Thickness-Dependent Seebeck Coefficient in Hybrid 2-Dimensional layers

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***Abstract*— The Seebeck coefficient in a single molecule is determined by the slope of the transport probability of the charge carrier at the Fermi level, which can result in high Seebeck coefficients. However, since single molecules can only generate a limited amount of power for thermoelectric applications. Hence, larger scale systems must be developed to provide enough power for real applications. In this work, we examine the effect of the dimensionality on the Seebeck coefficient of molecule/Au nanoparticle 2D arrays with a massive number of molecular junctions within the network system. This approach increases the complexity and interactions between the components as the system size scales. In this work, we observed that the multilayer structure of 2D hybrid arrays provides higher Seebeck coefficients than monolayer structures with same molecular linkers. In particular, Oleylamine (OAM) and thiolated anthraquinone derivatives (5AQ5) are used as molecular interlinkers between gold nanoparticles in the structure. Experimental results illustrate that a four-layer structure of OAM/Au 2D array yields a ~11x improvement in the Seebeck coefficient (S=38.21 µV/K) over the single-layer structure (S=3.36 µV/K), which, along with an improvement in the conductivity yields a power factor improvement of 635 times. The other set of results illustrate that a three-layer structure of anthraquinone-based norbornylogous bridge (5AQ5)/Au 2D array yields a ~26x improvement in the Seebeck coefficient (S=-3254 µV/K) over the single-layer structure (S=-127 µV/K), and a power factor improvement of 177 times. These findings demonstrate that it is possible to improve the thermoelectric performance of engineered nanostructures by controlling the number of layers.**

Keywords— Thermoelectric, nanomaterials, nanoparticles, supperlatice, Seebeck coefficient, power factor

I. INTRODUCTION

Thermoelectric devices produce electricity when exposed to a thermal gradient. This effect is called the thermoelectric effect and was discovered by Thomas Seebeck in 1821 [1]. Today, thermoelectric generators (TEGs) are extremely useful for supplying wearables and remote devices with energy by converting ambient wasted heat energy into electricity [2-6]. The figure of merit (ZT) defines the efficiency of thermoelectric generators and given by:

$$ZT = \frac{\sigma S^2 T}{\kappa} \quad (1)$$

where σ is electric conductivity, S is the Seebeck coefficient, T is the temperature, and κ is the thermal conductivity.

Nanostructured materials can enhance the thermoelectric properties of a system since both the electrical conductivity and thermal conductivity of the system can be tailored beyond the limitations of bulk materials. Quantum confinement phenomena and the programmable surfaces of nanomaterials are utilized to improve the efficiency of thermoelectric devices [7, 8]. In hybrid nanostructured systems, organic linkers on the surface of the nanoparticles limit phonon mode propagation through the lattice [4, 8-10], play an important role in the conductivity of the system [11-14], and determine the Seebeck coefficient in nanoparticle array (NPA) [8].

The Seebeck coefficient of a large molecular-nanoparticle system, as shown in Fig. 1(a), depends on the Seebeck coefficient of the individual molecular junctions and interactions of the components in the system. One potential method of engineering the thermoelectric efficiency is to take advantage of system dimensionality to create large Seebeck coefficients. Since modern nanofabrication techniques offer opportunities for producing large molecular-nanoparticle systems [12, 15-17], it is appropriate to utilize these techniques to study the effect of dimensionality on the thermoelectric performance of hybrid 2D arrays.

In this work, we investigate the effect of film thickness (the number of layers in the array) on the thermoelectric properties of hybrid molecules/Au nanoparticle films. In particular, we measure the Seebeck coefficient and power factor of the monolayers as well as multilayers of oleylamine (OAM) capped gold nanoparticles and anthraquinone-based norbornylogous bridge (5AQ5) capped gold nanoparticles. OAM is the initial ligand covered the surface of the gold nanoparticles after the synthesis process. 5AQ5 ligand is used as another ligand since it has a suitable length, and the quality of the layer remains almost intact after the solid-state ligand exchange process. Fig. 1 (b) presents an SEM image of a monolayer of oleylamine capped Au nanoparticles, Fig. 1 (c) and Fig. 1(d) shows the schematic structure of the monolayer and multilayer hybrid films.

