

論文の内容の要旨

論文題目 Stimuli-Responsive Hydrogels Packaging
Anisotropic Electrostatics
(異方的な静電力学を内包する刺激応答性ヒドロゲル)

氏名 金 娟秀

Introduction

In the field of materials science, various hydrogel actuators have been developed so far, however, their actuation has inherent limitation in efficiency, because of their primitive actuation mechanism simply relying on the volume changes through the swelling and deswelling of gel networks. The kinetics of such volume changes is governed by the transport of water and subsequent rearrangement of polymer chains, and therefore is generally slow. In addition, the volume changes are usually isotropic and not suitable to produce anisotropic motion. Furthermore, autonomous operation of such motion is an even greater challenge, although such motion is often observed for living organisms.

As a promising material to circumvent these limitations, Aida *et al.* recently reported an anisotropic hydrogel whose mechanical properties are dominated by ‘embedded electrostatic repulsion’ (**Figure 1**). This hydrogel is supported by a 3D network of an organic polymer incorporating unilamellar titanate nanosheets (TiNSs). This particular nanosheet, developed by Sasaki *et al.* in 1996, consists only of surface atoms adopting a single-crystal-like 2D array and therefore is ultrathin (0.75 nm). It is also characterized by an exceptionally high aspect ratio ($\sim 10^4$). TiNS is negatively charged and wrapped by tetraalkylammonium counterions to furnish an electric double layer in aqueous media. Unlike any other metal oxide nanosheets, TiNSs in an aqueous colloidal dispersion magnetically align cofacially (**Figure 1**, i). This

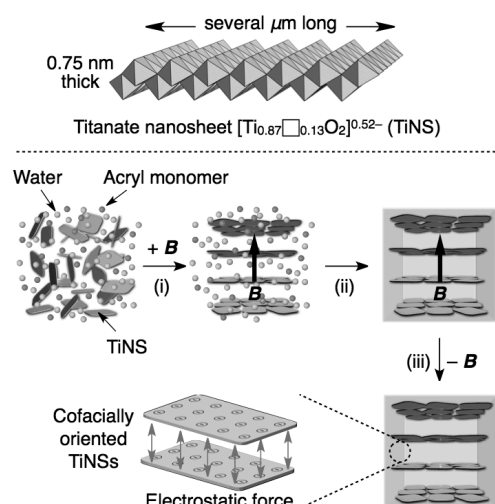


Figure 1. Schematic representation of the preparation of a hydrogel containing cofacially oriented TiNSs.

magneto-induced temporal structural ordering can be fixed by transforming the dispersion into a hydrogel by in-situ vinyl polymerization (**Figure 1**, ii).

Inspired by this work, the author envisioned that, if the 3D network of this hydrogel is composed of a stimuli-responsive polymer, the 3D network of the hydrogel would reversibly release and hold gelling water in response to external stimuli. Consequently, the polarity and dynamics of the gel matrix would be abruptly changed, which causes the switching of the intensity of the ‘embedded electrostatics’, thereby producing quick and anisotropic deformation of the hydrogel. In this philosophy doctoral (Ph.D.) thesis, the author describes stimuli-responsive hydrogels whose anisotropic actuation is driven by switching the intensity of embedded electrostatics acting among cofacially oriented TiNSs.

Chapter 1. Unidirectional actuation of a hydrogel driven by tunable anisotropic electrostatic repulsion among cofacially oriented inorganic nanosheets

As described in Introduction, the author aimed at introducing a thermoresponsive feature to the gel network of the anisotropic hydrogel with embedded electrostatic repulsion among cofacially oriented TiNSs. For the components of such a thermoresponsive gel network, the author chose *N*-isopropylacrylamide (NIPAM) as a monomer and *N,N'*-methylenebis (acrylamide) (BIS) as a crosslinker, whose lower critical transition temperature (LCST) is known to be 32–34 °C. The hydrogel containing cofacially oriented TiNSs was prepared according to the method we recently reported (**Figure 1**). Typically, an aqueous dispersion of 1.6 wt% TiNSs was hydrogelated in a 10 T magnetic flux by in-situ crosslinking polymerization of 8.0 wt% NIPAM and 0.48 wt% BIS. In the resultant hydrogel, TiNSs adopted a layered structure with a uniform plane-to-plane separation of 14 nm. A reference hydrogel containing randomly oriented TiNSs was also prepared in the same manner but without using a magnet.

