

Supporting Information

Deformable bi-compartmental particles and their application on controlling electric conductivity

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EXPERIMENTAL SECTION

Chemical and Materials

N-isopropylamide (NIPAM, 98%), trimethylolpropane triacrylate (TMPTA), *N,N'*-methylenebisacrylamide (BIS), *P*-toluenesulfonic acid, TMPTA 2-hydroxy-2-methylpropiophenone (HMPO) were obtained from Shanghai Macklin Biochemical Co., Ltd. 3,4-Ethoxylene dioxythiophene (EDOT) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HEMO) were purchased from InnoChem (Beijing, China). Polydimethylsiloxane (PDMS) was purchased from Weiss (Beijing, China). Ethanol absolute was purchased from Modern Oriental (Beijing, China). Syringe Pumps (XMSP-18, Nanjing Ximai Nano Technology Co., Ltd.) used to introduce the solution

into the microchannels. ITO conductive glass (Resistance $\leq 6\Omega$, South China Xiangcheng Technology Co., Ltd.)

Preparation of bi-compartmental particles using microfluidic device.

The microfluidic device is composed of two syringe needles (inner diameter: 0.09mm) inserted into a cylindrical silicone tube (inner diameter: 0.3mm), as shown in Figure S1. For preparing bi-compartmental particles, NIPAM and BIS were added into an aqueous solution with 5 wt% of HEMO, which was used as NIPAM solution. HPMO was added into TMPTA, which was used as TMPTA solution. Dimethyl silicone used as the outer continuous phase was injected into silicone tube by a micro-injection pump. NIPAM and TMPTA solutions were injected into syringe needles by micro-injection pumps and became droplets in dimethyl silicon, which were used as two dispersed phases. In the continuous phase, i.e., dimethyl silicone, the asymmetric droplets were shaped when the two different droplets connected with each other by pumping into the silicone tube. The UV light was put above silicon tube. The polymerization of NIPAM and TMPTA in two dispersed droplets was initiated with HEMO and HPMO respectively under UV light, resulting in bi-compartmental polymer particles. If EDOT was introduced into NIPAM solution while Fe_3O_4 was introduced into TMPTA solution, PNIPAM-PEDOT/PTMPT- Fe_3O_4 hybrid particles could be obtained with the fluidic technology.

Typically, an NIPAM solution was prepared as below: 2 g of NIPAM, 0.2 g of BIS and 0.05 g of HEMO, were dissolved into 2mL of water. 0.05 g of HPMO were dissolved into 4 g TMPTA for getting a TMPTA solution. The flow rate of dimethyl silicone, NIPAM solution and TMPTA solution was respectively set as 0.2 mL/h, 0.1 mL/h and

0.1 mL/h. Bi-compartmental PNIPAM/PTMPTA polymer particles with a flow ratio of 50% NIPAM solution in dispersed phases were collected under UV light when they left the silicon tube, which was washed with ethanol enough.

A typical bi-compartmental PNIPAM-PEDOT/PTMPTA-Fe₃O₄ particle was fabricated as below: 2g of NIPAM, 0.2g of BIS, 0.05g of HEMO and 2 of EDOT were dissolved into 2mL of mixture of water and ethanol with a ratio of 2:3 for getting an NE solution. 0.05g of HMPO was dissolved into 2g TMPTA for getting TMPTA solution, and 0.1g of Fe₃O₄. was dispersed into the above TMPTA solution for getting a magnetic solution (i.e., MT solution). The flow rate of silicon oil, NE solution and MT solution was respectively set as 0.2 mL/min, 0.1 mL/h and 0.1 mL/h. Bi-compartmental PNIPAM-PEDOT/PTMPTA-Fe₃O₄ hybrid particles with 50% NE ratio were collected under UV light when they left the silicon tube, which was washed with ethanol enough.

Characterization

The color and shape of bi-compartmental particles were characterized using an optical microscope (XSP-02, Jiangxi Fengning Optical Instrument Co., Ltd. Electronic Magnifying Glass (EMG, YF0012, Leyes company) was used to real-time monitor the particles. EMG connected with a laptop, using a HiView software for monitoring photo and video. SEM images of bi-compartmental particles were obtained with a JSM-7500F JEOL environmental scanning electron microscope (Japan Electronics Co., Ltd.) at a voltage of 5 kV and a current of 10 μ A after samples were sputtered with platinum. An Avometer of (Fluke 15B+, Fluke Test Instrument (Shanghai) Co., Ltd.) was used to measure the electric resistance of particles.

