

Thermoelectric performance of PbSe quantum dot films†

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The thermoelectric (TE) performance of films of colloidal lead selenide (PbSe) quantum dots (QDs) with metal-chalcogenide complex ligands is seen to change with QD size and temperature. Films of smaller QDs have higher Seebeck coefficient magnitudes, indicating stronger quantum confinement, and lower electrical and thermal conductivities. The thermoelectric figure of merit ZT is ~ 0.5 at room temperature and increases with temperature to 1.0–1.37 at ~ 400 K, where it is larger for smaller QD films. This is better than previous results for solution-prepared QD TE materials at these elevated temperatures.

Introduction

Low dimensional materials, such as those composed of quantum wells and quantum dots (QDs), can improve the energy conversion efficiency of thermoelectric (TE) generators, because the TE figures of merit ZT can be higher than those in the corresponding bulk materials, due to their increased carrier densities of states and increased relative rates of phonon scattering to carrier scattering.^{1–4} In particular, solution-based preparation methods, such as those using colloidal QDs (or nanocrystals), are promising because they entail fast, simple, production-scalable advantages, and provide good control of the particle size.⁵ However, these approaches have been limited by the low effective electrical conductivity of the films, due to the organic ligands on the colloidal QD cores. This electric conductivity limitation has been lessened in several recent studies. Colloidal films of Bi_2Te_3 QDs, whose organic ligands had been stripped by hydrazine, had $ZT \sim 0.2$ at room temperature.⁶ Films prepared with PbTe QDs that had been prepared with no organic ligands achieved $ZT \sim 0.3$ to 0.8 from 300 to 580 K.⁷ $(\text{Bi,Sb})_2\text{Te}_3$ alloy films prepared from annealed films of colloidal Bi_2S_3 QDs, whose ligands had been replaced by electrically-conducting Sb_2Te_3 metal chalcogenide complex (MCC) ligands before film formation, had $ZT \sim 0.7$ at 300 K.⁸

In addition to the well-studied telluride QD films, non-telluride QD films may show promise for TE generators, such as those composed of PbSe QDs, in part because PbSe shows promising TE performance in the bulk.^{9–12} From a practical perspective, Se is more commonly available and less expensive

than Te. Enhanced TE performance in nanostructured PbSe has been examined, but not extensively.^{13,14} In this study, the TE performance of films of colloidal PbSe QDs was investigated, using QDs after MCC-SnS₂ ligand exchange to improve the inter-QD electrical conductivity. The film electrical conductivity σ , Seebeck coefficient S , and thermal conductivity K were measured directly at temperature T , to obtain the TE figure of merit $ZT = S^2\sigma T/K$.

Experimental methods

PbSe QD preparation and ligand replacement

PbSe QDs were prepared by a quick-injection approach.¹⁵ The pills of selenium (Se) were first dissolved in the tri-octylphosphine (TOP) at 110 °C for 4 hours to form a clear 1 M TOPSe solution A. Then 2.16 g of lead acetate trihydrate and 7.3 mL of oleic acid were dissolved in 40 mL of squalane followed by degassing at 100 °C, which formed solution B. 18 mL of solution A was swiftly injected into solution B at 170 °C, and the temperature was reduced to 140–160 °C, allowing the QDs to grow to the desired size. PbSe QDs of several sizes were synthesized by adjusting the injection temperature (between 160 and 180 °C) and growth time (from 3 to 12 min), where higher injection temperature and longer growth time favored growth of larger QDs. The QDs were washed with ethanol–toluene non-solvent/solvent pair and finally dispersed in hexane. Metal chalcogenide complexes were used to replace the organic ligands following the methods in the literature.^{8,16} An $\text{SnS}_2\text{--N}_2\text{H}_4$ precursor (*Note:* Hydrazine is toxic and should be handled with appropriate protective equipment to avoid contacting with vapors or liquid) was stirred with PbSe QDs in hexane until the organic phase turned colorless and a stable colloidal solution of QDs in hydrazine phase was formed. The upper organic phase was carefully extracted by pipetting and then discarded. The final PbSe(SnS_2) QDs were washed in a glove box with ethanol (two times, with centrifuging) first, and then were transferred to the

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ambient environment and washed one more time with deionized water. The 7 nm, 9 nm, and 15 nm QDs were treated with MCCs from a Sn precursor, and the 18 nm QDs with MCCs from a SnS_2 precursor (see details in the ESI†). Both MCCs nominally had the same $(\text{N}_2\text{H}_5)_4\text{Sn}_2\text{S}_6$ concentration of 0.25 M. The thermoelectric performance of films of QDs treated in these two ways was compared and is discussed later.

