Supporting Information

Dimensionality-dependent charge transport in close-packed nanoparticle arrays: from 2D to 3D

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I. CURRENT-VOLTAGE CURVES MEASURED AT VARIOUS TEMPERATURES

To study the charge transport properties of nanoparticle arrays, we measured current-voltage (I-V) curves of each device at various temperatures. The samples were mounted on the sample holder of a cryostat. The temperature of samples could be controlled in the range from 3.5 K to room temperature.

Figure S1 shows I-V curves measured at various temperatures of device 1. Here, device 1 corresponds to the one we study in the main text. In our measurements, I-V curves were measured when the device had different thicknesses. To show typical I-V curves, we choose three thicknesses: monolayer, tetralayer, and pentadecalayer. Monolayer is a 2D system. Tetralayer is the finishing transition point from 2D to 3D. Pentadecalayer can be regarded as a real 3D system. The I-V curves of devices with these three thicknesses are shown in Fig. S1 a, b, c. For all measurements, the starting temperature was 3.5 K. Then, the temperature was increased and more I-V curves were measured. For all three thicknesses, the I-V curves are more and more nonlinear with decreasing temperature. At the same temperature, the current of tetralayer has a significant enhancement comparing with that of monolayer. However, there is not too much difference in current between tetralayer and pentadecalayer.

II. VARIABLE RANGE HOPPING AND SEQUENTIAL HOPPING FITTING FOR I-V CURVES AT LOW/MEDIUM TEMPERATURE.

To study the transport mechanism at different temperature ranges, we look at the temperature dependence of the zero-voltage conductance. Regardless of the thickness of nanoparticle arrays, the zero-vlotage conductance follows variable range hopping transport at low temperature, and sequential hopping transport at medium temperature.

Figure S2 shows typical results. We take a tetralayer as an example. Figure S2a plots the zero-voltage conductance as a function of $T^{-1/2}$ in a semi-log scale. The green line is the linear fitting curve. It is clear that the data at low temperature (30 K - 70 K) follow the $T^{-1/2}$ very well. However, the data at medium temperature (75 K - 130 K) start to deviate from the linear fitting. Instead, the zero-voltage conductance can be nicely fitted by Arrhenius behavior, as shown in Fig. S2b. The linear relationship between lnG_0 and $T^{-1/2}$ indicates that the data at low temperature can be understood in term of Efros-Shaklovskii variable-range-hopping (ES-VRH) model. On

