

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Experimental section

1. Materials. Poly(styrene-butadiene-styrene) (SBS, YH-792) was purchased from Sinopec Baling Petrochemical Co., Ltd (Hunan, China) and the ratio of styrene to butadiene was 40/60 (w/w). The raw carbon nanotubes (CNTs, >98%) and absolute ethanol (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Toluene, Formic acid (>88%), hydrogen peroxide (H₂O₂, 30% in water), polyethylene glycol-600 (PEG-600), acrylamide (AM), *N*-isopropylacrylamide (NIPAM), acrylic acid (AC), 3-(methacryloylamino) propyl-trimethylammonium chloride (MPTC), *N, N'*-methylenebisacrylamide (MBA), and α -ketoglutaric acid were obtained from Adamas-beta. The MBA and α -ketoglutaric acid were used as cross-linker and photo-initiator, respectively.

2. Synthesis of epoxidized SBS (ESBS). SBS was epoxidized according to the method in the literatures (*J. Appl. Polym. Sci.*, 2006, 99, 1975-1980; *Macromol. Symp.*, 2012, 315, 152-159). Typically, SBS (5 g, 0.0375 mmol) was dissolved in 50 mL toluene in a 250-mL three-necked round-bottom flask. 0.565 mL (0.0132 mol) formic acid and 0.05 mL (0.083 mol) of PEG-600 were added to the toluene solution. The mixture was stirred with a magnetic stir bar at 70 °C. After 1.5 mL hydrogen peroxide was dropped, the reaction mixture was stirred for 2 h at 70 °C. The solution was poured into a beaker after cooling. The solid product was obtained by precipitating with absolute ethanol, and washed several times with deionized water until the filtrate became neutral. The solid was dried at 35 °C in a vacuum oven overnight to give ESBS product.

3. Synthesis of acrylyl-opening ESBS (AESBS). 3.5 g (0.0257 mol) ESBS was dissolved in 35 mL toluene in a 250-mL three-necked round-bottom flask at 75 °C under magnetic stirring. We then prepared the mixture of 18.78 mL (0.274 mol) of acrylic acid and 0.0169 g (0.153 mol) hydroquinone and heated it to 75 °C in a round-bottom flask. The heated acrylic acid/hydroquinone solution was mixed with ESBS/toluene solution and stirred at 75 °C for 20 h. The reaction solution was poured into a beaker after cooling. After being precipitated with absolute ethanol, and washed several times with deionized water until the filtrate became neutral, the solid was dried at 35 °C in a vacuum oven overnight to give AESBS product.

4. Preparation of AESBS@CNTs film. 1.5 g (0.010 mol) AESBS, 0.0375g CNTs and 30 mL toluene were mixed in a 100-mL beaker. The mixture was vigorously stirred with a magnetic stir bar for 2 hours to give AESBS@CNTs/toluene solution. The AESBS@CNTs film was formed by spreading a certain amount of the solution on a glass slid (size: 65 mm × 15 mm × 1 mm) and heating at 35 °C for 1 hour in a vacuum oven.

5. Preparation of AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite. We first prepared AM@NIPAM solution by dissolving 1.36 g (0.012 mol) NIPAM, 0.14 g (0.002 mol) AM, 0.0016 g (0.010 mol) MBA, and 0.033 g (0.226 mol) α -ketoglutaric acid in 5 mL deionized water. The obtained solution was kept in a sealed container for use in the next step. We then prepared a series of AM@MPTC solutions by dissolving AM, MPTC, MBA, and α -ketoglutaric acid in 5 mL deionized water. The detailed information for the preparation of AM@MPTC solutions was shown in Table 1. Note that MBA acted as a cross-linker, while α -ketoglutaric acid was used as photo-initiator.

Table 1 Conditions for the preparation of AM@MPTC solution

Entry	AM (g)	MPTC (g)	MBA (g)	α -ketoglutaric acid (g)
1	1.5	0.1	0.0016	0.031
2	1.5	0.3	0.0016	0.033
3	1.5	0.6	0.0016	0.036
4	1.5	0.9	0.0016	0.039
5	1.5	1.2	0.0016	0.042

A silicone sheet with dimensions of 65 mm × 15 mm × 0.2 mm was cleaned by acetone. Its middle area of 60 mm × 12 mm was removed by a graver to give a rectangular framework. This silicone framework was

sandwiched between a pre-prepared AESBS@CNTs film and a glass slide to form a hollow transparent template. Note that the AESBS@CNTs film was not removed from the glass slide. The hollow area was vacuumized prior to the use. The AM@NIPAM solution was then injected into the hollow area. After that, the molded sample was irradiated with ultraviolet (UV) light ($\lambda = 365$ nm, intensity: 200 mW/cm²) for 40 min to give AESBS@CNTs/PAM@PNIPAM composite.

