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## Bioinspired Synthesis of Monolithic and Layered Aerogels

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### Abstract

**Aerogels are the least dense and most porous materials known to man, with potential applications from lightweight super-insulators to smart energy materials. To date their use has been seriously hampered by synthesis methods which are laborious and expensive. Taking inspiration from the life-cycle of the damselfly, we demonstrate a novel ambient pressure drying approach in which, instead of employing low surface tension organic solvents to prevent pore collapse during drying, sodium bicarbonate solution is used to generate pore-supporting carbon dioxide *in-situ*, significantly reducing energy, time and**

**cost in aerogel production. The generic applicability of this readily scalable new approach is demonstrated through the production of granules, monoliths and layered solids with a number of precursor materials.**

Lightweight and porous materials occur in many natural systems and their formation mechanism provides inspiration for the fabrication of man-made structures by energy efficient and ‘green’ synthesis routes. A major feature that distinguishes biomaterials from synthetic materials are mild synthesis conditions, employing ambient temperature and pressure, often in an aqueous environment. Aerogels are the lightest and the most porous materials known to man<sup>[1,2]</sup>, however their production is limited due to materials costs and laborious drying methods. Inspired by the life cycle of damselfly, particularly how their wings are produced rapidly in aqueous environments, we report replacement of surface tension reducing organic solvents in ambient pressure drying (APD) of aerogels by sodium bicarbonate solution, generating pore-supporting carbon dioxide *in-situ*, significantly reducing energy, time and cost in aerogel production. We anticipate that this new approach will prompt research into preparation of other porous materials, with potential for widespread application.

Aerogels are porous materials, with low bulk density and high specific surface area, prepared by using air to replace the liquid component of a wet gel.<sup>[1, 2]</sup> Their insulating properties and robustness against ageing, moisture and perforation make them ideal materials for insulation in buildings,<sup>[3]</sup> oil/gas wells and pipes.<sup>[1]</sup> Moreover, the potential to introduce functionality through compositional changes means that aerogel architectures can be developed beyond passive materials and exploited in many ‘smart’ applications such as CO<sub>2</sub> sorbents,<sup>[4]</sup> catalyst supports,<sup>[1]</sup> platforms for drug delivery,<sup>[5]</sup> perfect black materials for solar harvesting<sup>[6]</sup> etc. However, practical applications are still extremely limited owing to costly and laborious production methods.<sup>[1, 7]</sup>

The most common synthesis approach for aerogels involves extraction of liquid from a gel by critical point drying (CPD) with CO<sub>2</sub>, CH<sub>4</sub> etc. due to the low surface tension of supercritical fluids.<sup>[1]</sup> However, CPD requires expensive equipment and can be hazardous and time-consuming.<sup>[1, 8]</sup> Alternate methods include freeze drying<sup>[1]</sup> and sublimation of organic solvents<sup>[9]</sup> which are difficult to scale up due to the energy intensive requirements of vacuum for solvent sublimation and low temperature in the case of freeze drying. Ambient pressure drying (APD) is a less energy intensive alternative<sup>[10]</sup> and usually relies on replacing the original solvent used for gel preparation with organic low-surface-tension (LST) solvents, such as hexane, heptane, octane etc. In most APD approaches, surface modification is also introduced to replace hydroxyl groups by methyl groups at the gel surface for additional reduction of capillarity.<sup>[11]</sup> A common organic used for surface modification of silica gels is trimethylchlorosilane (TMCS), (CH<sub>3</sub>)<sub>3</sub>SiCl.<sup>[12]</sup> Surface modification by TMCS used in conventional APD always leads to the generation of hydrochloric acid requiring further organic solvents to remove. The result is that, although less energy intensive, current APD methods are nonetheless still time consuming and costly due to use of large quantities of organic solvents. These issues of scalability are primary limits to the large scale use of aerogels, for example in building insulation.

Many materials synthesis problems have been solved by biological systems and provide inspiration for design and production of man-made analogues.<sup>[13-16]</sup> Lightweight and porous materials are key elements of many biological structures: for example, the wings of Odonata – dragonflies and damselflies – which are among the fastest and most agile flying insects,<sup>[17, 18]</sup> consist of super-lightweight composites made of chitin microfibrils embedded in a protein matrix (resilin, an elastomeric protein) that have complex configurations at both macro and micro scale.<sup>[18]</sup> Typically, the wing weight is less than 2% of a dragonfly's total body mass.<sup>[19]</sup>

**Figure 1 (a-c)** presents Scanning Electron Microscopy (SEM) images of the wing of the damselfly *Lestes virens* (Odonata, Zygoptera: Lestidae) where a porous and layered structure similar to an aerogel-like material is observed. Dragonflies do not have a pupal stage – instead adults emerge directly from the larval skin during a final moult that takes place out of water.<sup>[20]</sup> During this process they leave behind the larval skin, the wings are expanded and the abdomen hardens. This process is very short compared with the under-water stage, and can last as little as one hour in the case of damselflies.<sup>[20]</sup> If one assumes that during the ‘underwater lifetime’, gelation and ageing of gel-like materials involved in wing membrane formation takes place, this implies that upon emerging from water, which is not a low surface tension solvent, a fast drying process produces these porous aerogel-like materials under ambient conditions.

