Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Supporting Information

## Highly conductive porous graphene film with excellent folding resilience for exceptional electromagnetic interference shielding

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## Experimental details

**Synthesis of graphene oxide with pre-oxidization process (PGO).**

$K_2S_2O_8$ (12.5 g) and $P_2O_5$ (12.5 g) were dissolved in concentrated $H_2SO_4$ (60 mL, 98%) at 80°C. And then graphite powder (15 g, 325 mesh, dried at 60°C for 24 h) was added to the acidic solution, and the resulting mixture was stirred at 80°C for 4.5 h. After cooling to room temperature, the solution was diluted with 2.5 L deionized water. The pre-oxidized graphite was obtained by filtration and dried at 100 °C for 12 h. This pretreated graphite powders (12 g) was put into concentrated $H_2SO_4$ (276 mL, 98%) in an ice bath (under 4°C), and then $NaNO_3$ (6 g) was added. After that, $KMnO_4$ (36 g) was gradually added within 30 min with stirring and keeping under 4°C. The mixture was then heated to 35 °C and kept for 4 h. After, deionized water (552 ml) was added into the mixture and the temperature of reactants was heated to 98°C for 15 min. The reaction was terminated by adding 552 mL deionized water and 30 mL $H_2O_2$ (30%) to reduce Mn(VII) species.

**Synthesis of conventional graphene oxide (CGO)**.

Graphite powder (12 g, 325 mesh, dried at 60°C for 24 h) was added to concentrated $H_2SO_4$ (276 mL) in an ice bath (under 4°C) with vigorous stirring, and followed by the slow addition of $NaNO_3$ (6 g). After that, $KMnO_4$ (36 g) was added over a period of 30 min and the oxidation was performed over 4 h under 35°C. The following oxidation process initiated by the addition of 552 mL $H_2O$ and kept at 98°C for 15 min. The reaction was terminated by the same method specified in the preparation of PGO.

**Synthesis of low temperature oxidized graphene oxide (LGO).**

Graphite powder (12 g, 325 mesh, dried at 60°C for 24 h) and $NaNO_3$ (6 g) were added to concentrated $H_2SO_4$ (276 mL) in an ice bath with vigorous stirring. After that, $KMnO_4$ (36 g) was added over a period of 30 min. The oxidation process was performed over 4 h at 20°C. After that, the reaction was terminated by pouring the reaction system into 1,000 mL 20°C deionized water and the slow addition of 30 mL 30% $H_2O_2$.

**Exfoliation and purification of the GO samples.**

The final mixture was centrifuged and subjected to several cycles of suspension in 10% HCl solution and separated by centrifugation until the pH value of the supernatant reached 7. The resulting solid was re-dispersed in deionized water and exfoliated by mild sonication at 20°C for 10 min, and subjected to dialysis to remove impurities for approximately 7 days. Then brown sticky GO dispersion was obtained. After that, the GO dispersion was diluted and subjected to another 3 cycles of centrifugation at 1000 rpm 20 min for each to remove the graphite powder and unexfoliated graphite oxide agglomerates. Finally, the GO dilute dispersion was concentrated by centrifugation at 10000 rpm for 1 h, generating the GO stock at solid content up to 1 wt.%.