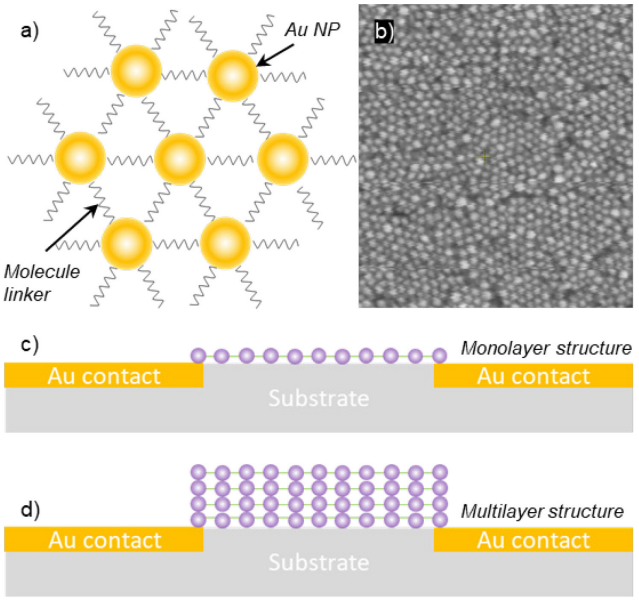

Fig. 1. (a) the schematic overview showing the structure of the molecule-Au nanoparticles; (b) SEM image of a 2D array of gold nanoparticles; (c) monolayer and (d) multilayer structures for measuring Seebeck coefficient and electric conductivity.

II. Results

The details of the Seeback coefficient and conductivity measurement methods are explained in a previous work [8]. Fig. 2(a) shows the optical image of a thermoelectric chip used for the measurements. A standard photolithography process is utilized to fabricate this chip. This chip contains resistive heaters to produce a temperature gradient, resistance thermometer devices (RTHDs) for measuring the thermal gradient through the device and calibrating the heater, and pairs of microelectrodes for measuring the generated thermoelectric voltage and device conductivity. All the devices on the chip are coated with a thin silicon nitride insulator layer except for the small area around the microelectrode gapa. This opening is required to make an electrical connection to the deposited layer for measurement purposes while the other conductors are isolated. An instrumentation amplifier is used to measure the generated thermoelectric voltage across two microelectrodes.

For characterizing the effect of the number of layers on the thermoelectric performance, we deposit 2D layers of molecule-capped gold nanoparticles on the surface of the thermoelectric chip. The ~15-nm gold nanoparticles are originally capped with oleylamine [18]. The deposition procedure begins with the creation of self-assembled, oleylamine-capped gold nanoparticle monolayers on the surface of the water, which are then transferred to the surface of a polydimethylsiloxane (PDMS) stamp in order to place the layer onto the thermoelectric chip. Fig. 2(b) shows an SEM image of the oleylamine capped gold monolayer deposited between microelectrodes.

In order to measure the Seebeck coefficient of 5AQ5-Au nanoparticles 2D layer, we first deposit a 2D monolayer of original oleylamine capped gold nanoparticles on the surface of the thermoelectric chip and then replace the OAM ligands with 5AQ5 molecules, as shown in Fig. 2(c), through a solid-state ligand exchange process [16, 19]. 5AQ5 comprises 4 thiols per each molecule and has high affinity to gold [20, 21] which facilitates the ligand exchange process.The process was performed by dipping the entire chip into an excess solution of 5AQ5 in dichloromethane overnight and then washing the sample with dichloromethane three times.

