Topical Review

Nanoscale self-assembly of thermoelectric materials: a review of chemistry-based approaches

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Abstract
This review is concerned with the leading methods of bottom-up material preparation for thermal-to-electrical energy interconversion. The advantages, capabilities, and challenges from a material synthesis perspective are surveyed and the methods are discussed with respect to their potential for improvement (or possibly deterioration) of application-relevant transport properties. Solution chemistry-based synthesis approaches are re-assessed from the perspective of thermoelectric applications based on reported procedures for nanowire, quantum dot, mesoporous, hydro/solvothermal, and microwave-assisted syntheses as these techniques can effectively be exploited for industrial mass production. In terms of energy conversion efficiency, the benefit of self-assembly can occur from three paths: suppressing thermal conductivity, increasing thermopower, and boosting electrical conductivity. An ideal thermoelectric material gains from all three improvements simultaneously. Most bottom-up materials have been shown to exhibit very low values of thermal conductivity compared to their top-down (solid-state) counterparts, although the main challenge lies in improving their poor electrical properties. Recent developments in the field discussed in this review reveal that the traditional view of bottom-up thermoelectrics as inferior materials suffering from poor performance is not appropriate. Thermopower enhancement due to size and energy filtering effects, electrical conductivity enhancement, and thermal conductivity reduction mechanisms inherent in bottom-up nanoscale self-assembly syntheses are indicative of the impact that these techniques will play in future thermoelectric applications.

Keywords: thermoelectrics, self-assembly, quantum dots, nanowires, mesoporous, thermal conductivity, bottom-up

(Some figures may appear in colour only in the online journal)

1. Introduction

In thermoelectric (TE) energy conversion, waste heat is directly converted into electricity. When a thermoelectric material is exposed to a temperature gradient, the charge carriers—electrons in n-type and holes in p-type materials—diffuse from one side of
the solid material to the other. In a power generation mode taking advantage of the Seebeck effect, a temperature gradient is used to generate electrical current as the diffusion of electrons is from the hot side towards the cold side and vice versa for holes. The opposite effect (using an electrical current to force a temperature gradient) can be used in a refrigeration mode and takes advantage of the Peltier effect (scheme 1).

The design of high performance thermoelectric materials can have a sizeable impact on the commercial industry as a sustainable energy recycler for the constant losses demonstrated by the excess waste provided by current manufacturing processes [1]. The performance of a thermoelectric material can be described by a non-dimensional quantity $zT$, defined as

$$zT \equiv \frac{S^2 \sigma}{\kappa} = \frac{S^2}{L} \cdot \left(1 + \frac{\kappa_l}{\kappa_e}\right)^{-1},$$

where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $L$ is the Lorenz number, $T$ is the absolute temperature, and $\kappa = \kappa_e + \kappa_l$ is the thermal conductivity comprised of electronic ($\kappa_e$) and lattice ($\kappa_l$) components. The energy conversion efficiency at optimum efficiency is related to the Carnot efficiency, $\eta_{\text{Carnot}}$, and figure of merit, $zT$, as indicated by the following equation [2]

$$\eta = \eta_{\text{Carnot}} \cdot \left(\frac{\sqrt{1 + zT_{\text{device}}} - 1}{\sqrt{1 + zT_{\text{device}}} + T_{\text{cold}}/T_{\text{hot}}}\right),$$

(2)

$$\eta_{\text{Carnot}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}},$$

where $T_{\text{hot}}$ and $T_{\text{cold}}$ are the temperatures at the hot and cold side of the device, respectively, and where the properties we are concerned with are taken across the range of temperatures over which the device operates, $zT_{\text{device}}$. A more detailed discussion of the relationship between temperature-dependent material properties and device efficiency is given in [3]. The graphical representation of the efficiency as a function of $zT_{\text{device}}$ is shown in figure 1 using a hot side temperature of 773 K and a cold side temperature of 300 K. Note that as an upper limit, this correlates to a Carnot efficiency of 61.2%. For an energy conversion technology to be considered practical, the efficiency should be greater than one third of the Carnot efficiency [1], hence the $zT_{\text{device}}$ required for practical energy conversion over the temperature range $T_{\text{hot}}$ to $T_{\text{cold}}$ can be expressed as

$$zT_{\text{device, practical}} = \frac{(T_{\text{cold}} + T_{\text{hot}}) \cdot (T_{\text{cold}} + 5T_{\text{hot}})}{4T_{\text{hot}}^2}.$$  

Comparison with state-of-the-art reports of $zT_{\text{device}}$ over this temperature, which is highest for top-down synthesized materials [4–7], demonstrates that while progress has been made to increase efficiency, materials performance is still the realm in which improvements must be made before thermoelectric energy conversion can become a practical technology. According to equation (1), emphasis in materials engineering should be placed on enhancing the power factor ($S^2\sigma$) while suppressing the thermal conductivity ($\kappa$). However, in reality, these properties are related to each other and act in opposite trends with respect to carrier concentration. As all
three of the transport properties ($S$, $\sigma$, and $k$) change interdependently, the carrier concentration can be adjusted to the value that leads to the maximum $zT$, which is carried out by deliberate $p$-type or $n$-type doping. For most cases, the optimum carrier concentration [8] is $\sim 10^{18}$–$10^{20}$ cm$^{-3}$. The carrier concentration needs to be optimized regardless of the material fabrication process (top-down or bottom-up). The carrier concentration needs to be optimized regardless of the material fabrication process (top-down or bottom-up) which can be dominated by presence of defects and vacancies [9].

Other than possessing a high $zT$, any developed synthesis approach should be capable of the mass production of thermally and mechanically stable materials at low cost. Developing these production techniques is crucial especially for potential operations in large industries such as petroleum refining and primary metals manufacturing. A majority of previous investigations are based on top-down (solid-state) methods for material preparation, and currently most of high $zT$ thermoelectrics have been obtained using solid-state synthesis processes [4–7, 10]. Each approach—solid-state or bottom-up—has its own advantages and limitations. Compared to the solid-state methods, bottom-up synthesis has been relatively overlooked and we argue that the highest potential for impact lays in investigations utilizing chemistry-based approaches. In contrast to thermoelectrics, solution-based approaches have long been utilized for various applications such as energy storage (batteries [11], supercapacitors [12]), solar cells [13–15] and catalysis [16]. There are many well-developed synthesis methods in these fields that can potentially be adapted to modify the electronic or thermal performance of nanostructured materials [17–19]. For instance, chemical routes have been discovered to control the shape, morphology, and dimensionality of inorganic materials that enable manipulation of their physico-chemical properties [20–23]. Ligand exchange techniques have been introduced for improvements of electrical properties in nanocrystals [24]. These are unique capabilities of bottom-up methods that have rarely been exploited for thermoelectric purposes. Bottom-up techniques such as microwave rapid synthesis also have inherent potential for mass-production. Ultra-high specific surface area nanomaterials such as mesoporous materials [25] offer the ability to tune transport both intrinsically and extrinsically on a macroscopic scale, yet these materials are difficult to synthesize through known top-down approaches with the exception of electroless etching of silicon [26, 27]. In addition, bottom-up synthesis offers the ability to leverage new transport phenomena into technology, such as thermal transport mechanisms at the organic–inorganic interfaces [28] and dissipationless surface-state transport phenomena [29–31].

A survey of obtained $zT$ values illustrating the current state-of-the-art for bottom-up processed thermoelectrics is shown in figure 2. The reports can be divided into three groups: (i) Bi/Sb-chalcogenides for low temperature applications (below 500 K), (ii) Pb-chalcogenides for medium to high temperature ranges (300–900 K), and (iii) oxide thermoelectrics for temperatures above 900 K. The obtained values are promising and indicate the potential of solution processed thermoelectrics. In regard to the goal of $zT_{\text{device}} > 1.75$ needed for practical energy conversion, more efforts are necessary. This survey emphasizes the potential of solution-processed thermoelectrics and the need for future investigations, including computational materials design efforts, on other materials apart from Bi or Pb-chalcogenides.

This review is focused solely on bottom-up synthesis approaches for thermoelectric materials and no discussion on top-down methods is surveyed unless it is required for explanation of basic principles or models. An interested reader can refer to the previously published review articles on...
thermoelectrics prepared via solid-state approaches [47–49]. Distinguished from the available review or feature articles discussing bottom-up thermoelectrics [50–53], this review provides the reader with a comprehensive survey of the recent literature, basic synthesis and thermoelectric concepts for low dimensional nanomaterials, and paradigms that can potentially be adapted for thermoelectric applications as well as suggestions for future investigations. First, common material synthesis methods including syntheses of mesoporous materials, quantum dots, solvothermal, and microwave processes are surveyed. Secondly, various routes for improving power factor, and decreasing thermal conductivity relevant to solution-process syntheses are reviewed. In addition, basic models, relevant equations, and advanced characterization methods have been incorporated.

2. Bottom-up synthesis of thermoelectric nanomaterials and related devices

2.1. Mesoporous materials: synthesis and thermoelectric applications

Mesoporous materials have long been used for a wide range of applications [54]. The term mesoporous refers to a material with a high surface area and a monodisperse pore size distribution from 2 to 50 nm. Soft-template and hard-template methods are the common routes for the synthesis of highly ordered materials (scheme 2). Surfactants or block copolymers containing both hydrophobic and hydrophilic head groups are used for the soft-template approaches [55, 56]. Interactions of the inorganic precursors and the surfactants are through non-covalent bonds such as hydrogen and electrostatic or electrovalent bonds [57]. The self-assembly process involves simultaneous hydrolysis and condensation of the precursors in a polar solvent. The elimination of the surfactant by thermal decomposition or other removal methods leaves the inorganic material with mesoporous long-range ordering [58]. In the soft-template method, condensation at the inorganic/surfactant interface is a time dependent process and the hydrolysis and condensation rates of the precursor are crucial factors. A rapid rate can lead to a disordered structure with a static or electrovalent bonds through non-covalent bonds such as hydrogen and electrostatic interactions of the inorganic precursors and the surfactants are

Figure 2. The reported high-\(zT\) thermoelectrics processed by using bottom-up synthesis approaches. The graph illustrates the temperature-dependent \(zT\) values for Bi/Sb chalcogenides for temperature ranges below 500 K (shown in red), for Pb chalcogenides for temperatures from 300 to 900 K (shown in blue), and for oxide thermoelectrics for temperatures above 900 K (shown in green). The curves are plotted based on: red colors: \(\text{Bi}_4\text{Sb}_3\text{Te}_5\) (Liu et al. [32] 2018, p-type), \(\text{Bi}_4\text{Sb}_3\text{Te}_5\) (Zhang et al. [33] 2017, p-type), \(\text{Bi}_4\text{Sb}_3\text{Te}_5\) (Zhang et al. [34] 2016, p-type), \(\text{Bi}_4\text{Sb}_3\text{Te}_5\) (Mehta et al. [35] 2012, p-type), \(\text{Bi}_2\text{Te}_3\) (Zhang et al. [36] 2012, n-type), \(\text{Bi}_2\text{Te}_3\text{Se}_0.2\) (Varghese et al. [37] 2016, n-type) blue colors: \(\text{PbS}_{0.72}\text{Te}_{0.28}\) (Ibáñez et al. [38] 2013, n-type), \(\text{PbTe}_{0.86}\text{Se}_{0.14}\)–\(\text{Cl}\) (Ibáñez et al. [39] 2015, n-type), \(\text{PbS}–\text{Ag}\) (Ibáñez et al. [40] 2016, n-type), \(\text{PbS}\) (Xu et al. [41] 2018, n-type) green colors: \(\text{TiO}_2\)–\(\text{TeO}_2\)–\(\text{TiO}_2\) (Ou et al. [42] 2015, n-type), \(\text{La}, \text{Nb}-\text{doped SiO}_2\) (Wang et al. [43] 2017, n-type), \(\text{Ca}_3\text{Ba}_{0.05}\text{Co}_4\text{O}_9\) (Carvillo et al. [44] 2015, p-type), \(\text{SrTiO}_3–\text{LaB}_6–\text{SrTiO}_3\) (Wang et al. [45] 2018, n-type), \(\text{ZnAl}_2\text{O}_4\) (Jood et al. [46] 2011, n-type). Notes: in Liu et al. [32], an average \(zT = 1.83\) was obtained based on measurements on five pellets. In the study by Jood et al. [46], the temperature-dependent thermal conductivity values were calculated using a modified Debye–Callaway model which extrapolated from a measured data point at \(\sim 300\) K.
hydrogen bonding is proposed where N\textsuperscript{0} is the non-ionic surfactant [62, 63]. The weaker non-ionic interactions can potentially result in thicker pore walls and more stable structures compared to the stronger ionic surfactants [63].

In a hard-template method also referred to as nano casting, the precursors are infiltrated through the template. Typically, highly ordered mesoporous silica [64, 65] are be used as templates although a desired polymer morphology can also be used as a template for the deposition of inorganic phases [56, 66]. Decomposition and crystallization of precursors takes place inside the template pores. After removal of the template, the final structure is obtained as a negative image of the parent template by etching the template in an aqueous solution of HF or NaOH for the silica templates or image of the parent template by etching the template in an aqueous solution of HF or NaOH for the silica templates or thermal calcination for carbon and polymer-based templates [67]. SBA-15 [68] is a well-known silica template with a two-dimensional (2D) structure of interconnected nanowires arranged in a p6mm mesostructure. KIT-6 [69, 70] is a high surface area silica template with a three-dimensional (3D) gyroidal mesostructure (Ia\textsuperscript{3}d). Both templates have tunable pore sizes below 10 nm and offer high thermal stability up to 1473 K [71] and 1173 K [72] for SBA-15 and KIT-6, respectively. The main challenge in the hard-template method is infiltration of the precursor into the pores of the template. Therefore, the precursor should be gaseous, highly soluble or liquid with certain qualities that can result in a high amount of loading without chemically reacting with the template [73]. An abundance of hydrogen bonds such as hydroxyl groups facilitates infiltration of precursors. Each method of soft-template or hard-template has challenges and is appropriate for different chemistries. For instance, in soft-templating, controlling the chemistry of the reaction is difficult which is why most inorganic structures are based on tetraethyl orthosilicate (TEOS) chemistries, and in hard-templating gaining a high-loading and selective template removal can be problematic.

