論文の内容の要旨

論文題目　Ultrastrong and Superelastic Nanolaminate Aerogels
（ナノ層状構造に基づく超剛性かつ超弾性のエアロゲル）

氏　名　孫　志方

Introduction

Aerogels are lightweight, 3D nanoporous materials composed mostly of air. Since the first report of aerogel in 1931, the unique structures and properties of aerogels have attracted great attention from material fields. Furthermore, the extremely low thermal conductivity of aerogels promises their application as ecofriendly insulation materials to replace the petroleum-based polymer foams, which would greatly contribute to the realization of sustainable society. However, conventional aerogels are generally very weak and brittle. The aerogel networks are usually composed of interconnected hard nanoparticles, and upon compression, cracks can be generated and quickly propagate in the networks, leading to the collapse of aerogels. In the field of aerogel, mechanical strength and elasticity are two important factors that determine their performance and applications; however, these two properties are mutually exclusive and thus far remaining a ground challenge to simultaneously achieve.

As represented by nacres and bones, many biological materials in nature exhibit exceptional toughness, although they are mainly composed of brittle components. The key design principle of such biomaterials is hierarchical nanolaminated structure, which efficiently suppresses the crack propagation and enhances the toughness. Inspired by such biological materials, the author hypothesized that aerogel networks can be likewise strengthened by nanolaminated structures. Recently, Aida *et al.* found that an aqueous dispersion of atomically thin 2D crystals, titanate nanosheets (TiNSs), can be cofacially aligned in a magnetic field to form confined nanolaminated structures. Using the nanolaminate confinements of TiNS, the author developed two kinds of nanolaminate aerogels, MS/TiNS$^{\mathrm{lam}}$ and MS$^{\mathrm{lam}}$. The MS/TiNS$^{\mathrm{lam}}$ aerogel exhibited unprecedentedly excellent mechanical properties, with simultaneously realizing ultrahigh compressive strength (>55 MPa) and superelasticity (elastic strain >80%) as well as excellent fatigue resistance (>100 cycles of 80% strain), which would be described in detail in Chapter 1. Another type of nanolaminated aerogel, MS$^{\mathrm{lam}}$ aerogel, exhibited even remarkable mechanical properties, which could be compressed up to 95% strain without losing its elasticity, where the stress reached to no less than 147 MPa. The details are described in Chapter 2.

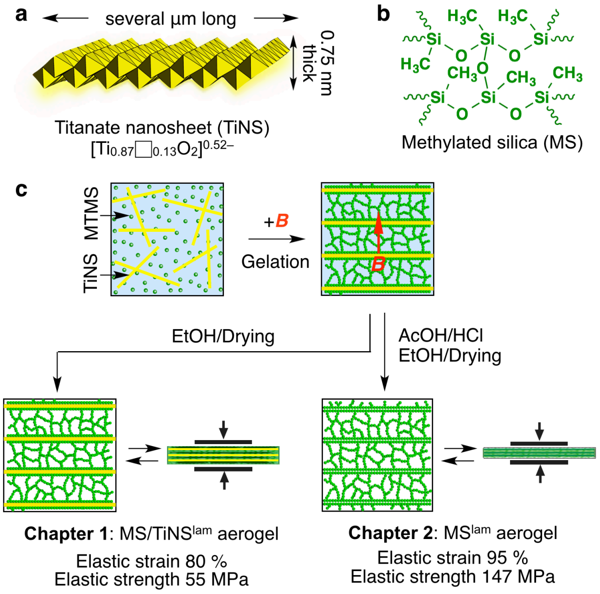

Figure 1. Schematic representation for the preparation of the ultrastrong and superelastic nanolaminate aerogels: (1) MS/TiNS$^{\mathrm{lam}}$ aerogel and (2) MS$^{\mathrm{lam}}$ aerogel.

