Tough and Recyclable Phase-Separated Supramolecular Gels via a Dehydration−Hydration Cycle

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ABSTRACT: Hydrogels are compelling materials for emerging applications including soft robotics and autonomous sensing. Mechanical stability over an extensive range of environmental conditions and considerations of sustainability, both environmentally benign processing and end-of-life use, are enduring challenges. To make progress on these challenges, we designed a dehydration−hydration approach to transform soft and weak hydrogels into tough and recyclable supramolecular phase-separated gels (PSGs) using water as the only solvent. The dehydration−hydration approach led to phase separation and the formation of domains consisting of strong polymer−polymer interactions that are critical for forming PSGs. The phase-separated segments acted as robust, physical cross-links to strengthen PSGs, which exhibited enhanced toughness and stretchability in its fully swollen state. PSGs are not prone to overswelling or severe shrinkage in wet conditions and show environmental tolerance in harsh conditions, e.g., solutions with pH between 1 and 14. Finally, we demonstrate the use of PSGs as strain sensors in air and aqueous environments.

KEYWORDS: *toughness, recyclable, supramolecular gel, phase separation, strain sensor*
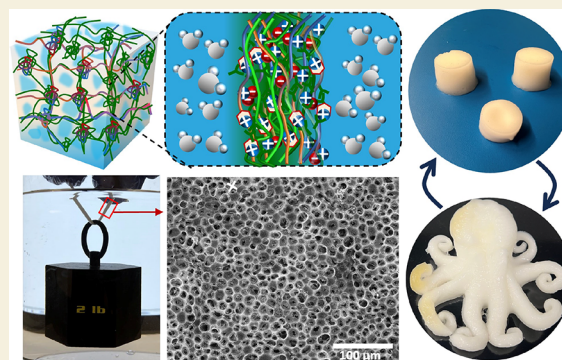
INTRODUCTION

Hydrogels are soft and elastic materials consisting of flexible polymer chains solvated in water. The unique combination of softness and hydration enables their impact on fields including, personal hygiene (e.g., diapers, personal healthcare products, etc.),[1,2] agriculture (e.g., carriers of agrochemicals),[3,4] environmental remediation (e.g., adsorbents and evaporators for water purification),[5,6] and food packaging systems.[7] Hydrogels can be functionalized and are also biocompatible, which are attractive features for applications at the interface of medicine and electronics, including drug delivery,[8,9] soft actuators,[10−12] strain sensors,[13−15] touch panels,[16] and artificial muscles.[17,18] Despite their tremendous potential and societal benefit, the growing consumption of hydrogels could contribute to environmental pollution as they are generally non-biodegradable under natural conditions.[19−21] Moreover, conventional hydrogels are covalently cross-linked, thus challenging to recycle and reprocess after use or damage.[22,23] One of the most effective approaches to resolve these shortcomings is to replace conventional covalent cross-linked gels with supramolecular hydrogels (SGs) cross-linked by dynamic hydrogen bonds.[24] Supramolecular hydrogels, however, are prone to overswelling and disintegration in aqueous environments because the presence of water molecules disrupts hydrogen bonds,[25,26] thus further weakening their mechanical strength. Such instability and poor mechanical properties inhibit the long-

term use and implementation of SGs. Therefore, constructing mechanically robust, yet recyclable gels that resist overswelling in a wide variety of aqueous environments is particularly attractive, but remains a significant materials challenge.

