Electronic Supplementary Information (ESI):

Multi-stage hydrogel rockets with stage dropping-off by thermal/light stimulation

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Supplementary videos description:

Video 1: Drops of water and driving solution on the surface of SDS/PA-*co*-PN hydrogel.

Video 2: The temperature-controlled process for dropping off small rockets step-by-step from the small rocket/GltAg0/small rocket/GltAg6 multi-stage hydrogel rocket. (driving solution: 150 mM NaCl, 100 mM $NaHCO_3$, and 50 mM glucose)

Video 3: The propulsion of two multi-stage hydrogel rockets, including small rocket/GltAg0/small rocket/GltAg6 and small rocket/GltAg16/small rocket/GltAg16. (driving solution: 150 mM NaCl, 100 mM $NaHCO_3$, and 50 mM glucose)

Video 4: The NIR laser-irradiation process for dropping off small rockets step-by-step from the small rocket/GNS-GltAg0/small rocket/GNS-GltAg6 multi-stage hydrogel rocket. (driving solution: 150 mM NaCl, 100 mM $NaHCO_3$, and 50 mM glucose)

Experimental methods and characterization

Preparation of hydrogel small-rockets. The multi-stage hydrogel rocket comprises two sections: glucose responsive SDS/PA-*co*-PN hydrogel (small rocket section) and gelatin/agar gels (sacrificial section). The small rockets were fabricated as follows. Firstly, a mold substrate with multiple rocket-shaped holes (8 mm in length, 4 mm in width, and 120^o of the arrow angle) was manufactured by utilizing silicone rubber. Note that small removable mold parts (2 mm in length, 4 mm in width, 2 mm in thickness, and 120^o of the arrow angle) were equipped for preparing the subsequent sacrificial hydrogel stages. Secondly, 5.0 mg of clay nanosheets (Laponite XLG, BYK Additives & Instruments) was dispersed in 1.0 mL of deionized water to form homogeneous dispersion by stirring for 0.5 h. 56.6 mg of *N*-isopropylacrylamide (J&K Chemical) was dissolved in the Laponite XLG dispersion, and then 19.1 mg of 3-acrylamidophenylboronic acid (Shanghai Macklin Biochemical Technology), 9.3 mg of *N*, *N'*-methylenebis(acrylamide) (J&K Chemical) and 17.3 mg of sodium dodecyl sulphate (SDS, Sigma-Aldrich) were added. Thereafter, 5.4 mg of photoinitiator (2,2'-azobis(2-methylpropionamidine) dihydrochloride, Sigma-Aldrich) and 10 μL of accelerator (*N, N, N', N'*-tetramethylethylenediamine, J&K Chemical) were added and purged with nitrogen gas for 10 min to remove oxygen. Thirdly, 20 μL of the prepared dispersion was injected into each hole and polymerized for 3 min under a UV lamp (1000 mW/cm^2, LDST230-1000, Dongguan Landun Electrical Equipment Technology). The hydrogel small-rockets were then produced and remained in the mold.

Gelatin/Agar mixture solutions. The preparation of Gelatin/Agar mixture with different proportions involves several steps. Briefly, 1.0 g of gelatin (from cold water fish skin 40-50% in H_2O, Sigma-Aldrich) was added into 500 μL of deionized water, and dissolved completely at 60 ^oC after 10 min. Meanwhile, a certain amount of agar (high gel strength (1000-1200 g/cm^2), Shanghai Macklin Biochemical) was added in 500 μL of deionized water, and dissolved completely at 90 ^oC after 30 min. Subsequently, the two solutions were mixed and then diluted to obtain the total solid content of 10 wt% with deionized water at 60 ^oC. The content of agar was varied in the range of 0~16 parts by weight (based on 100 parts by weight gelatin), which was named as GltAg0~GltAg16 according to the content of agar in the formula. The gelatin/agar mixture was dyed with butyl rosin B for clear observation. Additionally, 2 wt% of graphene nanosheets (ratio to the mass of gelatin/agar) was added to fabricate graphene incorporated gelatin/ agar gel, which was named as GNS-GltAg0~GNS-GltAg16.

Preparation of multi-stage hydrogel rocket. After producing the small rockets in the mold holes, the barriers (removable parts) were removed, and 20 μL each of gelatin/Agar mixed solution with different proportions was dripped into the interval vacant space of the hydrogel rockets and stored in the refrigerator at 4 ^{o}C for 4 h to promote gelation. Two types of multi-stage hydrogel rockets were prepared, including small-rocket/GltAg0/small-rocket/GltAg6 and small-rocket/GNS-GltAg0/small-rocket/GNS-GltAg6 multi-stage hydrogel rocket. The small-rocket/GltAg16/small-rocket/GltAg16 hydrogel rocket was fabricated to serve as control sample.

Enrofloxacin (ENR) release from multi-stage hydrogel rocket. Enrofloxacin (Zhejiang Guobang Pharmaceutical) was loaded in both driving stages and sacrificial stages of the small-rocket/GNS-GltAg0/small-rocket/GNS-GltAg6 hydrogel rocket. ENR loaded into the driving stages was achieved by following the above similar process, with 10 mg of ENR being pre-added into the Laponite XLG dispersion. Similarly, ENR loaded into the sacrificial stages was realized by adding 10 mg of ENR into the 10 wt% of GNS-GltAg solution. The drug release process of multi-stage hydrogel rockets is in the presence of 50 mM glucose and 150 mM NaCl at 28 ^{o}C and pH 8. The release profiles of enrofloxacin (maximum absorption peak 270 nm) were obtained by a UV-visible spectrometer (Shimadzu UV-240).

