Supporting Information

Optimizing impedance matching and interfacial characteristics of aromatic polyimide/graphene by molecular layer deposition for heat-conducting microwave absorption

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1. Experimental Section

1.1. Materials

Graphene obtained from Carmery Materials Technology (China) was fabricated through chemical intercalation-thermal expansion method. The precursors, including pyromellitic dianhydride (PMDA) and 4, 4′-diaminodiphenyl ether (ODA), were received from J&K Scientific. Natural rubber latex (35% dry rubber content, 0.25% ammonia content) was purchased from China Hainan Rubber Industry Group Co., Ltd. (Haikou, China). All chemicals purchased were used without any further purification.

1.2. Synthesis of PI/G by MLD

The PI/G samples were synthesized through the MLD method in a self-made atomic layer deposition (ALD) reactor. In order to obtain a reasonable vapor pressure, PMDA and ODA as precursors needed to be heated to 155 °C and 140 °C before entering the reactor, respectively. The deposition temperature was kept at 160°C. A complete deposition cycle includes the following steps: PMDA dose, N_2 purge, ODA dose, N_2 purge. For PDMA, the pulse, exposure and purging times are 5, 10 and 30 s, respectively. For ODA, the pulse, exposure and purging times are 3, 8 and 30 s, respectively. Finally, the collected samples were transferred to a tube furnace and calcined at 300 °C for 1 h with a heating rate of 3 °C/min to achieve complete imidization. By repeating the cycle 20, 40, 80 and 120 times, a series of samples were prepared, which were denoted as G-20PI, G-40PI, G-80PI and G-120PI, respectively.

1.3. Synthesis of PI/G/NR composites

First, PI/G (graphene mass content 5 wt%) was added into NR latex. To keep PI/G uniformly dispersed in the NR matrix, the mixture was continuously stirred with the aid of a surfactant, 0.1 wt.% sodium dodecyl sulfate (SDS). Then, the compounded latex was poured into a self-made mold and cured at room temperature for three days. For a comparative purpose, pure NR sample was prepared via the same method.

1.4. Characterization

Field emission scanning electronic microscopy (FESEM, Verios G4 UC) and transmission electron microscopy (TEM, JEOL JEM-2100) were carried out to analyze the morphology and microstructure of PI/G samples. Raman spectra as well as X-ray

diffraction (XRD) were acquired by using Renishaw inVia Reflex and Smart Lab II, respectively. X-ray photoelectron spectroscopy (XPS) was performed on an AXIS SUPRA instrument configured with a monochromatic Al Kα. The specific surface area and pore size distribution were measured through the Brunner-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH). Fourier transform infrared (FTIR) spectra were collected using a Bruker Tensor27 spectrometer. The relative complex permeability and permittivity values were detected using a vector network analyzer (Agilent N5230A) through the transmission/reflection coaxial line method ranging from 2 to 18 GHz. Uniformly mixing 5 wt% PI/G samples with paraffin wax, and then pressing the mixture into a coaxial ring with a size of 3.04 (inside) × 7.00 (outside) × 2.00 mm (height) to prepare specimens for evaluating electromagnetic performance. The thermal conductivity and thermal diffusivity values were tested by employing a thermal constant analyzer (Hot Disk TPS-2500S). The temperature of the composites was acquired using an infrared thermograph (FLIR E6).

1.5. RCS Simulation

CST Studio Suite 2019 was applied to simulate the radar cross section (RCS) of PI/G samples. The simulation model consists of the bottom perfect electric conductor (PEC) plate and the upper PI/G absorber layer. The thickness of the PEC plate is 2.0 mm. The thickness of the absorber layer is 1.7 mm corresponding to the optimal absorption performance. The length and width of the square shape model are set to 200 mm, which is large enough compared to the thickness. The model is placed on the X-O-Y plane, and linearly polarized plane waves incident from the positive direction of the Z axis to the negative direction of the Z-axis. The direction of electric polarization propagation is along the X-axis. Open boundary conditions are setting in all directions. The operating frequency is determined as 13 GHz corresponding to the optimal absorption properties. Single station and time domain solver are applied for calculation. The RCS values can be described by the following equation:

$$\sigma\left(dBm^2\right) = 10\log\left[\frac{4\pi S}{\lambda^2}\left|\frac{E_s}{E_i}\right|^2\right] \quad (1)$$

where S is the area of the simulated plate, λ is the length of the incident microwave, E_s

is the electric field intensity of transmitting waves, and E_i is the electric field intensity of receiving wave.