In another approach, phase separation has been exploited to improve the stiffness and restrict the overswelling of hydrogels by increasing the physical cross-linking density and reducing the flexibility of chain segments.[27,28] Recently, researchers have embarked on efforts to design phase-separated hydrogels that include a mechanism for energy dissipation, such as hydrogen bonding,[29] ionic bonding,[30,31] hydrophobic association,[31−33] or crystallization,[34] to increase strength and toughness. The most widely employed approaches to induce phase separation in hydrogels include the use of solvent exchange[35−37] or the addition of salt, i.e., the salting out effect.[33,38] However, the use of organic solvents and other chemicals is not environmentally benign nor are the gels reprocessable, which may further negatively impact the environment at the end of service life.
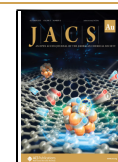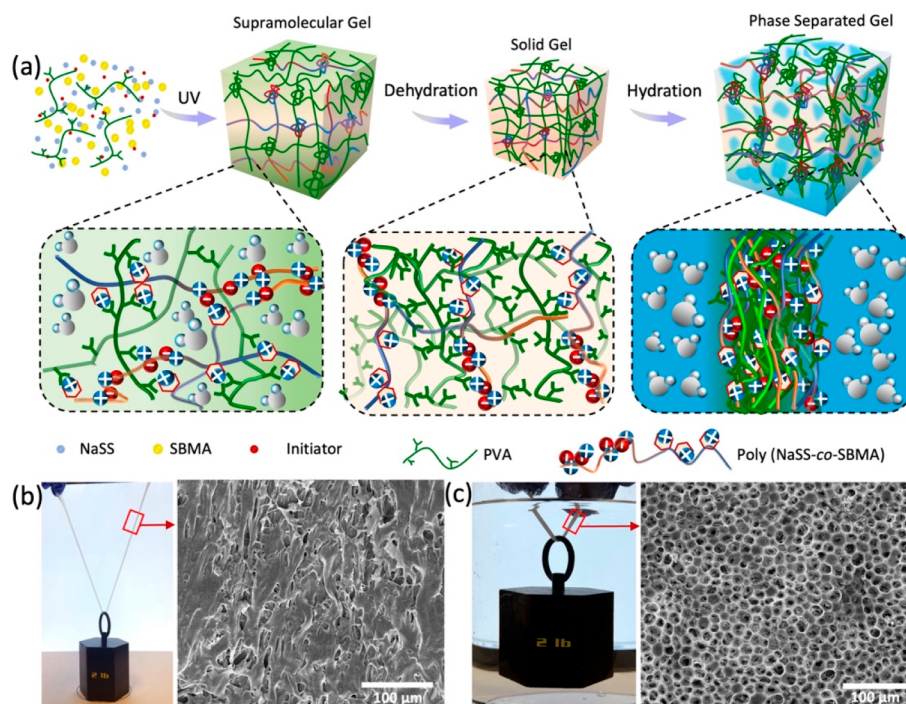
Figure 1. Fabrication and porous structures of the hydrogel. (a) Schematic of the fabrication route for PSGs. Lifting performance and microstructures of (b) SGs and (c) PSGs after dehydration–hydration treatment.

Finally, the structures of gels formed by these approaches are unstable when re-exposed to a wet environment.

With these considerations in mind, we introduce a dehydration–rehydration method to create tough and recyclable, phase-separated supramolecular hydrogels (PSGs). The PSG was prepared by copolymerization of sodium styrenesulfonate (NaSS) and sulfobetaine methacrylate (SBMA) in an aqueous PVA solution, followed by dehydration via air drying and rehydration via swelling in water (Figure 1a). The approach is facile, sustainable, and low-energy: all synthesis occurred in water, and the dehydration–rehydration process required no energy input. Upon dehydration, strong polymer–polymer interactions between PVA and poly(NaSS-co-SMBA) copolymer were activated, as illustrated in Figure S1. Subsequent, rehydration weakened hydrogen-bonding interactions between polymer chains while simultaneously promoting the aggregation of the hydrophobic polymer segments, leading to a PSG composed of water-rich and polymer-rich domains (Figure 1a). The polymer-rich domains acted as robust physical cross-links, which endowed the PSG with an unusual combination of material properties, including toughness, restricted swelling, and recyclability. The PSG exhibited stability in various environments, including mixed solvents containing ethanol, isopropyl alcohol (IPA), dimethyl sulfoxide (DMSO), and even extremely acidic/alkaline conditions with pH 1 and 14. We demonstrate PSG's performance as a flexible and recyclable strain sensor in both air and underwater.

RESULTS AND DISCUSSION

The synthetic route for tough and recyclable PSGs is illustrated in Figure 1a. In the first step, NaSS and SBMA monomers and Irgacure 2959, the initiator, were dissolved in an aqueous PVA (10 wt %) solution (see chemical structures in Figure S1). The aqueous solution transformed into a soft and light-yellow SG

after being irradiated by UV light at 365 nm for 2 h. The failure to form a gel using solely PVA or NaSS in the presence of SBMA highlights the essential role of the polymer interactions between PVA and poly(NaSS-co-SMBA) in the gelation process (Figure S2). The SG was weak and translucent because of the weak hydrogen-bonding interactions between the −OH groups of PVA and the −SO$_3^-$ groups of poly(NaSS-co-SMBA) copolymer (Figure 1b). In the second step, the SG was dehydrated via air-drying at room temperature and subsequently incubated in water for 12 h to form tough and recyclable PSG. Once immersed in water, the hydrophilic groups facilitated water diffusion into the dehydrated SG network. As the polymer backbone is hydrophobic, hydrogen bonding (between −SO$_3^-$ and −OH) and electrostatic interactions (between SO$_3^-$ and −N$^+$(CH$_3$)$_3$) favor the aggregation of polymer chains. These competing effects lead to phase separation and the resulting visual color transformation to opaque.

