Giant Thermal Rectification from Single-Carbon Nanotube–Graphene Junction

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Supporting Information

ABSTRACT: We describe the influence of the geometry parameters on the thermal rectification of single-carbon nanotube–graphene junction. The two-dimensional (2D) distribution of the thermal rectification with respect to the tube length and the side length of the graphene nanosheet are calculated and visualized. The maximum thermal rectification ratios of the designed single-carbon nanotube–graphene junction can reach 1244.1% and 1681.6% at average temperatures of 300 and 200 K, respectively. These values are much higher than those reported for single-material nanostructure-based thermal rectifiers. The thermal rectification ratios of the nanotube–graphene junction are fairly sensitive to geometry size and are almost entirely dominated by the degree of overlap of the power spectra under negative thermal bias. These findings could offer useful guidelines for the design and performance improvement of thermal diodes.

KEYWORDS: thermal rectification, carbon nanotube–graphene junctions, phonon density of states, standing wave, molecular dynamics

1. INTRODUCTION

As the most fundamental thermal controlling devices, thermal rectifiers have attracted considerable research attention due to their great potential in various applications, such as on-chip cooling, energy-saving buildings, and phononics applications.1−6 Numerous theoretical and experimental studies have predicted or demonstrated that thermal rectification (TR) exists in bulk or nanosized system, for example, shape-asymmetric structures,7−15 bisegment or bimaterial systems,16−19 hybrid structures,20,21 and systems based on phase change.22−26 However, the maximum rectification efficiency of these thermal rectifiers seems to be still much lower than that of their electronic counterparts.27 Accordingly, the development of more efficient thermal rectifiers is becoming of primary importance for their future applications.

In our recent study,28 we reported the considerable thermal rectification from the designed graded two-stage pillared graphene structures and preliminarily discussed the mechanism. Such kind of nanostructures can be considered to be constructed with building blocks of carbon nanotube–graphene junctions.29 However, the role played by the carbon nanotube–graphene junctions in the thermal rectification effect of the pillared graphene is not yet fully understood. Moreover, whether ultrahigh thermal rectification can be exhibited in a single-carbon nanotube–graphene junction is still unknown. Furthermore, how the thermal rectification is affected by its geometry parameters remains unknown and should be investigated, as this knowledge is crucial for successful design of thermal rectifiers with pillared graphene structures. It is worth mentioning that the thermal rectification of graded nanostructures is rather sensitive to their geometry size, but optimization is challenging due to the huge computational cost.

In this study, thermal rectification of two models of single-walled carbon nanotube (SWCNT)–graphene junctions with different boundary thermal contacts is investigated using nonequilibrium molecular dynamics (NEMD) simulations. The two-dimensional (2D) distribution of the thermal rectification with respect to the tube length and side length of the graphene nanosheet is calculated and visualized. We find that the values of the maximum thermal rectification ratios can reach 1244.1% and 1681.6% at average temperatures of 300 and 200 K, respectively.

2. MD SIMULATION METHOD

NEMD simulations are conducted for SWCNT–graphene junctions using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.30 To facilitate comparison with the literature data, the simulation details adopted are almost identical to those by Wang et al.7 and were also described in detail in our previous study.28 The schematics

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of the configuration of the two models of SWCNT–graphene junctions with different boundary thermal contacts, junction A and junction B, are illustrated in Figure 1a and 1d, in which the green, red, and cyan areas denote the fixed part, thermostated part, and free part of the system, respectively. The SWCNT–graphene junctions are considered to be constructed via an armchair SWCNT (6, 6), which is erected on and covalently joined to a graphene nanosheet with an appropriate hole. In our study, the graphene nanosheets within the SWCNT–graphene junctions have a square shape with the side length $L_2$ as shown in Figure 1a. Following the idea of Lee, the free part of the system is considered as the nanodevice and the thermostated parts are considered as the thermal contacts. In all simulations, the optimized Tersoff potential is adopted and a free boundary condition is used. The time step is set to 0.4 fs. Initially, the suspended junctions are relaxed in the NVT ensemble at $T_0$ for 2 ns using the Nose–Hoover thermostat. Then to establish a temperature gradient along the longitudinal direction of the tube, NEMD is performed for another 4.8 ns; the constant temperatures in the two heating bath zones are controlled by a Berendsen thermostat. The temperatures in the hot and cold bath zones are set to be $T_0(1+\Delta)$ and $T_0(1-\Delta)$, respectively, where $T_0$ and $\Delta$ represent the average temperature and the normalized temperature difference, respectively.

