances in materials science and the discovery of new materials with increased efficiency and sustainability, such as next-generation semiconductors and advanced thermoelectric materials, hold promise for the development of applications in energy, electronics and catalysis. Cu_2S (Copper Sulfide) and Cu_2Se (Copper Selenide) are remarkable thermoelectric materials due to their unique superionic phase transition, high electrical conductivity, and ultra-low lattice thermal conductivity. While significant progress has been made in understanding their structural, electronic, and thermal characteristics, challenges such as precise control over crystallization, defect engineering, and scalability persist. Addressing issues of long-term stability and environmental impact will also be critical for their practical implementation. In this context, the integration of computational modeling, machine learning, and novel synthesis techniques offers promising avenues for accelerating material discovery and optimization. Ongoing advances in computational and experimental techniques will be crucial to unlocking the full potential of these materials.

Acknonlements

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