The analysis of elements was measured by Organic Element Analyzer (EA, elemental vario EL cube) from Elementar Analysensysteme GmbH. Solid samples were burned under oxygen, and NO_2 , CO_2 , H_2O , SO_2 were analyzed for obtaining N, C, H, S elements contents by thermal conductivity detector.

Thermal stability of particles was measured using thermogravimetric analysis (TGA, Thermogravimetric Differential Thermocombination analyzer SII TG/DTA6300, Nippon Seikō Kabushiki Kaisha). A programmed temperature was used, and the samples were heated under nitrogen or oxygen atmosphere. The sample was heated to 210 °C for removing water and small molecules, and then an isothermal heating at 210°C was used for 20 minutes, finally the sample was heated to 700°C with 10°C/min. A lift platform (LGD60-L, Suqian Rui Morning Trading Co., Ltd.) was used to control the distance between two ITO conductive glass slides.

Supporting Figures



Fig. S1 A home-made microfluidic device at work.

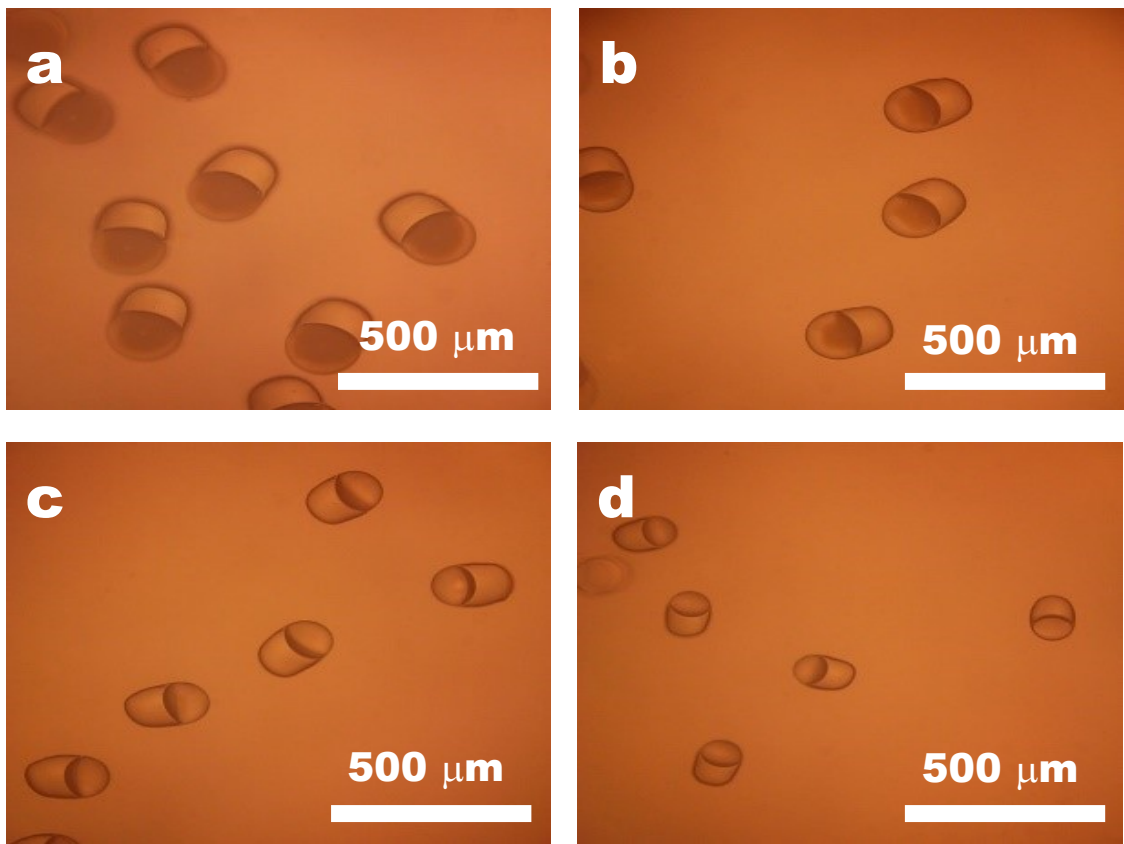


Fig. S2 PNIPMA/PTMPTA bi-compartmental particles prepared with different flow rates of continuous phase. a) 0.1 mL/h; b) 0.15 ml/h; c) 0.2mL/h; d) 0.25 mL/h. The flow rate of NIPAM solution and TMPTA solution was 0.1mL/h, respectively. The images were taken in polarized mode.