Atmospheric CO<sub>2</sub> dissolves in water over time and it is estimated that the dissolved pressure of CO<sub>2</sub> normalised to lake areas (habitats of Odonata) is  $\approx 800 \mu\text{atm}$ .<sup>[21]</sup> CO<sub>2</sub> dissolution in water establishes the following equilibrium:  $\text{CO}_{2(\text{aq})} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+$ . H<sub>2</sub>CO<sub>3</sub> can dissociate immediately into a proton and a bicarbonate ion, HCO<sub>3</sub><sup>-</sup>, reducing pH. At high pH, HCO<sub>3</sub><sup>-</sup> can further dissociate into a second H<sup>+</sup> and carbonate CO<sub>3</sub><sup>2-</sup>.<sup>[22]</sup> Damselfly (Zygoptera) larvae pump water in and out of the hindgut to deal with hypoxic stress (lack of oxygen in water),<sup>[23]</sup> the rate of which is affected by the concentration of NaCl in the surrounding medium.<sup>[24]</sup> In particular, the principal function of the hindgut and rectum of water insects is to support an exchange diffusion mechanism in which sodium ions are exchanged for ammonium ions and chloride ions for bicarbonate.<sup>[24]</sup> Therefore, it is possible that damselflies use bicarbonate-based solutions in some form as a non LST solvent in wing formation during the final moult. Release of CO<sub>2</sub> from bicarbonates compensates the change in environmental pressure when the damselfly emerges from underwater in order to balance blood pH.<sup>[25]</sup> This tentative hypothesis led us to use generation of CO<sub>2</sub> from sodium bicarbonate (NaHCO<sub>3</sub>) within the gel prior to drying to develop a new aerogel production process.

Capillarity is a key parameter dominating aerogel formation when silica gels dry<sup>[2]</sup>. If aerogel pores are modelled as cylinders, the capillary pressure in those pores ( $P$ ) satisfies the Young-Laplace equation (Equation 1).<sup>[26]</sup>

$$P = 2\gamma\cos\theta / R \quad (1)$$

where  $\gamma$  is the solvent surface tension,  $\theta$  the contact angle between solvent and surface, and  $R$  the pore surface radius in the wet gel.

In conventional APD, solvent present in the gel pores evaporates directly from the gel surface. Various low-surface-tension (LST) solvents have been investigated to reduce capillary pressure (e.g., refs 11, 14). **Figure 2a** presents a schematic of the conventional APD mechanism using a LST solvent. If, instead, of undertaking surface modification and solvent exchange we treat the wet gel with a combination of sodium bicarbonate solution and TMCS, carbon dioxide is generated within the bulk of the silica gel without surface modification occurring, as discussed in more detail below. Contact angle, Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Fourier Transform InfraRed (FTIR) spectroscopy measurements are presented in the Supporting Information and demonstrate the absence of any detectable surface functionalisation. The carbon dioxide formed is trapped in the wet gel with the pressure in the resulting bubbles opposing capillary pressure, preventing pore shrinkage and collapse during the drying step, as illustrated schematically in figure 2b. The absence of any surface functionalisation from the addition of sodium bicarbonate and TMCS, a step we characterise as ‘pre-drying’, leaves the final dried aerogel hydrophilic.

Figure 1(d and e) shows a typical silica aerogel produced using our novel APD approach. High translucency, a specific surface area of  $550 \text{ m}^2 \text{ g}^{-1}$  determined from nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method and a porosity of 87.5% was observed for a moderate concentration of TMCS (sample A1, see Experimental Section). At these TMCS concentrations the sample has a density of  $0.3 \text{ g cm}^{-3}$ , which does not reflect the density of the aerogel scaffold itself, but is a superposition with the density of sodium chloride, a by-product of the pre-drying reaction, trapped within the pores of the aerogel. A decrease in surface area and translucency (Figure 1f) coupled with an increase in density is observed for increasing quantities of TMCS (samples A2 and A3, described in the Experimental Section). X-ray diffraction (XRD), High-Resolution Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) confirms the presence of NaCl crystals within the bulk of such aerogels and not simply at the surface. However, the NaCl can be completely removed by washing the samples either before or after the drying procedures whilst retaining the aerogel structure, as confirmed by XRD, BET and TEM measurements (full details of characterisation are provided in the Supporting Information). Samples from which sodium chloride has been removed display typical densities of around  $0.06 \text{ g cm}^{-3}$ , typical of high quality aerogel samples. Removal of salts through washing of wet gels prior to drying has been reported for other synthesis routes<sup>[27]</sup>, however we find that washing prior to drying leads to a smaller average pore diameter and pore specific volume than washing the dried material, which retains the pore distribution of the original aerogel scaffold. We speculate that the change in pore distribution upon washing the wet gel may originate from some removal of trapped  $\text{CO}_2$  during the washing process. A full characterisation of the two washing approaches and comparison with as-produced material is presented in the Supporting Information.