2. Electromagnetic Formulas

The RL values at different thicknesses in the frequency range of 2–18 GHz can be calculated based on the transmission line theory through the following equations:

$$Z_{in} = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}tanh\left(j\frac{2\pi fd}{c}\sqrt{\mu_r\varepsilon_r}\right) \quad (2)$$

$$RL = 20\,log\left|\frac{Z_{in}-Z_0}{Z_{in}+Z_0}\right| \quad (3)$$

where Z_{in} is the input impedance, Z_0 is free space impedance, μ_r is the relative complex permeability, ε_r is the complex permittivity, f is the frequency of microwaves, d is the thickness of the absorber, and c is the velocity of light.

Debye relaxation (Cole-Cole plots) can be expressed as follows:

$$\left[\varepsilon' - (\varepsilon_s + \varepsilon_\infty)/2\right]^2 + (\varepsilon'')^2 = \left[(\varepsilon_s - \varepsilon_\infty)/2\right]^2 \quad (4)$$

where ε_s and ε_∞ stand for the static dielectric constant and relative dielectric constant at the high-frequency limit.

The attenuation constant (α) can be calculated by following equation:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu''\varepsilon' + \mu'\varepsilon'')^2}} \quad (5)$$

The impedance matching (Z) can be expressed as the equation:

$$Z = \frac{Z_{in}}{Z_0} = \sqrt{|\mu_r/\varepsilon_r|}\tan h\left[j(\frac{2\pi fd}{c})\sqrt{\mu_r\varepsilon_r}\right] \quad (6)$$

The minimum RL value can be obtained under a certain frequency (f_m) if the matching thickness (t_m) of the samples satisfies the following equation:

$$t_m = nc/(4f_m\sqrt{|\mu_r||\varepsilon_r|}) \ (n = 1, 3, 5\ldots) \quad (7)$$

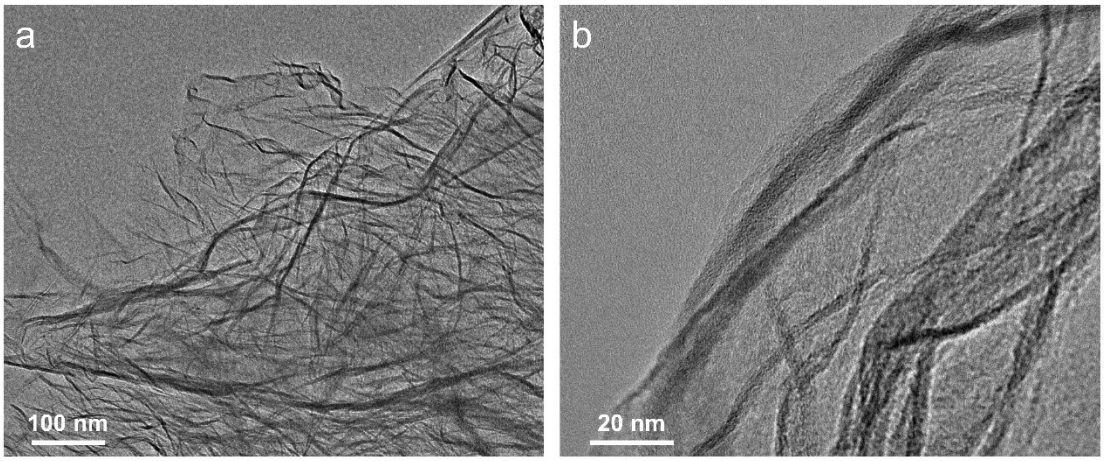

Fig. S1. TEM images of graphene.