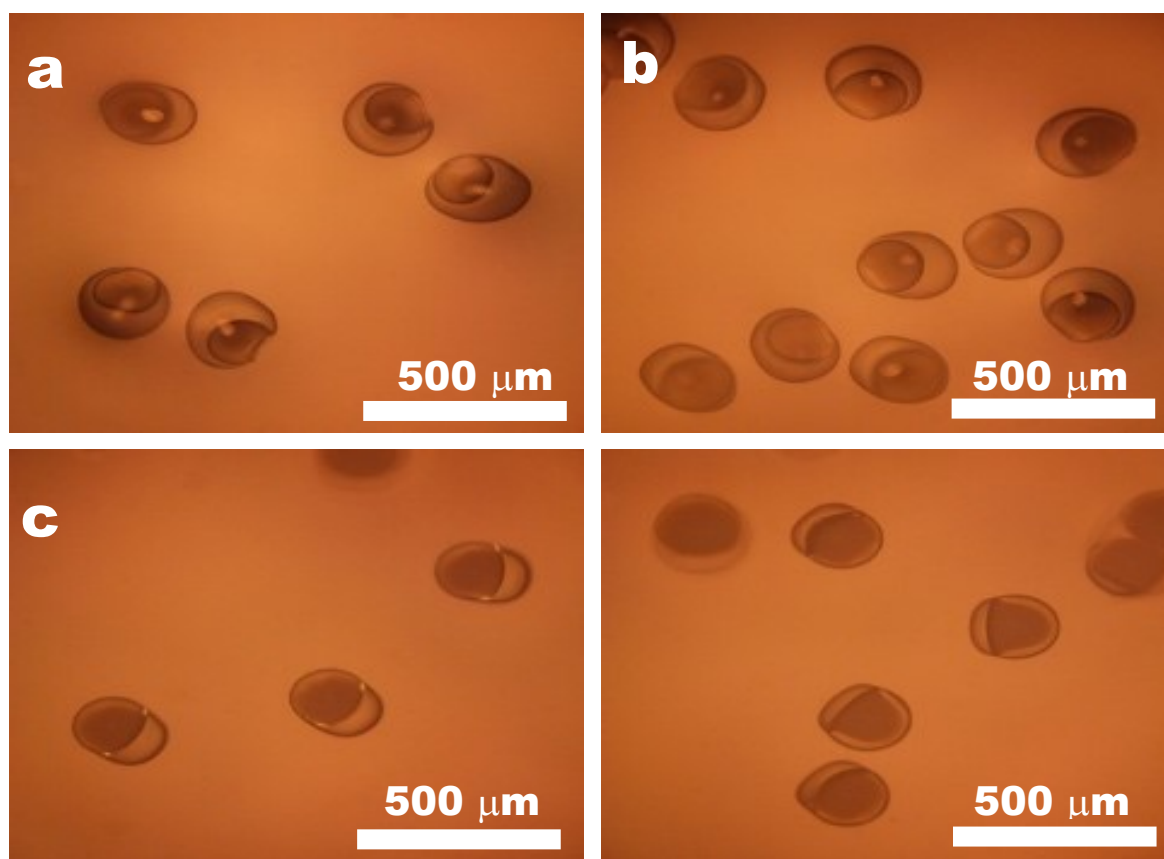


Fig. S3 PNIPAM/PTMPTA bi-compartmental particles with different ratios of two compartments prepared with different flow rates ratio of NIPAM solution to TMPTA solution. a) 1:2; b) 0.9:1.1; c) 1.1:0.9; d) 1.2:0.8. The flow rate of silicon continuous phase was kept as 0.1mL/h.

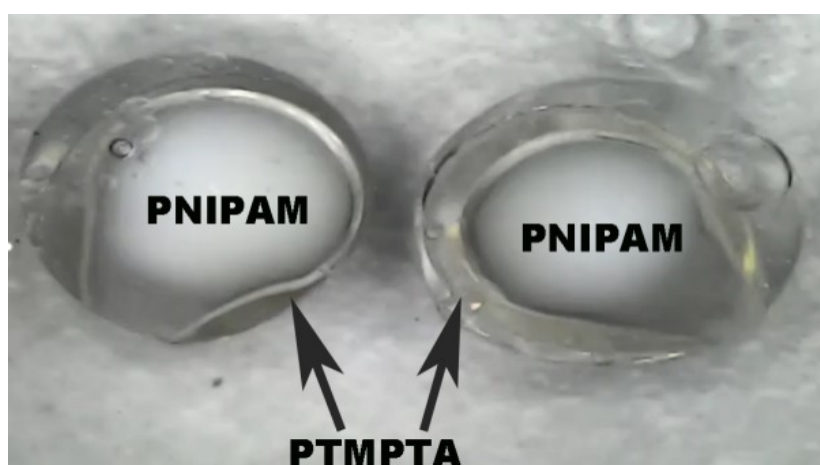


Fig. S4 The microscopic image of the bi-compartmental particles under transmitted light mode.