An important aspect of the new approach reported here is that its simplicity renders it readily scalable, with production of large batches of material becoming straightforward, as shown in

Section S7 of the Supporting Information. In addition to scalability, the production of monolithic aerogels is of importance for the development of a range of structural materials including insulation panels, windows etc.<sup>[3, 28-30]</sup> However, as a result of time and cost associated with their production currently the only commercially competitive aerogel monolith applications are in highly-specialised areas, such as use in Cerenkov radiation counters.<sup>[31]</sup> By using sodium silicate as a precursor we have prepared small-scale monolithic aerogels (Figure 1g) indicating the potential of our process for low-cost fabrication of larger free-standing aerogel materials. XRD of such aerogel monoliths demonstrates the absence of NaCl, which was removed before the drying procedure (Supporting Information and Methods section). The surface area of a typical aerogel monolith, obtained by the BET method, is  $700 \text{ m}^2 \text{ g}^{-1}$ , with an average pore diameter of 4.2 nm and a pore volume  $1.2 \text{ cm}^3 \text{ g}^{-1}$ , determined from nitrogen adsorption/desorption isotherms and the Barrett-Joyner-Halenda (BJH) method. The measured bulk density of these monoliths is  $0.051 \text{ g cm}^{-3}$  and the porosity was found to be 98.1%. SEM micrographs (Supporting Information) show high porosity and agree with the results obtained by the BJH method. Thermal conductivity was determined from room temperature to 425 K, with the value at room temperature found to be  $0.016 \text{ W m}^{-1} \text{ K}^{-1}$ , which is in the range of thermal performance of the other aerogels, substantially better than conventional insulating materials<sup>[28]</sup> and as good as silica aerogel monoliths produced by supercritical drying<sup>[29, 32]</sup>.

Layered silica aerogels can also be prepared by the same approach (**Figure 3**), enabling compositional variation through an aerogel monolith and providing a route by which large thickness monoliths may be built up. From nitrogen adsorption-desorption isotherms and pore size distribution analysis we find that the multi-layered silica aerogel films exhibit a surface area of  $520 \text{ m}^2 \text{ g}^{-1}$ . The isotherm curves display type IV behaviour, indicating mesoporous structure<sup>[33]</sup> with an average pore diameter of 15.6 nm and a pore volume of  $1.6 \text{ cm}^3 \text{ g}^{-1}$ . These layered aerogel structures display a remarkable similarity to the multilayered structure of

damsel fly wings, as might be expected given the original inspiration for the APD approach presented here. Layering the aerogel structure considerably increases aerogel durability – it was possible to produce free-standing aerogel monoliths with typical thicknesses of ~0.3 mm, whilst attempts to produce non-layered samples of similar thicknesses with the same composition and preparation approach failed as these more brittle samples broke up upon the most gentle of handling. These ultra-thin layered aerogel samples were sufficiently robust to allow for compression testing and were found to have a compressive elastic modulus of  $E_{\text{layered}} = 0.20 \pm 0.07$  GPa. Full details of characterisation and stress-strain measurements on the layered aerogels is presented in the Supporting Information. To demonstrate that the new APD approach is applicable to a broad range of aerogel compositions, we have also produced an alumina-based aerogel (dawsonite - sodium aluminium carbonate hydroxide) by the same method, as shown in Figure 1h. XRD and FTIR (see Supporting Information) are consistent with  $\text{NaAlCO}_3(\text{OH})_2$ , dawsonite.<sup>[34, 35]</sup> Nitrogen adsorption-desorption isotherms show that these dawsonite aerogels have a mesoporous structure with a surface area of  $345 \text{ m}^2 \text{ g}^{-1}$  and average pore diameter of 5.7 nm.

Figure 2c presents the proposed reaction mechanism underpinning the novel APD method. As described in the Methods section, TMCS is added to the wet gel containing sodium bicarbonate solution. When TMCS reacts with water hydrogen chloride is formed which reacts with sodium bicarbonate to produce sodium chloride, carbon dioxide gas in the pores of the silica gel and water. Moreover, the water produced reacts with remaining TMCS to further produce hydrogen chloride. This is a self-driving process allowing carbon dioxide to be released within the silica gel while hydrogen chloride slowly diffuses into the bulk. The reaction of the TMCS with the bicarbonate solution is sufficiently vigorous that it does not react with and functionalise the aerogel surfaces, instead forming trimethylsilanol (TMS),  $(\text{CH}_3)_3\text{SiOH}$ , after reaction with water. In the absence of a suitable catalyst, such as ammonia, TMS does not react with the silica



