Bioinspired Self-Growing Hydrogels by Harnessing Interfacial Polymerization

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The production of natural materials is achieved through a bottom-up approach, in which materials spontaneously grow and adapt to the external environment. Synthetic materials are specifically designed and fabricated as engineered materials; however, they are far away from these natural self-growing attributes. Thus, design and fabrication of synthetic material systems to replicate the self-growing characteristics of those natural prototypes (i.e., hairs and nails) remains challenging. Inspired by the self-growing behaviors of keratin proteins, here the fabrication of synthetic hydrogels (i.e., polyacrylamide (PAAm)) from the free radical polymerization at the interface between AAm precursor solution and liquid metals (i.e., eutectic gallium-indium (EGaIn)) is reported. The newly formed hydrogel materials at the EGaIn/AAm precursor interface gradually push the whole hydrogel upward, enabling the self-growing of these synthetic hydrogel materials. This work not only endows the fabrication of synthetic materials with unprecedented self-growing characters, but also broadens the potential applications of self-growing materials in actuation and soft robotics.

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1. Introduction

Bioinspired smart materials, featuring intriguing stimuli responsiveness and autonomous behaviors of natural prototypes, have become the basis for many new technological developments. The latest advancement in bioinspired smart materials has upended traditional design concepts and greatly expanded the application fields, including sensors,^[1] actuators,^[2] switches,^[3] robotics,^[4,5] human-machine interfacing,^[6] electronic devices,^[7] biomedical engineering,^[8] etc. For example, self-healing materials have been invented to mitigate damage through the reversible dissociation/association of covalent or dynamic covalent bonds.^[9,10] Shape memory materials are harnessing external triggers (i.e., thermal, optical or magnetic field) to activate the shape change of prefixed materials and structures.^[11] Strengthening materials are mainly achieved through the further polymerization, cross-

linking, or reorientation within the as-formed network structures.^[12,13] The fabrication process of these bioinspired smart materials always involves chemical synthesis, assembling, molding, mechanical machining, 3D printing, etc.

In nature, the living organisms are able to create various elegant and complex architectures with distinctive characters through a spontaneously self-growing mode under ambient conditions without extra high energy input. For example, keratin proteins, widely existing in the fingernails and hairs, are responsible for their self-growing behaviors (Figure 1a). When keratin cells at the root of the nail grow, they are slowly pushed forward by those newly formed cells jostling for space behind them. This process allows the fingernails to continuously grow at a rate of about 3 mm per month, while 1 mm per month for toenails.^[14,15] In sharp contrast to these completely dynamic and open systems observed in nature, synthetic materials continuously incorporate external components within one unit without compromising the materials' structural and mechanical integrity. Therefore, synthetic materials are generally considered as static and closed systems, suffering from their intrinsic selforganization mechanisms.[16,17]

Most recently, scientists and engineers are continuously fascinated by the self-growing characters of these natural prototypes, which could not be readily replicated in synthetic systems. One of the representative strategies, to endow synthetic materials with the living characters, involves the incorporation www.advancedsciencenews.com



Figure 1. Bioinspired design rationale for self-growing hydrogel materials. a) Schematic illustration of the underlying mechanism for the self-growing phenomena of keratin protein in human hairs. New cells are constantly forming in the hair bulbs, sticking together, and hardening. With more new hardened cells attaching to the hair from below, it is gradually pushed up out of the skin, at a rate of about 1 cm per month. b) Schematic illustration of our bioinspired self-growing hydrogels from free radical polymerization at the interface between liquid metal (i.e., EGaIn) and a monomer precursor solution (i.e., AAm). c) Snapshotted images recording the growing process of PAAm hydrogels within a glass tube (diameter of 3.5 mm and length of 100 mm) at 45 °C. The self-growing system is consisted of EGaIn (44.4 wt%) and AAm precursor solution (28.5 wt%). d,e) Microscale structural morphology of the PAAm hydrogel samples from self-growing reactions through ESEM observation for both the perpendicular and parallel directions. Scale bar: 25 μm.

of microorganisms or biological components (i.e., cells, bacteria, or enzymes) as a key component, aiming to engineer the natural processes of biological components within the synthetic materials.^[18–20] However, it poses harsh requirement on the external environments, in order to maintain the availability/ activity of these microorganisms or biological ingredients.^[21] Equally important, there are even fewer examples so far of practical synthetic versions of the self-growing materials.^[1,22–24]

Herein, we proposed a biological metabolism-inspired strategy to develop the self-growing hydrogel materials, by harnessing the continuous radical polymerization at the interface between liquid metal (i.e., eutectic gallium–indium (EGaIn)) and aqueous monomer (i.e., acrylamide (AAm)) solution. Gallium's atomic configuration of [Ar] 3d¹⁰4s²4p¹ is representative of odd electron species, making it a source of unpaired electrons as radical initiators for polymerization.^[25] The side product of hydrogen gas facilitates the formation of pores within the hydrogels, which further decreases the density of hydrogel materials. Moreover, newly formed hydrogel materials at the EGaIn/AAm monomer precursor interface gradually push the whole hydrogel structure upward, therefore, imparting the hydrogel materials with unprecedented self-growing characters. We have also demonstrated the potential of such self-growing

hydrogels as actuators, which could serve as a guideline for the control of prospective actuation and soft robotics.