Chapter 1. Development of Nanolaminate Aerogels Containing Titanate Nanosheets

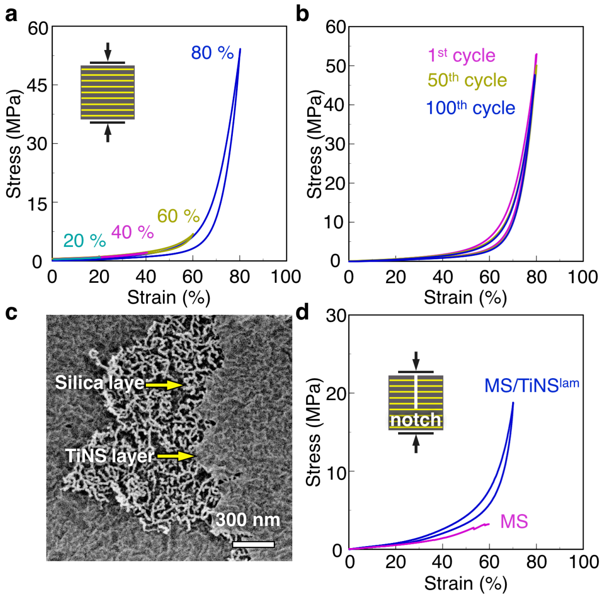

Figure 2. (a) Stress-strain curves of MS/TiNS^{lam} aerogel at various strains. (b) Stress-strain curves of selected cycles during repeated compression to 80% of MS/TiNS^{lam} aerogel. (c) SEM image of MS/TiNS^{lam} aerogel. (d) Stress-strain curves of notched aerogels.

Nanolaminate structures are ubiquitous in nature, such as nacres, bones and plants, which can effectively toughen the materials and make them crack-resistant. The author obtained inspiration from these biological materials to use the nanolaminate structure for toughening aerogels. As described in the introduction part, TiNSs dispersed in water can be cofacially aligned in a magnetic field to form nanolaminated confined spaces with a regular thickness of ~100 nm. On the other hand, it was recently reported that methylated silica aerogels (MS) made from a trifunctional silica source (methyltrimethoxysilane; MTMS) show much higher flexibility compared with the conventional silica aerogels made from tetrafunctional silica sources (*e.g.* TEOS). In the present study, the author attempted to form the nanolaminated MS network by polycondensation of MTMS within the confined spaces between magnetically oriented TiNSs in water to afford an MS/TiNS^{lam} hydrogel. Through solvent exchange with ethanol and supercritical CO$_2$ drying, MS/TiNS^{lam} hydrogel was converted into MS/TiSN^{lam} aerogel. As references, the corresponding aerogels without TiNS (MS aerogel) and with randomly oriented TiNSs (MS/TiNS^{ran} aerogel) were likewise prepared, by omitting the addition of TiNSs and the application of the magnetic field, respectively. All the aerogels show characteristic properties of usual aerogels, such as low density (0.18 g cm^{-3}), high porosity (>90%), and high surface area (~430 m^2 g^{-1}).

The compression tests revealed that MS/TiNS^{lam} aerogel show excellent mechanical properties toward compression. When a mechanical force was applied in the direction orthogonal to the TiNS plane, MS/TiNS^{lam} could be compressed up to 95% without fracture, and remained partially elastic and sprang back to ~50% of its original length when released from the compression. This observation motivated the author to estimate the strain region for MS/TiNS^{lam} aerogel to undergo perfectly elastic deformation. It was found that MS/TiNS^{lam} aerogel was perfectly elastic up to 80% strain (Figure 2a). Worth noting is that the stress at 80% strain reached to no less than 55 MPa, which is two orders of magnitude higher than the state-of-the-art elastic aerogels based on carbon materials, and *ca.* 4 times larger than MS aerogel. Furthermore, upon repeated compression, MS/TiNS^{lam} aerogel showed excellent fatigue-resistance. Even after 100 cycles of compression up to 80% strain, the maximum stress decreased only by 9% from the original value, and only 1.9% of plastic deformation occurred (Figure 2b).