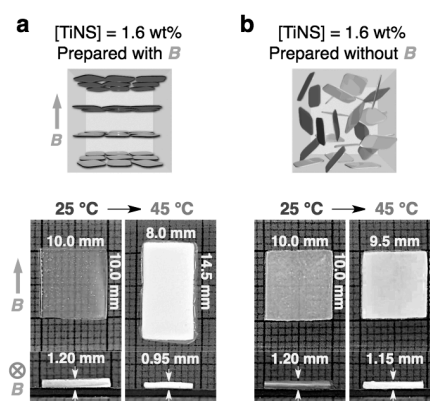


Figure 2. Thermo-responsive deformation of hydrogels containing (a) cofacially oriented TiNSs (1.6 wt%) and (b) randomly oriented TiNSs upon heating from 25 to 45 °C.

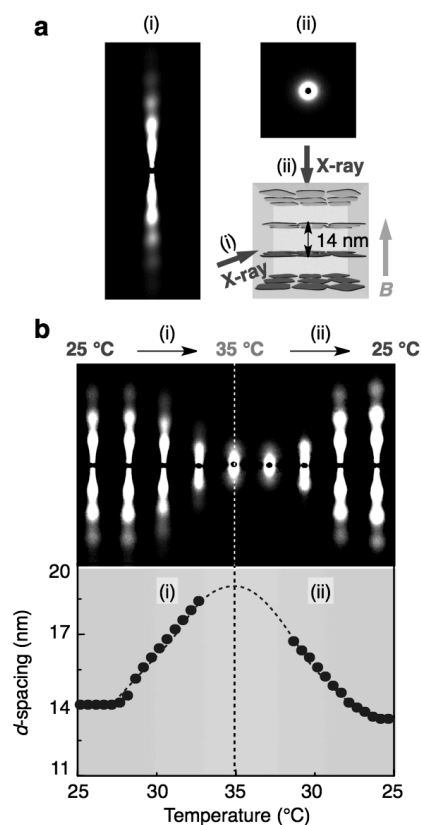


Figure 3. (a) 2D SAXS profiles of the hydrogel containing cofacially oriented TiNSs, where the incident X-ray beam was directed orthogonal (i) and parallel (ii) to the TiNS plane. (b) Changes in the 2D SAXS profiles upon repeated heating-cooling cycles.

When the hydrogel was heated from 25 to 45 °C, it became opaque at ~32 °C due to the hydrophilic–hydrophobic transition of the gel network, and then underwent the following anomalous deformation. To our surprise, the hydrogel expanded to ~150% in the direction orthogonal to the TiNS plane, unlike other poly(NIPAM)-based hydrogels that generally shrink when heated above their LCST. Concomitantly to this expansion, the hydrogel contracted to ~80% in the in-plane directions of the TiNS plane. Accordingly, the volume of the hydrogel was maintained through the deformation (**Figure 2a**). In addition, when the hydrogel thus deformed is cooled below 32 °C, the reverse deformation took place. Worth noting is that these deformations do not involve a long-range water transport and subsequent polymer rearrangement, and therefore are very quick, unlike the deformation of usual stimuli-responsive hydrogels. Furthermore, upon heating–cooling cycles, these deformations can be repeated without any detectable degradation. Such anomalous deformations occur only when TiNSs in the hydrogel are cofacially oriented. Indeed, a reference hydrogel containing randomly oriented TiNSs was heated above 32 °C, it did not exhibit such an anomalous deformation in the present time scale, but only gained its turbidity (**Figure 2b**). In order to confirm the hypothesized mechanism more directly, 2D small-angle X-ray scattering (2D SAXS) of the TiNS-oriented gel was measured with irradiating an X-ray beam parallel to the TiNS plane, so that the information on the plane-to-plane separation of the oriented TiNSs can be obtained. In the original state, the 2D SAXS image indicated that cofacially oriented TiNSs align with a uniform *d*-spacing of 14 nm (**Figure 3a**). When the TiNS-oriented gel was heated up to 35 °C, the layered structure of TiNSs expanded with gaining its *d*-spacing from 14 to >19 nm (**Figure 3b, i**). In the reverse cooling process, the layered structure reduced its *d*-spacing from >19 to 14 nm (**Figure 3b, ii**). The expansion and contractile of the layered structure could be repeated multiple times without serious structural degradation.

Chapter 2. Spatiotemporally controlled actuation of a hydrogel driven by the hybridization of anisotropically embedded electrostatics and a self-oscillating reaction