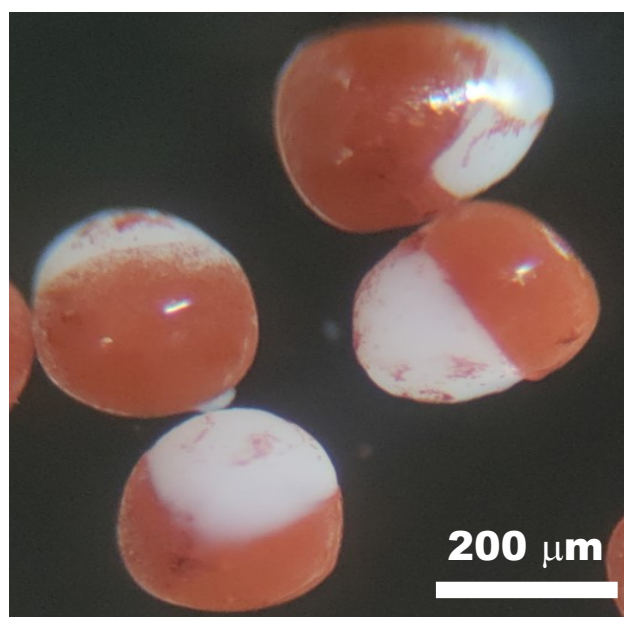


Fig. S5 PNIPAM/Fe₃O₄@PTMPTA bi-compartmental particles.

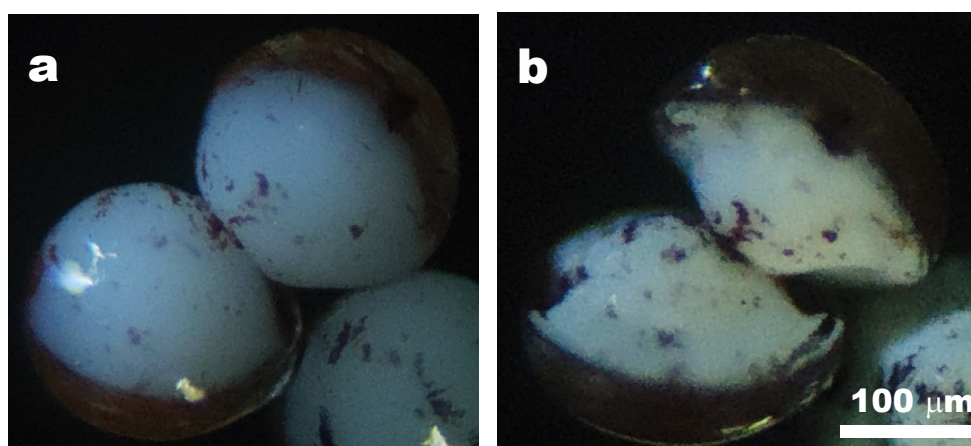


Fig. S6 The swelling and collapsed image of bi-compartmental PEDOT@PNIPAM/Fe₃O₄@PTMPTA particles. a) a microscopic image of swollen bi-compartmental particles in ethanol; b) the microscopic image of the dried collapsed bi-compartmental particles.