gel<sup>[36]</sup> and it is sufficiently volatile to be removed during the drying step. Carbon dioxide generated by the reaction between TMCS, sodium bicarbonate and water is trapped within the wet gel, as demonstrated by the FTIR spectra presented in **Figure 4**. A clear infra-red absorption peak is observed at  $2342\text{ cm}^{-1}$  in the wet gel, corresponding to the asymmetric  $\text{CO}_2$  stretch mode,<sup>[37]</sup> which is absent in the spectra from the dried gels obtained under the same conditions. During the drying step the  $\text{CO}_2$  trapped in the wet gel resists pore collapse due to capillary pressure, preventing densification. Comparison of average pore diameters and pore specific area with silica aerogel produced by conventional APD (**Table 1**), shows a reduction in pore size indicating that some compression may occur. However, low density and high specific area is maintained. It is possible to estimate the concentration of  $\text{CO}_2$  within the wet gel using the appropriate form of the Beer-Lambert Law and  $\alpha$ , the absorption coefficient of  $\text{CO}_2$  at  $\approx 2340\text{ cm}^{-1}$ . There are a range of different values for  $\alpha$  in the literature, for example in aqueous solution Jones and McLaren<sup>[38]</sup> find  $\alpha \approx 9 \times 10^5\text{ cm}^2\text{ mol}^{-1}$  and Falk and Miller<sup>[39]</sup> obtained a value of  $\approx 1.5 \times 10^6\text{ cm}^2\text{ mol}^{-1}$ , while for  $\text{CO}_2$  inclusions in rhyolitic glasses Behrens and co-workers<sup>[40]</sup> found that the absorption coefficient was  $\approx 1.2 \times 10^6\text{ cm}^2\text{ mol}^{-1}$ . These values of  $\alpha$  give a  $\text{CO}_2$  concentration of between  $1.2 \times 10^{-5}$  and  $1.9 \times 10^{-5}\text{ mol cm}^{-3}$ , which would correspond to a  $\text{CO}_2$  volume fraction of between 0.26 and 0.43 at standard temperature and pressure (STP). Proof of the proposed mechanism is provided in the Supplementary Material, which details control experiments of reactions between solid sodium bicarbonate, pure TMCS and water vapour from ambient air and presents data demonstrating that no surface functionalisation of the aerogel occurs within the limits of detectability, leaving the material hydrophilic. Although carbonate solutions, including sodium bicarbonate, have previously been employed in the synthesis of organic aerogels<sup>[41-45]</sup> their role has been limited to gelation. In resorcinol-formaldehyde aerogels they have been used as a catalyst to promote condensation and cross-linking,<sup>[41-43]</sup> in production of alginate aerogels as precursor and catalyst,<sup>[37]</sup> whilst

carbon dioxide formed during graphene oxide reduction prevented re-stacking of reduced graphene platelets during gelation.<sup>[44]</sup> However, in all these cases conventional drying approaches, in which the carbonates played no role, were used to produce aerogels from the hydrogel/lyogel precursors.

In summary, a novel approach to the production of aerogels through the use of sodium bicarbonate in APD has been demonstrated. The use of a range of precursors and demonstration of direct methods for preparing monoliths and free-standing porous layers shows that our novel approach to aerogel production has potential for wide applicability, with the resulting aerogels displaying physical properties very similar to those produced by conventional approaches. Moreover, the low cost of reagents coupled with the absence of specialised conditions results in a method which is both economical, with a materials cost of \$4 per kg of aerogel produced (costings are outlined in Section S7 of the Supporting Information) and scalable, overcoming the cost barrier which has prevented the widespread use of aerogels to date.<sup>[30]</sup> Moreover, the reduction in organic solvent use and low energy budget ensures that this aerogel production approach has a smaller environmental footprint compared with other methods. We believe that this simple method for aerogel production, and developments arising from it, can open the way for economical and routine application of these materials in a wide variety of functions from building insulation to energy storage, addressing pressing concerns in carbon emissions and sustainability.

## **Experimental Section**

### *Silica gel preparation (TEOS precursor)*

All materials and solvents were purchased from Sigma-Aldrich and used without further purification. Silica gels were prepared by hydrolysis of tetraethoxysilane (TEOS,  $\geq 98\%$ ), ethanol ( $\geq 99.5\%$ ) and de-ionised (DI) water at a molar ratio of TEOS:ethanol:H<sub>2</sub>O = 2:38:39.

To speed gelation, 1 ml of catalyst (ammonium hydroxide (28-30%), ammonium fluoride ( $\geq 98\%$ ) and DI water in a molar ratio  $\text{NH}_4\text{OH}:\text{NH}_4\text{F}:\text{H}_2\text{O} = 8:1:111$ ) was added to 34 ml of as-prepared precursor. After 5 minutes, silica gels were removed from the casting mould, washed with DI water, and aged with 500 ml of ethanol for 24 hours. After 24 hours of aging ethanol was replaced by 500 ml DI water and 22 g sodium bicarbonate ( $\geq 99.7\%$ ). Silica gels were soaked in the bicarbonate solution while stirring for 24 hours. At the end of the solvent exchange step the gels were removed from the sodium bicarbonate solution and trimethylchlorosilane (TMCS,  $\geq 97\%$ ) in quantities of 6, 8, or 10 ml was slowly poured onto them. After two minutes, ethanol was added as protecting solvent. The release of further  $\text{CO}_2$  was observed over the following 24 hours. Finally, the gels were dried at  $60^\circ\text{C}$  and ambient pressure with ethanol for 24 hours to obtain aerogels. The aerogels prepared by adding 6, 8 and 10 ml of TMCS are referred to as A1, A2 and A3, respectively. After addition of TMCS, sodium chloride is generated along with TMS and  $\text{CO}_2$  inside the aerogel. Samples were washed by two approaches: 1) washing with DI water after drying followed by a subsequent drying step at  $60^\circ\text{C}$  for 12 hours; 2) during the drying process, samples were washed with DI water between the completion of  $\text{CO}_2$  release and final drying. The drying procedure was then continued as before.