The morphological difference between SG and PSG was illustrated by scanning electron microscopy (SEM). The SG exhibited a rough and homogeneous structure (Figure 1b). In contrast, the PSG exhibited a continuous porous structure with uniformly distributed pores (Figure 1c). Another stark difference between SGs and PSGs is reflected in their mechanical performance. As illustrated in Figure 1b,c, we attempted to lift a 2 lb weight in water using an SG and PSG with a cylindrical structure (45 mm × 5 mm, Figure S3). The SG stretched but failed before lifting the weight. In contrast, the PSG was capable of lifting the weight. Notably, lifting tests were performed in water, implying PSG's viability for applications in aqueous environments. The difference in mechanical response is due to the difference in morphology. The phase-separated hard domains of PSG act as physical cross-links that strengthen the polymer network. Remarkably, the PSG achieves a desirable balance between mechanical
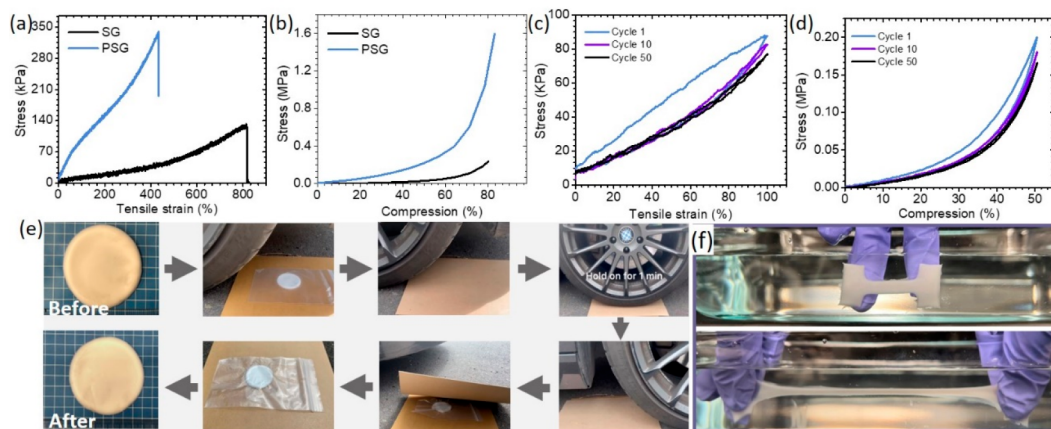
Figure 2. Mechanical characterization of the hydrogels. (a) Typical tensile stress−strain curves of SG and PSG. (b) Compressive stress−strain curves of SG and PSG. (c) Consecutive cyclic tensile stress−strain curves of the PSG for 50 successive loading−unloading cycles at a strain of 100%. (d) Consecutive cyclic compressive stress−strain curves of the PSG. (e) Photographs of a car-compression test. (f) Photographs of underwater stretchability of PSG at a strain of 50%.
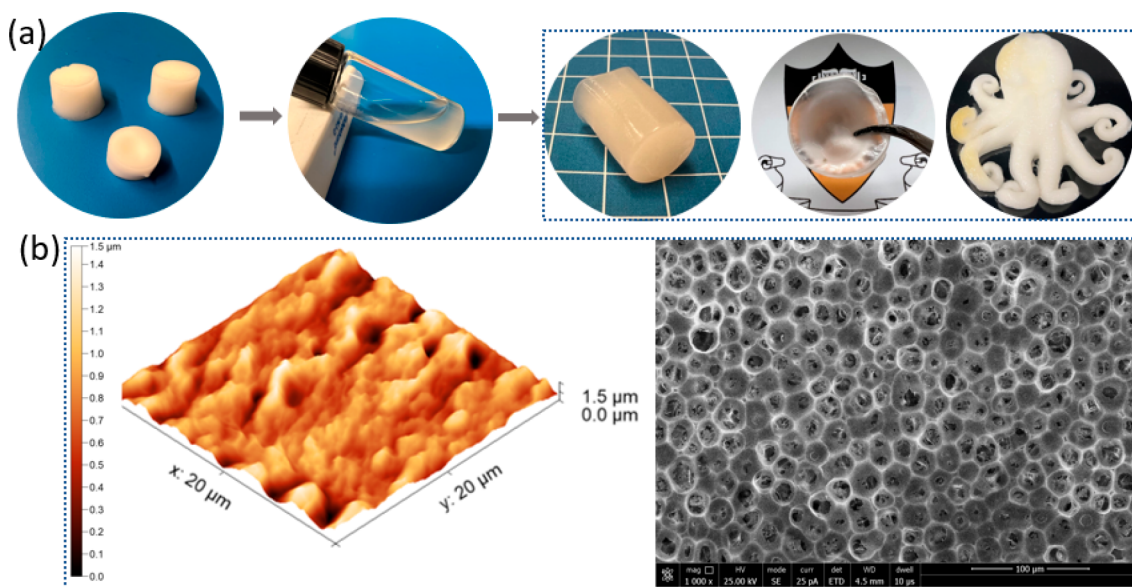