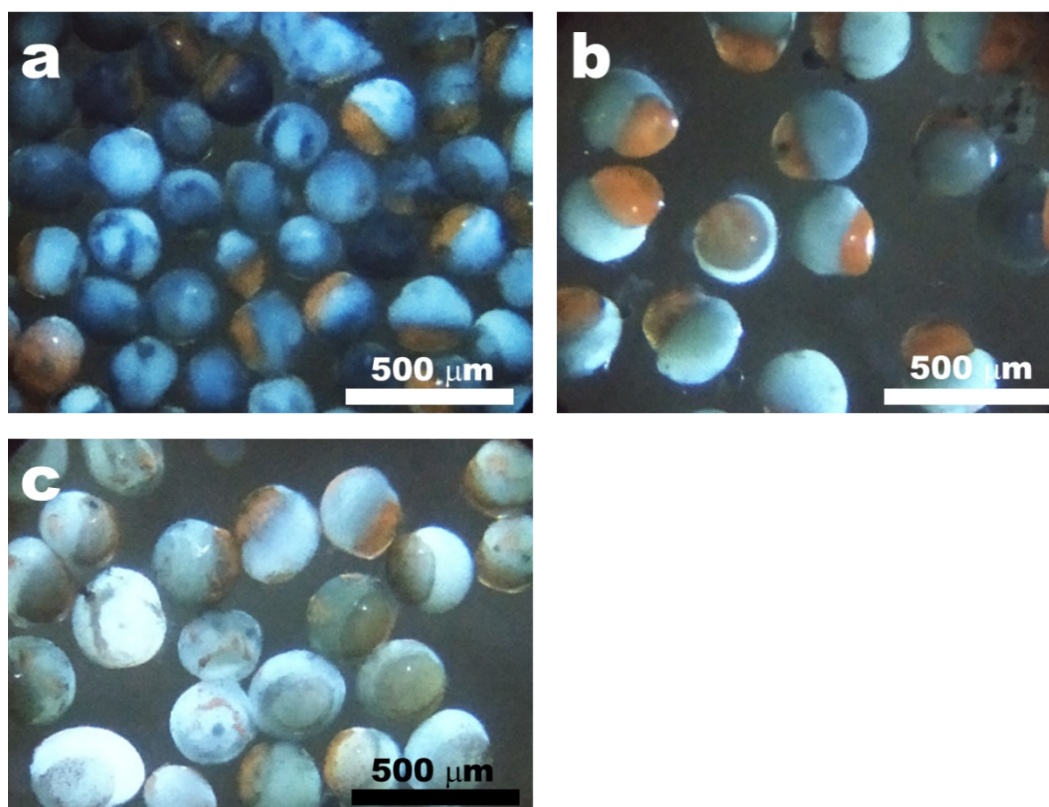


Fig. S7 PNIPAM-PEDOT/PTMPTA-Fe₃O₄ bi-compartmental particles prepared with different NE ratios. a) 60%, b) 70%, c) 80%.

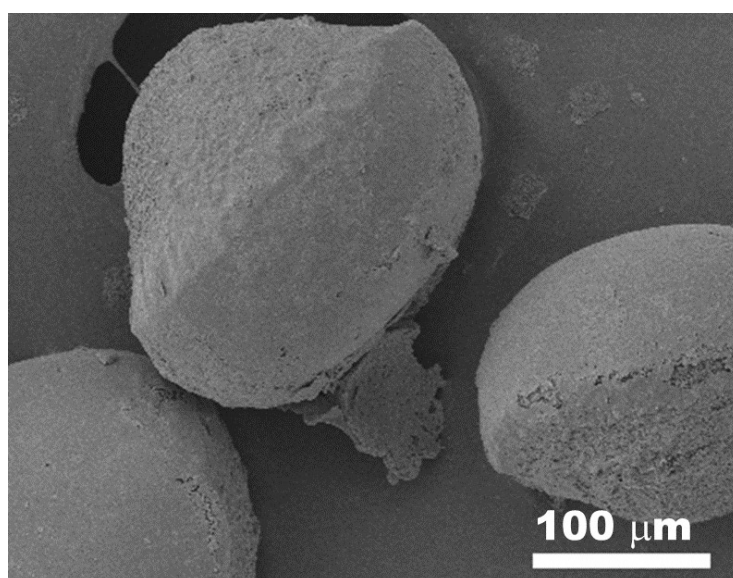


Fig. S8 SEM image of the dried PNIPAM-PEDOT/PTMPTA bi-compartmental particles with NE ratio at 60%.