We then opened the mold and replaced the silicone framework with a thicker one (thickness: 0.3 mm). The mold was again covered by a glass slide, in which a gap remained between the AESBS@CNTs/PAM@PNIPAM composite and the glass slide. After being vacuumized, the AM@MPTC solution was injected to fill in the gap. The sample was irradiated with UV light ($\lambda = 365$ nm, intensity: 200 mW/cm²) for 40 min to give AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite.

6. NMR spectroscopy and degree of epoxidation. The structural evaluation of chemically-modified SBS was characterized on AVANCE III 500MHz hydrogen nuclear magnetic resonance (¹H NMR) spectrometer (Bruker, Germany). 5 mg of SBS, ESBS, and AESBS was respectively dissolved in 0.6 mL deuterated chloroform (CDCl₃) for NMR measurement at 25 °C.

The degree of epoxidation of SBS was calculated according equation of $I_e / (I_e + I_d)$ (*J. Mater. Chem. C*, 2020, **8**, 14826-14833). The parameters were obtained from ¹H NMR spectra. I_e was the sum of intensities of proton peaks of the epoxy groups. I_d was the sum of intensities of proton peaks of the double bonds.

7. Infrared spectroscopy. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was carried out on infrared spectrometer of Thermo Scientific Nicolet IS10. We first prepared SBS, ESBS, AESBS and AESBS@CNTs into films, and cut the films to squares of 5 mm × 5 mm. The square films were measured at a wavenumber range of 4000-400 cm⁻¹.

8. Microscopic observation. The AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite were dried in a freeze-dryer (Model: FD-1A-50, Shanghai Bilon Instrument Manufacturing Co., Ltd). The composite were broken manually and attached to a silicon wafer with conductive glue. After gold coating, their cross sections were observed by scanning electron microscope (GeminiSEM 450, Zeiss) at an operating voltage of 5 kV. The micrographs were taken at room temperature and a pressure of 8.8×10^{-7} Pa.

9. Mechanical measurements. A tensile tester with a 50 N load cell (HY-0580, Shanghai Hengyi Test Instrument Co., Ltd.) was employed to perform the mechanical tensile testing and 90° peeling tests. The loading rate was constant at 50.0 mm/min for the both tests. For 90° peeling testing, AESBS side was fixed on a glass slide by double-sided tape, while the hydrogel side was covered with a rigid tape backing to prevent the elongation along the peeling direction. Thus, the measured interfacial adhesion is equal to the steady-state peeling force per width of the bilayer. The interfacial adhesion energy was determined by dividing the force (F) by the width of the sample (W).

10. Water contact angle (WCA). The water contact angles of SBS and AESBS films were performed on a dynamic contact angle measurement instrument (CA100A, Shanghai Innuo Precision Instruments Co., Ltd.). A 0.5 μL water droplet was dropped on the surface of films, and the image was immediately taken for WCA measurements. Each test was performed three times. The WCA was calculated based on the captured images by using Theta v4.1.9.8 (Biolin scientific, Stockholm, Sweden) software.

11. Water swelling ratio (WSR). The AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite were dried at 60 °C for 24 h, which were then weighed and immersed in deionized water until saturation with water sorption at room temperature. The WSR was calculated with the equation of $(W_s - W_d) / W_d$, where W_s and W_d were the weight of the swollen and dried composite, respectively.

12. Measurement of bending angle of actuators. The AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite was cut to a rectangular shape of 2.0 mm × 0.3 mm × 15.0 mm. When it was immersed in water, the PAM@PMPTC side adsorbed water and expanded rapidly, which induced the sandwich composite bending toward AESBS@CNTs side. The bending process was recorded by a common camera. We then tracked the bending angle with time to reflect the bending kinematics. The bending angle ($360^\circ - 2\theta$) was defined as shown in Fig. 4a.

