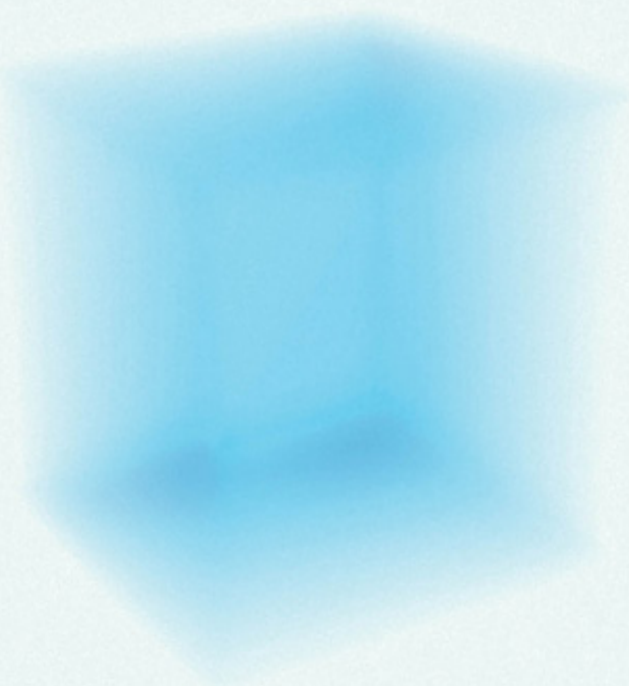


# **AEROGELS FOR ENERGY SAVING AND STORAGE**



EDITED BY **MELDIN MATHEW, HANNA J. MARIA,  
ANGE NZIHOU, AND SABU THOMAS**

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## **Aerogels for Energy Saving and Storage**



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*Edited by*

*Meldin Mathew  
Mahatma Gandhi University  
Kottayam, India*

*Hanna J. Maria  
Mahatma Gandhi University  
Kottayam, India*

*Ange Nzihou  
CNRS-IMT Mines Albi  
Occitanie, France*

*Sabu Thomas  
Mahatma Gandhi University  
Kottayam, India*

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey  
Published simultaneously in Canada

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*Library of Congress Cataloging-in-Publication Data*

Names: Mathew, Meldin, editor. | Maria, Hanna J., editor. | Nzihou, Ange, editor. | Thomas, Sabu, editor.

Title: Aerogels for energy saving and storage / edited by Meldin Mathew, Mahatma Gandhi University, Kottayam, India, Hanna J. Maria, Mahatma Gandhi University Kottayam, India, Ange Nzihou, CNRS-IMT Mines Albi, Occitanie, France, Sabu Thomas, Mahatma Gandhi University, Kottayam, India.

Description: Hoboken, New Jersey : John Wiley & Sons, Inc., [2023] | Includes index.

Identifiers: LCCN 2023024508 (print) | LCCN 2023024509 (ebook) | ISBN 9781119717638 (hardback) | ISBN 9781119717621 (adobe pdf) | ISBN 9781119717652 (epub)

Subjects: LCSH: Energy storage—Equipment and supplies. | Insulation (Heat)—Materials. | Aerogels.

Classification: LCC TK2945.A37 A38 2023 (print) | LCC TK2945.A37 (ebook) | DDC 621.402/4—dc23/eng/20240118

LC record available at <https://lcn.loc.gov/2023024508>

LC ebook record available at <https://lcn.loc.gov/2023024509>

Cover Design: Wiley

Cover Image: © dandesign86/Shutterstock

Set in 9.5/12.5pt STIXTwoText by Straive, Pondicherry, India

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## List of Contributors

### ***Golnoosh Abdeali***

Polymer Engineering Department  
Faculty of Chemical Engineering  
Tarbiat Modares University  
Tehran, Iran

### ***Basim Abu-Jdayil***

Chemical and Petroleum Engineering  
Department  
UAE University  
Al Ain, UAE

### ***Safa Ahmed***

Chemical and Petroleum Engineering  
Department  
UAE University  
Al Ain, UAE

### ***Bilkis Ajiwokewu***

Chemical and Petroleum Engineering  
Department  
UAE University  
Al Ain, UAE

### ***Ayşe Bayrakçeken Yurtcan***

Department of Chemical Engineering  
Atatürk University  
Erzurum, Turkey  
and  
Department of Nanoscience and  
Nanoengineering  
Atatürk University  
Erzurum, Turkey

### ***Elisa Belloni***

Department of Engineering  
University of Perugia  
Perugia, Italy

### ***Cinzia Buratti***

Department of Engineering  
University of Perugia  
Perugia, Italy

### ***Saheed Busura***

Chemical and Petroleum Engineering  
Department  
UAE University  
Al Ain, UAE

### ***Ai Du***

Shanghai Key Laboratory of Special  
Artificial Microstructure Materials and  
Technology  
Tongji University  
Shanghai, China  
and  
School of Physics Science and Engineering  
Tongji University  
Shanghai, China

### ***Ran Du***

School of Materials Science and  
Engineering  
Beijing Institute of Technology  
Beijing, PR China

**Piergiovanni Domenighini**

Department of Engineering  
University of Perugia  
Perugia, Italy

**Can Erkey**

Materials Science and Engineering  
Koç University  
Istanbul, Turkey  
and  
Chemical and Biological Engineering  
Koç University  
Istanbul, Turkey  
and  
Tüpraş Energy Center (KUTEM)  
Koç University  
Istanbul, Turkey

