Electronic Supplementary Information (ESI) for

Dual external fields-responsive polyaniline-coated magnetite/silica nanoparticles for smart fluid application

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Materials and methods

Materials

Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), oleic acid (98%), 1-octadecene (90%), hexane, Igepal-CO 520, tetraethylorthosilicae (TEOS, 98%), aniline (>99.5%), and silicone oil [poly(methylphenylsiloxane), viscosity = 100 cSt] were purchased from Aldrich Chemical Co. Sodium oleate (95%), Ammonium hydroxide (NH_4OH, 28.0~30.0%), ethanol, cyclohexane, and hydrochloric acid (35.0~37.0%) were purchased from Samchun Chemical. Co., Korea. All chemicals were used without further purification.

Synthesis of magnetite nanoparticles (Fe_3O_4 NPs)

Fe_3O_4 nanoparticles with a size of *ca*. 15 nm were prepared by thermal decomposition of iron-oleate complex as described in literature. Typically, Iron chloride hexahydrate (5.4 g) and sodium oleate (18.25 g) were dissolved in a solvent containing distilled water (30 mL), ethanol (40 mL) and hexane (70 mL). The mixture was heated to 68 °C for 4 h. The upper organic layer was washed three times with distilled water, and the solution was heated to evaporate hexane, which resulted in an iron-oleate complex. Subsequently, the resulting iron-oleate complex (18 g) and oleic acid (2.8 g) were added to 1-octadecene (200g). Under the nitrogen condition, the solution was refluxed to 320 °C with a heating rate of 3.3 °C min^{-1} and kept that temperature for 30 min. After cooling the solution, ethanol (300 mL) was added to precipitate the nanoparticles. Finally, the Fe_3O_4 NPs were dissolved in cyclohexane (~ 0.5 wt%).

Fabrication of Fe_3O_4/SiO_2 core/shell nanoparticles

Fe_3O_4/SiO_2 core/shell nanoparticles were fabricated by a reverse microemulsion method. Firstly, the Fe_3O_4 solution (0.5 mL), Igepal-Co 520 (0.5 g), and ammonium hydroxide (0.2 mL) were dissolved in cyclohexane (11 mL) with a vigorous stirring. Then, TEOS (0.28 mL) was added to the solution via an equivalently fractionated drop method (adding 40 μL per 2 h). The Fe_3O_4/SiO_2 core/shell NPs were collected by centrifugation and washed with methanol several times.

Fabrication of Fe_3O_4/SiO_2/PANI nanoparticles

Fe_3O_4/SiO_2/PANI NPs were fabricated by a seeded dispersion polymerization method. Firstly, the Fe_3O_4/SiO_2 core/shell NPs (0.3 g) were dispersed in distilled water (50 mL) using a sonication. Then, $FeCl_3$ (0.3 g) was added into the mixture. After 12 h, Fe^{3+} ion-coated Fe_3O_4/SiO_2 NPs were separated by centrifugation and dispersed in chloroform (50 mL). aniline (60 μL) was added into the solution and polymerized for 6 h. The resulting Fe_3O_4/SiO_2/PANI NPs were isolated with centrifugation and obtained after drying in a vacuum oven for overnight.

Characterization

The structural morphologies of nanoparticles were obtained using transmission electron microscopy (JEM–2100, JEOL). The surface morphologies and elemental composition of the nanoparticles were obtained by FE-SEM (JSM–6700F, JEOL) installed with an energy dispersive X-ray spectrometer (INCA energy). The crystal structures were examined using a SmartLab X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation source (λ = 1.541 Å) in the 2 θ range of 10–70 ° with a scan rate of 10 ° min^{-1}. FTIR spectra were acquired by a PerkinElmer FTIR spectrum 400 System. Thermogravimetric analysis (TGA) was conducted by TGA 2050 analyzer (TA instruments) in N_2 atmosphere, and measured from the temperature range of 100–800 °C. Magnetizations of the nanoparticles were obtained using a Physical property measurement system (PPMS–14, Quantum Design) at room temperature.

