Electronic Supplementary Information for

Asymmetric Geometry Composites Composed between Parallel Aligned and Interconnected Graphene Structure for High Efficient Thermal Rectification

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S1. Experimental Section

All chemicals were of analytical-reagent grade and were directly used. Natural flake graphite (NG) with an average particle size of 200 mesh and the purity can be over 99.9% was bought from Shenghua Research Institute (Changsha, China). potassium persulfate ($K_2S_2O_8$), potassium permanganate ($KMnO_4$), polyethyleneglycol6000 (PEG6000), phosphorus (V) oxide (P_2O_5), L-Ascorbic acid (L-AA), concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was offered by a Millipore water purification system.

S1.1 The preparation of GO: Using modified Hummers method. [S1-S3]

The first step: Preparation of pretreated graphite

Briefly, concentrated H_2SO_4 (30 mL) in a beaker of 250 mL was heated to 85 °C in the oil bath. $K_2S_2O_8$ (1.0 g) and P_2O_5 (1.0 g) were added in sequence with continuous stirring until the reactants were completely dissolved. And then, graphite powder (0.6 g) was added to the above solution kept magnetic stirring for 4.5 hours. After that, the resulting mixture was diluted with 200 mL of distilled water and left overnight. (Be careful, adding slowly with a syringe to prevent splashing). The obtained sample was filtered and washed using a Millipore filter to remove all other impurities and soluble substances. The corresponding pretreated graphite was dried under ambient conditions.

The second step: Preparation of GO

Concentrated H_2SO_4 (25 mL) was put in an Erlenmeyer flask of 100 mL and then $KMnO_4$ (1 g) was added slowly with stirring. Thereafter, the mixture was allowed to react in water bath heating at 35 °C for 2 hours. After that, transferring the reaction into an ice bath and then deionized water (40 mL) was slowly dropped into the flask with a syringe. Afterwards, the solution was transferred to the oil bath and kept stirring for half an hour at 95 °C. Next, an additional deionized water (60 mL) was added for dilution. Thereafter, 1.5 mL of H_2O_2 (30%) was added to the mixture at once. At this moment, the mixture resulted in a brilliant yellow color along with bubbling. Then the mixture was allowed to cool to ambient temperature and centrifuged with HCl (10%) solution twice and followed by deionized water three times to remove the excess acid. (Ultrasonic dispersion must be carried out before centrifugation. Until the solution formed a stable dispersion and then centrifugal. The purpose was to make the graphite oxide be stripped into graphene oxide.) The resulting product was dried under vacuum for the subsequent experiments.

S1.2 Preparation of graphene

Here, a simple chemical reduction method to obtain the graphene was introduced.[S4,S5] 50 mL (1mg mL^{-1}) of an aqueous dispersion of above prepared GO and 0.5 g of L-AA was placed into a flask of 250 mL under vigorous stirring at room temperature (~ 25 °C) for 30 h. In order to further prove that graphene was reduced fair enough, the FT-IR spectroscopy and UV-vis of GO and graphene were shown as following Fig. S1. It was evident that the FT-IR peaks corresponding to the oxygen functionalities, such as the stretching vibration peak of C=O (1726 cm^{-1}), the deformation (1404 cm^{-1}) peaks of O–H groups, the C–O (epoxy) stretching vibration peak (1226 cm^{-1}), and the C–O (alkoxy) stretching peak (1066 cm^{-1}), respectively in Fig. S1(a), decreased their intensities dramatically or disappeared entirely after 30 h reduction of the GO with L-AA. In Fig. S1(b), a strong absorption peak of the UV-vis absorption located at 230 nm from GO solution decayed gradually with the reduction progressing and disappeared after 30 h. Meanwhile, a new absorption peak (~ 270 nm) verified the aromatic structure of graphene might be restored gradually.

