Supplementary Information

Ultrathin flexible graphene films with high thermal conductivity and excellent EMI shielding performance using large-sized graphene oxide flakes

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Figure S1 Images of (a) folding, then unfolding, and (b) crumpling, then releasing of the PLG film; (c) folding, then unfolding, and (d) crumpling, then releasing of the LG-4 film.
Figure S2 SEM images of (a) double folding, (b-f) bending of PLG films; (g-h) cracks of the PLG film after repeated folding; (i-k) folding, (l) bending of the LG-4 film.
Figure S3 Fabrication of graphene films. (a) casting and drying of GO suspension; (b) the annealing furnace; (c) compression of porous graphene films.

Figure S4 EMI shielding performance testing equipment.

Figure S5 Bending testing of compressed graphene films: (a) before bending; (b) after bending.

As shown in Figure S5, the moving speed is 2 mm·s⁻¹ and free length of graphene films is around 27 mm. The bending radius is from ∞ to 0 mm and the bending speed is around 0.037 Hz. After repeated bending, no cracks or breakages were formed for the compressed graphene films.
Figure S6 EMI SE of (a) PU substrate, (b) graphene films compressed with two porous graphene films, (c) graphene films compressed with four porous graphene films, (d) small-size graphene films, (e) medium-size graphene films; SE$_{\text{ref}}$, SE$_{\text{abs}}$ and SE$_{\text{total}}$ of (f) the SG-4 film, (g) the MG-4 film, and (h) the LG-4 film; (i) A and R coefficients of the LG-4 film.

Table S1 The electrical conductivity of graphene films and the copper foil

| Samples | Electrical conductivity $10^4$ (S·cm$^{-1}$) | STDEV $10^4$ (S·cm$^{-1}$) | Samples | Electrical conductivity $10^4$ (S·cm$^{-1}$) | STDEV $10^4$ (S·cm$^{-1}$) |
|---------|---------------------------------|-----------------|---------|---------------------------------|-----------------|
| PSG     | 0.117                           | 0.011           | SG-2    | 0.540                           | 0.016           |
| PMG     | 0.121                           | 0.009           | MG-2    | 0.597                           | 0.010           |
| PLG     | 0.127                           | 0.016           | LG-2    | 0.674                           | 0.026           |
| SG-1    | 0.523                           | 0.009           | SG-4    | 0.541                           | 0.012           |
| MG-1    | 0.601                           | 0.017           | MG-4    | 0.585                           | 0.017           |
| LG-1    | 0.645                           | 0.023           | LG-4    | 0.696                           | 0.016           |
| Cu      | 50.2                            | 0.4             |         |                                 |                 |
### Table S2 Sheet resistance of GO films

| Samples | Sheet resistance \((10^8 \text{ } \Omega)\) | STDEV \((10^8 \text{ } \Omega)\) | Areal density \((\text{mg} \cdot \text{cm}^{-2})\) |
|---------|---------------------------------|-----------------|-------------------------------|
| SGO     | 26.13                           | 3.62            | 1.72                          |
| MGO     | 14.65                           | 2.11            | 1.69                          |
| LGO     | 8.07                            | 5.01            | 1.68                          |

### Table S3 The in-plane thermal conductivity of compressed graphene films

| Samples | Diffusivity \((\text{mm}^2 \cdot \text{s}^{-1})\) | STDEV \((\text{mm}^2 \cdot \text{s}^{-1})\) | Specific heat capacity \((\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1})\) | Density \((\text{g} \cdot \text{cm}^{-3})\) | Thermal conductivity \((\text{W} \cdot \text{K}^{-1} \cdot \text{m}^{-1})\) |
|---------|---------------------------------------------|-----------------------------|---------------------------------|----------------------|----------------------|
| SG-1    | 465.06                                      | 3.99                        | 0.708                           | 1.91                 | 628.9                |
| MG-1    | 475.31                                      | 8.34                        | 0.753                           | 2.02                 | 722.9                |
| LG-1    | 501.63                                      | 4.5                         | 0.781                           | 2.05                 | 803.1                |

