The design and investigation of hydrogel-based metamaterials with ultra large negative hygroscopic expansion ratio

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ABSTRACT

A design strategy for a mechanical metamaterial with large negative hygroscopic expansion (NHE) was proposed in this paper. Different from the reported structures, the present metamaterial is designed by constructing repeated lattice microstructure consisting of curved ligaments incorporating hydrogel active layers and polymer support layers and straight polymer bars. When immersed in the solution environment, the swelling of hydrogel layer of such composite structure induces the reversed bending of the ligament, leading to the overall ultra-large shrink (negative expansion) deformation of the metamaterial. Through the new structural design, large NHE effects can be achieved. The theoretical investigation and finite element analysis (FEA) were conducted to demonstrate the large negative expansion effects of such metamaterial. The results showed that the effective NHE ratio of the metamaterial is dependent on the curvature of the curved ligament and the size of both the ligament and the connecting rod. The ultra-large NHE ratios about −80% for the 2D structure and −90% for the 3D version can be obtained by adopting the structural parameters. The newly designed metamaterials have potential applications in medical and other fields.

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1. Introduction

Metamaterials, also known as structured materials, are artificially designed periodic or aperiodic structures with abnormal mechanical and physical properties, such as negative Poisson’s ratio (NPR) materials, negative thermal expansion (NTE) materials and negative hygroscopic expansion (NHE) materials. Those metamaterials have broad applications in many engineering fields [1–3]. The NPR metamaterials exhibit transverse expansion when it is stretched longitudinally, and transverse compression when it is compressed longitudinally. These abnormal deformation forms are dominated by applied external forces [4–6], which limit the use of metamaterials in self-driven fields such as tissue engineering [7], soft robotics [8] and biosensing [9]. The NTE and NHE effects of metamaterials are usually realized by environmental stimuli. The NTE metamaterials contract with increasing temperature, or expand with decreasing temperature. The early studies for the design of NTE metamaterials can be traced to 1995, Lakes [10] innovatively designed a 2D cellular structure and found that arbitrarily high thermal expansion coefficients could be obtained by designing cellular solid constructed by bilayer-ed structures with different expansion coefficients. Wu et al. [11] designed several antichiral structure-based 2D/3D NTE metamaterials and investigated the relationship between the geometry of the structure and the effective coefficient of NTE, proving a new method for obtaining tunable NTE metamaterials. Parsons et al. [12] designed and fabricated cellular metal composites
with tunable thermal expansion and optimized their specific stiffness. Li et al. [13] proposed two novel metastructures exhibiting auxetic behavior by designing a special unit cell, by which NTE and NPR can be realized simultaneously. Liu et al. [3] presented a new bucking-based mechanism to induce effective negative swelling effects and designed a new NTE soft metamaterial. The same design principles can be extended to different materials and stimuli such as pH and light.

Hydrogels are soft reactive materials with an extremely hydrophilic 3D network structure that swells rapidly in solution environment. Due to the hygroscopic expansion capacity, hydrogels have been widely applied in biomedicine [14], tissue engineering [15], precision instrument [16,17], agriculture [18] and other fields. The NHE metamaterials can be designed by using the swelling or shrinking capacity of hydrogels when exposed to solution environment. Hydrogel-based NHE metamaterials are specially designed structures, which contract with absorbing solvents, or expand with losing solvents. Ji et al. [19] prepared hydrogel-based structures with complex and controllable shape deformations by introducing secondary grooves on one side of featured structures, resulting in the bending or torsional deformation due to the asymmetric expansion. Zhang et al. [20] designed a class of soft mechanical metamaterials consisting of periodically distributed triangular lattices by introducing horseshoe-shaped composite microstructures composed of hydrogel and passive materials, and their NHE behaviors are produced by converting the hydrodynamic swelling deformation of the hydrogel layer into a bending deformation of the sandwiched configuration. Inspired by such design, Wei et al. [21] developed new 2D and 3D NHE hydrogel-based metamaterials by respectively designing tetragonal and cubical lattices and examined the deformation mechanism by finite element simulation and theoretical analysis. In addition to the self-driven bending-based design of the ligaments, the NHE effects can be achieved by fluid exchange inside and outside the hydrogel cell [22]. The NHE metamaterials have great potential for drug delivery, biocompatible stents, molecular sieves and other applications.

