Electronic Supplementary Information (ESI)

Synthesis of novel rambutan-like graphene@aluminum composite spheres and non-destructive terahertz characterization

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Schematic and Setup for the MPCVD approach

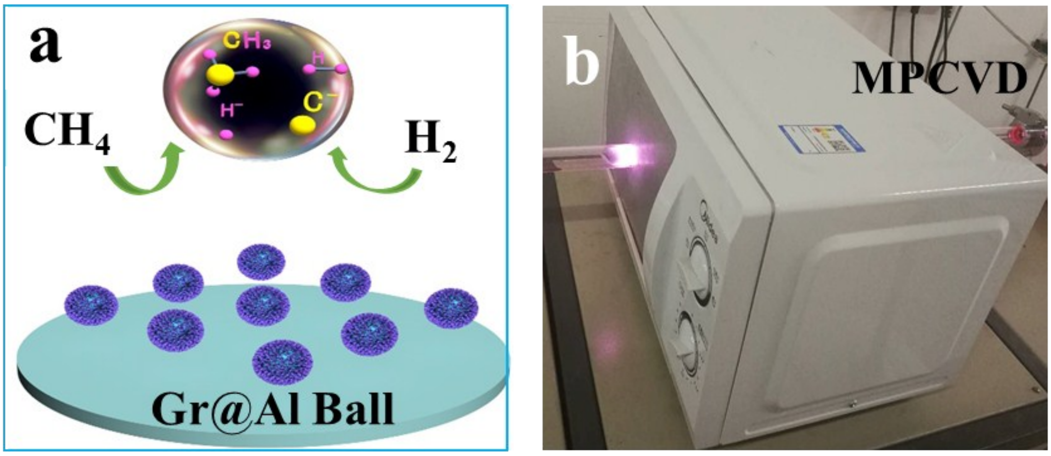

Fig. S1 Schematic and setup for the MPCVD approach. a) Schematic illustrating the principle of synthesizing graphene@Al spheres; b) Photograph showing the home-made setup for the MPCVD, in which a microwave oven is utilized. The plasma can be observed clearly inside the microwave oven.

Theoretical calculation, FDTD simulation and averaged spherical diameter derivation

Statistically, the thickness of the graphene shell on graphene@Al spheres can be approximated as the half of the diameter difference between the averaged diameter of graphene@Al spheres and Al spheres (100 μm in diameter). Therefore, once the averaged diameter of graphene@Al spheres is obtained, the thickness of the graphene shell can be easily calculated.

For polyethylene (PE) buried-Al spheres or -graphene@Al spheres samples, the distribution of Al spheres or graphene@Al spheres in PE is very similar to the system of particles suspended in solution. Therefore, the light scattering method used for measuring the size of particles suspended in solution with visible or near-infrared waves can be extended to measure the diameter of Al spheres or graphene@Al spheres with THz waves.[1] The parameters including scattering, absorption and extinction efficiencies of a sphere to a wave is important and must be known in the light scattering method for the calculation of the diameter of particles.

In the following text, we will first calculate the scattering efficiency of an Al sphere and a graphene@Al sphere by the Mie theory as well as by the finite-difference time-domain (FDTD) simulation, and then show how to obtain the averaged diameter of the synthesized graphene@Al spheres from the THz transmission spectra step by step, based on the light scattering method in THz region.

1. Theories for the calculation of the scattering efficiency

As the surface roughness of a graphene@Al sphere (Fig. 1d in the main text) is far less than the wavelength (λ) of THz waves (the wavelength for 1 THz is 300 μm), we can treat the rambutan-like graphene@Al sphere as a perfect sphere in the THz region. Thus, the efficiencies of scattering (Q_{sca}), extinction (Q_{ext}) and absorption (Q_{abs}) of such a sphere to THz wave can be analytical calculated by the Mie theory.[2] Q_{sca}, Q_{ext} and Q_{abs} can be calculated via:

$$Q_{sca} = \frac{2}{x^2}\sum_{n=0}^{\infty}(2n+1)(|a_n|^2+|b_n|^2) \qquad \text{(S1)}$$

$$Q_{ext} = \frac{2}{x^2}\sum_{n=0}^{\infty}(2n+1)Re(a_n+b_n) \qquad \text{(S2)}$$

$$Q_{abs} = Q_{ext} - Q_{sca} \qquad \text{(S3)}$$

where a_n and b_n are the Mie coefficients, and n, the natural number. a_n and b_n are functions of the size parameter (x) and the complex refractive index (m) of the sphere relative to the ambient medium. Readers can refer to the reference (2) for more details regarding the calculation of a_n and b_n. The size parameter, x, is expressed as

$$x = \pi D n_0 f/c \qquad \text{(S4)}$$

where D represents the diameter of the sphere, n_0, the refractive index of the ambient medium, f, the frequency of THz wave, and c, the speed of light in vacuum.