Contact angle measurements. 1 μL of water or driving solution (0.15 M NaCl, 0.10 M $NaHCO_3$, and 0.05 M glucose) were dropped to the surface of SDS/PA-*co*-PN hydrogel. The change of liquid drops was recorded by Contact Angle System (OCA20) and the contact angles were analyzed.

Dissolving temperatures of gelatin/agar gels. The dissolving temperatures of gelatin/agar gels with different formulas were determined by ball-dropping method. Briefly, the GltAg0~GltAg16 solutions (2 mL for each formula) were orderly injected into glass tubes with 15 mm in diameter, and gelled in the refrigerator of 4 ^{o}C for 4 h. Then a steel bead (4 mm in diameter) was placed on the gel surface of each tube. Subsequently, the samples were placed in a super thermostatic water bath cycle machine (HWY-501) with 25 ^{o}C of initial temperature and 1 ^{o}C/min of heating rate. Upon temperature increase, the gelatin/agar gel samples gradually dissolved, the steel balls slowly sank until reaching the bottom of the tube and then the gel samples completely turned into free-flowing solutions. The temperature when the bead reaching the tube bottom was defined as the dissolving temperature of gelatin/agar gel.

Motion study of multi-stage hydrogel rockets. To observe the motion of the multi-stage hydrogel rockets, 0.05 mol L^{-1} glucose solution was used as the driving energy fuel, whose pH value was adjusted close to 8.0 by sodium bicarbonate, ionic strength was regulated by 0.15 mol L^{-1} sodium chloride solution and initial temperature was set at 28 ^{o}C. The remote propulsion and detachment of small rockets from multi-stage hydrogel rockets were captured and recorded by using camera (CANON IXUS 220 HS). During the temperature-controlled process, small-rocket/GltAg0/small-rocket/GltAg6 rocket was propelled and the second GltAg0 stage dissolved by rising temperature to 31 ^{o}C to detach the first small rocket, and then the fourth GltAg6 stage dissolved by continuously rising temperature to 34 ^{o}C to detach the third small rocket, subsequently, the two released small rockets were propelled in the same environment. Meanwhile, during the NIR irradiation-controlled process, dissolving GNS-GltAg0 and GNS-GltAg6 stages of the small-rocket/GNS-GltAg0/small-rocket/GNS-GltAg6 hydrogel rocket was manipulated by NIR irradiation to detach the small rocket stages. The propulsion process of the control sample small-rocket/GltAg16/small-rocket/GltAg16 was recorded at 28 ^{o}C and the gelatin/agar gel stages (GltAg16) are insoluble. The trajectory and speed profiles of all rockets were traced and calculated by using the NIS-Elements AR 4.3 software.

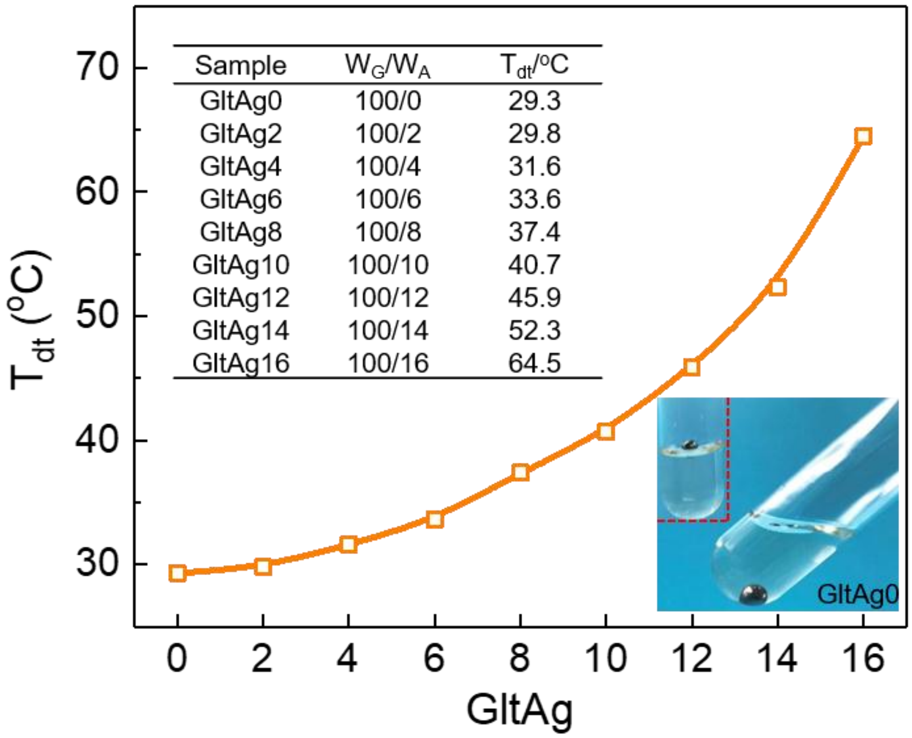

Fig. S1 The dissolving temperature (T_{dt}) of gelatin/agar gel with different formulas. The table shows the formulas of gelatin/agar gels, and their solid contents are 10 wt%. The inset image shows the gelling state at 4 ^oC (in the red box) and dissolving state of GltAg0 at high temperature of 29.3 ^oC.