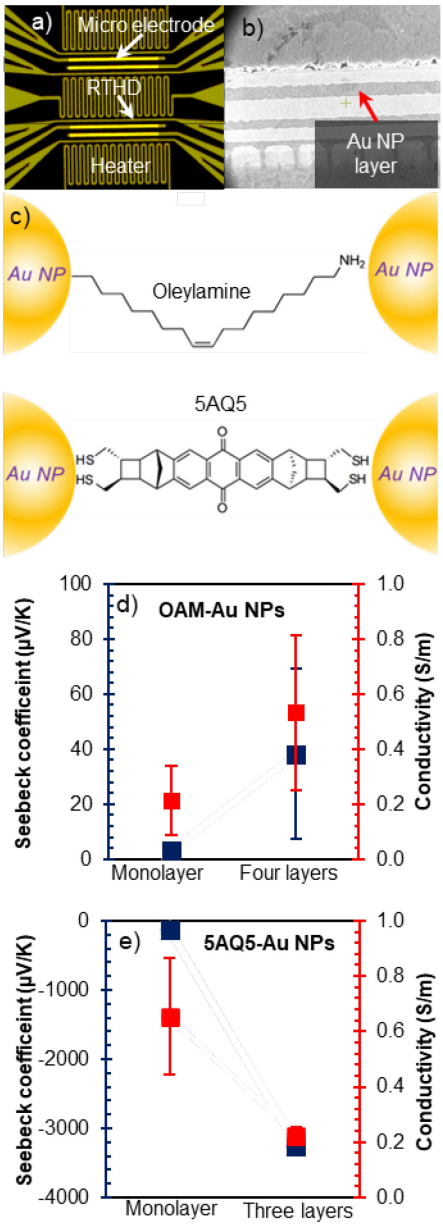

Fig. 2. Thermoelectric measurements of hybrid molecule-nanoparticle monolayers. (a) Optical image of thermoelectric chip consisting of heaters, resistance thermometer devices (RTHDs), and microelectrodes; (b) SEM image of the stamped monolayer on a thermoelectric chip; (c) molecular structure of oleylamine and 5AQ5 bridging two Au nanoparticles; (d) and (e) Seebeck coefficient (blue) and conductivity (red) of the monolayers and multilayer of OAM-Au NPs and 5AQ5-Au NPs.

The Seebeck coefficient measurement process starts by applying a controlled DC voltage to one of the heaters. This heater generates a thermal gradient between 0 and 0.6 K across

the molecule-Au array depending on the voltage level. The thermovoltage generated as a result of applied thermal gradient is used to determine the Seebeck coefficient for each device. The Seebeck coefficients extracted for each system are shown in Fig. 2(d) and Fig. 2(e) corresponding to OAM-Au NPs and 5AQ5-Au NPS, respectively. The Seebeck coefficient for a monolayer of oleylamine capped Au nanoparticles is a low positive number (S = 3.36 μV/K) indicating p-type transport, and the resulting conductivity is σ = 0.21 S/m.

The measurement on 5AQ5-Au layers shows that after replacing the oleylamine ligand with 5AQ5, the Seebeck coefficient of the monolayer increases by more than 37 times to S = -126.56 μV/K which is related to the behavior of the molecule itself. The negative Seebeck coefficient reveals n-type transport in the conduction process of the thin film of 5AQ5-AU NPs. The corresponding change in the Seebeck coefficient is an indicator of the success of the ligand exchange process. In another set of experiments, we increase the number of layers for both OAM-Au and 5AQ5-Au arrays. The Seebeck coefficient for the four-layer structure of OAM-Au NPs array improved by a factor of 11 reaching S=38.21 μV/K compared with the monolayer of the same material system. Similarly, the three-layer structure of 5AQ5-Au array shows a 26 times improvement in the magnitude of Seebeck coefficient reaching S=-3254 μV/K over the single-layer structure.