**Houssam El-Rassy**

Department of Chemistry  
American University of Beirut  
Beirut, Lebanon

**Wei Fan**

Key Laboratory of Synthetic and Biological  
Colloids, Ministry of Education  
School of Chemical and Material Engineering  
Jiangnan University  
Wuxi, PR China  
and  
State Key Laboratory for Modification of  
Chemical Fibers and Polymer Materials  
College of Materials Science and Engineering  
Donghua University  
Shanghai, PR China

**Nilay Gizli**

Chemical Engineering Department  
Ege University, İzmir, Turkey

**Mahaveer A. Halakarni**

Centre for Nano and Material Science  
Jain University  
Bangalore, India

**M. Manohara Halanur**

Centre for Nano and Material Science  
Jain University  
Bangalore, India

**Maryam Hasanpour**

Department of Chemical Engineering  
University of Bojnord  
Bojnord, Iran  
and  
Department of Mechanical Engineering  
Esfarayan University of Technology  
Esfarayan, Iran

**Mohammad Hatami**

Department of Mechanical Engineering  
Esfarayan University of Technology  
Esfarayan, Iran

**Aruchamy Kanakaraj**

Center for Nano and Material Sciences  
Jain University  
Bangalore, India

**Mahmoud Khalil**

Department of Chemistry  
American University of Beirut  
Beirut, Lebanon

**Sanna Kotrappanavar Nataraj**

Centre for Nano and Material Science  
Jain University  
Bangalore, India  
and  
Polymer Science and Engineering  
Chonnam National University  
Gwangju, South Korea

**Zili Li**

School of Information Science and  
Technology  
Fudan University  
Shanghai, China  
and  
School of Materials Science and  
Engineering  
Georgia Institute of Technology  
Atlanta, USA

**Zhiqun Lin**

School of Materials Science and  
Engineering  
Georgia Institute of Technology  
Atlanta, USA

**Tianxi Liu**

Key Laboratory of Synthetic and Biological  
Colloids, Ministry of Education  
School of Chemical and Material Engineering  
Jiangnan University  
Wuxi, PR China  
and

State Key Laboratory for Modification of  
Chemical Fibers and Polymer Materials  
College of Materials Science and Engineering  
Donghua University  
Shanghai, PR China

**Francesca Merli**

Department of Engineering  
University of Perugia  
Perugia, Italy

**Barbara Milow**

German Aerospace Center  
Linder Hoehe  
Cologne, Germany  
and  
Department of Aerogels and Aerogel  
Composites  
Institute of Materials Research, German  
Aerospace Center  
Cologne, Germany

**Özge Payanda Konuk**

Materials Science and Engineering  
Koç University  
Istanbul, Turkey

**Arun Prasad Murthy**

Department of Chemistry  
School of Advanced Sciences  
Vellore Institute of Technology  
Vellore, Tamil Nadu, India

**Ameya Rege**

Department of Aerogels and Aerogel  
Composites  
Institute of Materials Research, German  
Aerospace Center  
Cologne, Germany

**Ahmad Reza Bahramian**

Polymer Engineering Department  
Faculty of Chemical Engineering  
Tarbiat Modares University  
Tehran, Iran

**Juno A. Rose**

Center for Nano and Material Sciences  
Jain University  
Bangalore, India

**Meryem Samancı**

Department of Chemical Engineering  
Atatürk University  
Erzurum, Turkey

**Nataraj Sanna Kotrappanavar**

Center for Nano and Material Sciences  
Jain University  
Bangalore, India  
and  
Polymer Science and Engineering  
Chonnam National University  
Gwangju, South Korea

**Marina Schwan**

German Aerospace Center  
Linder Hoehe  
Cologne, Germany

**Selay Sert Çok**

Chemical Engineering Department  
Ege University, İzmir, Turkey

**Jin Tian**

State Key Laboratory for Modification of  
Chemical Fibers and Polymer Materials  
College of Materials Science and Engineering  
Donghua University  
Shanghai, PR China

**Costanza Vittoria Fiorini**

DIAEE Department of Astronautical,  
Electrical, and Energy Engineering  
“Sapienza” University of Rome  
Rome, Italy

***Chengbin Wu***

Shanghai Key Laboratory of Special Artificial  
Microstructure Materials and Technology

Tongji University

Shanghai, China

and

School of Physics Science and Engineering

Tongji University

Shanghai, China

***Orçun Yücel***

Material Technologies Department

Arçelik A.Ş., Central R&D

Istanbul, Turkey

***Michele Zinzi***

ENEA, Centro Ricerche Casaccia

Via Anguillarese

Rome, Italy

## Preface

Increasing population and high energy consumption per capita in many countries have steadily increased the global demand for energy. This follows several issues related to energy production, storage, and consumption. Recently, many industries have started to promote aerogel energy for purposeful applications, including thermal insulators, catalysis, energy storage devices, sensors, electrodes, and super capacitors. The specialties involved in aerogel technology have many possibilities to influence the scientific society by helping in research, industrial access, commercialization, and social development. Aerogels have attained worldwide attention from many research and industrial areas due to their fascinating properties – high porosity, low density, high specific surface area, and low dielectric permittivity, as well as extraordinarily low thermal conductivity. All of these special properties of aerogel are capable of promoting sustainable and successful development.

