Spontaneous and rapid electro-actuated snapping of constrained polyelectrolyte hydrogels

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INTRODUCTION

Nature provides elegant paradigms and inspirations to devise versatile soft actuators and robots (1–6). Especially, some plants capable of rapid and articulate actions have attracted extensive interest (7–11). For example, the leaves of Venus flytrap undergo a fast snapping upon stimuli, owing to the snap-through instability rooted in the bistable structural geometry (8, 9). Similarly, aquatic bladderworts take advantage of the fast release of elastic energy to capture small preys (10, 11); when stimulated, the initially concave bladder wall snaps and rapidly recoils to a convex configuration, resulting in intake of water. This fast snapping is crucial for soft actuators/robots, whose natural rates of deformation/motion are usually slow. By incorporating structures with snap-through instability, elastic energy can be efficiently stored, quickly released, and converted to kinetic energy (12–24). For example, Bende et al. (13) investigated the force-induced snap transition of a creased thin shell, in which the inherent geometry creates an energy barrier between isometric stable states. The unit capable of fast snapping has also been used to fabricate versatile devices, and a direct force is usually required to be in physical contact with the device and thereby trigger the snap transition or to reset the snapping structures (25–28). For example, a soft inflatable jumper has been fabricated, which is actuated by snapping of spherical elastomer caps when pressurized (28), similar to the rubber “popper toys” (27). The energy landscape for the isometric deformation is revealed by relating the applied force/pressure to the displacement of the snapping unit (13, 28). An autonomous earthworm-like walker is developed with a soft valve equipped with bistable elastomeric dome that is switchable by differential pressure (29, 30). Unlike natural organisms, however, these artificial systems are nonresponsive to external stimuli and thus often require external forces to flip between the mechanically stable states.

Different from elastomers, hydrogels are ideal materials for soft actuators/robots due to their diverse forms of responses, similarity to soft biological tissues, and versatile applications under aqueous and bio-relevant conditions (31–34). Nevertheless, the solvent migration–enabled deformation is usually slow, while mechanical instability such as snapping may significantly expedite the actuation/motion. For example, a bilayer composite comprising thermo- and pH-responsive hydrogels, which is made into a dome constrained by a prestretched hydrogel ring, snaps to opposite directions by pH or temperature stimulation (31), but the complex fabrication and different conditions for reversion may hinder the applications. Alternatively, photolithography is a powerful strategy to fabricate hydrogels with in-plane gradients; the swelling mismatch between different regions leads to out-of-plane buckling with intrinsic bistability (35–37). If the bistable hydrogel can be actuated by contactless stimuli such as light or an electric/magnetic field (38–41), then spontaneous and fast snapping should be expected. Around 30 years ago, Shiga and Kurauchi (42) found that a polyelectrolyte hydrogel strip showed bending deformation under an electric field. This phenomenon has been theoretically analyzed by Doi and other scientists (43–46). Although the general physics of differential osmotic pressure has been revealed in terms of ion migration inside the gel under an electric field, most existing models have not considered the coupled dynamics of ion and water migration and osmotic pressure has been revealed in terms of ion migration inside the gel under an electric field. It should be interesting to realize the electro-response of the gel coupled with the mechanical instability. Another substantial yet challenging task is to formulate a numerical model to reveal the underlying mechanism, which is more complicated than the electro-bending of polyelectrolyte gels.

Here, we present a bistable hydrogel that exhibits electric field–steered snapping transition. A composite hydrogel sheet is fabricated via photolithographic polymerization, in which a high-swelling polyelectrolyte gel disc is embedded in a nonswelling neutral gel. When immersed in a saline solution, due to swelling mismatch, the high-swelling region buckles into a domal configuration, which is naturally bistable. Under an appropriate electric field, the domal polyelectrolyte gel tends to bend in the opposite direction. Such an action, however, is prohibited by the surrounding constraint, and
the gel is trapped in a local energy minimum. The elastic energy gradually accumulates and ultimately leads to a fast snap-through upon reaching a threshold. This process is reversible and controllable through the applied electric field, which redistributes the ions, causing water migration and bending. Because of the bistable nature of the structure, the flipped state can be maintained without the need of sustained energy input. Furthermore, a transient model with fully coupled electromigration of ions and water and the deformation of polyelectrolyte gel is successfully developed and validated by quantitative analysis of the electro-actuated snap transition. The actuation is imposed through a pair of electrodes without physical contact and triggered spontaneously from internal of the hydrogel, just like the natural organisms. Using the reversible snapping, an autosensing catcher and a self-sustained pulse pump are developed. This work heralds a new strategy to devise hydrogel-based soft actuators and robots with fast responses.