Electrical conductivity and Seebeck coefficient measurement

Cr/Au (5 nm/50 nm) metal leads were patterned on insulating glass substrates by standard lithography, metallization and lift-off. The width of the metal leads was 5–20 μm and spacing between the electrodes ranged from 3–100 μm . The metal patterned substrates were cleaned by an O_2 plasma for 5 min, to improve surface hydrophobicity of the substrate. The $\text{PbSe}(\text{SnS}_2)$ QD solutions were drop cast on the substrates at 110 $^\circ\text{C}$ in multiple cycles to ensure the homogeneity and continuity of the QD films. The thickness of the QD films was characterized using a Dektak3 profilometer to a resolution of 1 nm. Normally, the thickness of the QD films ranged from 150 to 300 nm, as controlled by the number of cycles of the drop casting and the concentration of the QD solutions. Voltages and currents were measured in air using Protek B-845 digital multi-meters and the sample temperature was controlled using Nuova hot plates and T type thermocouples (± 1 $^\circ\text{C}$).

Thermal conductivity measurement

The $\text{PbSe}(\text{SnS}_2)$ QDs were spin coated on a Si substrate and the resulting QD film thicknesses were targeted from 100 nm to 800 nm. SiO_2 insulating layers with thicknesses of 180–200 nm were deposited on top of the QD films using a low temperature e-beam evaporator, which avoided damage to the QDs by plasma-assisted deposition. Cr/Au metals leads were deposited on the SiO_2 layers through a shadow mask. The length of the metal lines was 8 mm and their widths ranged from 30–80 μm . Measurements were performed in vacuum.

Results and discussion

1 Transmission electron microscopy and X-ray diffraction

Films prepared using QDs synthesized by the solution method have a very low ZT due to the electrically insulating organic ligands covering the QDs. To increase electrical conductivity and ZT of these QD films, these organic ligands were replaced by metal chalcogenide complexes following the method in the literature.^{8,16} The size and crystalline structure of the QDs were characterized by transmission electron microscopy (TEM) (JEOL JEM-100CX operated at 100 kV) and X-ray diffractometry (XRD) (Scintag X2). Four sizes of PbSe QDs were prepared, with diameters of 7 nm, 9 nm, 15 nm, and 18 nm, as determined by TEM as illustrated in Fig. 1. For example, Fig. 1(c) shows the TEM image of 15 nm QDs after MCC treatment. The inset shows the as-synthesized PbSe QDs with organic ligands. The average size of the QDs is 15 nm, and the size distribution has a standard deviation of less than 10%. After ligand replacement, the inter-QD distance decreases from 1.4 nm to <0.3 nm, while the QD shape and size remain the same.

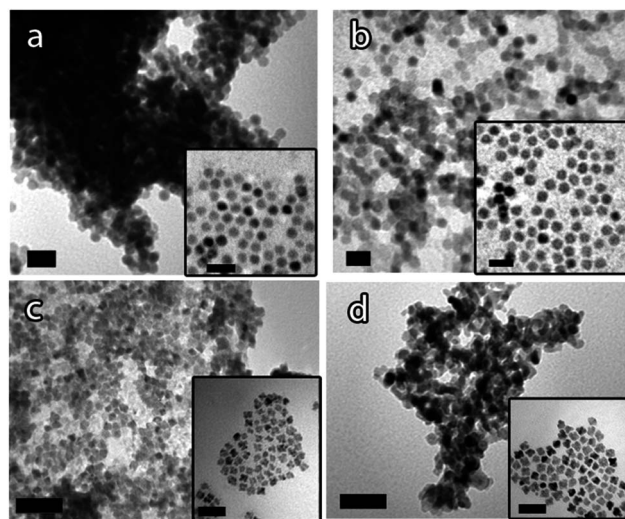


Fig. 1 TEM images of QDs after MCC treatment, with diameters (a) 7 nm, (b) 9 nm, (c) 15 nm, and (d) 18 nm. Insets are TEM images before MCC treatment. The scales bars are 20 nm for (a) and (b), and their insets; and 100 nm for (c) and (d), and 50 nm for their insets.