According to the Mie theory, the scattering, extinction and absorption efficiencies of a sphere are functions of the complex refractive index (m). For materials having high conductivities in the THz range (e.g., Al and graphene), the Drude model can be used to describe the frequency-dependent dielectric constants of Al[3] and graphene.[4] The dielectric constants of Al and graphene can be expressed by Eq. (S5) and (S6), respectively.

$$\varepsilon_{Al}(\omega) = 1 - \omega_{p,Al}^2/(\omega^2 + i\omega\gamma_{Al}) \qquad \text{(S5)}$$

$$\varepsilon_{graphene}(\omega) = 1 - \omega_{p,graphene}^2/(\omega^2 + i\omega\gamma_{graphene}) \qquad \text{(S6)}$$

where $\omega=2\pi f$ is the angular frequency of THz waves. In the equations, the plasma frequency ($\omega_{p, Al}$) and the scattering rate (γ_{Al}) of Al are set to 2.24×10^{16} rad s^{-1} and 1.24×10^{14} rad s^{-1}, respectively.[3] The plasma frequency ($\omega_{p, graphene}$) and the scattering rate ($\gamma_{graphene}$) of graphene are set to 2.64×10^{15} rad s^{-1} and 1.79×10^{13} rad s^{-1}, respectively.[4]

The frequency-dependent complex refractive index, m, obeys the relationship

$$m = \sqrt{\varepsilon(\omega)} \qquad \text{(S7)}$$

where $\varepsilon(\omega)$ is the dielectric constant of Al or graphene.

By the substitution of Eq. (S4-S7) into Eq. (S1), (S2) and (S3), respectively, we can obtain that the efficiencies of scattering, extinction and absorption of an Al sphere or a graphene sphere using the Matlab functions developed by Matzler.[5] From our calculations, it was observed that although m is the function of the frequency (f), the value of m in the THz range (0.1 - 2.8 THz safely) actually has no influence on the calculated efficiencies of scattering, extinction and absorption because the refractive index m of Al or graphene is very high in the THz range.

2. The relationship between the scattering efficiency and the diameter of the sphere

Based on the above-mentioned theories, we calculated the relevant parameters for individual Al or graphene spheres with diameter ranged from 80 μm to 140 μm. We found that the absorption efficiency (Q_{abs}) for the sphere is very small and the scattering efficiency (Q_{sca}) is just a little bit smaller than the extinction efficiency (Q_{ext}) (see Eq. (S3)); therefore we only focused on the calculation of the scattering efficiency of an Al sphere or a graphene@Al sphere in the following content. We also found that for both Al spheres and graphene spheres the scattering efficiency increases rapidly and monotonically with the size parameter (x) or the frequency (f) when x or f is below a certain value (defined as the "critical size parameter" or the "critical frequency"), and keeps nearly constant when x or f is beyond a critical value. Namely, the critical size parameter (x or f) is a constant for an Al sphere or a graphene sphere.

An example is shown in Fig. S2 for an Al sphere with a diameter of 100 μm embedded in PE. In this case, the scattering efficiency, Q_{sca}, increases rapidly with the size parameter (x) or the frequency (f) when x is below 1.1 or f is smaller than 0.8 THz, and keeps at a value of ~ 2.15 when x is larger than 1.1 or f is larger than 0.8 THz. It is necessary to point out that because the critical size parameter is a constant for an Al sphere, we can know that the critical frequency is inversely proportional to the diameter of the sphere according to Eq. (S4), which means the larger the diameter of the sphere the smaller the critical frequency. In other words, the thicker the graphene shell, the lower the critical frequency is.

