

Electronic Supporting Information

Conductive Magnetic-Patchy Colloidal Microparticles for High Performance Pressure Sensor

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Experimental section

Materials: Polyethylene glycol-diacrylate (PEGDA, M_w 700 g mol^{-1}), paraffin oil, sodium 4-vinylbenzenesulfonate (NaSS), 2-hydroxy-2-methylpropiophenone (Darocure 1173, 97%), polyacrylic acid (PAA, M_w 7.5×10^4 g mol^{-1}), poly(ethyleneimine) (PEI, $M_w \sim 7.5 \times 10^5$ g mol^{-1}) and Fe_3O_4 NPs were purchased from Sigma-Aldrich (USA). Cetyl PEG/PPG-10/1 dimethicone (Abil EM 90, Evonik, Germany) were used as received. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was kindly supplied from Daeha ManTech Co. (Korea). Hexyltrimethoxysilane (TCI, Japan) and 2-[methoxy (polyethyleneoxy) propyl]-trimethoxysilane (Gelest, USA) were used as received. All other chemicals used in this study were reagent grades and used without further purification.

Fabrication of glass capillary microfluidic devices: The glass capillary-based microfluidic device was fabricated from a round capillary tapered by heating and pulling a cylindrical glass capillary (outer diameter = 1.0 mm, inner diameter = 0.58 mm, World Precision Instruments, USA) with a pipette puller (Model P-97; Sutter Instruments, USA). For hydrophilic modification, a square capillary tube was treated with 2 wt% of 2-[methoxy (polyethyleneoxy) propyl]trimethoxysilane in a mixture of ethanol and water at pH 5. The round capillary was wetted for 1 min at room temperature with 1 wt% hexyltrimethoxysilane in toluene to make their surface hydrophobic. It was completely dried at 50 °C for 6 h. For production of monodisperse W/O emulsions, the tapered cylindrical capillary tube, which was used as the collection tube, was inserted into the square capillary tube (inner diameter = 1 mm,

Atlantic International Technology, USA). The diameter of the tapered capillary inner tube was trimmed to be 220 μm . Both ends of the square capillary were fit in with a needle (Cupdown needle, Korea Vaccine Co., Ltd., Korea) and completely glued with epoxy resin.

Synthesis of monodisperse magnetic-patchy conductive microparticles: Monodisperse water-in-oil (W/O) emulsions were generated through the capillary-based microfluidic device. In the typical synthetic procedure, the outer fluid (OF) consisted of paraffin oil and 1 wt% of Abil EM90. The dispersion fluid (DF) was formulated with 20 wt% PEGDA, 1 wt% Fe_3O_4 NPs, 10 wt% NaSS, and 1 wt% Darocur 1173, and 0.006wt% PAA in water. The flow rate of each fluid was precisely controlled with syringe pumps (Pump 11 Elite, Harvard Apparatus, USA). The generation of emulsion drops was monitored using an inverted microscope equipped with a high-speed camera (Phantom Miro eX2, Vision Research Inc., USA). The depletion-induced segregation of Fe_3O_4 NPs in the emulsion drops was obtained in the presence of PAA in 2 h at room temperature. The emulsion drops were then solidified by photo-polymerization by irradiation of UV light (365 nm) for 40 s (JHC1-051S-V2, A&D, Korea). After the polymerization, Paraffin oil and other additives were completely washed out by repeating centrifugation at 1500 rpm with a large amount of isopropyl alcohol (IPA). The magnetic-patchy microparticles were re-dispersed in deionized (DI) water. The sizes of the emulsion drops and magnetic-patchy microparticles were determined from analysis of their bright-field microscope images (Axio Vert.A1, Zeiss, Germany).