A large number of ordered mesoporous materials have been synthesized using both hard and soft-template approaches that are listed in specialized reviews [25, 58]. The majority of reported mesoporous crystalline materials are metal oxides with measured Brunauer–Emmett–Teller surface areas (S\textsubscript{BET}) on the order of 100–200 m\textsuperscript{2} g\textsuperscript{−1}. Examples include Nb\textsubscript{2}O\textsubscript{5} (p6mm, S\textsubscript{BET} = 196 m\textsuperscript{2} g\textsuperscript{−1}) [74, 75], SnO\textsubscript{2} (p6mm, S\textsubscript{BET} = 180 m\textsuperscript{2} g\textsuperscript{−1}) [74, 75], Co\textsubscript{3}O\textsubscript{4} (p6mm, S\textsubscript{BET} = 367 m\textsuperscript{2} g\textsuperscript{−1}) [76] produced using soft-templating, and Co\textsubscript{3}O\textsubscript{4} (p6mm, S\textsubscript{BET} = 101–122 m\textsuperscript{2} g\textsuperscript{−1}) [77, 78], Co\textsubscript{3}O\textsubscript{4} (Ia\textsuperscript{3}d, S\textsubscript{BET} = 92. 130 m\textsuperscript{2} g\textsuperscript{−1}) [79, 80], SnO\textsubscript{2} (p6mm, S\textsubscript{BET} = 160 m\textsuperscript{2} g\textsuperscript{−1}) [81]. ZnO (p6mm, I\textsubscript{4}1\textsubscript{3}2, S\textsubscript{BET} = 192–202 m\textsuperscript{2} g\textsuperscript{−1}) [82], WO\textsubscript{3} (p6mm, Ia\textsuperscript{3}d, S\textsubscript{BET} = 81.8, 54.3 m\textsuperscript{2} g\textsuperscript{−1}) [83–86], and MoO\textsubscript{3} (P6mm, S\textsubscript{BET} = 50–63 m\textsuperscript{2} g\textsuperscript{−1}) [87] produced using hard-templating. These ordered mesostructures provide an opportunity to reduce the relatively high thermal conductivities associated with large band gap oxide thermoelectrics [88, 89]. For instance, a linear suppression of thermal conductivity has been reported in SrTiO\textsubscript{3} by reducing the grain boundaries below 100 nm even approaching the minimum value calculated by Cahill’s model [90, 91]. This is promising regarding the fact that most reported oxide mesoporous materials have characteristic sizes tunable to below 10 nm. However, to the best of our knowledge, there has been no report investigating the use of mesoporosity in oxide thermoelectrics.

Chalcogenide compound semiconductors (group IV–VI and V–VI) such as the families of (Pb, Sn)(S, Se, Te) and (Bi, Sb)(S, Se, Te)\textsubscript{3} are among the most relevant for thermoelectric energy conversion [8]. An ordered mesoporous metal chalcogenide can be regarded as either a negative image of a quantum dot (QD) superlattice structure or an inverse image of nanowires. If such a highly ordered material is synthesized, there exists a possibility of tuning the electronic band gap by varying the wall thickness [92, 93]. Despite the successful routes developed for the synthesis of highly ordered mesoporous silicates and metal oxides, similar approaches for metal chalcogenides face many challenges. These include complicated chemistry, a compatible surfactant removal process, and a lack of compatible precursors for S, Se, and Te [25, 92] which demands more investigations before mesoporous materials in this category become widely available. For metal chalcogenides, both soft-template and hard-template methods have been tested but few successful highly ordered materials have been reported [25]. These successful attempts consist of mesoporous CdS,
MoS2 and WS2 through hard-templating [94, 95]. Another approach focuses on using cation exchange to convert a parent mesoporous material such as CdS into other mesoporous structures such as CuS and Ag2S [96, 97]. For the hard-template method, the challenge is, unlike the metal oxides, the template should be infiltrated with both precursors for the metal as well as the chalcogen which in most cases causes the blockage of the pores by the second precursor [25]. A single precursor containing both metal and chalcogen was shown to be successful by in situ conversions of [(Cu6(TePh)3(PPh3)Et)5] into Cu6Te [98], Cd(XPh)2TMEDA (X: S, Se, Te, TMEDA: tetramethylethylenediamine) into Cd(S, Se, Te) [99], and [Cd10(CN)2(C2H8N2O2S8)] into ordered mesoporous CdS (Soret = 160 m3 g−1, average pore size of 6 nm) [94]. In the case of CdS, ZnS, and In2S3, Lui et al [100] reported the formation of complex precursors using thiourea as the sulfur source and the appropriate metal nitrate precursor which were capable of filling pores in SBA-15 to create replicate mesoporous structures. A second method that has been developed is to fill the pores of the template with only the metal precursor and then thermochemically convert the metal complex using a gaseous precursor for the chalcogens, usually by a treatment in H2S or H2Se. This second method has produced highly ordered mesoporous MoS2 and WS2 with p6mm and Ia3d layered structures [95], ordered mesoporous MoSe2 [101], and first-row transition-metal sulfides FeS2, CoS2, and NiS2 [102]. Recently, a gaseous transformation of highly ordered double gyroid (Ia3d) mesoporous Nb2O5 to NbN by annealing under NH3 was carried out by Robbins et al [103] for superconductivity applications. Most impressive, the morphology of the free-standing films were preserved after high temperature NH3 treatment at 865 °C (figure 3). So far, none of these approaches have been investigated for thermal or thermoelectric energy conversion applications.

Bulk silicon has a thermal conductivity at room temperature with a broad spectral range of constituent phonon mean free paths (MFPs) [104], which has led to efforts to reduce its thermal conductivity by introducing low-dimensionality [26] or porosity. The broad spectral nature of phonon MFPs in Si, with 90% of bulk κ arising from phonons with MFPs up to 8 μm, makes this material particularly sensitive to size effects and mesostructure thus we will discuss Si as special case. We note that most thermoelectric materials exhibit more spectrally narrow κ distributions than silicon [105, 106], which means only sub-10 nm features may alter thermal transport properties. For Si, Lee and Grossman [107] predicted a two-fold increase in the thermopower at carrier concentrations less than 2 × 1019 cm−3, with an overall two-fold enhancement in zT at room temperature due to porosity. Their calculation predicted a 200-fold reduction in the lattice thermal conductivity with only a 2–4-fold increase in the electrical conductivity. In contrast to Si, numerical modeling of Si1-xGe1-x alloys predicted zT degradations due to the porosity arising from a strong reduction in the electrical conductivity despite the beneficial reduction in thermal conductivity and enhancement of Seebeck coefficient (due to the carrier filtering effect) [108]. Due to the contradictory conclusions of these computational predictions, and lack of experimental consensus, additional basic research is required to address the posed hypotheses. Experimental measurements of disordered nanoporous Si [109] showed several orders of magnitude reduction in electrical conductivity. This indicates the importance of having a highly ordered mesoporous material compared to a random disordered porous structure. Arens-Fischer et al [110] measured the thermal conductivity of electrochemically etched porous silicon with porosity in the range of P = 64%–89% using the 3ω technique. The porous structure and corresponding details

Figure 3. Retention of an ordered inorganic mesostructure after thermochemical conversion 850 °C: the case of Nb2O5 into NbN. (a) Pore size distribution of Nb2O5 (450 °C) and after conversion to NbN (700 °C, 850 °C). The double gyroid morphology of the free-standing films (b, e) after NH3 treatment at 700 °C, (c, f) after nitriding at 850 °C, and (d) Nb2O5 after calcination at 450 °C in air. Adapted from [103]. © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0.
were not described. As the porous material is a composite of solid and vacuum (or assumed medium with $\kappa = 0$), the relationship between measured (effective) and intrinsic (solid) thermal conductivity can be expressed as a function of the porosity. Thermal conductivity across interfaces is a function of adhesion energy [111, 112], thus many porous materials can be analyzed as follows especially for the case of single crystalline silicon frameworks, hot pressing, or spark plasma sintering (SPS). To gain a better understanding of the effects of porosity, Arens-Fischer et al. [110] used a simple equation to model the effective thermal conductivity of the porous Si, $\kappa_{\text{eff}}$ as [113]

$$\kappa_{\text{eff}} = \kappa_{\text{solid}} \cdot (1 - P)^3,$$  \hspace{1cm} (4)

where $P$ is the porosity, $\kappa_{\text{solid}}$ is the thermal conductivity of the solid phase within the porous medium. The measurements showed 3–5 orders of magnitude thermal conductivity reduction compared to the bulk Si values over a temperature range of 300–35 K. Several additional studies have been performed on the thermal conductivity of electro-chemically etched porous Si [114–120]. Song and Chen [121] reported temperature dependent (50–300 K) in-plane thermal conductivity of single crystal Si with periodically fabricated micropores, and a more than three-fold reduction in $\kappa$ (e.g. 40 W m$^{-1}$K$^{-1}$ at room temperature). Temperature dependent thermal conductivity scaling was observed even at the micron size level of the pores.

The Eucken [122, 123] and Russel [124] models can be used in order to estimate the effective thermal conductivity in porous media as

$$\kappa_{\text{eff}} = \kappa_{\text{solid}} \cdot \left(1 - \frac{1}{2}P\right)^3,$$  \hspace{1cm} (5)

and

$$\kappa_{\text{eff}} = \kappa_{\text{solid}} \cdot \frac{(1 - P^{2/3})}{(1 - P^{2/3} + P)},$$  \hspace{1cm} (6)

respectively. We note that this is in line with the paradigm of spectral thermal conductivity proposed by Minnich et al [104]. Most relevant to the ordered mesoporous materials prepared by nanoscale self-assembly, Fang et al. [125] reported the thermal conductivity of a mesoporous nanocrystalline Si thin film prepared via a magnesium reduction of polymer-templated silica with a porosity of 25%–35%, measured by the $3\omega$ method. The samples showed a reduction in $\kappa$ of 3–5 orders of magnitude compared to the bulk values. At low temperatures, the measured thermal conductivity showed a dependence of $\kappa \propto T^2$, similar to that predicted by the Cahill model [90] for the minimum lattice thermal conductivity of amorphous and disordered crystalline materials. An effective thermal conductivity expression was used in order to model the experimental data [126]

$$\kappa_{\text{eff}} = \kappa_{\text{solid}} \cdot \left(1 - \frac{1}{2}P\right)^3,$$  \hspace{1cm} (7)

where $\kappa_{\text{solid}}$ represents the thermal conductivity of the solid medium which was replaced by a combination of the effective medium approximation (EMA) [127, 128] and kinetic theory, or the minimum value by Cahill’s model [90].

So far, only two experimental investigations have reported thermoelectric properties of a mesoporous material: Tang and coworkers [129] reported the thermoelectric measurements of ‘holey silicon’ prepared by nano-sphere lithography and block copolymer lithography. The holey silicon membrane with 35% porosity exhibited a two orders of magnitude reduction in thermal conductivity approaching the amorphous limit, with a room temperature $\tau T$ of 0.4. The second study was carried out by Zhang, Stucky and coworkers [36] on an $n$-type $\text{Bi}_2\text{Te}_3$ monolith. Colloidal silica nanospheres (LUDOX) were used as the hard-template and was mixed with stoichiometric amounts of precursors. After crystallization under a H$_2$ atmosphere at 400 °C, a 4 M aqueous sodium hydroxide solution was employed in order to remove the silica hard-template. The transport measurements were conducted on hot-pressed pellets. Structural characterizations showed a disordered porous material with $\text{S}_{\text{BET}} = 28.4 \text{ m}^2 \text{g}^{-1}$ and pore size distribution between 5 and 30 nm. After hot-pressing, the original isotropic spherical nanopores were preserved and transformed into anisotropic ellipsoidal shapes. Compared to the bulk (condensed) sample, the mesoporous sample indicated a slightly lower electrical conductivity in the direction perpendicular to the pressing but exhibited a clear reduction in the parallel direction. However, the thermal conductivity was reduced by more than 50% (a 60% reduction in relative lattice thermal conductivity, a 20% in electrical conductivity) leading to a $\tau T$ of 0.7 at 480 K. This demonstrated a 45% enhancement compared to the measured value for the bulk sample over the range 400–500 K (figure 4).

Several studies of chemically synthesized thermoelectric materials [35, 38–40, 130, 131] have reported lower mass density compared to the theoretical values due to inter particle voids formed during cold-pressing, hot-pressing, or SPS. This type of porosity results in a lack of confidence when interpreting transport phenomena in even the highest performing top-down-synthesized thermoelectric, SnSe [6, 132], and should not be neglected during analysis of experimental results. A simple Maxwell–Eucken model [133, 134] has been developed and is commonly used to account for the effects of porosity in both electrical and thermal conductivities of pressed pelletized materials:

$$\kappa_{\text{eff}} = \kappa_{\text{solid}} \cdot \frac{(1 - P)}{(1 + \beta P)}.$$

where the 100% dense (corrected) solid conductivity value, $\kappa_{\text{solid}}$, is obtained from the measured porous (effective) conductivity, $\kappa_{\text{eff}}$, the porosity $P$, and the parameter $\beta$ which is in the range of 1–3 for spherical pores. Note that $\beta = \frac{1}{2}$ in the original Eucken model [122, 123] given by equation (5).

