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Structured Ultra-Flyweight Aerogels by Interfacial Complexation: Self-Assembly Enabling Multiscale Designs

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The rapid co-assembly of graphene oxide (GO) nanosheets and a surfactant at the oil/water (O/W) interface is harnessed to develop a new class of soft materials comprising continuous, multilayer, interpenetrated, and tubular structures. The process uses a microfluidic approach that enables interfacial complexation of two-phase systems, herein, termed as “liquid streaming” (LS). LS is demonstrated as a general method to design multifunctional soft materials of specific hierarchical order and morphology, conveniently controlled by the nature of the oil phase and extrusion’s injection pressure, print-head speed, and nozzle diameter. The as-obtained LS systems can be readily converted into ultra-flyweight aerogels displaying worm-like morphologies with multiscale porosities (micro- and macro-scaled). The presence of reduced GO nanosheets in such large surface area systems renders materials with outstanding mechanical compressibility and tailorable electrical activity. This platform for engineering soft materials and solid constructs opens up new horizons toward advanced functionality and tunability, as demonstrated here for ultralight printed conductive circuits and electromagnetic interference shields.

1. Introduction

Unlocking the full potential of multiphase soft materials can be facilitated by engineering their structure. Given their morphological tunability, emulsions are deemed as a versatile candidate for creating advanced structured multiphase soft materials with a combination of prescribed properties. However, in practice, emulsions are often formed by mixing of immiscible fluids via mechanical agitation or ultrasound techniques, limiting a precise control over morphology and domain size. The morphology and nonuniform nature of the dispersed phase in conventional emulsions prevent their use in applications where a large interfacial area is required, e.g., separation processes. Hence, many efforts have been made to develop hierarchical and structured emulsions; for example, by controlling the thermodynamics of the system or by employing novel processing techniques. For instance, with regard to thermodynamics, computational simulations performed back in 2005 predicted a new class of structured emulsions,[1] known as “bicontinuous interfacially jammed emulsion gels” (bijels), which were experimentally achieved in 2007.[2]

The formation of the bijels relies on the interfacial jamming of surface-active particles during spinodal decomposition of two fluids. Thus, continuous domains of oil adjacent to continuous domains of water coexist in the structure. Due to the large surface area of the interface, which is packed within a small volume,[3] bijels have been proposed as scaffolds for tissue engineering,[4] controlled release systems, and in the design of cross-flow microreactors and separation processors.[5] However, as a direct consequence of processing complexity (i.e., spinodal decomposition), bijels’ fabrication has been limited to a small number of materials and a judicious choice of fluids and particles must be made, which significantly limits their potential use.[5]

Concerning the emulsification process, the advent of microfluidic technology and 3D printing has facilitated accurate control over the emulsification process.[6–10] For instance, in a recent study,[11] hierarchical emulsions (e.g., double and triple emulsions with a tunable core number, size, and composition) were fabricated via a microfluidic 3D droplet-printing-in-droplet technique. Although microfluidic techniques are known to
be effective in forming emulsions,\cite{6–8,12} their structure is still restricted to a matrix-dispersed phase morphology. With an intent to extending the applications of emulsions for novel purposes, such as fabrication of ultralight aerogels with tunable micro/macroscale structures, a more controlled emulsification process is yet to be achieved.

By virtue of the characteristics of ultralight and highly porous aerogels, research interest has sparked application potentials, for example, for acoustic and thermal insulation,\cite{13–15} energy storage,\cite{16} air and water treatment,\cite{17} biomedical scaffolding,\cite{18} and lightweight electronics.\cite{19} Related aerogels can be obtained by supercritical drying of polymer/nanomaterial-incorporated liquids (e.g., suspensions, solutions, or emulsions). Nevertheless, engineering and associated scientific challenges have included design and fabrication of lightweight porous structures of practical dimensions while accurately controlling their porosity, from the nano to the macroscopic levels. That is, before drying, the structure of the precursor liquids must be tailored according to the desired application.