*Aerogels for Energy Saving and Storage* has huge relevance due to the efficient properties of aerogels that will satisfy multiple purposes in the future energy saving technology. The upcoming energy still exists as a question because of the progressing consumption of energy due to large population growth over the world. The energy storage, storage system, and energy consumption rate have much influence in these aspects. Aerogels offer several attractive properties for overcoming energy-related challenges.

This book discusses current and promising applications for energy-based aerogels. Chapter 1 illustrates the history and properties of aerogels in a detailed manner. The next chapter gives information about the overall outlook of aerogel in different conversion devices. Other chapters deal with aerogels based on materials such as metal, inorganic and organic materials, polymer, graphene, clay, silica, and so on. Moreover, hybrid, graphene, and CNT-based aerogels, including their applications, are detailed in other chapters. Theoretical modeling on thermal-mechanical structure and property is portrayed in Chapter 16. The book culminates with the future state of art and new challenges in aerogel research and study progression.

This is the first time such a comprehensive analysis using energy studies has been undertaken to understand the diverse applications possible with aerogels. Therefore, a reference book of this type is invaluable for recognizing the hidden possibilities of future energy and the storage in aerogel. Many industries, researchers, and students will benefit from this book because of the science-based perspective that we are offering on aerogel in future energy and storage.

Aerogel experts have been willing to share their knowledge through this book, which is of significant benefit to scientists and researchers around the world. It brings attention to new discoveries for researchers and students in the field of energy and environmental sustainability.

Of significant value, this book reviews the scientific literature published so far in order to study the energy of aerogel from the various branches of science. We cover all the advances developed from aerogels and the specialties relating their morphology, properties, processability, applications, and future perspectives.

We express our sincere thanks to the team at Wiley for their extreme support and encouragement throughout this journey. We also express our sincere thanks to the contributors who have put their maximum efforts and cooperation into the progression.

We would like to thank our parental institutions Mahatma Gandhi University, Kottayam, Kerala, India, and Institute of Mines Telecom, Albi-Carmaux, France. Moreover, we acknowledge all the reviewers and advisory experts who were involved in the successful completion of these chapters. We would like to thank our family members and motivators who stood with us and supported us. All above, we thank our Lord for his great kindness and blessings.

## 1

## The History, Physical Properties, and Energy-Related Applications of Aerogels

Ai Du<sup>1,2</sup> and Chengbin Wu<sup>1,2</sup>

<sup>1</sup>Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, Tongji University, Shanghai, 200092, China

<sup>2</sup>School of Physics Science and Engineering, Tongji University, Shanghai, 200092, China

Chinese physicist Prof. Kun Huang mentioned in his course “Solid State Physics” before 1964 that “here we only discuss the crystal, not because non-crystalline solids are unimportant but because they are over-complicated” (translated) [1]. Aerogels, normally nanoporous noncrystalline solids, exhibit numerous unique properties but are not fully understood. Among them, their physical properties are fundamental to aerogel science, which strongly affects the noncrystalline theory and related applications. The aerogel science has been booming recently. Plenty of aerogels with novel compositions, structures, properties, and applications have joined the community. Research papers and patents related to aerogels have increased sharply. A symposium mainly referring to aerogel was added to the 2017 MRS Spring Meeting & Exhibit, and two series of international conferences (International Seminar on Aerogels, and International Conference on Aerogel-Inspired Materials) and one series of regional conferences (Sino-International Symposium on Aerogels) has been held biennially. Many new findings and concepts have come to the fore but lack timely updates about the definition and theory.

Thus, in this chapter, we will briefly introduce the history, physical properties, and applications, especially for the energy-related applications. The definition of aerogels, mechanisms, and prospects will also be discussed. We hope the audience can learn something and perhaps come up with novel ideas based on the historical progress, developing theory, smart design for specific applications, and selected works in this chapter. We hope more researchers join us and paint a bright future for the aerogel science.

### 1.1 Definition and History of the Aerogels

#### 1.1.1 Basic Characteristics and Definition of Aerogels

The aerogel is a very special solid whose physics properties could be much different from its solid and gas components. One of the most notable samples is the sonic velocity in aerogels. As we know, the sound velocity through silica aerogels could be as low as  $100 \text{ m s}^{-1}$ , which is much lower than that in the dense silica ( $>5000 \text{ m s}^{-1}$ ) and the air ( $\sim 340 \text{ m s}^{-1}$ ) included. Therefore, in our

previous review, we suggested that aerogel is not only a novel material but also a new state of matter due to its unique position in the phase diagram and the diverse compositions [2].