Figure 3. (a) Photos demonstrating the recycling process for the PSG gel. (b) AFM and SEM images of the recycled PSG gel. SEM image shows homogeneous, evenly distributed pores within the recycled PSG gel.

robustness and water content (∼90% water by mass), which distinguishes it from conventionally cross-linked gels or SGs without molecular interactions. The dehydration−hydration approach and design strategy has been applied to additional chemistries to illustrate the generality of the approach (Figure S4).

To examine the quantitative effect of phase separation on the strength and toughness of the gels, tensile and compression tests were performed for SG and PSG samples (Figure 2). The SG exhibited an elongation at break of ∼820% and a fracture stress of ∼130 kPa (Figures 2a and S5). In contrast, a maximum stress up to 340 kPa and a high stretchability of 433% were observed for the PSG (Figures 2a and S5). Both SG and PSG exhibited substantial extensibility, as they can dissipate stress by dissociation of noncovalent physical bonds. The enhanced stiffness of PSG can be further improved by an order-of-magnitude by incubation in a salt solution due to the Hofmeister effect (Figure S7). This is a consequence of the complexes formed between introduced ions and water, leading

to significant aggregation and crystallization of the polymer chains. As shown in Figure 2b, the compressive strength of PSG (∼1.8 MPa at 80% compression) is ∼6 times greater than SG (∼0.3 MPa at 80% compression). After removal of the stress, the PSG rapidly recovered its original shape, while the SG exhibited only a slight recovery (Figure S6). Even after 50 continual loading−unloading cycles at a strain of 100% and a compression of 50%, the PSG maintained fatigue resistance, as revealed by the nearly constant hysteresis loops in Figure 2c,d. The PSG's remarkable elasticity was also demonstrated through an extreme compressibility test that was performed using a car, as seen in Figure 2e. The PSG, initially measuring 120 mm in diameter and 3 mm in thickness, was enclosed in a plastic bag and positioned between two plastic sheets to prevent slippage and surface contamination during the test. A four-wheel car with a total weight of ∼2200 kg was driven over the PSG repeatedly and held atop the PSG for 1 min (Video S1). After the car-compression test, no fracture or irreversible deformation was observed for the PSG. In addition, even in an
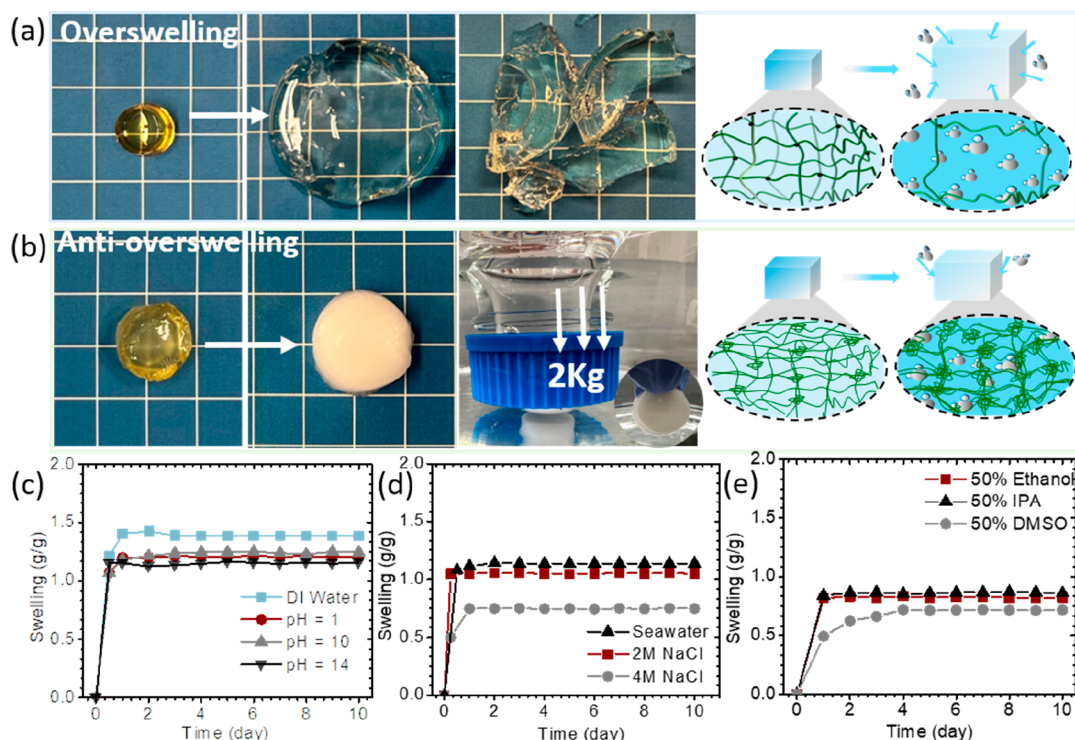
