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4 **Ultralight and Highly Elastic Graphene/Lignin-Derived Carbon Nanocomposite**  
5 **Aerogels with Ultrahigh Electromagnetic Interference Shielding Performance**  
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35 **Keywords:** Lightweight, porous architectures, graphene, EMI shielding, high  
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5 **Abstract:** Ultralight and highly elastic reduced graphene oxide (RGO)/lignin-derived  
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7 carbon (LDC) composite aerogels with aligned micron-sized pores and cell walls are  
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9 prepared using a facile freeze-drying method. The presence of a small fraction of  
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11 LDC in the cell walls enhances the interfacial polarization effect while almost  
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13 maintaining the amount of charge carriers and conductivity of the cell walls, greatly  
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15 boosting wave absorption capability of the cell walls. RGO/LDC aerogels also show a  
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17 greater number of large cell walls with better integrity than RGO aerogels, further  
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19 improving the multiple reflection ability of the aligned cell walls. Synergistic effects  
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21 of the multi-phase cell walls and the preferred microstructures of the RGO/LDC  
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23 aerogels lead to their high electromagnetic interference (EMI) shielding effectiveness  
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25 of 21.3 to 49.2 dB at the ultralow density of 2.0 to 8.0 mg/cm<sup>3</sup>. This corresponds to  
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27 surface specific SE (SE divided by density and thickness) up to 53250 dB·cm<sup>2</sup>/g,  
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29 which is higher than reported values for other carbon- and metal-based shields.  
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31 Furthermore, the critical roles that microstructures play in determining EMI shielding  
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33 performance are directly revealed through comparing shielding performance in  
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35 directions parallel and normal to cell walls, as well as in an in-situ compression  
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37 process.  
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## Introduction

Lightweight and compressible carbon-based porous architectures, which exhibit microcellular structures built with carbon nanomaterials, are currently attracting more and more attention as high-performance structural and functional materials.<sup>1-10</sup> These three-dimensional (3D) macroscopic structures are promising for many applications such as mechanical cushioning,<sup>10</sup> energy absorption,<sup>9</sup> and sensing.<sup>8,11</sup> EMI shielding is also recently emerging as an important application for such 3D porous architectures.<sup>12-16</sup> Different from solid films whose EMI shielding performance is mainly dependent on bulk material properties, the shielding effectiveness (SE) of 3D porous architectures are influenced by both the properties of their intrinsic constituents and microstructures.<sup>14, 17-19</sup> The micron-sized pores in the porous architectures not only lead to weight reduction of the shields, but also embark multiple reflection effect<sup>16, 20-22</sup>, resulting in extended path lengths of the incident waves in the porous architectures and hence increased absorption of electromagnetic waves by the constituents.

Since conventional metal-based shields typically suffer from high density and poor corrosion resistance, carbon nanomaterials such as carbon nanotubes (CNTs) and graphene have been intensively exploited for applications that require light-weight EMI shielding materials.<sup>16, 23-31</sup> In particular, graphene has a unique two-dimensional (2D)  $sp^2$  network structure, exceptionally high carrier mobility, low density, extremely large specific surface area, superb mechanical strength and outstanding anti-corrosion property.<sup>15,28-30,,32</sup> It is, therefore, considered as an ideal building block for

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3 constructing lightweight, robust and high-performance EMI shielding porous  
4 architectures, which are important for many application occasions such as aircraft,  
5 spacecraft, and portable electronics.<sup>15,16,18,33</sup> Specific SE (SSE), which is defined as  
6 the EMI SE divided by density of the shielding material, can be used to compare EMI  
7 shielding performance of materials with different densities.<sup>13, 14, 34</sup> Compared with the  
8 SSE of 10 dB·cm<sup>3</sup>/g for copper-based shields at 3.1 mm thickness,<sup>35</sup> SSE values of  
9 around 64 and 40 dB·cm<sup>3</sup>/g have been achieved for graphene embedded polystyrene<sup>17</sup>  
10 and polyetherimide<sup>18</sup> porous nanocomposites at 2.3-2.5 mm thickness, respectively.  
11 Graphene foams prepared by hydrazine foaming also showed higher SSE of 420  
12 dB·cm<sup>3</sup>/g and SE of 25.2 dB at thickness of 0.3 mm.<sup>33</sup> The good mechanical strength,  
13 high EMI SE and SSE of these graphene foams and polymer/graphene porous  
14 architectures can be attributed to the synergistic effects of their micron-sized pores  
15 and graphene constituents.

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EMI shielding performance of a material mainly depends upon its reflection, absorption, and multiple reflection capability, which are associated with mobile charge carriers, electric dipoles, and large interfaces/surfaces in the shielding architectures, respectively.<sup>32, 36-38</sup> Total SE (SE<sub>T</sub>) is the sum of shielding by reflection (SE<sub>R</sub>) and absorption (SE<sub>A</sub>), while multiple reflections can further enhance the absorption component owing to the extended path lengths of the waves in the shielding material. Generally, graphene-based porous macrostructures are constructed via either dispersing graphene layers into polymer matrices or directly assembling graphene-based foams. In the case of the former, interfaces are introduced between