The TR ratio is defined as

$$\eta = \frac{(J_+ - J_-)}{J_+} \times 100\%$$  \hspace{1cm} \text{(1)}$$

where $J_+$ is the heat current from the wide side to the narrow side, corresponding to $\Delta > 0$, and $J_-$ is the heat current from the narrow side to the wide side when $\Delta < 0$.

3. RESULTS AND DISCUSSION

First, we investigate the dependence of thermal rectification on the geometry size of the SWCNT–graphene junctions, which are characterized by the tube length $L_1$ and the graphene nanosheet $L_2$ (depicted in Figure 1a). The 2D gridded data of the thermal rectification by $L_1$ varying from 3.69 to 9.84 nm (15–40 unit cells) with a step of 5 unit cells and $L_2$ varying from 6 to 16 nm with a step of 2 nm are calculated by MD simulations. In all simulations, $T_0$ is set as 300 K and $|\Delta|$ is set as 0.5. Surprisingly, ultrahigh thermal rectification ratios with maximum values of 1244.1% and 1063% are observed by junction A and junction B with geometry sizes $L_1 = 4.9$ nm and $L_2 = 10$ nm, respectively. These thermal rectification ratio values are much higher than the rectification value of 790.8% established for the designed graded two-stage pillared graphene structures we reported in our previous study.

Then a cubic interpolation is performed on the gridded simulation results to obtain a smoother surface distribution of the thermal rectification ratio. The distribution of the thermal rectification with respect to $L_1$ and $L_2$ for junction A and junction B is illustrated in Figure 1b, 1c, 1e, and 1f, in which the thermal rectification of the nanotube–graphene junctions that is fairly sensitive to geometry size can be observed. $L_1$ varies from 3.69 to 9.84 nm (15–40 unit cells) and $L_2$ from 6 to 16 nm, which lead to changes in the values of the thermal rectification ratio of junction A and junction B from 69% to.
The objective of the wide and the narrow sides of the device, respectively. In Figure 1, where most of the regions with larger rectification values are located in the narrow areas of the connections of the two peaks. The causes for the ultrahigh thermal rectification in these junction nanostructures and for the sensitivity of thermal rectification to the geometry size also need to be elucidated. Thus, we analyze the dependence of the phonon spectra overlap of the thermal rectification on the geometry size of the junctions. It is worth noting that among the working principles of thermal rectification, phonon spectra overlap is most commonly used in analysis and explanation of TR in heterojunctions and graded systems. The phonon spectra are obtained via calculation of the vibration density of states (vDOS). In the calculations of the power spectra of the wide and narrow sides, we choose the atoms of the device in the first two unit cells away from each thermal contact. The overlaps ($S_\pm$) of the power spectra of the wide and narrow sides of the device are calculated as follows

$$ S_\pm = \frac{\int P_w(\omega) P_n(\omega) d\omega}{(\int P_w(\omega)^2 d\omega)^{1/2} (\int P_n(\omega)^2 d\omega)^{1/2}} $$

where $S_+$ and $S_-$ are the overlaps in the case of $\Delta > 0$ and $\Delta < 0$, respectively, and $P_w(\omega)$ and $P_n(\omega)$ are the power spectrum of the wide and the narrow sides of the device, respectively. In fact, the objective of $S_\pm$ is to quantify the analysis of the match or mismatch of the power spectra; thus, it can be calculated via both the definition of overlaps and the similarity measures. It should be noted that this equation proposed in this study is based on the cosine similarity measures and is different from those in previous studies. The $S_\pm$ calculated by this equation can well describe the match or mismatch of the power spectra with components of significant standing wave. This equation is explained and discussed in detail in the Supporting Information. In keeping with previous studies, $S_\pm$ calculated by this equation is still called overlaps.

