Unravelling the Impact of Graphene Addition to Thermoelectric SrTiO$_3$ and La-doped SrTiO$_3$ Materials: A Density Functional Theory Study

Supporting Information

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Electronic Transport Calculations

We performed transport calculations on the pristine and La-doped SrTiO$_3$ surface-slab models using the BoltzWann code$^{1,2}$ with an interpolated 50 $\times$ 50 $\times$ 1 $k$-point mesh. Due to the large number of bands and the semi-metallic nature of the surfaces with adsorbed graphene, we were not able to perform BoltzWann calculations on these models.

During the BoltzWann calculations, transport coefficients were calculated using maximally localized Wannier functions (MLWFs), which can be used for Wannier interpolation of the band energies onto a fine $k$-point sampling mesh.$^3$ Test calculations on bulk SrTiO$_3$ showed that Wannier projections onto the oxygen $p$ and titanium $d$ orbitals using atom-centered Gaussian-type orbitals yielded the best MLWFs. In each case the final spreads for the WFs were $< 1$ Å with convergence to $< 10^{-5}$ Å$^2$, and all the WFs were real. Figure S1 shows example Wannier functions obtained for the SrTiO$_3$ surface slab model.

The disentanglement method was used to freeze the bands around the Fermi level.$^4$ In this region of the band structure the Bloch states and therefore the bands are preserved, whereas in the outer energy window the Bloch states can change depending on the choice of unitary transformation. The disentanglement window was chosen to be between -6 eV below the Fermi level and $\sim$1 eV above the lowest-energy conduction band. The bands contained in the outer window are not relevant for transport properties as they lie more than a few $k_bT$ from the Fermi level.$^{2,5}$ For bulk SrTiO$_3$, projections onto the Ti $d$ and O $p$ orbitals give 14 WFs compared to the 15 bands calculated with DFT. Figures S2-S4 compare the band structures for bulk SrTiO$_3$ and the SrTiO$_3$ and La-doped SrTiO$_3$ slab models obtained by explicit computation of the band energies at strings of $k$-points along the band path and by Wannier interpolation.

Figures S5 and S6 compare the calculated Seebeck coefficients of bulk SrTiO$_3$ obtained using both methods as a function of carrier concentration at $T = 600$ and 1000 K, and as a function of temperature at a fixed carrier concentration of $10^{20}$ cm$^{-3}$, corresponding to the chemical potential at the bottom of the conduction band. Similarly, Figures S7 and S8 compare the calculated Seebeck coefficients of the SrTiO$_3$ and La-doped SrTiO$_3$ surface models as a function of carrier concentration at 600 and 1000 K and as a function of temperature at a carrier concentration of $-2.6 \times 10^{20}$ cm$^{-3}$, corresponding to $n$-type doping.

Finally, Figures S9 and S10 show additional calculations performed using BoltzTrap to investigate the Seebeck coefficient of bulk SrTiO$_3$ at zero carrier concentration (Figure S9) and the Seebeck coefficient, electrical conductivity and electronic thermal conductivity as a function of carrier concentration at 300 K, and as a function of chemical potential at 300, 600 and 1000K for pristine and graphene-adsorbed SrTiO$_3$ and La-doped SrTiO$_3$ surfaces (Figure S10).
**Figure S1.** Real-space plots of representative MLWFs obtained for the SrTiO₃ surface slab model, generated using the VESTA software.⁹ (a) $p$-type projection centered on an oxygen atom (red). (b) $d$-type projection centered on a titanium atom (bright green). Strontium atoms are shown in dark green.

**Figure S2.** Comparison of the band structures of bulk SrTiO₃ obtained by explicit computation of the electronic band energies at strings of $k$-points (red lines) and by Wannier interpolation with 14 Wannier functions (black). Both calculations predict the same indirect band gap of 1.65 eV.
**Figure S3.** Comparison of the band structures of the SrTiO$_3$ surface slab model obtained by explicit computation of the electronic band energies at strings of $k$-points (red lines) and by Wannier interpolation (black).