From the previous studies, the effective shrink linear strains of the existing NHE metamaterials are lower than 50% [20,21], and the metamaterials with relatively large shrink strain are seldom reported. Hence, the development of new metamaterials with a large NHE coefficient still remains a challenge. In this work, we proposed a new design strategy for soft hydrogel-based metamaterials with large NHE. The deformation behavior of the present metamaterial from 2D and 3D were carried out by theoretical analysis and finite element simulations. The results showed that the desired NHE deformations of the proposed metamaterials can be customized by tailoring the geometric parameters of the lattice microstructures.

2. Structural design and deformation analysis

2.1. Design concept and deformation principle

Inspired by the hydrogel swelling capacity and self-driven deformation mechanism of curved bilayer, a solution-driven hydrogel-based NHE multilevel structure was designed. Figure 1 illustrates the designed strategy of the soft network composite and presents a schematic illustration for the NHE deformation. The investigated structure is constructed in a periodic 2D inclined squared lattice configuration, as shown in Figure 1(a), and the
repeated microstructural unit cells (Figure 1(b)) consisting of four curved ligaments are connected by straight bars (dark blue) to form the entire network. As the active element, the curved ligament consists of active hydrogel layer (green) and relatively long passive polymer layer and the active layer is bonded to the middle of passive layer, as shown in Figure 1(c). When immersed in the solution, the hydrogel layers absorb solvents to induce the swelling deformations which can be converted into the mechanical deformation and reversed bending of ligaments (Figure 1(d)), resulting in the volume shrink of the lattice microstructure (Figure 1(e)). Finally, the effective NHE (volume shrink) of the entire network is produced, as shown in Figure 1(f). It is noted that the swelling-induced reverse bending of the bi-layered ligament requires that the hydrogel layer is well bonded to the polymer layer. In reality, two approaches are commonly adopted to ensure the perfect bonding of the hydrogel/polymer layer during the swelling-induced deformation process. The first method is to glue the two layers directly by a strong interface. For example, Zhou et al. [23] fabricated a hydrogel/elastomer bi-layered structure consisting of hygroscopic polyacrylamide (PAAm) layer and water-insensitive polydimethylsiloxane (PDMS) layer, and investigated the effect of intrinsic mechanical properties of the hydrogel on the resulting curvature. In their study, the hydrogel is strongly adhered to the polymer by Benzophenone. As an alternative approach, the perfect bonding between hydrogel and polymer layer can be achieved by constructing a special hydrogel-based composite structure where the hydrogel is encapsulated by a thin grooved elastomer membrane, ensuring the strong connection of the two layers [20,21].

For the metamaterials, the effective NHE ratios can be flexibly adjusted by tuning the design parameters of the lattice microstructure to meet specific requirements.
For the following mechanical analysis and finite element simulation, according to the work of Zhang et al. [20], the representative elastic modulus of the hydrogel and polymer layers are respectively 0.2 MPa and 65MPa, and the corresponding Poisson’s ratio are adopted by 0.5 and 0.4, respectively. Figure 2 illustrates the geometry evolution and structural parameters of a representative ligament with free-end driven by hydrogel swelling. Under the stimuli of experimental solution, the initially curved ligament with curvature radius $r_0$ (Figure 2(a)) is deformed to an equilibrated configuration with relatively large curvature radius (Figure 2(b)). It is noted that the equilibrated configuration with reversed bending mode (Figure 2(c)) is also possibly achieved as long as specific conditions are satisfied. From the geometry evolution of the ligaments, it is easily to observe that the magnitude of bending angle $\alpha$ is decreased for the equilibrated configuration with forward bending, whereas the angle evolves to a negative value for the equilibrated configuration with reversed bending.