2. Results and Discussion

2.1. Design and Fabrication of Self-Growing Hydrogels

To implement our design rationale, as depicted in Figure 1b, we choose AAm as the precursor, which is usually used to prepare hydrogel materials through free radical polymerization.^[26,27] As an active material with unpaired electrons,^[28] liquid metals of EGaIn have been widely exploited as a high-efficiency radical initiator for monomers like acrylamides or acrylates, in order to synthesize polymer or hydrogel materials. Therefore, a polyacrylamide (PAAm)/EGaIn hydrogel composites could be readily obtained by uniformly dispersing EGaIn nanoparticles (~100 nm in diameter) within AAm aqueous solution under ultrasonication.^[25] However, despite the spontaneous polymerization without extra initiators, such as ammonium persulfate or α -ketoglutaric acid, no self-growing characters could be detected (Figure S1, Supporting Information).

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Different from the dispersion of EGaIn micro-/nanoparticles within the AAm monomer solution,^[25] in our study here, bulkstate EGaIn was placed at the bottom of a glass vial due to its high density (4.9 g cm⁻³); therefore, a distinct and macroscopic interface between EGaIn and AAm solution was formed (Figure 1b). It deserves to mention that EGaIn can form H₂ in aqueous conditions (Figure S2, Supporting Information),^[25,29] which further generate pores within the PAAm hydrogels. The pores within the hydrogel serve as micro-/nanoscale channels, allowing the transportation of AAm monomers to the EGaIn/ PAAm interface. Moreover, the pores could efficiently decrease the density of the PAAm hydrogels, thus pushing the newly formed PAAm hydrogel materials upward, leading to continuous growing of the PAAm hydrogels, similar to the selfgrowing of fingernails or hairs (Figure 1a).^[14,15] Moreover, from the results of Fourier-transform infrared (FT-IR) and Raman spectra analysis (Figure S3 and Tables S1 and S2, Supporting Information), some AAm monomer residues were detected, which could be completely removed by soaking within excessive amount of water, prior to some specific biomedical uses.

The self-growing characters of our hydrogel systems were first validated in a slender glass tube (diameter of 3.5 mm and height of 100 mm, Figure 1c and Video S1 (Supporting Information)), filling with 28.5 wt% AAm monomer solution (0.73 g, 0.66 mL) and EGaIn (0.57 g, 0.12 mL). After an incubation period of 6 h, opaque hydrogel material was formed at the EGaIn/AAm monomer solution interface. With the reaction proceeding, new hydrogels continuously formed at the interface and forced the previously formed hydrogels to move upward, thus a 1D self-growing behavior along the glass tube was detected (Figure 1c and Video S1 (Supporting Information)). In the plane perpendicular to the self-growing direction, the PAAm hydrogel exhibited a honeycomb-like network structure with disordered yet open pores (Figure 1d), different from the closed-pore morphology of conventional PAAm hydrogels (Figures S4 and S5, Supporting Information), corroborating the role of H₂ in forming porous hydrogels. Meanwhile, preferential alignment of the pore walls was clearly detected along the self-growing direction (parallel, Figure 1e). Similar self-growing behavior was also detected in other containers, such as glass vial (diameter of 20 mm, height of 50 mm, Figure S6 and Video S2 (Supporting Information)), with slight difference in the growing kinetics (i.e., induction time and growing rate).

To further quantify the self-growing kinetics, we conducted the hydrogel growing tests within a slender glass tube (diameter of 3.5 mm and height of 100 mm), and monitored the whole growing process with a camera (**Figure** 2a). We then analyzed the self-growing kinetics by plotting the height of the asgrown PAAm hydrogel samples as a function of reaction time (Figure 2b). For a representative self-growing test with an AAm concentration of 28.5 wt%, the whole process could be distinctly divided into four stages, namely, the incubation stage (0–6 h), fast-growing stage (6–14 h), slow-growing stage (14–24 h), and growing-terminated stage (24–66 h).