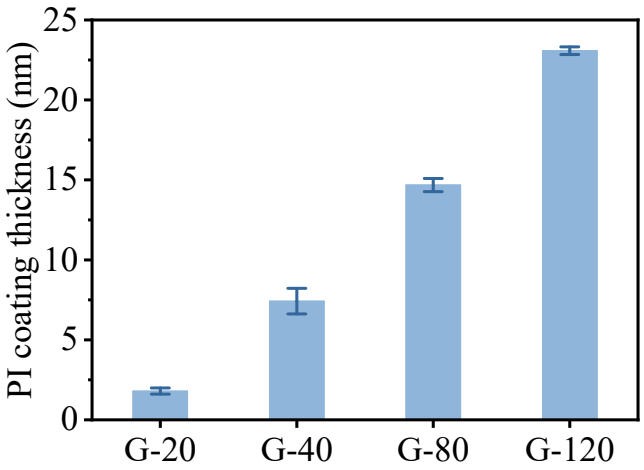

Fig. S2. The PI coating thicknesses of PI/G samples.

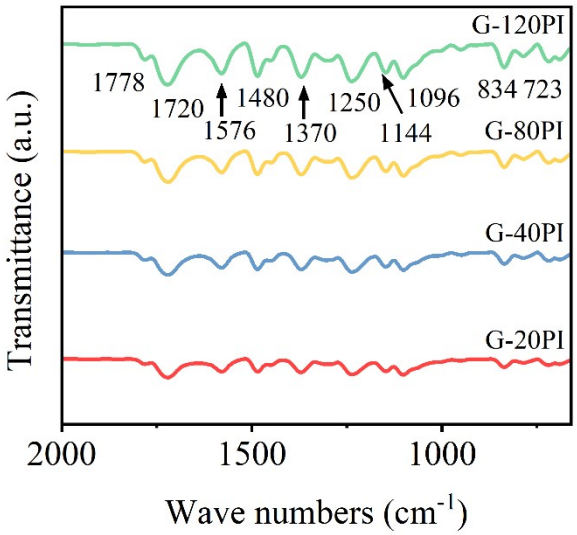

Fig. S3. FTIR of PI/G samples.

The characteristic peaks at 723, 1370, 1720 and 1778 cm^{-1} are allocated to imide ring, C−N−C bond of imide, symmetric C=O and asymmetric C=O, which verifies the presence of imine bond (CONCO), indicating PI films are successfully formed on the graphene. The characteristic peaks at 1580 and 1480 cm^{-1} can be seen as phenyl framework vibration. The band at 1250 cm^{-1} is associated with the characteristic structure of ether bond in ODA. The peaks at 1144 and 1096 cm^{-1} are assigned to oxygen-containing groups. The peak at 834 cm^{-1} is attributed to C−H bending vibration.

Table S1. BET surface area, Pore volume and average pore diameter of PI/G samples.

Samples	BET Surface Area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
G-20	85.42	0.198	9.26
G-40	75.37	0.168	8.89
G-80	71.75	0.150	8.36
G-120	63.55	0.142	8.91

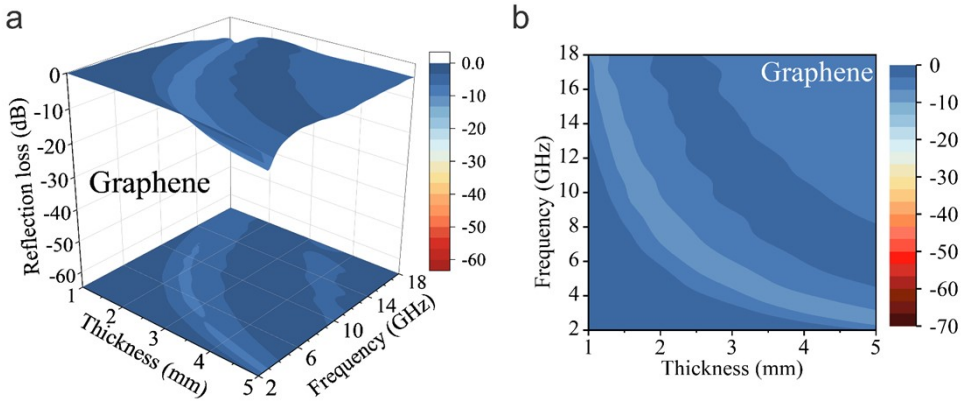

Fig. S4. RL values of graphene.

