Fast photothermal poly (NIPAM-*co*-β-cyclodextrin) supramolecular hydrogel with self-healing through host-guest interaction for intelligent light-controlled switches

Qiaofeng Gao^{1,2}, Jing Hu^{1,2}, Jianmin Shi³, Wenwei Wu³, Dereje Kebebew Debeli^{1,2}, Pengju Pan^{1,2}, Guorong Shan^{1,2, *}

¹State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China ²Institute of Zhejiang University-Quzhou, Quzhou 324000, China ³Ningbo Fengcheng Institute of Advanced Energy Material, Ningbo 315500, China Correspondence to: Guorong Shan (E-mail: shangr@zju.edu.cn)

S1 Synthesis of Acryloyl-β-cyclodextrin and Graphene Oxide.

The synthesis of AC- β -CD was shown as follows. First, β -CD (5 g, 4.41 mmol) was added to a solution of KOH (1.51 g, 26.88 mmol) in 100 mL deionized water to solubilize under stirring at room temperature. After β -CD was completely dissolved, the solution was cooled to 0 °C. Then, AC (1.08 mL, 13.2 mmol) was added dropwise to the solution for 20 min. The solution was stirred at 40 °C for about 10 h. After the reaction completed, the solution was filtrated, and the filtrate was collected. Most of the solvent was removed using a rotary evaporator, and the precipitate was washed with acetone three times and dried in a vacuum oven for further use.

The synthesis of graphene oxide (GO) was shown as follows 4g of graphite powder and 2 g of NaNO₃ were added to 94 mL of concentrated H_2SO_4 solution. The mixture was stirred in the ice bath for 1 h. After that, 12 g of KMnO₄ was slowly added with vigorous stirring at 0 °C for 2 h. Then the temperature of the mixture was raised to 35 °C for 2 h. Subsequently, 200 mL of deionized water was gradually added into the mixture, and the reaction was transferred to 98 °C for 0.5 h. Finally, 30 mL of 30% H_2O_2 was added to the mixture and then cooled to room temperature. The solution was neutralized with dilute hydrochloric acid. After ultrasonication for 40 min, the supernatant liquid was taken after centrifugation to obtain an aqueous graphene oxide solution, which was dried in vacuum for 24 h to obtain GO.

S2 Detailed Operation Steps of Kinetics Tests.

The wet hydrogels were weighed after water on the surface of hydrogels was removed, using wet filter paper. Then hydrogels were lyophilized until the weight no longer changes and weighed, and the swelling ratio (SR) is calculated by the following equation:

$$SR = \frac{W_S - W_d}{W_d}$$

where W_s is the mass of the wet hydrogel at different temperatures and W_d is the dry mass of the hydrogel.

The deswelling kinetics of the hydrogels was carried out in a water bath at 50 °C. The hydrogels were first immersed in deionized water until equilibrium was reached, then they were placed in a water bath at a temperature of 50 °C. The water on the surface of the hydrogels was removed with filter paper at a specific time, and weighed. Water retention (WR) is calculated by the following equation:

$$WR(\%) = \frac{W_{t50} - W_d}{W_0 - W_d} \times 100$$

where W_{t50} is the mass of the wet gel at a specific time at 50 °C, W_0 the mass of the wet gel at 25 °C after equilibrium, and W_d the dry mass of the hydrogel.

The hydrogel contracted in a 50 °C water bath was reswelled in deionized water at 25 °C, and the water on the surface of the hydrogel was removed using a filter paper at a specific time and weighed. The value of WR is calculated by the following equation:

$$WR(\%) = \frac{W_{t25} - W_d}{W_0 - W_d} \times 100$$

where W_{t25} is the mass of the wet gel at a specific time at 25 °C, and other terms are the same as defined above.



Figure S1 Comparison of FT-IR spectra between β -CD and AC- β -CD. Typical peaks of ester groups at 1720 cm⁻¹ (C=O) and 1210 cm⁻¹ (C=O) could be found on AC- β -CD curve, and double bonds (C=C) at 808 cm⁻¹ shown on FT-IR spectra of AC- β -CD.



Figure S2 NMR spectra of AC- β -CD.¹H NMR spectra of AC- β -CD showed proton signals of double bonds(C=C) were at 5.9 ppm, 6.1 ppm, and 6.3 ppm (H-a, H-b, H-c).



Figure S3 Comparison of FT-IR spectra of hydrogels with different cross-linking methods and partial enlarged.