We further investigated the effects of monomer concentration (c_0) and reaction temperature (*T*) on the self-growing kinetics of PAAm hydrogels (Figure 2b–d and Figures S7 and S8 and Tables S3 and S4 (Supporting Information)). A critical AAm concentration of 16.7 wt% was detected for the self-growing

reaction at 45 °C, below which no hydrogel could be spontaneously formed during an observation period of 144 h. When c_0 was set between 16.7 and 41.2 wt%, distinct self-growing behaviors were detected, and the growing rate v remained constant (8.81 ± 0.23 mm h⁻¹) despite the change in c_0 . Afterward, when c_0 was further increased above 44.4 wt%, the self-growing behavior was substantially inhibited with v of 0.06–0.20 mm h⁻¹. By contrast, the incubation period (t_0) exhibited a nonlinear effect on c_0 (Figure 2c). With c_0 increased, t_0 first dropped to a minimum value of 5 h at $c_0 = 33.3$ wt% and then gradually increased to 25 h at $c_0 = 50.0$ wt%, afterward, it remained ≈25 h.

Reaction temperature T is another key factor dominating the self-growing kinetics of the hydrogel materials (Figure 2d and Figure S8 and Table S4 (Supporting Information)). When T was lower than 25 °C, no hydrogel materials could be generated within the observation period of 144 h for c_0 of 28.5 wt%, but only few small bubbles observed at the interface. When T was increased up to 65 °C, small bubbles (diameter of 0.2-0.6 mm) were formed immediately at the interface within 1 h (Video S3, Supporting Information). Afterward, larger-sized bubbles (2.1–2.6 mm) were formed within the hydrogels (Video S3, Supporting Information), leading to porous hydrogels with microporous structure and low polymer network density (≈ 0.24 g cm⁻³). Consequently, self-growing PAAm hydrogels with structural collapse and inferior mechanical properties were obtained (Figure S9, Supporting Information). Within the optimal temperature range of 25–55 °C, with T gradually increased, v increased from 0.32 ± 0.04 to 25.28 ± 2.83 mm h⁻¹, while t_0 decreased from 72 to 2 h.

We also explored the effect of oxygen on the self-growing behaviors of PAAm hydrogels by carrying out the self-growing tests under both aerobic and anaerobic conditions (Videos S4 and S5 and Figure S10, Supporting Information). We found that the incubation period of AAm under anaerobic conditions was \approx 3.3–5.0 h, which was around 60% of that for aerobic conditions (≈4.0-8.7 h). Moreover, self-growing PAAm hydrogels under anaerobic conditions exhibited a faster self-growing rate (18.29 mm h^{-1} for anaerobic and 8.57 mm h^{-1} for aerobic conditions, Figure S10 (Supporting Information)). Therefore, removal of oxygen may facilitate the self-growing kinetics of PAAm hydrogels. Further improvement over t_0 could be rationally conducted by increasing the reaction temperature and/or deoxygenation. However, in order to ensure the simplicity and practicability, the following self-growing experiments were still carried out without deoxygenation treatment.

In nature, plants could regrow after grafting or transplanting only if the nutrients are continuously supplied. In our case, at the end of the growing reaction, when new precursor solution (AAm 28.5 wt%, 0.4 mL) was further fed into the glass tube, the self-growing behavior could be resumed, until the complete consumption of the newly added AAm monomers (Figure S11, Supporting Information). We also quantified the regrowing kinetics by adding a previously grown PAAm hydrogel into an AAm precursor solution (Figure 2e–h and Video S6 (Supporting Information)), and the whole growing process was recorded. Thanks to the residue of EGaIn at the bottom end of the previously grown PAAm hydrogel samples (Figure S12, Supporting Information), they could further act as the active sites to initiate the interfacial radical polymerization, thus the regrowing www.advancedsciencenews.com

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Figure 2. Self-growing and regrowing kinetics of the PAAm hydrogels. a) Schematic illustration of the self-growing experiment in a slender glass tube (diameter of 3.5 mm and length of 100 mm) to investigate the growing kinetics. b) Plotting of the growing height of PAAm hydrogels as a function of reaction time for precursor solutions with various AAm concentrations (c_0). c) Plotting of the growing rate (ν) and incubation period (t_0) as a function of AAm monomer concentration. The fitting function is presented in Figure S7 (Supporting Information). d) Plotting of ν and t_0 as a function of reaction temperature (T). The fitting function is presented in Figure S8 (Supporting Information). e) The schematic of regrowing experiment in a slender glass tube (diameter of 3.5 mm and length of 100 mm), by placing a previously grown PAAm hydrogel sample within a slender glass tube containing AAm precursor solution (28.5 wt%). f) Snapshotted images recording the regrowing process at different reaction times (AAm of 28.5 wt% and temperature of 45 °C). The previously grown PAAm hydrogel segment was stained with yellow dyes, in order to differentiate it from the newly grown PAAm hydrogel segment (opaque) through regrowing. Scale bar: 10 mm. g) Plotting of the growing height as a function of reaction time t_0 of both the regrowing and first-cycle self-growing PAAm hydrogels. Note: ν is defined as the slope of the linear region (fast-growing stage) of the growing kinetics curve. t_0 represents the incubation period of self-growing. Data in (c), (d), and (h) are means \pm S.D., n = 15.