Among different nanomaterials, 2D graphene nanosheets offer a great potential to form novel platforms, provided that they are properly integrated into macroscopic, highly porous complex structures. They have been shown to be successful for application in energy devices, high-performance pressure sensors, adsorbents, and electromagnetic wave absorbing materials, to name a few.\cite{20–25} The facile synthesis of GO and its suspension processability,\cite{26} coupled with morphological tunability, empower the functionality of GO-based aerogels. With the emergence of ultralow density (\(<10\, \text{mg cm}^{-3}\)) GO-based aerogels,\cite{27} the next goal is to fabricate ultra-lightweight aerogels (UFAs) with a density less than 1 mg cm\(^{-3}\), which is even lower than that of air at ambient conditions (1.2 mg cm\(^{-3}\)). UFAs have been achieved from low-concentration GO suspensions.\cite{28,29} However, due to the poor rheological and mechanical integrity, the macroscale design of low-concentration GO-based suspensions, e.g., to fabricate structured ultralight or ultra-weight aerogel, remains an arduous challenge.\cite{30} The incorporation of additives, such as surfactants, binders, and rheology modifiers, can address such challenges. However, these additives dramatically diminish the properties of the final products (conductivity, for example) and increase the density of the resultant aerogels.\cite{31}

To surmount the main challenges in processing and property development, we introduce a facile method to develop a new type of two-phase soft materials with tunable morphology, enabling the design of UFAs with controlled macroscale. This was accomplished by microfluidic extrusion of low-concentration aqueous GO suspensions in different nonpolar phases containing a surfactant. We named this technique as “liquid streaming” (LS) (see Table 1 for nomenclature).

By harnessing ES, not only did we generate uniform water-in-oil continuous emulsions with tunable morphology and domain size but also introduced novel types of two-phase soft materials, namely, multilayer, interpenetrated, tubular double emulsions. Solidified interfacial layers were created thanks to the rapid co-assembly of GO nanosheets and surfactant at the oil/water interface, imparting mechanical rigidity to the “sculpted aqueous phase. Such frozen interface locks in highly nonequilibrium shapes of the aqueous phase in the nonpolar phase. Such a process allows the manipulation of the structure of low-concentration aqueous GO suspensions, with sizes from the micrometer up to the centimeter scales. We demonstrate that the thin interfacial layers of GOs can hold the structure of the aqueous phase during one-step freeze-drying, leading to the formation of a novel class of highly porous and wormlike UFAs (WUFAs). The LS technique allows the fabrication of WUFAs with any desired shape. Moreover, the developed structured GO WUFAs can be thermally or chemically reduced, allowing the realization of applications for advanced electronics. Furthermore, as a proof of concept, the WUFAs are shown for their mechanical properties, which can be tuned by integrating polymers via various approaches (e.g., impregnation), resulting in the creation of soft, rigid, flexible, and compressible aerogels. Indeed, our proposed LS technique offers a programmable, facile, and flexible approach to translate the inherent physical properties of nanomaterials into 3D topologies and geometries, that can find applications in areas such as chemical separation, delivery, biphasic cascading reaction, and advanced electronics.

### Table 1. Abbreviations.

<table>
<thead>
<tr>
<th>System</th>
<th>Abbreviation</th>
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<tr>
<td>Liquid streaming</td>
<td>LS</td>
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<tr>
<td>Water-GO suspension</td>
<td>W-GO</td>
</tr>
<tr>
<td>Oil and water interface</td>
<td>O/W</td>
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<tr>
<td>Oil and (aqueous suspension of graphene oxide) interface</td>
<td>O/W-GO (x)(^{4})</td>
</tr>
<tr>
<td>Ultra-flyweight aerogel</td>
<td>UFA</td>
</tr>
<tr>
<td>Worm-like ultra-flyweight aerogel of GO derived from freeze-drying of the soft materials obtained by liquid streaming</td>
<td>WUFA-GO (x)</td>
</tr>
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</table>

\(^{4}\)x represents the concentration of GO in the aqueous phase.