**RESULTS**

**Electro-actuated snapping of constrained gel**

The patterned hydrogel sheet with a polyelectrolyte gel disc embedded in a neutral gel frame is fabricated by two-step photolithographic polymerization (fig. S1). Selection of hydrogels is based on the electro-response of the polyelectrolyte gel, as well as the balanced mechanical properties and large swelling mismatch between the high-swelling and nonswelling gels. Because of the swelling mismatch between poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonic acid) [P(AAm-co-AMPS)] gel and polyacrylamide (PAAm) gel, the high-swelling disc gel buckles out of plane (Fig. 1A). The buckled gel exhibits a bistable domal configuration and can be switched between the convex and concave states with equal elastic energy by a mechanical force (fig. S2). This snapping transition can also be triggered under an electric field, by placing the hydrogel in an aqueous solution of sodium sulfate (Na$_2$SO$_4$), between a pair of graphite electrodes with the dome facing to the cathode. When the domal gel is suspended in the saline solution by a soft thread, it drifts with the time, especially during the snap-through transition (fig. S3 and movie S1), and complicates the analyses. For simplicity, the domal gel is clamped at the two ends with glass substrates. Similar snapping transition is observed under the electric field. After applying a direct current electric voltage, which results in migration of mobile ions and the buildup and accumulation of internal stress in the constrained polyelectrolyte gel, the dome undergoes a sudden snap-through and buckles toward the anode to release the stored elastic energy (Fig. 1, B and C). The flipped configuration is stable after removing the electric field, in contrast to a popular "popper toy" (27). The snapping transition is reversible—when the electric field is reversed, the dome of the patterned hydrogel readily snaps back as expected.

Detailed snap-through transition of the gel is examined from the recorded movie (Fig. 1C and movie S2). The domal configuration shows no obvious change under the electric field (strength: 4 V cm$^{-1}$) for ~8 s. However, after 10 s, local concavity appears and gradually grows at the edge near the nonswelling region, while the overall direction of the dome is unchanged. A fast snapping occurs at 15 s. Specifically, one concavity rapidly grows and breaks the symmetry (13), and the sudden snapping completes within 0.1 s, similar to that of flytraps (8). The dome height $h$ is plotted as a function of time $t$ in Fig. 1D. $h$ slightly increases from 2.7 to 2.8 mm at the initial stage, from 0 to 7 s, and then gradually decreases to 2.5 mm before the snapping. The slight variation of $h$ results from the redistribution of mobile ions and the buildup of transient through-thickness gradient under the electric field, which will be discussed later. The snapping transition leads to a sudden and drastic drop in $h$ from 2.5 to ~2.9 mm. The moment with fastest change of $h$ is defined as the snapping time ($t_s$), i.e., the action time of electric field required for triggering the snap-through transition. We note that $t_s$ is not constant in successive actuations—it increases from 15 s in the first cycle to 34 s in the second one and slightly increases in the following ones (Fig. 1, E and F). This is because it takes time for water molecules to redistribute and recover the original state after removal of the electric field. However, $t_s$ reverts to 15 s by resting for 5 min before the next-round electrical stimulation. In the following section, $t_s$ refers to the first-cycle snapping transition of the domal gel from an equilibrium state.

Worth noting is that the domal hydrogel with two ends clamped has smaller $t_s$ than that of a free-standing gel (Fig. 1C and fig. S3). To better investigate the effect of clamping, we examine the influence of clamping distance $l$ (between the clamping glass substrate and the edge of the high-swelling gel) on the snapping time, $t_s$, of the domal gel. As shown in fig. S4, $t_s$ increases from 16 to 42 s, when $l$ increases from 1 to 7 mm. This is likely to be caused by the perturbation in the local curvature introduced by the clamps, which shallows the energy barrier against the snapping. In the following experiments, the clamping distance is kept as 1 mm to study the electro-actuated snap-through transition of the domal gel.