LbL deposition of conductive polymers on PU microparticles: To uniformly coat PEDOT:PSS on the magnetic-patchy microparticles, the layer-by-layer (LbL) deposition was employed. First, 45 mg of the magnetic-patchy microparticles were finely dispersed in a 10 mL vial. PEI solution was also prepared in a NaCl solution (0.5 M). The microparticles were immersed in 2 mL of PEI solution. The dispersion was then vortexed for 30 min at room temperature. After deposition of PEI, the particles were repeatedly washed with DI water for more than five times to completely remove the unreacted materials. Next, for the LbL deposition of PEDOT:PSS, PEDOT (0.5 wt%) and PSS (0.8 wt%) were dissolved in DI water, respectively. The same process was undergone with 2mL of a PEDOT:PSS solution for generation of a PEDOT:PSS layer on the PEI-coated microparticles. The surface morphology of magnetic-patchy conductive microparticles was observed with a scanning electron microscopy (SEM, S-4800, Hitachi, Japan).

Detection of precision pressure changes: ITO glasses were used as top and bottom electrodes with 20 mm \times 25 mm dimension. First, the ITO glasses were cleaned by sequentially sonicating with alcohol and acetone for 30 min. Then, their surfaces were exposed to oxygen plasma (Cute-B, Femto Science, Korea) at 70 W, 90 sec. The magnetic-patchy conductive microparticles dispersed in IPA

were spin-coated at 1000 rpm for 30 sec. The density of particles on the ITO glass was exactly controlled so as not to cause any current deviation that comes from the different contact number of particles between electrodes. For this, we set the concentration of particles as 30 mg in 1 mL IPA. After spin coating, the particles-coated ITO glass was covered with the other ITO glass as a top electrode. Each electrode was extended with an Au-Ni woven conductive fabric (SILTEX CNG Type, Solueta Co. Ltd., Korea) and fixed with a conductive copper tape. The distribution of microparticles on the ITO glasses was observed with an optical microscopy (BX-51, Olympus, Japan). Current of the sensing devices was measured with a source meter (2400, Keithley, USA). The applied force was controlled using a universal manipulator with 0.01N resolution (UMP 100, Teraleader Co. Ltd., Korea).

Experimental data



Figure S1. (A) Schematic illustration of a micro-capillary device for the generation of magnetic NPs-containing precursor W/O emulsion drops. (B) TEM image of Fe₃O₄ NPs.

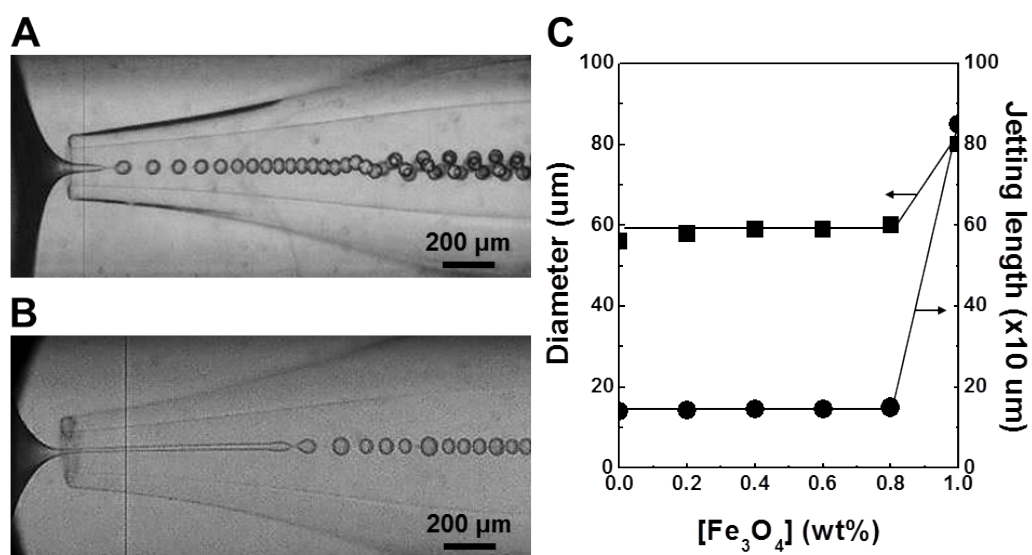


Figure S2. Optical microscope images showing the generation of the W/O emulsion drops containing Fe₃O₄ NPs: (A) 0.2 wt% and (B) 1 wt%. The flow rates were set with $Q_{OF} = 3000 \text{ uL h}^{-1}$ and $Q_{DF} = 200 \text{ uL h}^{-1}$. (C) Jetting length and drop diameter changes with varying the concentration of Fe₃O₄ NPs in the emulsion drops.