#### 2. Results and Discussion

##### 2.1. Emulsification and LS

Like graphene, graphene oxide (GO) nanosheets are essentially one-atom thick but can be as wide as tens of micrometers (Figure S1, Supporting Information).\cite{32–34} Recently, it was shown\cite{35} that GO nanosheets in water (W-GO, see Table 1 for abbreviations) instantaneously migrate and assemble at the oil/water (O/W) interface due to their tendency to spread over high-energy interfaces, to minimize the Helmholtz free energy.\cite{32,36} This propensity stems from the dual nature (hydrophobic and hydrophilic) of GO; the hydrophobic nature of GO nanosheets originates from the basal plane, i.e., carbon rings. Meanwhile, GO hydrophilicity is imparted by the functional groups, e.g., hydroxyl, carboxylic, and epoxy, that exit on the surface and edges of the GO.\cite{37,38} While the basal plane of GO is hydrophobic, segregating the GO to the interface replaces the exposure of the basal plane on both sides from water to one where one side is exposed to the hydrophilic oil, a far more favorable interaction.\cite{35} The GO interfacial network structure acts as a
The high elasticity of the O/W interface in the presence of GO nanosheets (Figure S2c, Supporting Information), even at extremely low concentrations (e.g., 0.04 vol%), makes the GO assemblies exceptional candidates for applications where stabilization of the O/W interface is essential. For instance, a recent work showed that interfacial elasticity plays a decisive role in emulsion stabilization.\cite{41} Thus, here, we achieved ultrastable oil-in-water emulsions at extremely low concentrations of the GO nanosheets by low energy (hand-shaking) emulsification (see Figure S2a,d, Supporting Information, corresponding to the digital and optical microscope images, respectively, of a 50:50 oil-in-water emulsion in the presence of 0.3 vol% GO). The fabricated emulsions were stable over the course of months.

Interestingly, following the same low energy emulsification process, upon the incorporation of 1 mg mL$^{-1}$ PSS-[3-(2-aminoethoxy)aminopropyl]heptaisobutyl substituted POSS (POSS-NH$_2$) into the silicone oil (O-POSS), a phase inversion occurred, leading to the formation of water-in-oil emulsions. Figures S2f and S3a (Supporting Information) show the 50:50 oil-in-W-GO emulsions in the presence of POSS. Figure S3b (Supporting Information) compares the interfacial properties of O/W-GO 0.04 vol% with and without POSS. With POSS dissolved in the silicone oil against W-GO 0.04 vol%, the equilibrium interfacial tension (IFT), the free energy penalty of exposing one immiscible liquid to another, was found to be $\approx 6$ mN m$^{-1}$, which is considerably lower than that of the pure silicone oil and W-GO 0.04 vol% ($\approx 35$ mN m$^{-1}$). This confirms that POSS molecules display activity at the O/W interfaces, where they assemble in high number density. Moreover, a solid interfacial skin, wrapping the aqueous phase, is observable during contraction of a pendent droplet of W-GO 0.04 vol% in the O-POSS phase (Figure S3b, Supporting Information). The wrinkles on the droplet's surface upon decreasing the volume conﬁrm the synergistic effect of the nanosheets and POSS at the interface, leading to the formation of a mechanically rigid interfacial skin with high binding energy that can withstand the compressive force. The solid skin can hold the droplets in highly non-equilibrium shapes, even with stable sharp edges (Figures S2e and S3d, Supporting Information), leading to the formation of structured emulsions (i.e., nonspherical dispersed phase).