13. Differential Scanning Calorimetry (DSC). DSC was performed with Q2000 DSC at a heating rate of 5 °C/min using DSC/TG pan of Al₂O₃. The temperature range was 5 to 50 °C and dry N₂ gas was used as carrier gas at a flow rate of 50 mL/min.

Supplemental Figures

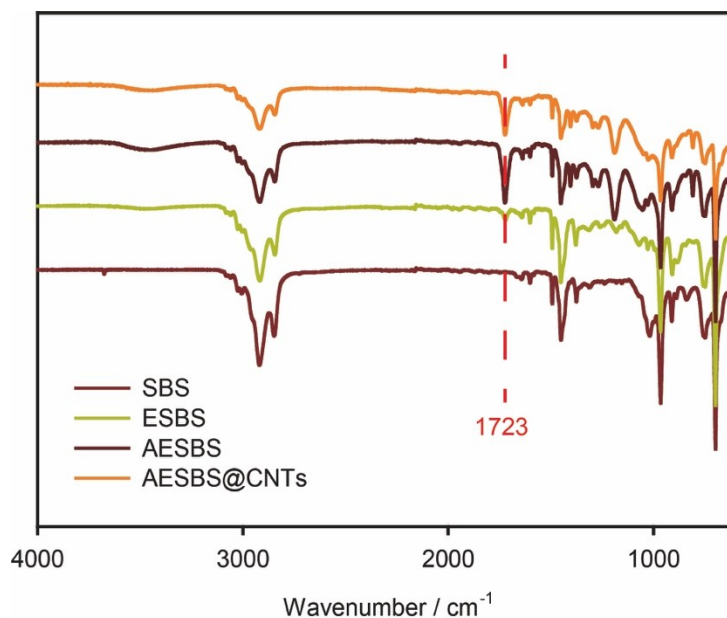


Fig. S1 ATR-FTIR spectra of SBS, ESBS, AESBS and AESBS@CNTs.

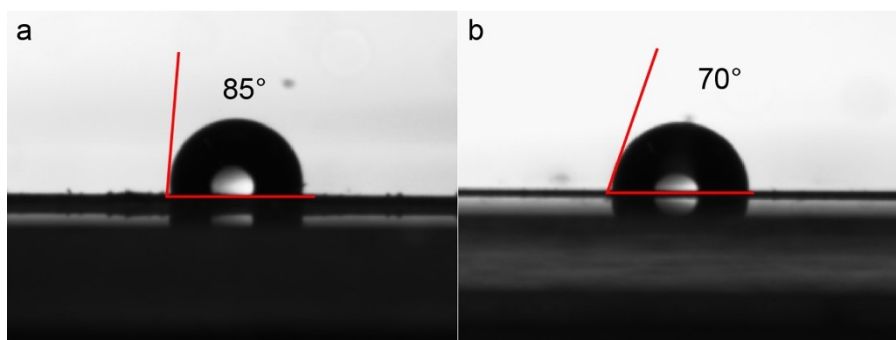


Fig. S2 The water contact angle of (a) SBS and (b) AESBS.

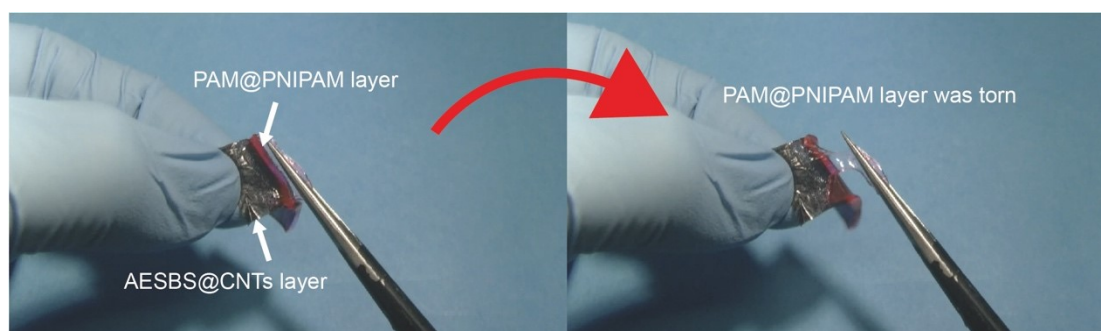


Fig. S3 Snapshots show the peeling process of the AESBS@CNTs/PAM@PNIPAM composite.