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3 the conductive graphene and insulating polymer matrices, and hence the interaction  
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5 between electromagnetic fields and interfacial dipoles can cause a significant  
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7 interfacial polarization loss, enhancing the  $SE_A$ .<sup>21, 32, 36, 38, 39</sup> However, the difficulty in  
8  
9 achieving nanoscale dispersion of graphene layers in polymers and relatively high  
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11 fractions of insulating polymers could result in a significant reduction of charge  
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13 carriers and poor conductivity of the porous nanocomposites, which are detrimental to  
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15  $SE_A$  and  $SE_R$ , respectively.<sup>13, 14, 17, 18, 20, 32</sup> In the case of graphene-based foams, the  
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17 presence of abundant charge carriers and excellent conductivity benefits the electric  
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19 loss<sup>37, 38</sup> to the electromagnetic waves, improving the EMI shielding performance.  
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21 However, it is desired to further improve the shielding performance of these foams by  
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23 both enhancing the penetration loss of incident waves in the cell walls and extending  
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25 path lengths of the incident waves in the foams via simultaneously manipulating the  
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27 phase structure of the cell walls and microstructures of the foams. For example,  
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29 CNT/ multilayered graphene hybrid foams fabricated by chemical vapor deposition  
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31 (CVD) method,<sup>15</sup> graphene embedded in the carbon-based foams prepared by phase  
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33 separation and graphitization,<sup>25</sup> multiwall carbon nanotube (MWCNT)/graphene  
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35 foams obtained by solvothermal method<sup>40</sup> were designed to improve penetration loss  
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37 ability of the cell walls. These composite or hybrid foams showed enhanced EMI  
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39 shielding performance or microwave absorption ability, such as ultrahigh SSE values  
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41 up to around  $10000 \text{ dB}\cdot\text{cm}^3/\text{g}$ . The pore structures of these foams were, however, not  
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43 tailored to further enhance their EMI shielding performance via boosting the multiple  
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45 reflection effect. Since the constituents and phase structure of the cell walls, the  
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3 morphology of the cell walls, and pore structure of the foams are all vitally important  
4 factors for enhancing EMI shielding performance, a new strategy needs to be  
5 designed to simultaneously manipulate these factors to realize mechanically robust  
6 graphene-based porous architectures that are efficient in multiple reflections<sup>39-44</sup>, and  
7 exhibit significant polarization loss while retaining abundant charge carriers and high  
8 conductivity.  
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11 In this work, to address the above issue, we designed and fabricated a novel 3D  
12 unidirectional porous architecture with cell walls composed of reduced graphene  
13 oxide (RGO) layers and lignin-derived carbon (LDC). Lignin, a type of natural  
14 macromolecules obtained as a byproduct in paper manufacturing industry,<sup>45</sup> has been  
15 used to construct various types of LDC-based porous architectures.<sup>47,48</sup> In our design,  
16 the presence of LDC in the RGO-based cell walls results in the formation of interfaces  
17 between the RGO layers and LCD and thus improves the interfacial polarization  
18 effect of the nanocomposites,<sup>32, 38</sup> while abundant charge carriers and high electrical  
19 conductivity of the graphene layers can be well retained with a low content of LDC;  
20 the LCD phase also provides additional intrinsic charge carriers. Furthermore, with  
21 lignin as “glue” between GO layers, extremely high and controlled porosity, and well  
22 aligned micron-sized pores can be created using a facile ice-templating method,<sup>7, 49-51</sup>  
23 resulting in thin yet tight unidirectional RGO/LDC cell walls after the carbonization,  
24 and hence leading to improved multiple reflection capability. Owing to these unique  
25 multi-phase and microstructural characteristics, the RGO/LDC foams can reach an  
26 EMI SE of 21.3 to 49.2 dB at a thickness of 2.0 mm and ultralow density of 2.0 to 8.0  
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3 mg/cm<sup>3</sup>, corresponding to the extremely high SSE of 10650 dB·cm<sup>3</sup>/g and surface  
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6 SSE (SSE divided by the thickness) of 53250 dB·cm<sup>2</sup>/g, which are higher than those  
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8 reported for other carbon- and even metal-based shields. In addition, the incorporation  
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10 of LDC and the honeycomb-like microstructure lead to significantly enhanced  
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12 mechanical strength and relatively high elasticity of the RGO/LDC aerogels. EMI  
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14 shielding performance of the aligned porous architectures is also measured in an  
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16 in-situ compression process, and the variation of the EMI shielding behavior with  
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18 compression demonstrates, directly, the critical influences of the microstructures on  
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21 the EMI shielding performance.  
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## 28 **Experimental Section**

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32 ***Fabrication of graphene based aligned porous architectures:*** Through a modified  
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34 Hummer's method, GO dispersed in water suspension was prepared with controlled  
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36 concentration.<sup>54</sup> The alkali lignin (USA, TCI product number: L0082, soft lignin)  
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38 water suspension with the same concentration as the GO suspension was adjusted and  
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40 mixed with various ratios by the magnetic stirring for 3 h. By freezing the mixed  
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42 aqueous suspensions in a mold with Teflon jacket and stainless steel bottom using  
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44 liquid nitrogen, the ice-crystal nuclei formed rapidly at the bottom of the mixed  
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46 suspensions, and the large temperature gradient could result in unidirectional growth  
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48 of the ice crystals towards the top of the mold. Simultaneously, the dispersed  
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50 GO/lignin in the suspension were excluded to stay between the ice crystals to form the  
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3 GO/lignin composite cell walls. Subsequently, through freeze-drying in a  
4 freeze-drying vessel ( $-80\text{ }^{\circ}\text{C}$  and  $10\text{ Pa}$ ) for 24 h to sublime the ice, porous  
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6 GO/lignin foams with aligned GO/lignin composite cell walls were formed. Finally,  
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8 the foams were heated at a rate of  $5\text{ }^{\circ}\text{C}/\text{min}$  in a tube furnace and carbonized at the  
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10 temperature of  $900\text{ }^{\circ}\text{C}$  for 2 h under argon atmosphere to obtain the aligned porous  
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12 RGO/LDC aerogels. Density of the GO/lignin foams and relevant RGO/LDC aerogels  
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14 could be controlled by adjusting the water fraction of the mixed aqueous suspension.  
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16 Lower water fraction could result in higher densities of the GO/lignin foams and  
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18 RGO/LDC aerogels. The content of the RGO/LDC in the aerogels could also be  
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20 controlled by tuning the ratio of the lignin to GO in the aqueous solution. For example,  
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22 by mixing  $7.5\text{ mg/ml}$  RGO and  $7.5\text{ mg/ml}$  lignin suspensions at equal amount and  
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24 treating the mixture following the procedure described above, the GO/lignin foams  
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26 with  $50\text{ wt}\%$  lignin and density of around  $12\text{ mg}/\text{cm}^3$  were prepared, and the  
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28 corresponding RGO/LDC composite aerogels were obtained by further carbonization.  
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30 Also, various shapes or sizes of the aerogels were obtained by selecting various  
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32 molds. After the same freeze-drying process and carbonization treatment of the GO or  
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34 lignin suspension, RGO or LDC aerogels were obtained as well.  
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46 **Characterization:** Microstructure of the porous architectures was investigated by  
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48 scanning electron microscopy (SEM, JSM-7600F). The resistance ( $R$ ) of the sample  
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50 was measured by four-probe method with a Keithley 4200-SCS Semiconductor  
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52 Characterization System (Keithley, Cleveland, Ohio, USA) at room temperature. The  
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54 electrical conductivity ( $\sigma$ ) was obtained by the equation  $\sigma = 1 / (R \cdot A)$ , where  $A$  and  $l$   
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3 are the effective area and length of the measuring electrode, respectively. The  
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6 compression behavior of the porous sample was evaluated using a dynamic  
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8 mechanical analyzer (DMA, TA Q800), and the loading applied was cyclic in DMA  
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10 strain rate mode. The dimensions of the tested samples were  $1 \times 1 \times 1 \text{ cm}^3$ , and at  
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12 least five specimens for each type of aerogels were tested. The carbon-based aerogels  
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14 were compressed in the transverse direction, i.e., the direction normal to the aligned  
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16 cell walls, and longitudinal direction, i.e., the direction parallel to the orientation  
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18 direction of the cell walls, respectively, and thus transverse and longitudinal  
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20 mechanical stress-strain curves were obtained, respectively. EMI SE characterizations  
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22 were carried out on the samples with size of  $22.86 \text{ mm} \times 10.16 \text{ mm}$  (length  $\times$  width)  
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24 in the frequency range of 8.2–12.4 GHz (X-band), by a waveguide method using a  
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26 vector network analyzer (Agilent E8363B PNA-L), and more than five specimens  
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28 were tested for each type of foams. The *S*-parameters of each sample were recorded  
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30 and applied to calculate the EMI SE. It is worth noting that the sample thickness could  
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32 be adjusted but it could not be larger than 9.46 mm because the waveguide chamber's  
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34 dimensions were  $22.86 \text{ mm}$  (length)  $\times$   $10.16 \text{ mm}$  (width)  $\times$   $9.46 \text{ mm}$  (thickness). The  
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36 electric field direction was in the width direction and the propagation direction of  
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38 tested wave was in the thickness direction of the waveguide chamber. In the case of  
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40 longitudinal EMI SE measurement, EMI SE values were measured when the incident  
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42 wave propagated parallel to the cell walls' direction (*Z* direction shown in Figure 1a).  
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In the case of transverse EMI SE measurement, the propagation direction of incident