For convenience, it is assumed that the lengths of both the active and the passive layers remain constant after swelling deformation. The curvature radius of the deformed ligament is given by [20]

$$r = \frac{1 + \left(\frac{E_h}{E_p}\right)^2 \left(\frac{h_h}{h_p}\right)^4 + 2 \frac{E_h}{E_p} \left(\frac{h_h}{h_p}\right)^2 \left(2 \left(\frac{h_h}{h_p}\right)^2 + 3 \frac{h_h}{h_p} + 2\right)}{1 + \left(\frac{E_h}{E_p}\right)^2 \left(\frac{h_h}{h_p}\right)^4 + 2 \frac{E_h}{E_p} \left(\frac{h_h}{h_p}\right)^2 \left(2 \left(\frac{h_h}{h_p}\right)^2 + 3 \frac{h_h}{h_p} + 2 + 3 \left(1 + \frac{h_h}{h_p}\right) \frac{h_h}{h_p} \varepsilon_h\right)} r_0 \quad (1)$$

where $E_h, h_h, E_p$ and $h_p$ are elastic modulus and thickness of hydrogel and polymer layer, respectively. $\varepsilon_h, r_0$ and $r$ are the strain of hydrogel, the initial bending radius and bending radius of the deformed ligament, respectively.

(a) Initial curved configuration with curvature radius $r_0$; (b) Equilibrated configuration with forward bending; (c) Equilibrated configuration with reversed bending

Inspired by the bending mechanism of hydrogel-polymer bilayer-ed ligament in aqueous solution and the deformation principle of the reentrant auxetic structures, a specific lattice microstructure with NHE effect was designed. Figure 3 illustrates the designed microstructure, structural parameters and geometry evolution. The new design is an improvement compared to the unit cells reported in [21]. The polymer layers of the lattice are denoted by dark blue, and hydrogel driving layers are represented by green, as indicated in Figure 3.

Figure 2. The schematic illustration of geometry evolution and structural parameters of the ligament with free-end. (Active hydrogel layer, green; Passive polymer layer, blue).
Figure 3. The schematic illustration of the microstructure, structural parameters and geometry evolution of the microstructural lattice (Active hydrogel layer, green, thickness $t_2 = 0.4$ mm; Passive polymer layer, blue, thickness $t_1 = 0.6$ mm; out-of-plane width $t = 1$ mm). (a) Initial configuration; (b) Equilibrated configuration with forward bending of ligaments; (c) Equilibrated configuration with reversed bending of ligaments.

Similar to the geometry evolution of ligament with free-end (Figure 2), the lattice microstructure (Figure 3(a)) may be deformed to an equilibrated configuration with forward bending of ligaments (Figure 3(b)), accompanied with the relatively large curvature radii of the ligaments under the stimuli of solution. In addition, the equilibrated configuration with reversed bending of ligaments (Figure 3(c)) is also possibly achieved when the swelling actuation is sufficiently large.

The structural parameters of the lattice microstructure in the initial configuration depicted in Figure 3(a) are defined as follows. $L_0$ is the initial distance between the two ends of the ligament, $H_0$ is the initial distance between the end of the ligament and the apex of the ligament, $b$ represents the length of the straight bar, $d_0$ denotes the distance between the end of the ligament and the adjacent end of the active hydrogel layer, $l_0$ denotes the initial distance of the microstructure lattice in vertical or horizontal direction. The bending angle of the curved hydrogel layer is initially set to 90°($\frac{\pi}{2}$). For the sake of discussion in what follows, the sum of $d_0$ and $r_0$ is denoted by $D_0$. As seen from Figure 3(a), once $D_0$ and $r_0$ are assigned in the design, the structural parameters ($H_0$, $L_0$, $l_0$) can be readily obtained respectively.

$$H_0 = \left(1 - \frac{1}{2}\right)r_0 + \frac{\sqrt{2}}{2}D_0 \quad (2)$$

$$L_0 = \sqrt{2}D_0 \quad (3)$$

$$l_0 = 2b + 2H_0 + L_0 \quad (4)$$

For the designed metamaterial, with a certain of solvents imbibition into the hydrogel layer, the microstructural lattice may be deformed to an equilibrated configuration with forward bending of ligaments where the initial structural parameters ($L_0$, $H_0$, $l_0$) evolve to ($H_1$, $L_1$, $l_1$) which are respectively given by

$$H_1 = h_1 + h_2 \quad (5)$$
In Equations (5)-(7), \( h_1 \) is the vertical projection length of the active layer, \( h_2 \) is the difference between the vertical projection length of the entire ligament and the vertical projection length of the active layer, \( r_1 \) is the bending radius of the deformed ligament in equilibrated configuration with forward bending of ligaments, \( \theta_1 \) is the bending angle of the deformed ligament in equilibrated configuration with forward bending of ligaments.