of PAAm hydrogels. For a better visual effect, we stained the previously grown PAAm hydrogel with a ginger yellow fluorescent dye (3,4-ethylenedioxythiophene-2-hexyl-[1,2,3]triazolo[4,5*c*]pyridine-3,4-ethylenedioxythiophene (EDOT-2HPTz-EDOT)). Due to the hydrophobic essence of EDOT-2HPTz -EDOT, there was no diffusion out of the dye molecules, thus a distinct color

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difference between the previously grown and newly grown PAAm hydrogel sections. An induction time of 32.0 ± 0.5 h was detected, afterward, the PAAm hydrogel gradually grew at a speed of 3.1 ± 0.2 mm h⁻¹, which was slightly slower than the first-cycle growing process (Figure 2g,h). Therefore, we could expect that by designing the reactant supplying system, the self-growing behavior of the hydrogel materials could proceed continuously as long as the raw reactants are available.

2.2. Mechanical Properties of Self-Growing Hydrogel

We then conducted uniaxial tensile tests on the self-growing hydrogel materials from various AAm precursor solutions (**Figure 3a**–c and Table S5 (Supporting Information)). For the hydrogel samples from AAm concentration of 37.5 wt%, cracks initiated when the strain reached 40%, and gradually propagated till the fracture strain of 50% (Figure 3a). Young's modulus and fracture strain increased with the AAm concentration from 28.5 to 37.5 wt% (Figure 3b and Figure S13 and Table S5 (Supporting Information)). However, when the AAm concentration was further increased to 41.2 wt%, the Young's modulus and fracture strain decreased to 206 \pm 63 kPa and 40 \pm 5%, respectively. It is deserved to mention that when the AAm content was less than 28.5 wt%, the as-formed hydrogel material was too fragile to quantify the mechanical properties (Figure S14, Supporting Information).

When comparing with natural and synthetic materials in terms of their mechanical properties, such as strength and toughness, one might consider that our self-growing PAAm hydrogels exhibit inferior performance. To validate the generality of our self-growing strategy, we also tested the selfgrowing behaviors with other monomers, and it is shown that this strategy also works with other acrylate monomers, such as 2-hydroxyethyl methacrylate (HEMA) (Figure S15 and Videos S7 and S8, Supporting Information). Moreover, PAAm/alginate hydrogels, a well-established tough hydrogel system reported by Suo and co-workers^[26] could also be fabricated through our self-growing strategy (Figure S16 and Videos S9 and S10, Supporting Information). Moreover, the self-growing PAAm/alginate hydrogels display comparable tensile strength and higher Young's modulus (Figure 3c,d) to the classical PAAm/alginate tough hydrogels, despite the difference in chemical composition (i.e., solid fraction, AAm/alginate ratio, calcium crosslinking density). Thus, it indicates the great promise of our self-growing strategy in fabricating hydrogel materials with a variety of chemical composition, as well as mechanical performance, allowing for the rational design and fabrication of hydrogel materials with tailored properties.

In Figure 3e and Table S6 (Supporting Information), we compared the mechanical properties of our self-growing hydrogels with other hydrogels from natural or synthetic materials. Hydrogels from animal tissues generally exhibit lower fracture strain (from 28.3% to 72.7%) and Young's modulus (from 349.3 to 544.7 kPa).^[27] Natural hydrogels also exhibit a broad range of fracture strain from 20% to 1190% and a moderate Young's modulus (from 17 to 600 kPa).^[26,27,38,40,41] Synthetic hydrogels with ultrahigh fracturing strain (for example, 2340% for alginate/PAAm hydrogel) and a broad range of Young's

modulus (1.5–550 kPa) have been widely reported.^[26,35,41–43] In our work here, these self-growing hydrogels exhibit a higher Young's modulus of 140–873 kPa, which is comparable to that of caudicle, muscle, and hydrogels made of chitosan or cellulose (Figure 3f and Table S6 (Supporting Information)).^[26,27,40] Moreover, these self-growing hydrogels also exhibit a fracture strain (from 12% to 50%) similar to that of skin, muscle, and hydrogels made of gellan gum or chitosan (Table S6, Supporting Information).^[27,40] Therefore, the mechanical properties of self-growing hydrogels could be rationally tailored to that of biological materials.

