

# Development of Agricultural-Based Nano-Structured Aerogels

Subjects: Materials Science, Biomaterials

Contributor: Syaifullah Muhammad, Esam Bashir Yahya, H. P. S. Abdul Khalil, M. Marwan, Yonss M. Albadn

Aerogels are an exceptional form of porous materials with extraordinary unique properties. The aerogel has been fabricated from different inorganic and organic materials and incorporated with a variety of novel compounds for specific applications and to enhance its performance in the desired application.

Keywords: aerogels ; porous materials ; agricultural activated carbon

## 1. Introduction

Aerogels are open-celled and mesoporous forms of materials composed of inter-connected nanostructured networks exhibiting a porosity of more than 50% <sup>[1]</sup>. Aerogels have steadily developed since S. Kistler fabricated aerogels for the first time from silica gel in 1931 <sup>[2]</sup>. Abdul Khalil et al. <sup>[3]</sup> presented the chronological development of aerogel materials from inorganic silica aerogel until the current forms of nano-structured aerogels. The term nano is applied to materials that have at least one dimension in the nano-meter range (1 to 100 nm). Nano-structured aerogels are said to be materials with pores of less than 50 nm in diameter <sup>[4]</sup>. Having such a character, nano-structured aerogels possess an ultra-light weight and extremely high surface area, making them attractive materials for several advanced functionalities.

## 2. Classification and Properties of Nano-Structured Aerogels

The history of aerogel materials commenced with the fabrication of a silica aerogel by Kistler in 1931, who replaced the liquid in "Hydrogel" with gas without inducing any shrinkage <sup>[5]</sup>. Owing to the unique properties that suit particular applications, these materials have been widely utilized in several applications, including acting as: carriers for the delivery of different drugs <sup>[6]</sup>; electrodes in batteries <sup>[7]</sup>; filters for wastewater treatment <sup>[8]</sup>; and catalyst supports in fuel cells <sup>[9]</sup>. Several methods have been used to classify aerogels since there is no standard IUPAC classification yet for them <sup>[10]</sup>. The most convenient classification for aerogels is based on the precursor/s and/or the additives, which can be classified into three main groups, including inorganic, organic and composites <sup>[11]</sup>. Inorganic aerogels are the initial form of the materials prepared from metal alkoxides and/or metal salts to form metal oxide aerogels, chalcogenide aerogels and metallic aerogels. Organic aerogels are derived from several form of carbon, including biopolymers, phenol formaldehyde resin, etc to form biopolymeric aerogels, carbon nanotubes, graphene aerogels and other polymeric aerogels <sup>[12]</sup>. However, the third form of aerogels is formed by combining both inorganic and organic precursors to form composite aerogels (Table 1).

**Table 1.** Classification of aerogels based on the precursor material/s.

Type of Aerogel	Sub-Type	Example	Ref.
Inorganic based aerogels	(1) Inorganic oxide aerogels	Gold/iron oxide aerogel	<sup>[13]</sup>
	(2) Metallic aerogels	Vanadium nitride nanosheets aerogel	<sup>[14]</sup>
	(3) Chalcogenide aerogels	Chalcogenide aerogel CuSb <sub>2</sub> S <sub>4</sub>	<sup>[15]</sup>
	(4) Silica aerogels	Transparent silica aerogel fibers	<sup>[16]</sup>
	(5) Carbon aerogels	Shaddock peel-based carbon aerogel	<sup>[17]</sup>
Organic based aerogels	(1) Biomass aerogels	Marine biomass-derived aerogel	<sup>[18]</sup>
	(2) Synthetic organic aerogels	Poly lactide aerogel	<sup>[19]</sup>
	(3) Biopolymeric aerogels	Nanocellulose/Chitosan aerogel	<sup>[20]</sup>

Type of Aerogel	Sub-Type	Example	Ref.
Composites aerogels	(4) Mixed metal oxide aerogels	Magnetic iron oxide/graphene aerogel	[21]
	(1) Mixed organic aerogels	Alginate-chitosan aerogel	[22]
	(2) Mixed inorganic aerogels	Mesoporous Fe-silica aerogel	[23]
	(3) Organic/inorganic aerogels	Nanocellulose/silica aerogel	[24]
	(4) Other composite aerogels	Nanocellulose/poly ethylenimine aerogel	[25]