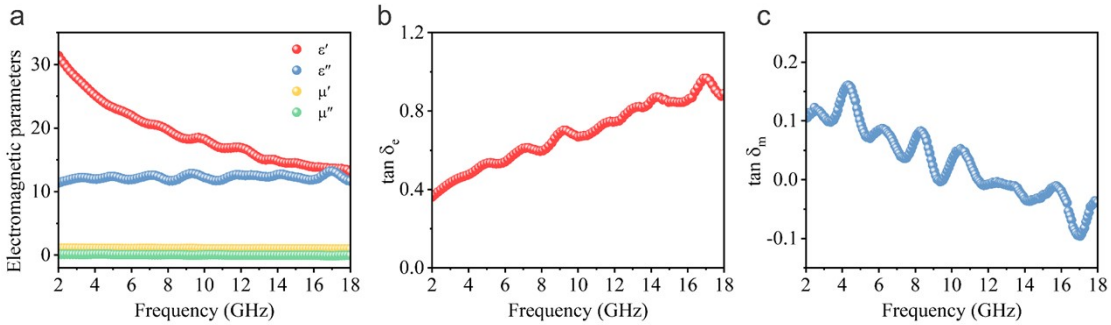

Fig. S5. (a) Electromagnetic parameters, (b) dielectric loss tangent and (c) magnetic loss tangent of graphene.

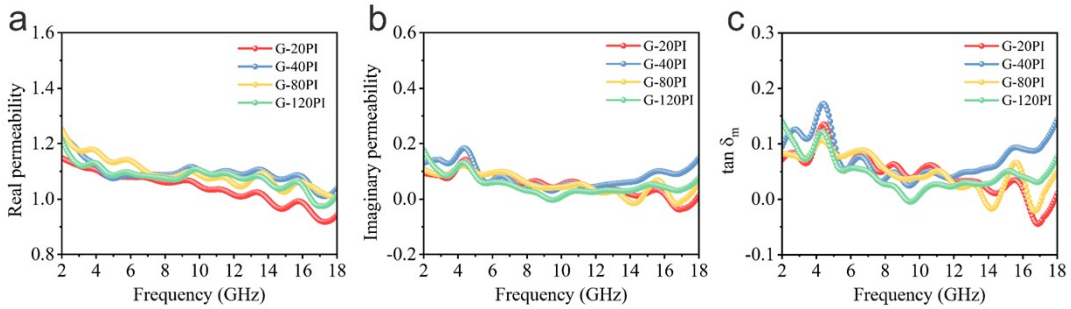

Fig. S6. The frequency dependence of (a) real permeability, (b) imaginary permeability and (c) magnetic loss tangent of PI/G samples.