We further investigate the effects of the applied electric field ($E$), feeding fraction of AMPS ($f_a$), and concentration of Na$_2$SO$_4$ in the solution ($C_s$) on the snapping time $t_s$. $E$ influences the fluxes of mobile ions without changing the initial geometry of the hydrogel dome. Thus, the energy barrier against the snapping transition is almost constant. As shown in Fig. 1G, $t_s$ decreases from 58 to 8 s as $E$ increases from 2.5 to 6.0 V cm$^{-1}$. It takes more time to overcome the energy barrier under lower $E$; the snapping transition cannot be triggered when $E$ is lower than 2.5 V cm$^{-1}$. $f_a$ influences $t_s$ by varying the charge density of the polyelectrolyte gel (fig. S5) and the mechanical and swelling properties. The relatively small swelling ratio of the gel with $f_a < 6$ mole percent (mol %) leads to weak out-of-plane buckling; the snapping transition of corresponding domal gel is easily affected by small perturbation and thus difficult to quantify. On the other hand, the swelling ratio of the gel with $f_a > 14$ mol % results in an energy barrier too large to overcome for snapping. Therefore, snapping transition is only observed in the gel with $f_a$ of 6 to 14 mol %; as $f_a$ increases from 6 to 10 mol %, $t_s$ increases from 8 to 16 s, which slightly increases to 18 s with further increase in $f_a$ (Fig. 1H). The effect of $C_s$ is also examined. Snapping only happens when $C_s$ is between 0.04 and 0.16 M. Similar to $f_a$, $C_s$ also influences $t_s$ in terms of ion distribution and initial geometry of the dome. With the increase in $C_s$, $t_s$ first decreases and then increases, with a minimum value of 16 s at $C_s = 0.1$ M (Fig. 1I). Both $f_a$ and $C_s$ affect the dome height $h$ and thus the energy barrier for snapping transition, as confirmed by the mechanical force–induced snapping (fig. S6). We should note that the differential Young’s moduli of the high-swelling P(AAm-co-AMPS) gel and the nonswelling PAAm gel not only account for the formation of hydrogel dome but also influence the snap-through transition to some extent. However, in experiments, the swelling mismatch and stiffness difference cannot be changed independently. Instead, we change the mechanical and...
swelling properties of the polyelectrolyte gel by varying the feeding fraction of AMPS and the saline concentration of the bath (fig. S7) while leaving the PAAm gel unchanged. In the experimental range, the electro-snapping of the domal gel is severely influenced by the swelling mismatch, while the effect of modulus ratio is found to be minor.

**Electro-bending of a free-standing gel strip**

On the basis of these results, it is rational to correlate the snapping of a domal structure with the bending of a gel strip under an electric field. The snapping of a domal gel with or without clamping (i.e., a geometrically constrained polyelectrolyte gel) is induced by the sudden release of elastic energy when a critical condition is met, in contrast to the gradual deformation of an unconstrained gel strip. To better understand the snapping mechanism and validate the numerical model, we systematically investigate the electro-bending of a free-standing P(AAm-co-AMPS) gel strip under the same conditions (Fig. 2, A and B, and movie S3), although similar phenomena have been investigated in different polyelectrolyte gels (42, 45). The electric field motivates directional motions of mobile ions in the gel and the solution. However, the significantly less populated counterions in the polyelectrolyte gel creates a barrier for counterion transportation, leading to gradient distribution of mobile ions and differential osmotic pressure through the thickness of the gel, which drives the bending of the gel under the electric field.
In our experiment, the thickness of the polyelectrolyte gel strip is identical to the domal gel, and the width is 3 mm, above which the bending behavior becomes insensitive to the width (fig. S8). Variation of the gel curvature $\kappa$ with the action time of the electric field is shown in Fig. 2. Under an electric field, $\kappa$ increases rapidly before reaching a peak value, $\kappa_m$, and then gradually decreases and plateaus, because of the decrease in the fluxes and the equilibration of mobile ions. The bending speed, $\nu_b$, is characterized by the initial changing rate of $\kappa$ at $t < 30$ s. Here, we focus on the bending behavior of the gel strip before reaching the maximum curvature by considering the similar time scale (<60 s) and the maximum driving force for the snapping transition of the domal gel. Specifically, as $E$ increases from 2.0 to 6.0 V cm$^{-1}$, $\nu_b$ and $\kappa_m$, respectively, increase from 0.7 to 3.4 cm$^{-1}$ min$^{-1}$ and from 0.7 to 2.1 cm$^{-1}$ (Fig. 2C), due to the increased fluxes of mobile ions. The variation of $f_a$ shows minute influence on $\nu_b$ and $\kappa_m$ (Fig. 2D), suggesting the little impact of fixed-ion density (fig. S5) on electro-actuated bending deformation. The influence of $C_s$ is shown in Fig. 2E. As $C_s$ increases from 0.04 to 0.16 M, $\nu_b$ and $\kappa_m$ decrease from 4.3 to 1.4 cm$^{-1}$ min$^{-1}$ and from 2.7 to 1.0 cm$^{-1}$, respectively. The effect of $C_s$ is complicated since it affects both the initial state and time evolution of ion distribution under the electric field. Governed by Donnan equilibrium, the overall ion concentration increases with $C_s$, leading to higher conductivity. However, higher $C_s$ results in a less obvious difference in mobile ion concentration at the gel/solution interface. In concentrated Na$_2$SO$_4$ solutions, the swelling ratio of the polyelectrolyte gel is less sensitive to the change of $C_s$ (fig. S9) and hence offers a smaller driving force for electro-bending.