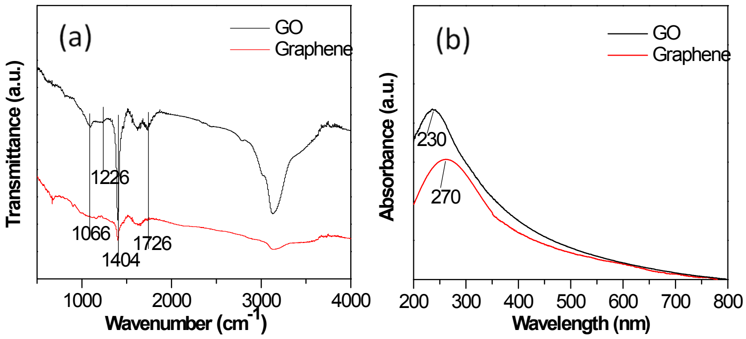

Fig. S1 FT-IR (a) and UV-vis (b) spectra of GO and graphene respectively.

S1.3 The preparation of G/PEGs

Method for preparing interconnected G/PEGs (i-G/PEGs): Interconnected netlike G/PEGs were prepared through simply mixing PEG and the suspension solution of graphene, then evaporated at a high temperature and air-dryed at ambient temperature. More concretely, as-prepared graphene (0.5 g) was dispersed into the deionized water (100 mL) via ultrasonication (KQ-400KDB, 40 kHz, 400W) with 1 h in order to form the homogeneous suspension. Then the suspension was dripped into a flask of 250 mL which has been contained white flakes of PEG (PEG6000, 6.667 g). Next, the mixture was followed by refluxing and vigorous stirring in the oil bath at 80 ^{o}C for 5 h. Finally, after ultrasonic for 2 h with the aim of getting rid of air bubbles in solution, the ultimate dispersed suspension was transferred to another wide-mouth container to fastly evaporate excess water and form a gelatinous structure over 5 hours at 80 °C. After air-drying, the novel architecture of interconnected netlike graphene assembled in the PEG matrix was formed.

Method for preparing parallel aligned G/PEGs (p-G/PEGs): Typically, graphene (0.5 g) was dispersed in deionized water (100 mL) via ultrasonication with 1 h to form a homogeneous suspension. Then the suspension was dripped into a flask of 250 mL which has been contained white flakes of PEG (PEG6000, 6.667 g). Next, the mixture was stirred at room temperature (~ 25 °C) for 5 h. Finally, after the ultrasonic for 2 h to get rid of air bubbles in solution, the resultant mixture was poured into the mould and slowly air-dried to constant weight under ambient temperature to gain parallel aligned graphene assembled in the PEG matrix.

Method for preparing binary asymmetric geometry composites composed between parallel aligned and interconnected G/PEGs: Firstly, the above i-G/PEGs and p-G/PEGs were both constructed into bulk cube structure with the dimensions of 1×1×0.5 cm^3, respectively. Secondly, a PEG (PEG6000) flake (~ 1mm of thickness) with a 1 cm^2 of square was put between i-G/PEGs and p-G/PEGs to form the sandwich structure. Finally, the whole was placed in the oven at 70 °C for 30 min with the aim of making the PEG melted to obtain the connected complex.

S2. Thermal conductivity measurement

The as-prepared p-G/PEGs samples were combined into two pieces with the same size. Before measurement, the detector of hot wire was closely clamped with two samples. The temperature of p-G/PEGs and detector was monitored by using a programmed software. Until the temperature fluctuations rate is less than 50 mK/5 min, the measurement would start. Each measurement is tested 5 times at a giving temperature. Two parallel measurements should have an interval of 10 minutes to guarantee that the internal sample can reach equilibrium state of the measured temperature. The i-G/PEGs samples were tested by the same method.

S3. Thermal rectification test system

The triangular G/PEG composites are suspended on the two heating plates. G/PEGs and heating plate are adhesion together using silver glue (Kyocera Chemical CT285) to establish good thermal contact between heaters and samples. Two thermocouples (TPK-01) are placed on both sides of sample to indicate the temperature (Fig. S2). Furthermore, the heaters are placed in the foam to reduce the heat leakage.

