Electronic Supplementary Information (ESI) for

Heat Collection and Supply of Interconnected Netlike Graphene/ Polyethyleneglycol Composites for Thermoelectric Device

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S1. Experimental Section

S1.1 Chemicals and materials

All chemicals were analytical-reagent grade and were directly used without further purification. Natural flake graphite (NG) with an average particle size of 200 mesh and a purity of over 99.9% was purchased from Shenghua Research Institute (Changsha, China). polyethyleneglycol6000 (PEG6000), phosphorus (V) oxide (P_2O_5), potassium persulfate ($K_2S_2O_8$), potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water (18.2 MΩ•cm) was provided from a Millipore water purification system.

S1.2 Procedures for graphene oxide

The graphene oxide powder was prepared from natural graphite flakes by a classically Hummers method with minor modifications.[S1,S2] Briefly, $K_2S_2O_8$ (2 g) and P_2O_5 (2 g) are added into the concentrated H_2SO_4 (60 mL) heated to 85 °C with stirring in a 500 mL of beaker. Then, Graphite powder (1.2 g) is added to the above solution kept at 85 °C for 4.5 hours. Next, the mixture diluted with 400mL of deionized water and left overnight. The obtained sample is filtered and washed using a Millipore filter to remove all other impurities. The pretreated graphite is dried under ambient conditions. For the synthesis of graphene oxide,

H_2SO_4 (50 mL) is placed into a 500mL of Erlenmeyer flask and the pretreated graphite (0.2 g) is added to the acid and stirred. $KMnO_4$ (2 g) added slowly and dissolved with stirring, the mixture is then allowed to react at 35 °C for 2 hours after which distilled water (80 mL) is added. **Notice:** the addition of the water causes the temperature of the mixture to rise rapidly. After adding all the deionized water, the mixture is transferred to oil bath at 95 °C and kept stirring for 0.5 hours at which point an additional 120 mL of deionized water is added. Immediately after the dilution with 120 mL of water, 3 mL of 30% H_2O_2 is added to the mixture resulting in a brilliant yellow color along with bubbling. The mixture is allowed to cool to ambient temperature. The remaining mixture is centrifuged and washed with 10% HCl solution twice and followed by deionized water three times to remove the acid. The resulting solid is dried under the condition of vacuum for the subsequent experiments.

S1.3 Preparation of graphene

To avoid the irreversible graphene agglomerates in the preparation of individual graphene sheets through aqueous solution based chemical reduction of GO.[S3,S4] Here we reduced the GO with the L-Ascorbic acid (L-AA) at room temperature (~ 25 °C) according to the reported method with minor modications,[S5] and found that the as-prepared reduced GO sheets can be suspended stably in water at room temperature for several days without adding any capping reagent. Briefly, 0.1g of L-AA was added to 100 mL (0.1 mg mL^{-1}) of an aqueous dispersion of the GO under vigorous stirring. The reduction was confirmed by UV-vis and FT-IR spectroscopy. As shown in Fig. S1a, the intensities of two UV-vis absorption peaks located at 230 and 300 nm from the GO decayed gradually with the reduction progressing and disappeared after 24 h. Meanwhile, a new absorption peak (~270 nm) verified the aromatic structure of graphene might be restored gradually. In Fig. S1b, the FT-IR peaks corresponding to the oxygen functionalities, such as the stretching vibration peak of C=O (1726 cm^{-1}), the vibration (3395 cm^{-1}) and deformation (1410 cm^{-1}) peaks of O–H groups, the C–O (epoxy) stretching vibration peak (1226 cm^{-1}), and the C–O (alkoxy) stretching peak (1052 cm^{-1}), respectively, decreased their intensities dramatically or disappeared entirely after 30 h reduction of the GO with L-AA. All these observations confirmed that GO was reduced successfully and the as-prepared graphene still kept quite good dispersion in the water.

Fig. S1 UV-vis (A) and FT-IR (B) spectra of GO and graphene.