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3 wave was normal to the cell walls' direction (normal to Z direction), and the electric  
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5 direction was parallel to the cell walls' direction (Z direction).  
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## 10 **Results and Discussion**

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12 To prepare the RGO/LDC aerogels, GO with average lateral size of 10  $\mu\text{m}$  was  
13 synthesized and uniformly dispersed in water (Figure S1a), followed by mixing with a  
14 lignin suspension (**Figure 1a-i**). Zeta potentials of the GO and mixed suspension with  
15 GO/lignin mass ratio of 1:1 are lower than -30 mV, showing moderate stability of the  
16 suspensions and indicating their feasibility for freeze-drying process (Figure S1b). In  
17 the freezing process, the steep temperature gradient results in the rapid formation of  
18 ice-crystal nuclei at the bottom of the mixed suspensions and unidirectional growth of  
19 ice crystals towards top, and the dispersed GO sheets and lignin molecules are  
20 excluded to form cell walls between ice crystals (Figure 1a-ii). After the freeze-drying  
21 process, the ice crystals are sublimated and thus the GO/lignin foams with aligned  
22 micron-sized pores and cell walls are obtained (Figure 1a-iii, Figure 1b-e). Herein the  
23 parallel and perpendicular directions to the growth direction of ice crystals in the  
24 suspension are defined as the longitudinal (Z direction) and transverse directions (X  
25 or Y direction), respectively, and hence the resultant porous architectures have  
26 aligned cell walls in longitudinal direction. In a subsequent carbonization treatment  
27 (Figure 1a-iv), majority of oxygen-containing groups in GO is removed and the lignin  
28 is carbonized (Figure S2, Figure S3, Table S1), resulting in the formation of  
29 RGO/LDC aligned porous aerogels (Figure 1f-i). Compared with GO/lignin  
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3 nanocomposites with smooth cell walls, RGO/LDC aerogels have wrinkled cell walls  
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5 (Figure 1e, i). In addition to tuning macroscopic shape and size (Figure 1b, f),  
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7 porosity and density of the foams can be controlled easily by adjusting water fraction  
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9 in the suspension before freezing. The outstanding mechanical property of  
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11 interconnected cell walls and the adjustable high porosity lead to the production of  
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13 stable, large-dimension, free-standing RGO/LDC aerogels with ultralow density down  
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15 to 2.5 mg/cm<sup>3</sup> (Figure 1f-i, Figure S4).  
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21 Synergistic actions of the graphene layers and LDC lead to the improvements in  
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23 macroscopic performance and microscale structures. Owing to the vast weight loss of  
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25 the lignin in the carbonization process (Figure S5a), the LDC aerogels have severe  
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27 volume contractions (**Figure 2a**, Figure S5b). However, outstanding mechanical  
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29 modulus of the graphene layers can result in enough strength of cell walls to sustain  
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31 the RGO/LDC or RGO aerogels, and provide dimensional stability. Nonetheless, after  
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33 carbonization, pure LDC aerogels show much higher density, resulted from large  
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35 volume shrinkage. GO/lignin nanocomposites, on the other hand, produce RGO/LDC  
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37 aerogels with relatively lower densities (Figure 2b). The lower conductivity and C/O  
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39 ratio of the carbon, compared with those of the RGO, also result in slightly lower  
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41 conductivity for the RGO/LDC aerogels made from GO/lignin composites with higher  
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43 lignin contents (Figure 2b,c, Table S1). After the same carbonization treatment of GO,  
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45 lignin and GO/lignin foams with the similar densities (~ 12 mg/cm<sup>3</sup>) (Figure S6),  
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47 RGO, LDC and RGO/LDC aerogels, with evident aligned cell walls, are obtained,  
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49 respectively (Figure 2d-f, Figure S7). Owing to the molecular nature of lignin, it gives  
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3 stronger interactions between the constituents than GO, leading to thicker cell walls  
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5 and better integrity for the lignin foams, while thinner and holey cell walls are  
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7 observed for the GO foams (Figure S6a-b). In GO/lignin foams, the composite of the  
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9 lignin and GO leads to relatively thin cell walls, while the integrity of the cell walls is  
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11 maintained simultaneously (Figure S6c). Therefore, RGO/LDC aerogels own more  
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13 intact cell walls with better integrity than RGO aerogels (Figures S7a, c, d, e), and  
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15 thinner cell walls (tens of nanometers) than LDC aerogels (around hundreds of  
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17 nanometers) (Figure S7b). If the lignin content is too high, the RGO/LDC aerogels  
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19 will shrink significantly, and hence have thicker cell walls and smaller spacing  
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21 between the cell walls than those of neat RGO aerogels. Nevertheless, abundant  
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23 composite cell walls with good integrity can be obtained by adjusting the initial lignin  
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25 content, which would result in large effective cell-wall surface area for multiple  
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27 reflection (Figure 2f, Figure S7c, e), and hence potentially improve the multiple  
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29 reflection capability of the RGO/LDC aerogels.  
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38 Microstructures of the foams also play critical roles in determining their  
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40 compressive modulus and elastic performance. For all the foams studied in this work,  
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42 longitudinal modulus obtained by compressing the sample in the longitudinal  
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44 direction is much higher than the transverse one, attributed to more sustained cell  
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46 walls in the longitudinal direction (Figure 2g, Figure S8). However, RGO/LDC  
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48 aerogels show complete recovery and excellent reversibility after the application of  
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50 various compressive strains even up to 70 % in the transverse direction (Figure 2g),  
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52 while they cannot recover fully under the compressive strain of 50 % in the  
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3 longitudinal direction (Figure S8). Even after 300 compression cycles in the  
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5 transverse direction, compressive stress of the RGO/LDC aerogels at a high strain of  
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7 50 % is only decreased by less than 10 %, which displays their high elasticity and  
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9 good cycling stability (Figure 2h,i).<sup>2</sup> Similar compressive behavior is observed for  
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11 RGO and LDC aerogels; however, the mechanical strength and modulus of  
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13 RGO/LDC aerogels are improved over their RGO counterparts due to the presence of  
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15 a small amount of LDC in RGO aerogels (Figure S9). The LDC aerogels have higher  
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17 compressive modulus because of their significantly higher density. However,  
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19 compared with RGO and RGO/LDC aerogels, LDC aerogels display higher stress  
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21 reduction ratio under the cyclic compressive curve probably because LDC-based cell  
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23 walls with lower modulus have poorer elastic performance<sup>2</sup> (Figure 2i). In short, the  
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25 RGO/LDC aerogels exhibit considerable mechanical strength and good elasticity due  
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27 to their microstructural character, which is of vital importance for achieving robust  
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29 EMI shielding materials for practical applications.  
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38 EMI SE is measured first when incident wave propagation is parallel to the  
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40 transverse direction of the aligned porous aerogels. SE is almost independent of the  
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42 frequency, implying the uniform microstructure and conductivity of the porous  
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44 architectures (**Figure 3a**).<sup>52</sup> Initially, EMI SE of the RGO/LDC aerogels increases  
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46 with increasing LDC content, whereas after reaching a maximum it starts to decrease  
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48 at higher LDC contents. LDC and RGO aerogels show SE of 6.1 dB and 22.3 dB,  
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50 respectively, at the thickness of 2 mm. RGO/LDC aerogels made from the GO/lignin  
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52 foams with small fraction of lignin ranging from 9.1 wt% to 25 wt%, on the other  
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3 hand, all show higher EMI SE (30.9 to 26.9 dB) than both LDC and RGO aerogels at  
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5 the same thickness. Although slight decrease in  $SE_R$  of RGO/LDC aerogels is  
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7 observed with increased LDC content, which is because of decreased conductivity,  
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9 the  $SE_A$  show more notable increase and hence the EMI SE increases (Figure 3b). The  
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11 RGO/LDC aerogels made from GO/lignin foams with 9.1 wt% to 25 wt% lignin  
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13 exhibit  $SE_A$  ranging from 26.4 dB to 22.2 dB. By contrast, the RGO foams show  $SE_A$   
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15 of only 17.7 dB. Higher lignin content, e.g., 50.0 wt%, in GO/lignin composites may  
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17 be more detrimental to conductivity and also reduce charge carriers in the  
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19 corresponding RGO/LDC aerogels significantly, resulting in a decrease in total EMI  
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21 SE (14.3 dB).  
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28 The data presented above indicate that the introduction of LDC into the cell  
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30 walls of the RGO-based aerogels has played critical roles in improving the EMI  
31  
32 shielding performance of the aerogels. Firstly, the addition of a small fraction of LDC  
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34 to RGO/LDC aerogels does not noticeably reduce the amount of charge carriers or  
35  
36 deteriorate bulk conductivity. Secondly, the LDC can introduce substantial interfacial  
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38 area between the carbon and graphene layers in the cell walls. According to  
39  
40 Maxwell-Wagner-Sillars polarization principle,<sup>32</sup> the conductivity mismatch between  
41  
42 the LDC and RGO in the composite cell walls can result in polarization and charge  
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44 accumulation at their interfaces in the electromagnetic field, which can further interact  
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46 with the incident electromagnetic waves. Therefore, high electric loss of the  
47  
48 composite cell walls to the incident electromagnetic waves derived from the  
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50 maintained conductivity and charge-carrier amount, and the effective interfacial  
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3 polarization<sup>22, 23</sup> resulted from the interfaces between LDC and RGO can both  
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5 improve intrinsic absorption ability of the RGO/LDC composite cell walls. Moreover,  
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7 the presence of LDC also leads to larger effective cell-wall surface area for reflection,  
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9 causing enhanced multi-reflection of the incident waves. Thus, even with a small  
10  
11 fraction of LDC, the coexistence of these characteristics can lead to significantly  
12  
13 higher  $SE_A$  and  $SE_T$  of the RGO/LDC composite aerogels than those of RGO. For  
14  
15 example, EMI SE values of neat RGO aerogels are only 22.3 and 14.2 dB at the  
16  
17 densities of 4.5 and 3.0 mg/cm<sup>3</sup>, respectively, while the RGO/LDC aerogel with a  
18  
19 small fraction of LDC, which was made from GO/lignin with 25 wt% lignin, exhibits  
20  
21 EMI SE of 30.0 and 21.3 dB at the densities of 4.5 and 2.0 mg/cm<sup>3</sup>, respectively  
22  
23 (Figure 3c); the thickness is 2 mm for both types of aerogels.