2.1.1. Outlook. The main advantage of using mesoporous materials for thermoelectric applications is their ability to suppress the lattice thermal conductivity. This reduction needs to be more than any possible degradation in electrical conductivity. There is a possibility of enhancing the thermopower due to the electron confinement effect if a highly ordered material can be synthesized. Despite the promise of this mesostructural class of
materials, few studies have reported the effects of mesoporosity on thermoelectric properties. For the bulk thermoelectrics, the study of mesoporous Bi₂Te₃ [36] indicated the existence of the mesopores even after hot-pressing. The benefit of having a high surface area is not limited to effects on phonon scattering. Having access to the surface of a material provides many advantages for thermochemical processing [103] and extrinsic control over the chemical potential [135]. For instance, the pores can be filled with a properly designed secondary phase in order to induce the filtering effect of low energy charge carriers. Due to the contradictory conclusions of the few available computational predictions, and lack of experimental consensus with only two studies available for validation, additional basic research efforts are required to address the posed hypotheses of the effect of mesoporosity on thermal and thermoelectric performance. Synthesis methods for mesoporous heavy metal chalcogenide materials, improving the electrical properties, and improving the mechanical and thermal stabilities are the major challenges for future investigations.

2.2. Quantum dots (QDs): synthesis and thermoelectric applications

Quantum dots (QDs, mainly semiconductor nanocrystals) have received significant attention in different scientific fields...
and for varied technological applications mainly because their physical properties can be tuned by controlling their size, shape, composition, and modification of their surface chemistry. A typical QD synthesis procedure consists of three components: (i) precursors (the sources of inorganic materials), (ii) surfactants (ligands), and (iii) solvents [20]. Generally, a ligand’s role is to passivate the surface of the nanocrystals. During the synthesis, precursors decompose upon heating at the reaction temperature, and form a superset of saturation of monomers. Monomers are molecular species originating from dissolution of the precursor which can either join or leave the nucleated nanocrystals later in the reaction, resulting in their growth or shrinkage. The formation of monomers is followed by a nucleation step. Monomers present in the reaction join the formed nucleation seeds and cause them to grow which eventually shapes the final nanocrystals through a rearrangement of the atoms [20]. Crystallization occurs during the reaction. The reaction temperature is important and should be high enough to allow precursor decomposition and nanocrystal annealing/crystallization and low enough to avoid instability of common organic materials present in the reaction (temperatures are in the range of 200 °C–400 °C) [20]. This relatively low temperature range overcomes the cohesive energy per atom and, therefore, nanocrystals crystallize because the cohesive energy is related to the melting temperature of nanoparticles which, in turn, is a function of size—smaller size corresponds to a lower melting point [20, 136]. At any given monomer concentration, there exists a critical size at which the particle dissolution rate is equal to the growth rate. Particles smaller than the critical size are not stable and have negative growth rates whereas larger particles have positive growth rates. The critical nanoparticle size is a function of the monomer concentration in such a way that higher concentrations correspond to smaller critical size [137]. As figure 5(a) illustrates, both high and low monomer concentrations exhibit maximum peaks in their growth rate—size relationship. This is due to the fact that when particles grow and become larger, the growth rate becomes slower because continuing the growth requires more atoms to join [20]. Two mechanisms are proposed in order to explain the kinetics of the growth process with high and low monomer concentrations: (i) growth by diffusion (narrowing, or focusing) [138] and (ii) the Ostwald ripening effect [139] (broadening, or defocusing). According to the former model, and because a high monomer concentration corresponds to a smaller critical size, it is more likely that the particle size distribution range does not fall into the critical size regime. Because the growth rate is inversely proportional to the particle radius, smaller particles grow faster than the larger ones and therefore the obtained size distribution can be focused [140]. In contrast, a low monomer concentration corresponds to both slower growth and a larger critical size. This dictates that the smaller particles are not thermodynamically stable and tend to deplete into the solution, releasing monomers which deposit onto the surface of larger particles (known as Ostwald ripening effect [139]). This model assumes that the solubility of the particles is a function of their size, in which smaller particles dissolve in the solution and are consumed by larger ones [141]. In other words, at the beginning of the reaction and upon dissolution of the precursor, the monomer concentration is enhanced above the critical value required for the nucleation to start. By proceeding with the reaction, monomers are consumed due to nanocrystal nucleation and growth and the monomer concentration falls below the nucleation critical value causing nucleation events to cease. At this point the monomer concentration is still higher than the monomer critical value needed to avoid the dissolution of smaller particles, and as nucleation has already been stopped the remaining monomers are consumed for the growth of
existing nanocrystals. If the reaction continues further, the monomer concentration falls below the equilibrium critical value. Once this happens, the particles smaller than the critical size are not thermodynamically favorable anymore and will deplete in the form of monomer back in the solution (Ostwald ripening) [142].

In general, hot-injection and heat-up (also known as non-injection) methods are the most common techniques for the synthesis of nanocrystals. Hot-injection involves rapid nucleation of monomers by an injection of a room temperature precursor into a hot solution of surfactants (figure 5(b)) [140]. The main feature of this method is that the nucleation and growth are separated which leads to a more focused size distribution. This separation is followed by an inevitable reaction temperature drop due to the injection. The disadvantage of this technique is that both scalability and reproducibility are difficult. For instance, the temperature drop upon injection does not have a linear relationship with the volume injected. Unless automated, the injection time varies from person to person which will affect the reproducibility [142]. In contrast, in the heat-up technique all the precursors are present at the beginning of the reaction. At room temperature, the nucleation rate should be negligible and as the reaction proceeds further, the nucleation rate increases. The heating rate and the precursor reactivities are the two important parameters. Although the heat-up method is more favorable for reproducibility and scalability, the main challenge is the overlap between the nucleation time and the growth period which can result in a broad size distribution (figure 5(c)). A rapid heating rate will result in a smaller average size and narrower size distribution. In such a situation, the nucleation is much faster than the growth which leads to a high concentration of nuclei. As the growth is distributed among a larger total number of nanocrystals, the size distribution can focus. A moderately reactive precursor is more favorable compared to a precursor with a high or low reactivity because of the balance created between nucleation and growth periods [142].

Ligands (surfactants) are used in order to passivate and stabilize the surface of QDs, compensating for their high surface-to-volume ratios [137, 143]. Proper use of a surfactant can also increase the surface tension at the solvent-nanoparticle interface and lead to a narrower particle size distribution [137]. The adhesive energy of the surfactant is a key factor that plays an important role in the crystal growth which can alter the reaction kinetics [144] and nanocrystal morphology [145]. The surfactant adhesion energy should allow the surface of the nanoparticle to be accessible for growth while the entire particle is protected against aggregation [20]. In addition, recent synthesis advancements have demonstrated the ability to epitaxially connect and couple all the QDs in the form of a superlattice structure [146–149]. First, ligand-capped superlattices are synthesized, and then, are attached by a selective binding of the ligand to a specific crystal facet. Removal of the ligand, causes the nanocrystals to fuse together in the specific orientation [149] (figure 6).

2.2.1. Outlook. Many studies have reported synthesis of QD materials that are attractive for thermoelectricity such as PbS [150, 151], PbSe [148], PbTe [152], Bi$_2$Te$_3$ [153], Bi$_2$S$_3$, SnS [154], SnSe [155, 156], and SnTe [157] mainly for photovoltaic purposes. Controlling the kinetics of the reaction as well as using proper surfactants and precursors can result in a narrow size distribution. A narrow size distribution, can potentially boost the thermopower and reduce the lattice thermal conductivity through size effects. Most promising, synthesis of a defect-free QD superlattice as per [149] can improve electrical properties through delocalization of charge transport.

2.3. Hydro/solvothermal and microwave synthesis of thermoelectric nanomaterials

In a hydro/solvothermal process, the synthesis constituents such as precursors, solvents, surfactants, and reduction agents are allowed to react under a high-pressure and temperature, usually in a sealed Teflon autoclave. In microwave synthesis, the reaction is sealed and heated by microwave radiation allowing for faster processing on the order of minutes. Several studies have reported the use of hydro/solvothermal synthesis of materials for thermoelectric applications such as PbTe [158], Bi$_2$Te$_3$ [159, 160], La$_{0.2}$Bi$_{1.8}$Te$_3$ [161], CoSb$_3$ [162], PbTe nanowires [163], nanoboxes [164], and nanocubes [165], Sb$_2$Te$_3$ [166–170], Sb$_2$Te$_2$–Te [171], (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ [172–174], S-doped Ag$_2$Te [175], Sn$_2$Sb$_2$Te$_5$ [176], and p-type Sb$_2$Te$_3$/poly(3,4-ethylenedioxythiophene) [177]. The hydro/solvothermal method can also be used as a post-synthesis treatment to modify already made materials via grain boundary engineering. Ji and Tritt et al [160] reported modification of commercial p-type (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ powders by a hydrothermal treatment in a solution of AOH, and ABH$_x$, where A = Na, K, and Rb (figure 7). The untreated and treated x-ray diffraction data showed no extra peaks and suggested no intercalations or formation of a new crystalline phase. However, a hump feature was observed which was attributed to an amorphous constituent of a new phase which dramatically changed thermoelectric properties. Selected area electron diffraction (SAED) patterns of the treated samples showed cubic symmetry about the hexagonal symmetry of the un-treated samples, suggesting the existence of a secondary crystallinity from the bare materials along with a non-crystalline phase. An interesting observation was that this coating layer could be easily removed by a short ultrasonication, suggesting that the coating layer is loosely bound to the parent material which also introduces an elastic mismatch at the boundaries. Transport measurements indicated that the power factor was retained upon post-synthesis hydrothermal surface treatment, and even increased for Rb treatment. The electrical conductivity was improved due to an enhancement of carrier concentrations resulting in overall improvement of the thermoelectric power factor, $\sigma S^2$. All surface-treated samples exhibited lower thermal conductivities compared to those of the bare (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$. In
the case of Na treatment, a 15% reduction in room temperature thermal conductivity was reported.

Microwave rapid-synthesis methods have been used for preparation of a large variety of materials \[178-180\]. Studies that used microwave-assisted synthesis for thermoelectric applications include Sb$_2$Te$_3$ \[181, 182\], TiNiSn \[183\], TiNiSb$_{0.05}$Sn$_{0.5}$ \[184\], Bi$_2$Se$_3$ \[185\], Cu$_3$(Sb$_{0.94}$In$_{0.06}$)Se$_4$ \[186\]. Thermoelectric measurements of a TiNiSn and TiCoSb ternary intermetallic system prepared via a rapid microwave-assisted method showed $zT$ values $\sim$0.4 at a temperature of 780 K \[187\]. Mehta and Ramanath \textit{et al} \[35\] reported synthesis of sulfur-doped $n$- and $p$-type pnictogen (Bi, Sb) chalcogenide nanoplates by a microwave assisted method. In the synthesis, thioglycolic acid (CH$_2$COOHSH) was used as the structure directing agent which also acted as the source of sulfur-doping. It was observed that increasing the microwave dose resulted in larger plates with little changes in their thickness ($\sim$5–20 nm). The dried powders were packed into a pellet using a hydraulic press, resulting in a density $\sim$60%–70%. The pellets were then sintered under vacuum at $10^{-7}$ Torr and 300°C–400°C in order to obtain compacted pellets with relative densities of $\sim$92%. The samples showed high room temperature electrical conductivities in the range from 300 to 2500 S cm$^{-1}$. Bismuth chalcogenide samples exhibited $n$-type behavior and antimony chalcogenide samples showed $p$-type behavior, although Bi$_2$Te$_3$ is known to be $p$-type in the presence of bismuth anti-site defect acceptors common in bulk synthesis \[8, 188\] and $n$-type in the presence of chalcogen vacancies \[189\] and oxidation \[190\] such as has been reported for single-crystal (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ nanoplates \[135, 191\]. The observed change in the behavior of the microwave-synthesized materials was attributed to the sulfur doping. Having high power factors and very low thermal conductivity ($0.5 \leq \kappa \leq 1.4$), the microwave synthesized samples demonstrated high thermoelectric performance with $zT$ as high as 1.1, which is 25%–250% higher than those of bulk counterparts and alloys \[8\].

2.3.1. Outlook. Hydro/solvothermal and microwave-assisted syntheses can be used for large-scale production of thermoelectric nanomaterials. Both methods show a flexibility for tailoring structures and controlling bulk and surface chemical compositions. Similar to all solution-based methods, there is a possibility of self-doping during synthesis through reaction components such as impurities in the precursors, solvents, and surfactants and can be either beneficial or detrimental to thermoelectric performance. The work conducted by Mehta
And Ramanath et al. [35] showed that the traditional view of bottom-up materials as possessing too low a quality—especially regarding electrical conductivity—to perform well as thermoelectrics is not appropriate. Using proper additives to dope the samples, e.g. with sulfur, and with a post-treatment method to remove the insulating organics, e.g. thermal annealing, can greatly enhance the electrical conductivity. This indicates the adaptability of microwave-assisted synthesis for mass productions, where even a domestic microwave can perform the reaction in a time period of \( \sim 30-60 \) s.

2.4. Flexible thermoelectrics

Flexibility for thermoelectric devices opens opportunities for daily applications such as wearable modules that can operate using body heat and cooling by natural convection. Although device efficiencies and power densities are low, we will review important advancements in this application area where bottom-up synthesis is uniquely suited to make advances in this technology. Fabrication of a flexible thermoelectric for power generation was demonstrated by coating PbTe onto flexible glass fibers [192]. In the process, fibers were placed into a PbTe colloidal nanocrystal solution. After drying, the native insulating ligand was exchanged in a solution of 0.1 M hydrazine diluted with acetonitrile. After washing with anhydrous acetonitrile, the samples were dried again. The procedure was repeated until the desired thickness of PbTe was obtained (figure 8).