2.3. Self-Growing Hydrogels as Actuators

Living organisms are capable of uptaking external nutrients and incorporating them as part of their structural integrity through a self-growing mode, in sharp contrast to that of synthetic materials with static appearance, shapes, and functions. In our work here, we have demonstrated the capability of self-growing PAAm hydrogels as high as ≈80 mm (depending on the height of glass tube), without any extra high energy input. Similar to the natural vine climbing up along a scaffold (Figure 4a), we are expecting that the PAAm hydrogels could grow vertically along a predesignated microscale channel. To validate this hypothesis, we filled the channels with AAm monomer precursors, with EGaIn located at the bottom of the channel (Figure 4b). To track the whole growing process, we stained the AAm monomer precursors with traceable amount of indicator, such as phenolphthalein (base sensitive) in right channel and litmus (acid sensitive) in the left channel (Figure 4c and Figure S17 (Supporting Information)). A "buoy" was placed on the top of the AAm precursor solution, and employed as a marker to track the selfgrowing process. On the other hand, top of the apple-shaped containers was filled with base (potassium hydroxide (KOH) solution) and acid solution (citric acid solution), respectively. As recorded in Video S11 (Supporting Information), after an incubation period of ≈4.5 h, opaque hydrogel materials were generated and growing spontaneously and continuously, pushing the buoy upward (purple and yellow) along the channels. At \approx 7–10 h, the hydrogel material reached the apple-shaped container, the color of the hydrogel changed from transparent white (or opaque) to purple (right channel, Figure 4d) and red (left channel, Figure 4e), respectively. Afterward, the hydrogel continued to fill the apple-shaped containers until all the AAm precursors were completely consumed within ≈15 h (Figure 4f). The self-growing behaviors of the PAAm hydrogels could successfully mimic the natural vine climbing phenomena, exhibiting great promise in soft wall-climbing robotics.^[44] Notably, our self-growing hydrogels exhibit distinct advantages over traditional soft robotics in dredging those small curved pipes, especially for those microchannels that cannot be operated by large-scale machinery.

The self-growing process of hydrogels can also generate forces for soft actuation, similar to the natural prototype's making its way, such as the small plant breaking through the soil (**Figure** 5a). Inspired by such kind of natural "power," we proposed a high-efficiency soft actuator based on selfgrowing hydrogels to convert the growing "power" into the





Higher Young's modulus

Figure 3. Mechanical properties of the self-growing hydrogels. a) Snapshotted images of the self-growing PAAm hydrogel sample (diameter of \approx 3.5 mm and length of \approx 20 mm, AAm concentration of 37.5 wt%) during uniaxial tensile test till fracturing at a maximum strain of 50%. b) Nominal stress-strain curve of the PAAm hydrogels from various AAm monomer concentrations (28.5, 33.3, 37.5, and 41.2 wt%). All these PAAm hydrogel samples were prepared within glass tubes (diameter: 3.5 mm, length: 100 mm, EGaIn content of 44.4 wt% and temperature of 45 °C) through self-growing. c) Nominal stress-strain curve of self-growing PAAm/alginate double network (DN) hydrogels and conventional PAAm/alginate DN hydrogels. All these samples were prepared within glass tubes (diameter of 3.5 mm, length of 100 mm, and temperature of 45 °C). The AAm/(Aam + alginate) ratio was set as 96.8 wt%. The fraction of the covalent cross-linker MBAA and initiator (EGaIn for self-growing PAAm/alginate hydrogels and ammonium persulfate for conventional PAAm/alginate hydrogels) were fixed at 0.02 and 17.1 wt% that of acrylamide, respectively. The weight ratio of CaSO₄ was fixed at 0.00028 wt% that of alginate. d) Summary of the Young's modulus, fracture strain, and tensile strength of these hydrogels. e) Ashby plot of the Young's modulus for various elastomers and hydrogels. The data used for the plotting are summarized in Table S6 (Supporting Information). Data in (d) are means \pm S.D., n = 15. Data of other hydrogel systems showed in (e) were compiled from the literature.^{(26,27,30-39]}

corresponding strong actuation force (Figure S18, Supporting Information). As shown in Figure 5b,c and Video S12 (Supporting Information), we set the EGaIn/AAm precursor solution within a home-design mold, and the system was sealed with a cap, for which a force of 53 N was required to open

it. Thanks to the self-growing essence, the PAAm hydrogel reached the cap at t = 2.3 h. A crack was formed at the cap at t = 3 h, and the crack further propagated until the whole cap was opened at t = 4 h. We also compared the power density (actuation force per volume) of our self-growing hydrogels with