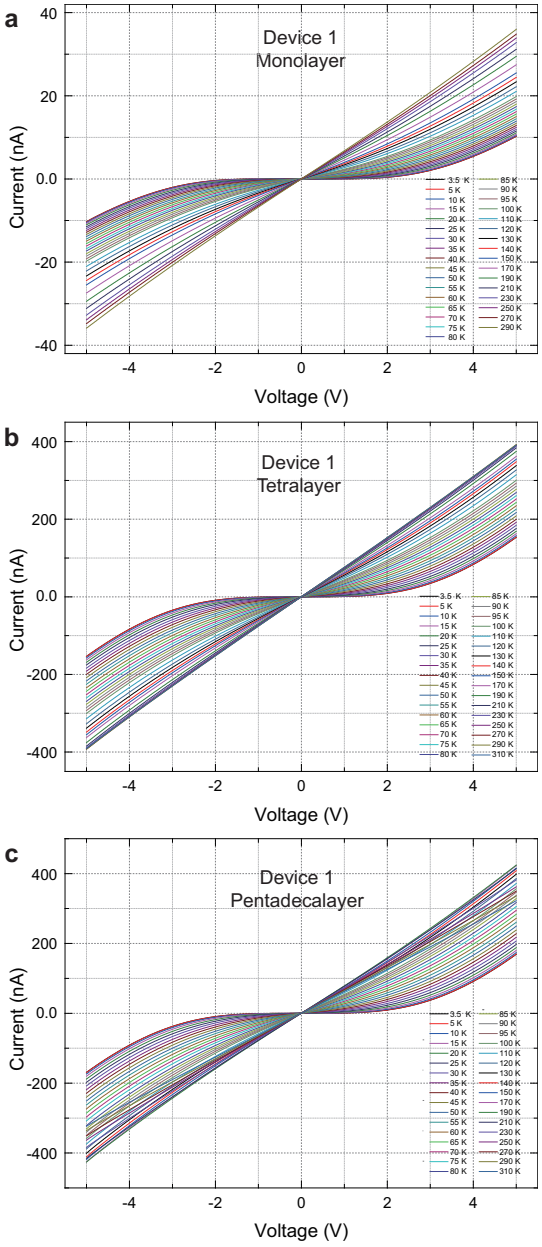

FIG. S1: **Current-voltage curves measured at various temperatures.** I-V curves of devices with different thickness: monolayer (**a**), tetralayer (**b**), and pentadecalayer (**c**).The temperature was controlled in the range from 3.5 K to room temperature.

the other hand, The Arrhenius behavior suggests the sequential hopping mechanism at medium temperature. Note that all data of different thicknesses have the similar behavior, although only the data of tetralayer are shown here. This justifies the rationality of the data treatment at low/medium temperature in the main text.

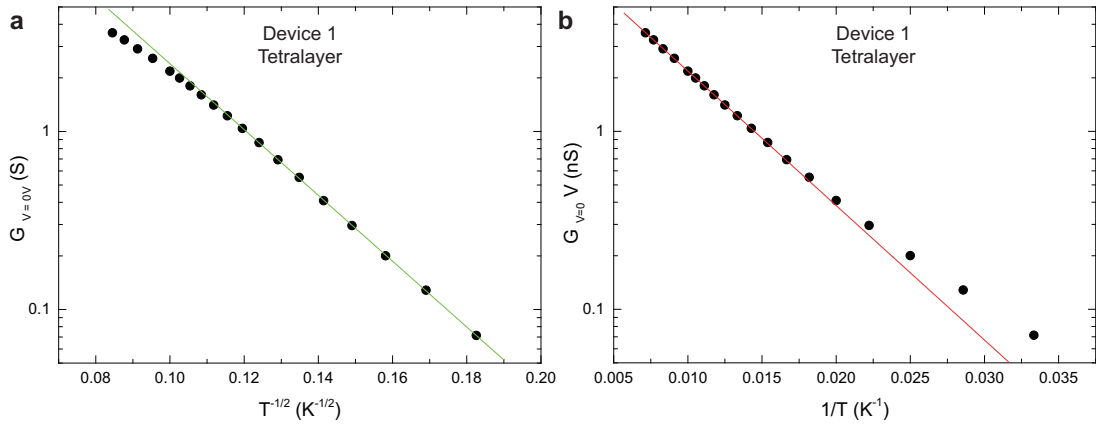

FIG. S2: **ES-VRH and SH fitting for I-V curves at low/intermedium temperature. a,** The zero-voltage conductance of a tetralayer as a function of $T^{-1/2}$. The green line is the linear fitting for the data points at low temperature. **b,** The zero-voltage conductance as a function of T^{-1}. The red line is the linear fitting for the data points at medium temperature.

III. COEFFICIENT β_D AS A FUNCTION OF ARRAY THICKNESS FOR DEVICE 2

For another device (device 2), we did the same treatment on the data measured at low temperature as device 1. Figure S3a shows the zero-voltage conductance of nanoparticle arrays with different thickness as a function of $T^{-1/2}$ in the temperature range from 30 K to 70 K. The data show that the logarithm of the zero-voltage conductance is linearly proportional to $T^{-1/2}$ regardless of the thickness of the arrays at low temperature. Another feature of the data sets is that the conductance increases obviously from monolayer to few multilayers, but starts to level off after stacking 4-5 monolayers. These features are similar to that we observe on device 1.