The interfacial film formation has been previously investigated by various means including grazing incidence X-ray scattering, atomic force microscopy, and X-ray photon correlation spectroscopy.\cite{42-45}

Herein, the interfacial skin formation can be attributed to strong interactions between rigid POSS molecules and GO nanosheets (i.e., hydrogen bonding between the amino groups of POSS and superficial functional groups of GO). Moreover, the existence of POSS changes the charge at the interface from being negative to positive.\cite{39} Thus, interfacial jamming induced by electrostatic interactions between nanomaterials and oppositely charged surfactants, e.g., ammonium-carboxylate ion pairing, can be another reason for the strong film formation of negatively charged GO nanosheets at the POSS incorporated interfaces (i.e., interfacial complexation).\cite{46}

The electrostatic interactions between nanoparticles and surfactants at interfaces have been studied in details in a recent study by Luo et al.\cite{47} What is more, the rigid structure of POSS molecules, cubic inorganic silica-cage core with side chains, significantly contributes to the mechanical strength of the GO/POSS interfacial film. Further discussion on the performance of GO with and without POSS at the O/W interface using different techniques (IFT and interfacial rheology) can be found in the Supporting Information.

The mentioned characteristic of the O-POSS/W-GO interfaces, i.e., rapid interfacial skin formation, prompted us to develop a facile method for devising new types of soft material with controlled morphology. In this method, named liquids streaming (LS), with the aid of a 3D printer, or a simple pump, aqueous suspensions of GO can be jetted into an O-POSS phase, see Videos S1 and S2 (Supporting Information). In other words, the water phase is extruded out of a nozzle, at a controlled flow rate, into the oil phase. The rapid co-assembly of the GO nanosheets and POSS prevents Plateau-Rayleigh instabilities\cite{48} i.e., the break-up of the jetted aqueous phase into drops due to minimization of the surface energy, leading to the formation of aqueous tubules wrapped by the continuous GO/POSS interfacial skin (Figure 1a,b), which are stable over the course of months (Figure 1c). It is worth mentioning that the tubes’ formation and their mechanical integrity stem solely from the rapid GO/POSS interfacial skin formation, rather than the bulk rheology of the suspensions, which is the primary origin of the typical filament formation in direct ink writing/printing of hydrogels.\cite{49,50,51,52} Figure 1d and Video S3 (Supporting Information) clearly show the flowability of the GO suspensions at four different concentrations. Following a recent work by Russell and co-workers\cite{32} and for simplicity, we named these structured liquids as “sculpted emulsions.” We obtained this type of two-phase system even at extremely low concentrations, as low as 0.04 vol% (see Figure 1e and Video S2, Supporting Information). Thus, the co-assembly of GO nanosheets and POSS at the interface of O/W creates a mechanically-rigid, solidified interfacial layer encasing the aqueous liquid (see Video S4, Supporting Information).

The formation of the tubules significantly relies on the pressure of the injection. Figure 1f schematically shows that at low or high enough injection pressures, droplet formation takes place rather than tubule formation (see Videos S5, S6, S7, S8, and S9, showing the injection at 50, 70, 90, 110, and 150 psi, respectively). The transition from a continuous jet to a stream of droplets relies on the viscosity $\mu$, density $\rho$, surface tension $\gamma$, and the jet diameter $d$, which can be estimated by Ohnesorge number $Oh = \mu/\sqrt{\rho \gamma d}$. When $1 < Oh$ or $Oh < 0.1$, instability sets in, and the liquid jet breaks apart into droplets. See Figure S5 (Supporting Information) and the corresponding discussion for further information.

Indeed, the LS technique provides a versatile platform for designing two-phase soft materials with continuous domains. More importantly, the domain size, combination, and macroscale design are highly tunable. For instance, by manipulating the flow rate, needle size, and the printing head’s speed, the tubules’ size can be readily controlled (see, for instance, Figure 1i; Figures S6 and S7, Supporting Information).
Moreover, by virtue of the precise control of this platform, new classes of soft materials can be formed, namely multilayer (Figure 1g) and interpenetrated (Figure 1h) tubules. The latter were fabricated by simultaneous injection of different aqueous suspensions (0.04 and 0.3 vol% GO) through separated nozzles into the O-POSS. A myriad of application prospects emerges given the possibility of loading these GO suspensions with different materials (e.g., magnetic particles,[35] metal–organic frameworks,[36] etc.) and injecting them through different needles simultaneously. They can also expand the range of materials bestowed with multi-functionally, via the LS process. All in all, the proposed customizable LS technique opens new avenues to design novel uniform, multifunctional two-phase soft materials featuring different orders or shapes. We postulate