Actually, Li et al. concluded that the thermal rectification ratio is related to the match or mismatch of the corresponding power spectra and follows the equation $TR = (J_+ - J_-)/J_+ \approx (S_+/S_-)^{\delta_R} - 1$ with $\delta_R = 1.68 \pm 0.08$, where, $J_+$ and $J_-$ are the heat flux in the cases with a positive thermal bias ($\Delta > 0$) and a negative thermal bias ($\Delta < 0$). These results have important implications in the design of thermal diodes and suggest that the thermal rectification ratio can be improved by increasing the value of $S_\pm$ or decreasing that of $S_-$. The distribution of $S_\pm$, $1/S_\pm$, and $(S_+/S_-)^{\delta_R} - 1$ with respect to the geometry sizes $L_1$ and $L_2$ for model junction A are calculated (Figure 2a, 2b, and 2c). We find that $S_\pm$ is insensitive to the geometry size (Figure 2a). Conversely, $S_-$ is rather sensitive to the geometry size (Figure 2b), and the variations of $1/S_-$ with geometry size are similar to those of the thermal rectification ratio (Figure 1c). Accordingly, our results indicate that the strong effect of the geometry size on the thermal rectification ratio is dominated by $S_-$ and has an insignificant relationship with $S_+$. The distribution of $(S_+/S_-)^{\delta_R} - 1$ ($\delta_R = 1.8$) is also calculated and shown in Figure 2c, which follows the equation $TR = (J_+ - J_-)/J_+ \approx (S_+/S_-)^{\delta_R} - 1$. Moreover, the distribution of $J_+$ and $1/J_-$ with respect to geometry size is also established in our study (Figure 2d and 2e). Although $J_+$ increases with increasing $L_2$ and decreases with increasing $L_1$, its variation is much smaller than that of $1/J_-$. The latter is more sensitive to the geometry size, and its distribution with geometry size appears to be similar to that of the TR ratio and $(S_+/S_-)^{\delta_R} - 1$. Thus, we can conclude that the decrease of $S_-$ is more important for improving the TR ratio than increasing $S_+$. The distribution of $S_\pm$, $1/S_\pm$, and $(S_+/S_-)^{\delta_R} - 1$ with respect to the geometry sizes $L_1$ and $L_2$ for model junction A are calculated (Figure 2a, 2b, and 2c). We find that $S_\pm$ is insensitive to the geometry size (Figure 2a). Conversely, $S_-$ is rather sensitive to the geometry size (Figure 2b), and the variations of $1/S_-$ with geometry size are similar to those of the thermal rectification ratio (Figure 1c). Accordingly, our results indicate that the strong effect of the geometry size on the thermal rectification ratio is dominated by $S_-$ and has an insignificant relationship with $S_+$. The distribution of $(S_+/S_-)^{\delta_R} - 1$ ($\delta_R = 1.8$) is also calculated and shown in Figure 2c, which follows the equation $TR = (J_+ - J_-)/J_+ \approx (S_+/S_-)^{\delta_R} - 1$. Moreover, the distribution of $J_+$ and $1/J_-$ with respect to geometry size is also established in our study (Figure 2d and 2e). Although $J_+$ increases with increasing $L_2$ and decreases with increasing $L_1$, its variation is much smaller than that of $1/J_-$. The latter is more sensitive to the geometry size, and its distribution with geometry size appears to be similar to that of the TR ratio and $(S_+/S_-)^{\delta_R} - 1$. Thus, we can conclude that the decrease of $S_-$ is more important for improving the TR ratio than increasing $S_-$.
If a device exhibiting large rectification is to be designed, the solutions attempted to decrease $S_{-}$ should be preferentially considered.

To further understand the underlying mechanism of the strong geometry size effect on $S_{+}$, we calculate the power spectra and the velocity autocorrelation function (VACF) for three junctions A with different geometry sizes, which are presented in Figure 3a-l. In the calculations, the atoms groups used for the calculations of $S_{+}$ and $S_{-}$ described above are selected. In Figure 2c, the geometry size sets selected are labeled as follows: for A, $L_1 = 4.9$ nm and $L_2 = 10$ nm; for B, $L_1 = 6.1$ nm and $L_2 = 8$ nm; for C, $L_1 = 9.84$ nm and $L_2 = 16$ nm.

