Supporting Information

Biothermal Sensing Torsional Artificial Muscle

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Experimental sections

Chemicals: The N-isopropylacrylamide (NIPAM), N-succinimidyl acrylate (NSA), N,N′-methylene bis(acrylamide) (BIS), sodium dodecyl sulfate, ammonium persulfate (APS), glucose, glucose oxidase (GOx) from *Aspergillus niger*, horseradish peroxidase (HRP), and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) used were purchased from Sigma-Aldrich. A 20 mM phosphate buffer containing 0.14 M NaCl (PBS) was prepared daily. All solutions were made using fresh deionized water from a Milli-Q Plus water purification system (Millipore, Bedford, UK).

Synthesis of the Poly(NIPAM-co-NSA) particle: Poly(NIPAM-co-NSA) hydrogel particles were synthesized using a free-radical precipitation polymerization method reported elsewhere[25, 26]. The molar composition of the monomer mixture solution was 96% NIPAm, 2% NSA, and 2% BIS. All polymerizations were carried out in a three-neck round bottom flask. A total monomer concentration of 70 mM and 2 mM of SDS was filtered and added to the flask, which was then heated to 70 °C. The solution was purged with Ar gas and stirred

vigorously until the temperature remained stable. After 30 min, the reaction was initiated by injecting a 1 mL solution of the 2 mM APS. The reaction continued for 4 h under Ar with constant stirring. Following the synthesis, the synthesized nanoparticle solution was dialyzed against deionized water for 1 week using dialysis tubing with MWCO = 3500, with the deionized water being exchanged every 12 h. The dialyzed solution was filtered using a 0.2 μm syringe filter before the fabrication of the PNIPAm–GOx/MWCNT yarn.

Preperation and characterization of PNIPAm-GOx particles: To immobilize the catalytic enzymes on the poly(NIPAM-co-NSA) particle, 1 mg/ml of poly(NIPAM-co-NSA) particle in deionized water and 2 mg/ml of GOx in a 20 mM phosphate buffered solution were mixed at 36 °C for 2 h. The conjugation of the GOx with the copolymerized NSA was self-assembled. The fabricated PNIPAM–GOx particle was then filtered three times using VIVASPIN 20 300K MWCO centrifugal concentrators (Sartorius Stedim Biotech, Göttingen, Germany) to remove any unbound enzyme for further analysis. Dynamic light scattering measurements were performed to examine the evolution of the particle size and phase transition temperature using a Malvern Nanosizer, (Malvern Instruments Ltd., Malvern, UK). The exothermic reaction of the enzyme catalysis was measured using isothermal calorimetric titration analysis using a MicroCal™ VP-ITC Microcalorimeter (TA Instruments, New Castle, USA).

Fabrication and characterization of biomolecular-responsive biscrolled yarn: Three layers of 7 mm width MWCNT sheets were drawn from the sidewalls of MWCNT forests and a nanoparticle solution was injected into the contact space between the MWCNT sheet and an attached glass slide to float the MWCNT sheets. After injection, the samples were dried at 60 °C and the enzyme solution was injected onto the surface of the PNIPAm-

modified MWCNT sheets, which were then incubated for 2 h at 36 °C. The sheets were washed carefully using 20 mM phosphate buffered saline, and finally, the enzyme-immobilized PNIPAm/MWCNT sheets were twisted into yarn using a low speed motor with 4,000 turns per meter and 40 μm diameter PNIPAm–GOx/MWCNT yarns were obtained. In order to quantify the loading weight of the guest materials in the fabricated yarn, the weight of bare MWCNT yarns and biscrolled yarns, which were fabricated by using same width and the number of layers of the MWCNT sheets, were measured using ultra micro balance (Mettler-Toledo, Colombus, USA) and the weight percentage is calculated by comparing them. The fabricated PNIPAm–GOx yarn was cut to a length of 5 mm and the catalytic activity of the immobilized GOx was assayed by standard hydrogen peroxide determination in PBS (20 mM, pH = 6.0) using HRP, ABTS, and glucose (in the concentration range 5–80 mM) at room temperature (25 °C). The increase in absorbance at λ = 414 nm determined using a DU®730 Life Science UV/VIS Spectrophotometer (Beckman Coulter Inc., Fullerton, USA) was monitored for 6 min. The glucose-responsive change in length of the PNIPAm–GOx/MWCNT yarn was measured using an EXSTAR TMA/SS7100 thermomechanical analyzer (SII NanoTechnology, Tokyo, Japan). The strain–stress curves were determined using an Instron 5966 tester (Instron Engineering Corporation, Canton, USA) at a strain rate of 50 um min^{-1} and initial gage length of 1 cm.