Figure 1. a) Digital image demonstrating tubule formation upon injection W-GO (0.3 vol%) in silicone O-POSS (1 mg mL⁻¹). Digital images of the two-phase O-POSS/W-GO system (0.3 vol%) b) soon after formation at two magnifications and, c) after two months. d) GO suspension at different concentrations and their liquid-like behavior (flowability). e) O-POSS/W-GO (0.04 vol%) system at two magnifications. f) Schematics demonstrating the co-assembly of GO nanosheets and POSS at the O/W interface and the effect of injection pressure on the morphology and domain size of the system. g) Multilayer emulsion, bottom and top layer: W-GO (0.04 vol%), middle layer: W-GO (0.3 vol%). h) Interpenetrated tubules of W-GO (0.3 vol%) and W-GO (0.04 vol%) in O-POSS. i) Optical microscopy images showing the diameter tunability of the tubules by changing the print head speed rate. Single tubule at different printing speeds was printed (similar to Video S12, Supporting Information, and Figure 4h) for imaging. The scale bars in (i) are 500 μm.
that these novel types of soft materials can greatly expand the application of multiphase systems.

2.2. Aerogel Formation

The emulsions in the previous section were formed by injection of the aqueous phase into a low-viscous silicone oil. In this section, in order to fabricate the aerogels, the silicone oil was replaced with a volatile nonpolar liquid. This decision roots from our observation that the LS technique worked well with different volatile nonpolar phases, including toluene and hexane. Herein, for brevity, we report on the interfacial skin formation results of LS in hexane (Figure S8, Supporting Information), noting that a similar phenomenon was observed in other cases. Figures S8 and S9 (Supporting Information) and the corresponding discussion in Supporting Information present the interfacial characterization of hexane/W-GO with and without POSS. As delineated in the former section, the same procedure was used here for the fabrication of the sculpted emulsions, i.e., injection of the GO suspensions through a needle inside the hexane-POSS phase. Afterward, the system was dried utilizing one-step freeze-drying, noting that prior to such drying, the samples were kept in a freezer overnight.

Figure 2a and Figure S10 (Supporting Information) show the digital images of the resultant structured aerogel. As can be seen, the aerogels feature a unique worm-like structure. The aerogels’ domain size can be tuned by controlling the tubules diameter during the LS process (for instance, compare Figure 2a and Figure S10, Supporting Information). Figure 2b shows the SEM images of the worm-like aerogels. Clearly, a layer of GO encased a highly porous structure, primary porosity (see the arrow in Figure 2b). The porosity of the inner structure of the tubules is inherited from the ice crystal templates in the freezing process and can be controlled by the concentration of the GO in the precursor suspension (see the SEM images in Figure S11, Supporting Information). For instance, a porous structure is observable in the aerogel tubules

![Figure 2](https://www.advancedsciencenews.com/doi/10.1002/smll.202002200)

Figure 2. a) Digital images obtained from different angles of a worm-like ultra-flyweight aerogel (WUFA) of GO after freeze-drying of hexane-POSS/W-GO (0.3 vol%) and its b) SEM images at different magnifications. The yellow arrow is used to show the micro-scale porosity inside the tubules. The specified area (red contour) shows the macroscale voids/pores between the tubules. c) 3 mL W-GO suspension and d) its sculpted emulsion counterpart. e) Confocal images of the sculpted emulsion shown in (d). f) Digital images demonstrating the lightness of a WUFA-GO and that the electrostatic charges on a plastic marker hold the WUFA-GO (density of ~4 mg mL⁻¹).
(Figure 2b), derived from freeze-drying of hexane-POSS/W-GO 0.3 vol%. While the tubules of the aerogel derived from hexane-POSS/W-GO 0.1 vol% are mostly hollow (see Figure S12, Supporting Information), indicating that at low concentrations, the majority of the nanosheets migrate to the O/W interface.