#### *Synthesis of silica aerogels (sodium silicate precursor)*

Silica hydrogels were synthesised by the sol-gel method then dried by the novel APD. Water glass (sodium silicate, Sigma Aldrich:  $\text{Na}_2\text{O} \sim 10.6\%$ ,  $\text{SiO}_2 \sim 26.5\%$ ) was diluted with deionised water at different volume ratios (1:3, 1:3.5, 1:4, 1:4.5 and 1:5). Ion exchange was carried out with Amberlite. The silica sol had pH in the range of 2 -3 after ion exchange. The sol was transferred to a beaker and stirred for 5 min. For the gelation step, ammonium hydroxide and ammonium fluoride solution was used to modify the pH of the sol to pH 6. The silica sol was then transferred to a plastic mould for gelation. Gelation completed within 15 min,

following which the hydrogel was soaked with deionised water for 24 hours for aging. The water was exchanged with sodium bicarbonate solution (4.4 g for each 100 ml water). The gel was treated with a mixture of 6 ml TMCS and 150 ml ethanol for 24 hours, soaked in ethanol for 8 hours to remove unreacted TMCS and residual HCl then rinsed with water several times to remove the salt produced during the reaction between TMCS and sodium bicarbonate. Finally, the gel was soaked in ethanol for 24 hours with the ethanol refreshed every 12 hours and dried at 60°C for 24 hours. To obtain monolithic silica final addition of TMCS with ethanol was to a wet gel (the wet-gel was soaked in TMCS and ethanol mixture for 24 hours followed by soaking in pure ethanol). Ethanol was exchanged twice and the aerogel dried at 60°C for 24 hours and at 100°C for 1 hour.

#### *Synthesis of dawsonite aerogels*

Synthesis of dawsonite aerogels involved three main steps: preparation of the alcogel; treatment with sodium bicarbonate and TMCS and solvent displacement; removal of trapped solvent from the pores by APD. The sol was prepared by mixing aluminum sec-butoxide, deionised water, ethyl acetoacetate and ethanol in a molar ratio of 1:0.6:0.58:16, for 45 min at 60°C. Hydrolysis and condensation was carried out by mixing the sol with a mixture of methanol, water, acetic acid, and N,N-dimethylformamide (DMF) in a weight ratio Sol:MeOH:H<sub>2</sub>O:DMF of 1:0.2:0.003:0.03. 1 mL of acetic acid was added for each 30 ml of mixture while stirring for 30 min at room temperature. The resulting homogeneous sol was transferred to airtight boxes and kept for 7 days at room temperature to complete gelation. After gelation completed the gel was soaked in sodium bicarbonate solution (4.4 g for each 100 ml water) while stirring for 2 h. CO<sub>2</sub> was generated within the aerogel by soaking in ethanol solution containing TMCS (14 ml TMCS in 100ml ethanol) for 24 h at room temperature. The gel was rinsed with ethanol to remove the unreacted TMCS, soaked with water and stirred for 8 h. Finally, the gel was

immersed in ethanol for 24 h and dried at room temperature for 72 h followed by 100°C for 2 h under ambient pressure.

#### *Synthesis of multi-layered silica aerogel films*

Multi-layered silica aerogel films were synthesised from tetraethoxysilane (TEOS) using the same method and molar ratios detailed in the section describing silica gel preparation with TEOS precursor, above. Briefly: cling film was pulled tight over a petri dish to create a flat surface and the silica sol dripped on the film by pipette. To prepare uniform films, 1 ml of sol was spread using a glass rod. Once gelation of the first layer was complete, another layer of silica sol was dripped on the gel surface until gelation was completed. The process was repeated until the required number of layers was complete. After completing gelation, the cling film was placed inside the petri dish and the gel soaked with ethanol for 8 hours. After ageing, ethanol was replaced by a mixture of deionised water and sodium bicarbonate for 8 hours. The gel was then soaked in a TMCS and ethanol mixture with a 16:100 volumetric ratio for 4 hours. Following this, the gel was rinsed with ethanol to remove unreacted TMCS. Finally, the gel film was dried at ambient pressure and room temperature for 12 hours, then at 100°C for 1 hour. Attempts to produce a single aerogel layer of the same overall thickness as the multi-layered aerogel samples produced materials which were too brittle to successfully remove from the cling-film support.