The excellent fatigue resistance of MS/TiNS^{lam} aerogel might be attributed to the nanolaminated structure, which is generally known to efficiently dissipate energy and suppress crack propagation. As shown in Figure 2c, the SEM image of the MS/TiNS^{lam} aerogel taken from the out-of-plane direction clearly shows the alternate silica and TiNS nanolaminates. These nanolaminate structures are very similar to that of natural materials, such as nacres, bones and woods, which can efficiently suppress the propagation of cracks and also enhance the interfacial interactions between building blocks, leading to the toughening of materials. Bearing this in mind, the author investigated the notch tolerance of the MS/TiNS^{lam} aerogel. As shown in

Figure 2d, the notched sample of MS/TiNS^{lam} aerogel could be compressed to 70% and fully sprang back, showing maximum stress of 18.7 MPa. Collapse of the sample started to occur only when the applied strain was increased to 80%. In sharp contrast, notched MS aerogel fractured when compressed to 60% strain, with a low stress of 3.2 MPa. These results clearly demonstrate that the MS/TiNS^{lam} aerogel exhibits excellent crack tolerance. Thus, it can be concluded that alternate nanolaminates of silica network and TiNSs can synergistically strengthen the network and sufficiently suppress the crack propagation once generated inside.

Chapter 2. Development of Nanolaminate Aerogels Free of Titanate Nanosheets

In Chapter 1, the author demonstrated that the alternate nanolaminates of silica network and TiNSs can synergistically strengthen the composites aerogel, making it ultrastrong and superelastic. However, several points are still elusive, such as the role of silica nanolaminate and the structural differences between the silica networks of MS and MS/TiNS^{lam} aerogels. The author envisioned that, if the TiNS in the MS/TiNS^{lam} aerogel can be selectively etched, the resultant material would be helpful to understand the mechanism on how the silica nanolaminates affect the mechanical properties in the MS/TiNS^{lam} aerogels. Bearing this in mind, the author discovered a method, using corrosive acid (CH_3CO_2H:HCl = 9:1, v/v), to selectively dissolve TiNSs in MS/TiNS^{lam} hydrogel. After repeated washing with ethanol and supercritical drying, a nanolaminate aerogel composed of only MS, named as MS^{lam} aerogel, can be prepared.

Cyclic compression tests of MS^{lam} aerogel were conducted at varying strain ranges from 0–65%, 0–80% and 0–95%. To our surprise, the MS^{lam} aerogel underwent perfectly elastic deformation up to 95% strain and fully sprang back to its original shape when released from the compressive force (Figure 3a). Such a large elastic strain region has never been observed before for nanoporous materials (Figure 3b). Furthermore, the maximum stress applicable to MS^{lam} aerogel (at 95% strain) reaches to 147 MPa, which is one order higher than MS aerogels (at 80% strain) and around 3 times larger than the MS/TiNS^{lam} aerogel (at 80% strain). Repeated cyclic compression tests suggested that MS^{lam} aerogel is highly durable to this ultralarge strain, and retain 95% of its maximum stress after 10 cycles (Figure 3c and 3d). The absorbed energy per cycle of MS^{lam} aerogel was 8 times larger than MS aeroegel and 3 times larger than MS/TiNS^{lam} aerogel. Thus, by using nanolaminated structure, the author developed an unprecedented aerogel composed solely of silica, which exhibit both ultrahigh strength and superelasticity never achieved before. Considering the porosity and density of the aerogel, the compressive strain of 95% is close to the theoretical limit. Thus, upon compression to 95% strain, the aerogel becomes like monolithic solids, in terms of porosity and density. The perfect spring back from such a condensed state is quite surprising.

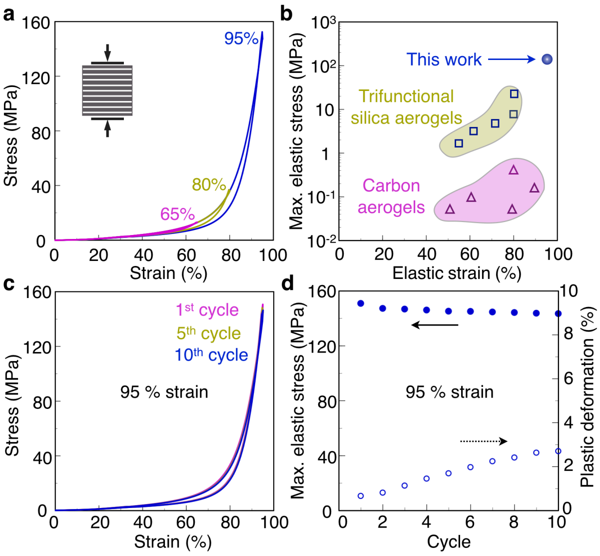

Figure 3. (a) Stress-strain curves of MS^{lam} aerogel at various strains. (b) Ashby chart plotting maximum elastic stress versus maximum elastic strain for the MS^{lam} and other previously reported aerogels. (c) Stress-strain curves of the selected cycles during repeated compression to 95% of the MS^{lam} aerogel. (d) History of maximum elastic stress and plastic deformation for the MS^{lam} aerogel during repeated compression at 80% strain.