The unique entangled morphology of the tubules (following worm-like contours) creates voids or a secondary macro-scale porosity (see the areas indicated with red lines, Figure 2b), forming an appealing morphology for applications where a large surface area is required, e.g., for gas sorption. The size and volume of the larger pores are dictated by the diameter of the tubules; these pores add more structural flexibility to the solid constructs fabricated by the LS technique.

The secondary pores are occupied by the oil phase in the emulsions. Figure 2c, for instance, shows that for a 3mL GO suspension, the volume increased to more than 5 mL in the case of its sculpted emulsion counterpart (Figure 2d). The green phase in the confocal images of the sculpted emulsions shown in Figure 2e also indicates the inclusion of the secondary pores by the oil phase. This increase in the volume by the secondary porosity significantly reduces the density of the resultant worm-like aerogels. These aerogels are among the lightest reported and is due to the fact that precursor constituents were low-concentration GO suspensions (0.04–0.3 vol%). As shown in Figure 2f, few cotton fibers or a plastic marker can hold the worm-like aerogels by electrostatic charges. The density of the structured aerogels was estimated to be in the range of ≈0.5 to ≈4 mg cm⁻³ (depending on the concentration of GO in the precursor emulsion and the diameter of the tubules), placing our worm-like aerogels in the category of ultra-flyweight aerogels.

Figure S11 (Supporting Information) shows the digital and SEM images of the regular GO aerogels derived from GO suspensions at various loadings of the nanosheets. As the GO concentration decreased from 0.3 to 0.2 vol%, the freeze-dried aerogels were not able to sustain their structure, and an extensive shrinkage and deformation took place (Figure S11, Supporting Information). This can be attributed to the extremely low concentration of the nanosheets in the precursor suspensions, which means that the regular GO aerogels failed to retain the structure during freeze-drying. However, interestingly, no deformation was observed in the WUFAs, even for those obtained at the lowest concentration (Figures S12 and S13, Supporting Information). Moreover, no shrinkage was observed in WUFA-GO (0.1 vol%) (Figure S12, Supporting Information) and the shrinkage was negligible for WUFA-GO (0.04 vol%) (Figure S13, Supporting Information). Hence, our proposed method offers structural tunability for UFA fabrication, and these aerogels feature superior structural stability during freeze-drying, thanks to the strong GO interfacial assembly. In addition, it will be shown that worm-like structure bestows excellent mechanical properties to our WUFAs.

Here, to achieve a much lighter WUFA, we injected a (50:50 (V:V) hexane (pure)-in-(W-GO)) emulsion (the same as Figure S2a, Supporting Information) into the hexane-POSS, instead of injecting GO suspensions. This type of emulsion is inspired by double emulsions. Nonetheless, instead of encapsulating oil-in-water droplets, the oil droplets were trapped by continuous tubules of aqueous W-GO in the hexane-POSS phase (see Figure 3a,b). Thus, these emulsions can be considered as oil-in-water-in-oil double emulsions, named as “tubular double emulsions.” As 50 vol.% of the tubules is filled with a volatile hexane phase, the resultant aerogels are 50% lighter than their counterparts from the sculpted emulsions prepared by pure GO suspensions. Thus, the density reduced to ≈0.25-≈2 mg cm⁻³. This approach adds more tunability to
the microstructural features of the worm-like aerogels, as the porosity can also be tailored by the amount and size of the dispersed hexane phase in the aqueous tubules. Figure 3c–h illustrates the digital and SEM images of the WUFAs derived from the tubular double emulsions. These tubules are flyweight, and they can be actuated by electrostatic fields (see Figure 3g,h and Video S10, Supporting Information). Moreover, these tubules were strong enough to bear the weight of the entire structure (see Figure 3h). Structures with smart, stimuli-responsive (electrostatic, electrical, thermal, and photonic signals) features are essential in the design of advanced electronics.[56] With a recently proposed approach,[56] these tubules can be used as primary units in nonwoven structures, with a great capability for next-generation wearable systems.