A foldable thermoelectric device was fabricated by embedding polyaniline (PANI), and poly(3-hexylthiophene) (P3HT) in a matrix of Au-doped carbon nanotubes (CNTs) [193] (figure 9). This device demonstrated a \( zT \) of 0.2 and a power generation of 1.74 \( \mu \text{W} \) were measured in a module of seven \( p-n \) junctions with a 20 K temperature difference operating at room temperature. Although this advancement is promising, we note the maximum power density of \( \sim 0.4 \mu \text{W cm}^{-2} \) is, by nearly two orders of magnitude, too low for practical applications.

CNT-based flexible thermoelectrics have also been demonstrated using \( n \)-type Ag\(_2\)Te nanoparticles [194]. After the composite nanoparticle/CNT was synthesized, the thiol-capping ligands on the sample surfaces were removed by thermal annealing at 400 °C. A reduction in the electrical conductivity data was observed due to the phase change of Ag\(_2\)Te from a monoclinic structure (\( \beta \) phase) to a face-centered cubic one (FCC, \( \alpha \) phase). Samples showed a Seebeck coefficient in the range of \(-30 \sim -228 \mu \text{V K}^{-1}\), electrical conductivity of 100–200 S cm\(^{-1}\), and total thermal conductivity as low as 0.7 W m\(^{-1}\)K\(^{-1}\) over the temperature range of 325–525 K [194]. To create flexible materials based on semiconducting inorganic nanomaterials alone, a five-step vacuum filtration fabrication of a Cu\(_{1.75}\)Te nanowires/poly(vinylidene fluoride) (PVDF) (2:1) composite was developed [195] which incorporated high pressure processing to increase the interparticle conductance (figure 10). A room-temperature thermopower of 9.6 \( \mu \text{V K}^{-1}\) and electrical conductivity of 2490 S cm\(^{-1}\) with a power factor of 23 \( \mu \text{W m}^{-1}\)K\(^{-2}\) were measured [196].

Paper-based thermoelectric generators have also been developed through impregnation by dipping cellulose paper into solutions of \( p \)- and \( n \)-type colloidal QDs (PbS and
Figure 8. Flexible glass fibers coated with thermoelectric nanocrystals. (a) SEM image of the obtained coating of PbTe on glass fibers as a flexible thermoelectric material. (b) $zT$ values over the temperature range of 300–400 K. Adapted with permission from [192]. Copyright 2012 American Chemical Society.

Figure 9. Foldable Au-doped CNT/polymer thermoelectrics. (a) Schematic of the fabrication process and thermoelectric module geometry. (b) Maximum power output (black), maximum power output per area (red), and maximum power output per weight (blue) as a function of temperature difference $\Delta T$ at near room temperature. (Inset) Corresponding device current versus power curves. Adapted with permission from [193]. Copyright 2016 American Chemical Society.

Figure 10. Schematic of the sample fabrication process for an inorganic nanowire-based flexible composite thermoelectric film. (a) Cu$_{175}$Te nanowires are first vacuum filtered in order to form a film. (b) The obtained film is transferred onto a sacrificial glass substrate and is pressed under 30 MPa and (c) subsequently annealed at 150 °C under vacuum. (d) A poly(vinylidene fluoride) (PVDF) solution is drop-cast onto the dried sample. (e) By heating at 80 °C, the composite is peeled from the substrate and (f) the flexible thermoelectric composite is obtained. Reprinted with permission from [195]. Copyright 2015 American Chemical Society.
Bi-doped PbTe, respectively) [197]. To remove the native oleic acid ligands from the QDs, subsequent ligand exchange was performed by placing the paper into 0.1 M KOH in methanol for PbS QDs, and into 0.1 M NH4I in methanol for Bi-doped PbTe QDs. Preparation of a wearable fabric-based thermoelectric generator was reported using cotton and polyester yarns as the matrix, which was dip-coated by a composite of aqueous polyurethane, CNTs, and PEDOT:PSS [198]. The generators showed low values of optimal electrical conductivity (~138 S cm⁻¹) and thermopower (~10 μV K⁻¹), leading to a power factor of just 1.41 μW m⁻¹ K⁻² at room temperature. Modification of the PEDOT:PSS polymer thermoelectric [199] was demonstrated by adding small amount of chemically exfoliated MoS2 nanosheets, resulting in a Seebeck enhancement from 15 to 20 μV K⁻¹ without a significant reduction in electrical conductivity. Thus, a power factor more than 30 times higher than the CNT/PEDOT:PSS composite [198] was obtained (45.6 μW m⁻¹ K⁻²) with only a 4 wt% addition of MoS2 [199]. Other investigations on flexible thermoelectrics include Te nanowires/reduced graphene oxide (rGO) [200], n-type Cu doped Bi2Se3 nanoplates [201], Ni/PVDF nanocomposites [202], and multiwall carbon nanotubes/PVDF [203].

2.4.1. Outlook. Although these results demonstrate a low $zT$, and also very low power outputs, the synthesis techniques could be promising for other material chemistries or composites at optimum doping concentrations, such as increasing the conductivity of flexible oxide-based composites [196]. Substrates such as PVDF, cotton, polyester, carbon nanotubes and rGO can all be used as flexible supports. Despite the practical production issues for daily use of these composites as wearable fabrics [204–206], many questions and concerns remain such as weight, cost, biological compatibility, stability, and efficiency require continued and thorough investigation. An encouraging production method is to design inks containing materials printable on flexible and robust fabrics [207–210]. Although promising in terms of applications, the expectation for power production is still bound the Carnot limit of efficiency. For instance, the Carnot efficiency for an irreversible heat engine connecting a human at 37°C and an ambient environment at 20°C is 5.48%. If one uses the entire body surface area [211] (1.79 ± 0.181 m², error calculated as ± one pooled standard deviation [212] from different populations) and a daily energy output of 14.51 MJ day⁻¹ [213], we can estimate an adult will generate a heat on the order of 167.9 W (corresponding to a flux of 9.4 ± 0.9 mW cm⁻²). In the Carnot (upper) limit of efficiency, this corresponds to power output of 9.2 W (corresponding to 513 ± 6 μW cm⁻²). For $zT_{\text{device}}$ on the order of 1, the efficiency will be on the order of 0.96% and power output will be on the order of 1.61 W (corresponding to 90 ± 1 μW cm⁻²). With a goal of producing 5 W from a wearable thermoelectric skin, $zT_{\text{device}}$ will need to be improved to at least 10. Our estimate of the upper limit of power density that can be produced from human-based thermoelectric power generation is shown in figure 11.

3. Thermoelectric phenomena related to enhancing performance in self-assembled nanomaterial systems

3.1. Quantum confinement effects for thermopower enhancement

Quantum confinement effects are responsible for modification of the electron density of states (DOS) in low dimensional thermoelectrics as described by e.g. Hicks and Dresselhaus for Bi2Te3 nanowires [214, 215] and thin films [214]. If the size of a semiconductor is significantly small, then the constraining morphology will affect the electron wavelength. In photovoltaic applications, the quantum confinement effect is well known as a phenomenon that occurs when the particle is smaller than the Bohr radius of an exciton (electron–hole pair) [216]. In thermoelectric applications, the quantum confinement effect is of interest because it can change the band gap, DOS, and Seebeck coefficient [216–218]. To explain this for the cases of metals and degenerate semiconductors, the Mott formula for the Seebeck coefficient can be used [219]

$$S = \frac{\pi^2 k_B^2 T}{3q} \left\{ \frac{d \ln |\sigma(E)|}{dE} \right\}_{E=E_F},$$

where $S$ is the Seebeck coefficient, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the charge of the carriers ($-e$ for electron and $+e$ for holes), $\sigma$ is the electrical conductivity, $E$ is the energy and $E_F$ denotes the Fermi
energy). It should be mentioned that the Mott formula is chosen rather than the general Seebeck coefficient equation derived from the Boltzmann transport equation for the sake of simplicity of understanding the argument. Because the electrical conductivity is related to the carrier concentration and mobility through \( \sigma = ne\mu \), where \( n \) is the carrier concentration and \( \mu \) is the mobility, one can rewrite equation (9) as:

\[
S = \frac{\pi^2 k_B^2 T}{3q^2} \left\{ \frac{1}{n} \frac{d n(E)}{dE} + \frac{1}{\mu} \frac{d \mu(E)}{dE} \right\}_{E=E_F}.
\] (10)

From equation (10), it is understood that the Seebeck coefficient can be enhanced by two ways: (i) increase the energy dependence of the carrier concentration and (ii) increase the energy dependence of the mobility, both at the Fermi energy. The carrier concentration depends on the DOS at the Fermi energy. This means that a perturbation in the DOS near the Fermi level will increase the energy dependence of carrier concentration and therefore the Seebeck coefficient. This is also suggested using Mahan and Sofo’s [217] theory which a Dirac delta function-shaped DOS near the Fermi level was predicted to maximize the figure of merit. In practice, this can be achieved by having a distortion in the DOS resulting from resonant-level doping [220] or by having a delta-function-like DOS. This DOS, highly localized in energy, can be obtained through the quantum confinement effect. It is important to remember that, in both cases, the DOS singularity has to be properly aligned within \( \pm 2.4k_BT \) of the Fermi level in order to maximize \( zT \) [217]. They also found that having two delta-functions or a background DOS will lower the ideal maximum \( zT \). The effect of the background DOS will be significant, a 25% decrease in the maximum \( zT \) was predicted for only a 10% contribution from background DOS near the Fermi energy.

Another feature of the confinement effect is the widening of the electronic band gap when the particle size becomes smaller than its exciton’s Bohr radius [221]. Figure 12 illustrates size dependency of the optical band gap in (Cd, Pb)(S, Se, Te)-family QDs [222].

The measured optical band gap \( E_g^{\text{opt}} \) from the absorption spectra can be related to the actual transport band gap \( E_g \) by the Brus theoretical particle-in-a-box model equation [224]

\[
E_g = E_c - E_v = E_g^{\text{opt}} + 1.786 \cdot \frac{q^2}{4\pi \varepsilon_0 QD R}.
\] (11)

where \( E_c \) is the conduction band minimum, \( E_v \) is the valence band maximum, \( q \) is the carrier charge, \( R \) is nanoparticle radius which can be measured by TEM or determined from the empirical correlations based on the first maximum absorption peak [225–227], \( \varepsilon_0 \) is the dielectric constant of the QD and \( \varepsilon_0 \) is the vacuum permittivity. Thus, the enhancement of nanocrystal optical band gap is an indication of an electronic transport band gap widening. If the change in band gap is much larger than the changes in the Fermi energy due to size effects, the band edges distance themselves from the Fermi energy as the nanocrystal size decreases. As a result, the difference between the Fermi energy and the average energy of the mobile carrier increases, and this means that the Seebeck coefficient will increase [228]. This can be better understood by deriving the Seebeck coefficient expression starting from Boltzmann transport equation with the relaxation time approximation as [229]

\[
S = \frac{1}{qT} \cdot \left[ \frac{1}{E=0} \frac{\partial f_0}{\partial E} \cdot D(E) \cdot E \cdot (E - E_F) \cdot \tau(E) \cdot dE \right]^{-1},
\] (12)

where \( f_0 \) is the Fermi–Dirac distribution, \( D \) is the DOS, and \( \tau \) is the relaxation time. This equation indicates that Seebeck coefficient is proportional to the average energy difference from the Fermi level. This difference is weighted by the differential electrical conductivity at each level (integrand in the denominator of equation (12)) [229]. Therefore, if the Fermi level remains unchanged, decreasing of the crystal size
The transport energy level $E_T$ is defined as the energy at which the hopping mobility is above zero, and for a $p$-type material $A$ is a roughly temperature independent constant called the ‘heat-of-transport’. In nanocrystals, unlike the bulk materials, $E_T$ is not necessarily the edge of the DOS because of the low probability of finding a state with an energy difference smaller than $k_BT$. Here $E_T$ is defined as the energy level that the carrier can hop with a noticeable mobility [231]. It is fruitful to understand the physical meaning of each term in equation (14). The first term indicates the average entropy change of the system due to thermal excitation of charge carriers to the transport level, and the second term is proportional to the average vibrational energy of the carriers beyond $E_T$ as they hop, weighted against their contribution to the total conduction [231, 232] (see figure 14). The value of $A$ lies between 1 and 2 for bulk semiconductors and can be larger for the case of QD systems which have a sharper DOS profile [230, 231, 233, 234]. The curvature of the optical absorption data, as the optical DOS, can be used to estimate the energy dependency of DOS and therefore the value of $A$ [231]. By plotting the Seebeck coefficient against the inverse temperature, one can extract $E_T$ from the slope, and $A$ from the ordinate intercept which corresponds to $T\to\infty$. There can be other contributions to the ordinate intercept such as the temperature dependency of DOS [235–238] or $E_F$ [233, 239]. Ko and Murray [231] used the Fritzsche general expression [230] in order to examine $E_T–E_F$ as a function of size in $p$-type PbTe QDs. The largest QDs with an average size of 11.5 nm, they found that the value of $E_T–E_F$ was smaller than half of the optical band gap energy showing that the Fermi energy position was below the mid-gap energy. As the size of the QDs decreased, the band separation increased due to quantum confinement effects (see figure 14). As the authors stated, knowing the value of $E_T–E_F$ can be beneficial, because for a known effective DOS and electrical conductivity, one can use this to estimate the carrier concentration. In addition, if $E_T$ is estimated, the change in position of $E_T$ can be tracked.