**Figure S4.** Comparison of the band structures of the La-doped SrTiO$_3$ surface slab model obtained by explicit computation of the electronic band energies at strings of $k$-points (red lines) and by Wannier interpolation (black).
Figure S5. Comparison of the Seebeck coefficient of bulk SrTiO$_3$ as a function of carrier concentration obtained using BoltzTraP and BoltzWann at 600 and 1000 K. The plots show excellent agreement, indicating that our choice of Wannier functions is suitable. Experimentally, SrTiO$_3$ is intrinsically an $n$-type semiconductor with a negative Seebeck coefficient, corresponding to a negative $p$-$n$.\textsuperscript{7}

Figure S6. Comparison of the Seebeck coefficient of bulk SrTiO$_3$ as a function of temperature for a fixed carrier concentration of $10^{20}$ cm$^{-3}$, corresponding to the chemical potential at the bottom of the conduction band, obtained using the BoltzTraP and BoltzWann codes. Both the calculated Seebeck coefficient and its increase in magnitude as a function of temperature, in agreement with other theoretical modelling and experiments.\textsuperscript{8-10}
Figure S7. Comparison of the Seebeck coefficient as a function of carrier concentration for the SrTiO$_3$ (a/b) and La-doped SrTiO$_3$ (c/d) surface slab models obtained using the BoltzTraP and BoltzWann codes at $T = 600$ (a/c) and 1000 K (b/d).
Figure S8. Temperature dependence of the Seebeck coefficients of the SrTiO\textsubscript{3} (a) and La-doped SrTiO\textsubscript{3} (b) surface model at a fixed carrier concentration of $-2.6 \times 10^{20}$ cm\textsuperscript{-3} (i.e. \textit{n}-type doping), obtained using the BoltzTraP and BoltzWann codes.

Figure S9. Temperature dependence of the Seebeck coefficient of bulk SrTiO\textsubscript{3} obtained using BoltzTraP at a carrier concentration $p$-$n = 0$. 
Figure S10. (a-c) Calculated Seebeck coefficient $S$ (a), electrical conductivity $\sigma/\tau$ (b) and electronic thermal conductivity $\kappa_{el}/\tau$ (c) as a function of carrier concentration for pristine and graphene-adsorbed SrTiO$_3$ and La-doped SrTiO$_3$ surfaces at $T = 300$ K, obtained using the BoltzTraP code. (d-l) Calculated Seebeck coefficient $S$ (d/g/j), electrical conductivity $\sigma/\tau$ (e/h/k) and electronic thermal conductivity $\kappa_{el}/\tau$ (l/i/l) as a function of chemical potential for pristine and graphene-adsorbed SrTiO$_3$ and La-doped SrTiO$_3$ surfaces at $T = 300$, 600 and 1000 K, obtained using the BoltzTraP code.
Rotation of Surfaces and Group Velocities

The surface-slab models employed in this work are rotated with respect to bulk SrTiO$_3$ (Figure S11). The thermal conductivity and related tensor quantities computed for the rotated cell, denoted $\kappa_{ij}^m$, can be related to the original cell, $\kappa_{ij}$, as outlined below.

For our surface $\kappa_{ij}^m$ is given by:

$$
\kappa_{ij}^m = \frac{j \kappa_{ij}^T}{\text{det}(J)}
$$

Eq. S1

$$
\begin{pmatrix}
\kappa_{xx}^m & \kappa_{xy}^m & 0 \\
\kappa_{yx}^m & \kappa_{yy}^m & 0 \\
0 & 0 & \kappa_{zz}^m
\end{pmatrix} =
\begin{pmatrix}
\kappa_{xx} \cos^2 \theta + \kappa_{yy} \sin^2 \theta & (\kappa_{xx} + \kappa_{yy}) \sin \theta \cos \theta & 0 \\
(\kappa_{xx} + \kappa_{yy}) \sin \theta \cos \theta & \kappa_{yy} \cos^2 \theta + \kappa_{xx} \sin^2 \theta & 0 \\
0 & 0 & \kappa_{xx}
\end{pmatrix}
$$