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25 To further verify contribution of the LDC to the EMI shielding performance,  
26  
27 theoretical EMI SE values ( $M-SE_T$ ,  $M-SE_R$ ,  $M-SE_A$ ) calculated based on the  
28  
29 conductivity of a homogeneous shield (the calculation method is shown in Supporting  
30  
31 Information) are compared with the measured SE values ( $SE_T$ ,  $SE_R$ ,  $SE_A$ ) in Figure 3b.  
32  
33 Without LDC, the calculated  $M-SE_T$  is higher than the experimentally measured  $SE_T$   
34  
35 of the RGO aerogel, which may be attributed to the detrimental effect of the very high  
36  
37 porosity (Table S1) on the shielding performance. By contrast, in the case of  
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39 RGO/LDC composite aerogels with optimized cell walls, the experimentally  
40  
41 measured  $SE_A$  values are much higher than the corresponding  $M-SE_A$  values because  
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43 the latter are calculated without considering the multi-phase structure of the  
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45 RGO/LDC cell walls and their large effective surface area for multiple reflection.  
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3 Since the differences between  $M-SE_R$  and  $SE_R$  of these composite aerogels are very  
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5 small at similar conductivities, the experimentally measured  $SE_T$  values are also much  
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7 higher than the corresponding  $M-SE_T$  values.  
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10 In addition to the LCD content, the density and thickness of the RGO/LDC  
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12 composite aerogels can also be controlled easily to adjust their EMI SE values. Since  
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14 higher density or larger thickness of the composite aerogels can lead to more charge  
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16 carriers and interfacial dipoles interacting with the incident electromagnetic waves,  
17  
18 EMI SE of the aerogels typically increases with the density and thickness. For  
19  
20 example, EMI SE of this composite aerogel made from GO/lignin with 25 wt% lignin  
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22 can reach as high as 49.2 dB at a density of  $8.0 \text{ mg/cm}^3$ . The ultralight RGO/LDC  
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24 aerogel with density  $2.5 \text{ mg/cm}^3$  also shows an EMI SE as high as around 80 dB at the  
25  
26 thickness of 9 mm (Figure 3d). It is also worth noting that at the thickness of only 2  
27  
28 mm and ultralow density of  $2.5 \text{ mg/cm}^3$ , EMI SE of the RGO/LDC aerogel is well  
29  
30 above 20 dB, which is high enough for commercial EMI shielding applications.  
31  
32 Considering the influences of the density and thickness on the EMI shielding  
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34 performance, in order to make a clearer comparison,  $SSE/d$  (SE normalized by  
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36 thickness and density) of typical shielding materials as a function of density are  
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38 presented in Figure 3e, and a comprehensive comparison with more reported data is  
39  
40 given in Table S2. The excellent EMI SE of the graphene-based porous architectures  
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42 reported in this work, which are achieved at an ultralow density and low thickness,  
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44 results in exceptionally high values for SSE and  $SSE/d$  (Table S2). The SSE values of  
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46 the RGO/LDC aerogels can reach as high as  $32000 \text{ dB}\cdot\text{cm}^3/\text{g}$ , which are much higher  
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4 than those of other previously reported shielding materials at the similar thicknesses.  
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6 For example, some reported superb SSE values include  $500 \text{ dB}\cdot\text{cm}^3/\text{g}$  for  
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8 graphene/PDMS composite foams,<sup>16</sup>  $1148 \text{ dB}\cdot\text{cm}^3/\text{g}$  for CNT/WPU foams,<sup>14</sup>  $1100$   
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10  $\text{dB}\cdot\text{cm}^3/\text{g}$  for a CNT sponge,<sup>43</sup>  $3122 \text{ dB}\cdot\text{cm}^3/\text{g}$  for graphene/PEDOT:PSS composite  
11  
12 foams,<sup>53</sup> and  $6600\text{-}11300 \text{ dB}\cdot\text{cm}^3/\text{g}$  for CNT/graphene foams,<sup>15</sup> which are all lower  
13  
14 than the aforementioned SSE values of our RGO/LCD aerogels (Table S2). The  
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16 SSE/*d* values of the RGO/LDC aerogels range from  $30750$  to  $57200 \text{ dB}\cdot\text{cm}^2/\text{g}$ , which  
17  
18 far exceed those of most shielding materials. For example, even satisfying the  
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20 commercial EMI SE level, SSE/*d* of the RGO/LDC aerogels with 2-mm thickness can  
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22 reach as high as  $53250 \text{ dB}\cdot\text{cm}^2/\text{g}$ , which is comparable to recently reported extremely  
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24 high values of  $40000 \text{ dB}\cdot\text{cm}^2/\text{g}$  for the CNT/multilayer graphene foams<sup>15</sup> and  $30830$   
25  
26  $\text{dB}\cdot\text{cm}^2/\text{g}$  for the  $\text{Ti}_3\text{C}_2\text{T}_x$  film<sup>34</sup>, as well as  $30555 \text{ dB}\cdot\text{cm}^2/\text{g}$  for a pure metal (Al foil)<sup>34</sup>.  
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28 Furthermore, the controllability of the density and thickness for these aerogels is also  
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30 an important feature which allows us to easily obtain adjustable and controllable SE  
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32 and SSE. This feature, along with good mechanical performance of these aerogels,  
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34 brings about great potentials for these graphene-based aligned porous aerogels for  
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36 practical applications.  
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45 To thoroughly analyze the roles that micron-sized pores play in the EMI  
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47 shielding performance of the porous architecture, the longitudinal EMI SE ( $L\text{-SE}_T$ ,  
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49  $L\text{-SE}_A$  and  $L\text{-SE}_R$ ), referring to SE when wave propagation is parallel to the  
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51 longitudinal direction, is compared with the transverse SE ( $T\text{-SE}_T$ ,  $T\text{-SE}_A$  and  $T\text{-SE}_R$ ).  
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53 The  $\text{SE}_T$ ,  $\text{SE}_A$ , and  $\text{SE}_R$  of the RGO/LDC aerogels (made from GO/lignin foams with  
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4 25 wt% lignin) at 10 GHz and at the thickness of 6 mm are shown as functions of  
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6 sample density in both directions (Figure 3f). We can observe that  $T-SE_A$  is much  
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8 higher than  $L-SE_A$ , while  $T-SE_R$  and  $L-SE_R$  are similar. Therefore, for aerogels at the  
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10 same thickness and density,  $T-SE_T$  is much higher than  $L-SE_T$ . In the case of the  
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12 aligned porous aerogels, the incident waves passing along the transverse direction can  
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14 interact with significantly more cell walls. As a result, considering the good  
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16 absorption ability of the cell walls,  $T-SE_A$  becomes much larger than  $L-SE_A$ .  $SE_R$ ,  
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18 however, is related to conductivity which is similar in both directions, hence the  
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20 corresponding values are similar. Therefore,  $T-SE_T$  becomes much higher than the  
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22  $L-SE_T$ , thanks in large to  $SE_A$ . For example,  $L-SE_A$  and  $T-SE_A$  can reach 33.5 dB and  
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24 67.2 dB, respectively, which can result in  $L-SE_T$  and  $T-SE_T$  values of 35.8 dB and  
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26 71.0 dB, respectively. Significant difference in the longitudinal and transverse  
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28 absorptions, therefore, well demonstrate the important influence of micron-sized  
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30 pores on the EMI shielding performance.  
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38 To further investigate the influences of the micron-sized pores on the EMI  
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40 shielding performance, the EMI SE is obtained for RGO/LDC aerogels subjected to  
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42 compression in transverse direction. With an increased compressive strain, more voids  
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44 disappear from the aerogels and interconnections and contacts between the cell walls  
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46 are increased (**Figure 4a**), resulting in increased density and electrical conductivity  
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48 for the aligned porous architectures (Figure 4b). Compression-induced increase in the  
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50 conductivity of aerogels leads to an enhanced  $SE_R$ . By contrast, owing to decreased  
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52 cell-wall surfaces that are squeezed together with increased compression strain, the  
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3 compression reduces the pores and in turn the multiple reflections and, as a result,  
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5  $SE_A$  reduces. As absorption dominates total shielding, EMI  $SE_T$  decreases with  
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7 increased compressive strain. In short, compressing aerogels, which changes  
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9 microstructure and in turn the contributions from different EMI shielding mechanisms,  
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11 provides another direct proof on the critical roles that micron-sized pores play in the  
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13 EMI shielding performance. Moreover, EMI SE can still be maintained without  
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15 noticeable deterioration even after 100 deformation cycles up to 50 % compressive  
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17 strain (Figure 4c), demonstrating the durability of our robust RGO/LDC aerogels for  
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19 EMI shielding applications. Based on the results presented above, we propose a  
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21 mechanism to explain the exceptionally high EMI shielding performance of the  
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23 ultralight weight RGO/LDC aerogels (Figure 4d). Owing to the unidirectionally  
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25 aligned cell walls and their good integrity, the incident electromagnetic waves can  
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27 meet and interact effectively with much larger area of cell-wall surfaces in the  
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29 transverse direction, leading to a significantly enhanced multiple reflection ability of  
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31 the aerogels. This, combined with the high absorption ability of the cell walls derived  
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33 from interfacial polarization at RGO-LDC interfaces and abundant charge  
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35 carriers-induced electric loss in the RGO/LDC composite cell walls, gives our  
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37 RGO/LDC aerogels excellent EMI SE at ultralow density and thereby super high SSE  
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39 and  $SSE/d$ .