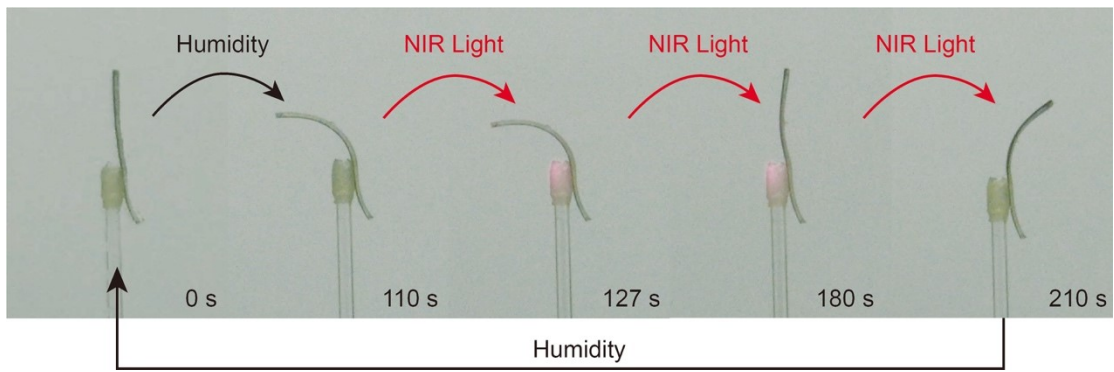


Fig. S4 the process of reversible and controlled motion of AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite.

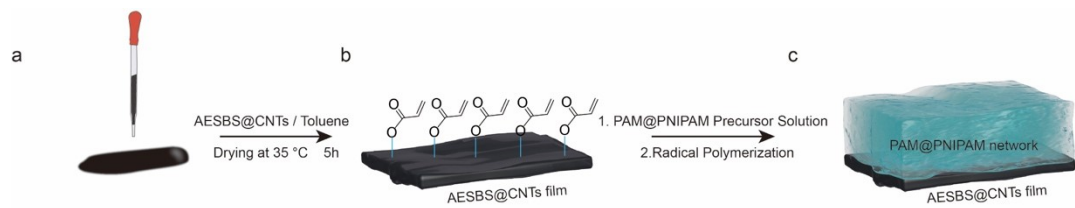


Fig. S5 The synthetic process of AESBS@CNTs/PAM@PNIPAM composite.

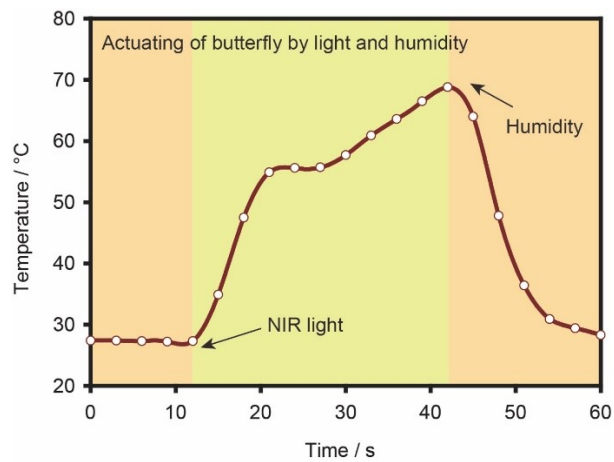


Fig. S6 The temperature change of the butterfly actuator under alternative stimulation of humidity and NIR light.

Movie Legends

Movie S1. Manual peeling testing. The hydrogel layer was torn instead of being peeled off from the surface of AESBS@CNTs layer. The video was displayed at its original speed.

Movie S2. Standard 90° peeling testing of the AESBS@CNTs/PAM@PNIPAM composite, further showing the strong interfacial adhesion between AESBS@CNTs and PAM@PNIPAM. The video was displayed at its original speed.

Movie S3. The reversible motion of AESBS@CNTs/PAM@PNIPAM/PAM@PMPTC sandwich composite. The video was displayed at its twenty times speed.

Movie S4. A butterfly-like soft actuator mimicking the movements of the left/right wings of a butterfly. The video was displayed at its twenty times speed.

Movie S5. A flower-shaped actuator mimicking the blooming and closing of a flower. The video was displayed at its twenty times speed.

Movie S6. A claw-shaped actuator that bended its claws to grasp the object. The video was displayed at its original speed.

Movie S7. Movements of a miniature robot driven by humidity/water and NIR light. The video was displayed at its twenty times speed.