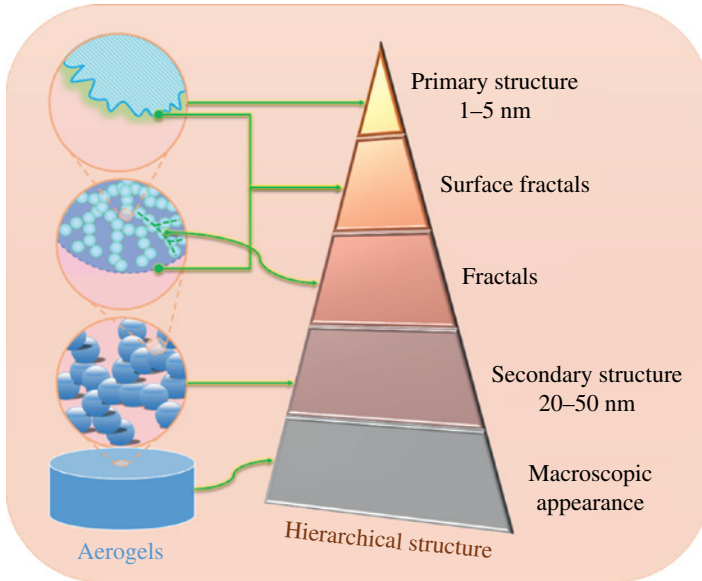
There is no uniform definition of the term *aerogel* since the concept is still developing. Traditional academicians think that aerogel is a supercritical fluid-dried gel, while the gels with freeze drying, air drying, and ambient drying without large shrinkage are regarded as cryogel, xerogel and ambigel, respectively. The public may think the classifications are complex and prefer simple and identifiable definitions. Thus, the aerogel is defined as “a light, highly porous solid formed by replacement of liquid in a gel with a gas so that the resulting solid is the same size as the original” and “a solid material of extremely low density, produced by removing the liquid component from a conventional gel” by Merriam-Webster Dictionaries and Oxford Dictionaries, respectively. These definitions indicate a wet process the aerogel has undergone and a distinctive feature of ultralight. Similarly in the *Aerogel Handbook*, Pierre applied the initial idea of Kistler to define it as the “gels in which the liquid has been replaced by air, with very moderate shrinkage of the solid network” [3]. A longer definition in Hüsing’s review (also in Ullmann’s Encyclopedia of Industrial Chemistry) designates the aerogel as the “materials in which the typical structure of the pores and the network is largely maintained . . . while the pore liquid of a gel is replaced by air.”

Recently, several studies have used the term *aerogel* to refer to the solid formed from a gel by nonsupercritical drying [4]. Thus, the academic community of aerogel science tends to approve the definition of the aerogels identified by the specific structure but not the preparation or drying method. IUPAC (international union of pure and applied chemistry) gave aerogel a definition of “gel comprised of a microporous solid in which the dispersed phase is a gas,” seeming not to mention the forming or drying method [5]. However, the word *gel* refers to a wet sol-gel process. Indeed, most aerogels reported are derived from the wet gel via a sol-gel process. Some are not, however. For example, Gao’s group developed a “sol-cryo” method to construct ultra-flyweight carbon aerogels by direct cryodesiccation of the aqueous, fluid solutions of carbon nanotubes (CNTs) and graphene oxide(GO) without undergoing the gelation process. That means the aerogel is not necessarily derived from a gel [6]. The other representative sample is that Aliev et al. developed a dry method (catalytic chemical vapor deposition) to prepare straight sidewalls of multi-walled nanotube forests and corresponding transparent carbon nanotube aerogel. The wet sol-gel process is not necessary to form an aerogel as well. Thus, in a broad sense, aerogel-related porous materials classified originally as xerogel or cryogel are gradually accepted as aerogels. Nowadays, aerogel is increasingly recognized as a matter with gel-like structure and unique characteristics, without considering the preparation or drying method.

Here, the definition of an aerogel in a broad sense should be regarded as *a state of matter whose structure is similar to the solid networks of a gel with gas or vacuum in-between* [2]. This definition ensures the aerogel in a high-vacuum environment could be still called “aerogel.” Moreover, this definition does not emphasize the wet sol-gel process but focuses on the gel-like structure. According to IUPAC, *gel* means a “non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid.” To induce the concept of gel-like structure could further avoid discussing the preparation process.

But it is not easy to describe the gel structure due to its complexity. In our opinion, as shown in Figure 1.1, a typical gel-like structure should have the following characteristics: (i) highly dispersed, coherent, and randomly distributed networks and pores that are expanded throughout its whole volume; (ii) hierarchical structure ranging from nanoscale primary structure (building blocks and pores) to its monolithic appearance; (iii) fractals in-between different hierarchies; (iv) normally composed of noncrystalline or nanocrystalline matter. Normal nanoporous powders with porosity could not be identified as the aerogel since they cannot be monolithic.





**Figure 1.1** Typical gel-like structure of aerogels.

Traditional foams or cellular solids, even though their density is ultralow, cannot be recognized as aerogels probably due to the closed pores or large primary structure. Biology-derived porous materials with fine and hierarchical structure (like woods) could not be regarded as aerogels because of their relatively ordered structure and lack of microscopic fractal features. It is worth noting that fractals are emphasized because they are usually derived from multi-body random movements of the building blocks normally limited by diffusion or reaction. The forming process, named self-organized criticality by Bak, leads to a significantly complex structure, which may be extremely important for the unique properties or special behavior of the aerogel [7].

The gel-like structure leads to some property characteristics of aerogels, such as ultralow density, ultralow thermal conductivity, ultralow modulus, ultralow refractive index, ultralow dielectric constant, ultralow sound speed, high specific surface area and ultrawide adjustable ranges of physical properties. As one frequently mentioned characteristic, apparent density of the aerogel could be lower than air density. However, ultralow density is not a necessary feature, since many kinds of aerogels show relatively high density. Also, the aerogel could be, but not necessarily, formed as a monolith. The common forms of the aerogel include thin film, granule, powder, and sheet, for example.