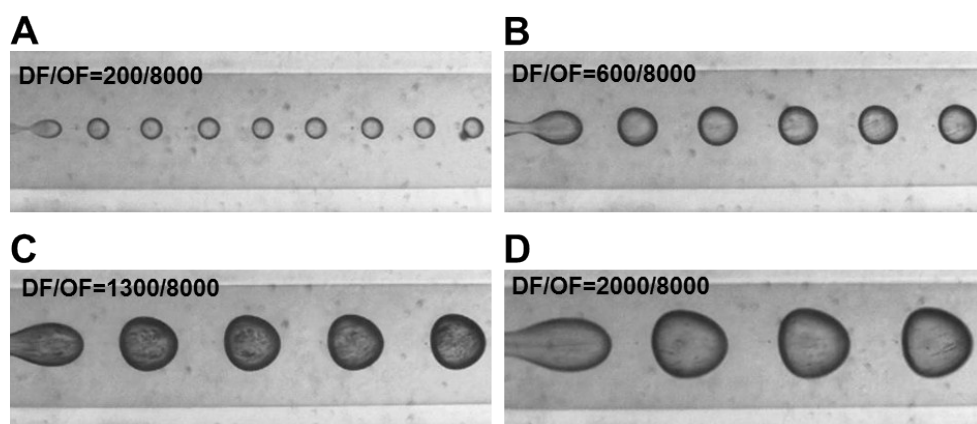


Figure S3. Control over the drop size of W/O emulsions by regulating the relative flow rate of the dispersion fluid (DF) over the continuous fluid (CF) in the micro-capillary device. (A) $Q_{DF}/Q_{OF} = 200 \text{ uL h}^{-1}/8000 \text{ uL h}^{-1}$, (B) $Q_{DF}/Q_{OF} = 600 \text{ uL h}^{-1}/8000 \text{ uL h}^{-1}$, (C) $Q_{DF}/Q_{OF} = 1300 \text{ uL h}^{-1}/8000 \text{ uL h}^{-1}$, and (D) $Q_{DF}/Q_{OF} = 2000 \text{ uL h}^{-1}/8000 \text{ uL h}^{-1}$.

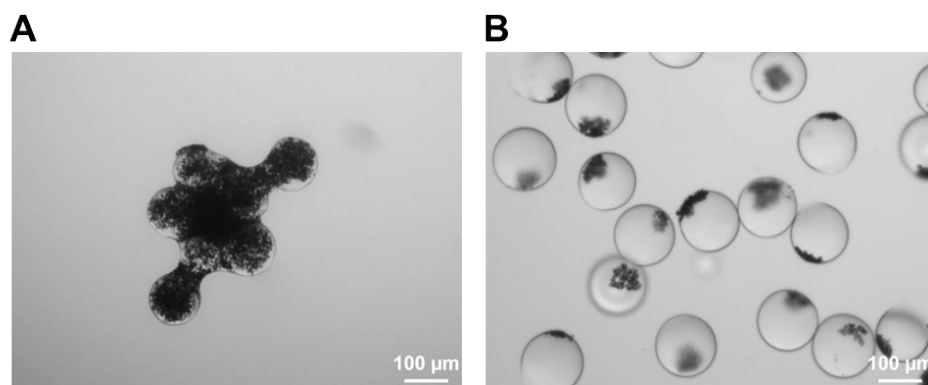


Figure S4. (A) Irreversible coalescence of typical magnetic-patchy microparticles. (B) Stable dispersion of magnetic-patchy microparticles of which surface was negatively charged by copolymerization of NaSS (10wt% against PEG dispersion fluid).