In this situation, the effective linear strain \( \varepsilon_1 \) of the lattice microstructure is formulated as

\[
\varepsilon_1 = \frac{l_1 - l_0}{l_0} = \frac{2 \left[ b + r_1 \left( 1 - \cos \frac{\theta_1}{2} \right) + \frac{4(D_0 - r_0)}{\pi - 2\theta_1} \left( \cos \frac{\theta_1}{2} - \frac{\sqrt{2}}{2} \right) \left( 1 + \frac{1}{\tan \left( \frac{\theta_1}{4} + \frac{\pi}{8} \right)} \right) + r_1 \sin \frac{\theta_1}{2} \right]}{2b + 2 \left( \sqrt{2D_0} + (1 - \sqrt{2})r_0 \right)} - 1
\]

The final equilibrated configuration (Figure 3(c)) with reversed bending of ligaments may be achieved by further swelling of the hydrogel active layers. The corresponding structural parameters \((H_2, L_2, l_2)\) shown in Figure 3(c) are expressed by

\[
H_2 = \left( 4 - 2\sqrt{2} \right) \frac{(D_0 - r_0)}{\pi + 2|\theta_2|}
\]

\[
L_2 = \frac{8(D_0 - r_0)}{\pi + 2|\theta_2|} \left( \sin \frac{|\theta_2|}{2} + \frac{\sqrt{2}}{2} \right) + 2r_2 \sin \frac{|\theta_2|}{2}
\]

\[
l_2 = 2(b - h_s) + 2H_2 + L_2
\]

where \( h_s \) is the distance due to the inward contraction of the straight bar because of the reversed bending of the ligaments, \( r_2 \) is the bending radius of the deformed ligament in final equilibrated configuration, \( \theta_2 \) is the reversed bending angle of the ligaments in this configuration. For the sake of distinction with the configuration with forward bending angle \( \theta_1 \) of the ligaments, the sign of the reversed bending angle \( \theta_2 \) of the ligaments is negative. In other words, the bending angle \( \theta \) of the ligaments for the equilibrated configuration can be divided into two cases, that is

\[
\theta = \begin{cases} 
\theta_1, & (0 < \theta < \frac{\pi}{2}) \\
\theta_2, & (-\pi < \theta < 0) 
\end{cases} 
\]

\[
\text{forward bending mode} \\
\text{reversed bending mode}
\]
When the equilibrated configuration with reversed bending of ligaments is achieved, the corresponding effective linear strain \( \varepsilon_2 \) of the lattice microstructure is written as

\[
\varepsilon_2 = \frac{l_2 - l_0}{l_0} = \frac{2(\pi + 2|\theta_2|) \left( b - h_s + r_2 \sin \frac{|\theta_2|}{2} \right) + 8(D_0 - r_0) \left( 1 + \sin \frac{|\theta_2|}{2} \right)}{(\pi + 2|\theta_2|) \left\{ 2b + 2 \sqrt{2D_0} + (1 - \sqrt{2})r_0 \right\}} - 1
\]  

(15)

It is obvious that the effective linear strain of the microstructure lattice remains a minimum value when the length \( b \) of the straight bar is identical to the inward contraction depth \( h_s \) which can be determined from the geometric relationships as implied in Figure 3.

\[
b = h_s = \begin{cases} 
0, & (0 > \theta > \frac{\pi}{2}) \text{ forward bending mode} \\
1 - \cos^2 \frac{|\theta_2|}{2} \left( \frac{4(D_0 - r_0)}{\pi + 2|\theta_2|} + \frac{m_0}{2|\theta_2|} \right), & (-\pi > \theta > 0) \text{ reversed bending mode}
\end{cases}
\]

(16)

Recalling the assumption of the inextension of hydrogel layer, we can obtain

\[
\theta_1 r_1 = |\theta_2| r_2 = \frac{\pi}{2} r_0
\]

(17)

It is well accepted the final equilibrated configuration dominated by the ligament bending angle \( \theta \) varies with the typical microstructural parameters of the designed lattice. In order to more accurately describe the deformed configuration of the metamaterial, we introduce a function in terms of an initially designed parameter \( s_0 \) which is defined as the ratio of the initial bending radius \( r_0 \) of ligament to the initial distance \( L_0 \) between the two ends of the ligament. We have

\[
\theta = f(s_0)
\]

(18)