So far, exceptional features such as large surface area, tunable mechanical properties (will be shown in Figure 4), good structural stability, and robust interface formation were obtained. Coupling these characteristics with the superior electrical properties of the graphene nanosheets broadens the range of potential applications of WUFAs, e.g., lightweight advanced electronics and electromagnetic interference (EMI) shields. We produced electrically conductive WUFAs via a double thermal/chemical reduction process explained in Supporting Information (see Figure S14, Supporting Information, and Figure 4). The samples were reduced via both thermal and chemical reduction to show the durability of the WUFAs. The collapse of the reduced graphene (rGO) aerogels upon reduction at elevated temperatures has been recently reported.[57] Interestingly, no deformation or shrinkage was observed in the WUFAs after thermal treatment at 1100 °C (see Figure 4a and Figure S14, Supporting Information). This can be considered as a great advantage over direct ink writing of suspensions containing rheological modifiers (e.g., polymer), as they suffer from deformation and/or cracking induced by thermal stresses due to thermal expansion coefficient mismatch.[31]
Figure 4b,d shows a 3-mg reduced worm-like aerogel, before and after holding a 22500 mg weight, demonstrating an excellent mechanical performance, which has rarely been found in other full graphene aerogels (see Figure S15, Supporting Information). Video S11 (Supporting Information) and Figure 4e confirm the compressibility of the reduced WUFA. Based on Figure 4e, the reduced WUFA can recover its initial shape after cyclic compression at deformations ranging from 20% to 80% (Figure S14c, Supporting Information, shows the shape recovery). To the best of our knowledge, this outstanding compressibility has never been reported for pure regular rGO aerogels. In fact, it is well known that rGO aerogels lack any mechanical properties and are fragile as a direct consequence of the weak interfaces formed by nanosheets, even at high concentrations.\(^{[5]}\) This limits practical applications of traditional rGO aerogels. Figure S15 (Supporting Information) confirms that the traditional rGO aerogels, derived from freeze-drying of W-GO 1.0 vol% suspension, do not recover their shape after compression. Zhao et al.\(^{[20]}\) also reported a great compressibility for millimeter-scale graphene aerogel spheres (GSs) with a core–shell structure and a density of 5.0–7.8 mg cm\(^{-3}\) prepared by a coagulation method. The extremely better compressibility of the GSs compared to regular graphene-based aerogels was attributed to the dense and continuous shell structure, preventing serious deformation damages. Hence, it can be postulated that the outstanding compressibility of the reduced WUFA stems from their unique worm-like structure (strong network of nanosheets encasing a highly porous structure). Of note, the mechanical properties of the WUFAs can be readily tuned by the inclusion of various polymers into the aerogels, allowing the fabrication of rigid to flexible structures (see Figures S16 and S17, Supporting Information). More importantly, the weight of the WUFAs decreased (≈40%, see the TGA graph in Figure S14b, Supporting Information) by removing the oxygen-containing functional groups upon reduction, resulting in a further density reduction (≈0.15–1.2 mg cm\(^{-3}\)).

The reduced WUFAs were used to fabricate EMI shielding circuits. Aerogels prepared from the sculpted emulsions of rGO 0.3 vol% showed an appreciable average EMI shielding effectiveness (SE) of ≈ 29 dB over the X-band frequency range at a thickness of 5 mm (Figure 4f), meaning that it can shield 99.8% of the incident wave. This excellent SE was achieved at an extremely low solid content, leading to an extraordinary specific SE (SE/thickness/density) of ≈ 24 000 dB cm\(^{2}\) g\(^{-1}\) (Figure S14e, Supporting Information, compares this value with the literature). As can be seen in Figure 4g, the dominant mechanism of shielding is absorption, i.e., absorbance (\(A\)) > reflectance (\(R\)), in the probed frequency window, making our aerogels a wave absorber, a versatile candidate for medical and military applications.\(^{[9]}\) Indeed, due to the low density of the shields, the EM waves can penetrate the structure. Then, the penetrated waves will be trapped by the primary and secondary pores via wave scattering and multiple reflections at the abundant solid–air interfaces, leading to prolonging the trajectory and, thus, dissipation of the EM waves.\(^{[6]}\)