Analysis of electrorheological and magnetorheological response

ER activity was examined using a rheometer (AR 2000 Advanced Rheometer, TA instruments) installed with a cup (radius = 15.0 mm and height = 30.0 mm), a concentric cylinder conical geometry (radius = 14.0 mm and height = 30.0 mm), a high-voltage generator (Trek 677B), and a temperature controller. MR activity were investigated using a magneto-rheometer (MCR 301, Anton Paar, Austria) equipped with a magnetic field generator. A magnetic field was applied between the parallel plates by a magnetorheological device (PS-MRD/5A, Anton Paar, Austria). The diameter of a parallel plate and a gap between parallel plates were 20 mm and 0.1 mm, respectively. The dual stimuli-responsive activity of Fe_3O_4/SiO_2/PANI-based fluid was investigated using the rheometer (AR 2000 Advanced Rheometer) by applying the electric and magnetic fields in the parallel direction. Because the direction of electric fields was normal to a rotator (or cup), we needed to remove the undesired fields. So, we partially coated the cup with the insulating materials including RTV silicone and insulating tape. After this step, the electric and magnetic fields were applied in the parallel direction. Moreover, the EMR activity of the fluid was examined using the rheometer (AR 2000 Advanced Rheometer) by applying the electric and magnetic fields in the perpendicular direction. In this case, the coating of insulating materials was not necessary. Namely, the direction of electric fields was normal to the geometry. The magnetic fields were applied from the bottom of the concentric cylinder conical geometry. In this way, the electric and magnetic fields were applied in the perpendicular direction during the measurement.

1. SEM images and EDS analysis

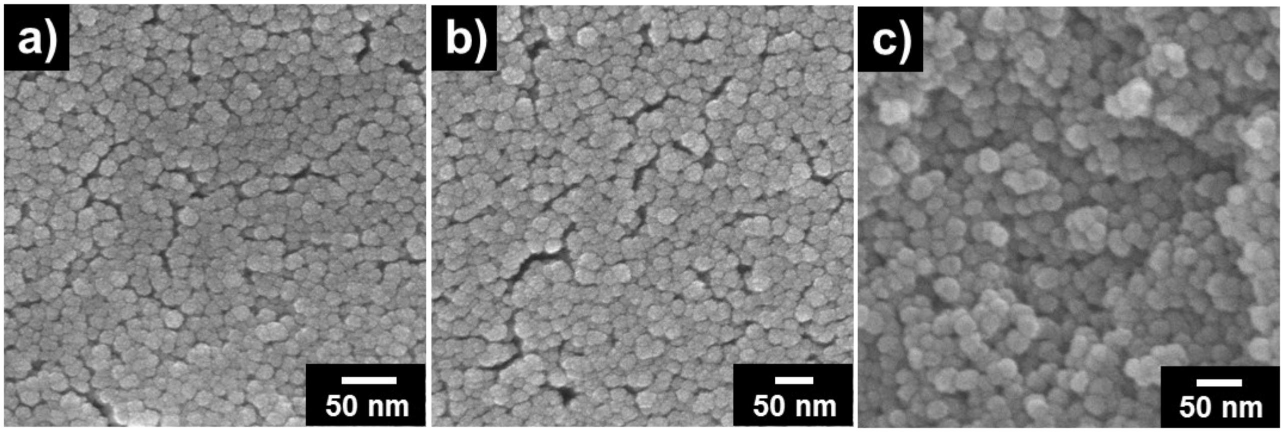

Fig. S1 SEM images of (a) Fe_3O_4, (b) Fe_3O_4/SiO_2, and (c) Fe_3O_4/SiO_2/PANI nanoparticles.

Table S1. Elemental analysis of Fe_3O_4, Fe_3O_4/SiO_2, and Fe_3O_4/SiO_2/PANI nanoparticles.

Samples	Atomic %[a]					
	C	N	O	Si	Fe	Total
Fe_3O_4	3.80	0.00	52.1	0.00	44.1	100.0
Fe_3O_4/SiO_2	1.50	0.00	63.7	10.3	24.5	100.0
Fe_3O_4/SiO_2/PANI	15.9	3.10	45.6	16.3	19.1	100.0

[a]Atomic percentages of the samples were obtained by Field Emission Scanning Electron Microscope (JSM-6701F, JEOL) installed with Energy Dispersive X-ray spectrometer (INCA Energy, Oxford Instruments Analytical Ltd.).