Aerogels have been developed from almost every material, which determines the properties of that aerogel. However, the lack of novel properties in a single material limits the multifunctionality of many pure aerogels. Therefore, composite aerogels provide a solution for many potential applications to enhance, introduce and develop novel materials for many new applications. Nanoparticles of silica were impregnated with a network of polymers and loaded with model drugs [26]. This composite aerogel possesses an excellent drug release properties, which can be a potential drug carrier for many medical applications, such as wound dressing [26]. A silica–gelatin aerogel hybrid was fabricated and incorporated with the anticancer drug methotrexate [27]. The incorporation of the drug to the composite aerogel provided an excellent control for drug release. Other composite aerogels have been also used in the field of adsorption, separation and filtration, such as the removal of antibiotics from polluted water using nanocellulose/graphene oxide hybrid aerogel [28], and the same composite aerogel has been used for water purification [29]. Gonçalves and co-workers developed a composite aerogel based on alginate by incorporation of an alginate biopolymer with some drugs in the form of microparticles for mucosal administration. The authors reported that drug release from the alginate-based hybrid was faster than in previous polymer hybrids such as alginate/pectin [30].

The silica aerogel is the first prepared inorganic aerogel characterized with extraordinary properties, which opened a new pathway to many potential applications. The high cross-linked structure, high porosity and ultra-low density of silica-based aerogels raised a lot of interest in many applications [31]. They are mainly composed of air (more than 95%) and only the rest are silica, therefore, it exhibits poor thermal conductivity, and a high surface area [32][33], and being a novel material with unusual properties, has a promising and bright future in many important fields. Several precursors have been used for the preparation of silica aerogels including;  $\text{Na}_2\text{SiO}_3$ ,  $\text{Si}(\text{OR})_4$ , MTMS, TEOS, and TMOS [34]. The production expenses of silica aerogels minimized their usage at the time they were discovered. However, in recent years, silica aerogels have been prepared from cheaper precursors, such as bamboo leaf [35], fly ash [36], oil shale ash [37], water glass [38], agricultural wastes, such as wheat husk [39] and bagasse ash [40] instead of with expensive organoalkoxysilanes [39]. Moreover, instead of using expensive, health risky supercritical drying in the large-scale production of aerogels, which is expensive may pose a risk to health, numerous researches have used alternative methods such as ambient pressure [41], freeze drying [42] and microwave drying [43]. The fabrication of flexible, smokeless, super thermal insulators have been always a novel objective for humankind. However, Kim, Y.-G., et al. [44] developed a silica-based aerogel which exhibited an ultra-low thermal conductivity compared to previous fabrications. Similarly, an unexpansive silica aerogel was developed from rice husk and incorporated into cement for thermal insulation purposes [45]. The authors observed an excellent thermal insulation in their aerogels, which may potentially be used as green materials for building applications.

### 3. Fabrication of Agricultural Carbon Nano-Structured Aerogels

Several polymeric materials can easily form gels when they are suspended in water, such as carrageenan, gelatine, and starch, etc., but others, such as cellulose and synthetic polymers require a cross-linker for this purpose [3]. However, aerogels can be simply prepared from both types of materials, with or without the formation of a wet-gel of the material. The shape of particles can be preservative and fixed during the drying phase either by the formation of wet-gel or by freezing of the suspension. The fabrication of an aerogel can be initiated by dissolving or dispersing the precursor material/s in distilled water or any other liquid solvent. The homogenization of precursor materials are required for a non-solvable material to achieve homogeneous suspension; the solution then requires some time for the aging process to form a wet-gel [46]. The precursor particles are linked together during the aging process, forming a viscous semi-solid material known as wet-gel. This material is formed by the network of precursor/s surrounded by the solvent. The next step is to remove the solvent without shrinking or disturbing the structure of that network. In order to achieve this, the wet-gel is frozen to keep the structure integrity intact, and then the frozen material is either freeze-dried or supercritical-dried. Freezing of the wet-gel will result in removing the liquid from the system, leaving the precursor network, which appears as a porous 3D material known as aerogel [47]. Li et al. [48] fabricated cocoon-based carbon aerogel by pyrolyzing the initially prepared aerogel at 800 °C for two hours. The authors were able to achieve a nano-porous structure with excellent catalytic activity for their carbon aerogel. The porosity, pore size and volume of the aerogel can be determined by the type

and concentration of the precursor material/s. The fabrication technique and the conditions of preparation also highly affect the physical, chemical, and mechanical properties of the aerogels.