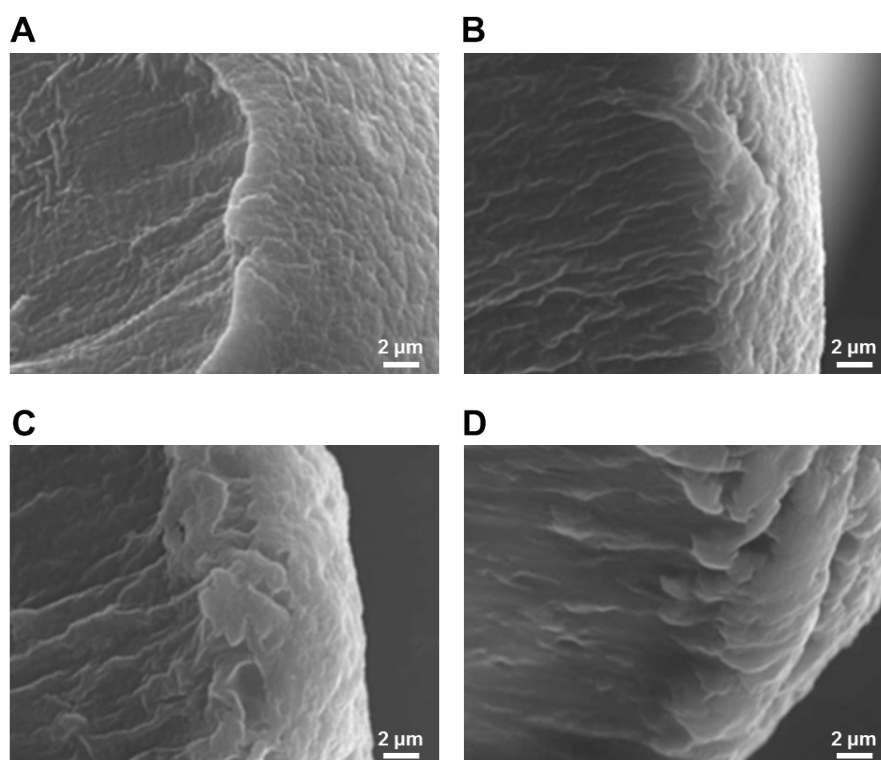


Figure S5. SEM images of chopped magnetic-patchy conductive microparticles with a different number of PEI/PEDOT:PSS layers. (A) $n=1$, (B) $n=2$, (C) $n=4$, and (D) $n=5$.

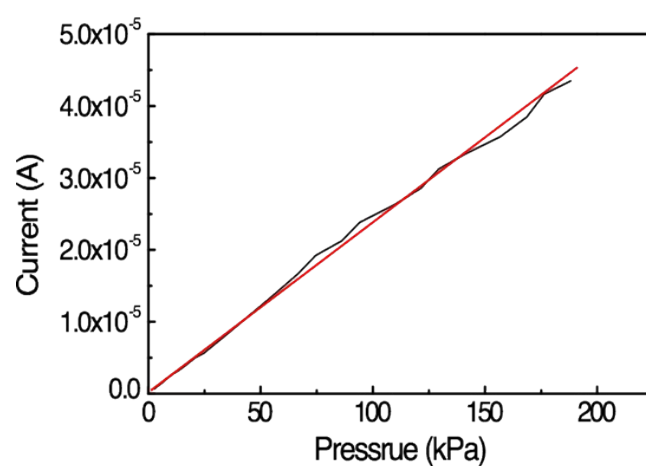


Figure S6. Current changes of conductive magnetic-patchy microparticles as a function of the applied pressure. The microparticles were coated with 10 PEI/PEDOT:PSS layers.