Combining Equation (10), Equation (15) – (18), the effective linear strain of the entire metamaterial is reformulated as

\[
\varepsilon_{\text{min}} = \begin{cases} 
\frac{m_0}{r_{\text{f}(s_0)}} \left( 1 - \cos \frac{r_{\text{f}(s_0)}}{2} \right) \left( \frac{\pi + 2|\theta_2|}{4} \frac{\cos \frac{r_{\text{f}(s_0)}}{2}}{2} \left( 1 + \frac{1}{\tan \frac{r_{\text{f}(s_0)}}{4}} \right) + \frac{m_0}{2r_{\text{f}(s_0)}} \sin \frac{r_{\text{f}(s_0)}}{2} \right) + 2(\pi + 2|\theta_2|) \left( \frac{4(D_0 - r_0)}{\pi + 2|\theta_2|} + 8(D_0 - r_0) \left( 1 + \sin \frac{r_{\text{f}(s_0)}}{2} \right) \right)}{(\pi + 2|\theta_2|) \left\{ 2(1 - \cos \frac{r_{\text{f}(s_0)}}{2}) + 4(D_0 - r_0) + 2 \sqrt{2D_0} + (1 - \sqrt{2})r_0 \right\}} - 1, & (0 < f(s_0) < \frac{\pi}{2}) \\
2(\pi + 2|\theta_2|) \left( \frac{m_0}{2r_{\text{f}(s_0)}} \sin \frac{r_{\text{f}(s_0)}}{2} \right) + 8(D_0 - r_0) \left( 1 + \sin \frac{r_{\text{f}(s_0)}}{2} \right) - 1, & (f(s_0) = 0) \\
2(\pi + 2|\theta_2|) \left\{ 2(1 - \cos \frac{r_{\text{f}(s_0)}}{2}) + \frac{m_0}{2r_{\text{f}(s_0)}} \right\} + 2(\pi + 2|\theta_2|) \left( \frac{4(D_0 - r_0)}{\pi + 2|\theta_2|} + \frac{m_0}{2r_{\text{f}(s_0)}} \right) + 2 \sqrt{2D_0} + (1 - \sqrt{2})r_0 - 1, & (-\pi < f(s_0) < 0)
\end{cases}
\]

(19)

3. Results and discussion

3.1. The effects of microstructural parameters on the effective NHE strain

The overall contraction deformation of the lattice microstructure is driven by the swelling of hydrogel. Different curvature radius of the lattice microstructures correspond to different lengths of the hydrogel. Therefore, the microstructures designed with different curvature radii of ligaments leads to different NHE ratios.
In order to quantitatively investigate the effects of geometric parameters on the deformation of the lattice microstructure, the finite element simulations were conducted by ABAQUS FE package to compute the deformation of the lattices. In the FE simulations, \( D_0 \) is set to a constant 21 mm, and the curvature radius was initially set between 2 and 16 mm with intervals of 1.0 mm for the designed microstructure.

Many attempts have been made in the field of the swelling-induced deformation modeling of smart hydrogels [24–26]. Yang [27] et al. proposed a constitutive model and formulated a user-defined hyperelastic material subroutine (UHYPER) in ABAQUS to simulate the chemo-mechanically coupled deformation of the hydrogels. In this work, we adopted the above material model and the 8-node element C3D8H for simulation. Figure 4 shows the initially designed microstructure and the simulated final configurations of lattice microstructures with varying ratios \( s_0 \) and curvature radii \( r_0 \). More detailed dimensions of initial and final configurations are listed in Table 1.

It can be observed from Table 1 that the bending angles vary with the curvature radius of the ligaments. When immersed in the solution, the hydrogel layers absorb solvents to induce the bending deformations of ligaments, resulting in the obvious variations of the angle \( \theta \) and the shrink (NHE) of the lattice microstructure. The simulated bending angles for the different microstructures and the fitted polynomial function are shown in Figure 5. It is readily observed that the bending angles \( \theta \) first decrease and then increase with the increasing ratio \( s_0 \). When the ratio is below a critical value, the computed angle \( \theta \) is positive, indicating that the ligaments exhibit forward bending. Meanwhile, the simulated bending angle \( \theta \) is negative when the ratio is relatively large, indicating that the ligaments exhibit reversed bending and the lattices shrink sharply. However, the bending angles do not vary monotonously with the ratio. For the reversed bending mode, the angles first decrease and then increase with the increasing ratio \( s_0 \). This is attributed to the fact the ligament will contact to the adjacent one when the ratio \( s_0 \) increases to a certain degree, and the maximum shrink of the lattice is achieved in this situation where the magnitude of the negative hygroscopic expansion ratio reaches the maximum value for the 2D metamaterial. If the ratio \( s_0 \) further increases, the magnitude of the reversed bending