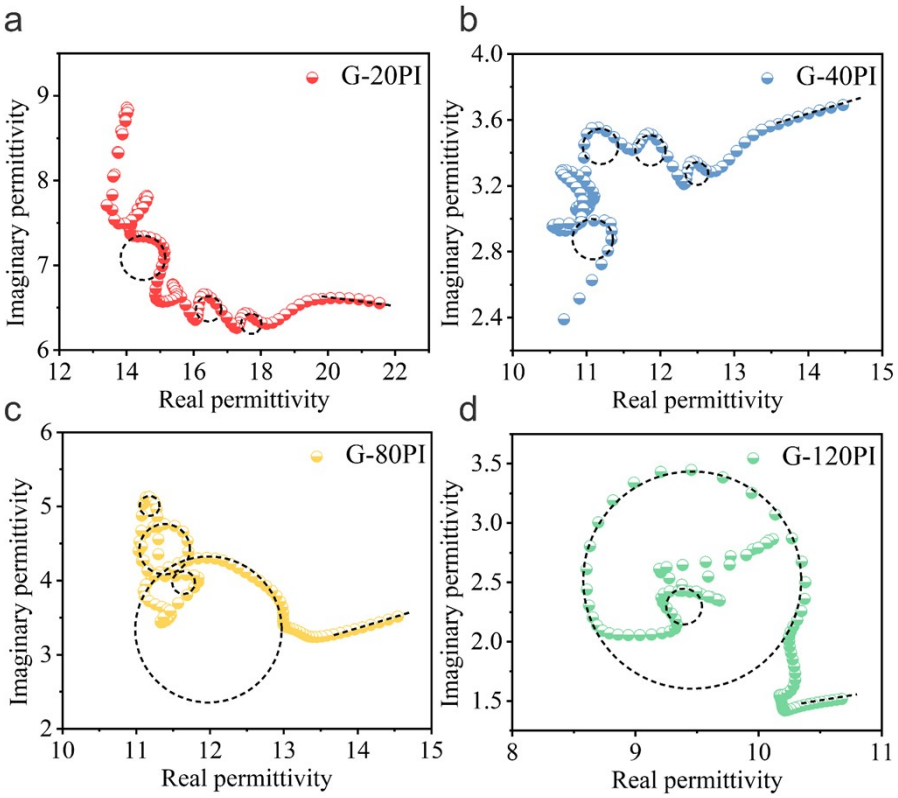

Fig. S7. The Cole-Cole plots of (a) G-20PI, (b) G-40PI, (c) G-80PI and (d) G-120PI.

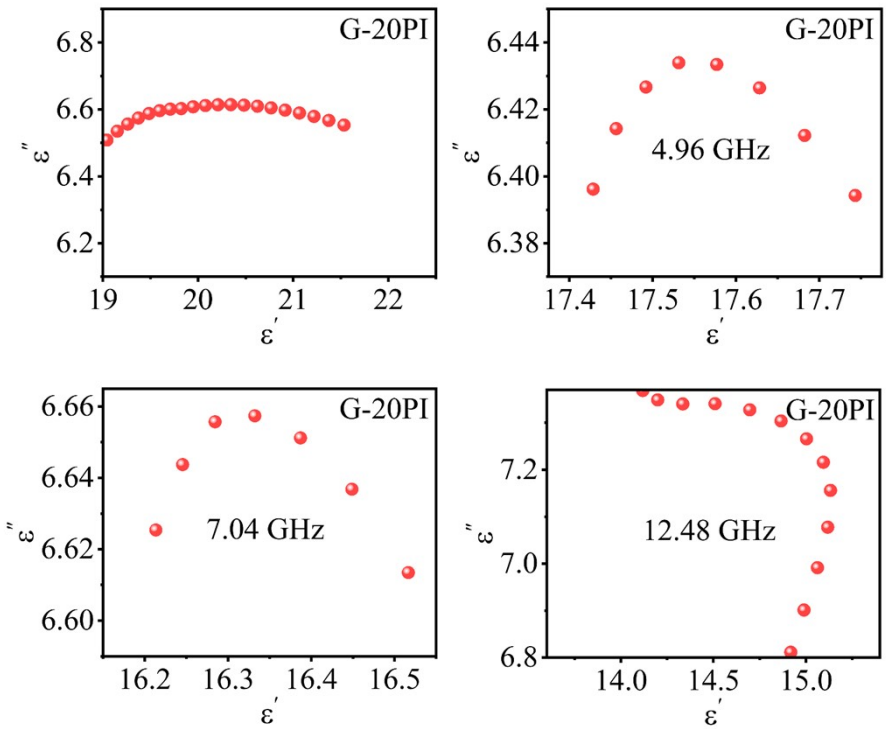

Fig. S8. The Cole-Cole plots of G-20PI.

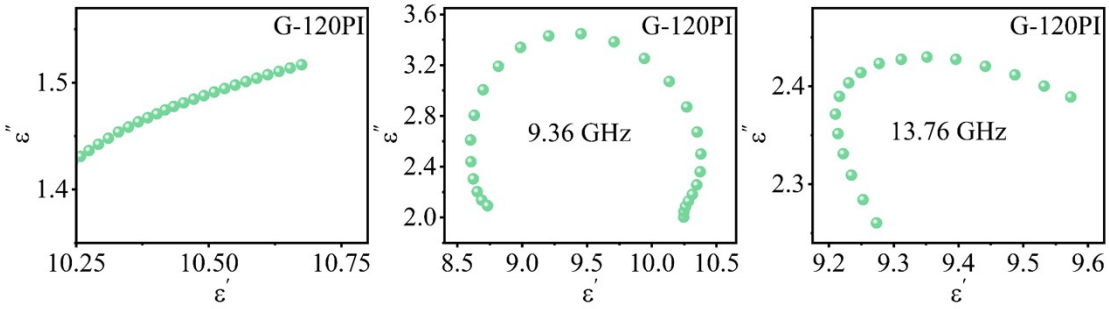

Fig. S9. The Cole-Cole plots of G-120PI.