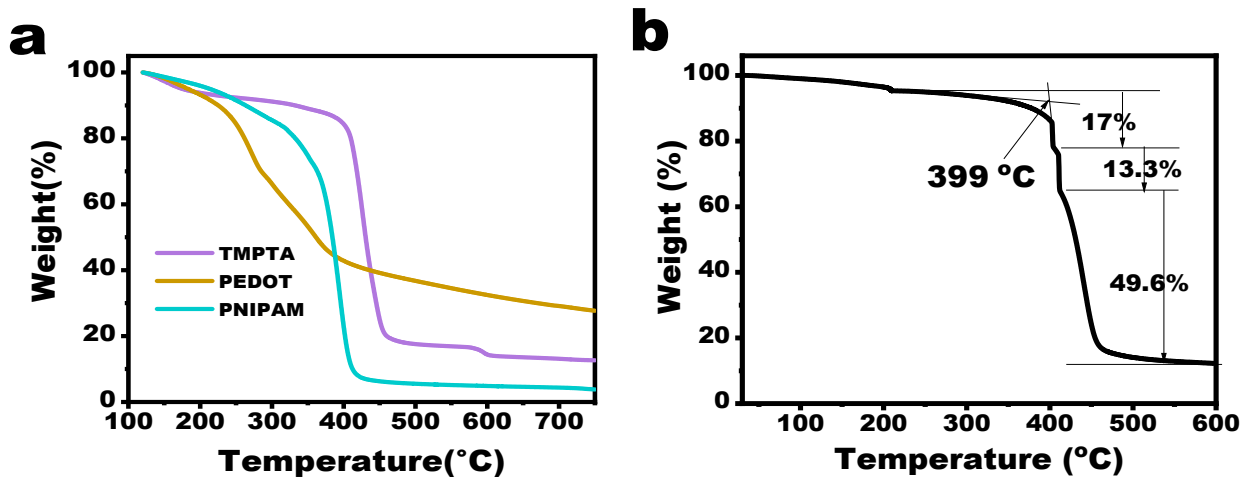


Fig. S9 TGA curves of Polymers. a) PNIPAM, PEDOT and PTMPTA; b) PEDOT@PNIPAM/Fe₃O₄@PTMPTA bi-compartmental particles with NE ratio at 50%, which was heated isothermally at 210 °C for 20 min in the measurement. The TGA measurements were performed in nitrogen.

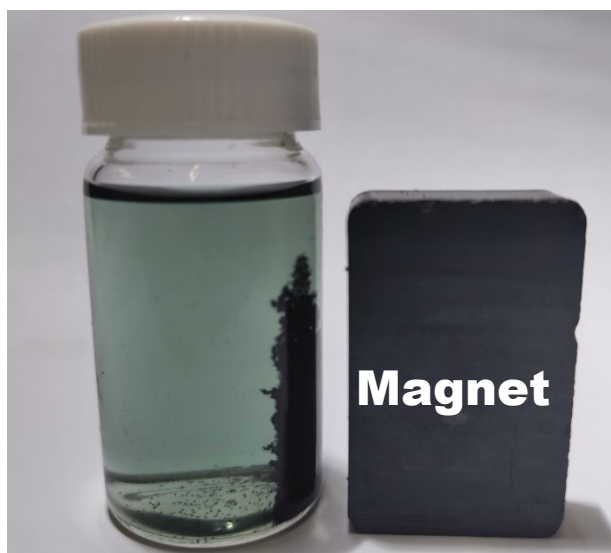


Fig. S10 The response of PEDOT@PNIPAM/Fe₃O₄@PTMPTA bi-compartmental particles to magnetic field.

Table S1. Element analysis of bi-compartmental particles prepared with different NE ratios

NE ratio	N %	C %	H %	S %
50%	0.385±0.065	53.545±0.125	6.215±0.0290	0.776±0.046
60%	0.605±0.055	55.215±0.105	6.557±0.0350	1.0555±0.0275
70%	0.635±0.045	49.425±0.0950	6.8905±0.0305	1.1075±0.0355
80%	0.745±0.045	52.36±0.1000	6.299±0.0260	1.1825±0.0245