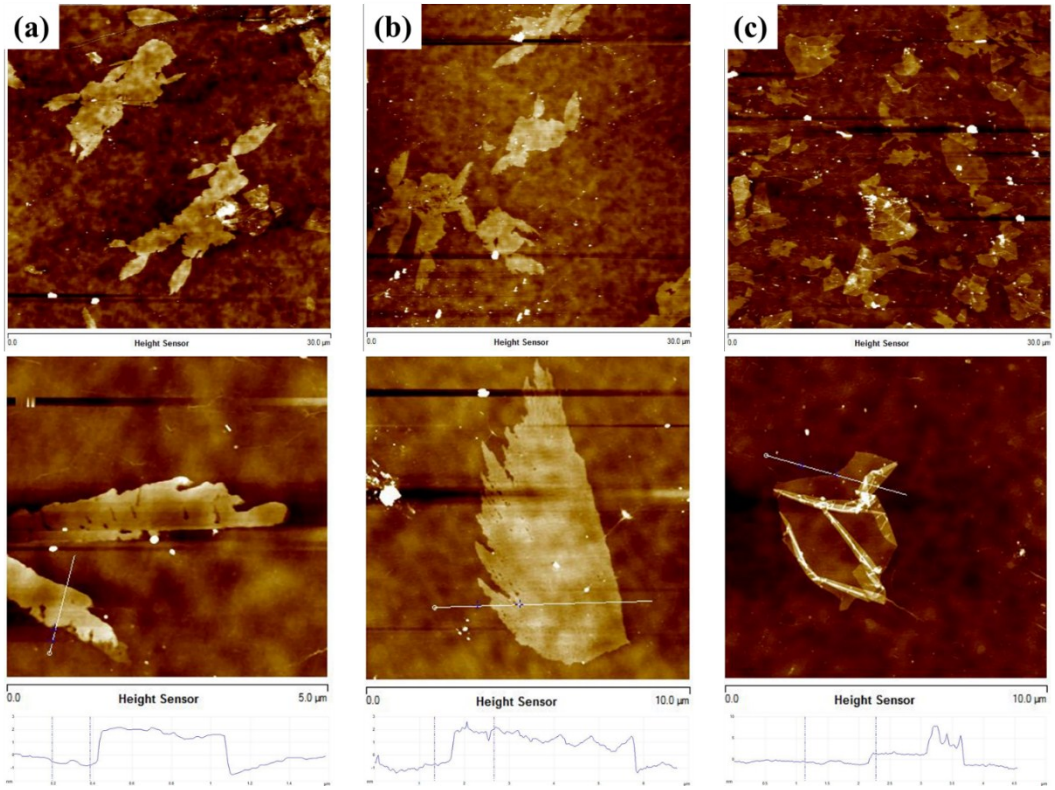


**Figure S1.** Typical AFM images and height profiles of GO sheets: (a) PGO, (b) CGO and (c) LGO.

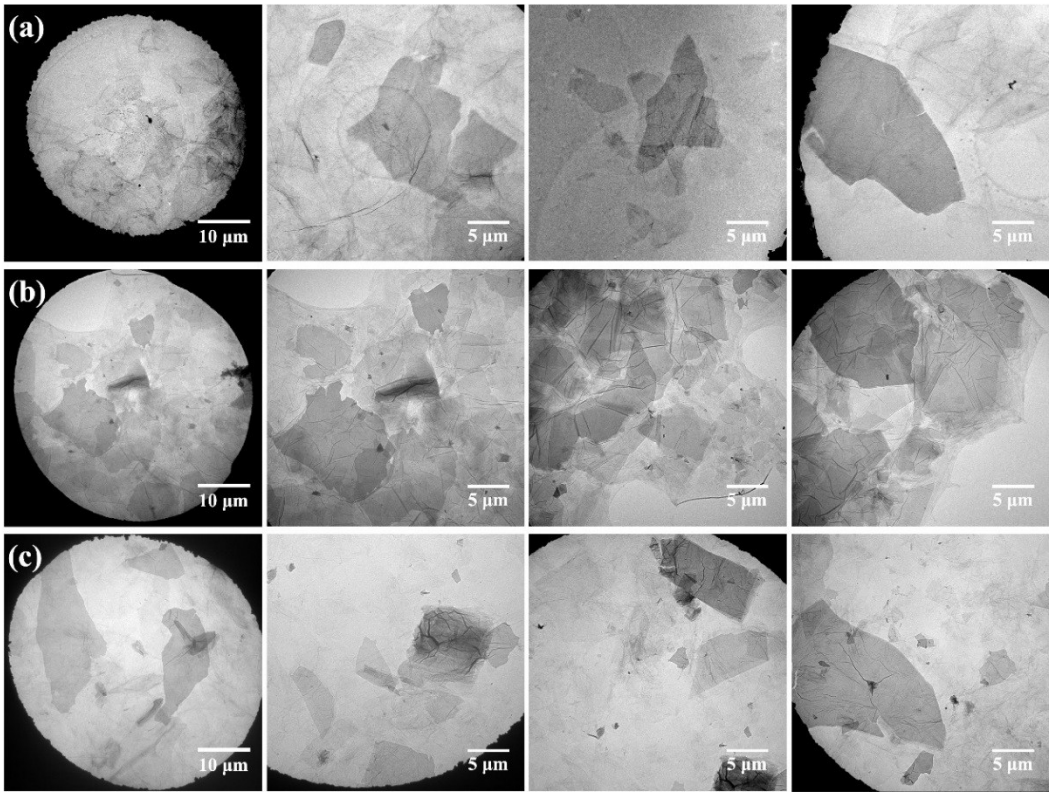


**Figure S2.