2. Dynamic light scattering (DLS) analysis of the nanoparticles

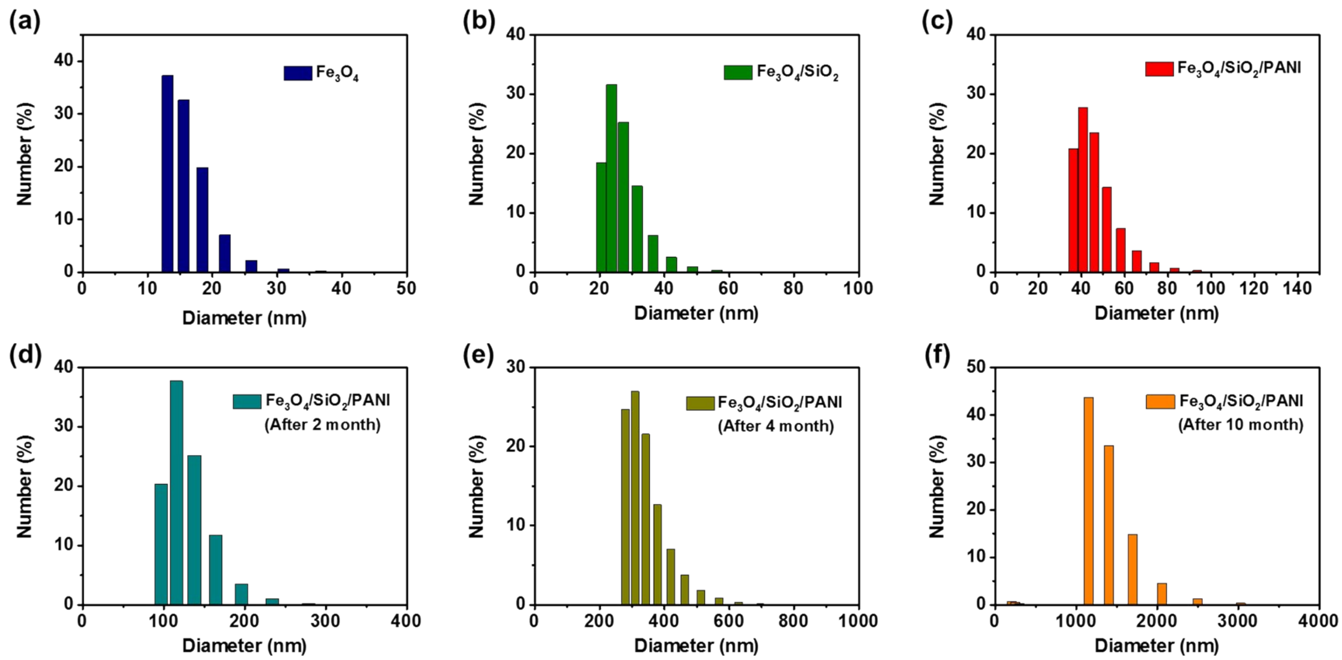

Fig. S2 The dynamic light scattering (DLS) analysis of (a) Fe_3O_4, (b) Fe_3O_4/SiO_2, and (c) Fe_3O_4/SiO_2/PANI. The DLS analysis for the Fe_3O_4/SiO_2/PANI nanoparticles fabricated (d) 2, (e) 4, and (f) 10 months ago.