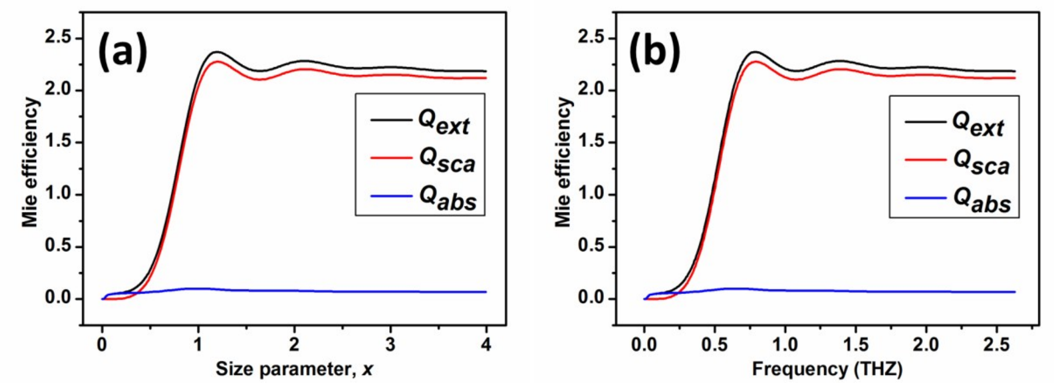

Fig. S2 Theoretical calculations of the Mie efficiencies (extinction, scattering and absorption) for an Al sphere (100 μm in diameter) embedded in PE. The Plots of Mie efficiencies versus (a) the size parameter (*x*) and (b) the frequency (*f*). The efficiencies of extinction, scattering and absorption are denoted by Q_{ext}, Q_{sca} and Q_{abs}, respectively. Q_{ext} is the sum of Q_{sca} and Q_{abs}.

The calculation of the scattering efficiency of a graphene@Al sphere is very similar to an Al sphere for the reasons below: (1) graphene has a very high conductivity and the THz wave cannot penetrate through a graphene shell with a thickness of the order of microns in our system; (2) no occurrence of scattering at the interface between the inside Al sphere and the outside graphene shell for our synthesized graphene@Al sphere, which means all the scattering occurred at the surface of the graphene@Al sphere and that the graphene shell is responsible for the scattering; and (3) the calculation of the scattering efficiency for a graphene@Al sphere can be treated as for the calculation of the scattering efficiency of a graphene sphere with the same diameter as the graphene@Al sphere.

By taking a graphene@Al sphere (a 4 μm thick graphene on an Al sphere with a diameter of 100 μm) and an Al sphere (108 μm in diameter) as an example, we found that the scattering efficiencies of them are almost the same in the range of 0.1 - 2.8 THz (see in Fig. S3) due to the high conductivity of Al and graphene in the THz region, and that the scattering efficiencies keep at a value of ~ 2.15 when x is larger than 1.1 or f is larger than 0.74 THz. The above-mentioned rule of the diameter of the sphere is inversely proportional to the critical frequency is also applicable to the graphene@Al sphere.

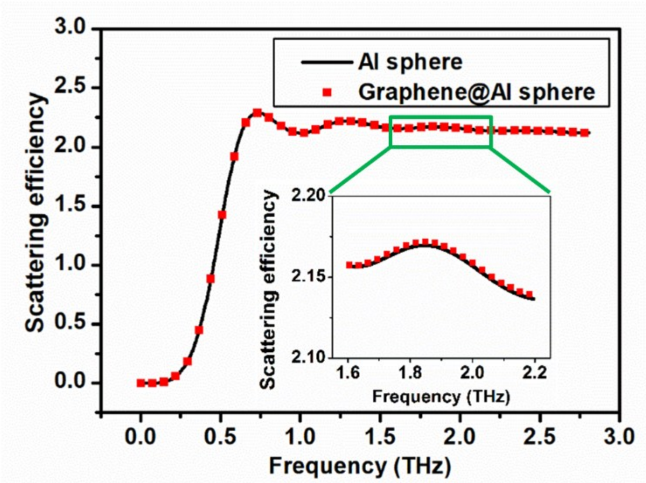

Fig. S3 Calculation of the scattering efficiency of an Al sphere (108 μm in diameter, black curve) and a graphene@Al sphere (red square), embedded in PE. The graphene@Al sphere was constructed by wrapping a 4 μm thick graphene shell on an Al sphere with a diameter of 100 μm. Inset is zoomed-in from the region marked by the green rectangle, showing that the scattering efficiencies of the Al sphere and the graphene@Al sphere are nearly the same in the region between 1.6 - 2.2 THz.

3. The scattering efficiency for two adjacent spheres

3.1 The distance between the centers of two adjacent spheres embedded in PE

In the light scattering method for the particles in solution, the distance between two particles is far enough, thus each particle can be regard as an individual scattering center and the scattered light from one particle has no interaction with other particles.[1]

In our samples, Al spheres or graphene@Al spheres were thoroughly mixed in PE, respectively; and the mixture was pressed into a disk (see the section of "***THz transmission spectrum***

***measurement*"** in the main text). It can be assumed that Al spheres or graphene@Al spheres were evenly distributed in the sample in a layer by layer manner. Below we take Al spheres in PE as an example to show how to estimate the averaged distance between two spheres. The averaged distance (d) between two adjacent spheres can be calculated via the following equations:

$$d = (V/N)^{1/3} \tag{S8}$$

$$V = \pi D_{disk}^2 H/4 \tag{S9}$$

$$N = M/(\rho\pi D_{Al}^3/6) \tag{S10}$$

where V, D_{disk}, and H are the volume, diameter and thickness of the disk-like sample, respectively; and N, M, ρ, D_{Al} are the number, mass, density and averaged diameter of the Al sphere, respectively.