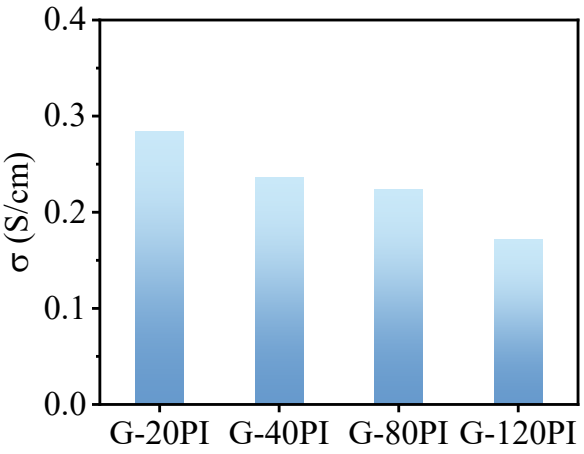

Fig. S10. The conductivity of PI/G samples.

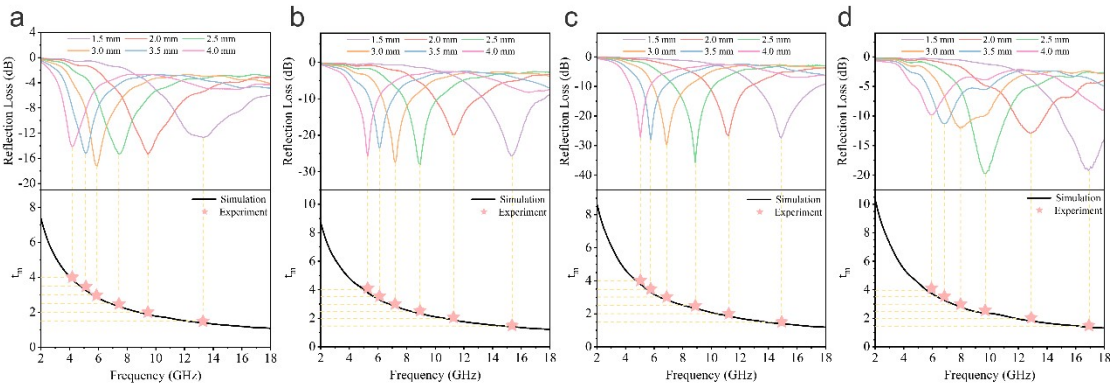

Fig. S11. The RL and dependence of matched thickness (t_m) on matched frequency (f_m) at λ/4 wavelength of PI/G samples.

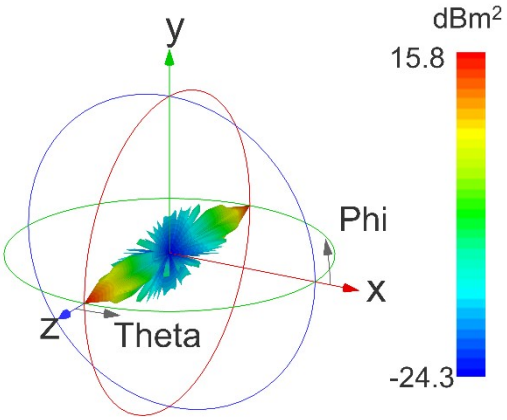

Fig. S12. CST simulation results of PEC.

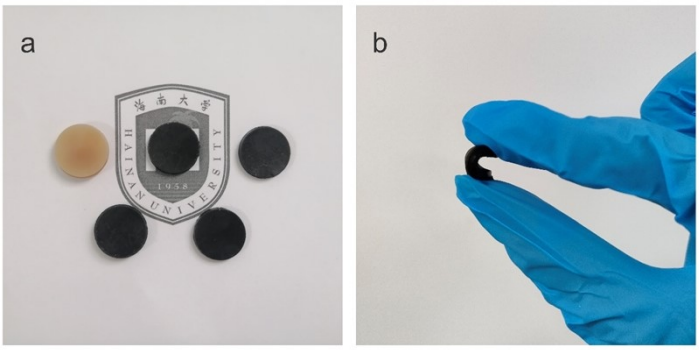

Fig. S13. The optical photographs of NR and PI/G/NR composites.