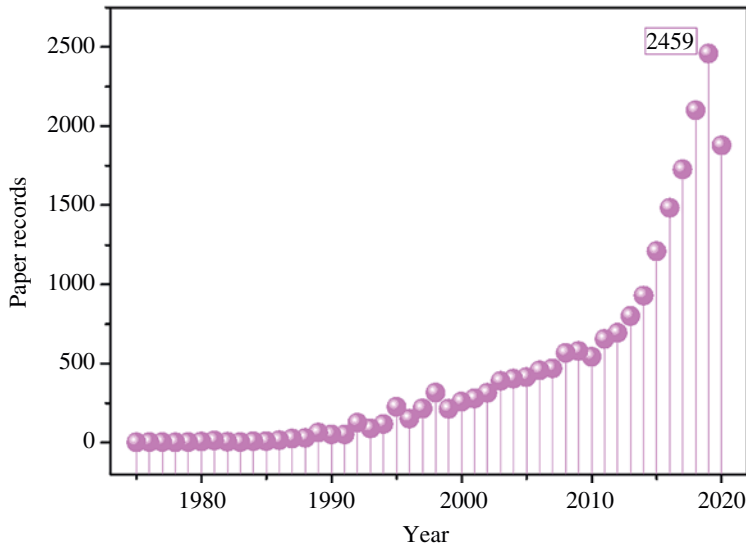
The gel-like structure could be characterized by using different characterizations, among which nitrogen adsorption/desorption and small-angle X-ray scattering (SAXS) analysis are the most powerful tools in our opinion. By using BET (Brunner–Emmet–Teller), BJH (Barrett–Joyner–Halenda), DFT (Density Functional Theory), or FHH (Frenkel–Halsey–Hill) method to treat nitrogen adsorption/desorption results, we could statistically analyze the pore structure, getting abundant information including specific surface area, pore volume, average pore size, surface interaction, pore size distribution, micropore size distribution, surface fractal dimension, and so on [8]. The fractal types and fractal dimensions in different sizes, and characteristic lengths of hierarchical structure could be statistically obtained by analyzing the intensity-wave vector relationship of SAXS results [9–12].

### 1.1.2 Brief History and Evolution of the Aerogel Science

The history of the aerogel science was introduced in detail in our previous review [2]. Here we just make a brief introduction and update. As we know, aerogel was invented and named by Kistler in 1931. The roots of “aerogel” include *aero* and *gel*, which means the wet gel replaces the liquid inside with the air without damaging its solid microstructure [13]. Although a series of different aerogels were prepared, and some fascinating properties were shown, the following research was limited before the 1970s, probably because of complex and time-consuming preparation processes [14]. After that, in the period of the 1970s and 1980s, organic precursors developed by Teichner’s group in 1968 and Russo et al. in 1986 simplified the preparation, leading to a fast development of aerogel science [15, 16]. At the same period, novel sol-gel methods and carbon dioxide supercritical fluid drying also promoted the development significantly [17]. The first and second international symposiums on aerogels (ISA) were held in 1985 and 1988, respectively. In the 1990s, the birth of organic and carbon aerogel and surface-modified ambient drying aroused broad interest from both academic and industrial communities [3, 18–20]. The third to sixth ISA continued to promote aerogel research, generating various ideas for potential applications that are still developing now. From the early twenty-first century to the present, many great achievements in aerogel science were realized. Numerous novel advances – including versatile sol-gel methods for preparing oxide aerogels, complex gradient aerogels, and ingeniously designed composite aerogels – have been developed and successfully applied in the fields of energy, environment, architecture, medicine, and aerospace [21–42]. Moreover, Brock et al. first prepared the chalcogenide aerogel via reverse micelle synthesis and supercritical fluid drying, arousing a broad interest in developing the single-component aerogels with novel composition [43–45]. After that, a series of novel aerogels, including CNT aerogel, graphene aerogel, carbide aerogel, diamond aerogel, single-element aerogels, hybrid aerogels, biomass aerogels, polymeric aerogels, and bio-inspired aerogels were added into the aerogel communities in succession [6, 41, 46–99]. In addition, the properties, applications, industrialization, and commercialization of the aerogel were widely developed in this period. Several series of academic conferences mainly concerning aerogels were held recently and produced many novel ideas.

As shown in Figure 1.2, there are 20,354 papers recorded in Science Citation Index (SCI, Web of Science WOS Core Collection) from 1975 to 2020, searching with the keyword “aerogel” or “aerogels” as the topic on October 14, 2020. The number of papers published increased sharply from 1975 to 2020. The one-year record in 2019 is 2459, higher than the total papers published during 1975–2001 (2287 in total for 27 years), showing that aerogel science has become a relatively hot topic.

Also, aerogel science becomes more and more interdisciplinary, affecting fundamental science to applied science. As shown in Figure 1.3, in the early period of 1975–1984, the top five fields include physics, instruments, nuclear science, chemistry, and electrochemistry. More than 70% of the papers belong to physics-related areas. But during 1985–1994, the proportion of physics-related areas decrease to less than one-half. Materials science and chemistry increases significantly, according to the data in Figure 1.3b. After that, the proportion of physics-related areas tends to decrease continuously, and the proportion of chemistry and materials science reaches about 50%. At the same time, engineering researches increase obviously to about one-fifth of the top five fields. To further analyze the interdisciplinarity, the “interdisciplinary index” is introduced by calculating the quotient of the total number of research areas divided by the article counts. As shown in Figure 1.4, the interdisciplinary index increased significantly from 2.18 in 1985–1994 to 4.33 from 2015 to 2020, which means that on average, each article covered 4.33 research areas during 2015–2020.