3. The directions of electric and magnetic fields in the rheometers

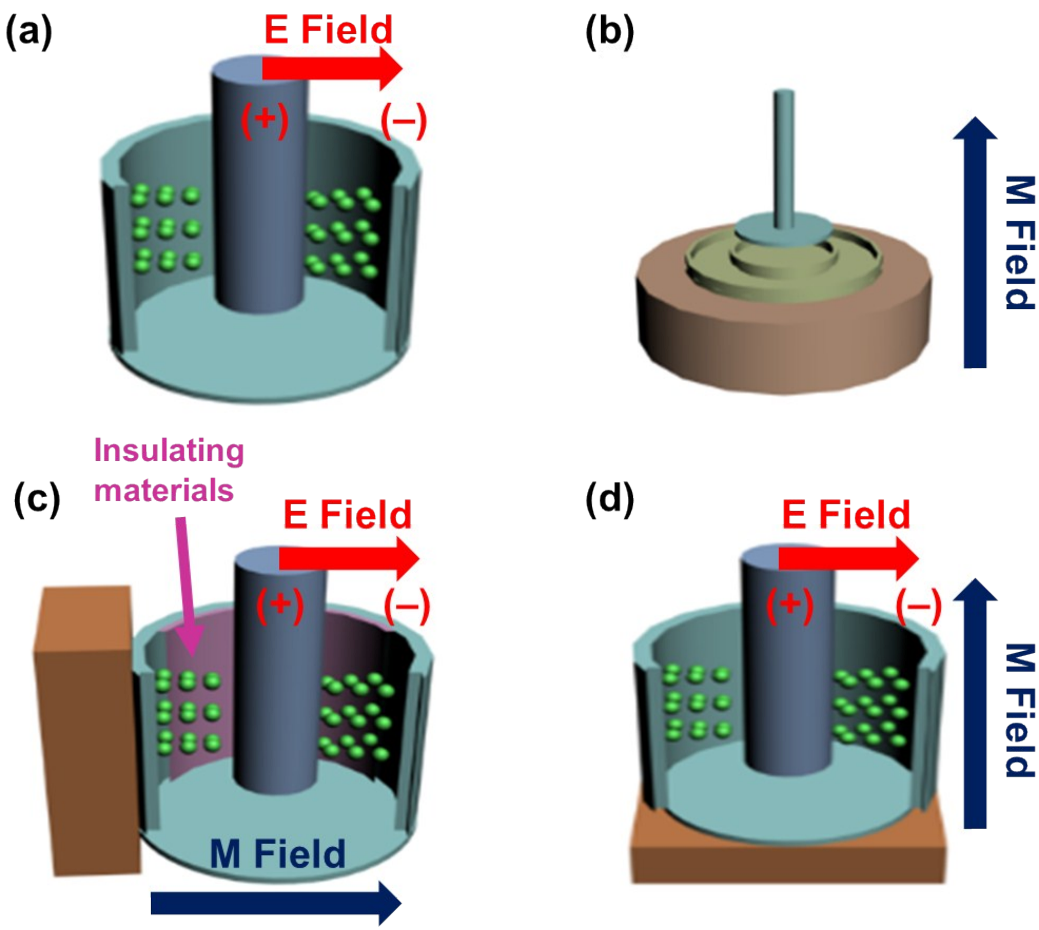

Fig. S3. The direction of electric and magnetic fields in the rheometers. (a) The electric fields were perpendicular to the concentric cylindrical conical geometry. (b) The magnetic fields were normal to the parallel plates. (c) The electric and magnetic fields were applied in the parallel direction. In this case, the cup was partially coated with RTV silicone and insulating tape to remove the undesired direction of electric fields. (d) The electric and magnetic fields were applied in the perpendicular direction.

4. Electrorheological activity of Fe_3O_4/SiO_2-based fluid

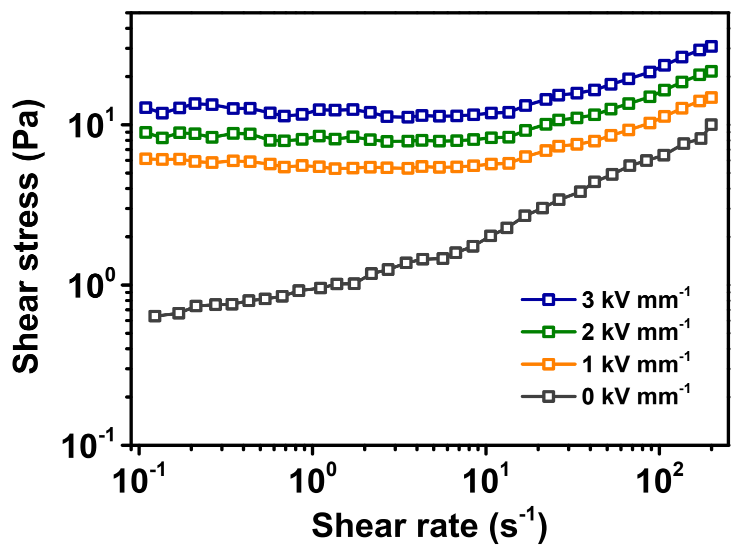

Fig. S4 Shear stresses of Fe_3O_4/SiO_2-based fluid as a function of shear rate measured at various electric field strengths.