## 40 41 42 43 44 45 46 47 48 49 50 51 52 53 **Conclusions**

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3 Ultralight, highly elastic, and robust RGO/LDC aerogels, featuring aligned  
4 micron-sized pores and cell walls, are fabricated using a simple freeze-drying method.  
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6 RGO/LDC aerogels show a greater number of large cell walls with good integrity  
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8 than RGO aerogels, and thinner and more cell walls than LDC aerogels. A larger  
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10 amount of tight cell walls results in larger effective cell-wall surface area for  
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12 reflection, improving the multiple reflection ability of the aerogels. The enhanced  
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14 multiple reflection effect, combined with high wave absorption ability derived from  
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16 abundant charge carriers and interfacial polarization dipoles in the cell walls, result in  
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18 exceptionally high EMI shielding performance of these lightweight aerogels. The  
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20 density and size of our RGO/LDC aerogels also show good controllability for  
21  
22 achieving a wide range of EMI SE. EMI SE of the 2 mm thick RGO/LDC composite  
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24 aerogels can reach up to 49.2 and 21.3 dB at ultralow low densities of 8.0 and 2.0  
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26  $\text{mg}/\text{cm}^3$ , respectively. At a density of 2.5  $\text{mg}/\text{cm}^3$ , the RGO/LDC aerogels can also  
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28 show high EMI SE of 80.0 to 23.2 dB by adjusting the thickness of the samples. The  
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30 SSE/*d* value can achieve up to 53250  $\text{dB}\cdot\text{cm}^2/\text{g}$  that is higher than values reported for  
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32 other of carbon- and even metal-based shields. Furthermore, by comparing shielding  
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34 performance of the aerogels in transverse and longitudinal directions, as well as in a  
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36 compression process, it is directly proved that the micron-sized pores play a critical  
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38 role in determining the absorption ability of the RGO/LDC composite cell walls.  
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40 These 3D macrostructures with optimized microstructures in terms of cell walls and  
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42 micron-sized pores, combined with ultralow density, high electrical conductivity,  
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44 considerable mechanical strength, and high elasticity, underscore the great potential of  
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3 these RGO/LDC aerogels as ultralight, robust, and ultrahigh performance EMI  
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5 shielding materials for practical applications.  
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## 10 ASSOCIATED CONTENT

### 11 (S) Supporting Information

12  
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14  
15  
16 Optical images of as-prepared GO, FTIR, Raman, XPS, SEM, TGA and  
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18 mechanical properties of as-prepared aerogels, theoretically calculated EMI  
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20 shielding performance of a homogeneous shield, and the table for EMI shielding  
21  
22 performance of various shielding materials are included in the **Supporting**  
23  
24 **Information**, which is available free of charge on the **ACS Publications website** at  
25  
26 **<http://pubs.acs.org>**.  
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### 44 Conflicts of interest