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3. Conclusion

Inspired by the growth of keratin protein, we have developed a design rationale to engineer conventional hydrogel materials with unprecedented self-growing characters. A growing model of interfacial radical polymerization has been proposed to interpret the underlying mechanism of the self-growing process. Such kind of self-growing mechanism is applicable to a variety of monomers, and the mechanical properties of these self-growing hydrogels could be rationally tailored to the magnitude of biological materials. The current study addresses a long-standing challenge in the development of smart hydrogel materials with self-growing attributes, which are only observed in those natural systems, and have not yet been achieved in synthetic materials. Moreover, the self-growing performance as a new kind of actuation route is also expected to serve as a guideline for the control of prospective actuation and soft robotics.

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а

С

е

10 h

0 h

b

Growing

Objective region

Reactant B

Reactant A

Self-growing

AAm solution

7 h

15 h

EGaln

d

f

5 mm







Figure 5. Self-growing hydrogels as soft actuators. a) Image showing a mushroom growing and breaking out of the soil. b) The snapshotted images recording the process of self-growing PAAm hydrogels for soft actuation. The self-growing PAAm hydrogel system was set within a 3D printed mold. The whole process recorded the moment when the PAAm hydrogel reached the cap (t = 2.3 h), a crack formed at the cap (t = 3 h), and the crack propagated until the whole cap was opened (t = 4 h). The AAm concentration is fixed at 28.5 wt%. The weights of EGaIn and AAm solution are fixed at 0.64 and 10 g, respectively. c) The actuation force generated by the self-growing process was measured as a function of reaction time. Inset is the schematic illustration for the setup of the actuation force experiment. A 3D printed mold, filled with EGaIn and AAm solution, was loaded within a tensile machine, while the actuation force was recorded in situ. d) Ashby plot of the actuation power density for various hydrogel-based actuation systems. The data used for the plotting are summarized in Table S5 (Supporting Information). Data of other hydrogel systems showed in (d) were compiled from literature.^[45-52]

4. Experimental Section

Materials: Unless otherwise specified, the materials and chemicals used in this work were used directly without further purification. AAm (AR, 99.0%) and HEMA (AR, 99.0%) as monomer, N,N'-methylene diacrylamide (MBAA), AR, 97%) as cross-linker, ammonium persulfate (APS) (AR, \geq 98.0%) and α -ketoglutaric acid (AR, 97%) as initiators, N, N, N', N'-tetramethylethylenediamine (TEMED) (AR, >98.0%) as catalyst, EGaIn (melting point of 16 °C) as self-growing initiator, sodium alginate (AR, viscosity of 200 ± 20 mPa s), ionic cross-linker two hydrated calcium sulfate (CaSO₄·2H₂O) (AR, 99.0%), and phenolphthalein (1.6 wt%) were purchased from Sigma-Aldrich or Alfa Aesar. KOH (AR, Beijing Chemical Reagent), citric acid monohydrate (AR, Sinopharm Chemical Reagent), litmus (Sinopharm Chemical Reagent) were purchased from commercial chemical reagent companies. Nanosuperhydrophobic self-cleaning coating (ZXL-CSS) was purchased from Shandong Laiyang Zixilai Environmental Protection Technology Co., Ltd. Milli-Q water (18.25 M Ω) was used for all aqueous polymerizations.

Preparation of Conventional PAAm Hydrogels: A precursor solution was prepared by mixing AAm (5 g), MBAA (700 μ L, 0.023 wt%), APS (102 μ L, 0.2 M), and TEMED (8.2 μ L) in 10 mL Milli-Q water under stirring at room temperature until a clear solution was obtained. The precursor solution was then poured into a homemade acrylic mold and then covered with a glass plate, which was pretreated with superhydrophobic self-cleaning coating. The hydrogel was cured under ultraviolet irradiation (power of 15 W, wavelength of 254 nm, power density of $1.2 \times 10^4 \,\mu$ J cm⁻²) within a UV reactor (XL-1500, Spectronics).

