Giant Volume Change of Active Gels under Continuous Flow

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Supporting Information

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S1 Fabrication of microgels

Materials

2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), *N,N'*-methylene-bis-acrylamide (BIS, **5**), *N*-isopropylacrylamide (NIPAAm, **4**) (≥99%) were purchased from Sigma-Aldrich. NIPAAm was purified by recrystallization before use. All the ruthenium catalysts **1**, **2** and **3** were synthesized as reported in previous publications.[1]

Fabrication of Gel_a microgels

NIPAAm (**4**, 40 mg), BIS (**5**, 0.7 mg) and Ru catalyst (**1**, 3.8 mg) were charged into a 0.5 mL eppendorf. Methanol (190 μL) and water (50 μL) were added into the eppendorf and the mixture was mixed well. Methanol solution of Irgacure 2959 (10 μL, 10 mg/mL) was added into the mixed solution. The mixture was injected into a polycarbonate-glass mold and sealed. After applying a mask on the glass side of the mold, the set-up was immersed in a shallow ice-water bath and exposed under an Omicure light source for 10 mins. The microgels were detached from the mold and immersed in DI water for dialysis for 3 days before further tests.

Fabrication of Gel_b microgels

Fabrication of Gel_b microgels is the same as the fabrication of Gel_a microgels, except that Ru catalyst (**2**, 3.6 mg) instead of Ru catalyst **1** was added to the reaction mixture.

Fabrication of Gel_c microgels

NIPAAm (**4**, 40 mg) and Ru catalyst (**3**, 2 mg) were charged into a 0.5 mL eppendorf. Then the same procedure as in the fabrication of Gel_a and Gel_b was followed. The exposure time to Omicure light source was extended to 30 min. After dialysis, Gel_c microgels were obtained for further tests.

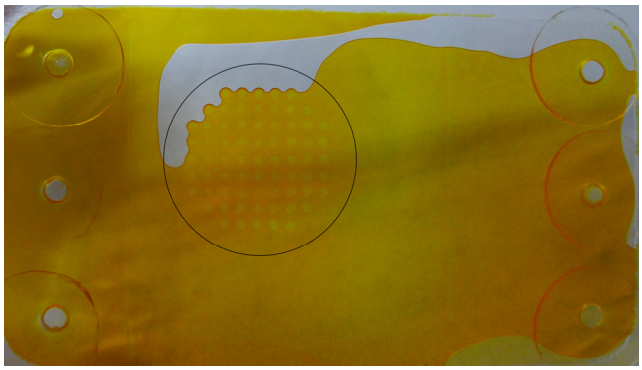


Figure S1. Optical image of the fabrication set-up with microgels inside (black circle part).

S2 Characterization of the microgels

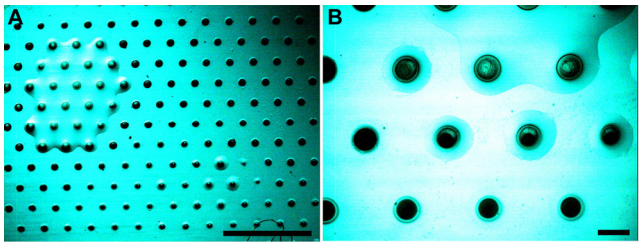


Figure S2. (A) Optical image of a batch of microgels (Gel_a) (scale bar is 5 mm) before detachment from the glass slide and (B) an extended image (scale bar is 500 μm).

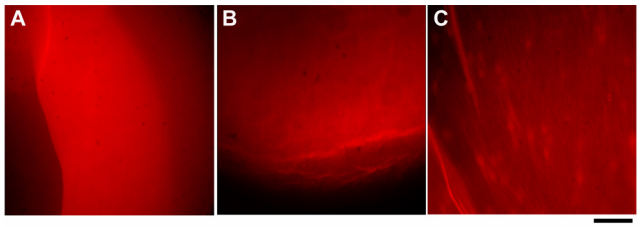


Figure S3. Fluorescent images of thin slice of microgels, (A) Gel_a, (B) Gel_b and (C) Gel_c (scale bar is 10 μm).