** Typical TEM images of (a) PGO, (b) CGO and (c) LGO sheets.

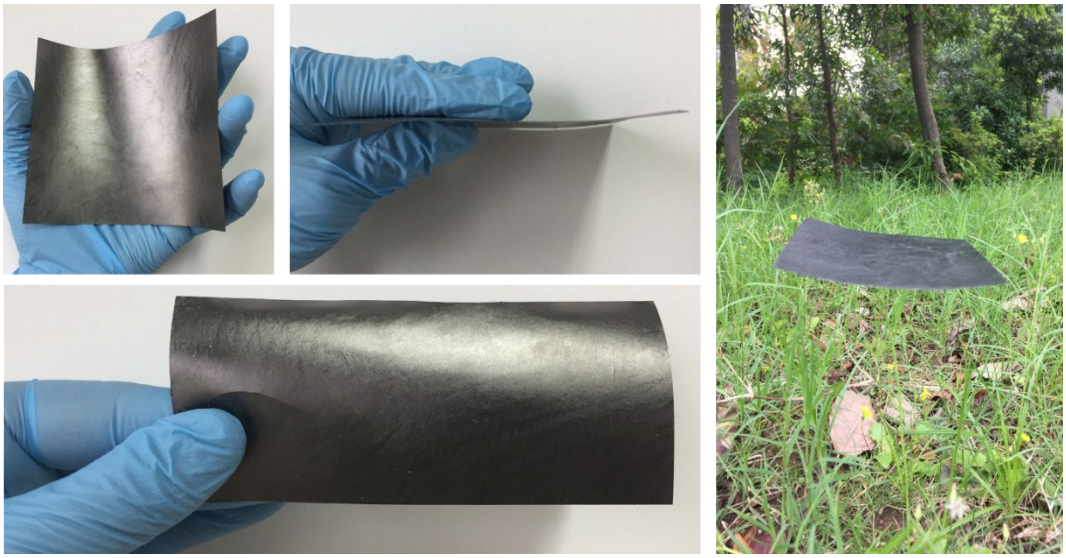

**Figure S3.** Typical photographs of large-scale porous graphene film with a dimension of 100 mm × 100 mm and a thickness of 100 μm.