Preparation of Self-Growing Hydrogel: The self-growing PAAm hydrogel was prepared exploiting the interfacial free radical polymerization of AAm precursor solution with EGaIn as the radical initiator. Glass vials (20 mm in diameter, 50 mm in height) and glass tubes (3.5 mm in diameter, 100 mm in height) were employed as the reactor. In the glass

vial, a precursor solution was prepared from the mixture of 2 g AAm (28.5 wt%) with 5 g Milli-Q water, together with 4 g EGaIn (44.4 wt%). In order to measure the growing kinetics, AAm precursor solutions of various weight fractions (i.e., 16.7, 23.1, 28.5, 33.3, 37.5, 41.2, 44.4, 50.0, 54.6, and 60.0 wt%) were used. 0.57 g EGaIn and 0.73 g AAm precursor solutions were added into the glass tube. A distinct interface formed immediately due to the intrinsic difference in density between the EGaIn (\approx 4.9 g cm⁻³) and AAm precursor solution (\approx 1.1 g cm⁻³). The self-growing reaction was conducted under a predesignated temperature (i.e., 25, 35, 45, 55, and 65 °C) within an incubator (DNP-9272, Jinghong, China), and a digital camera was used to record the entire self-growing process. The self-growing of poly(2-hydroxyethyl methacrylate) (PHEMA) and PAAm/ alginate hydrogels were carried out following the same protocol. For the self-growing of PHEMA hydrogel under 65 °C, a HEMA monomer solution (28.5 wt%) and EGaIn (44.4 wt%) was used. For the self-growing PAAm/alginate hydrogels under 45 °C, an AAm/alginate mixture (AAm/ (AAm + alginate) ratio of 96.8 wt%) and EGaIn (17.1 wt% of acrylamide) was used. The weight of the covalent cross-linker MBAA was fixed at 0.02 wt%, and the weight ratio of $CaSO_4$ was fixed at 0.00028 wt%.

Regrowing of the PAAm Hydrogel: In the glass tubes (3.5 mm in diameter, 100 mm in height), the regrowing kinetics was quantified by adding a previously grown PAAm hydrogel (3.5 mm in diameter, 25 mm in height) into an AAm precursor solution (28.5 wt%, 0.55 g). It was deserved to mention that some EGaIn remained at the bottom end of the previously grown PAAm hydrogel samples (Figure S12, Supporting Information), which further acted as the active sites to induce the interfacial radical polymerization. The regrowing reaction was conducted under 45 °C within an incubator (DNP-9272, Jinghong, China). The whole growing process was recorded with a camera. For a better visual effect, the previously grown PAAm hydrogel was stained with ginger yellow fluorescent dye (EDOT-2HPTz-EDOT), which was used in the previous work.^[53]

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X-ray Photoelectron Spectroscopy (XPS): To evaluate the chemical composition and confirm the surface oxidation of Ga, the self-growing hydrogel was further characterized using XPS (K-Alpha, Thermo Scientific, America) with a vacuum of 3×10^{-7} mbar and working voltage of 12 kV. The self-growing hydrogel was dried at 60 °C for 24 h in a vacuum oven (ZKGT-6053, AODEMA, China) and ground into a powder before characterization.

Micromorphology Characterization: The microscale morphologies of the self-growing hydrogels were characterized using an environmental scanning electron microscope (ESEM) (Quattro S, ThermoFisher, Netherlands) at 10 kV acceleration voltage, low vacuum (chamber pressure of 0.53 Torr), and low-temperature environment (-15 °C). These hydrogel samples were immersed in liquid nitrogen for 2.5 h prior to imaging. All hydrogel samples were frozen with liquid nitrogen, and then fractured immediately at the frozen state, and the cross-sectioned surface was then characterized.

Porous Structure Analysis: The pore size distribution of these selfgrowing hydrogels was quantified using mercury intrusion porosimetry with a high-performance automatic mercury porosimeter (Autopore 9520, Micromeritics, America). These hydrogel samples were freeze-dried with a lyophilizer (SCIENTZ-10N/A, Ningbo SCIENTZ Biotechnology, China) under vacuum (1.0 Pa) at -80 °C for at least 3 days, until all of the solvent was sublimed.

Mechanical Tests: Tensile test of the self-growing hydrogel samples was conducted with a tensile machine (WDW-2, Changchun Kexin Test, China), equipped with a 10 N load cell. For each data point, at least 15 parallel samples were tested. Cylindrical-shaped hydrogel samples (diameter of 3.5 mm, length of 30 mm) were used. Paperboard (specifications of 300 g) was used as a gripping intermediate and a pair of homemade aluminum alloy (6061) clamps was used as fixtures, in order to mitigate the influence of centering error of the microtester gripers. All mechanical tests were performed in air at room temperature. In both the loading and unloading tests, the deformation rate was kept constantly at 5 mm min⁻¹, and the tensile elastic modulus was fitted within the strain range of 5%.