In addition, the sets A, B, and C refer to the first peak, the second peak, and the point with the maximum geometry size, respectively, in Figure 1b. Significant low-frequency peaks at 14.5 THz are observed in the power spectra of the narrow side for geometry size sets A, B, and C under negative thermal bias and the higher peak leads to larger TR ratio. These significant low-frequency peaks have been found to occur only when the narrow end of the graded nanostructure is subjected to a temperature that is higher than that of the wide end.6,9,10,28 In this study, they are demonstrated to be of standing wave nature by VACFs as shown in Figure 3c, 3g, and 3k. The standing wave greatly hinders the propagation of phonon waves and the

Figure 3. vDOS per atom and normalized velocity autocorrelation functions for junction A with geometry size sets A, B, and C: (a, e, and i) vDOS when $\Delta = -0.5$; (b, f, and j) vDOS when $\Delta = 0.5$; (c, g, and k) VACF for narrow sides; (d, h, and l) VACF for wide sides.

Figure 4. (a) Phonon (12.5−16.5 THz) spatial distribution of the atoms of the free part of the system for junction A with geometry sizes set A when $\Delta = -0.5$ and 0.5; (b) phonon (0−30 THz) spatial distribution of the atoms of the free part of the system for junction A with geometry sizes set A when $\Delta = -0.5$ and 0.5; (c) calculated natural frequencies of junction A with geometry sizes sets A, B, and C.
transfer of thermal energy, which indicates that formation of the standing wave is sensitive to the geometry size and stronger standing wave leads to smaller $S_{−}$.

In general, the thermal rectification can also be explained by phonon localization, visualized by the spatial distribution of phonon modes equivalent to the weight distribution of the specific modes. The weight of a specific range ($\Lambda$) of phonon modes on the whole spectral range for the $ith$ atom can be expressed as

$$w_{\Lambda,i} = \frac{\int_{\Lambda} P(\omega) d\omega}{\int_{0}^{\infty} P(\omega) d\omega} \quad (3)$$

The phonon spatial distribution of the atoms of the nanodevice part of the system are illustrated in Figure 4a and 4b at $\Delta = −0.5$ and $\Delta = 0.5$ with $\Lambda = 12.5−16.5$ THz and $\Lambda = 0−30$ THz, respectively. As can be seen in the figure, the phonon spatial distribution is almost uniform in the case of $\Delta = 0.5$. However, the phonon localization is substantial when $\Delta = −0.5$, and atoms with higher $w_{i}$ are located in the region near the tube ends. The higher $w_{i}$ result from the extremely high peaks of vDOS at 14.5 THz which are of standing wave nature as discussed above. These findings indicate that the standing waves in the area near the tube end are vigorous and decay fast along the heat transfer direction. We also calculated the natural frequencies of junction A with geometry size sets A, B, and C, which are depicted in Figure 4c. It is apparent from this figure that the natural frequencies of 14.5 THz coincides with the peaks of 14.5 THz in Figure 3a, 3e, and 3i for the vDOS and the frequencies of standing waves in Figure 3c, 3g, and 3k. This means that the standing wave is a resonance at the natural frequencies of the junction, and smaller peaks with a frequency of 29 THz may be harmonic with the doubled frequency also caused by the resonance at the natural frequency of 14.5 THz.

To illustrate the standing wave more clearly that formed along the junction, the free part of the system of junction A has been used, and four atom groups (each consisting of 48 atoms) are chosen and labeled 1−4 (see Figure 5a). The VACF are calculated for atom groups 1−4, as shown in Figure 5b. In the heat transport direction (from the narrow side to the wide side when $\Delta = −0.5$), the strength of the standing wave continuously decreases and gradually disappears at the region of atom groups 3 and 4, thus suggesting that the standing waves decay fast along the heat transport direction of the free part. Figure 5c shows a plot of the temperature profile along the transport direction for junction A with geometry size set A. This indicates that the two curves of the temperature profile are asymmetric when $\Delta = −0.5$ and 0.5. A temperature jump at the structure region between SWCNT and graphene for $\Delta = 0.5$ can also be seen, which is much larger than that in the case of $\Delta = −0.5$. More importantly, for $\Delta = −0.5$, an undulation of temperature can be observed. Such a behavior of the

Figure 5. Illustrations for the standing wave formed and temperature profile along junction A with geometry sizes set A: (a) the free part of the system for junction A and chosen atom groups 1−4; (b) VACF calculated for group 1−4 when $\Delta = −0.5$; (c) temperature profile of junction A along the heat transport direction.