The slopes of the data set shown in Fig. S2a were extracted and shown in the inset of Fig. S3b with respect to the number of printed nanoparticle monolayers. To obtain 6.5 for β_D in the case of monolayer, the effective dielectric constant ε has to be 7. This is little bit high for octanethiol-capped gold nanoparticle arrays. However, the value of the effective dielectric constant does not change the evolution trend of the coefficient β_D as a function of the thickness of nanoparticle arrays, as shown in Fig. S3b. Again, just as the device 1, the coefficient β_D decreases deeply in the first 4-5 nanoparticle layers, and starts to fluctuate in thicker arrays. In detail, the coefficient is 6.5 for the 2D array and decreases to 3.7 for the pentalayer array. When the number of layers is more than 5, the coefficient fluctuates between 3.4 and 3.7 up to 15 layers.

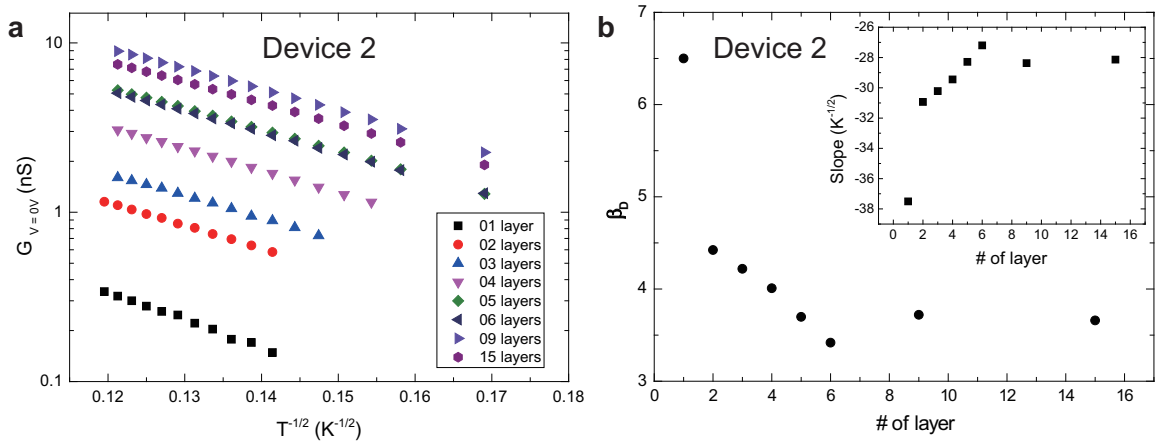

FIG. S3: **Coefficient β_D as a function of array thickness for device 2. a,** Temperature-dependent conductance at low voltage bias in a semi-log scale. The logarithm of the zero-voltage conductance of all nanoparticle arrays is linearly proportional to the $T^{-1/2}$ at low temperature regardless of the layers of the nanoparticle arrays. **b,** The coefficient β_D in ES-VRH model, which is supposed to depend on the system dimensionality D, as a function of the number of nanoparticle monolayers. Inset: Slopes of the ln(G)-$T^{-1/2}$ curves shown in **a** plotted as a function of number of nanoparticle monolayers.

IV. ACTIVATION ENERGY E_a AS A FUNCTION OF ARRAY THICKNESS FOR DEVICE 2

The inset of Fig. S4 shows the zero-voltage conductance between 75 K and 130 K as a function of inverse temperature for device 2. It is clear that the zero-voltage conductance follows Arrhenius behavior. The activation energies E_a determined by data fitting are shown in Fig. S4 as a function of the number of printed monolayers. Our data show that the activation energy decreases deeply with increasing the thickness of the nanoparticle array for the first five layers from 12.3 meV to 9.0 meV. Afterward, the activation energy fluctuates between 8.7 meV and 9.0 meV with increasing more nanoparticle monolayers. The change trend is similar to that of the coefficient β_D, as shown in Fig. S3b.