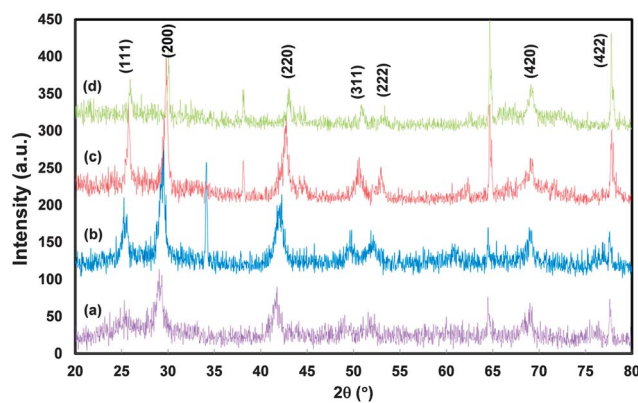


Fig. 2 XRD patterns of (a) as-synthesized 15 nm QDs capped with organic layers, and (b) 15 nm, (c) 9 nm, and (d) 7 nm QDs after organic ligand removal and MCC ligand replacement.

Fig. 2 shows the XRD pattern of the PbSe QDs, both for the 15 nm as-synthesized QDs capped with organic layers in (a), and the 15 nm, 9 nm, and 7 nm QDs after organic ligand removal and MCC ligand replacement in (b)–(d). The XRD patterns confirm that the QDs have a rock salt crystal structure and that the MCC-hydrazine treatment does not change the crystalline structure of the QDs. Ostwald ripening would be expected if hydrazine were used to strip the initial ligands and the resulting QD surfaces were not protected; however in our procedure the initial ligands are continuously being replaced by MCC complexes on the QD surfaces so ripening is not expected here, as is confirmed in Fig. 1 for the 15 nm QDs.

2 Electrical conductivity

A two-probe test was performed to verify the removal of organic ligands by the MCC treatment. Fig. 3(a) shows two probe I – V curves in log-scale of the 15 nm PbSe QD film in air with and

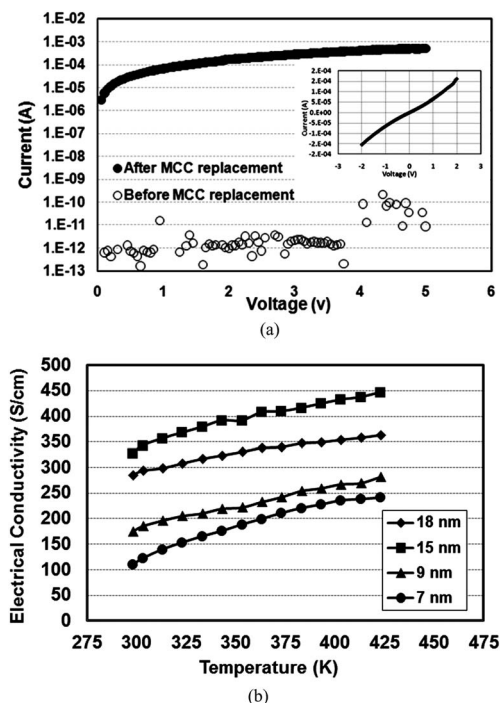


Fig. 3 (a) Two probe I - V curves of films of the 15 nm QDs before (hollow circles) and after (solid circles) MCC replacement, with the inset showing the I - V curve in linear scale, and (b) temperature dependence of the electrical conductivity of films of different sized PbSe(SnS₂) QDs.

without MCC replacement. The conductance increased by over eight orders of magnitude after the MCC treatment. The inset to Fig. 3(a) shows the I - V curve of the PbSe QD film after the MCC treatment plotted using linear scales. The approximately symmetric and linear curves in the negative and positive voltage regions indicate that the contact between the metal and film is ohmic, as is the film itself. The electrical conductivities of the PbSe(SnS₂) QD films in air for the four QD sizes are plotted in Fig. 3(b), measured using the four-probe method. The data plotted represent an average of typically two to four measurements on one film for each particle size, with run-to-run variations in σ normally <10%. The run-to-run variations of the measurements of S and K were similar. Within experimental error, measurements of σ , S , and K were the same for runs during which T was increased or decreased, and were the same after several cycles of increasing and then decreasing T . (See the ESI.†) The films have high electrical conductivity, 110–320 S cm⁻¹ at room temperature, which is comparable to or higher than that measured for previous solution-based QD films.^{6,8,14,16} The electrical conductivity generally increases with QD diameter (Fig. 3(b)), as in previous experiments.^{13,17} (The 18 nm QD film had slightly lower σ than the 15 nm QD film, perhaps due to effects attributable to using different MCCs, as mentioned in the experimental section. There are similar small deviations from monotonic behavior in the Seebeck and thermal conductivity measurements.) The electrical conductivity is observed to increase with T , which is consistent with the published results on solution-processed nanostructured materials.^{6,14,18}