| \( r_0 \) (mm) | \( s_0 \) | \( \theta \) (rad) | \( l_0 \) (mm) | \( l_1(l_2) \) (mm) | Effective linear strains (%) |
|---|---|---|---|---|---|
| 2 | 0.07 | 0.85 | 57.74 | 56.35 | –2.4 |
| 3 | 0.10 | 0.58 | 56.90 | 54.55 | –4.1 |
| 4 | 0.13 | 0.25 | 56.08 | 51.87 | –7.5 |
| 5 | 0.17 | –0.07 | 55.25 | 48.81 | –12 |
| 6 | 0.20 | –0.43 | 54.76 | 44.72 | –18 |
| 7 | 0.24 | –0.77 | 55.68 | 42.63 | –23 |
| 8 | 0.27 | –1.11 | 58.49 | 42.00 | –28 |
| 9 | 0.30 | –1.45 | 60.32 | 39.97 | –34 |
| 10 | 0.34 | –1.78 | 61.99 | 37.45 | –40 |
| 11 | 0.37 | –2.12 | 63.64 | 34.93 | –45 |
| 12 | 0.40 | –2.43 | 65.18 | 32.40 | –50 |
| 13 | 0.44 | –2.69 | 66.26 | 29.42 | –55 |
| 14 | 0.47 | –2.76 | 66.15 | 28.22 | –57 |
| 15 | 0.51 | –2.69 | 64.70 | 28.29 | –56 |
| 16 | 0.54 | –2.58 | 63.22 | 28.53 | –55 |
angle decreases, resulting in the relatively small shrink of the lattice. Based on the FE simulation results, the bending angle function \( f(s_0) \) in terms of initial ratio \( s_0 \) is polynomially fitted by the least square method, that is

\[
f(s_0) = 59.732s_0^3 - 43.483s_0^2 - 0.6957s_0 + 1.0317
\]  

(20)

According to the theoretical formulation Equation (19) and FE simulated results, Figure 6 shows the variations of minimum effective linear strain \( \epsilon_{\min} \) with the increasing ratio, and the theoretical prediction is in good agreement with the FE results. It can be observed that

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{The initially designed lattice configuration and the computed final configuration of lattice microstructures with different ratios \( s_0 \) and initial curvature radii \( r_0 \).}
\end{figure}
magnitude of the magnitude of the effective linear strain decreases with the decreasing ratio $s_0$, due to the fact that the microstructural lattice is less prone to shrink on account of a weak swelling actuation of the relatively short hydrogel layer. When the ratio $s_0$ reaches 0.47, that is, $r_0$ equals to 14 mm, the magnitude of the effective linear strain achieves the maximum, which implies that the adjacent ligaments just touch each other. In this situation, the effective linear contraction strain reaches 57%, and the depth $h_s$ of the inward contraction of the straight bar is 9.2 mm. As the ratio $s_0$ increases further, the adjacent ligaments are gradually squeezed, preventing the lattice to shrink even more. Therefore, we choose the optimal design by setting $s_0$ to 0.47 ($r_0 = 14$ mm) and $b$ to 9.2 mm to achieve the 2D metamaterials with largest NHE ratio. In subsequent sections, we extended the microstructure lattice to 2D and 3D metamaterials and conduct the FE simulations for more investigations.