To determine the concentrations of the catalysts within the gels, we used a UV-vis spectrophotometer to measure the absorption of catalysts at λ = 450 nm, which helps to quantify the amount of unreacted catalysts monomer. By measuring the weight of the dried gel polymerized from a given volume of prepolymerization solution, we calculate the polymerization rate of NIPAAm (trace amount of BIS in Gel_a and Gel_b is ignored). Based on these data, we estimate that the polymerization conversion of NIPAAm in Gel_a is around 14% with a molar ratio of Ru-catalyst (**1**)/NIPAAm of 0.6%; the polymerization conversion of NIPAAm in Gel_b is around 23% with a molar ratio of Ru-catalyst (**2**)/NIPAAm of 0.5%, and the polymerization conversion of NIPAAm in Gel_c is around 11% with a molar ratio of Ru-catalyst (**3**)/NIPAAm of 5%.

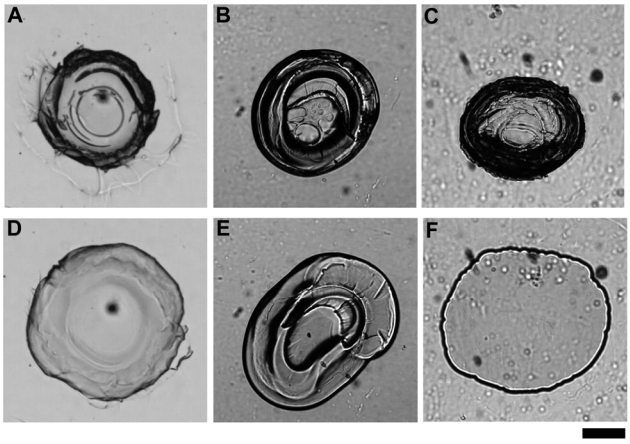


Figure S4. Optical images of gels in the reduced state before and after several hours of BZ reaction. Gel_a at (A) 0 and (D) 6 hof BZ oscillation; Gel_b at (B) 0 and (E) 4 h of BZ oscillation; Gel_c at (C) 0 and (F) 6 h of BZ oscillation (scale bar is 100 μm).

S3 Setup of microfluidic flow cells

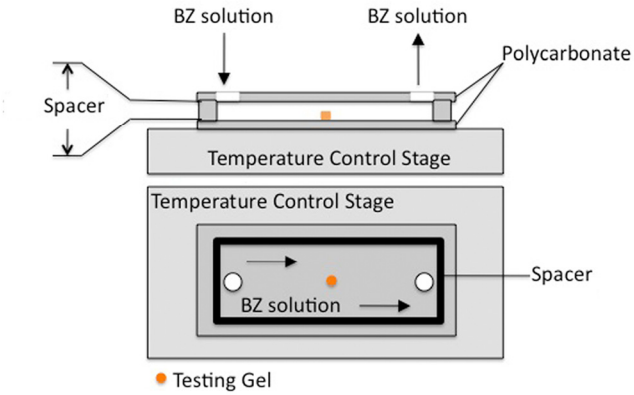
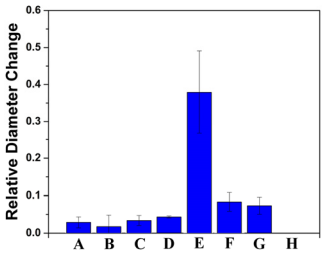


Figure S5. Cartoon illustration of the set-up of the microfluidic flow cell for detection of chemomechanical oscillation of the microgels under a bright field microscope and on a temperature control stage.