Figure 4. Swelling properties in various liquids. (a) Overswelling behavior of conventional PolyNaSS hydrogels. (b) Anti-overswelling of PSG and demonstration of toughness and shape recovery upon loading of a 2 kg weight. (c−e) Swelling kinetics of PSG in water, pH 1, 10, and 14, seawater, and organic solvents.

aqueous environment, the PSG possessed excellent stretchability of 420% (Figure 2f), which ensured its viability for applications in different environmental conditions.

The network formation of PSGs is enabled by noncovalent interactions, which enable recyclability and reprocessability of the gel. Reprocessing is accomplished in a two step process: (1) heating the PSG and (2) performing the dehydration−hydration process (Figure S8). Heating to ∼80 °C disrupts the hydrogen bonds and hydrophobic interactions within the PSG and enhances polymer mobility. The first step results in a translucent liquid, which upon cooling can be reformed into various shapes via the second step, i.e., the dehydration−hydration process (Figure 3a). The morphology of the reprocessed gel after dehydration−hydration was examined by AFM and SEM. The structure is consistent with that of the original material (Figures 3b and S9).

The stability of PGSs in an aqueous environment is a major criterion for their practical use. Visualization of PSGs after swelling in water was compared to a covalently cross-linked polyNaSS hydrogel and noncovalent SGs without the dehydration−rehydration process (Figures 4 and S10). The polyNaSS hydrogel (5 mol % cross-linking density) expanded significantly in water with a swelling ratio of ∼20 g/g and broke into pieces when gently agitated (Figure 4a). The SG softened when submerged in water and eventually fully dissolved (Figure S10). In contrast, the PSG absorbed water and reached an equilibrium swollen state within 24 h and remained unchanged in water for a minimum of 10 days, i.e., the length of the experiment (Figure 4c). No overswelling or dissolution was observed. In pure water, the abundance of $-SO_3^-$ groups within PSG caused a higher osmotic pressure and strong electrostatic repulsion, which facilitated water molecule penetration and network expansion. However, the phase-separated hard domains act against expansion by limiting excess water adsorption. On balance, the two competing effects resulted in a material with an anti-overswelling behavior. The anti-overswelling of PSG is distinctive and indicates that the phase-separated domains can stabilize the supramolecular bonds in a wet environment and maintain a stress (Figure 4b).