The variations in transport parameters vs. size and temperature shown in Fig. 3(b) are similar to those seen in other studies of highly polycrystalline and granular structured films, but different from those of similar homogeneously disordered films,^{6,19} due to the grain boundaries and interfaces, and possible trap states at interfaces.

The film electrical conductivity generally increases with larger QD diameter (Fig. 3(b)), which is in agreement with the theoretical calculations²⁰ and the previous experiments on nanostructured films.^{13,17} Films with reduced crystal size have more interfaces, which increases carrier scattering and decreases carrier mobility.

The electrical conductivity increases with T in Fig. 3(b), which is consistent with the published measurements on solution-processed nanostructured materials.^{6,14,18} In contrast, in homogeneous materials electrical conductivity generally decreases with T if the carrier density is constant, because the phonon density increases and carriers suffer more frequent phonon scattering. The carrier density would be expected to be independent of T in the regime studied here because impurities should be fully ionized at room temperature due to the large dielectric constant ($\epsilon \sim 250$) and small effective mass (m^*) of PbSe.²¹ However, in nanostructured materials there can be interfacial energy barriers between the QDs, such as grain boundaries, interfacial boundaries, and traps states, that can block the transport of low energy carriers;^{22,23} this and related models of carrier blocking² have sometimes been termed carrier energy filtering. Low energy carriers are trapped, while the high energy carriers overcome the energy barriers and contribute to σ , even at lower T . When T increases, the low energy carriers can overcome the energy barriers, which would explain the increased σ with T in our films. In fact, σ is seen to decrease with T in bulk PbTe and PbTe:Ag, but to increase with T in nanocomposite PbTe:Ag,¹⁸ as is seen here. The decrease in σ in nanostructured PbSe films at very high T ,¹⁴ which is not seen here, was attributed to oxygen desorption that decreases p-type doping or to defect creation.

3 Seebeck coefficient

The Seebeck coefficients of QD films were measured in air using mesoscopic devices patterned with micro-heaters and thermometers that also served as the electrodes for electrical measurements. These mesoscopic devices can probe low dimensional materials with high spatial resolution.²⁴ Fig. 4(a) shows the top view scanning electron microscopy (SEM) image of the Seebeck device patterns with (false) colored metal lines and Fig. 4(b) shows a schematic illustration of the device for the Seebeck coefficient measurement. By applying current to the heater, a temperature gradient ΔT was induced across the QD films *via* joule heating of the microheater. The localized temperatures, T_1 and T_2 were measured by probing the four-probe resistances as functions of T and were calibrated before the Seebeck coefficient measurements. The thermoelectric voltage V corresponding to $\Delta T = T_1 - T_2$ across the QD films was measured and the Seebeck coefficient was consequently obtained by $S = -V/\Delta T$.

Fig. 5 shows the Seebeck coefficients of the PbSe(SnS₂) QD films. The sign of the Seebeck coefficient of the PbSe(SnS₂) QD

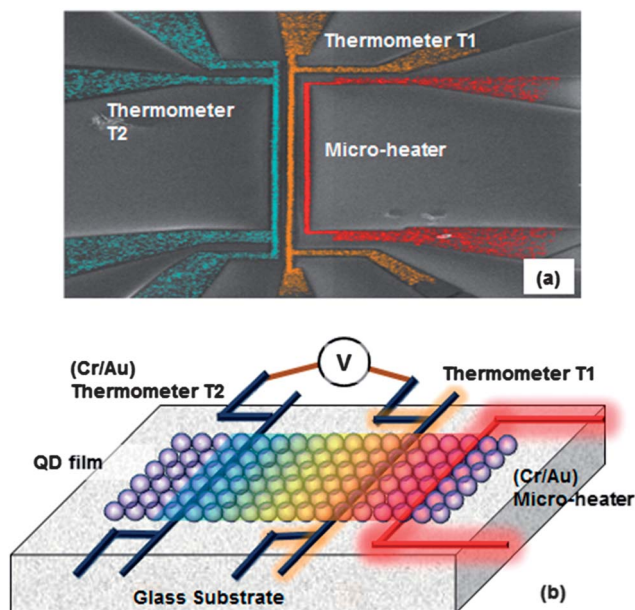


Fig. 4 (a) SEM image of the Seebeck measurement patterns with false colored metal lines, and (b) schematic illustration of the mesoscopic device for Seebeck coefficient measurements.