With regard to EMI shields, recently, it has been shown that the multilayer gradient assembly of conductive rGO nanosheets adds to the total EMI SE and improves the absorption of the waves.\(^{[6]}\) Indeed, the multilayer sculpted emulsions make the fabrication of the gradient aerogels possible (Figure S18, Supporting Information), opening new opportunities in the field of lightweight EMI shields. Moreover, inspired by liquid-in-liquid printing,\(^{[60,63-66]}\) the sculpted tubes can be structured in any desired shape (see, for instance Figure 4h and Videos S12 and S13, Supporting Information), and the resultant WUFA (Figure 4i) can be chemically or thermally reduced (rGO), realizing applications in ultralight conductive circuits (Figure 4k).

3. Conclusions

The development of ultra-flyweight aerogels (UFAs) by facile processing technologies that also lead to controllable macroscale structures is still a major challenge. Likewise, the structural stability of the UFAs is difficult to achieve during fabrication, i.e., preventing shrinkage or deformation. These limitations were overcome in this work by using the surface activity of graphene oxide (GO) nanosheets and 3D assembly of liquid and solid constructs with controlled nano-, micro-, and macroscale designs. We showed that a super elastic interfacial skin of GO is formed when GO aqueous suspensions are exposed to POSS-incorporated nonpolar liquids (e.g., toluene, hexane, and silicone oil). This strong interfacial skin stems from the coexistence of hydrogen bonding and electrostatic interactions between GO and POSS in the opposite phases. We developed a unique class of water-in-oil soft materials (named continuous, multilayer, interpenetrated, and tubular double “sculpted emulsions”) via rapid interfacial co-assembly of GO/POSS combined with a microfluidic approach (named liquid streaming, LS). By using one-step freeze-drying of the mentioned soft materials, worm-like ultra-flyweight aerogels (WUFAs) with stable and tunable morphologies were produced. The proposed LS approach will lead to the design of practical devices that will generate new technological opportunities, e.g., by combining unique morphological flexibility and functional performance. To further the application of these materials, we need an accurate control of surface chemistry and particle size to enable the formulation of LS.

4. Experimental Section

**Synthesis Proceeded:** GO was synthesized via a modified Hummers’ method.\(^{[87]}\) The detailed synthesis procedure and characterization can be found in the Supporting Information.

**Oil Phase:** Silicone oil (1 cSt, Clearco #63148-62-9) and hexane (Sigma-Aldrich, #107-83-5) were used as the oil phase for fabrication of the soft materials.

**Oil-POSS Phase:** PSS-[3-(2-aminoethyl)amino]propyl-heptaisobutyl substituted POSS (POSS-NH\(_2\); POSS-NH\(_2\); Sigma-Aldrich) ligands were dissolved in the oil phase for LS.

**Printing:** A BIOX 3D printer (Cellink, Sweden) equipped with a pneumatic print head was used for LS. The samples were loaded into a 3 mL plastic syringe and extruded through a 32 G steel dispensing needle.

**Emulsification and LS:** Soft materials were fabricated by extrusion of the aqueous phase in the oil phase (liquid streaming (LS) technique) using a 3D printer equipped with a 32 G steel dispensing needle. The domain size/shape of the sculpted emulsions was controlled by various factors including the pressure of the injection, diameter of the nozzle,
Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

graphene oxide, interfacial assembly, liquid streaming, ultra-flyweight aerogels

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Conflict of Interest

The authors declare no conflict of interest.