Why the nanolaminate aerogel has simultaneously high compressive strength and high elastic strain? To address this issue, the author systematically investigated the structural characteristics of the MS^{lam} aerogels. During the sol-gel process of the MS/$TiNS^{lam}$ gel, polycondensation takes place within the confined spaces of the TiNS nanolaminates, in which the distance is 90 nm. Because the tetramethylammonium counterions on the TiNS can catalyze the polycondensation of silica, a MS layer first grows onto the TiNS, and further polycondensation proceeds to fill the remaining confinements of 60 nm, which can only accept 4 MS particles. Thus, numerous struts formed, which can be regarded as the pillars (Figure 4a). Upon compression of MS^{lam} aerogel, the nano-pillars can enhance the modulus, and longer silica nanofibers has less structural defects to initiate the cracks. Even some cracks generated inside the MS^{lam} network, the nanolaminate structure can efficiently suppress its propagation, making the MS^{lam} aerogel superelastic (Figure 4b). To further prove the role of silica nanolaminates, morphology of the MS^{lam} aerogel was investigated by SEM before and after compression to 95% strain. Before compression, MS^{lam} aerogel had a well-connected, continuous long nanofibrillar network (Figure 4c). After compression by 95% strain, the network remained intact and showed no notable difference (Figure 4d). The excellent mechanical properties of MS^{lam} aerogel is attributable to such continuous network with less structural defects, which might be originated from the template effects of the TiNSs during the *in situ* hydrogelation of silica. Therefore, the key to these outstanding mechanical performances is the nanolaminate structures of the silica network, which can sufficiently suppress the crack propagation once generated inside the aerogel networks.

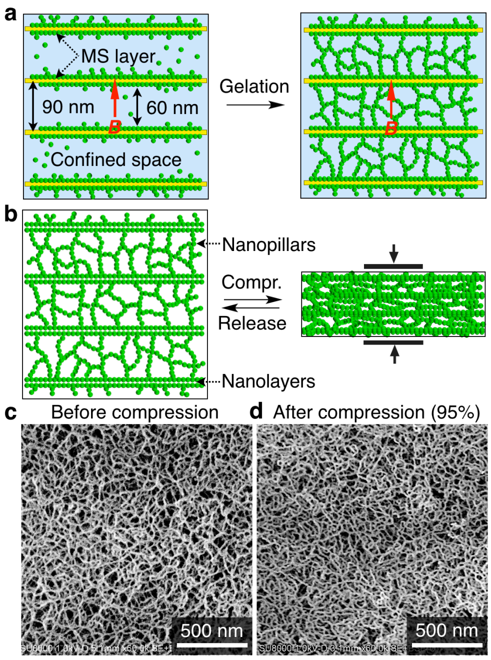

Figure 4. (a) The growth and gelation of silica network during the sol-gel process of the MS^{lam} gel. (b) Upon compression, silica struts confined in nanolaminates efficiently boost the modulus, and cracks can be suppressed by the MS nanolaminates. (c,d) SEM images of the MS^{lam} aerogel before (c) and after (d) being compressed by 95% strain.

Summary

The author succeeded in developing unprecedented nanolaminate aerogels with concurrent ultrahigh strength and ultralarge elasticity, as well as excellent fatigue resistance. Besides, in contrast to conventional silica network, the nanolaminate aerogels can retain excellent mechanical properties even when notched. Furthermore, the nanolaminated aerogels can retain all the excellent intrinsic properties characteristic of silica aerogels, such as low-density, high porosity, high surface area and low thermal conductivity. The present discoveries are significantly important in the following aspects: (i) Utility of nanolaminate structures for toughening materials is clarified. (ii) An exception is posed for the preconceived notion that high strength and high elasticity are trade-off for low-density materials. (iii) General problems of aerogels that hamper their practical use are shown to be resolved by proper material design.