Wang and Majumdar et al [228] reported the first thermopower measurements of a solution-based $p$-type PbSe QD superlattice with a strong quantum confinement effect. It was observed that as the nanocrystal size decreased from 8.6 to 4.8 nm, the thermopower increased from 700 to 1150 $\mu V K^{-1}$ due to the quantum confinement effect. This size reduction also resulted in an order of magnitude decline of the electrical conductivity due to a decrease in the carrier concentration. Upon exposure of their material to oxygen, the conductivity increased by about an order of magnitude due to $p$-type doping, with a commensurate decrease in thermopower from 760 to 440 $\mu V K^{-1}$. Additionally, post-treatment in the presence of hydrazine induced $n$-type doping. A transformation of Te nanowires to PbTe nanowires in a solvothermal reaction in a Teflon lid autoclave was reported by Tai and Guo et al [163] in their proposed reaction, Pb$^{2+}$ cation were reduced to Pb atom in the presence of hydrazine which then reacted with Te and formed PbTe nanowires with diameters ~20–40 nm. The transport properties measurements were carried out on thin films, showing a high thermopower of 628 $\mu V K^{-1}$ at room temperature. Performed DFT calculations indicated an enhancement of the local DOS near the Fermi level as the
nanowires diameter decreased from 2.305 to 0.326 nm. Yan and Ma et al. [240] reported a single step solvothermal synthesis of PbTe nanowires with a diameter range of 10–30 nm. Measurements of the transport properties of thin films on glass substrates showed a high thermopower of $S > 470 \mu V K^{-1}$ at $T = 375$ and 425 K but a high resistivity of $2 \times 10^{-3} \Omega m$ at room temperature. No measurements for the mobility were reported.

Additional studies of quantum confinement effects yield qualitatively similar results, although the effect is less intense for nanowire-based systems compared to QD systems. Zhou and Yan et al. [241] reported the transport properties of PbTe–PtTe$_2$ multilayer nanoparticles sprayed on glass substrates. They observed that as the phase ratio of PbTe to PtTe$_2$ was increased from 0.33 to 0.67, the average particle size grew from 30 to 52 nm. The Seebeck measurements of the pure PbTe particles exhibited a $p$-type material with $S > 500 \mu V K^{-1}$ over a temperature range of 300–600 K. Quantum confinement effects were suggested as the reason for the high thermopower. The introduction of Pt to the nanoparticles, changed the material from $p$-type to $n$-type. As the phase ratio of PbTe decreased from 0.67 to 0 (pure PtTe$_2$), the maximum of thermopower declined from 155 to 5 $\mu V K^{-1}$. Thermopower of the samples with a PbTe ratio of 0.67 and 0.5 were 50%–100% higher than that of bulk $n$-type PbTe with similar charge carrier concentrations. As the ratio of PbTe decreased, the electrical conductivity increased and for the ratio of 0.5, a maximum electrical conductivity of $1 \times 10^{10} S m^{-1}$ was reported. Maksym and Talapin et al. [242] synthesized PbTe nanocrystals capped with Sb$_2$Te$_3$ molecular metal chalcogenide complexes (MMCs) by replacing the oleic acid ligands. Another approach involved preparation of single phase (Bi, Sb)$_2$Te$_3$ and bi-phase PbTe–Sb$_2$Te$_3$ starting from Bi$_2$S$_3$ and PbS. The conversion of Bi$_2$S$_3$ and PbS to Bi$_2$Te$_3$ and PbTe was completed through an anion exchange of $S^2$ by $Te^2$ by reacting Bi$_2$S$_3$ and PbS with Sb$_2$Te$_3$ molecular metal chalcogenide complex containing excess Te. PbTe capped with Sb$_2$Te$_3$ showed a large $p$-type thermopower of $750 \mu V K^{-1}$, more than a two-fold increase versus that of the bulk PbTe at a comparable carrier density ($1.3 \times 10^{19} cm^{-3}$) [242].

The quantum confinement effect was proposed as an explanation for the high value of the Seebeck coefficient due the small size of the PbTe nanocrystals (2–30 nm) and a large exciton Bohr radius of 46 nm for PbTe [242, 243]. Unlike Wang and Majumdar et al.’s [228] study on PbSe, the hydrazine treatment of MMC-capped PbTe did not transform the material from $p$-type to $n$-type owing to the excess of Te in Sb$_2$Te$_3$ MMCs [242]. The measurements of (Bi, Sb)$_2$Te$_3$ thin films exhibited $p$-type Seebeck coefficients of 170–250 $\mu V K^{-1}$. An $n$-type Seebeck of $-245 \mu V K^{-1}$ was obtained through Se doping in the form of (Bi, Sb)$_2$(Te, Se)$_3$. We note that for larger diameter QD systems, doping will have a greater impact on tuning the thermopower than size control. For example, altering the carrier concentration by doping with iodine was found to dominate the thermopower of $n$-type PbTe QDs with diameters of 12, 29, and 48 nm, and negligible size dependency was found for this diameter range [244].

3.1.1. Outlook. Thermoelectric materials with large exciton Bohr radii [216] such as PbS (20 nm) [216], PbSe (46 nm) [216], PbTe (46 nm) [242, 243], InAs (34 nm) [216], and InSb (54 nm) [216] are good candidates for increased thermopower through quantum size effects. Considering the characteristic sizes needed to gain from this effect, bottom-up synthesis techniques are the optimal tools for the preparation of materials with crystal sizes capable of exhibiting confinement effects. Many synthetic recipes capable of tailoring the crystal size in different configurations such as quantum dots [18, 152, 245–247], thin nanosheets [248, 249], nanowires [250, 251], and nanorods [252–254] have been successfully developed. The electronic band gap widening measured by the absorption spectra of nanocrystals alone might not be sufficient to attribute thermopower enhancements to confinement effects. In this regard, an assessment of mobility and carrier concentration measurements is essential because a thermopower enhancement can be the result of a change in carrier concentration as well. In addition, the confinement effect does not necessarily guarantee a high thermoelectric

Figure 14. Fritzsch analysis of the Seebeck coefficient of QD systems. (a) Absorption spectra of PbTe QDs with different diameters. The data was used to calculate the curvature of the optical DOS for the heat-of-transport estimation. (b) Thermopower measurements plotted against the inverse temperature. The slope is an indication of the $E_F$–$E_T$ values. (c) Schematic of the evolution of $E_F$–$E_T$ as a function of size due to quantum confinement effects. Reprinted with permission from [231]. Copyright 2011 American Chemical Society.
power factor. The location of the chemical potential is the other factor that should be controlled carefully in these materials.

### 3.2. Energy filtering effects for thermopower enhancement

An additional approach to enhance the Seebeck coefficient is to increase the second term in equation (10), i.e. by increasing the energy dependence of the mobility at the Fermi energy. Starting from the Boltzmann transport equation with the relaxation time approximation and applying Ohm’s law in the presence of an electric field, the carrier mobility for a semiconducting material can be written in the form of [229]

$$\mu = -\frac{2q}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} \cdot D(E) \cdot E \cdot \tau(E) \cdot \text{d}E,$$

where \( q \) and \( m \) are the electron/hole charge and mass, respectively, \( \tau \) is the relaxation time, and \( f_0 \) is the Fermi–Dirac distribution. Equation (15) clearly shows that the energy dependence of mobility at the Fermi level can be enhanced by increasing the energy dependence of the scattering time i.e. \((\partial \tau/E)|_E\). This implies that the charge carriers should be scattered differently according to their energies which is called the carrier energy filtering effect. Using the relaxation time approximation for small deviations from equilibrium, applying to elastic scatterings where energy is conserved, and for an isotropic scattering of a two-particle system, one can neglect the spatial non-uniformity and derive the following for the distribution function

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}, \text{ hence } f = f_0 + C \cdot \exp\left(-\frac{t}{\tau}\right),$$

where \( C \) is a constant of integration. This expression indicates that the relaxation time is the time needed for a system to relax from a nonequilibrium distribution function to an equilibrium state

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the Seebeck coefficient through a hole-filling effect in Ag/oxide/Sb$_2$Te$_3$–Te heterostructures with $zT \approx 1$ at 460 K. With an intermediate oxide layer consisting of aluminum oxide ($\sim 1–2$ nm) and hafnium oxide ($\sim 1$ nm), a metallic silver phase was coated on a telluride layer (figure 17). Due to the high solubility of silver in tellurium, the oxide layers were used to prevent the formation of silver and tellurium alloys which might take place during annealing at a mild temperature on the order of 200 °C. The silver layer was grown by electron beam evaporation and rapid thermal annealing. The oxide layers were deposited using atomic layer deposition (ALD). Sb$_2$Te$_3$ films with excess Te were synthesized using a hydrazine-based chemistry technique. The hafnium oxide layer was deposited in order to protect the aluminum oxide layer against etching in hydrazine. The thickness of this oxide layer was deemed critical because a very thin layer could not prevent alloying of silver with tellurium, which will increase the carrier concentration of Sb$_2$Te$_3$–Te and therefore lower the Seebeck coefficient as the material becomes a degenerate semiconductor. On the other hand, an overly thick layer can interfere with the efficient transmission of carriers through the barrier and thus decrease the electrical conductivity. Transport properties for three samples of Sb$_2$Te$_3$–Te (without an energy barrier), Ag/Sb$_2$Te$_3$–Te (with Ag as energy barrier) and Ag/oxide/Sb$_2$Te$_3$–Te were reported, with the highest electrical conductivity and lowest Seebeck coefficient measured in the sample with the Ag layer and without oxide protection due doping. The sample with the Ag layer as the energy barrier and the oxide layer to avoid any unwanted...
doping showed the maximum power factor, around \(10 \mu W \text{cm}^{-1} \text{K}^{-2}\) at 300 K, which was attributed to hole-filtering effects. Even with the protection of the oxide layer, a slight amount of hole-doping was observed due to Ag impurities. The Ag concentration was \((3-6) \times 10^{19} \text{cm}^{-3}\) in the oxide-protected sample compared to \(1.6 \times 10^{20} \text{cm}^{-3}\) in the sample without any oxide layer protection.

The use of high energy carrier filtering effect in the bottom-up thermoelectric materials is not limited to the low temperature chemistry of the metal chalcogenides in hydrazine. In an study carried out by Scheele and Weller et al [131], PbTe nanoparticles were synthesized in a solution of diphenylether capped by oleic acid as the ligand. A slight amount of acetic acid was necessary in order to obtain the octahedral structures whereas only cubic structures were obtained in its absence. The organic ligand was exchanged with phosphonic acid in a hexan solution which was then removed by adding a solution of anhydrous ammonia in methanol. The obtained powder with nanoparticle sizes of \(~30 \text{ nm}\) was compacted into pellets with densities of 89% of the theoretical density using SPS. EDS analysis revealed presence of oxide species originated from the reaction environment. A density-functional calculation along with XPS data [271] have shown that such oxygen complexes form chemical bonds by transferring charge from tellurium atoms in PbTe. Upon oxidation, the material was depleted of Te and became Pb-rich. The calculation confirmed that PbTe is less resistant to oxidation than PbS. The chemisorbed surface oxygen can cause trapping of carriers at grain boundaries and form energy barriers that inhibit the conduction of charge carriers between grains [258, 272]. This means that these oxide layers can reduce the electrical conductivity and enhance the Seebeck coefficient. An electrical resistivity one order of magnitude larger than that of the bulk PbTe and a large thermopower of \(625 \mu W \text{cm}^{-1} \text{K}^{-2}\) (\(S \sim 615 \mu V \text{K}^{-1}\)) at room temperature was reported [131]. The authors argued that it was unlikely that such a high Seebeck coefficient was a result of a low carrier concentration because the Seebeck coefficient dropped to a value of \(~10 \mu V \text{K}^{-1}\) at high temperature (550 K). This decline indicated that more of the low energy holes were possibly able to escape the barrier at high temperature. A barrier height of \(E_B = 140 \text{ meV}\) was estimated by using Seto’s equation [273] for modeling the effective mobility of carriers trapped in grain boundaries of a polycrystalline material

\[
\mu_{\text{eff}} = L q \cdot (2 \pi m^* k_B T)^{-1/2} \cdot \exp \left( - \frac{E_B}{k_B T} \right),
\]

where \(L\) is the crystallite characteristic size and \(m^*\) is the carrier effective mass. This height of the barrier did not result in an optimal trade-off between decreasing the electrical conductivity and increasing the Seebeck coefficient. The investigators lowered the barrier height by replacing the oxide layer with a shell composed of PbS in a PbTe–PbSe core–
shell structure with a larger average crystal size. The structure was found to be nano stars with tip-to-tip lengths of ~75 nm, and with tellurium in the core and selenium in the arms. Adding this layer of PbSe did not prevent surface oxidation, as oxygen was detected by EDS. The first cycle measurement of electrical conductivity and Seebeck coefficient revealed a strong temperature dependency. The Seebeck coefficient decreased from 530 μV K⁻¹ at room temperature to 0 at 470 K. The material became n-type with a maximum Seebeck coefficient of −360 μV K⁻¹ at 500 K and decreased to −100 μV K⁻¹ at 575 K. The authors suggested that due to a thermal alloying of the two chalcogen phases (PbSe, PbTe), Se acted as an n-type dopant at high temperatures in the originally p-type PbTe, causing the Seebeck coefficient to change sign. Another reason was attributed to an elimination of the oxide barriers by thermal annealing during the first cycle. In the second cycle, however, the sign inversion in the Seebeck coefficient was not seen. This observation indicates the importance of post-synthesis processing such as high-temperature annealing and SPS in order avoid thermally induced solid-state chemical reactions during material performance measurements, and to improve material stability. Post-synthesis processing needs to be optimized and conducted at temperatures high enough for any irreversible solid-state reactions or organic species decompositions to occur prior to evaluating thermoelectric performance. This is essential for stability and reproducibility of the results, as the sign inversion in the Seebeck coefficient measurement of Scheele and Weller et al [131] was irreversible and only observed in the first measurement cycle. Analyses such as thermal gravimetric analysis (TGA)/differential scanning calorimetry (DSC) should be performed in order to track thermal reactions, phase changes, and decompositions as well as determining the proper post-synthesis temperature limit. A change in sign of the temperature dependent Seebeck coefficient has been reported in a number of bottom-up thermoelectric studies [38–40, 274, 275].