**Theoretical analysis and numerical simulations**

It is known from physics that mobile ions migrate toward corresponding electrodes under an electric field. The nonuniform distributions of mobile ions lead to differential osmotic pressure, driving water diffusion and thus deformation of the polyelectrolyte hydrogels. Similar electro-bending behavior has been studied theoretically by modeling the time evolution of ion concentration profiles under an electric field (42, 43). However, a gel is simplified either into blocks with homogeneous ion concentration (42) or just by looking at the one-dimensional through-thickness profile (43). Osmotic pressures are estimated without modeling water migration or gel deformation. For electro-snapping, structural instability exists in the domal polyelectrolyte gel due to the geometric constraint of the surrounding neutral gel; therefore, the modeling is more challenging than the electro-bending. Here, we modify the field theory for transient behavior of polyelectrolyte gels by insisting electroneutrality, develop a model for the coupled transportation of mobile ions and water molecules and the deformation of polymer network, and study the electro-actuated bending and snapping of hydrogel strips.
The dynamic electro-actuation process of a polyelectrolyte gel in an aqueous solution is modeled by solving the coupled equations of nonlinear elasticity and ion/mass transport. Detailed description of the numerical model is provided in Materials and Methods.

The basic working mechanism can be understood as follows, with a polyanion gel as an example. Because of the existence of immobile polyanions, the concentration of co-ions (mobile anions) is relatively low in the gel, creating a barrier for co-ion migration. The co-ions thus accumulate near the cathode side of the gel-solution interface and diminish on the other side. The electroneutrality dictates that counterions also accumulate in and evacuate from the same regions, as shown by simulations (Fig. 3A). The ionic concentration difference on the anode/cathode side creates a differential osmotic pressure that drives water into/out of the gel, causing the local swelling/deswelling. The polyanion gel thus bends toward the cathode as observed in experiments. Nevertheless, the process is nonequilibrium and dependent on the directional motion of ions. If no sources of co-ions or counterions are provided, as they gradually equilibrate and hand the role of charge carriers to the electrochemically active and much less populated H⁺ and OH⁻ ions, then the gel strip relaxes and bends back. Using the model, the dependence of the bending speed on the current, fixed ion concentration, and solute concentration is studied numerically. The results, plotted in terms of dimensionless quantities (which are noted by the same symbols with overbars) in Fig. 3 (B to D), agree well with the experimental results in Fig. 2, demonstrating the validity and effectiveness of our coupled field theory and numerical model.

In the case of a buckled domal gel, the mobile ion distribution in the polyelectrolyte gel and the solution undergoes a similar transition, and the osmotic pressure builds up a through-thickness stress gradient. By using the abovementioned model, we simulate the redistribution...
of cations and corresponding morphing details of the hydrogel dome during the snapping transition (Fig. 3E). After applying the electric field, the differential osmotic pressure tends to swell the cathode side of the gel and shrink the other side and would thus bend the gel if no constraint is present. The geometric constraint from the nonswelling gel prohibits the bending through a large energy barrier, until the snapping-through when the osmotic pressure–induced bending moment exceeds a critical value. Figure 3F shows the variations of dimensionless total elastic energy $U_{S}$ and dome height $h$ of the hydrogel as a function of dimensionless action time $I$ of the electric field. The sudden decrease in $U_{S}$ and $h$ indicates the snapping transition.

Detailed snapping process with the variations of solvent and stress gradients is provided in Fig. S10. When the swelling ratio and stress gradient through the thickness increase beyond a critical level, the structure symmetry of the dome is broken, and a local concavity appears near one of the two constrained edges of the gel dome. With the continuous application of the external electric field, the entire dome quickly flips with the concave region grows at the expense of the center convex region, releasing the high in-plane stress of the gel (Fig. 3E and movie S4). The simulation result agrees well with the experimental observations (Fig. 1C) and reveals the detailed mechanism of electro-snapping.

To compare with the experimental results in Fig. 1, we carry out a numerical study systematically and plot the snapping time $t_s$ against the parameters $I$, $C_{fix}$, and $C_s$ (Fig. 3, G to I). The dependence of $t_s$ on $I$ (or similarly the electric field) is in good agreement with experiments, while that on $C_{fix}$ or $C_s$ does not agree well. The discrepancies can be attributed to the inaccuracy of the simple material model in capturing the swelling behavior of a polyelectrolyte gel. The change in $C_{fix}$ or $C_s$ affects the initial geometry (e.g., the height of buckled dome) and the bending kinetics simultaneously. As shown by the simulations (fig. S11), the two effects exhibit opposite trends and the competition leads to a nonmonotonic dependence of the observed $t_s$ on $C_{fix}$. As the material parameters are directly extracted from experimental conditions, the crossover between the two effects may not lie in the range simulated and is thus not seen in the numerical results. To improve modeling accuracy, one can carry out independent tests (e.g., free swelling, constrained swelling, and mechanical tests) to characterize the mechanical properties and the energy of mixing function for the specific type of polyelectrolyte gel and then insert it to the current model for electro-actuation prediction.