#### *Materials Characterisation*

A FEI XL30 ESEM-FEG (Environmental Scanning Electron Microscope-Field Emission Gun) was used to image samples in high vacuum mode with a 10 kV accelerating voltage. Before SEM imaging, the samples were coated with gold to increase electrical conductivity. Coulter™ SA 3100™ Surface Area and Pore Size Analyzers were used to measure surface area of silica aerogels prepared by TEOS (samples A1, A2 and A3) by measuring nitrogen adsorption-

desorption isotherms at 77 K. Specific surface area was determined by the Brunauer-Emmett-Teller (BET) method from the adsorption curve and pore size distribution found with the Barrett-Joyner-Halenda (BJH) method using the desorption curve. All other samples were characterised by a Thermo Scientific™ SURFER. Uncertainties in the measured quantities are  $\pm 20 \text{ m}^2 \text{ g}^{-1}$  for BET surface area,  $\pm 0.1 \text{ nm}$  for average pore diameter and  $\pm 0.02 \text{ cm}^3 \text{ g}^{-1}$  for pore specific volume. A PANalytical X'Pert Pro Multipurpose Diffractometer (MPD) was used for X-ray powder diffraction (XRD) analysis. High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) experiments were carried out using a Tecnai F30 300keV microscope at the Materials Science Centre, University of Manchester. Samples for HRTEM and STEM were prepared by ultrasonication of silica aerogels in de-ionised water until there were no large pieces of aerogel visible to the naked eye. Thermal conductivity measurement were carried out by the hot disk method (Hot Disk TPS2500S). Compression tests were carried out on layered silica aerogels with an overall thickness, measured by SEM, to be approximately  $\sim 0.3 \text{ mm}$ . Five samples were tested using a Tinius-Olsen mechanical testing frame at a crosshead speed of  $0.5 \text{ mm min}^{-1}$ . Compression, the slope of the stress-strain curves, was used to calculate the compressive elastic modulus. The surface area needed for determination of moduli was determined with optical microscopy.

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#### Conflict of Interest

The authors declare no conflict of interest.