The preparation techniques of aerogels are divided into two major classes; conventional preparation techniques, which include those techniques that do not involve computer aid and follow fully manual lab-based routes. Advanced preparation techniques (rapid prototyping techniques), include those techniques that involve the aid of a computer in the fabrication process, as described below <sup>[49]</sup>.

Conventional preparation techniques of aerogels such as supercritical CO<sub>2</sub> drying, freeze-drying and thermal-induced phase separation, etc., do not involve any computer aid and are fully controlled by technicians. Since they are fully manmade materials, these techniques have the drawback of preparing accurate shapes for particular applications. However, due to their cost effectiveness and simplicity, many of these approaches are still in use even now. These techniques are associated with several issues, including time consumption and manpower requirements; thus, the past two decades have witnessed the development in the computer-aided design of aerogels in term of composition ratios and the final shape of the material. Such fabrication techniques are referred to as rapid prototyping techniques, due to the ease of preparation compared with traditional techniques. Moreover, using the computer in mixing the precursor material also helps in determining the optimal combination of each hybrid, in addition to the control of the physical, morphological and mechanical properties of the aerogels <sup>[50]</sup>. **Table 2** highlights the main differences between traditional and advanced bioaerogel fabrication techniques.

**Table 2.** Comparison between conventional and advanced bioaerogel fabrication techniques.

Functionality	Conventional Techniques	Rapid Prototyping Techniques
Time consuming and computer-aid	Consume longer time, without computer aid	Rapid fabrication with computer-aid
Easiness and Manpower requirements	Require more manpower	Minimize manpower required
Aerogel homogeneity	Difficult to obtain homogeneous structures	Easier to obtain homogeneous structures
Accurate controllable properties and aerogel shape	Relatively unspecific	Highly specific
Aerogel porosity and pore shape	Random and irregular pores shape	Highly regular and interconnected pores
Aerogel toxicity	Depending on the technique (more toxic)	Less toxic in some techniques
Production costs	More expensive, consume more materials	Consume minimum materials, generally low cost of production

## References

1. Mariana, M.; Abdul Khalil, H.P.S.; Yahya, E.B.; Olaiya, N.; Alfatah, T.; Suriani, A.; Mohamed, A. Recent trends and future prospects of nanostructured aerogels in water treatment applications. *J. Water Process Eng.* 2022, 45, 102481.
2. Ziegler, C.; Wolf, A.; Liu, W.; Herrmann, A.K.; Gaponik, N.; Eychmüller, A. Modern inorganic aerogels. *Angew. Chem. Int. Ed.* 2017, 56, 13200–13221.
3. Abdul Khalil, H.P.S.; Adnan, A.; Yahya, E.B.; Olaiya, N.; Safrida, S.; Hossain, M.; Balakrishnan, V.; Gopakumar, D.A.; Abdullah, C.; Oyekanmi, A. A review on plant cellulose nanofibre-based aerogels for biomedical applications. *Polymers* 2020, 12, 1759.
4. Wang, H.-L.; Hsu, C.-Y.; Wu, K.C.; Lin, Y.-F.; Tsai, D.-H. Functional nanostructured materials: Aerosol, aerogel, and de novo synthesis to emerging energy and environmental applications. *Adv. Powder Technol.* 2020, 31, 104–120.
5. Yahya, E.B.; Alzalouk, M.M.; Alfallous, K.A.; Abogmaza, A.F. Antibacterial cellulose-based aerogels for wound healing application: A review. *Biomed. Res. Ther.* 2020, 7, 4032–4040.
6. Yahya, E.B.; Jummaat, F.; Amirul, A.; Adnan, A.; Olaiya, N.; Abdullah, C.; Rizal, S.; Mohamad Haafiz, M.; Abdul Khalil, H.P.S. A review on revolutionary natural biopolymer-based aerogels for antibacterial delivery. *Antibiotics* 2020, 9, 648.
7. Dong, X.; Zheng, X.; Deng, Y.; Wang, L.; Hong, H.; Ju, Z. SiO<sub>2</sub>/N-doped graphene aerogel composite anode for lithium-ion batteries. *J. Mater. Sci.* 2020, 55, 13023–13035.

