Supporting Information

Lightweight, Mechanically Flexible and Thermally Superinsulating rGO/Polyimide Nanocomposite Foam with Anisotropic Microstructur

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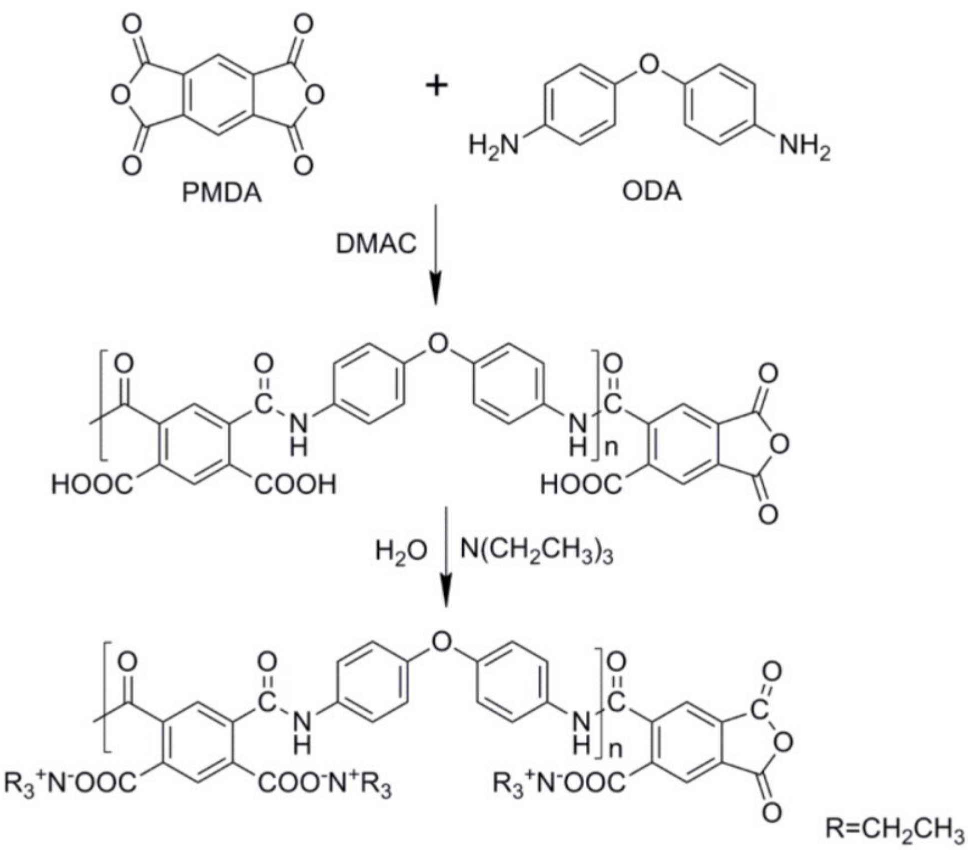

Scheme S1. Reaction scheme of water-soluble polyimide precursor.