45  
46 There are no conflicts of interest to declare  
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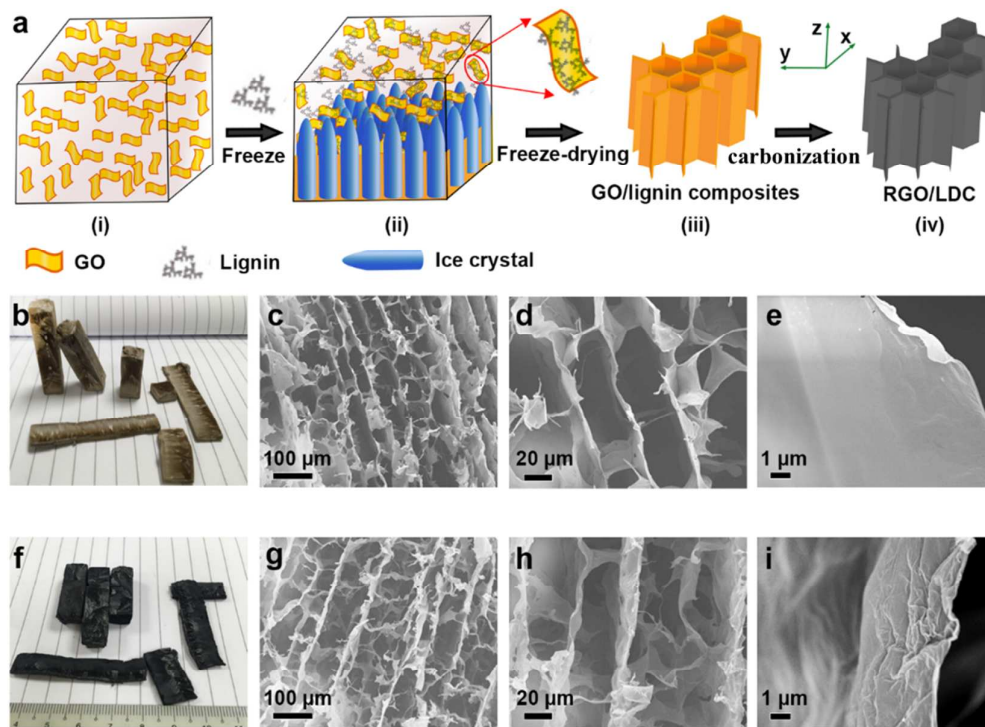
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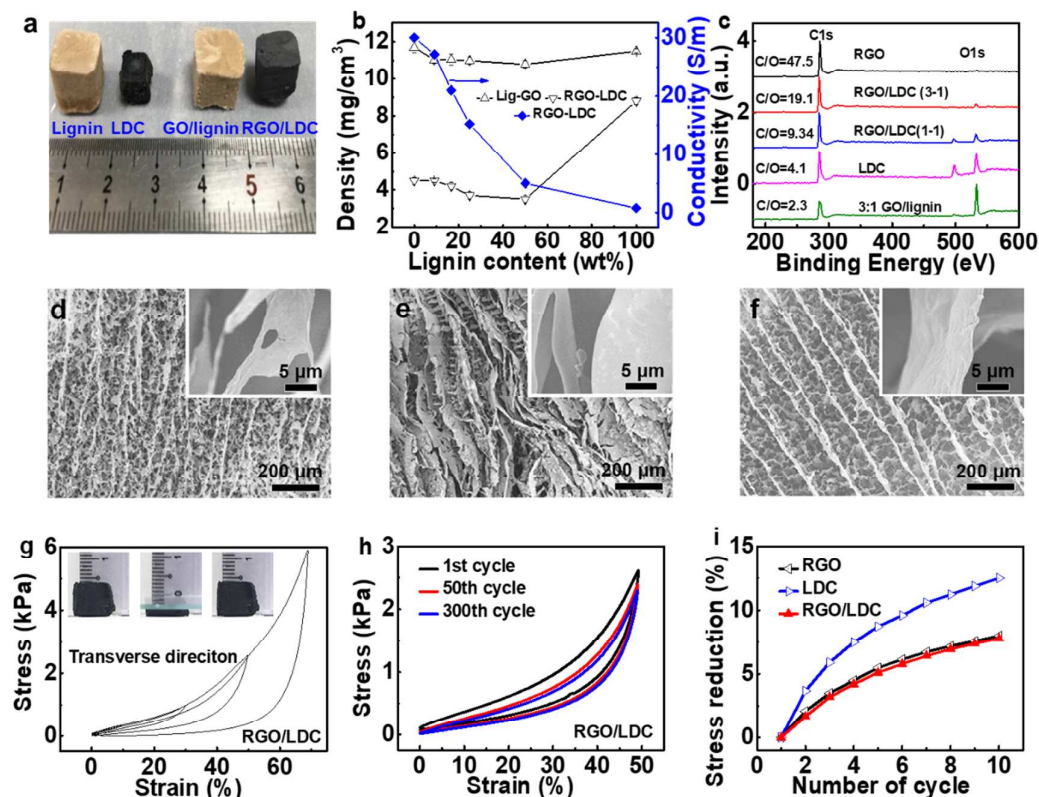
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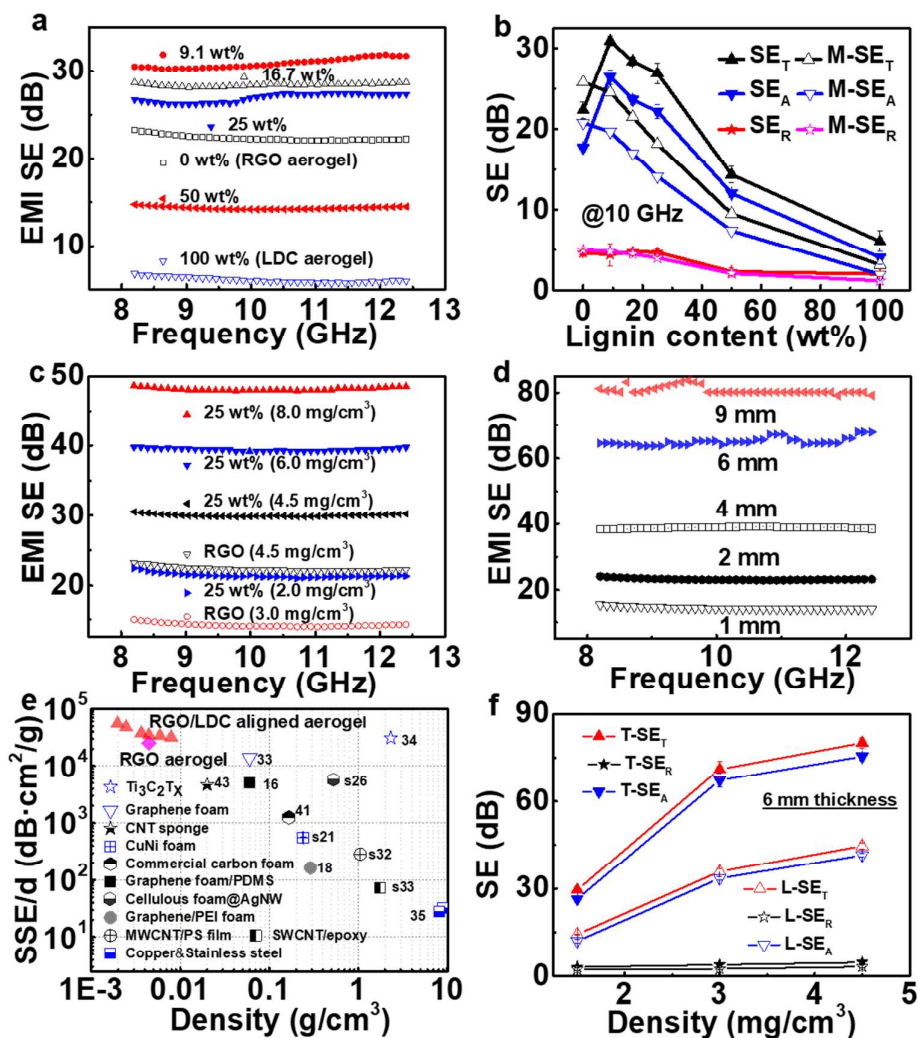
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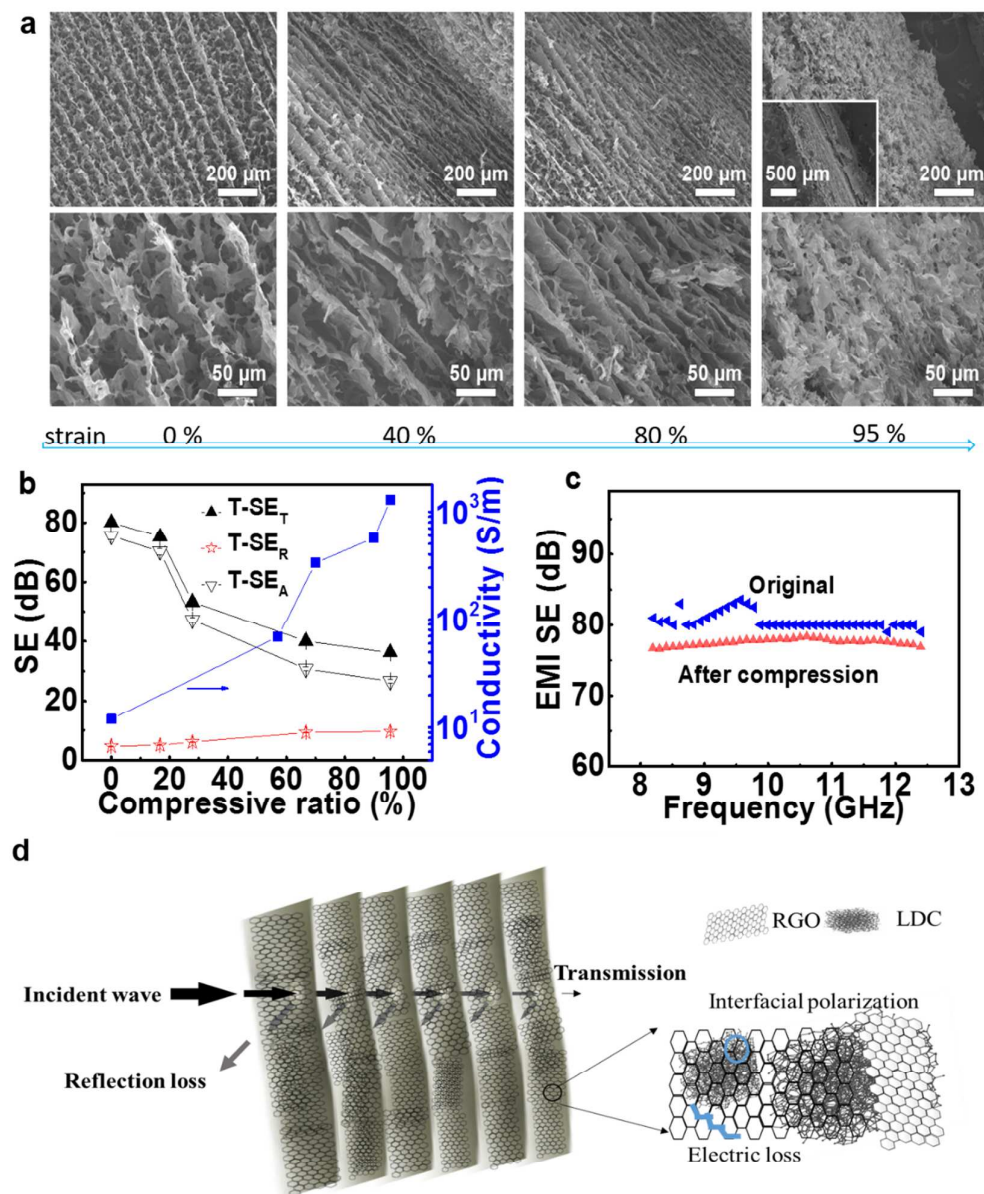
**Figure 1.** (a) Schematics showing the fabrication process of RGO/LDC aerogels: (i) GO aqueous dispersion, (ii) freezing process of the GO/lignin mixed aqueous suspension, (iii) GO/lignin composite foam, (iv) RGO/LDC aerogel (Z is defined as longitudinal direction, while X and Y are defined as transverse directions). Optical images showing various shapes of (b) GO/lignin porous composite foams with 25 wt% lignin ( $\sim 12 \text{ mg/cm}^3$ ) and (f) the corresponding RGO/LDC porous architectures ( $\sim 3.7 \text{ mg/cm}^3$ ) after carbonization; SEM images taken from the transverse direction showing microstructures of (c, d, e) the GO/lignin composite foams and (g, h, i) the corresponding RGO/LDC composite porous architectures.