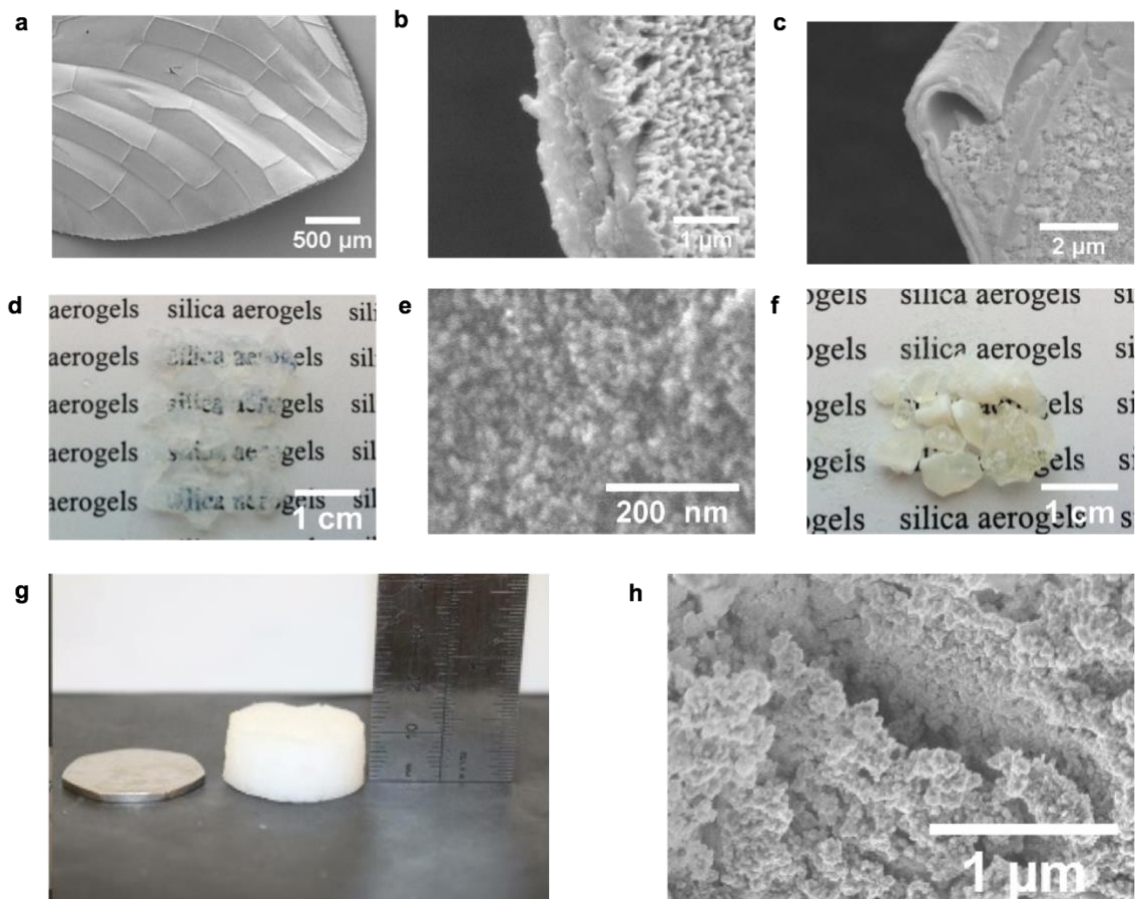
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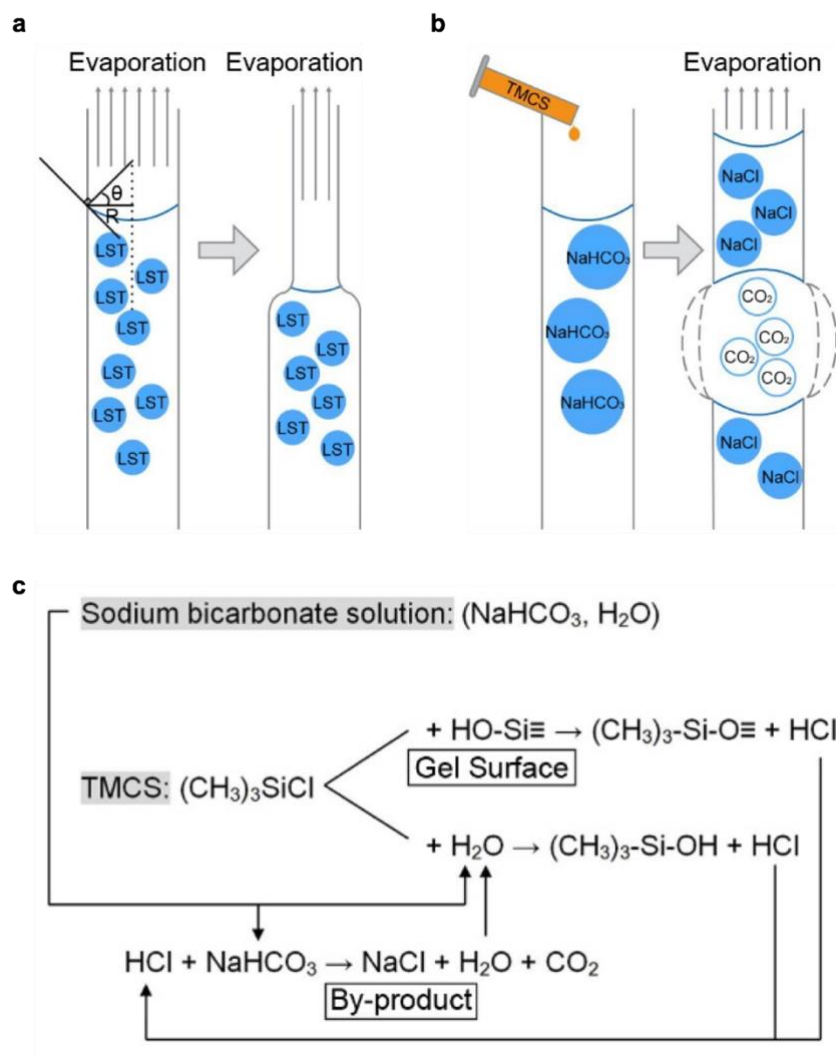
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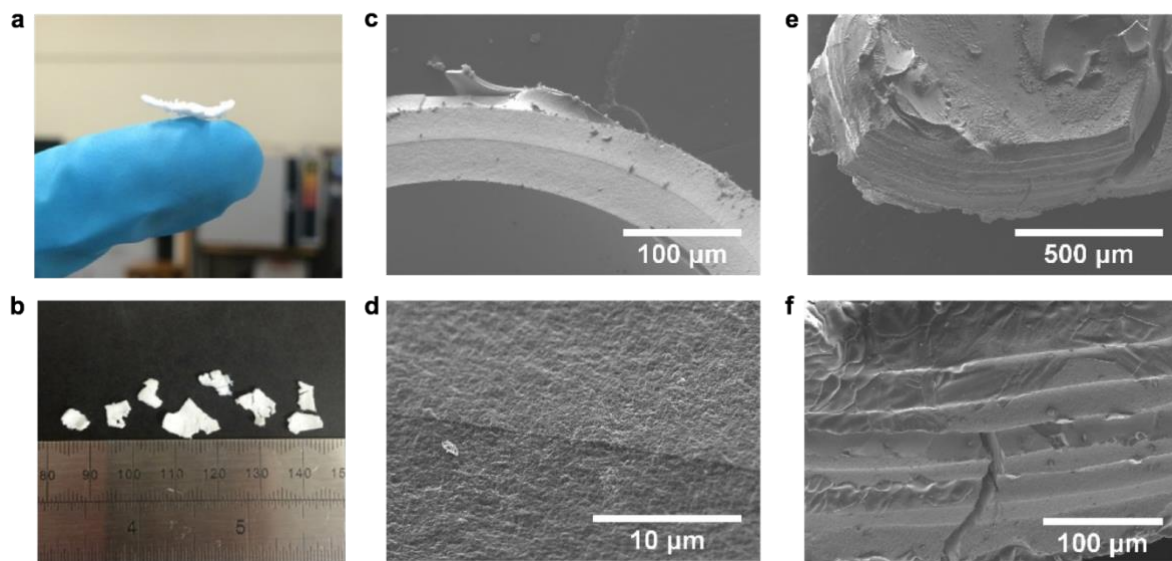
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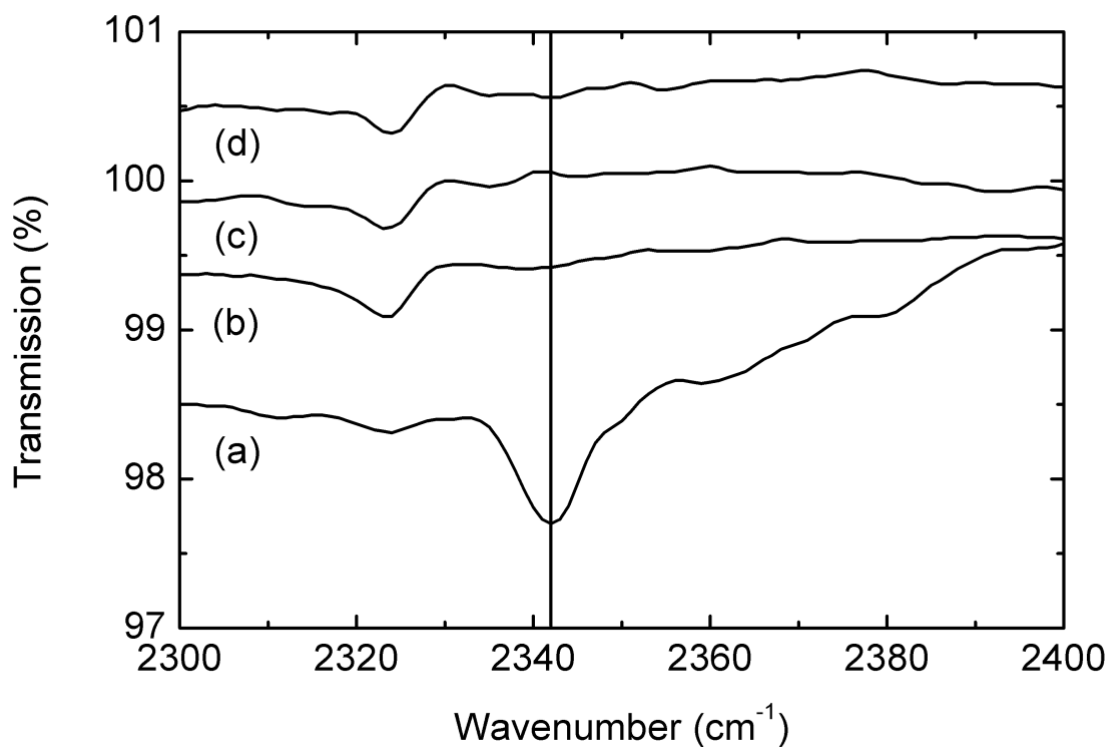
**Figure 1.** (a-c) SEM images of the membrane of the damselfly *Lestes virens* (Odonata, Zygoptera: Lestidae): (a) base of the wing; (b) multi-layered structure (5 layers are visible) of the base of the wing; (c) two layer structure of the end of the wing. It is clear that the thickness of membrane varies across the wing and the wings are made from porous tuctile multilayers. (d-f) Silica aerogels produced from TEOS precursor: (d,e) using 6 ml TMCS; (f) using 10 ml TMCS, showing increasing opacity with TMCS and hence NaCl concentration within the aerogel. (g) Monolithic silica aerogel prepared with water glass (sodium silicate precursor) with bicarbonate solution and TMCS. (h) SEM image of Dawsonite ( $\text{NaAlCO}_3(\text{OH})_2$ ) aerogels synthesised with aluminium sec-butoxide.