Biothermal sensing artificial muscle fabrication: A twisted bare MWCNT yarns that helped to return the paddle to its initial angle as a torsional spring were fabricated with same width and number layers of MWCNT that we used for biscrolled yarn. the bare MWCNT yarn and a biomolecular-responsive PNIPAm–GOx/MWCNT biscrolled yarn were used to fabricate a two-tethered configuration of yarn artificial muscle. Since the 2 × 1 mm^2 area

paddle was attached near to the yarn center, both ends of the yarn were fixed using waterproof epoxy glue to fabricate the 2 cm long yarn artificial muscle.

Method and apparatus for actuation testing: The yarn artificial muscles were installed in a custom-built flow injection system, as shown in Supplementary Figure 1, and trialed for at least 1 h to stabilize the structure of the yarn at the target temperature. The method for injecting the PBS solution containing glucose and the pure PBS solution used a three-way cock. The reaction cell was placed in a water bath to control the ambient temperature. The flow was supplied by peristaltic pump (LongerPump® LEAD-2, Baoding Longer Precision Pump Co., Ltd, Baoding, China) to reduce the pulse wave on the reaction cells. The torsional actuation was recorded using a microscopic movie camera and the angles were measured using the ImageJ software package (http://imagej.nih.gov/ij/).

Supplementary Figures

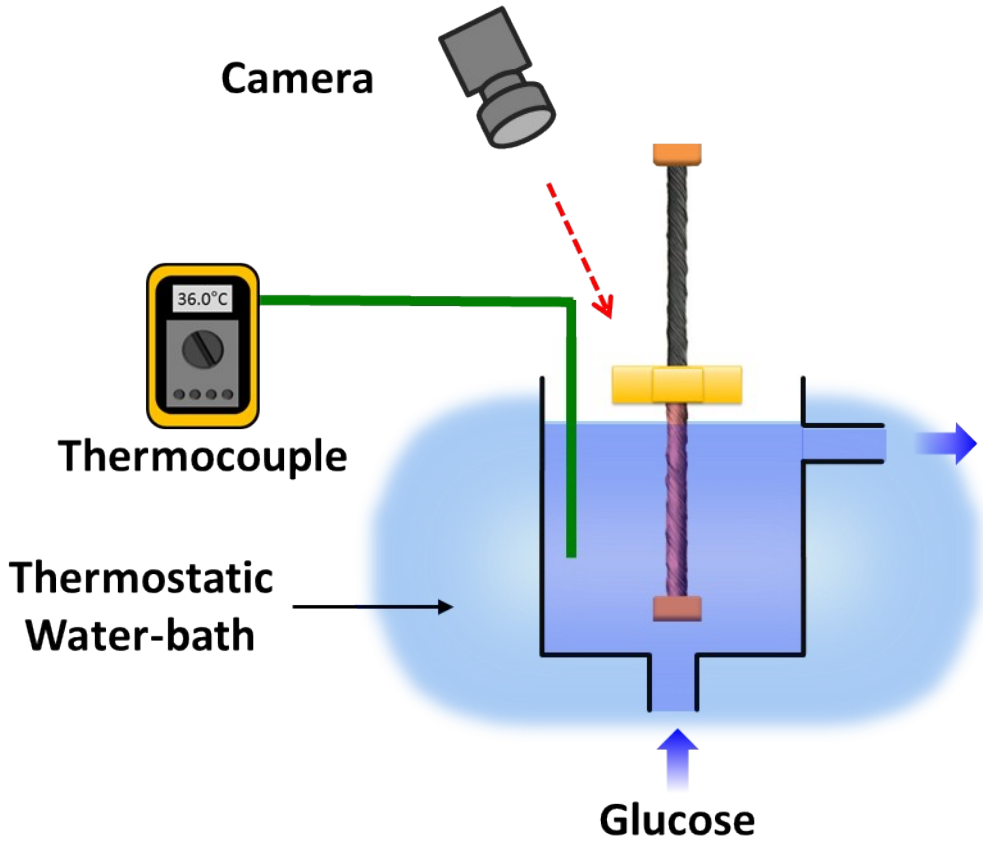

Figure S1. A schematic drawing of the custom-built flow injection system.

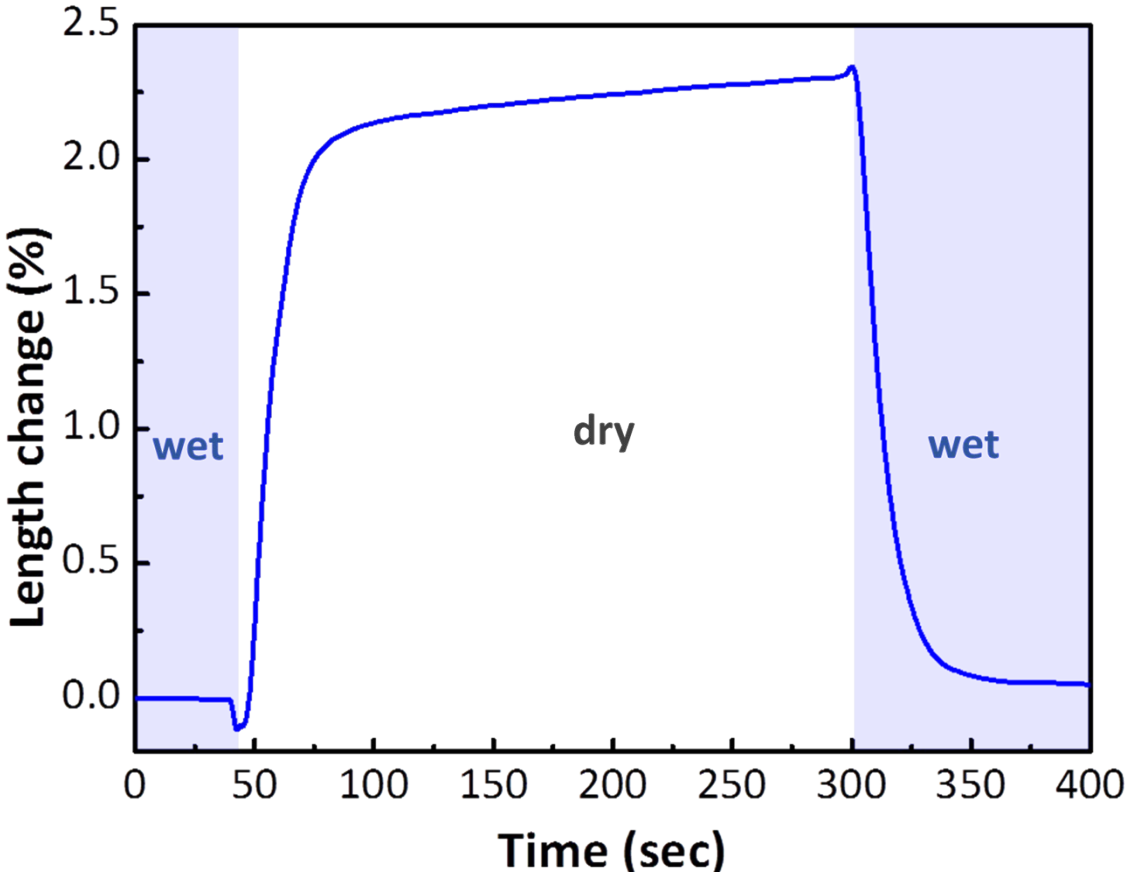

Figure S2. The change in length of the yarn correlated to the wetting and drying of the entrapped PNIPAm–GOx particle versus time.