**Hydrogel devices based on electro-actuated snapping**

The electro-actuated snapping transition enables designs of versatile devices with switchable states, in which rapid action and large-amplitude deformation are triggered by external stimuli such as the electric field. As a proof-of-concept example, the domal gel is used as an optical switch. When the dome faces upward, the laser path is blocked, and the optical switch lights up the light-emitting diode (LED). When the dome snaps downward under the electric field, the blocked path of laser is relaxed, and the LED is turned off (Fig. 4, A and B, and movie S5). The optical switching is reversible by controlling the direction of electric field that dictates snap-through transition of the domal gel. When compared to the optical control based on low-speed deformations (49), the fast action of snap transition affords precise and high-efficiency switching between two states. Electro-snapping of the dome is also feasible with only one side clamped, resulting in a relatively large stroke and “kicking” a ball underwater (fig. S12 and movie S6). To mimic the predation of Venus flytrap, an autonomous hydrogel catcher is devised by integrating two domes as the “leaves” (Fig. 4, C and D). Once the “prey” enters the responsive region and blocks the laser, the optical feedback triggers the action of the electric field and then the rapid closure of the two leaves for predation. The catcher can be reset by applying an electric field in the opposite direction for next round sensing and predation (movies S7 and S8). More precise location of the prey that triggers the predation can be realized by an optical sensing system with crossed lasers. Such a speedy catcher relies on electro-response of polyelectrolyte gel and mechanical instability of domal structure and thus is a close analogy to the rapid closure of flytraps, in which the accumulated action potentials trigger the fluid transportation inside the leaves, thereby leading to heterogeneous swelling and snap-through transition (3, 8). The hydrogel actuator presented here, which shows similar scenario and performance as the flytrap, outperforms most existing artificial systems (17, 50, 51).

Furthermore, the electro-snapping can also be used as a pump piston to intermittently pressurize and transport fluid. An autonomous system capable of pumping fluid in and out of a chamber is devised by harnessing the electro-actuated snapping transition, mimicking the function of mammalian hearts to pulsate and pump the blood. A domal gel is adopted as the driving unit of the pulse pump (Fig. S4E and figs. S13 and S14). After applying the electric field for 29 s, the convex dome undergoes a sudden inward snapping, pumping out the fluid through the right check valve (Fig. 4F). The direction of electric field is automatically switched by using the optical switch as described above. After another 35 s under the switched electric field, inverse snapping takes place that pumps in the fluid through the left check valve, which also completes a feedback loop with the dome facing upward. Therefore, the pulsed pump works continuously to intermittently pump in and out the fluid (Fig. 4F and movie S9). As expected, the stroke volume of fluid pumped in and out of the chamber both equal approximately 0.08 ml (Fig. 4G). We should note that the required action time of electric field for each snapping gradually increases during the continuous process, consistent with the trend found in a single domal gel (Fig. 1, E and F). With hydraulic resistance, the liquid level in a vertical tube is raised by 18.5 mm after sequential actuations of electro-snapping (fig. S15).

**DISCUSSION**

We have demonstrated the fast and reversible action of hydrogel actuators by using an electric field to direct ion and water migration in the polyelectrolyte gel and thereby trigger the snapping transition of the bistable configuration. A gel sheet of in-plane pattern, with polyelectrolyte gel surrounded by neutral gel, is fabricated through photolithographic polymerization. The swelling mismatch and geometrical confinement lead to out-of-plane buckling of the high-swelling polyelectrolyte region to form a domal configuration with mechanical bistability. Under the electric field, the polyelectrolyte gel intends to bend to the opposite direction yet is initially hindered by the geometric constrain. After the accumulated elastic energy is above a critical value, a fast snapping takes place. Systematic experiments are conducted to investigate the influences of gel composition, electric field, and salt concentration of the bath on the snapping transition. The snapping mechanism is further analyzed by numerical
simulations, and a transient model with coupled electromigration of ions and deformation of polyelectrolyte gel is successfully developed and validated. This electric field–steered snapping has promising applications as optical switch, automatic catcher, and pulse pump, as demonstrated by experiments. Another noteworthy point is that the electro-actuated snap-through transition is also feasible when the domal gel is placed in phosphate-buffered saline (PBS; fig. S16), suggesting the potential biomedical applications of this snap-through-based actuator. Although a polyanion gel is used as an example in this work, polycation gels with opposite electro-responsiveness can be integrated to form complex systems (fig. S17 and movie S10). Sequential snap-through of multiple domes to certain directions at distinct times should afford sophisticated actuation of integrated devices in a spatiotemporal way. Since the electro-snapping and hysteresis between successive actuations are related to the migration of mobile ions and water, these processes can be sped up to some extent by reducing the thickness of the hydrogel (fig. S18), which, together with the feedback control loop, should merit the design of versatile soft actuators and robots. The overall efficiency for electro-actuated bending or snapping is relatively low, because most electrical energy has been wasted by molecule/ion migration in the solution and electrochemical reaction around the electrodes. To weaken or avoid the electrochemical reaction, the applied voltage needs be reduced to an appropriate level by miniaturizing the hydrogel system to shallow the energy barrier, which should be an interesting subject for further studies.