SGs are typically unstable in water,[23] salt solutions,[39] organic solvents,[40] and acidic/alkaline conditions.[25,41] For instance, Wang et al. developed a tough SG of poly(methacrylamide-*co*-methacrylic acid) by utilizing hydrophobic methyl groups to stabilize hydrogen bonds.[25] The gel was stable in neutral or weakly alkaline conditions (pH ≤ 9.6) but dissolved in strongly alkaline conditions. Creating hydrogels that can remain stable in harsh environments remains a challenge. PSGs are structurally stable under various environmental conditions, including extreme acidic/alkaline solutions, seawater, concentrated salt solutions, and mixed solvents (Figures 4d,e and S11−S13). For instance, PSGs exhibited similar swelling behavior in pure water and pH = 1, 10, and 14 solutions. In seawater, the PSG's swelling ratio was slightly lower than that in pure water and decreased further in more saline solutions (Figure 4d). Finally, upon exposure to various mixed solvents, the PSGs maintained a similar swelling ratio and shape (Figures 4e and S13). The remarkable stability in diverse conditions can be attributed to the combination of osmotic pressure, anti-polyelectrolyte,[42−44] and Hofmeister effects[45−48] (further explanation can be found in the Supporting Information).

The integration of antifouling properties into mechanically strong hydrogels is crucial for their use in many applications, including as flexible strain sensors.[49,50] Here, we demonstrate the incorporation of antifouling within the suite of synergistic
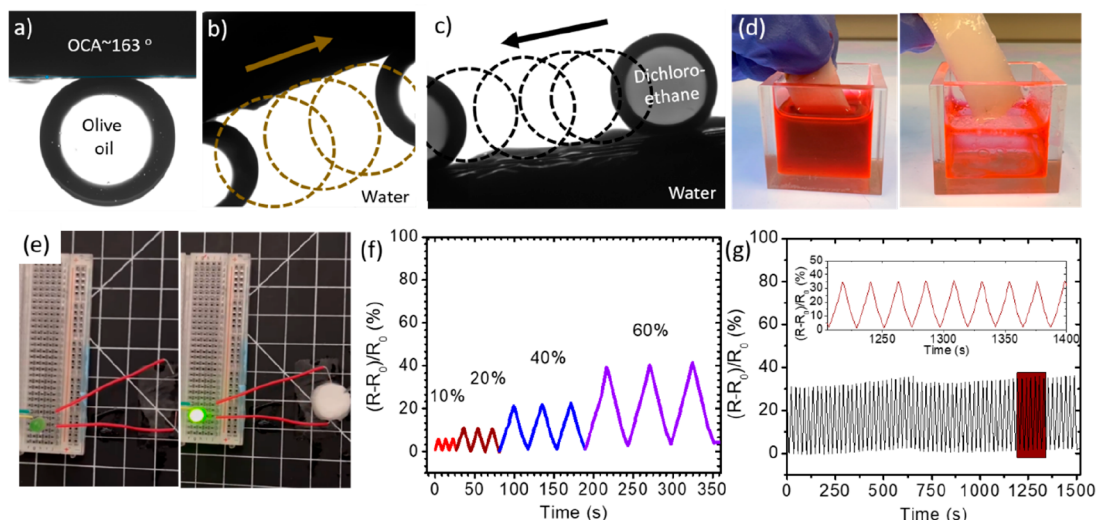
Figure 5. Antifouling and self-cleaning property. (a) Underwater−oil contact angle (OCA) of olive oil on the PSG. (b) Underwater sliding behavior of (b) olive oil and (c) 1,2-dichloroethane droplets on the PSG. (d) Photos of the PSG contaminated by Nile red-labeled olive oil before and after being washed with water. (e) Demonstration of conductivity of PSG. (f) Relative resistance changes of PSG in air under different strains. (g) Real-time resistance variations of the PSG upon stretching to 50% strain for 70 cycles.

properties of PSG. The underwater−oil contact angles (OCA) of PSG were measured after being immersed in water (Figure 5a). An OCA of ∼163° for a high viscosity olive oil was observed, indicating PSG's underwater superoleophobicity. When the PSG was tilted at a small-angle underwater, the oil droplets rolled quickly over the PSG surface (Figures 5b,c and S14). This effect was attributed to the zwitterionic components' ability to form a hydration layer, which acted as a lubricant to decrease the oil adhesion force and penetration.[51−53] In a water environment, a jet of 1,2-dichloroethane spontaneously bounces off the surface of the PSG without any noticeable oil residue remaining (Figure S15). When exposed to a pure oil, the PSG surface was initially partially wetted with olive oil but was restored to a pristine state by washing with water (Figure 5d). This property is vital for the use of hydrogels in strain sensors and biomedical applications.[49,54−56]