Eq. S2

where $J$ is the Jacobian matrix of the coordinate transformation between the rotated and original surfaces, and for rotation around the $z$ axis perpendicular to the surface:

$$
J = \begin{pmatrix}
\cos \theta & \sin \theta & 0 \\
-sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

Eq. S3

We can solve the simultaneous equations in Eq. S2 to obtain expressions for the tensor elements for the rotated surface in terms of those of the original surface to obtain $\kappa_{xx}$, $\kappa_{yy}$, and the off-diagonal term $\kappa_{xy} = 0$:

$$
\kappa_{xx}^m = \kappa_{xx} \cos^2 \theta + \kappa_{yy} \sin^2 \theta
$$

Eq. S4
\[
\kappa_{yy}^m = \kappa_{yy} \cos^2 \theta + \kappa_{xx} \sin^2 \theta \quad \text{Eq. S5}
\]
\[
\kappa_{xy}^m = (-\kappa_{xx} + \kappa_{yy}) \sin \theta \cos \theta \quad \text{Eq. S6}
\]

As \( \cos^2 \theta + \sin^2 \theta = 1 \), we can substitute \( \cos^2 \theta = 1 - \sin^2 \theta \):

\[
\kappa_{xx}^m = \kappa_{xx}(1 - \sin^2 \theta) + \kappa_{yy} \sin^2 \theta \quad \text{Eq. S7}
\]
\[
\kappa_{yy}^m = \kappa_{yy}(1 - \sin^2 \theta) + \kappa_{xx} \sin^2 \theta \quad \text{Eq. S8}
\]
\[
\kappa_{xy}^m = -\kappa_x \sin \theta \cos \theta + \kappa_y \sin \theta \cos \theta \quad \text{Eq. S9}
\]

We now proceed to rearrange Eq. S7 so that:

\[
\kappa_{xx}^m = \kappa_{xx} - \kappa_{xx} \sin^2 \theta + \kappa_{yy} \sin^2 \theta \quad \text{Eq. S10}
\]
\[
\kappa_{yy}^m \sin^2 \theta = \kappa_{xx}^m - \kappa_{xx} + \kappa_{xx} \sin^2 \theta \quad \text{Eq. S11}
\]

We similarly rearrange Eq. S8 to obtain:

\[
\kappa_{yy}^m = \kappa_{yy} - \kappa_{yy} \sin^2 \theta + \kappa_{xx} \sin^2 \theta \quad \text{Eq. S12}
\]
\[
\kappa_{xx}^m \sin^2 \theta = \kappa_{yy}^m - \kappa_{yy} + \kappa_{yy} \sin^2 \theta \quad \text{Eq. S13}
\]

Substituting Eq. S13 into Eq. S10 gives:

\[
\kappa_{xx}^m = \kappa_{xx} - (\kappa_{yy}^m - \kappa_{yy} + \kappa_{yy} \sin^2 \theta) + \kappa_{yy} \sin^2 \theta
\]
\[
= \kappa_{xx} - \kappa_{yy}^m + \kappa_{yy} - \kappa_{yy} \sin^2 \theta + \kappa_{yy} \sin^2 \theta
\]
\[
= \kappa_{xx} - \kappa_{yy}^m + \kappa_{yy} \quad \text{Eq. S14}
\]