Fig. 4. Hydrogel devices by harnessing electro-steered snapping transition. (A and B) Schematic of the device (A) and experiment results (B) of the domal gel as an optical switch to control the state of LED. LED is turned on when the laser is blocked by the dome and off when the dome snaps downward to relieve the laser. (C and D) Schematic (C) and experiment observations (D) of swift catcher comprising a pair of domal gels. The catcher is activated when the prey enters the responding region and blocks the laser that triggers the action of electric field to induce snapping transition of domal gels. (E) Schematic of pulse pump with a negative feedback system. (F) Snapshots showing the autonomous pumping in and out of fluid after successive snapping upward and downward. Solution inside the chamber is dyed for better visualization of fluid transportation under ultraviolet (UV) light. (G) Stroke volume of fluid pumping out/in of the chamber as a function of action time of the electric field. Scale bar, 5 cm.
MATERIALS AND METHODS

Materials
Acrylamide (AAm), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), N,N′-methylenebis(acrylamide) (MBAA), methacrylamide, and neutral red solution [4 weight % (wt%) solution] were used as received from Aladdin Chemistry Co. Ltd. The 2,2′-azo-bis-(2methylpropionamide) (V-50) and potassium persulfate were purchased from Macklin Inc. N,N,N′,N′′-tetramethylthelylenediamine and 3-(methacryloxy)propyl-trimethylammonium chloride (MPTC; 50 wt % solution) were used as received from Sigma-Aldrich. Sodium sulfate (Na₂SO₄), PBS, and fluorescein sodium were purchased from Sinopharm Chemical Reagent Co. Ltd. Millipore deionized water was used in all the experiments.

Fabrication of patterned composite hydrogels
Patterned composite hydrogel was fabricated via multistep photolithographic polymerization. A precursor solution containing AAm, AMPS, MBAA (chemical cross-linker), and V-50 (photoinitiator) was injected into a reaction cell assembling by two glass substrates that were separated by a frame of 0.5-mm-thick silicon rubber. A photomask prepared by inkjet printing was placed atop the reaction cell to direct the photopolymerization at the specific region. The ultraviolet (UV) exposed area formed hydrogel after irradiation under UV light for 45 s. After removing the unreacted solution, another precursor solution that contained AAm, MBAA, and V-50 was injected into the interspace around the preformed P(AAm-co-AMPS) hydrogel and immediately placed under UV light for 60 s. The resultant patterned composite PAAM/P(AAm-co-AMPS) hydrogel was incubated in sodium sulfate (Na₂SO₄) solution of different concentrations. The swelling mismatch led to out-of-plane buckling of the high-swelling disc hydrogel and the formation of domal structure. The recipes of precursor solutions and the detailed dimensions of the as-prepared composite hydrogels are shown in table S1 and fig. S1. To increase the contrast between the P(AAm-co-AMPS) and PAAm gel regions, 2.5% volume fraction of neutral red was added to the first precursor solution. Composite hydrogel with polycation gel as the high-swelling unit was fabricated in a similar procedure by using MPTC as the charged monomer instead of AMPS. The recipes of precursor solutions for the gel synthesis are shown in table S2.

Assembly of electro-actuated pulse pump
The pulse pump was assembled from a chamber, two check valves, a stiff hydrogel, and a domal composite hydrogel, as shown in fig. S13. The stiff poly(methacrylamide-co-methacrylic acid) hydrogel was prepared according to the protocol described in the literature (52). Snapping inward or outward of domal hydrogel [i.e., P(AAm-co-AMPS) disc gel embedded in PAAm gel] steered by the electric field resulted in the liquid pumping out/in with the assistance of check valves that ensured unidirectional transportation of fluid. The direction of the electric field was automatically switched by the DC power controller (dual power automatic transfer switch) with an optical sensor, which was associated with the snapping transition of the domal hydrogel. The initial bending speed of the disc gel outward under an electric field, the laser was relieved and the pump was supplied by DC power 1 to generate an electric field with switched direction. When the dome snapped outward, the laser was blocked and the pump was supplied by DC power 2 to generate an electric field with direction opposite to that of DC power 1 (fig. S14). The strokes of pumping in or pumping out fluid were measured by the mass after successive snapping upward and downward of the domal gel.