3.2. The NHE behaviors of 2D multilevel metamaterials

By arranging the microstructure lattices vertically and horizontally, 2D multilevel metamaterial can be obtained. Also, the negative expansion behavior of 2D multilevel metamaterials can be predicted by finite element simulations which can effectively guide the design of hydrogel-driven metamaterials. Figure 7 shows the configurations of the representative 2D multilevel metamaterial before and after swelling deformation. The result shows that the representative 2D multilevel metamaterial has extremely large NHE behavior. It can be observed that the edge length of the 2D multilevel metamaterial shrinks from 200.4 mm to 86.2 mm, and the maximum effective linear strain (~57%) and the corresponding effective NHE ratio (up around ~80%) are achieved.
In order to capture the deformation evolution of a representative 2D multilevel metamaterial immersed in solution, Figure 8 shows several typical simulated configurations at different stages of the representative lattice (Figure 8(a)) and the multilevel metamaterial (Figure 8(b)) during a hygroscopic process. It can be seen that the curved ligaments of the material first deform with the tendency to being flat, then bend toward to opposite direction, and finally the equilibrated configuration of the metamaterials with ultra large NHE ratio is obtained.

Figure 6. The variations of minimum effective linear strain with the increasing ratio $s_0$.

Figure 7. The configurations of 2D multilevel metamaterials (a) Initial configuration; (b) Final simulated configuration.
The NHE behaviors of the extended 3D metamaterials

The design of the 2D microstructural lattice examined in previous sections can be readily extended to 3D cases. The designed initial geometry and the simulated equilibrium configurations of the representative 3D lattice microstructure and the corresponding multilevel metamaterials are shown in Figure 9. The representative 3D lattice microstructure sketched in Figure 9(a), is composed of three identical 2D lattice microstructures that are distributed in cross each other. When immersed in solution, the three 2D lattices shrink simultaneously along three mutually orthogonal planes, leading to significant NHE of the 3D lattice microstructure, as shown in Figure 9(a). By extending the 3D lattice microstructure along three orthogonal directions (x, y and z), the 3D multilevel metamaterials can be constructed. Figure 9(b,c) respectively illustrate the configurations of multilevel metamaterial (3 × 3 × 1) with arrangement of three 3D lattices along two orthogonal directions and the multilevel metamaterial (3 × 3 × 3) with three 3D lattices arranged in three orthogonal directions. For comparison purposes, the initially designed structures and computed equilibrium configurations are given both in isometric and lateral views.

Table 2 lists the FE simulation results of the dimensional change for NHE deformations of the representative 3D lattice microstructure and two 3D multilevel metamaterials. It is easily recognized that the effective linear strain (≈57.3%) of the 3D lattice microstructure is comparable to that of the 2D lattice microstructure. The effective linear strains of two 3D multilevel metamaterials are respectively −56.7% (3 × 3 × 1) and −56.4% (3 × 3 × 3), the magnitude of which is slightly lower than that of the 3D lattice, on account of certain structural constraints. Due to the simultaneous contractions along three orthogonal directions, the effective hygroscopic expansion ratio of 3D lattice microstructure

**Figure 8.** Typical simulated configurations at different stages of the representative lattice and the multilevel metamaterial during a hygroscopic process. (a) Lattice microstructures; (b) 2D multilevel metamaterials.

**3.3. The NHE behaviors of the extended 3D metamaterials**
significantly reaches $-92.2\%$, approaching to the theoretical limit $-100\%$. Correspondingly, the effective hygroscopic shrink ratio of the two 3D multilevel metamaterials (91.9\% for $3 \times 3 \times 1$ array and 91.7\% for $3 \times 3 \times 3$ array), is roughly consistent with the that of the 3D lattice microstructure.

### 4. Conclusion

In this work, a new design strategy for 2D/3D soft hydrogel-based metamaterial with ultra-large NHE is proposed. Theoretical analysis and finite element simulations are conducted to demonstrate the negative hygroscopic expansion behaviors. Based on the theoretical analysis and the FE simulations, the deformed configuration and the effective NHE ratios of the designed metamaterials can be well predicted by tailoring the key design parameter $s_0$ of the ligaments. The results show that the effective linear strain may reach up to $-57\%$ and the corresponding area strain is up to $-81\%$ for the designed 2D lattice microstructure. For the extended 3D lattice microstructure, the effective hygroscopic expansion ratio reaches up to around $-92\%$, very close to the theory limit $-100\%$. The numerical results show that 2D/3D mechanical metamaterials with ultra large NHE ratio greater than that reported in previous studies, can be achieved by the present novel design strategy which provides an insight into how structural design increases the NHE ratio of hydrogel-based
metamaterials. Notably, the negative expansion behaviors of the designed metamaterials are scale-independent and the present design concepts show wide potentials in macro-micro-nanoscale applications such as electronic and biomedical engineering.

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