Self-Growing Hydrogels Mimicking the Climbing Behaviors of Nature Vines: The mold used for the climbing-up demonstration consisted of three parts (as shown in Figure S17 in the Supporting Information), which were all made of acrylics. The first part was the front side of the model, including a layer of 75 mm \times 90 mm \times 2 mm black acrylic plate shell to decorate the appearance (Number 1). Another layer of 2 mm thick transparent acrylic plate was used to encapsulate the channels (Number 2), in which two holes were used to load liquid reactants within the apple-shaped reaction chamber. The second part was the main body of the model, including a layer of fruit-tree-type channels made of 75 mm \times 90 mm \times 5 mm transparent acrylic plate (Number 3) for the hydrogel growing, another layer of 75 mm \times 90 mm \times 2 mm black acrylic plate as the background (Number 4), a back cover made of a 75 mm \times 90 mm \times 2 mm transparent acrylic plate for encapsulation (Number 5). The third part was the rear storage tank of the mold made of transparent acrylic board (Number 6) and a rear cover made of a 2 mm thick acrylic board (Number 7). These three parts were bonded together with super glue, and it should be noted that EGaIn was added within the left and right channels prior to packing. For a better visual effect, a buoy (5 mm \times 5 mm \times 8 mm) was placed at the top of aqueous precursor solution as a marker to track the self-growing process.

Phenolphthalein (0.05 g, 1.6 wt%) and 2 g AAm were dissolved within 5 g Milli-Q water until the homogeneous precursor AAm Solution 1 was obtained. Litmus powder (2 g) was added to 100 mL of Milli-Q water under stirring for one day until a saturated litmus solution was obtained. Saturated litmus solution (0.05 g) and 2 g AAm were added to 5 g Milli-Q water to prepare the precursor AAm Solution 2. Precursor AAm Solution 1 and acid solution (citric acid monohydrate, 0.05 M) were loaded within the left branch and apple channel, respectively. Meanwhile, precursor AAm Solution 2 and alkali solution (KOH, 0.05 M) were loaded within the right branch and apple channel, respectively. Finally, the mold was placed within an incubator (DNP-9272, Jinghong, China) with a temperature of 45 °C.

FT-IR Spectroscopy Analysis: The chemical structures of AAm precursor and self-growing PAAm hydrogel samples were characterized by using an infrared spectrometer (Nicolet iS5, Thermo Scientific, America) with potassium bromide as an internal reference. The self-growing PAAm hydrogels were directly dried at 60 °C for 24 h in a vacuum oven (ZKGT-6053, AODEMA, China) and ground into powders prior to FT-IR measurement.

Raman Spectra: The Raman spectra of the AAm precursor and self-growing PAAm hydrogel samples were recorded using a Raman spectrometer (LabRAM HR Evolution, HORIBA Scientific, Japan) with 785 nm laser source. The laser power was varied from 1% to 10% with a 10 s exposure time. Indication of the strength of the Raman lines was given by referring them to the strongest band, which was given an intensity of 10. The self-growing PAAm hydrogels were directly dried at 60 °C for 24 h in a vacuum oven (ZKGT-6053, AODEMA, China) and ground into powders prior to Raman measurement.

Self-Growing Hydrogels as Soft Actuators: As shown in Figure S18 (Supporting Information), setup for the soft actuator was consisted of a small bucket, a large bucket, and a cap. Two buckets were assembled into a double nested structure. Dimension details of each section are listed in Figure S18 (Supporting Information). 0.64 g EGaIn, 10 g 28.5 wt% AAm precursor solution, and the small bucket were placed in the big bucket, and then, the big bucket was sealed with the cap. It was noted that a small hole was punched on the top of the cap as an outlet to release the gas generated during self-growing process. Thus, the contribution from the inner air pressures was eliminated. The soft actuator setup was placed within an incubator (DNP-9272, Jinghong, China) with a temperature of 45 °C.

Quantification of the Actuation Force: The actuation force generated by the hydrogel self-growing process was monitored as a function of the reaction time. The schematic illustration for the setup of the actuation force experiment is shown in the inset of Figure 5c. A 3D printed mold, filled with 0.64 g EGaIn and 10 g AAm solution (28.5 wt%), was loaded in a tensile machine, while the actuation force was recorded during the whole self-growing process. The test was conducted within a thermal chamber at a predesignated temperature (45 °C).

Statistical Analysis: All the results in this study were presented as mean \pm standard deviation (S.D.), and all the mechanical properties presented in this study were measured from at least 15 parallel samples. Data distribution was assumed to be normal for all the parametric tests, but not formally tested, and no significant difference analysis was performed. The statistical analyses were carried out with the OriginPro software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Author Contributions

N.N.J., J.L., and K.Z. proposed the key idea of this paper. N.N.J. carried out the experiments and theoretical analysis with the assistance of L.Z., J.L., and K.Z. R.G., L.Z., Y.S., and Y.X. discussed the applications with the assistance of N.N.J. All the authors contributed to the writing of the paper.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

actuation, eutectic gallium-indium (EGaIn), interfaces, radical polymerization, self-growing hydrogels

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