Zhang and Wu et al [276] reported a solution based synthesis of Te–Bi₂Te₃ barbell nanowire heterostructures that exhibited energy filtering effects with a thermal conductivity as low as 0.309 W m⁻¹ K⁻¹ at 400 K. After synthesizing Te nanowires in a 3-neck flask continuously purged with N₂ in a Schlenk line, with hydrazine as the reducing agent, bismuth nitrate pentahydrate was added as the source of Bi and the heterostructure was obtained at the end of the reaction. PbTe–Bi₂Te₃ heterostructure was also prepared by adding lead acetate tributyrate. The measurements were carried out on a 63% dense pellet made by a hot press technique. Hwang and Lee et al [277] used metal acetate precursors (Co, Mn, Zn, Pd, Ni, Tb and Mo acetate) in an ethyl acetate medium in order to create embedded nanoparticles in Bi₀.₅Sb₁.₅Te₁. The starting material was prepared using a typical solid-state synthesis. This study used a solution chemistry technique as a complementary process to the solid-state material preparation. The zT of the starting material was improved from 1 to 1.4 in the Mn decorated sample, close to room temperature. Thermopower enhancement due to the energy filtering effect can be ideally followed by a decrease in the lattice thermal conductivity due to the phonon scattering [277]. In a recent study, Jo and Lee et al [278] used Te in order to modify the interfaces in a Bi₀.₅Sb₁.₅Te₃ starting material. Te was chosen because of its appropriate work function with respect to the main material, as a barrier, and its low solubility in (Bi, Sb)₂Te₃ which is necessary to avoid any unwanted doping at high temperatures. The ball-milled starting materials was mixed with a solution of Te₂⁺ polyanion, prepared by mixing Te powder with ethanethiol and ethylenediamine. Both thin films and SPS prepared pellets were tested. The samples with Te interfacial layers had higher motilities than the bulk sample indicating improved charge carrier transport across interfaces. The carrier concentrations of the materials with Te interfaces were higher than that of the bulk sample which was attributed to an increase in the distance between E₈ and the valence band by the band bending effect at the interfaces. All the samples showed improved power factors compared to that of the bulk with a maximum of 6-fold improvement. A Pisarenko plot of the data showed enhancements of the effective masses for all the Te-treated materials compared to the bulk (figure 18). For the SPS-pelleted samples, power factor and zT improvements of 28%–42% and 40%, respectively, with a zT of 1.3 were measured. The corresponding formula for Pisarenko plot is expressed as [279]:

\[
S = \frac{\pi^2 k_B^2 T^3}{3q} \left( \frac{8m^*}{\hbar^2} \right) \left( \frac{\pi}{3n} \right)^{2/3} \left\{ 1 + \frac{d \ln \lambda_s}{d \ln E} \right\},
\]

where \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(m^*\) is the carrier effective mass, \(q\) is the carrier charge, \(h\) is Planck’s constant, and \(n\) is the carrier concentration, and \(\lambda_s\) is the scattering distance [280]. In the limit of single parabolic band and energy-independent scattering assumptions, the term \(d \ln \lambda_s/d \ln E\) is zero [48].

In a recent study performed by Lee et al [281], Au nanodots were used as the energy barriers in n-type Bi₂Te₃ nanotubes achieving a 67% zT improvement due to a 27% enhancement in power factor and a 22% reduction in thermal conductivity at 440 K, and a maximum zT of 0.95 was reached at 480 K (figure 19). A Pisarenko plot of the data showed that Au–Bi₂Te₃ exhibited a ~25% higher effective mass than the untreated Bi₂Te₃ nanotubes, bulk n-type Bi₂Te₃, and previously reported Cu [282] and Pt [283] embedded in n-type Bi₂Te₃. One reason might be due to the lower work function of Au compared to Pt with respect to Bi₂Te₃. The barrier energy of Pt is \(E_B = 250\) meV whereas for Au, \(E_B = 100\) meV.

In a recent study by Zaia and Urban et al [284] the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) was used to introduce Cu islands to Te nanowires as barriers, in the form of Cu₁.₇₅Te alloy. The barrier height was 150–300 meV. Because the height of the barrier was higher than the optimum value of 100 meV, some of the hot carriers were expected to be scattered as well. The Seebeck coefficient was 16% higher than unalloyed nanowires and was higher than previously
reported for Cu_{1.75}Te nanowires [195]. The authors attributed this enhancement to the energy filtering effect by transportation of the holes from Te through the Cu coating and suggested that some of the holes might leak through the polymer as its height was 150 meV which was lower than that of the Cu_{1.75}Te barrier.

A small molecule, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO–OH), was also demonstrated as an energy barrier for poly(3,4-ethylenedioxythiophene) doped with poly (styrenesulfonate) (PEDOT:PSS) polymers by Tomlinson and Hilsmier et al [285] TEMPO–OH was chosen because its singularly occupied molecular orbital (SOMO) energy level was

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**Figure 18.** Grain boundary engineering for enhanced thermoelectric power factor in (Bi_{0.25}Sb_{0.75})_{2}Te_{3}. (a) Scanning electron microscopy image and (b) EDS elemental mapping of adjacent crystalline grains and their interfaces. (c) Band diagram at the interface between (Bi_{0.25}Sb_{0.75})_{2}Te_{3} and elemental tellurium. (d) Pisarenko plot of Seebeck versus carrier concentration for different loadings of Te. The density of states effective mass was calculated by equation (18) as m_{d}^{*}/m_{0} = 0.57, 0.98, 0.76, and 0.59 for 0, 5, 10, and 25 wt% Te, respectively, where m_{0} is the electron rest mass. Reprinted from [278], Copyright 2016, with permission from Elsevier.

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**Figure 19.** Dependence of the energy filtering effect on the metal work function. (a) Pisarenko plot showing Seebeck coefficient versus carrier concentration used in order to calculate the charge carrier density of states effective mass. Solid lines are the calculations for m_{d}^{*}/m_{0} = 0.8, 1.0, and 1.2, where m_{0} is the electron rest mass. A comparison between the work function of (b) Au and (c) Cu with respect to Bi_{2}Te_{3}. Au can act as a barrier whereas for Cu no energy barrier is formed. Adapted from [281] with permission of The Royal Society of Chemistry.
5.4 eV from vacuum, higher than the highest occupied molecular orbit (HOMO) of PEDOT:PSS (5.1 eV). The SOMO level of TEMPO–OH were calculated with cyclic voltammetry (CV) by using the equation \( E_{\text{HOMO}} = -(1.4 \pm 0.1)qV_{\text{CV}}-(4.6 \pm 0.08) \), where \( qV_{\text{CV}} \) is the product of elemental charge and molecular oxidation voltage relative to a reference solute in units of eV [286]. \( E_{\text{HOMO}} \) can also be measured by ultraviolet photoelectron emission spectroscopy (UPS) by measuring the ionization energy of the molecules, which is equal to \( E_{\text{HOMO}} \). The thermopower of the PEDOT:PSS sample with 2 wt% TEMPO–OH was 22 \( \mu \)V K\(^{-1} \) compared to 14 \( \mu \)V K\(^{-1} \) for the sample with 0 wt% of the open-shelled molecule. Other work regarding the concept of barrier energy filtering effect in bottom-up thermoelectrics include using composites of sodium carboxymethyl cellulose surfactant in Bi\(_2\)Se\(_3\) platelets [287], polyaniline (PANI) in multivall carbon nanotubes (MWCNT) [288], heterostructured grains in Bi\(_2\)Te\(_3\) [289], Te nanodots in Sb\(_2\)Te\(_3\) [290], PS in Bi\(_2\)Te\(_2\)S\(_0.3\) nanoplatelets [291], \( \gamma \)-Sn–Te in Sb\(_2\)Te\(_3\) [292], PbS nanoparticles in TiS\(_3\) [293], defective grain boundaries in exfoliated Bi\(_2\)Se\(_3\) [294] and PbTe [165], cetyltrimethylammonium bromide (CTAB) in electro deposited Sb\(_2\)Te\(_3\) films [290], and PANI in Au-doped CNT [193] and graphene/polymer/inorganic nanocrystal heterostructures [294].

### 3.3. Measurements of energy levels in semiconductors

A purposeful design and modification of a thermoelectric material requires comprehensive knowledge of the electronic band structure. Thus, we will discuss methods to experimentally obtain positions of the valence and conduction band edges, DOS, and the chemical potential. This information can be useful in order to design a material that can benefit from carrier filtering and size effects as discussed in the previous two sections. Figure 20 shows a schematic of the energy levels existing in semiconducting QDs as described in detail by Jasieniak and coworkers [223]. The same notation is kept here. If the vacuum energy level \( E_{\text{vac}} \) is taken as the reference zero point, the valence band energy is defined as the negative of ionization energy \(-IE\) and the conduction band edge is the negative electron affinity \(-EA\). The quasi particle band gap is defined as the difference between the ionization energy (IE) and electron affinity (EA), i.e. \( E_{\text{gap}}^{\text{QP}} = \text{IE} - \text{EA} \). The quasi-particle band gap of a QD consists of the bulk quasiparticle band gap \( E_{\text{gap}}^{\text{QP}}(\infty) \), the contributions of electron and hole quantum \((\epsilon^0)\) and dielectric confinement \((\Sigma^{pol})\) as \( E_{\text{gap}} = E_{\text{gap}}^{\text{QP}}(\infty) + \epsilon^0 + \sum^{pol} + \epsilon_{\text{h}}^0 + \sum^{pol}_{\text{h}} \). The quasi particle band gap can also be written in terms of the optical band gap \( E_{\text{gap}}^{\text{opt}} \), the direct Coulomb interaction in the electron–hole pair \( J_{\text{dir}} \) and the dielectric polarization energy \( J_{\text{pol}} \) as \( E_{\text{gap}} = E_{\text{gap}}^{\text{opt}} + J_{\text{dir}} + J_{\text{pol}} \). Using the Brus model with an effective mass approximation [221, 296] the direct Coulomb interaction and dielectric polarization terms can be replaced to derive the following approximation [223]

\[
EA \simeq IE - E_{\text{gap}}^{\text{opt}} = 1.786 \frac{q^2}{4\pi\varepsilon_{\text{QD}}\varepsilon_0 R} \left( \varepsilon_1^{-1} - \varepsilon_0^{-1} \right),
\]

\[
E_{\text{gap}}^{\text{opt}} = \frac{q^2}{4\pi\varepsilon_0 R} \left( \varepsilon_1^{-1} - \varepsilon_0^{-1} \right),
\]
3.3.1. Outlook

Measurements of the energy levels in semiconductors is essential in order to design a high-performance thermoelectric material. These measurements can be used to validate *ab initio* calculations of the band structure which are essential to predict thermoelectric properties. UPS is the most popular method among those discussed as it provides comprehensive information on the band structure of occupied energy levels, chemical potential, and valence band edge. However, samples which are not robust may be affected by the high exposure of ultraviolet light needed in UPS [320]. CV is the most convenient technique for sensitive samples, however, its accuracy is difficult to estimate and depends on the experimental conditions used [223, 286].

3.4. Electrical conductivity

Electrical conductivity is related to electronic mobility (μ) and carrier concentration (n) through \( \sigma = ne\mu \) where \( e \) is the elementary electric charge. Mobility, defined by equation (15), is
an indication of the average ability of the charge carriers to move in the presence of an electric field. In semiconductors, the carrier concentration is determined by the position of Fermi level. To understand the relationship between the carrier concentration and Fermi level, one can use the estimation for a non-degenerate semiconductor with a single parabolic band [321]

\[ n = 2 \cdot \left( \frac{2\pi m^* k_B T}{h^2} \right)^{3/2} \cdot \exp \left( - \frac{E_F - E_0}{k_B T} \right), \]  

(20)

where \( m^* \) is the effective electron mass which is inversely proportional to the curvature of the band. Although flat bands with high effective masses can potentially result in a high Seebeck coefficients due to their large DOS, the mobility decreases due to this flatness. Decreasing mobility can be easily shown from \( \mu = e\tau_m/m^* \) where \( \tau_m \) is the momentum relaxation time. As described by Ioffe [322], the optimal carrier concentration \( n_o \) is a function of temperature and is expressed according to the following equation [322]:

\[ n_o = 2 \left( \frac{2\pi m^* k_B T}{h^2} \right)^{3/2} \cdot \exp(r), \]  

(21)

where \( r \) is defined according to \( l = l_0(T)E \) and \( l \) is the electron free path. Equation (21) is derived from \( \partial n/\partial n(zT) = 0 \) with the assumption that electronic thermal conductivity is small compared to lattice thermal conductivity, and therefore, thermal conductivity was considered independent of carrier concentrations. Corrections to this assumption and parameters for \( r \) can be found in [322].