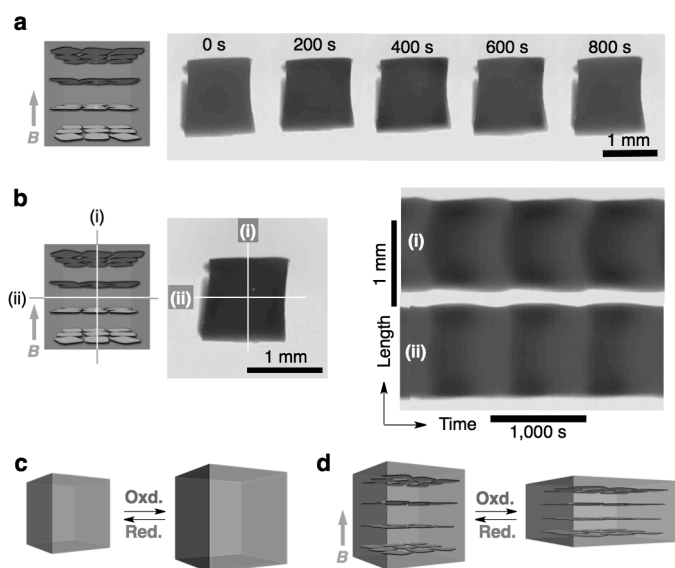


Figure 4. (a) Time-course images of the hydrogel containing Ru(bpy)₃ units and cofacially oriented TiNSs viewed from the direction parallel to the TiNS plane. (b) Spatiotemporal patterns constructed by lining up the one-line images along the perpendicular (i) and parallel (ii) direction to the TiNSs plane sequentially with time. (c) Schematic illustration of the self-oscillating behavior of conventional self-oscillating hydrogel based on poly(NIPAM) and Ru(bpy)₃ and (d) that of the hydrogel containing Ru(bpy)₃ and cofacially oriented TiNSs.

As described in Chapter 1, the author succeeded in developing a hydrogel actuator that exhibits large, quick, and unidirectional motion in response to external thermal stimuli. A remaining challenge for this hydrogel is “autonomy”, which is a crucial difference generally observed between artificial soft actuators and living organisms. According to the method established in Chapter 1 with some modification, the target hydrogel was synthesized, whose gel network embedded with cofacially oriented TiNSs was covalently modified with Ru(bpy)₃ units. The hydrogel was processed in a rectangular shape, where one of the sides became orthogonal to the TiNS plane, while the others are parallel to the TiNS plane. When the hydrogel was immersed in an aqueous medium containing the BZ substrates, the self-oscillating BZ reaction started in the hydrogel after a while (**Figure 4a**). In order to evaluate the anisotropy of this autonomous actuation, the time-series image analysis of the hydrogel was performed (**Figure 4b**) along the perpendicular (i) and parallel (ii) directions to the TiNS plane. Thus, from each frame of the movie taking whole shape of the hydrogel, a one-line image along either of the two directions (i or ii) was extracted and lined up sequentially with time, so that two spatiotemporal patterns were constructed. When the hydrogel turned to the oxidized state (Ru³⁺-state) where the hydrogel appeared green, the hydrogel showed notable contraction in the direction orthogonal to the TiNS plane. Synchronously to the contraction, the hydrogel expanded in the in-plane directions to the TiNS plane. When the hydrogel turned to the reduced state (Ru²⁺-state) where the hydrogel appeared orange, the reverse deformation occurred. These deformations were autonomously repeated in an oscillatory manner without degradation (**Figure 4b**). Worth noting is that the actuation mechanism of the present hydrogel is totally different from that of conventional self-oscillating hydrogels based on the BZ reaction, in terms of volume change and anisotropy. In the case of conventional self-oscillating hydrogels oxidative state of the Ru(bpy)₃ units (Ru²⁺ ⇌ Ru³⁺), which causes the changes in hydrophilicity and LCST of gel matrices and subsequent swelling and deswelling of their gel networks (**Figure 4c**). Therefore, such conventional hydrogels generally swell in the oxidized (Ru³⁺) state and shrunken in the reduced (Ru²⁺) state in an isotropic manner so long as the effects of their macroscopic shapes are negligible. In sharp contrast, the actuation of the present hydrogel does not involve swelling and deswelling of its gel network, but proceeds in an isovolumetric manner (**Figure 4d**). Considering the fact that the present hydrogel contracts in the direction orthogonal to the TiNS plane in the oxidized (Ru³⁺) state, an electrostatically attractive force between Ru(bpy)₃ units and TiNSs switches depending on the valence of ruthenium center, which causes the observed deformations.

Summary

The author succeeded in developing hydrogel actuators operated in unprecedented mechanism, which realizes efficient, unidirectional, and even autonomous motion. These hydrogels incorporate negatively charged inorganic nanosheets that are oriented cofacially with one another, where an anisotropic electrostatic repulsion emerges among the nanosheets. The oriented nanosheets are noncovalently packaged by 3D polymer networks of stimuli-responsive polymers, which can switch the electrostatic permittivity of the gel matrices in response to externally or internally controlled stimuli. These hydrogels, having many similarities to muscular tissues in actuation profiles and in mechanism, would contribute to the progress of studies on artificial soft actuators, both in fundamental and practical aspects.