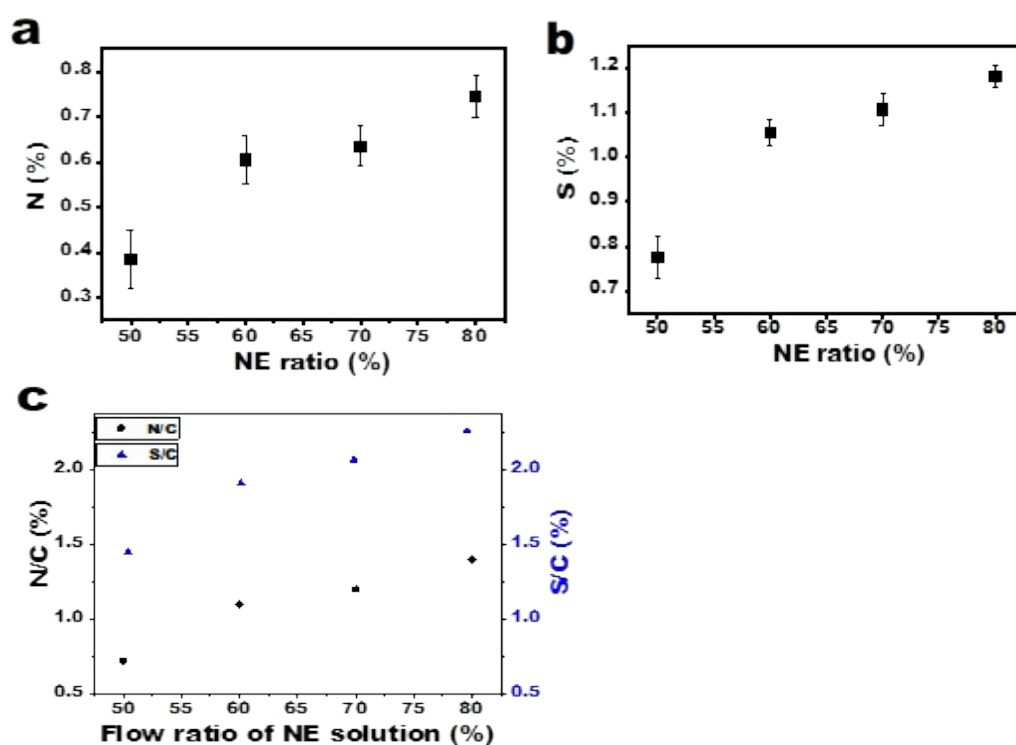


Fig. S11 The elemental contents measured with EAC. a) Nitrogen; b) Sulphur; c) the ratios of Nitrogen to Carbon and the ratio of Sulphur to Carbon.

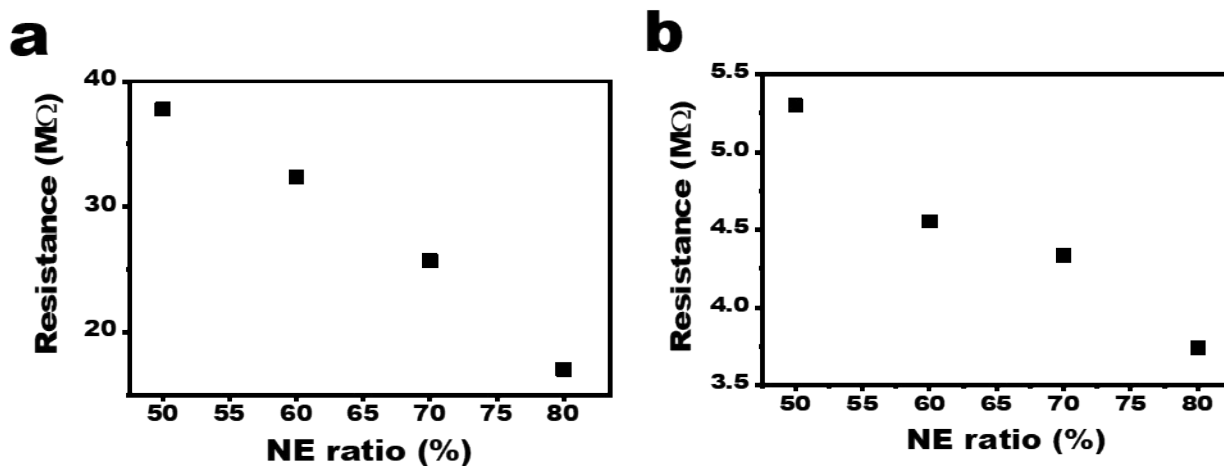


Fig. S12 Conductivity of bi-compartmental hybrid particles with different NE ratios. a) the electric resistance of one hundred bi-compartmental particles, b) the electric resistance of five hundred bi-compartmental particles.

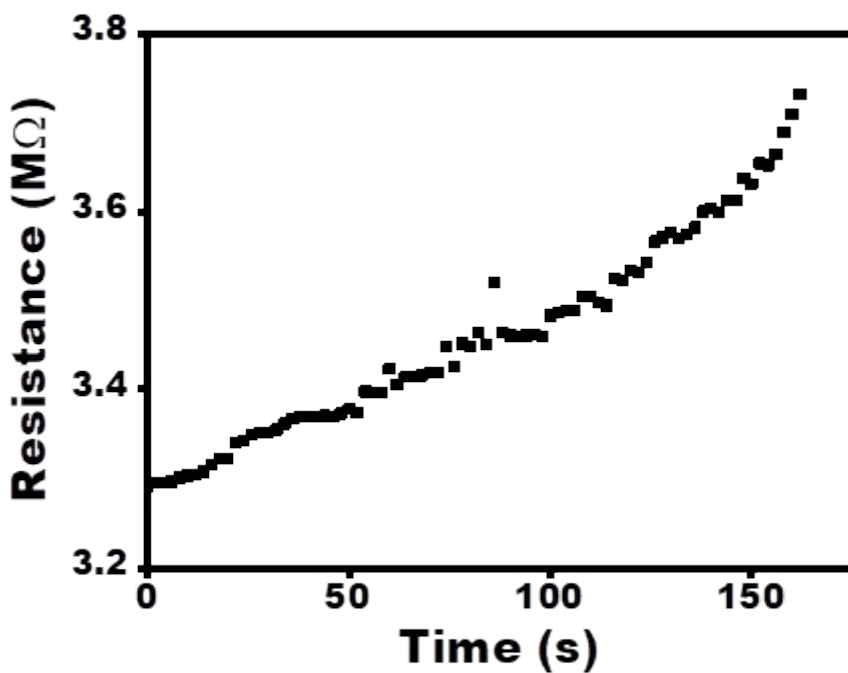


Fig. S13 Electric resistance of 500 bi-compartmental particles dependent on measuring time without magnetic field.