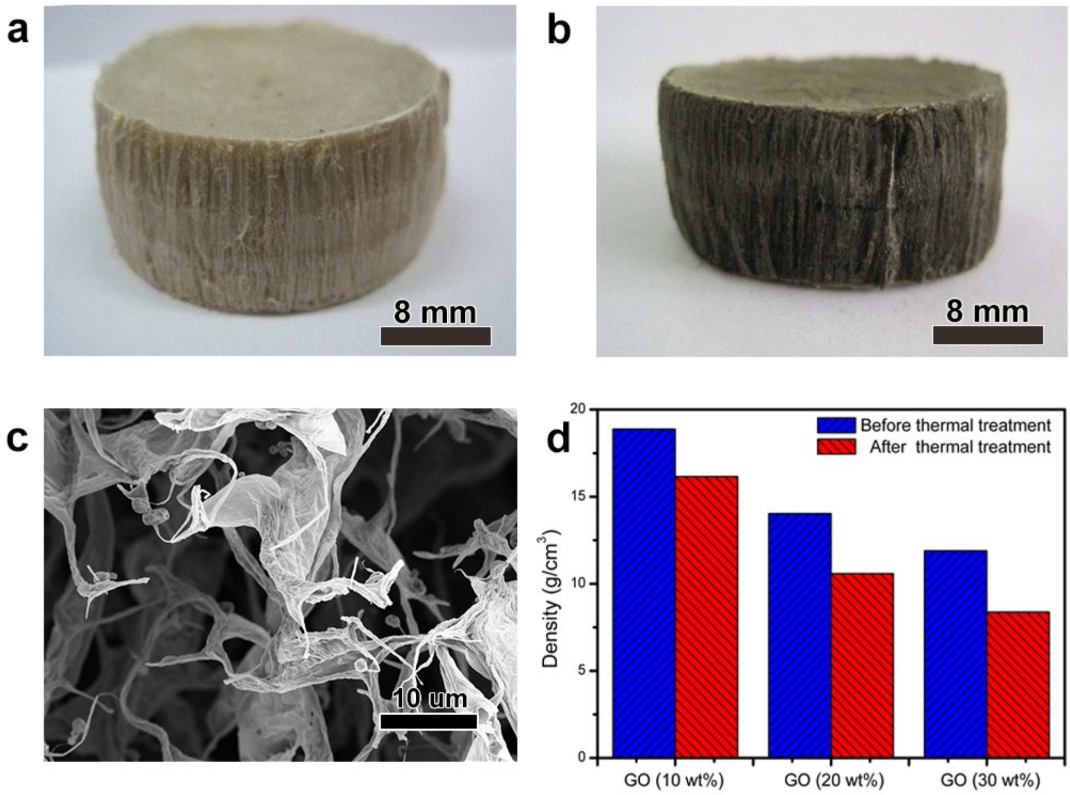

Figure S1. a-b) Optical images of rGO/PI nanocomposite foam before (left) and after thermal annealing (right). c) SEM image of rGO/PI nanocomposite (GO 10 wt%) shows crimped structure with some ripples and wrinkles. d) The density of rGO/PI thermally insulating foam with different content of GO (10-30 wt%) before and after thermal annealing.