5. Comparison of the electrorheological properties

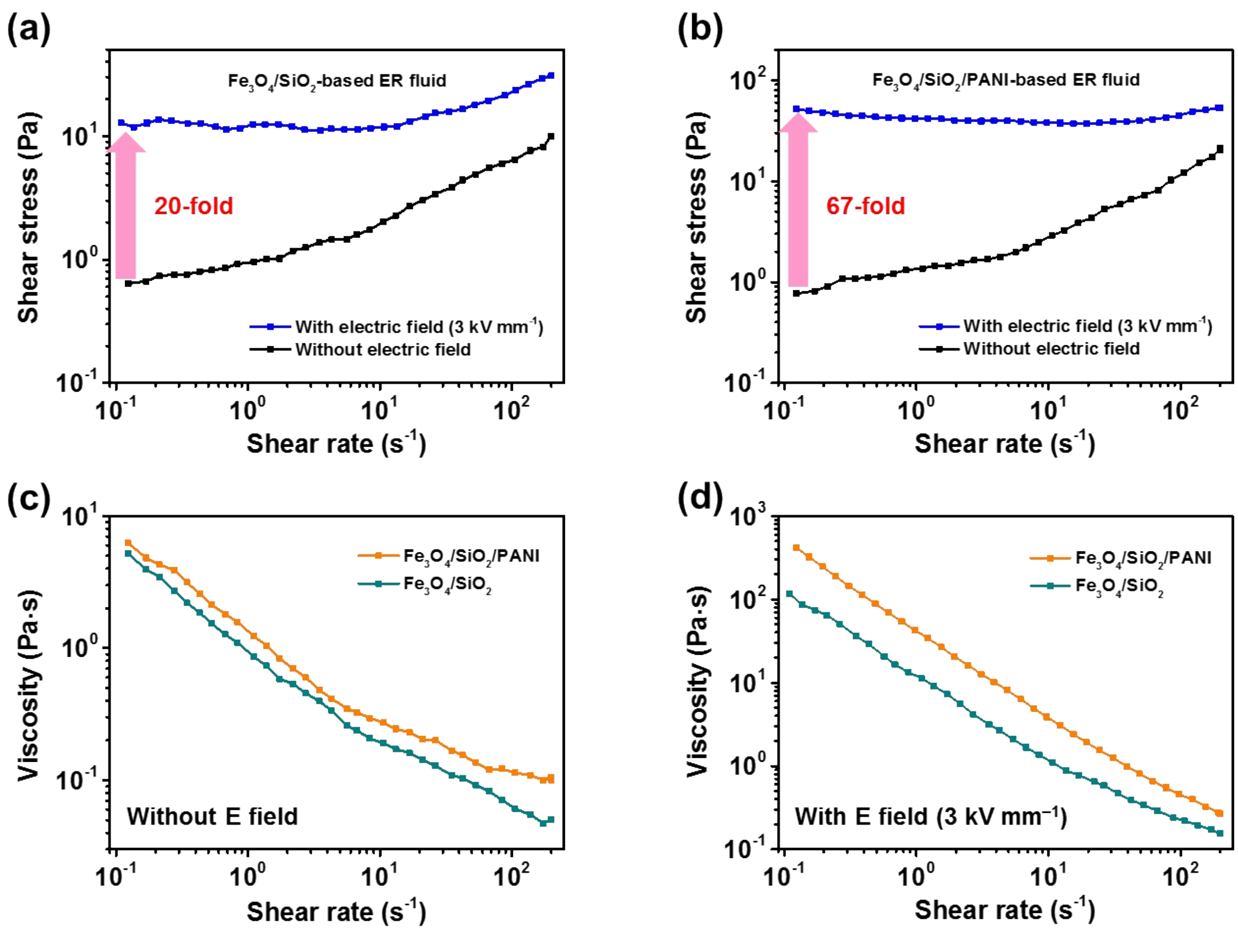

Fig. S5 Shear stresses of (a) Fe_3O_4/SiO_2 and (b) Fe_3O_4/SiO_2/PANI-based fluid (5 wt % in silicone oil) as a function of shear rate, measured with and without an electric field strength of 3 kV mm^{-1}. The insets show the enhancement of shear stress of each fluid. Viscosities of the fluids as a function of shear rate (c) without an electric field and (d) with an electric field of 3 kV mm^{-1}.