8. Yu, Y.; Shi, X.; Liu, L.; Yao, J. Highly compressible and durable superhydrophobic cellulose aerogels for oil/water emulsion separation with high flux. *J. Mater. Sci.* 2021, 56, 2763–2776.
9. Öner, E.; Öztürk, A.; Yurtcan, A.B. Utilization of the graphene aerogel as PEM fuel cell catalyst support: Effect of polypyrrole (PPy) and polydimethylsiloxane (PDMS) addition. *Int. J. Hydrogen Energy* 2020, 45, 34818–34836.
10. Salimian, S.; Zadhoush, A.; Naeimirad, M.; Kotek, R.; Ramakrishna, S. A review on aerogel: 3D nanoporous structured fillers in polymer-based nanocomposites. *Polym. Compos.* 2018, 39, 3383–3408.
11. Alwin, S.; Sahaya Shajan, X. Aerogels: Promising nanostructured materials for energy conversion and storage applications. *Mater. Renew. Sustain. Energy* 2020, 9, 7.
12. Yahya, E.B.; Amirul, A.; Abdul Khalil, H.P.S.; Olaiya, N.G.; Iqbal, M.O.; Jummaat, F.; AK, A.S.; Adnan, A. Insights into the role of biopolymer aerogel scaffolds in tissue engineering and regenerative medicine. *Polymers* 2021, 13, 1612.
13. Wang, C.-T. Photocatalytic activity of nanoparticle gold/iron oxide aerogels for azo dye degradation. *J. Non-Cryst. Solids* 2007, 353, 1126–1133.
14. Zhang, H.; Han, W.; Xu, K.; Zhang, Y.; Lu, Y.; Nie, Z.; Du, Y.; Zhu, J.; Huang, W. Metallic sandwiched-aerogel hybrids enabling flexible and stretchable intelligent sensor. *Nano Lett.* 2020, 20, 3449–3458.
15. Ahmed, E.; Rothenberger, A. Enhancement in CO<sub>2</sub> adsorption capacity and selectivity in the chalcogenide aerogel CuSb<sub>2</sub>S<sub>4</sub> by post-synthetic modification with LiCl. *Microporous Mesoporous Mater.* 2016, 220, 247–252.
16. Du, Y.; Zhang, X.; Wang, J.; Liu, Z.; Zhang, K.; Ji, X.; You, Y.; Zhang, X. Reaction-spun transparent silica aerogel fibers. *ACS Nano* 2020, 14, 11919–11928.
17. Gu, W.; Sheng, J.; Huang, Q.; Wang, G.; Chen, J.; Ji, G. Environmentally friendly and multifunctional shaddock peel-based carbon aerogel for thermal-insulation and microwave absorption. *Nano-Micro Lett.* 2021, 13, 102.
18. Yang, L.; Li, N.; Guo, C.; He, J.; Wang, S.; Qiao, L.; Li, F.; Yu, L.; Wang, M.; Xu, X. Marine biomass-derived composite aerogels for efficient and durable solar-driven interfacial evaporation and desalination. *Chem. Eng. J.* 2021, 417, 128051.
19. Chen, P.; Bai, D.; Tang, H.; Liu, H.; Wang, J.; Gao, G.; Li, L. Polylactide aerogel with excellent comprehensive performances imparted by stereocomplex crystallization for efficient oil-water separation. *Polymer* 2022, 255, 125128.