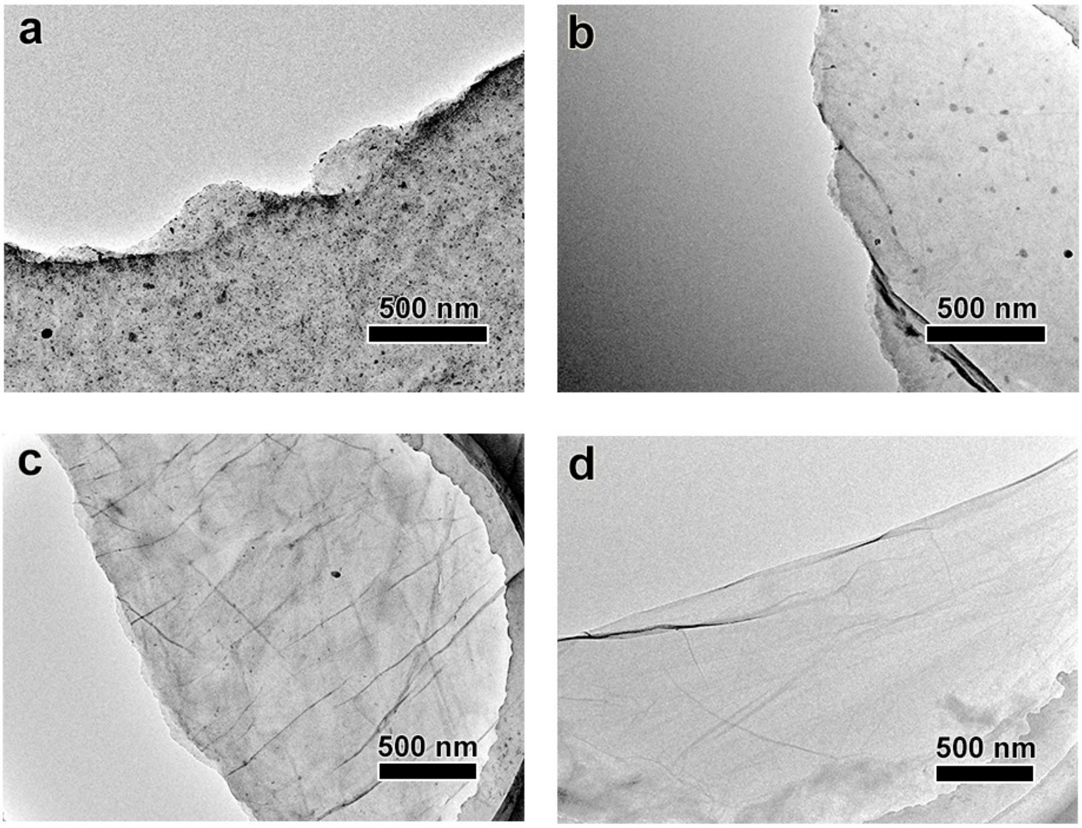

Figure S2. a-c) TEM images of rGO/PI thermally insulating nanocomposite foams with different content of GO (10 wt%-30 wt%). d) TEM images of rGO aerogel after thermal annealing.

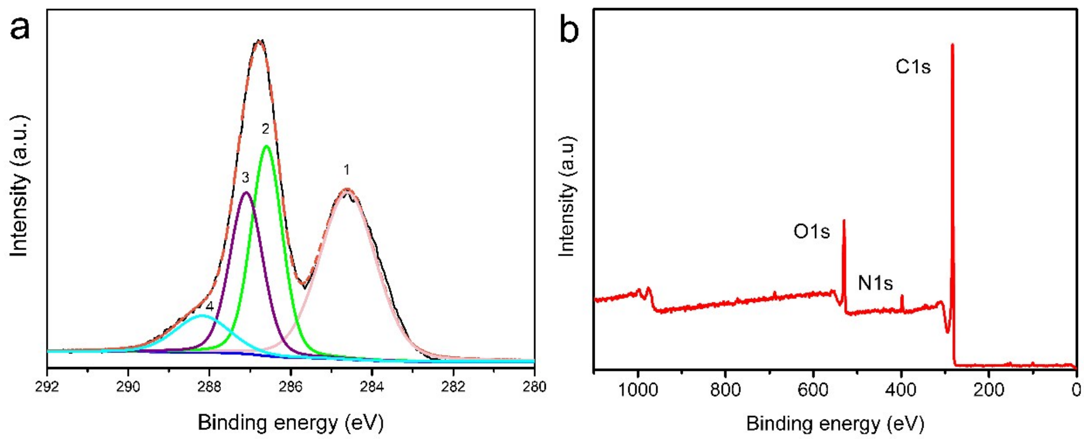

Figure S3. a) XPS spectroscopy of GO foam before thermal treatment. b) Wide-scan XPS survey spectroscopy of the rGO/PI thermally insulating nanocomposite.

Thermal conductivity measurements of rGO/PI nanocomposites

Thermal transport measurements were performed by Hot Disk TPS 2500S. The transient plane source (TPS) technique, which is based on the use of a transiently heated plane sensor (Figure s4a), is used to evaluate the thermal insulating property of the investigated sample. The plane sensor acts as a continuous plane heat source and a dynamic temperature sensor.[44] During the measurement, a plane sensor is sandwiched between two identical pieces of sample. A small electrical current is needed to increase the temperature of the plane sensor. Simultaneously, the temperature increase as a function of time is recorded by measuring the resistance. As for anisotropic nanocomposite, the thermal properties in the axial and radial directions can be obtained at the same time (Figure s4b). Before thermal conductivity measurements, the rGO/PI nanocomposites were kept at 22 ^{o}C and 55% relative humidity for 24 h. The thermal conductivities of rGO/PI nanocomposite were measured with a 6.4 mm hot disk sensor and the parameters were set to 20 mW output power and 4s test time.