**Figure 2.** A schematic comparison between ambient pressure drying methods for aerogels. (a) conventional APD using an organic LST solvent. (b) APD using inorganic sodium bicarbonate solution. When a bubble of carbon dioxide forms in a pore of the gel the gas opposes capillary pressure. Hence it is possible to successfully fabricate aerogels without commonly used LST solvents. Sodium chloride, which is the by-product of this process is more environmentally friendly than HCl. (c) A proposed net-chemical-reaction route in the sodium bicarbonate solution APD method with TMCS ((CH<sub>3</sub>)<sub>3</sub>SiCl).



**Figure 3.** Bioinspired wing-membrane-like multi-layered silica aerogels. (a-b), Photos of silica aerogels formed by the sodium bicarbonate solution based APD method using TEOS precursor. (c) SEM micrograph of bilayer aerogel material, note the similarity to the structure in Figure 1c from *Lestes virens*. (d) SEM micrograph of the interface in the bilayer aerogel: the porosity and excellent tuctility of the interface is clear. (e,f) nine layer porous aerogel structures.



**Figure 4.** FTIR spectra of (a) wet silica aerogel; (b) as prepared silica aerogel containing sodium chloride (SA); (c) silica aerogel with salt removed by a post-drying wash (SA-WAD); (d) silica aerogel with salt removed by a pre-drying wash (SA-WBD). A clear peak at  $2342\text{ cm}^{-1}$  is observed in the spectrum of the wet gel, corresponding to the asymmetric stretch of  $\text{CO}_2$ , which is absent from the spectra of the aerogels. Spectra have been shifted vertically for clarity.

<i>Sample</i>	<i>Surface area (m<sup>2</sup> g<sup>-1</sup>)</i>	<i>Pore specific volume (cm<sup>3</sup> g<sup>-1</sup>)</i>	<i>Average pore diameter (nm)</i>
<b>APD (hexane)</b>	500	1.5	10.6
<b>New approach</b>	580	1.0	7.0

**Table 1.** Surface area and pore size analysis for silica aerogels produced by conventional APD and the new approach reported here.