20. Rizal, S.; Yahya, E.B.; Abdul Khalil, H.P.S.; Abdullah, C.; Marwan, M.; Ikramullah, I.; Muksin, U. Preparation and Characterization of Nanocellulose/Chitosan Aerogel Scaffolds Using Chemical-Free Approach. *Gels* 2021, 7, 246.
21. Dang, N.H.; Tu, T.H.; Linh, V.N.P.; Thy, L.T.M.; Nam, H.M.; Phong, M.T.; Hieu, N.H. Preparation of magnetic iron oxide/graphene aerogel nanocomposites for removal of bisphenol A from water. *Synth. Met.* 2019, 255, 116106.
22. Batista, M.; Gonçalves, V.S.; Gaspar, F.; Nogueira, I.; Matias, A.A.; Gurikov, P. Novel alginate-chitosan aerogel fibres for potential wound healing applications. *Int. J. Biol. Macromol.* 2020, 156, 773–782.
23. Tang, R.; Hong, W.; Srinivasakannan, C.; Liu, X.; Wang, X.; Duan, X. A novel mesoporous Fe-silica aerogel composite with phenomenal adsorption capacity for malachite green. *Sep. Purif. Technol.* 2022, 281, 119950.
24. Zuo, K.; Wu, J.; Chen, S.; Ji, X.; Wu, W. Superamphiphobic nanocellulose aerogels loaded with silica nanoparticles. *Cellulose* 2019, 26, 9661–9671.
25. Mo, L.; Pang, H.; Tan, Y.; Zhang, S.; Li, J. 3D multi-wall perforated nanocellulose-based polyethylenimine aerogels for ultra-high efficient and reversible removal of Cu (II) ions from water. *Chem. Eng. J.* 2019, 378, 122157.
26. Follmann, H.D.; Oliveira, O.N.; Lazarin-Bidóia, D.; Nakamura, C.V.; Huang, X.; Asefa, T.; Silva, R. Multifunctional hybrid aerogels: Hyperbranched polymer-trapped mesoporous silica nanoparticles for sustained and prolonged drug release. *Nanoscale* 2018, 10, 1704–1715.
27. Nagy, G.; Király, G.; Veres, P.; Lázár, I.; Fábrián, I.; Bánfalvi, G.; Juhász, I.; Kalmár, J. Controlled release of methotrexate from functionalized silica-gelatin aerogel microparticles applied against tumor cell growth. *Int. J. Pharm.* 2019, 558, 396–403.
28. Yao, Q.; Fan, B.; Xiong, Y.; Jin, C.; Sun, Q.; Sheng, C. 3D assembly based on 2D structure of cellulose nanofibril/graphene oxide hybrid aerogel for adsorptive removal of antibiotics in water. *Sci. Rep.* 2017, 7, 45914.
29. Wei, J.; Gui, S.-H.; Wu, J.-H.; Xu, D.-D.; Sun, Y.; Dong, X.-Y.; Dai, Y.-Y.; Li, Y.-F. Nanocellulose-Graphene Oxide Hybrid Aerogel to Water Purification. *Appl. Environ. Biotechnol.* 2019, 4, 11–17.
30. Gonçalves, V.S.; Gurikov, P.; Poejo, J.; Matias, A.A.; Heinrich, S.; Duarte, C.M.; Smirnova, I. Alginate-based hybrid aerogel microparticles for mucosal drug delivery. *Eur. J. Pharm. Biopharm.* 2016, 107, 160–170.
31. Iswar, S.; Malfait, W.J.; Balog, S.; Winnefeld, F.; Lattuada, M.; Koebel, M.M. Effect of aging on silica aerogel properties. *Microporous Mesoporous Mater.* 2017, 241, 293–302.