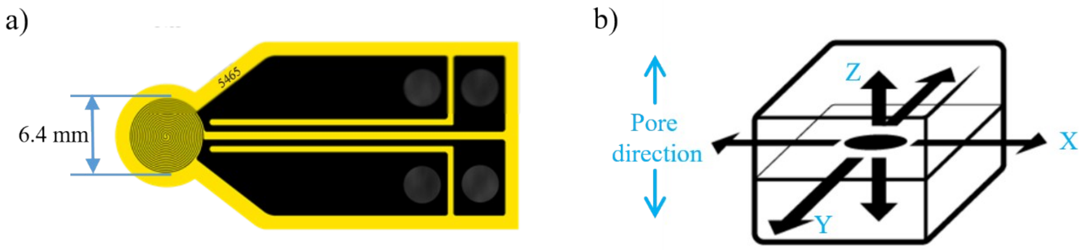

Figure S4: Schematic illustrations of hot disk sensor and the sensor position between anisotropic sample pieces. a) Hot Disk Kapton insulation sensor with a diameter of 6.4 mm. b) Schematic illustrations of the anisotropic thermal conductivity measurement. The X, Y direction represents to the radial (in-plane) direction of the nanocomposite, while the Z direction corresponds to the axial (out-of-plane) orientation. (The illustration images were taken from the website of Hot Disk AB, www.hotdiskinstruments.com).”

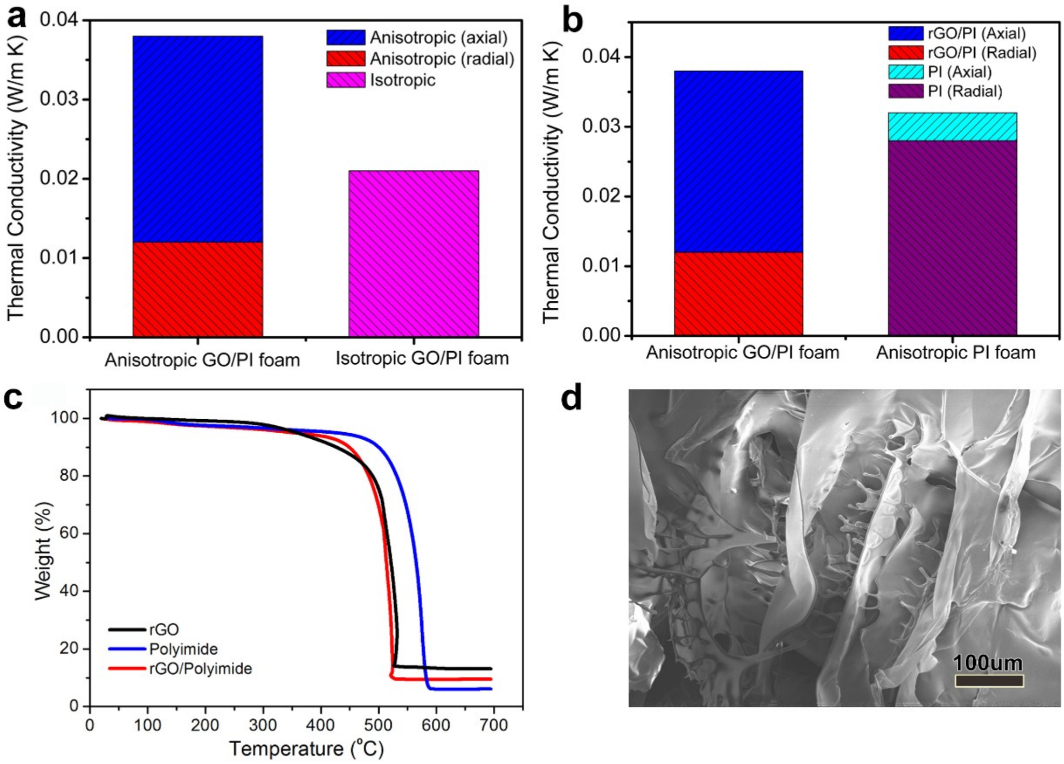

Figure S5. a) The comparison of thermal conductivity between anisotropic and isotropic rGO/PI nanocomposite with identical composition. b) The comparison of thermal conductivity between anisotropic rGO/PI nanocomposite and PI foam. c) TGA date of rGO, polyimide and rGO/polyimide samples. d) Figure S5d. SEM image of PI foam