S4 Volume change of Gel_a under different conditions



	[BrO_3^-]	[MA]	[H^+]
A	0.2M	0.4M	0.1M (HNO_3)
B	0.2M	1.2M	0.1M (HNO_3)
C	0.2M	0.4M	0.2M (HNO_3)
D	0.2M	0.6M	0.3M (HNO_3)
E	0.2M	0.4M	0.4M (HNO_3)
F	0.2M	1.2M	0.4M (HNO_3)
G	0.2M	0.4M	0.6M (HNO_3)
H	0.2M	0.4M	0.8M (HNO_3)

Figure S6. The relative volume change of the oscillating Gel_a at same continuous-flow rate (10 μL/min) in the same microfluidic channel but different BZ reactant (listed in the table) at 10 °C.

S5 Volume change profiles of microgels under the same BZ flow at different temperatures

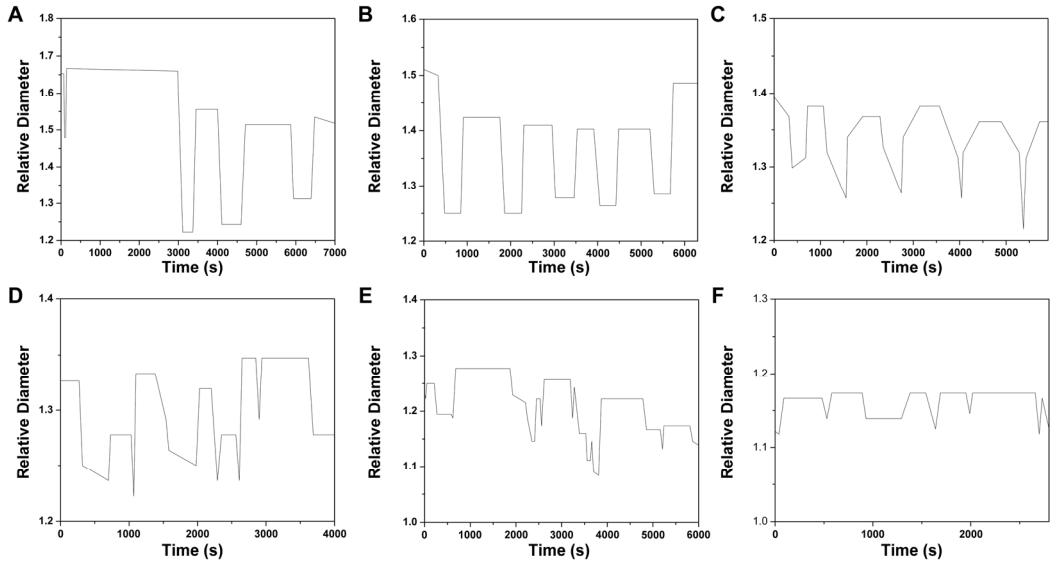


Figure S7. Oscillating volume change profile of Gel_a under a flow of BZ solution (10 μL/min, $[NaBrO_3]$ = 0.2 M, $[CH_2(COOH)_2]$ = 0.4 M, and $[HNO_3]$ = 0.4 M) at (A) 10 °C, (B) 14 °C, (C) 18 °C, (D) 22 °C, (E) 26 °C and (F) 30 °C.