Substituting Eq. S11 into Eq. S12 gives:

\[
\kappa_{yy}^m = \kappa_{yy} - (\kappa_{xx}^m - \kappa_{xx} + \kappa_{xx} \sin^2 \theta) + \kappa_{yy} \sin^2 \theta
\]
\[
= \kappa_{yy} - \kappa_{xx}^m + \kappa_{xx} \sin^2 \theta + \kappa_{yy} \sin^2 \theta
\]
\[
= \kappa_{yy} - \kappa_{xx}^m + \kappa_{xx} \quad \text{Eq. S15}
\]

Dividing Eq. S9 by \( \sin \theta \cos \theta \) gives the following relations:

\[
\kappa_{yy} = \kappa_{xx} + \frac{\kappa_{xy}^m}{\sin \theta \cos \theta} \quad \text{Eq. S16}
\]
\[
\kappa_{xx} = \kappa_{yy} - \frac{\kappa_{xy}^m}{\sin \theta \cos \theta} \quad \text{Eq. S17}
\]

Substituting Eq. S16 in to Eq. S14 yields:
\[ k_{xx}^m = k_{xx} - k_{yy}^m + k_{xx} + \frac{k_{yy}^m}{\sin \theta \cos \theta} \quad \text{Eq. S18} \]

\[ k_{xx} = \frac{k_{xx}^m}{2} + \frac{k_{yy}^m}{2} - \frac{k_{xy}^m}{2(\sin \theta \cos \theta)} \quad \text{Eq. S19} \]

Similarly, substituting Eq. S17 into Eq. S15 gives:

\[ k_{yy}^m = k_{yy} - k_{xx}^m + k_{yy} - \frac{k_{xy}^m}{\sin \theta \cos \theta} \quad \text{Eq. S20} \]

\[ k_{yy} = \frac{k_{xx}^m}{2} + \frac{k_{yy}^m}{2} + \frac{k_{xy}^m}{2(\sin \theta \cos \theta)} \quad \text{Eq. S21} \]

These relationships can be applied to both the thermal conductivity and the constant relaxation-time approximation function defined in Eq. 16 in the text to obtain the xx and yy components in terms of the bulk SrTiO₃ axes, and thence the in-plane average.

**Convergence of \( K_{\text{latt}}/\tau^{\text{CRTA}} \) with respect to the q-point sampling mesh**

As described in the text, we computed for each of the four surface-slab models the function \( K_{\text{latt}}/\tau^{\text{CRTA}} \) defined in Eq. 16. As depicted in Figure S12, we found that the convergence of this function with respect to the q-point sampling mesh was somewhat erratic. To handle this, we calculated the function over a large number of meshes with systematically increasing numbers of subdivisions. We then calculated the mean value at each temperature, over all the mesh sizes tested, and removed outliers for which the calculation was more than a standard deviation from the mean. Finally, we then recalculated the standard deviation and took this as a measure of the spread, which is shown in Figure 6 in the text.
Figure S12. Convergence of the function $\kappa_{\text{latt}}/T^{\text{CRTA}}$ (in-plane average) as a function of the $q$-point sampling mesh for the (a, b) SrTiO$_3$, (c, d) graphene-adsorbed SrTiO$_3$, (e, f) La-doped SrTiO$_3$ and (g, h) graphene-adsorbed La-doped SrTiO$_3$ surfaces. Plots in the left-hand column show the functions calculated for all the mesh sizes tested (a, c, e, g), while those in the right-hand column show the functions obtained after “masking” to remove the outliers as described above (b, d, f, h).
Figure S13. Convergence of the function $\bar{N}_2$ as a function of the q-point sampling mesh for the (a, b) SrTiO$_3$, (c, d) graphene-adsorbed SrTiO$_3$, (e, f) La-Doped SrTiO$_3$ and (g, h) graphene-adsorbed La-doped SrTiO$_3$ surfaces. Plots in the left-hand column show the $\bar{N}_2^{(1)}$ functions calculated for collision processes (a, c, e, g), while those in the right-hand column show the $\bar{N}_2^{(2)}$ functions calculated for decay processes (b, d, f, h).
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