Table S1 Solid conduction and interfacial thermal resistance R_k values of nanocomposite components

Component	Solid conduction λ_g (W·m^{-1}·K^{-1})	R_k (10^{-8} W·m^{-1}·K^{-1})	d (nm)	Solid conduction λ_{sol}^* (W·m^{-1}·K^{-1})
Graphene oxide	8.8 [19]	3[19]	1-3	0.07
Polyimide	0.22 [35]	3.9[35]	3	0.057

The thermal conduction of the graphene-based thermally insulating nanocomposite can be divided into two parts: the gas conduction (λ_g) and the solid conduction (a weighted average of the effective solid conduction values λ_{sol}^* of the individual components of the thermally insulating monolith).

The λ_g within the channels of the highly ordered graphene-based foams can be neglected in the following analysis

$$\lambda_g = \frac{\lambda_{g0}\Pi}{1 + 2\beta K_n} \tag{1}$$

Where λ_{g0} = 25 mW·m^{-1}·K^{-1} represents the thermal conductivity of gas in free space, Π represents the porosity of the nanocomposite monoliths, and $\beta(\approx 2)$ is the air in the monoliths. K_n is the Knudsen number

$$K_n = \frac{l_m}{\delta} \tag{2}$$

Where l_m is the mean free path of a gas and δ is the pore size, respectively. l_m is about 10 nm in the cell walls of the monolith (75 nm in free space).

The solid conduction of the rGO/PI nanocomposite can be estimated by a weighted average of the solid conduction values (λ_{sol}) of each individual components. For a bulk materials with the same composition as the rGO/PI nanocomposite (30 wt.% GO and 70 wt.% PI), the weighted average solid conduction is estimated to 2800 mW m^{-1}·K^{-1} based on the individual solid conductivities (Table S1).

Considering the interfacial phonon scattering effect of nanosized materials, the effective solid conductivity values λ_{sol}^{*} can then be calculated by the following equation

$$\lambda_{sol}^{*} = \frac{\lambda_{sol}}{1 + \lambda_{sol}\frac{R_K}{d}} \tag{3}$$

Where d is the particle size and R_K (Kapitza resistance) denotes the interfacial thermal resistance of the individual components (GO and PI) of the nanocomposite (Table S1). For the estimation of λ_{sol}^{*} in radial orientation (thermal transport across the highly ordered cell walls of the nanocomposite), the R_K values of GO and PI of the nanocomposite were taken from literature and the particle size was assumed to be approximately the thickness of PI and GO sheets (based on the SEM observations). The effective thermal conductivity of the rGO/PI nanocomposite can be estimated by the weighted average of the solid conduction based on the sample composition.

The thermal conductivity in the radial direction of rGO/PI nanocomposite is close to 60 $mW \cdot m^{-1} \cdot K^{-1}$, which is of the same order of magnitude as the experimental value.

Compared with isotropic structure, highly ordered microstructure in thermal insulation materials could enhance efficient thermal dissipation in the axial direction, leading to the prevention of local overheating and the reduction of heat flow across the aligned channels in the radial direction. This ordered microstructures would be helpful for the improvement of thermal insulation. The pores of honeycomb-like cellular structure run as channels parallel to the freezing direction throughout the nanocomposite. Admittedly, this highly ordered structures would be beneficial for the thermal transport along the channels, leading to a higher thermal conductivity in the axial direction. However, the anisotropic pore and wall structure formed by the strong orientation effect can effectively impede thermal transport across the channels and dramatically reduce thermal conductivity in the radial direction. Also, carbonaceous materials exhibited as efficient infrared absorbers, which were frequently used to reduce the radiative contribution in insulating materials. So, GO can act as a main components in thermally insulating nanocomposite.