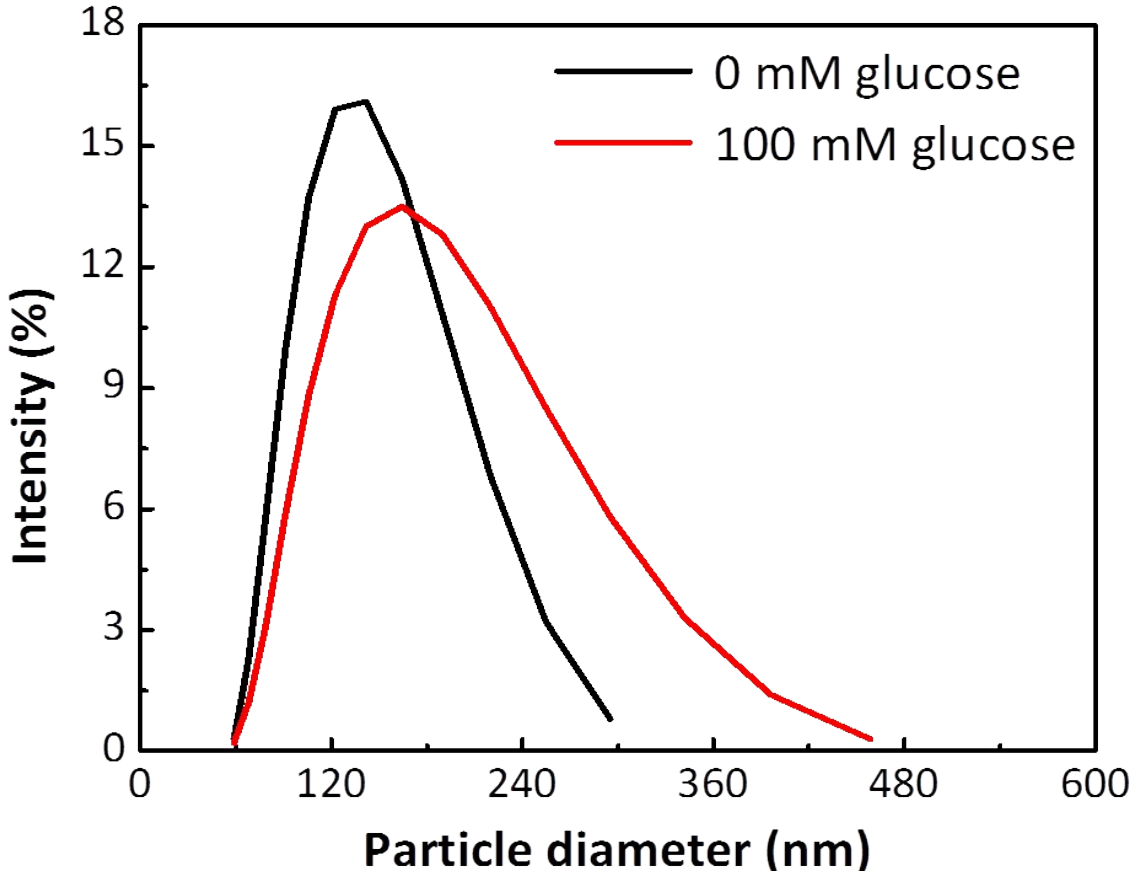

Figure S3. The particle size distribution of PNIPAm–GOx hydrogel in a pure PBS solution (black) and in a PBS solution containing 100 mM glucose at 36 °C (red).

Supplementary Movies

Movie S1. Biothermal sensing torsional actuation of a carbon nanotube yarn. Two-tethered half-biscrolled homochiral configuration of a torsional artificial muscle is tested in a custom-built flow injection system at 36 °C.

References

25. J. Gao, B. J. Frisken, *Langmuir,* **2003,** 19, 5212-5216.

26. W. H. Blackburn, L. A. Lyon, *Colloid. Polym. Sci.,* **2008,** 286, 563-569.