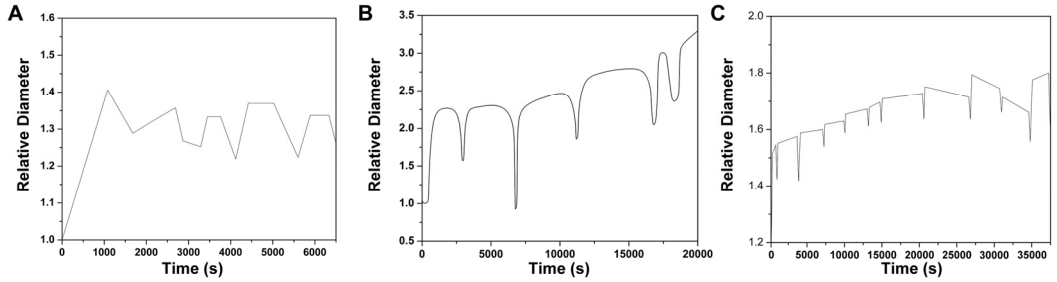


Figure S8. Oscillating volume change profile of Gel_b under a flow of BZ solution (10 μL/min, $[NaBrO_3]$ = 0.2 M, $[CH_2(COOH)_2]$ = 0.4 M, and $[HNO_3]$ = 0.4 M) at (A) 14 °C, (B) 22 °C and (C) 30 °C.

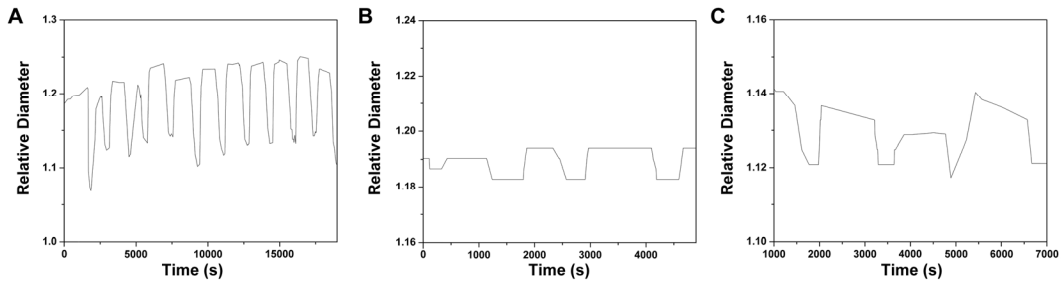


Figure S9. Oscillating volume change profile of Gel_c under the flow of BZ solution (10 μL/min, $[NaBrO_3]$ = 0.2 M, $[CH_2(COOH)_2]$ = 0.4 M, and $[HNO_3]$ = 0.4 M) at 10 °C (A), 14 °C (B) and 18 °C (C).

S6 Volume change profiles of the microgels under continuous flow and stationary conditions

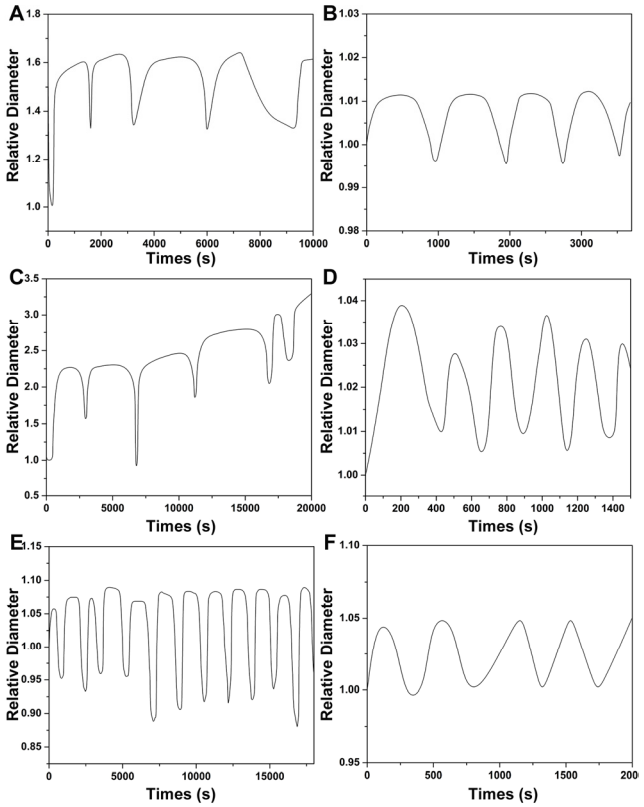


Figure S10. Oscillating volume change profiles of (A) Gel_a, (C) Gel_b and (E) Gel_c with continuous flow, (B) Gel_a, (D) Gel_b and (F) Gel_c without flow under optimal BZ conditions.