**Figure 2.** (a) Optical images of the porous architectures before and after carbonization; (b) densities of the GO/lignin foams and the corresponding RGO/LDC aerogels as a function of initial lignin content, as well as the electrical conductivity of the RGO/LDC aerogels; (c) XPS spectra of the GO/lignin foam with 25 wt% lignin and the carbon foams with different contents of LDC (RGO/LDC (3-1) and RGO/LDC (1-1) are made from the GO/lignin foams with 25 and 50 wt% lignin, respectively); SEM images of (d) RGO, (e) LDC and (f) RGO/LDC aerogels, of which the RGO/LDC aerogels are made from the GO/lignin foams with 25 wt% lignin; Mechanical performance of the RGO/LDC aerogels made from GO/lignin foams with 25 wt% lignin: (g) compressive behavior of the composites in transverse direction (the insert displays the compression and recovery processes), (h) transversal stress-strain curves of the architectures subjected to cyclic compression, (i) change of the maximum stress of three kinds of aligned porous aerogels in transverse direction in the first 10 compression cycles with a strain of 50 %.



**Figure 3.** (a) X-band EMI SE of the aligned porous carbon architectures made from GO/lignin foams with different contents of lignin; (b) measured SE ( $SE_T$ ,  $SE_A$  and  $SE_R$ ) and theoretically calculated SE ( $M-SE_T$ ,  $M-SE_A$  and  $M-SE_R$ ) values at 10 GHz for the aligned porous carbon architectures of 2-mm thickness made from GO/lignin foams with different lignin contents; (c) X-band EMI SE of RGO and RGO/LDC composite aerogels of 2-mm thickness; (d) X-band EMI SE of the RGO/LDC aerogels at the density of 2.5 mg/cm<sup>3</sup> and various thickness; (e) SSE/d as a function of density of typical shielding materials (with cited reference); (f) longitudinal and transverse EMI SE at 10 GHz for the RGO/LDC aerogels of 6-mm thickness as a function of density. For (c)-(f), the RGO/LDC aerogels are made from GO/lignin foams with 25 wt% lignin.



**Figure 4.** Microstructure and properties of the RGO/LDC aerogels under various compression ratios along transverse direction: (a) SEM images showing microstructures of the composite aerogels (the compression ratio increases from left to right), (b) EMI SE and electrical conductivity of the aerogels under various compression ratios; (c) EMI SE of the RGO/LDC aerogels before and after compression with 50 % strain for 100 cycles; (d) proposed EMI shielding mechanism for the RGO/LDC aerogels with the incident wave in the transverse direction.

# Ultralight and Highly Elastic Graphene/Lignin-Derived Carbon Nanocomposite Aerogels with Ultrahigh Electromagnetic Interference Shielding Performance

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## Table of Contents / Graphic Abstract