Mechanical force–induced snapping of domal polyelectrolyte gel
External force–induced snapping transition of the domal hydrogel was investigated using a tensile tester to generate controllable compressive strain at room temperature. The hydrogel dome was clamped at two ends by two pairs of glass plates. A cylinder glass bar with the diameter of 6 mm was used as the compressive indenter, which moved downward to compress the gel dome with a constant rate of 10 mm min⁻¹. As shown in fig. S2, under a certain of compressive strain, the hydrogel dome underwent an asymmetric deformation before the snapping transition. The force-displacement curve was recorded, and the energy barrier was calculated by integrating the area under the curve. After each measurement, the homogenous dome was flipped to make the dome face upward against the glass indenter for the next-round force-induced snapping transition. The energy required for snapping transition varied little during the cyclic tests. The force-induced snapping transition of domal poly-electrolyte hydrogel with different feeding molar fraction of AMPS, fₐ, and concentration of Na₂SO₄, Cₛ, was also examined under the same condition, and corresponding energy required for snapping transition was estimated from the force-displacement curves and presented in fig. S6.

Electro-actuated snapping of domal polyelectrolyte gel
A pair of graphite electrodes were assembled face to face with a spacing of 10 cm and placed in Na₂SO₄ aqueous solution. The two ends of the hydrogel dome were clamped by two pairs of glass plates, which was placed between the graphite electrodes with the dome facing toward the cathode. After the application of the electric field with different strength, snapping transition of the domal hydrogel was recorded by a video camera. The moment when the hydrogel underwent a fast snapping was defined as the snapping time, tₛ. The effects of E (intensity of electric field), fₐ, and Cₛ on tₛ were examined by controlled experiments with one parameter varied yet other ones kept constant (reference experimental conditions: E = 4 V cm⁻¹, fₐ = 10%, and Cₛ = 0.1 M). The electro-snapping has good reproducibility, as independently confirmed by at least five experiments for each condition.

Electro-actuated bending of polyelectrolyte gel strip
Slender strips of P(AAm-co-AMPS) hydrogel (length: 20 mm) were cut from the equilibrated gel sheet (thickness of as-prepared gel: 0.5 mm). The free-standing gel strip was placed in Na₂SO₄ solution between the graphite electrodes with the long axis parallel to the electrodes. After the action of electric field, the gel strip gradually bent toward the cathode. The bending curvature of the strip, κ, which varied with the action time, t, of the electric field, was examined using ImageJ to analyze the snapshots taken with 10-s intervals. During this process of electro-actuated bending deformation, the gel strip bent with increasing curvature to a maximum value, κₘ, and then slightly relaxed. The initial bending speed of the gel strip, v₀, was estimated from the slope of κ-t plot with t < 30 s. Influences of experiment conditions and gel parameters, including E, fₐ, and Cₛ, on the electro-actuated bending of the gel strip were investigated from the recorded behaviors. In addition, the effect of gel strip width on the bending deformation was also examined. As
shown in fig. S8, the bending behavior became insensitive to the width of the gel strip when the value was above 3 mm. Thus, the width of the gel strip was kept as 3 mm in the following experiments.

**Measurements of swelling ratio and Young’s modulus of the gels**

The as-prepared PAAm and P(AAm-co-AMPS) hydrogel sheets with different compositions were cut into disc shape and then swelled in a large amount of water or saline solutions with different concentration of Na₂SO₄, Cₗ, for 3 days to reach the equilibrium state. The swelling ratio in length of the hydrogel, S, was calculated as $S = l/l_0$, in which $l$ and $l_0$ refer to the diameter of the disc gel in the equilibrated and as-prepared states, respectively. Mechanical properties of the hydrogels equilibrated at different conditions were measured by tensile and compression tests using a tensile tester (Instron 3343). For tensile tests, the samples were cut from the hydrogel sheet into dumbbell shape with initial gauge length of 12 mm and a width of 2 mm. For compression tests, the samples were cut from the hydrogel sheet into disc shape with diameter of 8 mm. The tests were performed at room temperature to gel samples at a constant deformation rate of 100 mm min⁻¹ for tensile measurements and 0.2 mm min⁻¹ for compression measurements. Nominal stress and strain were recorded, and Young’s modulus of the hydrogel was estimated from the slope of stress-strain curve below a strain of 10% (fig. S7).

**Theoretical modeling**

The dynamic electro-actuation process of polyelectrolyte gels in an aqueous solution was modeled by solving the coupled equations of nonlinear elasticity and mass transportation (42, 43). Despite the fast dynamics at the very moment of snapping through, we neglect the inertia and distributed body forces and assume the nominal stress field $s(X, t)$ to be in equilibrium at all time for mathematical simplicity

$$\nabla \cdot s = 0 \quad (1)$$

Such an approximation may cause inaccuracy in predicting the time of response and other dynamic behaviors but should capture the process up to the point of snapping instability.

Here and throughout the paper, all spatial differentials are taken with respect to the geometry in the reference configuration, denoted by coordinates $X$. The nominal stress is related to the deformation gradient, $F = \partial x(X, t)/\partial X$, as well as the concentrations of mobile ions and solvent via the equations of state, $s = \partial W/\partial F$. We adopt the additive assumption and write the Helmholtz free energy density $W$ as the sum of the contributions from stretching the polymer chains and mixing water with polymer and mobile ions (47). Lack of inertial terms, to stabilize the snap-through process and avoid singularity, we added a minute viscous term to the stress (48).