S7 Profiles of the volume change of Gel_a at different flow rates of the BZ solutions in microfluidic channels having different widths

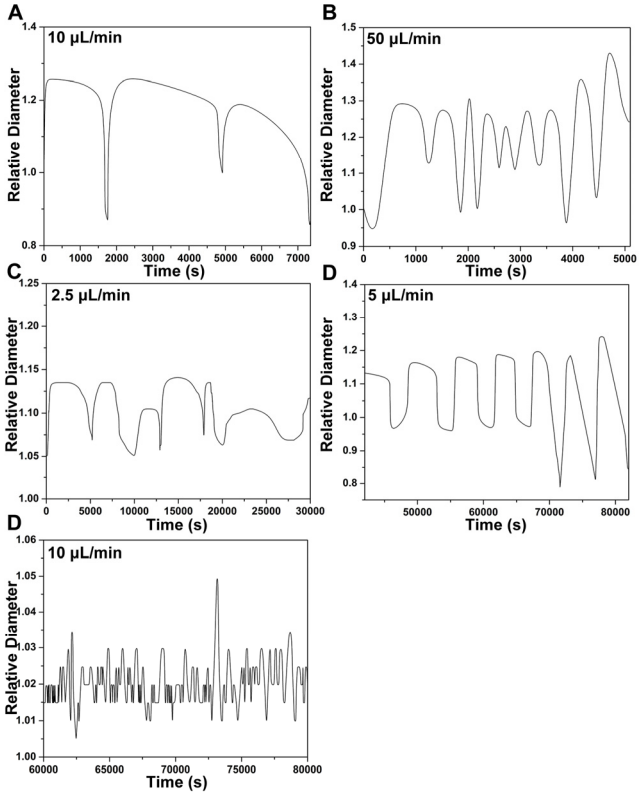


Figure S11. Time dependent relative diameter profiles of Gel_a in a microfluidic channel with a width 40 times the diameter of Gel_1 at a flow speed of (A) 10 µL/min, (B) 50 µL/min, and a channel with a width 10 times the diameter of Gel_a at a flow speed of (C) 2.5 µL/min, (D) 5 µL/min and (E) 10µL/min. (w, width of microfluidic channel; d, diameter of microgel.)

S8 Volume change profiles of Gel_a during counter ion exchange

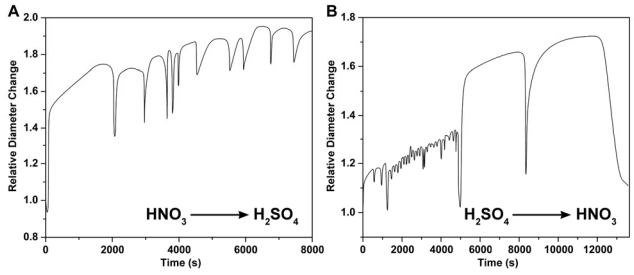


Figure S12. Relative volume change profiles of Gel_a at same continuous-flow rate (10 µL/min) but with counter ion exchange (A) from HNO_3 to H_2SO_4 and (B) from H_2SO_4 to HNO_3.

Movie S1 Volume change of Gel_b under continuous flow of BZ solution in the microfluidic channel

Movie S2 Volume change of array of Gel_a under continuous flow of BZ solution in the microfluidic channel

(1) Zhang, Y.; Zhou, N.; Akella, S.; Kuang, Y.; Kim, D.; Schwartz, A.; Bezpalko, M.; Foxman, B. M.; Fraden, S.; Epstein, I. R. et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 11494-11498; Delgado, J.; Zhang, Y.; Xu, B.; Epstein, I. R. *J. Phys. Chem. A* **2011**, *115*, 2208-2215.