Generally, bottom-up thermoelectrics are known to have poor electrical properties due to high interfacial densities and impurities which result in low electronic mobility. The low mobility originates from the defective or polycrystalline nature of some of these materials and impurities present in the precursors, solvents or ligands. The poor electrical conductivities and low mobility in these materials can be observed in their electrical conductivity versus temperature behavior [323, 324], which can be regarded as the main disadvantage of the bottom-up approach. However, many studies have reported dramatic improvements by applying post-treatment techniques as discussed in this section. Most of these investigations were conducted in aspiration for high performance photovoltaic or field effect transistor applications. The approach, however, can be adapted and benefit thermoelectric applications. A simple approach related to QDs is to remove the long and insulating native ligands used during the synthesis (e.g. oleic acid) and replace them with shorter and more conductive ligands. Talapin and Murray [325] reported that just by removing a fraction of the oleic acid, the interparticle spacing and electrical conductance changed from 1.5 nm and 10⁻¹¹ S cm⁻¹ to 1.1 nm and 3 × 10⁻¹⁰ S cm⁻¹, respectively for PbSe QDs. The conductance was further increased by 10 orders of magnitude through a post-treatment with a 1 M solution of hydrazine in acetonitrile, and a high field-effect electron mobility of 0.95 cm² V⁻¹ s⁻¹ was reported. However, after heat treatment at 100 °C, the material changed from n-type to p-type with a hole mobility of 0.12–0.18 cm² V⁻¹ s⁻¹ due to the desorption of hydrazine. Extending this methodology to a thermoelectric investigation of PbSe quantum dots demonstrated similar results; an 8 orders of magnitude improvement in the electrical conductivity was observed through a ligand exchange with Sn amalgamating solutions [326]. Kanatzidis et al [39] reported the removal of oleic acid ligands from the surface of PbTe₆S₇₋ₓ@PbS core–shell nanocrystals by room temperature.

Figure 23. Molecular metal chalcogenide complexes can be used as semiconducting ligands for QDs and other solution-based nanomaterials. Various colloidal nanocrystals are stable after ligand exchange with different metal chalcogenides. From [327]. Reprinted with permission from AAAS.
treatment in a solution containing HCl. The electrical conductivity improved by about 4-fold with a transition from semiconducting behavior to metallic because of the n-doping of the material by Cl\(^1\). A maximum \(zT\) of \(\sim 0.94\) at 700 K was reported.

In addition to ligand exchange, assembly of binary QD systems can reduce the interparticle distances and therefore improve the electrical conductivity. Urban and Murray et al [246] reported an assembly of PbTe and Ag\(_2\)Te QDs with a 100-fold increase in the conductance relative to the sum of each individual component. The improvement was correlated to an interparticle distance reduction from 1.7 to 0.3 nm on average. The ideal target is to connect the dots in the form of a superlattice with a complete delocalization of charge carriers.

A coherent and defect free structure, with complete delocalization of charge carriers throughout the superlattice, can lead to emerging and interesting physical properties such as Dirac cones [329, 330]. Recently, the first observation of charge transport through a highly ordered PbSe superlattice was reported by Whitham and Hanarath et al [149]. Colloidal PbSe nanocrystals of 6.5 nm diameter in hexane were dispersed on ethylene glycol. Then, the oleic acid ligand was replaced by ethylenediamine. It was proposed that this ligand selectively binds to Pb on [100] surfaces, causing these unprotected facets to orient and fuse together (see figure 6). The study confirmed delocalization of electrons due to the heterogeneity of the connections. As a demonstration of this approach for thermoelectric materials, a high \(zT\) value of 1.7 at 850 K was reported by Sheele and Weller et al [323] by ligand removal in sub-10 nm Bi\(_2\)Te\(_3\) nanoparticles. The removal process was performed using hydrazine hydrate etching followed by SPS. The material showed significantly reduced thermal conductivities with similar electrical conductivities as for bulk n-type Bi\(_2\)Te\(_3\). A post-synthesis treatment of Pb-chalcogenide nanocrystals with ALD has also been investigated [331]. The long length ligands were replaced by short ligands forming ordered nanocrystals with chalcogen rich surfaces. The unstable chalcogen rich surface was then transferred to a stable lead rich shell by using PbCl\(_2\). A high field-effect electron mobility of 4.5 cm\(^2\) V\(^{-1}\) s\(^{-1}\) was reported. To remove insulating ligands or other organic species, thermal annealing followed by a cold-press, hot-press, or SPS have been used for bulk nanostructured materials [35, 38] although this will lead to grain ripening and growth in addition to improving the interfaces. Another approach involves the use of a second phase in order to fill the voids between the interfacial boundaries of nanocrystals and weld them by SPS or hot-pressing under a high presser and temperature [332]. The successful implementation of such a strategy requires that nanoparticles react with the surface of the secondary phase and remain uniformly dispersed to avoid formation of a segregated phase. If this happens, there is a possibility of changing the electronic properties of the native material. In one ligand exchange process, Bi nanocrystals capped with (N\(_2\)H\(_4\))\(_3\)Sb\(_2\)Te\(_2\) were mixed and annealed with the ball milling beads with compositions of Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) and Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_{3.2}\) (7% excess Te) and mechanically reacted during the process [333]. The observation indicated that the inorganic ligand-capped Bi nanocrystals did not form a separate phase and acted as the glue for the grain boundaries of the main material. Measurements demonstrated that the NCs p-type doped the host material from 2.1 × 10\(^{-9}\) to 8.3 × 10\(^{-9}\) cm\(^{-3}\) and slightly decreased the mobility. For a case that the hole concentration of the NCs was less than the main material, the NCs acted as a donor dopant and an opposite and weaker trend in carrier concentration was observed. In one case the sample with 5% NCs showed a room temperature electrical conductivity 1100 S cm\(^{-1}\). In a separate study [40], using Ag metallic nanoparticles in PbS nanocrystals, the electrical properties were improved through injection of electrons and improved mobility. Favorably, the use of Ag nanoparticles reduced the thermal conductivity as well. Another strategy to improve the electrical properties is to hybridize the material with conducting polymers [334], carbon nanotubes [335], exfoliated graphene [336], or reduced graphene oxide [337].

3.4.1. Outlook. The main challenges in improving electrical conductivity are the presence of defects, disorders, and insulating organic species used in the synthesis process. The paradigm of replacing long hydrocarbon-based ligands with more conductive and shorter ligands has been shown to be indeed effective. Improving the current state of QD superlattices to a highly ordered and defect free material with observable carrier delocalization is a desirable target for research efforts. For bulk bottom-up thermoelectrics, using post-treatment schemes is necessary. The idea of ‘gluing’ the grain boundary is compelling provided that a uniform coating is formed. It should be noted that increasing the electrical conductivity usually involves simultaneously decreasing the Seebeck coefficient and increasing the electronic contribution to the thermal conductivity. Therefore, any improvement in electrical conductivity should be in an optimum range in order to lead to an overall \(zT\) enhancement. Interested readers are referred to the discussion on optimizing \(zT\) by tuning the carrier concentration given in [48].

3.5. Thermal conductivity

As can be realized from equation (1), \(zT\) is inversely proportional to thermal conductivity. Thus, it is favorable for a thermoelectric material to have a low thermal conductivity which is essential for maintaining the temperature gradient. Using the Boltzmann transport equation with relaxation time approximation, the following expression for the electronic contribution known as Wiedemann–Franz law [229, 255] can be derived:

\[
\kappa_e = \sigma LT,
\]

where \(L\) is the Lorenz number, \(\sigma\) is the electrical conductivity. For metals and the degenerate limit of semiconductors, the Lorenz number can be calculated according to the Sommerfeld expression [321], \(L_0 = \pi^2k_B^2/(3e^2) = 2.45 \times 10^{-8} \text{ W} \Omega \text{K}^{-2}\). For non-degenerate semiconductors, \(L\) deviates from this value.
as ambipolar conduction increases the effective value of $L$ by up to a magnitude above $L_0$ [191]. Larsen and Prytz [338] have estimated the Lorenz number for a single parabolic band as a function of carrier concentration, different scattering mechanisms, temperature and chemical potential. For an unknown carrier concentration using single parabolic band and electron- acoustic phonon dominant scattering assumptions, both $L$ and $S$ can be defined as parametric functions of the reduced chemical potential $\mu/(k_BT)$. For such a situation, Kim and Snyder et al [339] derived the simple correlation based on experimental observation

$$L = 1.5 + \exp(-|S|/116),$$

(23)

where $L$ is in units of $10^{-8}$ WΩK$^{-2}$ and $S$ is in units of $10^{-6}$ VK$^{-1}$. This empirical relationship was reported by the authors to have a 5% uncertainty for a single band material and 20% uncertainty for materials with multiple bands, multiple non-parabolic Kane bands, or dominated by different scattering mechanisms.

The Wiedemann–Franz law suggests that any attempt to reduce the electronic contribution to thermal conductivity can directly reduce the electrical conductivity. In other words, any attempt to suppress $\kappa_e$ will also affect the power factor $S^2\sigma$ because they are both related to carrier concentration. A sharp peak in the DOS can prevent this problem as described by Mahan and Safo [217]. In such a situation the Wiedemann–Franz law loses its validity [340], which has been described as the relaxation of the Wiedemann–Franz law [341]. The reason for this is that a sharp DOS will cut off the high-energy end of the Fermi distribution which results in a reduction of $\kappa_e$. This can be understood by realizing that the heat carried by an electron is proportional to the difference between its energy and the chemical potential [340]. This was described by Humphrey and Linke [340] as the best approach towards maximizing $e\tau$ by decreasing $\kappa_e$ without simultaneously decreasing $\sigma$. The proportionality between $\kappa_e$ and $\sigma$ turns most of the attention to reduction of phonon contributions to $\kappa$.

Following kinetic theory in the diffusive regime using the relaxation time approximation to the Boltzmann transport equation, one can derive the following for the phonon contribution to the thermal conductivity in an isotropic material [229]:

$$\kappa_l = \frac{1}{3} \sum_{\omega=0}^{\omega_{\text{max}}} C_{\omega} \nu_{\omega}^2 \tau_{\omega},$$

(24)

where $C$ is the volumetric specific heat, $\nu$ is the phonon group velocity, $\tau$ is the phonon relaxation time, and the subscript $\omega$ indicates phonon angular frequency which is related to energy by the reduced Planck constant as $E_{\text{phonon}} = h\omega$. We note that this model, referred to as the ‘kinetic theory’ picture of thermal transport, may not be appropriate for materials where non-resistive scattering [342] or four phonon scattering [343] are appreciable, or with crystallographic anisotropy [135, 191, 344–353].

These physical properties are required to be manipulated in order to make the desired changes in lattice thermal conductivity. For the specific heat in an isotropic material, the Debye model is more appropriate for the three acoustic phonon modes (one longitudinal and two transverse). Einstein’s model, assuming the same frequency for all oscillators, is a more appropriate treatment for the optical phonons [229]. Although, the optical phonons contribute to the specific heat, their contribution to the lattice thermal conductivity is less than acoustic phonons due to their lower group velocity and particle density. Equation (24) reveals that one way to suppress the phonon contribution is to reduce their relaxation time $\tau$, e.g. by scattering with nanostructures of sizes comparable to the mean free path $l = v_\tau$. Generally, at low temperatures the lattice thermal conductivity is dominated by its proportionality to the specific heat and phonon boundary scattering [354] $\kappa_l \propto C \propto T^3$, whereas at high temperatures intrinsic phonon–phonon scattering is dominant [355] and $\kappa_l \propto T^{-1}$. In imperfect crystals, defect scattering will also influence thermal conductivity [135, 191, 351, 352, 356]. In practice, the high temperature dependence is usually [229] $\kappa_l \propto T^{n-1}$ with $n = 1–1.5$. Further details and models such as the Morelli–Callaway model are not discussed in this review and can be found elsewhere [357–360].

Generally, the large band gap semiconductors have a larger lattice thermal conductivity which is disadvantageous for thermoelectric applications. Thus, the large band gap semiconductors are ideal candidates for thermal conductivity reduction through materials engineering approaches. On the other hand, bipolar conduction—or the effects of minority carriers—can be considered the main disadvantage of the small band gap semiconductors. According to Mahan’s theoretical calculations [361], the maximum achievable $e\tau$ for a material saturates as its band gap energy surpasses $E_g > 10k_BT$. For example, ideally the band gap should be near or above 0.45 eV at 250 °C and near or above 1.1 eV at 1000 °C.

The lower limit of the lattice thermal conductivity corresponds to that of amorphous materials and disordered crystals. The concept of minimum lattice thermal conductivity was first introduced by Roufosse and Klemens [362], and Slack [363]. In such situations, the phonon mean free path approaches the interatomic spacing [363, 364]. Instead of waves carrying heat, thermal conductivity is modeled by assuming that heat is carried by oscillators with random phases and vibrational attenuations comparable to the interatomic distances. Einstein’s model is modified with a Debye DOS and a representative scattering length of half the vibrational wavelength. This idea, known as Cahill’s model [90, 365, 366], predicted the experimental results of disordered solids to within 20%–40% for $T > 30$ K. At high temperatures, the predicted minimum value approaches

$$\kappa_{\min} = (\pi/48)^{1/3}k_Bn^{2/3}(v_1 + 2v_1),$$

(25)

where $n$ is the number density of atoms and $v_1$ and $v_1$ are the longitudinal and transverse group velocities, respectively [365]. The minimum value of lattice thermal conductivity can be regarded as a limit for designing thermoelectric materials. One route to surpass the minimum thermal conductivity has been demonstrated by Chiritescu and Johnson et al [367]. A room temperature thermal conductivity of just 0.05 Wm$^{-1}$K$^{-1}$, six times smaller than the predicted...
minimum lattice thermal conductivity, was measured for crystalline layered WSe\(_2\) sheets with disordered stacking. Although the measured cross-plane electrical conductivity was poor, the result of this study opened a window of possibilities for crystalline materials with ultra-low thermal conductivities. Quantum confinement [368–371] and stress engineering [353, 372, 373] may offer routes to optimize the electronic and thermoelectric transport properties in this class material.