V. TURNING POINTS IN THE TEMPERATURE COEFFICIENT OF CONDUCTANCE FOR DEVICE 2

The appearance of the turning point of the temperature coefficient of conductance at high temperatures when the dimensionality of nanoparticle arrays crosses over from 2D to 3D is a universe phenomenon. Figure S5 shows the zero-voltage conductance of nanoparticle arrays with different

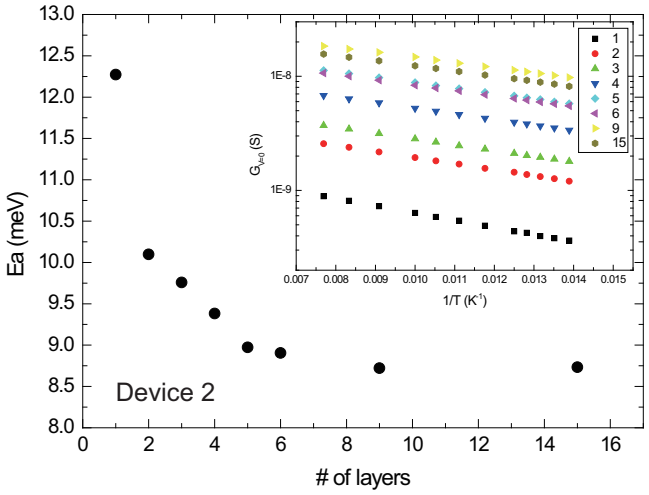

FIG. S4: **Activation energy E_a as a function of array thickness for device 2.** The Coulomb charging energy of nanoparticle arrays with different number of monolayers. Inset: The zero-voltage conductance of nanoparticle arrays with different thickness as a function of inverse temperature at medium temperature ranging from 75 K to 130 K.

thicknesses as a function of temperature. The shaded box indicates the temperature region where the turning point appears when the thickness of nanoparticle arrays is more than 3-4 nanoparticle monolayers.

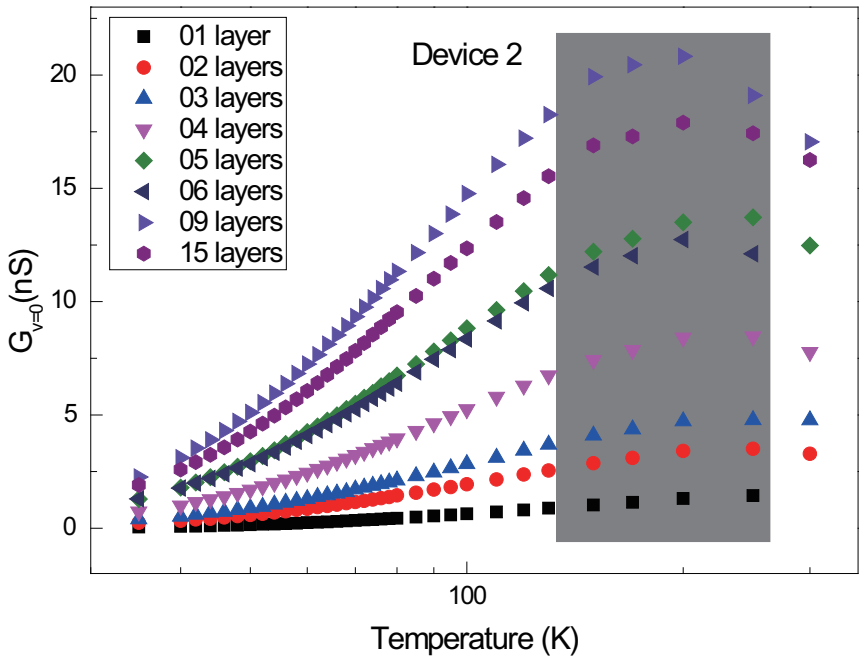

FIG. S5: **Turning points in the temperature coefficient of conductance for device 2.** The zero-voltage conductance of nanoparticle arrays with different thickness is plotted as a function of temperature. To see the turning point more clearly, a semi-log scale is used. The shaded box indicates the temperature region where the turning point appears when the thickness of nanoparticles is more than 3-4 nanoparticle monolayers.