The good ionic conductivity of the PSG suggests its use as a sensor (Figure S7b). Ionic conduction characteristics were observed for the PSG by integration into a circuit with a light-emitting diode (LED) indicator. As shown in Figure 5e, the LED indicator lit under a 3 V power supply by the PSG. As a strain sensor, the relative resistance changes of PSG in air were investigated under stepped cyclic strains of 10%, 20%, 40%, and 60% (Figure 5f). The relative resistance change rate at different strains recovered the initial value, indicating the strain-sensing reversibility. More importantly, the PSG exhibited durability and fatigue resistance: the resistance change remained consistent during continuous stretching (∼70 cycles) at a fixed strain of 50% (Figure 5g). The PSG's stability was also revealed by the consistent current obtained from chronoamperometry experiments under prolonged cathodic potential sweeps (Figure S16). Remarkably, the PSG is amenable for use in an underwater environment owing to its stability in wet environments. As shown in Figure S17, significant differences in electrical signal were clearly observed upon stretching the PSG to strains of ∼20% and ∼50% in distilled water. The PSG sensor did not suffer any lag or attenuation upon continuous stretching, which indicates a stable cycle performance and short response−recovery time.

Therefore, incorporating phase separated segments into a hydrogel shows great potential for addressing the primary issue of long-term underwater sensing stability in hydrogel-based sensors.

■ CONCLUSION

In this study, we developed a tough and recyclable PSG through a dehydration−hydration method using water as the only solvent. The approach is facile and environmentally benign and could be applied to various hydrogels. In general, traditional hydrogels are usually weakened upon hydration, shrink severely upon solvent exchange, and cannot be recycled. In contrast, the PSG's hydrophilicity favors water absorption, and its phase-separated domains inhibited overswelling in aqueous solution and stiffen the polymer network. The phase-separated structure also enabled the PSG to achieve enhanced toughness and excellent stability in various liquid environments such as seawater, organic solvents, and extremely acidic/alkaline solutions. Additionally, the PSG exhibited antifouling and self-cleaning properties. These characteristics make the PSG highly adaptable for applications in challenging environments. As demonstrated, the tough and recyclable PSG has great potential for use as a strain sensor in air and underwater, thus furthering the potential for applying hydrogel materials in smart sensors and electronic devices. Overall, this work introduces a highly effective dehydration−hydration method for developing phase-separation-induced tough gels that are recyclable.

■ METHODS

Preparation of PSG Gels

PSGs were synthesized by *in situ* photoinitiated polymerization of NaSS and SBMA in a PVA aqueous solution. By variation of the feed monomer ratios of NaSS and SBMA in the corresponding mixtures while keeping the mass ratio of PVA at 10%, several types of SGs with different mechanical properties were fabricated. Briefly, 10% PVA was first prepared by dissolving PVA powder in water at 80 °C. Then, NaSS, SBMA, and Irgacure 2959 were dissolved in 10% PVA solution under magnetic stirring. The mixture above was sealed and illuminated with UV light for 2 h to induce polymerization.

Subsequently, the gels were dehydrated in air and soaked in deionized (DI) water overnight at room temperature for rehydration. After this dehydration−rehydration process, white gels were obtained. To demonstrate that this approach can be applied to other hydrogels, we also fabricated poly(*N,N*-dimethylacrylamide)/PVA, poly(acrylamide-*co*-SBMA)/PVA, and poly(acrylamide)/PVA hydrogels. In addition, the conventional covalently cross-linked PolyNaSS hydrogel was fabricated in DI water using the same procedure described above but with the addition of a 5% Bis cross-linker.

■ ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon request. All other data needed to evaluate the conclusions in this study are provided in either the article or the Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.3c00326.

> Detailed experiments including synthetic procedures, materials characterizations, and more data (PDF)
>
> Video S1: a car-compression test (MP4)

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Author Contributions

R.D.P. coordinated the project; X.X. synthesized materials and conducted characterization with aid from Y.L.E., K.S.S.C., N.C., and A.L.M.; all authors discussed and interpreted the results and contributed to writing the manuscript.

Notes

The authors declare no competing financial interest.

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