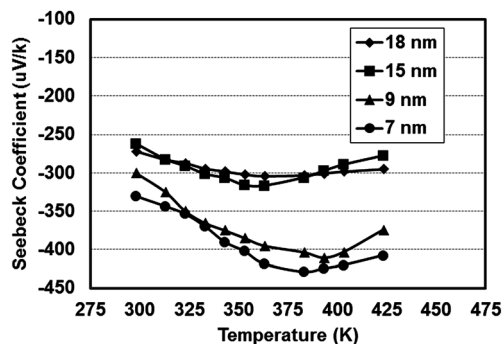


Fig. 5 Temperature dependence of the Seebeck coefficient of films of different sized $\text{PbSe}(\text{SnS}_2)$ QDs.

films is negative over the entire temperature range, which indicates solely dominant n-type conduction, maybe due to the MCC complexes.¹⁶ (Significant oxygen doping by air contamination could have made the film p-type.²⁵) As the QD size decreases from 18 nm to 7 nm, the magnitude of the film Seebeck coefficient generally increases from ~ 260 to $330 \mu\text{V K}^{-1}$ at room temperature. As T increases from room temperature, $|S|$ reaches the maximum at about 375 K and then decreases.

The increase in film Seebeck coefficient with decreasing QD size (Fig. 5) is consistent with the theory²⁰ that accounts for quantum confinement in the QDs²⁶ (for a domain size that decreases with decreasing QD size). The exciton Bohr radius in PbSe is known to be 46 nm,²⁷ so these QDs are in the strong quantum confinement regime; furthermore, the QD band gaps are much larger than that of bulk PbSe . Usually, the Seebeck coefficient is proportional to the difference between the carrier average energy E_{ave} and the Fermi level E_{f} .²³ The band gap E_{g}

increases as the QD size decreases due to carrier confinement, so the band edge moves away from the Fermi level, and thus E_{ave} , $E_{\text{ave}} - E_{\text{f}}$ and the Seebeck coefficient increase.¹³

The nanostructure of such films also affects the Seebeck coefficient in other ways, due to the potential presence of interfacial energy barriers that can block low energy carriers.²³ Only high energy carriers contribute to electrical conduction because of such barriers, so that the average carrier energy E_{ave} is even larger and consequently $|S|$ increases even more for films of smaller QDs. Furthermore, blocking of low energy carriers (even in some bulk materials) can increase $|S|$ because the sign of the contribution to S is the opposite sign for low and for high energy carriers.²

The magnitudes of the Seebeck coefficients for films formed with the four sizes of QDs show similar temperature dependences in Fig. 5: an increase, followed by a decrease at ~ 375 K. In nanostructured Bi_2Te_3 ,⁶ $|S|$ increases with T (up to measured upper limit of 280 K). In nanocomposite PbTe:Ag films,¹⁸ $|S|$ increases with T and then decreases, even as σ continues to increase, as is also seen here. In nanostructured PbSe films,¹⁴ $|S|$ and σ increase and then decrease with T (in contrast to what is seen here for σ , as explained above). In general, $|S|$ increases with T due to the increase of the overall average carrier energy with T . However, when T is higher than a certain value, the lower energy carriers are released from interfacial states, which will counter this effect (and the energy filtering effect noted in ref. 2 due to the difference signed contributions of lower and higher energy carriers) and could lead to a decrease in $|S|$. Also, at higher T , there could be increased densities of minority carriers (holes here), which would increase σ but decrease $|S|$. The inverse relation of $|S|$ and σ expected from the Mott relation for homogeneous materials²⁸ would not be strictly valid for nanostructured materials because of these latter two effects.

Changing the MCC treatment, by forming MCCs using different precursors, does not impact S significantly, with films of 15 nm and 18 nm QDs having similar S ; however, there are larger differences in their electric (Fig. 3(b)) and thermal (Fig. 7(a)) conductivities. The reason for this could be that S is dominated relatively more strongly by quantum confinement effects that depend on the QD size, and relatively less on the surface ligand species.