From Eq. (S8-S10), it is easy to obtain the distance (d) between the centers of any two adjacent spheres in the sample, as below:

$$d = (\rho \mathrm{H}\pi^2 D_{Al}^3 D_{disk}^2/M/24)^{1/3} \tag{S11}$$

In our experiments, D_{disk} = 13.0 mm, H = 1.16 mm, M = 20 mg, ρ = 2.7 g cm^{-3} and D_{Al} = 100 μm. By the substitution of these values into Eq. (S11), the averaged distance, d, between the centers of any two adjacent Al spheres can be calculated to be 219 μm. As a first approximation, the distance between any two adjacent graphene@Al spheres in PE buried graphene@Al sphere samples is estimated to be ~200 μm, based on the following reasons: (1) the size of the graphene@Al spheres is very close to that of Al spheres in our experiments (see Fig. 1 in the main text); (2) the mass (20 mg) of graphene@Al spheres used for preparing PE buried sphere sample is the same as that of Al spheres; (3) and the size of PE buried sphere sample is fixed (D_{disk}=13.0 mm and H=1.16 mm).

3.2 FDTD simulation for the scattering efficiency of an individual sphere and two spheres

The frequency-dependent scattering efficiencies of one Al sphere and two adjacent Al spheres (100 μm in diameter) embedded in PE were investigated using the FDTD method. Briefly, a plane wave with a spectral region of 0.1 - 2.8 THz was illuminated on the individual sphere or two Al spheres embedded in PE. The distance between the centers of the two spheres is 219 μm. The electric field direction of incident THz wave is arbitrarily for an Al sphere due to its spherical symmetry whereas parallel to the vector formed by two sphere centers. The complex refractive index (*m*) of Al was taken from the Drude model above (Eq. (S7)), and the refractive index of the PE was set to 1.45 for the range of 0.1 - 2.8 THz. A mesh size of 0.5 μm × 0.5 μm × 0.5 μm was set to guarantee the accuracy of simulation. Six monitors were surrounded the individual sphere or the two spheres in the *X*, *Y* and *Z* directions to collect the entire scattered THz wave.

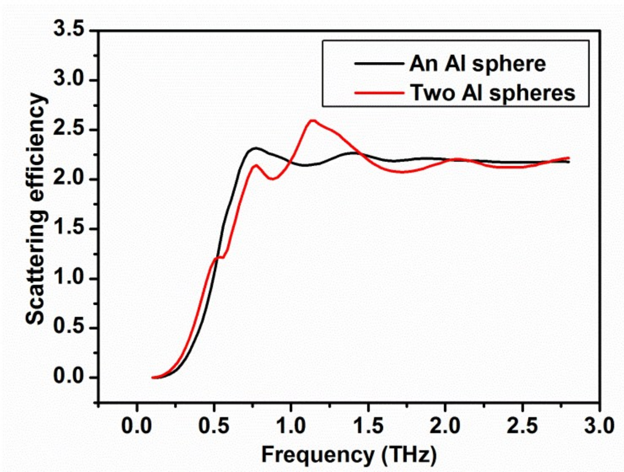

Fig. S4. FDTD simulation of the scattering efficiency of an Al sphere (100 μm in diameter, black curve) embedded in PE and two Al spheres (219 μm between their centers, red curve) embedded in PE.

From FDTD simulations (Fig. S4), we observe that: (1) the scattering efficiency of an individual Al sphere is highly consistent with that calculated from the Mie theory (See Fig. S2b), confirming the effectiveness of our FDTD simulation; (2) when the frequency is above 1.5 THz, the scattering efficiency of the two spheres is highly similar to that of one sphere and can be regarded as constant. Therefore, theoretically, we can ignore the influence between Al spheres in the analysis of PE-buried Al sphere samples when the THz frequency is above 1.5 THz. This approximation is also applicable to PE-buried graphene@Al sphere samples.