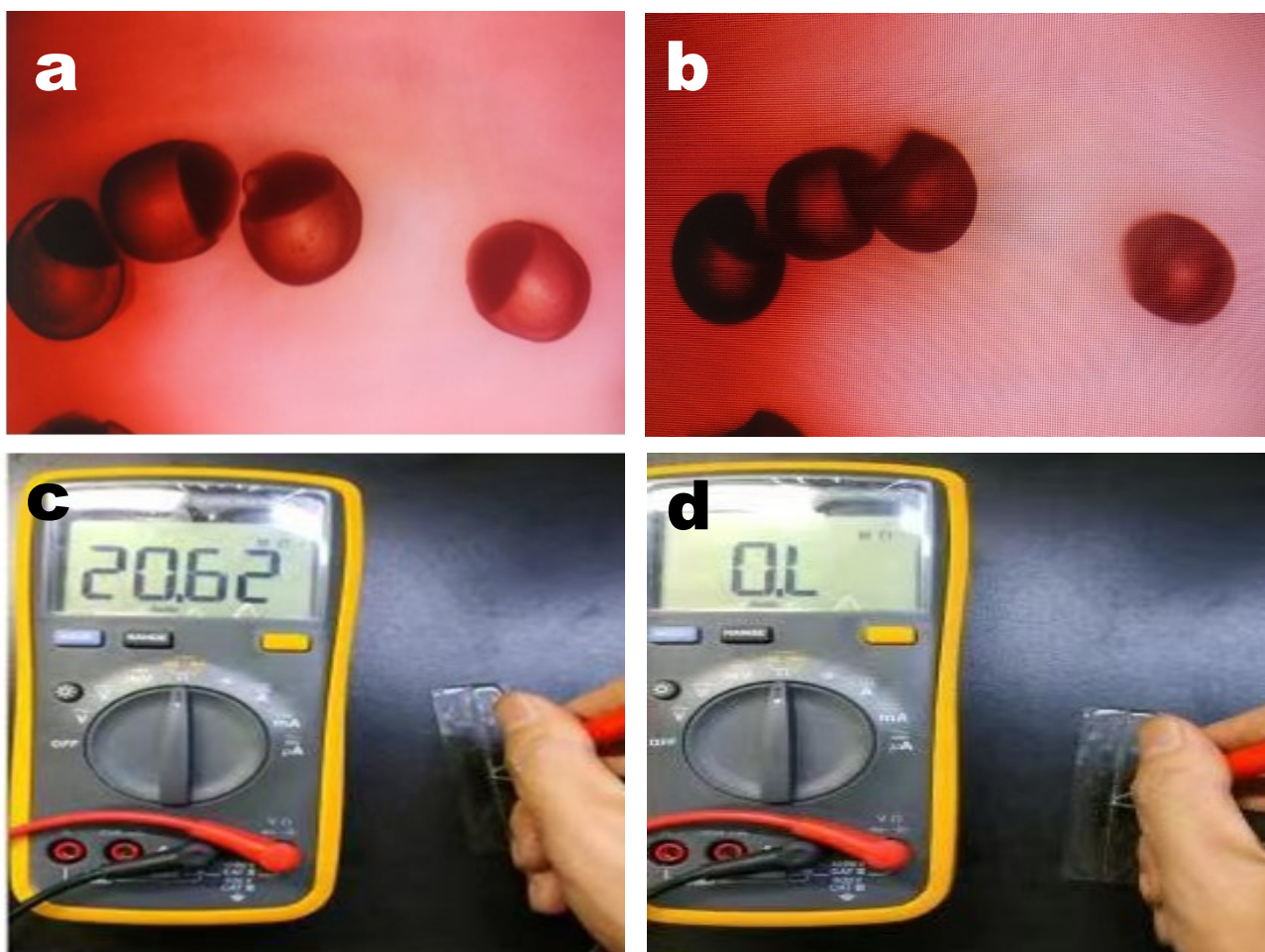


Fig. S14 The responsiveness of conductive bi-compartmental particles at different temperatures. a) Microscopic picture of bi-compartmental particles at 30 °C; b) Microscopic picture of bi-compartmental particles at 60 °C; c) picture of measuring resistance of bi-compartmental particles in a scotch on glass slide at 30 °C; d) picture of measuring resistance of bi-compartmental particles in a scotch on glass slide after heated at 60 °C.