Another effective approach to reduce the lattice contribution is through phonon-boundary scattering at interfaces with sizes comparable to phonon MFPs, shown extensively for nanowires [374–381]. First principle calculations of thermal conductivity accumulation suggested that nanostuctures of less than 10 nm are needed to effectively lower the thermal conductivity for PbTe, PbSe, SnS, and SnSe at 300 K [105, 106, 382]. Figure 24 shows that for SnS and SnSe, the mean free path values corresponding to 50% lattice thermal conductivity accumulation are only about 5 nm. At high temperatures, these values become even smaller (from 4.9 nm at 300 K to 1.9 nm at 750 K in SnSe, along the b-axis) [106]. For PbSe and PbTe, phonons with MFPs smaller than 10 nm are responsible for about 80% and 90% of the lattice thermal conductivity, respectively [382]. These computational investigations are valuable, indicating the true potential of bottom-up approaches for thermal conductivity reduction. Mesoporous, nanowire, and QD syntheses, which can realize size control on the order of these small MFPs, for instance through persistent micelle templating [383, 384], are the ideal tools in order to create materials with characteristic sizes on the order of those of the heat carrying phonons in thermoelectric materials.

Feser and Urban et al [385] investigated the thermal conductivity of CdSe thin films prepared from colloidal nanocrystals with different sizes between 3 and 6 nm. The thermal conductivity data as a function of the size was predicted by Cahill [90] and Morelli–Callaway [358] models. For nanocrystals smaller than 6 nm, the measured thermal conductivities fell below the predicted amorphous limit whereas the Morelli–Callaway model successfully estimated the measured values (figure 25). The lower thermal conductivity predicted by the Morelli–Callaway model seems to be in contrast with the fact that the scattering rate in the Cahill model which assumes that the average phonon scattering rate is a half of the period (\(\frac{1}{\tau} = \omega/\pi\)). The authors explanation referred to the fact that Cahill’s model implicitly assumes that all states have the same group velocity and therefore participate in heat conduction, whereas optical phonons and small wavelength acoustic phonons have small group velocities and their contribution is implicitly neglected in Morelli–Callaway model [385]. However, it is important to remember that the argument should not imply that one model is more successful than the other. These models use different assumptions that are relevant to different material systems.

Due to the presence of the ligands and other organic species in materials prepared by bottom-up techniques, an understanding of the thermal transport across organic/inorganic interfaces is crucial. This discussion can be extended to the thermal transport across organic materials or even molecular species. In a pioneering study, Losego and Braun et al [386] investigated the effect of chemical bonding strength across the interfaces using ultra-fast pump–probe techniques including time-domain thermorelectance and picosecond acoustics. The configuration consisted of a self-assembled monolayer (SAM) in between quartz and an Au transferred-printed film. The \(\alpha\)-ends of the SAMs were silane-based and in contact with quartz, while the chemistries of the \(\omega\)-end were varied while keeping the chain length constant. The most striking results were in conductance contrast between one \(\omega\)-end with a strong covalent-like bonding of thiol functionality and another methyl \(\omega\)-end with a weaker van der Waals attraction towards Au. Thermal conductances of 68 and \(36 \times 10^6\) W m\(^{-2}\)K\(^{-1}\) were measured for the thiol- and methyl-terminated SAMs, respectively. An interesting observation was that as the number of the covalent bonds (Au–thiol) increases, the interfacial thermal conductance increases and plateaus at a thiol:methyl end-group fraction of 0.75:1. The study suggested that as the bond strength reaches a critical value, all the heat-carrying phonon frequencies are coupled due to the high stiffness of the spring constant across the interface (figure 26), and thus offers a design route to lower interparticle thermal energy transfer.

Other reports on thermal transport across the interfaces include molecular chains [387], organic nanomolecular monolayers at metal/dielectric interfaces [388], thermal transport...
across metal/phosphonic acid/sapphire interfaces [389], SAMs [390], the role of hydrogen bonds [391], and inorganic/organic hybrid superlattices [392].

Ong et al [393] reported a thermal transport study of several types of self-assembled nanocrystal arrays (figure 27). Their investigation revealed several important observations as follows. (i) Frequency domain thermal reflectance (FDTR) measurements showed that the thermal conductivity in CdSe QDs (4.8 nm diameter) and PbS QDs (7.5 nm diameter) can be tuned by changing the chemistry of the ligand interfaces. By replacing the organic ligands tetracetylated phosphonic acid (TDPA) and oleic acid (OA) with shorter inorganic ligands In$_2$Se$_4$, AsS$_3$, and N$_2$H$_2$, the thermal conductivity was increased by 50%. (ii) The thermal conductivity of CdSe nanocrystal arrays was independent of the film thickness showing that thermal transport was dominated by short-wavelength diffusive phonons. (iii) The thermal conductivity of the nanocrystal arrays was enhanced by increasing the size of the core in all various core materials (PbS, PbSe, CdSe, Fe$_3$O$_4$, and Au). (iv) The thermal conductivities of the nanocrystal arrays were insensitive to the bulk thermal conductivity of the core materials. (v) Several models were applied in order to predict the thermal conductivity of the samples as a function of the core diameter. EMAs were used to account for the contributions of the two constituents—inorganic cores and organic ligands (oleic acid)—based on their volume fractions and thermal conductivities, where the thermal conductivity of lead oleate was used instead of oleic acid because the ligand forms a different structure in the array. (vi) The temperature dependence of the thermal conductivity increased with temperature from 10 to 200 K and plateaued above 200 K. These plateaus occurred at temperatures close to the Debye temperatures of the core materials. The authors proposed that heat diffuses through elastic coupling between the cores and the ligands in the composite material. As the temperature increases, more common frequencies between the ligand and core are activated which results in increasing the thermal conductivity. When the temperature surpasses the Debye temperature of the core material, the activated ligand frequencies are not coupled with any additional common frequencies in the core materials. The authors postulate that the observed plateau is an indication that the thermal transport is dominated by elastic vibrations,
Figure 27. Thermal conductivity in a ligated QD solid is dominated by elastic coupling between core and ligand. (a) Schematic of the frequency domain thermal reflectance thermal conductivity measurements of nanocrystals arrays. The two constituents contributing to the thermal conductivity are the inorganic core and organic ligand. (b) The thermal conductivities of all samples increased with increasing core diameter. The inset shows the thermal conductivities of the bulk materials. (c) A comparison between the experimental data and different models—Maxwell Eucken (ME) [395], effective medium theory (EMT) [395], Hashin LB [396], Minnich [397], and a modified version of ME developed by Hasselman and Johnson [398]. (d) Temperature dependence of the thermal conductivity. Plateaus above ~200 K were attributed to saturation of the coupled frequency states between the core and the ligand. (e) The thermal conductivity of a Fe₂O₃ sample with a higher Debye temperature exhibits a plateau at a correspondingly higher temperature. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [393], Copyright 2013.

Figure 28. Room temperature thermal conductivity of PbS QD solids functionalized with different ligands. (a) Thermal conductivity of 3.3 nm diameter QDs treated with different ligands depicted in (b). (b) Chemical structure of the different ligands, where TBAI is used for I⁻ surface termination, and CTAB is used for Br⁻ surface termination. Adapted with permission from [399]. Copyright 2015 American Chemical Society.
and the inelastic contributions are negligible in these materials [393, 394].

To further test the effect of ligand chemistry on thermal transport, Liu and Wang et al. [399] replaced the thiol organic acid ligand with several different ligands of 1,2-ethanedithiol (EDT), 1,4-butanedithiol (BDT), 1,6-hexanedithiol (HDT), 1,8-octanethiol (ODT), ethylenediamine (EDA), tetrabutylammonium iodide (TBAI), and cetrimonium bromide (CTAB) in PbS nanocrystals. The measurements showed that PbS nanocrystals with EDT ligands had a lower thermal conductivity than those with EDA ligands. This was despite the fact that EDT with thiol groups can induce stronger covalent bonding with PbS (figure 28). The other observation was that surface treatment with TBAI and CTAB (halide ligands containing I\(^-,\)Br\(^-\)) resulted in similar thermal conductivity although the PbS–Br\(^-\) bonding is expected to be stronger than PbS–I\(^-\) bonding as determined by UPES [306]. In addition, as the ligand length decreased from eight carbon atoms to four, the thermal conductivity increased from 0.20 to 0.27 W m\(^{-1}\)K\(^{-1}\).

Recently, thermal transport in superatomic crystals (SACs) was reported by Ong et al. [400]. The temperature-dependent measurements of unary Co\(_6\)X\(_6\)(PET\(_3\))\(_6\) and binary [Co\(_6\)X\(_6\)(PET\(_3\))\(_6\)]\(_2\olu\) superatoms, where X = S, Se, or Te, showed a transformation from an amorphous to a crystalline behavior by controlling orientational ordering in the materials. All the unary samples exhibited nearly temperature independent thermal conductivity as predicted by Cahill’s minimum thermal conductivity model [90]. The authors’ claim that the binary [Co\(_6\)Te\(_6\)][Co\(_6\)]\(_2\) samples showed an amorphous like thermal transport behavior similar to the unary materials, whereas [Co\(_6\)Se\(_6\)][Co\(_6\)]\(_2\) exhibited crystalline behavior below 200 K followed by transition to an amorphous like state with temperature independent thermal conductivity at temperatures above ~200 K. The explanation proposed by the authors was based on an XRD-observed transformation in the crystal symmetry from P3\(_1\)m1 to P3 as the temperature decreased below 190 K (see figure 29).

The effects of ligand surface chemistry on the low-frequency acoustic phonon vibrations of CdSe QDs was investigated by Mork and Tisdale et al. [401] figure 30 shows that changing the length of the ligands of straight-chain alkanethiols from 1-hexanethiol (C\(_6\)) to 1-octadecanethiol (C\(_{18}\)) resulted in a red shift of the low-energy phonon frequencies (radial breathing mode of the spherical particles denoted \(l = 0\), where \(l\) denotes the quantum number) relative to the shortest ligand. The experimental observations also revealed that this phonon frequency was insensitive to the environment surrounding the QDs, such that being in a thin film, in PMMA, in octadecene, or in a colloidal solution did not affect this frequency substantially. In contrast, the mass of the ligands noticeably affected the phonon frequency which has also been reported by others [402]. These results showed that the more massive ligands are the more resistance they provide against the contraction and expansion of the core during vibrational oscillations.

The majority of crystalline bottom-up thermoelectric materials show low values of thermal conductivities compared to those of the bulks. These low values are reported in studies including Bi\(_{23+\delta}\)S\(_8\)Te\(_3\) and PbTe–Sb\(_2\)Te\(_3\) nanocrystals [242],

![Figure 29. Thermal transport in superatomic crystal (SAC) compounds of dissimilar nanocrystal constituents.](image-url)
PbTe–Bi$_2$Te$_3$ heterostructure nanowires [404], solution-prepared nanostructured CdSe and In$_2$Se$_3$ [405], Ag$_2$Te–PbTe nanocrystals [274], PbS–Ag nanocomposites [40], cold-press PbTe–PbS core shell QDs [38], solvothermally prepared Ag and Sb co-doped PbTe [406], Bi$_2$Te$_3$ nanopolyhedra [407], Bi$_2$Te$_3$ and SPS pelletized Bi$_2$Se$_3$ nanoflakes [408] and Bi$_2$Te$_3$ and Bi$_2$Se$_3$ multishells [409].

3.5.1. Outlook. Effective medium theory with a reduced interface density has successfully predicted the experimental data observed for elastic thermal transport across ligand-inorganic core interfaces [393]. However, more questions have been raised from this experimental study. For instance, what are the exact ligand structures in the array and their corresponding thermal conductivities? What is the effect of changing Debye temperature of the ligands? What is the effect of different core atomic arrangements and their exposed crystal facets? What are the individual contributions of thermal transport through the inorganic core, organic ligand matrix, and core-ligand interfaces? In what circumstances does the contribution of the inelastic vibrations dominate the thermal transport? Some of these questions have been addressed by simulations after the experimental demonstration [394, 410–412].

4. Conclusion and prospects for future avenues of investigation

Expanding the knowledge of bottom-up methods of material preparation is highly advantageous for thermoelectric applications utilizing the unique properties of nanomaterial constituents such as nanowires or quantum dots. This review outlined the achievements in using bottom-up techniques for thermoelectric purposes. Useful experimental characterization techniques and simple-to-implement theoretical models were reviewed. New guidelines for improving figure-of-merit were discussed that can guide predictive materials design efforts achievable under current understanding of thermoelectric behavior. The reviewed literature emphasized that solution-based synthesis will be a fruitful field of research for exotic thermoelectric materials, especially for bringing size-effects to high temperature oxide or wide band gap thermoelectrics through ordered nanoporosity. Tailoring structure using bottom-up methods was shown to be capable of achieving thermoelectrics with thermal conductivities below the minimum value of disordered or amorphous materials. The reviewed work on flexible thermoelectrics illustrated the promise of using thermoelectric solution inks on a variety of substrates in roll-to-roll manufacturing lines for large-scale productions.

Furthermore, thermoelectric and thermal transport in superatomic crystals with delocalized electrons is not currently understood, as the reaction schemes for synthesis of these materials is only being developed. This is a particularly attractive route for inorganic chemists who have already developed robust synthesis techniques for complementary alternative energy solutions such as photovoltaics and catalysis. Improving the material and device performance through synthesis still remains as the main challenge for future investigations, where integrated self-assembly of nanowires and quantum dots may provide a system capable of demonstrating the elusive enhancements in
thermoelectric energy conversion efficiency predicted more than two decades ago.

Lastly, using post-synthesis treatments at the desired operating temperature range prior to measurement and operation is crucial in order to assure reproducibility of obtained results. High-temperature annealing or SPS can be very effective in removing organic species and remaining solvents. Analyses such as temperature-dependent or temperature-controlled XRD, XPS, TGA, and DSC can be very useful in detecting and avoiding any phase transition, weight loss, or irreversible solid-state reactions during cycling. It is highly recommended that transport properties be reported for multiple measurements on various samples, and $zT$ values and corresponding error analyses to be reported based on statistical analysis of such measurements.

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