4 Thermal conductivity

A three omega (3ω) method²⁹ was used to characterize the thermal conductivity of the QD films in vacuum. This 3ω technique has been verified and is now extensively used to measure the thermal conductivity of bulk, thin film materials and multilayer structures.^{30–32} The experimental setup is shown in Fig. 6. The inset shows a top view SEM image of a typical sample. The details of the 3ω method are given in the ESI.†

Fig. 7(a) shows that the thermal conductivities of the QD films are ~ 0.77 to $1.15 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, which is comparable to those for nanostructured $(\text{Bi,Sb})_2\text{Te}_3$ alloy films ($\sim 0.89 \text{ W m}^{-1} \text{ K}^{-1}$).⁸ In the present test data, film thermal conductivity generally decreases with decreasing QD size and increases with increasing T . The 18 nm QDs were treated by

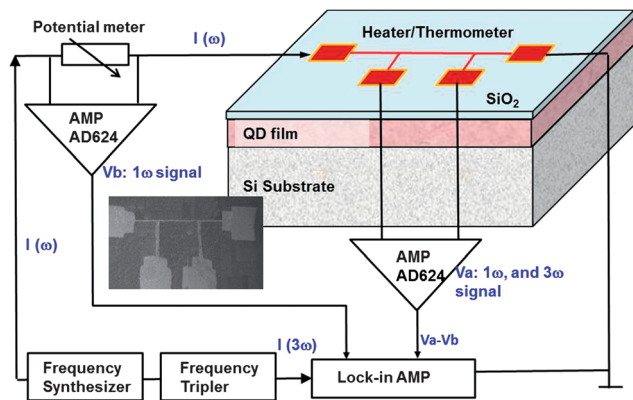


Fig. 6 Schematic of the 3ω thermal conductivity measurement apparatus and (inset) an SEM image of the measurement pattern.

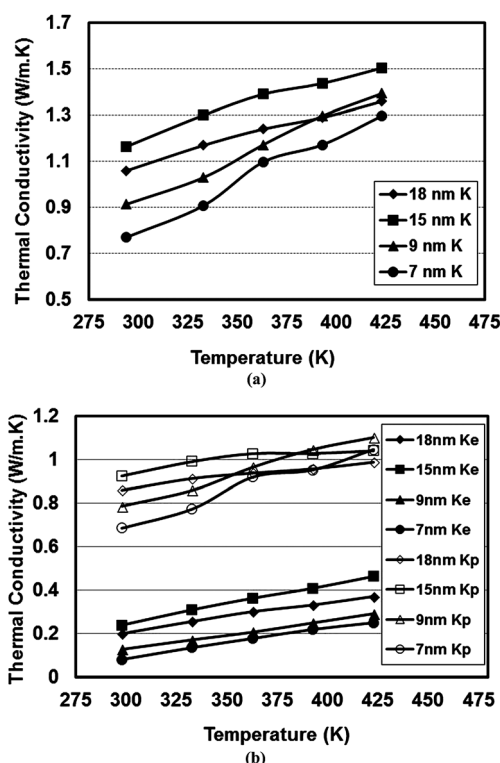


Fig. 7 Temperature dependence of the (a) total thermal conductivity and (b) lattice and electron thermal conductivity coefficients of films of different sized PbSe(SnS₂) QDs.

MCCs prepared from SnS₂, and the film composed of them had a lower thermal (Fig. 7(a)) and electric (Fig. 3(b)) conductivity. As noted before, the reason for this could be the different activities of these two types of MCCs, which may leave different amounts of residue SnS₂ on the QD surface after washing. In this study, the concentrations of these two types of MCCs were nominally the same, but the mole stoichiometry of active MCC ligands may have been different and affected the thermoelectric performance of films prepared using them. The investigation of the effect of different MCCs on final thermoelectric performance is underway and will be reported in the future.

The contribution to the thermal conductivity from electrons in these n-type films K_e , is estimated using Fig. 7(a) and the Wiedemann–Franz law: $K_e/\sigma T = L$, where L is the Lorenz number ($2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$). The lattice (or phonon) contribution to the thermal conductivity would then be $K_p = K - K_e$. Fig. 7(b) shows that $K_p > K_e$ and that both film K_p and K_e increase with QD size, in agreement with theoretical predictions and expectations due to smaller interface density. In the corresponding bulk materials, the phonon mean free path is ~ 10 to 100 nm ,³³ and is expected to be smaller in our films due to scattering by QDs that are smaller than this length range. Aside from its effect on S , TE performance cannot be improved unless the increased electron scattering due to QD interfaces is proportionately less than that for phonon scattering.