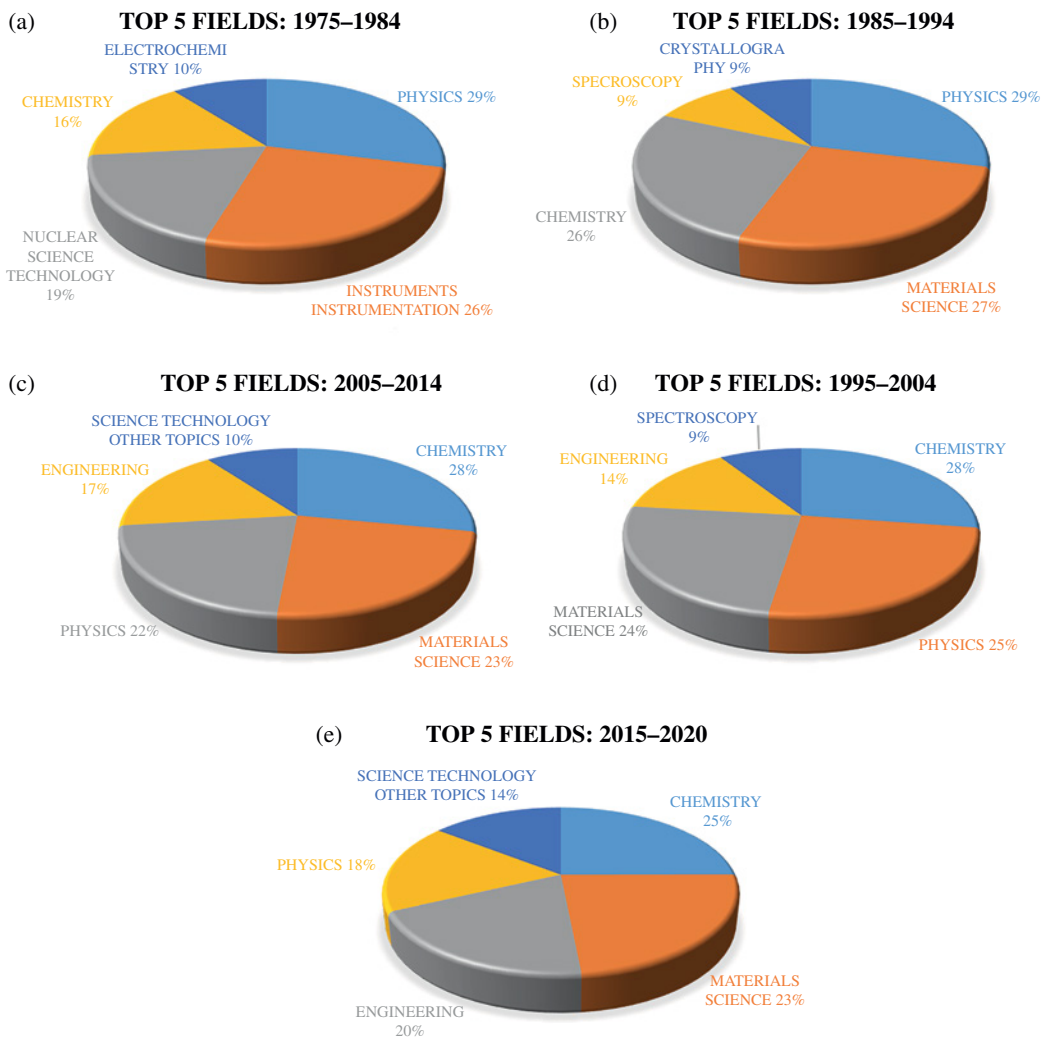
**Figure 1.2** Papers recorded in Web of Science Core Collection from 1975 to 2020.

The *Journal of Non-Crystalline Solids*, *ACS Applied Materials & Interfaces*, *Journal of Sol-Gel Science and Technology*, *RSC Advances*, *Journal of Materials Chemistry A*, *Carbon*, *Chemical Engineering Journal*, *Nuclear Instruments Methods in Physics Research Section A*, *Microporous and Mesoporous Materials*, and *Chemistry of Materials* are the top 10 journals published aerogel-related articles. Interestingly, in the early period of 1985–1994, the top 5 journals include *Journal of Non-Crystalline Solids*, *Journal de Physique*, *Physical Review Letters*, *Physical Review B*, and *Journal of Sol-Gel Science and Technology*, in which the physics-related researches dominate. However, from 2018 to 2020, the top 5 journals changed to *ACS Applied Materials & Interfaces*, *Chemical Engineering Journal*, *Journal of Materials Chemistry A*, *Carbon* and *Carbohydrate Polymers*, in which the chemistry-related researches dominate. *Journal of Non-Crystalline Solids* ranks over 30 during 2018–2020, indicating a dramatic change in aerogel science. The average number of citations per paper is 26.6, according to the data from WOS core collection. High average citations and wide distribution of frequent journals indicate that aerogel research has gotten broad attention. More and more scientists, engineers, businesspeople, investors, government officers, and the public pay close attention to the aerogel field, which ensures a bright future of aerogel science.