3.3 Relationship between the transmission value and the thickness of graphene shell

The light scattering method has been successfully used to measure the size and particles suspended in solution by visible lights.[6] A key point of using this method is that the light scattering from one particle has no influence on other particles. As we verified in section "***3.2 The Scattering efficiency for two adjacent spheres***" that the light scattering from each individual Al sphere or graphene@Al sphere has no influence on other Al spheres or graphene@Al spheres when the frequency is above 1.5 THz, therefore the light scattering method used for the analysis of particles in solution can be extended to analyze the size of Al spheres or graphene@Al spheres embedded in PE in the terahertz region (f > 1.5 THz) in principle. Then we have the following equation to theoretically calculate the transmission terahertz intensity ($I_{sample,\ theory}$) of PE buried Al sphere samples or PE buried graphene@Al sphere samples via:[1]

$$I_{sample,\ theory} = I_0(1-R)^2\exp(-\pi H D^2 N(D) Q_{sca}(\lambda, m, D)/4) \quad \text{(S12)}$$

where I_0 is the intensity of incident THz wave, R the reflectivity of PE, $N(D)$ the number of Al spheres or graphene@Al spheres per unit volume of the disk-like PE buried Al sphere or graphene@Al sphere sample, D the average diameter of Al spheres or graphene@Al spheres, and m the complex refractive index of Al or graphene.

The measured refractive index (n_0) for PE by our THz-TDS system is about 1.45, and the reflectivity of the disk-like sample surface (dominated by PE) can be calculated to be 0.03 via:

$R = (n_0\text{-}1)^2/(n_0+1)^2$ (S13)

Thus, the THz intensity loss due to the reflectivity of the disk-like sample surface can be neglected. As R is very small, so the term $(1\text{-}R)^2$ in Eq. (S12) can be approximated to 1.

As shown in Fig. 1d in the main text, the morphology of graphene shell on Al sphere is very likely graphene flakes (powered graphene). Because the density of powered graphene (0.0215 g/cm^3) is much less than the density of Al (2.7 g cm^{-3}),[7] and the thickness of graphene wrapped on Al sphere is much less than the diameter of the Al sphere, therefore the mass of graphene wrapped on the Al sphere can be ignored. Consequently, the parameter H, $N(D)$ and $Q_{sca}(\lambda,m,D)$ are constant when THz frequency is larger than 1.5 THz.

As a result, the theoretical transmission terahertz intensity ($I_{t,\ theory}$) for graphene@Al spheres of different synthesis durations can be simplified as below:

$I_{t,theory} = I_0\exp(-bD_t^2)$, (S14)

$b = \pi HN(D)Q_{sca}(\lambda,m,D)/4$, (S15)

where b is defined as the decay factor and D_t is the average diameter of the graphene@Al spheres with different synthesis durations. From Fig. S2, we find that Q_{sca} can be regarded as a constant in the range of 1.6 - 2.2 THz. By the substitution of H(0.13 cm), $N(D)$(9.19×10^4 cm^{-3}) and the averaged value of $Q_{sca,\ average}(\lambda, m, D)$(2.15) calculated from Fig. S2 into Eq.(S15), we obtained the decay factor, $b = 7.20 \times 10^4$ cm^{-2}, which is a constant here.

In real experiments, however the decay factor is smaller than that obtained from the theoretical calculation (Eq. (S15)) due to likely occurred forward scattering.[8] As a result, the decay factor obtained from theoretical calculation should be corrected. Correspondingly, the transmission THz intensity for PE-buried graphene@Al spheres with different synthesis durations can be calculated by the following formula:

$I_{t,experiment} = I_0 \exp(-b_{cf} D_t^2)$. (S16)

$T_{t,experiment} = I_{t,experiment}/I_0 = \exp(-b_{cf} D_t^2)$ (S17)

$T_{t,theory} = I_{t,\ theory}/I_0 = \exp(-bD_t^2)$ (S18)

where b_{cf} is the corrected decay factor (a constant) for the analysis of the experimental data, $T_{t,\ experiment}$ and $T_{t,\ theory}$ are the experimentally measured transmission value and the theoretical calculated transmission value, respectively.

The theoretically calculated transmission value, T, for Al spheres with a diameter of 100 μm for the range of 1.6 - 2.2 THz is calculated to be 0.165 through the Eq. (S18); and the experimentally measured averaged transmission ($T_{0\ min,\ experiment}$, Fig. 6 in the main text) for the range of 1.6 - 2.2 THz for Al sphere sample is 0.279. By comparing Eq. (S17) and (S18), we obtain the correction decay factor, b_{cf}, to be 5.11×10^4 cm^{-2}. Eq. (S17) is used in the main text for the calculation of the averaged diameter of graphene@Al spheres with different synthesis durations.

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