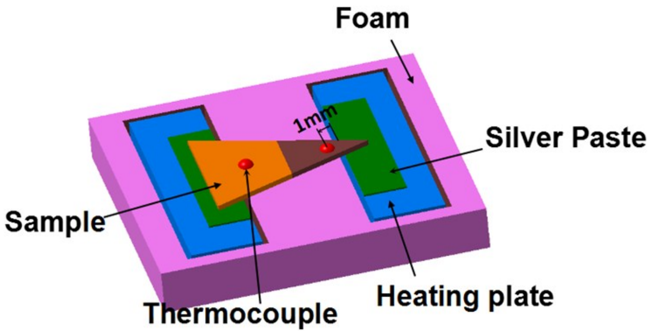

Fig. S2 A simple schematic of measure system for triangular G/PEGs structure.

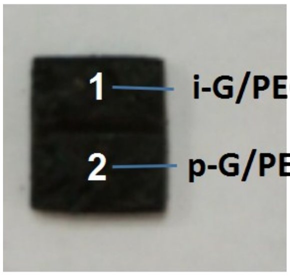

Fig. S3 Digital photograph of the binary asymmetric composites composed between i-G/PEGs and p-G/PEGs with rectangular structure.

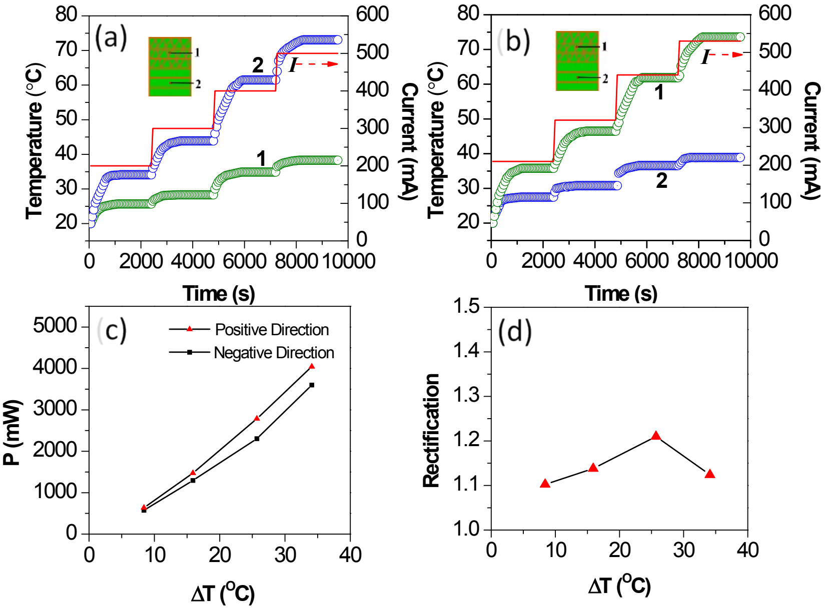

Fig. S4 Testing results on the thermal rectification phenomenon of the binary asymmetric G/PEG composites with rectangular structure. The temperature (left vertical axis) and current (right vertical axis) varies with time in (a) negative direction and (b) positive direction. (c) Heat power versus temperature bias. (d) Thermal rectification coefficient varies with different temperature bias.

S4. Characterization

The field emission scanning electron microscopy (FE-SEM) images were achieved by using a FEI Sirion-200 SEM. XRD patterns were obtained by using a Philips X'Pert Pro Super diffractometer with Cu-Ka radiation (λ=1.54178 Å). The samples characteristics of FT-IR spectral were performed using a Thermo-Fisher IS10 instrument. The absorption spectra of GO and graphene solution were measured using a Shimadzu UV-2550 spectrometer. The thermal conductivity was carried out with hot-wire thermal conductivity instrument using the type specification of Xiatech TC3000.

References

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