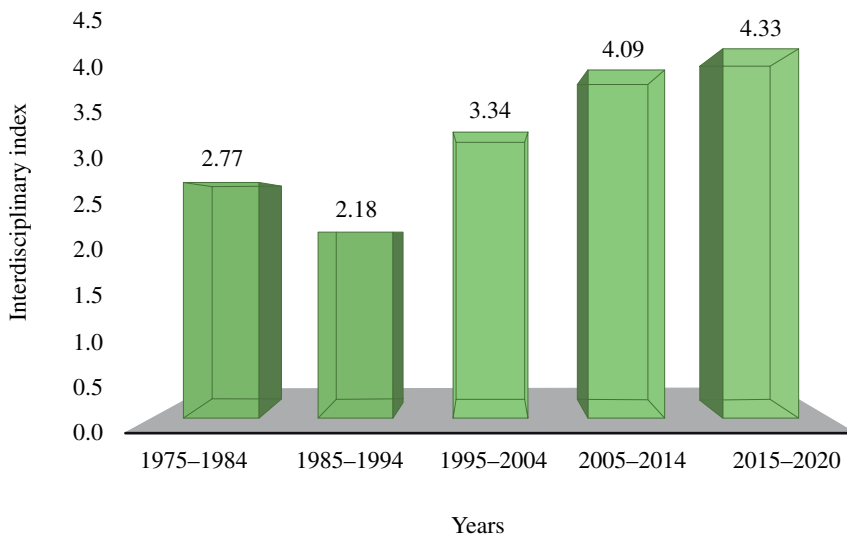
## 1.2 The Physics Properties of the Aerogels

One of the most fascinating things of aerogels lies in their unique properties. According to incomplete statistics, there are more than 10 property records held by silica aerogels among solid state matter, including lowest reflective index, lowest sound speed, lowest modulus, lowest dielectric constant, and broadest adjustable range of several kinds of properties. Today the records may be refreshed by other materials, but most of them are other kinds of aerogels. Thus, aerogels are truly interesting materials, worth being regarded as a new state of matter [2].

Here we will briefly update the physics properties of the aerogels, including the mechanical, thermal, optical, electrical, and acoustic properties. We will focus on the discussion about why the



**Figure 1.3** Top five field distributions during (a) 1975–1984, (b) 1985–1994, (c) 1995–2004, (d) 2005–2014, and (e) 2015–2020.



**Figure 1.4** Interdisciplinary index of aerogel science during different periods.

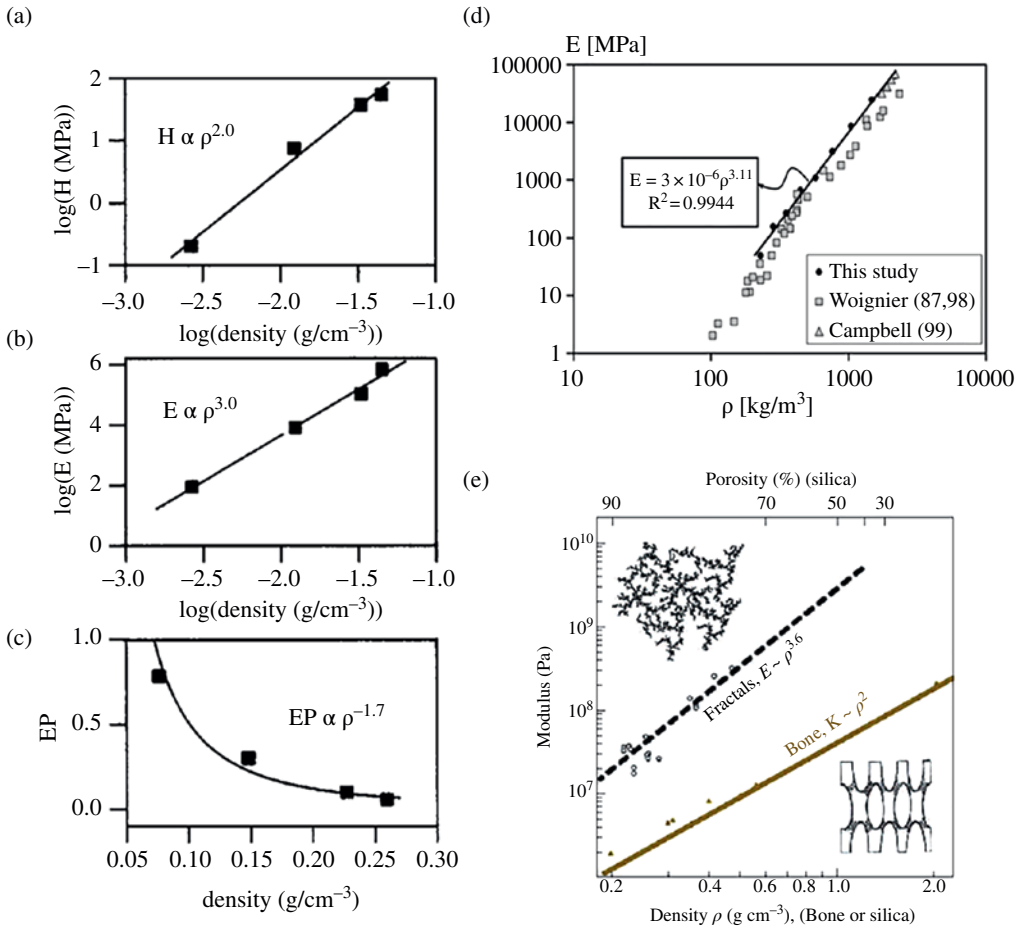
different kinds of aerogels exhibit unique properties and attempt to clarify the relationship between the microstructure and properties. Since there are far too many studies about the different properties, only the most relevant works will be chosen for this chapter. Most of them relate to aerogels with a single component but not composites in order to give a simple physical picture and possible mechanism.