As an indicator of the performance of the TEG device, thermoelectric power factor σS^2 is frequently reported [17, 22, 23]. The value of the thermoelectric power factor σS^2 of all four samples is presented in Fig. 3. The four-layer structure of oleylamine capped Au nanoparticles improves the power factor by about three orders of magnitude from 2.67 pW/mK^2 for the single-layer film to 1.69 nW/mK^2 for the four-layer film. Further results show that the three-layer structure of 5AQ5 capped Au nanoparticles improves the power factor by more than 176x from 14.5 nW/mK^2 for the single-layer film to 2.56 μW/mK^2 for the three-layer film. This final value is on par with materials such as zinc antimonide film [24], polysilicon [25], naphthalene derivatives [26], benzodifurandione paraphenylenevinylidene (BDPPV) derivatives [25, 27]. Since the electrical conductivity for both samples is not significantly changed, this improvement is primarily dictated by the changes in the Seebeck coefficient.

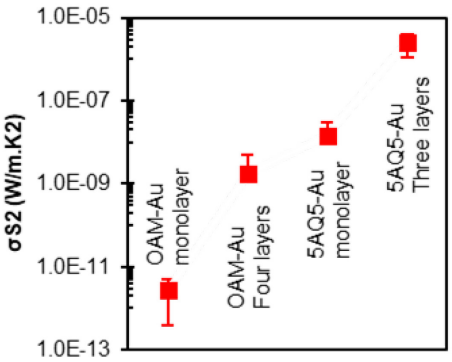

Fig. 3. Power factor as a function of conductivity for four types of samples showing higher performance for multilayer devices.

III. Conclusion

In summary, we studied the effect of dimensionality on the thermoelectric performance of molecule-Au, 2D layers. In this study, we used oleylamine-Au NP arrays and 5AQ5-Au NP arrays to show that multilayer structures can significantly enhance the overall thermoelectric performance of the device. The stack of a few layers of the same structure resulted in an improvement of the power factor of ~633 times for OAM-Au NPs structure and that of about 177 for 5AQ5-Au NPs structure. The results show promising opportunities for the design of high-efficiency thermoelectric devices based on the dimension of the array. In these experiments, the conductivity of the multilayer 5AQ5 is less than that of the single layer structure showing that the multiple deposition and ligand exchange process can adversely affect the layer quality. The efficiency of the device can be further improved during the fabrication process by depositing high quality multilayer structures.

IV. Experimental Section

A. *Nanoparticle synthesis*

Inside the glovebox at inert condition, ~15 nm Au nanoparticles were synthesized by rapidly injecting a solution of 150 mg of tetrachloroauric acid ($HAuCl_4$) in 3.6 mL of technical grade oleylamine and 3.0 mL of toluene into a boiling solution of 8.7 mL of technical grade oleylamine in 147 mL of toluene. The color of the solution changed to bright yellow and then gradually to deep red. Heating is stopped after 2 hours and 450 mL of methanol is added to precipitate the product. The particles were isolated by centrifugation and washed at least two times to remove unreacted starting materials and biproducts. The washing process involves dispersion in Toluene via vortex and precipitation in methanol via centrifuge [28].

B. *Monolayer preparation method*

To perform the monolayer self-assembly, the prepared Au nanoparticle solution was diluted with toluene in a 1:4 (Au NP:toluene) ratio to make a working solution. Next, for each nanoparticle array, 12 mL of distilled water was poured in a 14 mL centrifuge tube. 250 μL of working solution was then deposited onto the surface of the distilled water. The monolayer was formed in less than 4 hours. Acube of polymethyldisiloxane (PDMS) was then pushed through the surface of the distilled water to extract the Au arrays. The process was followed by lightly spraying the cube with N_2 gas to remove any excess air bubbles on the surface. Finally, the surface of the PDMS stamp with the array was carefully rolled over the surface of the thermoelectric chip to transfer the Au nanoparticle array to the chip.

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