Figure 6. TR ratio and heat flux for junction A with geometry sizes $L_1 = 4.9$ nm and $L_2 = 10$ nm: (a) TR ratio and corresponding heat flux vs $|\Delta|$; (b) TR ratio and corresponding heat flux vs average temperature.
temperature has been reported and was also confirmed to be the result of the standing wave.\textsuperscript{9,10}

For junction A with geometry sizes $L_1 = 4.9$ nm and $L_2 = 10$ nm, the TR ratio versus $|\Delta l|$ and the average temperature are shown in Figure 6a and 6b, respectively. The TR ratio increased almost linearly with $|\Delta l|$, which corresponded to the fast and low increase rate of $J_1$ and $J_-$. Even under a small thermal bias $|\Delta l| = 0.1$, a rectification ratio as high as 188.6% can be achieved. The rectification ratio of junction A at $|\Delta l| = 0.1$ is slightly higher than that of the designed graded two-stage pillared graphene structure PGN-B we reported earlier;\textsuperscript{28} however, the rectification ratio of junction A at $|\Delta l| = 0.5$ is much higher than that of PGN-B. These results indicate that the rectification ratio of junction A increases faster than that of PGN-B with $|\Delta l|$.

It is noteworthy that the rectification ratio of junction A decreased linearly with the elevation in the average temperature and reached 1681.6% and 912.7% at temperatures of 200 and 400 K, respectively. This can be explained as the weakening effect of Umklapp scattering. In a typical U process, randomization of the heat flow direction occurs and the net heat flux along the axis of the tube is reduced. With increasing temperature, scattering of the phonons steadily increases and the geometric asymmetry effect of the thermal rectification will steadily decrease, thus resulting in decreasing TR with temperature.

Before closing, we would like to emphasize that the geometry size of the designed graded two-stage pillared graphene nanostructures (PGN) in our previous study\textsuperscript{28} was not optimized. Thus, it is not appropriate to make a direct comparison between the thermal rectification of the pillared graphene structures and that of the optimized single-carbon nanotube–graphene junction studied in this work. However, the rectification effect exhibited by a single-carbon nanotube–graphene junction should relate with the giant thermal rectification from the designed graded two-stage pillared graphene structures. It should also be noted that the obtained optimized geometry parameters for the single-carbon nanotube–graphene junction cannot be directly used to obtain an optimized design of the pillared graphene-based thermal rectifier because the coupling of the phonons of the junctions needs to be considered and further studied. We have shown that both designed single-carbon nanotube–graphene junction and graded two-stage pillared graphene nanostructures can exhibit giant thermal rectification and would therefore be excellent thermal rectifiers. In reality, however, assembling such a small device is still quite challenging. Advanced technology, such as atomic force microscopy, can already manipulate single junctions or single molecules will be helpful for fabricating such a small nanodevice.

4. CONCLUSIONS

In summary, the effect of the geometry size on the thermal rectification of single-carbon nanotube–graphene junctions has been investigated. Additionally, the distribution of the thermal rectification with respect to the tube length and side length of the graphene nanosheet was calculated and visualized. The optimized carbon nanotube–graphene junction was found to have an ultrahigh thermal rectification ratio. In addition, the maximum thermal rectification ratios for junction A under $|\Delta l| = 0.5$ can reach 1244.1% and 1681.6% at average temperatures of 300 and 200 K, respectively. These are much higher than those of other reported single-material nanostructure-based thermal rectifiers. The thermal rectification of the nanotube–graphene junctions is fairly sensitive to the geometry size and almost completely dominated by the degree of overlap of the power spectra under negative thermal bias. Our findings could offer useful guidelines for the design and improvement of the performance of thermal diodes.

ASSOCIATED CONTENT

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b04464.

Comparison and discussion on the different equations for the calculation of overlaps of the vDOS (PDF)

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Notes

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