### Table S4 The out-plane thermal conductivity of compressed graphene films

| Samples | Diffusivity \((\text{mm}^2 \cdot \text{s}^{-1})\) | Thickness \((\mu\text{m})\) | Thermal conductivity \((\text{W} \cdot \text{K}^{-1} \cdot \text{m}^{-1})\) |
|---------|---------------------------------------------|----------------------------|----------------------|
| SG      | 2.47±0.05                                   | 45.4                      | 3.34±0.07            |
| MG      | 2.51±0.04                                   | 46.1                      | 3.82±0.06            |
| LG      | 2.53±0.09                                   | 47.2                      | 3.98±0.14            |

### Table S5 The tensile tests of graphene oxide films and compressed graphene films

| Sample | Strength \((\text{MPa})\) | STDEV \((\text{MPa})\) | Elongation at break \((\%)\) | STDEV \((\%)\) |
|--------|---------------------------|------------------------|-------------------------------|-----------------|
| SGO    | 35.60                     | 2.67                   | 1.15                          | 0.61            |
| MGO    | 46.54                     | 3.13                   | 1.73                          | 0.45            |
| LGO    | 52.62                     | 4.61                   | 1.93                          | 0.52            |
| SG-4   | 27.08                     | 2.27                   | 4.91                          | 0.61            |
| MG-4   | 33.70                     | 4.12                   | 5.70                          | 0.40            |
| LG-4   | 42.61                     | 5.29                   | 7.85                          | 0.62            |
Figure S7: The tensile tests of graphene oxide films and compressed graphene films.

Figure S8: TGA spectrum of the SGO, MGO and LGO films.
Figure S9 Complex permittivity and loss tangent (tan δ) of compressed graphene film. The real part ε’ and imaginary part ε” of complex permittivity for (a) SG-4, (b) MG-4 and (c) LG-4 films; tan δ of these graphene films.

Dielectric constant of the samples is tested by the wave-guide method in the X band (8.2-12.2 GHz). Graphene films are attached on the PU foam, with dimensions of 22.8 mm x 10.2 mm x 3 mm. PU is almost transparent to the waves. As shown in Figure S9, dielectric properties of compressed graphene films are characterized. The real part ε’ and imaginary part ε” of complex permittivity of graphene films declined when frequency increased, due to relaxation effect. Because of better electrical conductivity and fewer defects, delocalized π electron of the LG-4 films are more likely to form electric dipole and be polarized, leading to higher dielectric constants than the SG-4 and MG-4 films. Moreover, tan δ of the LG-4 films is also high than other two films, as shown in Figure S9 (d).

Table S6 Specific EMI shielding performance optimized with thickness of varied shielding materials