The conservation of mobile species, including water molecules and the mobile ions, requires that the changing rate of the nominal concentration $C$ of species $\alpha$ is related to its flux $J^\alpha$ by

$$\frac{\partial C^\alpha(X, t)}{\partial t} = -\nabla \cdot J^\alpha \quad (2)$$

Kinetic relations are further assumed that the diffusion fluxes are proportional to the negative gradient of chemical potential $\mu^\alpha$ with $M^\alpha$ being a mobility tensor. While the migration of different types of mobile species may affect each other, and thus the diffusion fluxes may be interdependent on the gradients of chemical potentials of different species, here we neglect the complex kinetics just to show the dominating players. The chemical potentials of mobile ions are given by the equations of state, which are also derived from the free energy function $W$: $\mu^\alpha = \partial W/\partial C^\alpha$.

It is further assumed that molecular incompressibility holds true for both polymer chains and water, and, thus, the water concentration $C^W$ and volume expansion are directly related as

$$\Omega(C^W - C^W_0) = \det F - 1 \quad (4)$$

Here, $\Omega$ is the volume occupied by each water molecule and $C^W_0$ is the initial water concentration in the as-prepared gel. Equation 4 is substituted into Eq. 2 to eliminate $C^W$ from the unknown fields. The volumes of the mobile ions are neglected for simplicity.

Last, as ionic conductors, both the polyelectrolyte gel and the electrolyte solution are electroneutral in most part of the bulk, except in a thin layer on the gel-solution interface or the surface of electrodes. The extremely thin nonneutral layers, known as the electric double layers, have a characteristic thickness of nanometers or even thinner for the ionic concentrations of interest and are thus believed to have little effect to the bending of the millimeter-thick gel strips. Therefore, following Doi et al. (43), we neglect the electric double layers and enforce the entire gel and the solution to be electroneutral by using a Lagrange multiplier $\phi$ and including the term

$$e\phi(\sum z^\alpha C^\alpha + z^f C^f) \quad (5)$$

where $e$ is the elementary charge, $z^\alpha$ is the valence of mobile ions, and $z^f$ and $C^f$ are the valence and the concentration of fixed ions. The Lagrange multiplier $\phi$ can be recognized as the electric potential and contributes to the electrochemical potentials.

A similar set of governing equations are prescribed in the liquid solution surrounding the gel, except the mechanical equilibrium for stress (Eq. 1). A moving arbitrary Lagrangian–Eulerian mesh is introduced in the solution domain and deforms with the gel at the interface to enable the equations in the Eulerian frame. Because of the omission of the electric double layers, the electric potential $\phi$ is no longer continuous through the gel-solution interface. Instead, a local equilibrium is assumed across the interface, such that the electrochemical potentials of the mobile species, $\mu^\alpha$, are assumed to be the same. Omitting the electric double layers near the electrodes, it is difficult to prescribe a physically meaningful boundary condition in terms of electric potential. Instead, the electrochemical potentials of both types of mobile ions on one electrode are taken to be the references, where $\mu^\alpha = 0$, while the fluxes are prescribed on the other side, with equal magnitude but opposite signs for the two types of ions. The other boundaries of the solution domain are treated as impermeable and insulating.

To facilitate numerical calculation and generalize the results, all variables and equations are written into dimensionless forms. Concentrations are normalized with the inverse of the volume of a water molecule $\Omega$, e.g., $C_\ell = \Omega C_\ell$; energies and chemical potential with $kT$, $\mu^\alpha = \mu^\alpha/kT$. Without resolving the electric double layer, the model lacks an intrinsic length scale. We normalize all lengths...
by the original thickness of the hydrogel sheet $H$ and correspondingly all times with $H^2/D$, with $D$ being the diffusion coefficient of water. The governing equations are implemented into a finite-element code in the commercial platform COMSOL. Multisphysics 5.4 and solved numerically in a fully coupled manner to obtain the time evolution processes of the gel structures.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at https://science.sciencemag.org/content/8/466/eaab9608.full.

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Acknowledgments

Funding: We acknowledge financial support from National Natural Science Foundation of China (51971389, 52173012, and 11972505) and Natural Science Foundation of Zhejiang Province of China (LR19C030002). Author contributions: Z.L.W. and C.Y.L. conceived this concept and designed the experiments. C.Y.L., S.Y.Z., and X.P.H. performed the experiments and analyzed the data. W.H. carried out theoretical and numerical analyses. C.Y.L., W.H., Q.L., and Z.L.W. contributed to the interpretation of the results. C.Y.L., W.H., and Z.L.W. wrote the paper. Z.L.W. and W.H. supervised the research. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Submitted 25 October 2021
Accepted 24 February 2022
Published 13 April 2022