### 1.2.1 Mechanical Properties

Nanoporous structure is one of the characteristics of aerogels [3], and porosity over 90% gives the aerogel many unique characteristics. The first one is the extremely low density. The apparent density of silica aerogel can be as low as  $1\text{--}3\text{ mg cm}^{-3}$ , which is close to the density of air [100]. It is possible to prepare aerogels with even lower density. Mecklenburg et al. prepared an aerogel-like materials called aerographite by depositing carbon on an adjustable ZnO template [101]. The metal Zn reduced by hydrogen gas evaporates and leaves an ultralight aerographite with the lowest density of  $0.18\text{ mg cm}^{-3}$ . Gao's group even developed an all-carbon aerogel with the lowest density of  $0.16\text{ mg cm}^{-3}$  by directly freeze-drying aqueous solutions of CNTs and giant graphene oxide sheets [6]. The aerogel is currently the lowest-density solid, and its density can be normally determined by the ratio of reagents and the shrinkage ratio. The adjustable range of density and relative properties are quite broad, which could be designed in the ingenious gradient density aerogel [102]. Aerogels also have the properties of large specific surface area, good macroscopic uniformity, and strong doping adsorption capacity mainly due to its nanoscale structure and ultralow density.

However, the ultralow density leads to some characteristics, among which mechanical properties are unique. Normally, the aerogels are ultra-soft (low modulus) and extremely fragile, which may limit their applications. Thus, the mechanical properties of aerogels are of great concern. The mechanical performance could be evaluated from different aspects, such as tensile strength, bending strength, impact strength, and hardness. It is not hard to understand that these mechanical properties are closely related to the density of the aerogel. Due to the brittleness of the nanoporous structure and framework particles, the aerogel has low rigidity, high brittleness, and low tensile and compressive strength, and these mechanical properties are highly dependent on density. Studies have shown that there is a power function relationship between mechanical parameters such as Young's modulus, hardness, and the elastic parameters (EP) of silica aerogels, and density [103]. In one study, silica gels were produced by hydrolysis and polycondensation of tetramethoxysilane (TMOS) diluted in acetone in a one-step synthesis mode, and dried by supercritical drying method. Figure 1.5 shows that the low-density aerogels are more elastic, while the high-density aerogels are more rigid [104, 105]. In lower densities, within a range of  $80\text{--}150\text{ kg m}^{-3}$ , the silica aerogels can withstand up to 70% of the compressive strain and restore to the original volume; at higher densities, they tend to break under small strains and exhibit glass-like behavior [106]. To understand the viscoelastic behavior of the aerogels, DMA/DMTA (dynamic mechanical analysis or dynamic mechanical thermal analysis) is one of the most commonly used methods. DMA/DMTA can be used to measure the storage modulus, loss modulus, and loss factor, which are three important factors of dynamic mechanical properties [107]. Tensile or compressive testing is another widely used method, by which the Young's modulus, tensile strength, and elongation at break can be measured.

There is a well-known scaling law between the modulus and density of silica aerogels. The exponent could be larger than 3, which means the modulus of the aerogels could be much lower than that of other porous materials or cellular solids [108, 109]. Brinker et al. mentioned that the ultra-high modulus-density scaling exponents ( $\sim 3.6$ ) of the silica aerogels may be due to dangling



**Figure 1.5** (a) Hardness, (b) Young's modulus, and (c) elastic parameters of the aerogel with different density [103] / with permission of AIP Publishing; (d) simulated elastic modulus vs. density for silica aerogels [106] / with permission of Elsevier; (e) modulus-density scaling relationships of highly porous gels and human bone [107] / With permission of Springer Nature.

skeletons without load bearing [105]. This explanation may be the best understanding about the ultralow modulus of the silica aerogel and ultralow sound speed from the statics. However, there must be a special mechanism of the scaling law, but not the other forms like linear or just positively related. Murillo et al. simulated the density-modulus relationship of the modeled silica aerogels and obtained the exponent larger than 3 (3.11) [104]. It was nice data, which approximately coincided with the experimental results. However, the study lacks enough evidence for structural similarity between the silica aerogels and the model samples formed through 3000 K thermal treatment and cooling down of  $\beta$ -cristobalite. There is still no study considering the microscopic mechanism of the scaling law.

Researchers have done fruitful works in enhancing the mechanical properties of aerogels. One commonly adopted method is to design fiber-enhanced doped aerogel composites [110]. The brittleness of the silica aerogel can be traced to the weak interparticle connecting zones. Therefore, it is reasonable to enhance the interparticle connection to improve the toughness of aerogels. In this respect, to bridge the nanoparticles could improve the mechanical properties and behaviors of