32. Chandradass, J.; Kang, S.; Bae, D.-S. Synthesis of silica aerogel blanket by ambient drying method using water glass based precursor and glass wool modified by alumina sol. *J. Non-Cryst. Solids* 2008, 354, 4115–4119.
33. Lee, K.-J.; Choe, Y.-J.; Kim, Y.H.; Lee, J.K.; Hwang, H.-J. Fabrication of silica aerogel composite blankets from an aqueous silica aerogel slurry. *Ceram. Int.* 2018, 44, 2204–2208.
34. Gurav, J.L.; Jung, I.-K.; Park, H.-H.; Kang, E.S.; Nadargi, D.Y. Silica aerogel: Synthesis and applications. *J. Nanomater.* 2010, 2010, 409310.
35. Kow, K.-W.; Yusoff, R.; Aziz, A.A.; Abdullah, E. From bamboo leaf to aerogel: Preparation of water glass as a precursor. *J. Non-Cryst. Solids* 2014, 386, 76–84.
36. Shi, F.; Liu, J.-X.; Song, K.; Wang, Z.-Y. Cost-effective synthesis of silica aerogels from fly ash via ambient pressure drying. *J. Non-Cryst. Solids* 2010, 356, 2241–2246.
37. Gao, G.-M.; Liu, D.-R.; Zou, H.-F.; Zou, L.-C.; Gan, S.-C. Preparation of silica aerogel from oil shale ash by fluidized bed drying. *Powder Technol.* 2010, 197, 283–287.
38. He, P.; Gao, X.-D.; Li, X.-M.; Jiang, Z.-W.; Yang, Z.-H.; Wang, C.-L.; Gu, Z.-Y. Highly transparent silica aerogel thick films with hierarchical porosity from water glass via ambient pressure drying. *Mater. Chem. Phys.* 2014, 147, 65–74.
39. Liu, S.-W.; Wei, Q.; Cui, S.-P.; Nie, Z.-R.; Du, M.-H.; Li, Q.-Y. Hydrophobic silica aerogel derived from wheat husk ash by ambient pressure drying. *J. Sol-Gel Sci. Technol.* 2016, 78, 60–67.
40. Nazriati, N.; Setyawan, H.; Affandi, S.; Yuwana, M.; Winardi, S. Using bagasse ash as a silica source when preparing silica aerogels via ambient pressure drying. *J. Non-Cryst. Solids* 2014, 400, 6–11.
41. Shi, F.; Wang, L.; Liu, J. Synthesis and characterization of silica aerogels by a novel fast ambient pressure drying process. *Mater. Lett.* 2006, 60, 3718–3722.
42. Hyun, S.; Kim, T.; Kim, G.; Park, H.-H. Synthesis of low-k porous silica films via freeze drying. *J. Mater. Sci. Lett.* 2000, 19, 1863–1866.
43. Nocentini, K.; Achard, P.; Biwolé, P.; Stipetic, M. Hygro-thermal properties of silica aerogel blankets dried using microwave heating for building thermal insulation. *Energy Build.* 2018, 158, 14–22.
44. Kim, Y.-G.; Kim, H.S.; Jo, S.M.; Kim, S.Y.; Yang, B.; Cho, J.; Lee, S.; Cha, J.E. Thermally insulating, fire-retardant, smokeless and flexible polyvinylidene fluoride nanofibers filled with silica aerogels. *Chem. Eng. J.* 2018, 351, 473–481.
45. Abbas, N.; Khalid, H.R.; Ban, G.; Kim, H.T.; Lee, H.-K. Silica aerogel derived from rice husk: An aggregate replacer for lightweight and thermally insulating cement-based composites. *Constr. Build. Mater.* 2019, 195, 312–322.
46. Zheng, Q.; Tian, Y.; Ye, F.; Zhou, Y.; Zhao, G. Fabrication and application of starch-based aerogel: Technical strategies. *Trends Food Sci. Technol.* 2020, 99, 608–620.
47. Abdul Khalil, H.P.S.; Yahya, E.B.; Jummaat, F.; Adnan, A.; Olaiya, N.; Rizal, S.; Abdullah, C.; Pasquini, D.; Thomas, S. Biopolymers based Aerogels: A review on revolutionary solutions for smart therapeutics delivery. *Prog. Mater. Sci.* 2022, 131, 101014.
48. Li, C.; Sun, F.; Lin, Y. Refining cocoon to prepare (N, S, and Fe) ternary-doped porous carbon aerogel as efficient catalyst for the oxygen reduction reaction in alkaline medium. *J. Power Sources* 2018, 384, 48–57.
49. Smirnova, I.; Gurikov, P. Aerogel production: Current status, research directions, and future opportunities. *J. Supercrit. Fluids* 2018, 134, 228–233.
50. Chia, H.N.; Wu, B.M. Recent advances in 3D printing of biomaterials. *J. Biol. Eng.* 2015, 9, 4.