S1.4 Fabrication of assembled G-PEGs

1. Preparation of assembled G-PEGs (93wt % of PEG).

Interconnected netlike G-PEGs composites was prepared by simple full mixing the PEG and graphene suspensiton, and then by evaporation at high temperature and air-drying methods under ambient temperature. Typically, above prepared graphene powders (1 g) were dispersed in deionized water (300 mL) with 1h ultrasonication (KQ-400KDB, 40 kHz, 400W) to form a homogeneous suspension. Then the graphene suspension was dripped into melted liquid PEG (PEG6000, 13.3 g) which has been preheated to 80 ^{o}C in a flask during stirring followed by vigorous stirring at 80 ^{o}C for 5h. Finally, after the ultrasonic for 1-2h to get rid of air bubbles in solution, the resultant mixture was poured into the mould at 80 ^{o}C in oven for another 5 h and air-dried to constant weight under ambient temperature to obtain interconnected netlike graphene/ polyethyleneglycol composites.

2. Preparation of assembled G-PEGs (85 wt % of PEG) and assembled G-PEGs (70 wt % of PEG).

The synthetic procedure was similar to that of the assembled G-PEGs (93 wt % of composite) except that the amounts of PEG6000 were changed to 7 g and 3.5 g, respectively.

S2. Heat collection and supply performance for thermoelectric device

A simple home-designed setup was used for the thermoelectric conversion measurement. It was composed of a 4-cm side length commercial square Seeback thermoelectric power generation piece connected to a LED bulb or a digital multimeter to directly monitor real-time current or voltage caused by temperature difference between two ends, a vacuum cup filled with ice water (0 ^{o}C), an assembled square graphene/polyethyleneglycol composite and two Polystyrene foam plastic boards used as fixture and preservation respectively. The ice water is used as cold source direct contacted with the cold end of power slice. The as-prepared square graphene/polyethyleneglycol composite used as heat source was firstly heated to 80 ^{o}C and then transferred quickly to the hot side face power slice.

S3. Characterization

XRD patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu-Ka radiation (λ = 1.54178 Å). The field emission scanning electron microscopy (FE-SEM) images were performed by using a FEI Sirion-200 SEM. Absorption spectra of the GO and graphene solution were measured using a Shimadzu UV-2550 spectrometer. FT-IR spectral characteristics of the samples were collected using a Thermo-Fisher IS10 instrument. For differential scanning calorimeter (DSC) measurements, the samples were sealed in an aluminum pan for characterization by the NETZSCH DSC 200 F3 instrument with a heating/cooling rate of 10 °C min^{-1}.

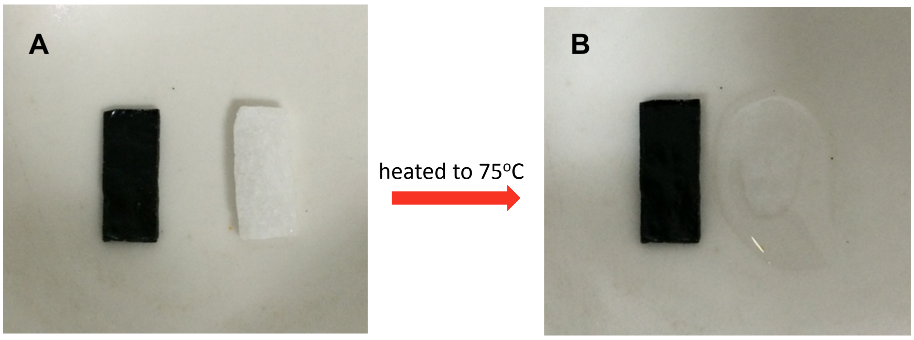

Fig. S2 Digital photographs of the assembled G-PEGs (93 wt% of PEG, black rectangular sample) and pristine PEG (white sample), respectively.

As shown in Fig. S2, by observing heating process, obviously, the pristine PEG begins melt into a fluid (Fig. S2B) from the original shaped solid (Fig. S2A) after the temperature is over its melting point, and in contrast, G-PEGs still keep original shape (Fig. S2A, B) without any distortion or leak of liquid PEG from it. The result proved that the PEG was well confined in 3D interconnected netlike graphene skeleton, which enables the composite excellent cyclic performances for heat collection, transport, and supply in thermoelectric power conversion.

References

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