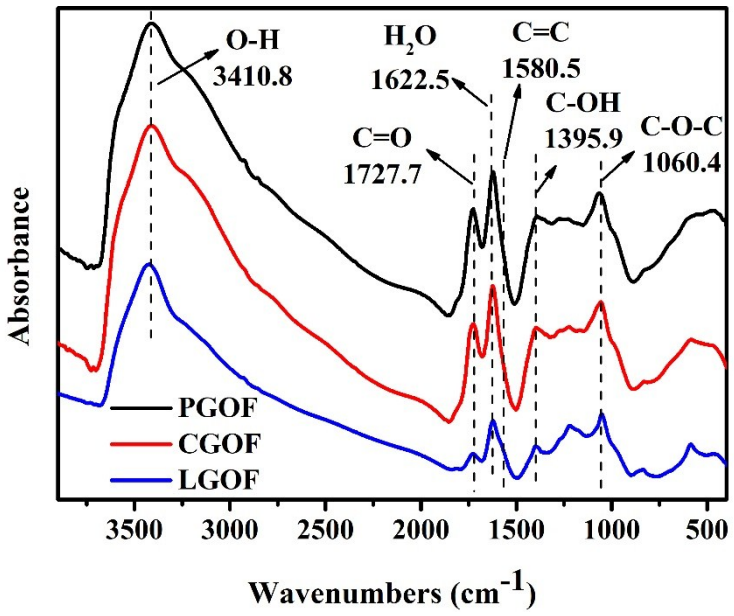


**Figure S4.** FTIR spectra of GO films.

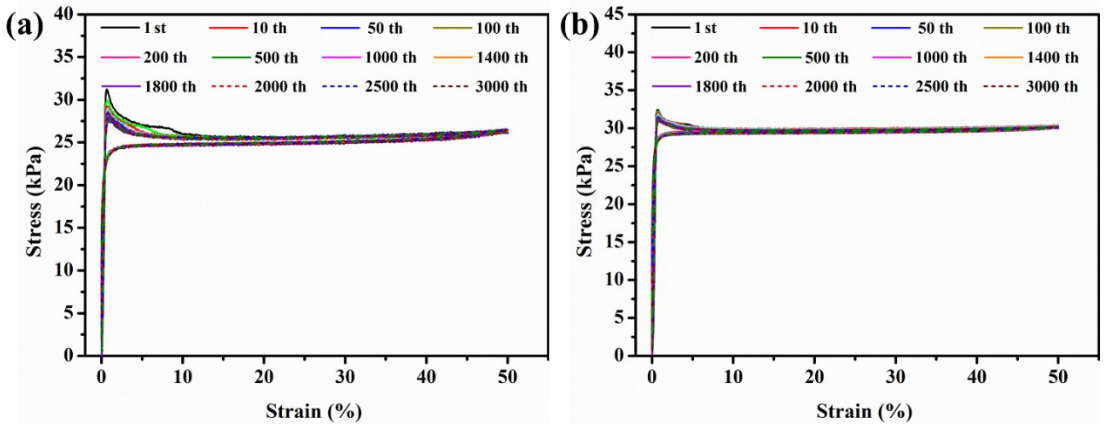


**Figure S5.** The cyclic compressing performance of 200 μm-thick porous graphene films of (a) PPGF and (b) CPGF.

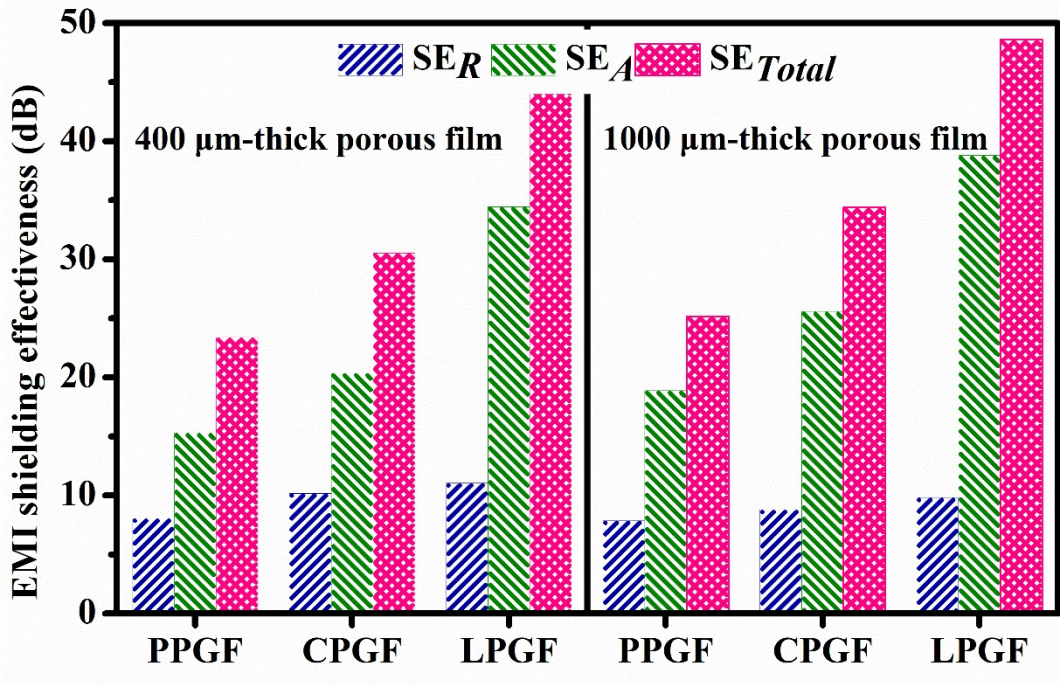


**Figure S6.** The average EMI shielding effectiveness of the porous graphene films with different GO precursors and film thicknesses of 400 and 1000 μm.