| Materials type          | Frequency (GHz) | Density (g cm⁻³) | t (mm) | SE (dB) | SSE/t (dB·cm²·g⁻¹) | Ref |
|-------------------------|----------------|-------------------|--------|---------|-------------------|-----|
| Graphene/PDMS           | 8-12           | 0.06              | 3      | 30      | 1667              | [1] |
| Graphene/PEI            | 8-12           | 0.29              | 2.3    | 11      | 164.9             | [2] |
| Graphene/PI             | 8-12           | 0.28              | 0.8    | 21      | 93.75             | [3] |
| rGO/PANI/PEI            | 8-12           | 0.4               | 2.5    | 18.2    | 180               | [4] |
| rGO/PEDOT               | 8-12           | 0.8               | 0.8    | 21      | 841               | [5] |
| CNT/WPU                 | 8.2-12.4       | 0.125             | 2.3    | 50      | 1739              | [6] |
| CNT/phenolic            | 12-18          | 0.51              | 0.14   | 32.4    | 4537.8            | [7] |
| CNT/pp                  | 8.2-12.4       | ~0.92             | 2.2    | 48.3    | 238.6             | [8] |
| CNT sponge              | 2-18           | 2.38              | 22     | 4622    |                   | [9] |
| CNT sponges             | 8.2-12.4       | 0.01              | 1.8    | 54.8    | 30444             | [10]|
| Carbon foam             | 8.2-12.4       | 0.06              | 0.3    | 25.2    | 14000             | [11]|
| Carbon foam             | 0.75-1.12      | 0.8               | 2      | 40      | 1250              | [12]|
| Carbon foam             | 8-12           | 0.0058            | 0.8    | 24      | 51700             | [13]|
| Material                      | Thickness | Density | Strength | E-Modulus |
|-------------------------------|-----------|---------|----------|-----------|
| Graphene foam                | 2-18      | 0.120   | 100000   | [14]      |
| Graphene film                | 8-12      | 1.07    | 60       | 11214     | [15]      |
| Graphene film                | 8-12      | 2.1     | 0.008    | 20        | 11904     | [16]      |
| Graphene film                | 0-18      | 0.120   | 0.018    | 55        | 14550     | [17]      |
| Expanded graphite            | 8.2-12.4  | 1.75    | 0.13     | 65        | 4545.5    | [18]      |
| Graphene/CNT                 | 2-18      | 1.45    | 0.05     | 15        | 26480     | [19]      |
| MWCNT/SWCNT film             | 8.2-12.4  | 0.111   | 0.13     | 65        | 4545.5    | [20]      |
| CNT                          | 8.2-12.4  | 0.26    | 0.6      | 56        | 3589      | [21]      |
| Graphene film/Fe₃O₄          | 8.2-12.4  | 0.78    | 0.3      | 21-24     | 1033      | [22]      |
| CuNi-CNT                     | 8-12      | 1.5     | 54.6     | 1580      | [23]      |
| Ag nanowires/PI              | 8-12      | 5       | 35       | 2416      | [24]      |
| Silver                       | 8.2-12.4  | 0.0033  | 0.0002   | 43        | 645600    | [25]      |
| Silver/MWCNT                 | 0.5-1.0   | 0.51    | 0.0066   | 24.5      | 72700     | [26]      |
| Al                           | 8.2-12.4  | 2.705   | 0.008    | 66        | 30555     | [27]      |
| Cu                           | 8.974     | 0.010   | 70       | 7812      |
| Ti₃C₂Tₓ                      | 2.394     | 0.011   | 68       | 25863     |
| Ti₃C₂Tₓ                      | 2.317     | 0.008   | 57       | 30830     |
| PSG                          | 8.2-12.2  | 0.0205  | 0.0335   | 54.2      | 88850     |
| PMG                          | 8.2-12.2  | 0.0240  | 0.0347   | 57.6      | 84710     |
| PLG                          | 8.2-12.2  | 0.0253  | 0.0356   | 62.0      | 87320     |
| SG-1                         | 8.2-12.2  | 0.1969  | 0.0034   | 26.4      | 39440     |
| MG-1                         | 8.2-12.2  | 0.2018  | 0.0035   | 29.3      | 41490     |
| LG-1                         | 8.2-12.2  | 0.2049  | 0.0035   | 33.1      | 46160     |
| SG-2                         | 8.2-12.2  | 0.2009  | 0.0068   | 43.8      | 32060     |
| MG-2                         | 8.2-12.2  | 0.2052  | 0.0069   | 46.2      | 32630     |
| LG-2                         | 8.2-12.2  | 0.2060  | 0.0071   | 51.1      | 34940     |
| SG-4                         | 8.2-12.2  | 0.1962  | 0.0134   | 61.7      | 23470     |
| MG-4                         | 8.2-12.2  | 0.2045  | 0.0138   | 68.4      | 24240     |
| LG-4                         | 8.2-12.2  | 0.2050  | 0.0140   | 73.7      | 25680     |

t represents for thickness; The thickness is measured by micrometer.
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