In contrast to what is often seen for bulk materials, the thermal conductivity of our PbSe(SnS₂) QD films increases with T . Similar observations are reported in ref. 6 and 8. In particular, this dependence has been seen for p-type (Bi,Sb)₂Te₃ nanocomposites in several studies.^{13,34,35} In ref. 6, K and K_p increase with T (up to the measured upper limit 200 K) in nanostructured Bi₂Te₃, presumably due to an increase in the lattice contribution to the specific heat in this temperature range. For the lattice contribution, $K_p = c_v v \lambda_p / 3$, where c_v is the specific heat per unit volume (due to the lattice), v is the speed of sound, and λ_p is the phonon mean free path. Ref. 36 shows that for bulk PbSe little increase in c_v is expected above 250 K . However, for most of the QD films (and particularly for those with the larger QDs), the larger increase K in Fig. 7(b) with T is, in fact, due to the electronic term and not the phonon term. This is expected in disordered materials where heat conduction involves the hopping of localized excitations.^{37,38} Furthermore, the increase of K_e with temperature is associated with the enhanced electrical conductivity at elevated T , *i.e.* lessening energy filtering.

5 TE figure of merit

Fig. 8 shows the thermoelectric figure of merit $ZT = S^2\sigma/K$ of the PbSe(SnS₂) QD films. At room temperature, $ZT = 0.42\text{--}0.56$, which is slightly lower than that reported for nanostructured (Bi,Sb)₂Te₃ alloy films ($ZT \sim 0.7$),⁸ and which compares favorably to that of other films made using other solution based

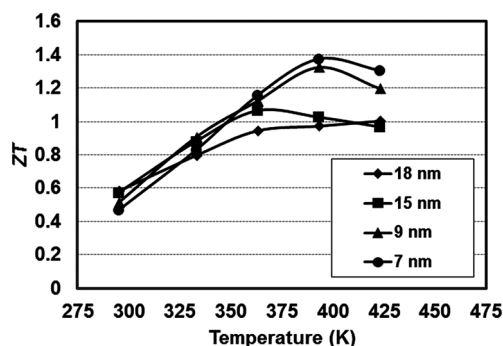


Fig. 8 Figures of merit ZT of the studied PbSe(SnS₂) QD films, as a function of temperature.

methods: ~ 0.2 for Bi_2Te_3 QD films,⁶ 0.22–0.45 for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ films,³⁹ and 0.2–0.27 for PbTe QD films.⁷ Above 400 K, our QD films have high ZT values ~ 1.0 to 1.37, which are higher than those reported for other colloidal QD films, such as ~ 0.6 to 0.7 in ref. 8. Films of smaller $\text{PbSe}(\text{SnS}_2)$ QDs (7 and 9 nm) have higher ZT, particularly at a higher T , than films of larger QDs (15 and 18 nm). Theory suggests ZT increases with smaller domain size (and eventually decreases for very small domain sizes).¹⁹ In the present films, ZT increases from 300 K to ~ 400 K and then either decreases or is roughly constant to 425 K, depending on particle size. An increase in ZT with T , followed by a decrease with T is predicted in theories of granular semiconductors.¹⁹ ZT for $(\text{Bi,Sb})_2\text{Te}_3$ alloy films formed using QDs after MCC ligand exchange is less dependent on T than for our QD films, and is ~ 0.65 above 400 K.⁸ The higher ZT here suggests possible advantages of $\text{PbSe}(\text{SnS}_2)$ QD films over others in this important elevated temperature region, because large values of ZT at the higher operating temperatures of TE generators is essential.

Conclusions

In summary, we have shown that films of colloidal PbSe QDs that have undergone SnS_2 -MCC ligand exchange have relatively high electrical conductivities, Seebeck coefficient magnitudes, and thermoelectric performance. Films of the smallest QDs (7 nm) have the lowest thermal and electrical conductivities and highest Seebeck coefficients. Their thermoelectric figure of merit ZT increases from ~ 0.5 at room temperature to 1–1.37 at 400 K, which is promising. This is higher than those of previously reported QD films, and suggests advantages in using $\text{PbSe}(\text{SnS}_2)$ QD films for thermoelectric generators at elevated temperatures.

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