**Table S1.** Comparison of the shielding capacity of graphene-based materials.

| Types | Materials | Matrix | Graphene contents (wt.%) | Density ($g/cm^3$) | Thickness (mm) | EMI SE (dB) | SSE/t ($dB \cdot cm^2/g$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Graphene-polymer solid materials | Graphene | PS | 7 | 1.04 | 2.5 | 45.1 | 173 | 1 |
| | Graphene | PEDOT : PSS | 25 | 1.04 | 0.8 | 70 | 841 | 2 |
| | Graphene | PEI | 10 | 1.28 | 2.3 | 22 | 75 | 3 |
| | Graphene | PMMA | 8 | 1.19 | 3.4 | 30 | 74 | 4 |
| | Graphene | PMMA | 4.70 | 1.18 | 2.9 | 63.2 | 184.7 | 5 |
| | Graphene | WPU | 7.7 | 1.43 | 2 | 32 | 112 | 6 |
| | Graphene | WPU | 7.5 | 1.43 | 2 | 34 | 119 | 7 |
| | Graphene | WPU | 7.5 | 1.43 | 2 | 38 | 133 | 8 |
| | Graphene | PS | 10 | 1.04 | 2 | 29.7 | 142.8 | 9 |
| | Graphene | PS | 14.9 | 1.02 | 2 | 24.5 | 120 | 10 |
| | Graphene @ $Fe_3O_4$ | PVA | 35 | 0.75 | 0.3 | 15 | 66.7 | 11 |
| | Graphene | PVA | 15 | 0.75 | 0.3 | 10 | 43.3 | 11 |
| | Graphene | UHMWPE | 1.5 | 0.94 | 2.5 | 28.3 | 120 | 12 |
| Graphene films | Graphene @ $Fe_3O_4$ | / | Bulk | 0.77 | 0.3 | 24 | 1033 | 13 |
| | Graphene film | / | Bulk | 1.09 | 0.018 | 55 | 28032 | 14 |
| | Graphene film | / | Bulk | 0.67 | 0.05 | 60 | 18300 | 15 |
| | Graphene film | / | Bulk | 1.85 | 0.08 | 77.2 | 5216 | 16 |
| | Graphene film | / | Bulk | 2.10 | 0.0088 | 37 | 20021 | 17 |
| Graphene foams | Graphene | PEI | 10 | 0.29 | 2.3 | 12.8 | 191.3 | 3 |
| | Graphene | PS | 30 | 0.45 | 2.5 | 29.3 | 257.6 | 18 |
| | Graphene | PS | 10 | 1.04 | 2.8 | 18 | 62 | 19 |
| | Graphene | PMMA | 5 | 0.79 | 2.4 | 19 | 100 | 20 |
| | Graphene | PI | 16 | 0.28 | 0.8 | 21 | 937.5 | 21 |
| | Graphene @ $Fe_3O_4$ | PEI | 10 | 0.4 | 2.5 | 18.2 | 182 | 22 |
| | Graphene | PU | 10 | 0.03 | 20 | 19.9 | 332 | 23 |
| | Graphene aerogel film | / | Bulk | 0.41 | 0.12 | 65 | 13211 | 24 |
| | Porous graphene film | / | Bulk | 0.06 | 0.3 | 25.2 | 14000 | 25 |
| | Graphene aerogel | PDMS | 3.07 | 1.0 | 2 | 54.26 | 271.3 | 26 |
| | Graphene aerogel | EPOXY | 0.33 | ~1.6 | 4 | 35 | 54.7 | 27 |
| | Graphene | PDMS | 0.8 | 0.06 | 1 | 20 | 3333 | 28 |
| | Graphene | Carbon texture | 42 | 0.07 | 1 | 15 | 2140 | 29 |
| | Graphene | PEDOT : PSS | 17.85 | 0.076 | 1.5 | 91.9 | 8040 | 30 |
| | Graphene | Melamine | Bulk | 0.019 | 12 | 27.3 | 119 | 31 |
| | Graphene | PU | 1 | 0.092 | 2.5 | 23 | 101 | 32 |
| | **LPGF** | **/** | **Bulk** | **0.142** | **0.1** | **37.43** | **26302** | |
| | **LPGF** | **/** | **Bulk** | **0.075** | **0.2** | **43.82** | **29178** | **This** |
| | **CPGF** | **/** | **Bulk** | **0.076** | **0.2** | **28.89** | **19007** | **work** |
| | **PPGF** | **/** | **Bulk** | **0.078** | **0.2** | **22.00** | **14103** | |

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