6. Yield stress of the Fe_3O_4/SiO_2/PANI-based fluid (ER response)

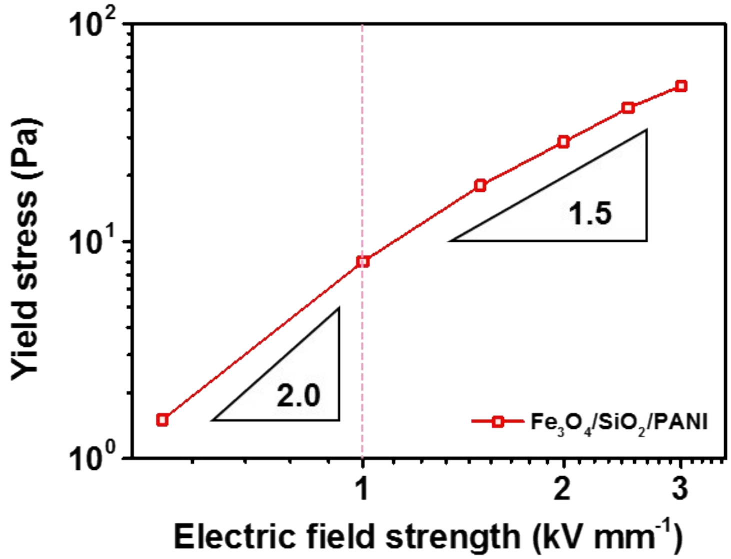

Fig. S6 Yield stress of the Fe_3O_4/SiO_2/PANI-based fluid (5.0 wt% in silicone oil) as a function of the electric field strength. The yield stress is proportional to *ca*. 2.0 power of the electric field strength below 1.0 kV mm^{-1} ($\tau_y \propto E^{2.0}$). However, the yield stress increases proportionally to *ca*. 1.5 power of the electric field strength above 1.0 kV mm^{-1} ($\tau_y \propto E^{1.5}$). This ER activity corresponds to the non-linear conductivity model.[1]

7. Yield stress of the Fe_3O_4/SiO_2/PANI-based fluid (MR response)

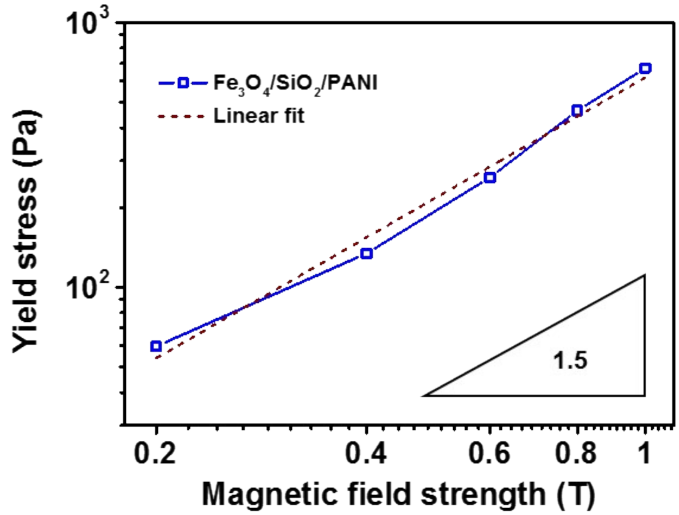

Fig. S7 Yield stress of the Fe_3O_4/SiO_2/PANI-based fluid (5 wt% in silicone oil) as a function of the magnetic field strength. The yield stress was proportional to *ca*. 1.5 power of the magnetic field strength ($\tau_y \propto H_0^{1.5}$).

The relationship between the yield stress and magnetic field strength

The yield stress depending on the applied magnetic field strength is expressed as follows.[2]

$$\tau_y(H_0) = \alpha H_0^2 \left(\frac{\tanh\sqrt{H_0/H_C}}{\sqrt{H_0/H_C}}\right)$$

$$\tau_y = \alpha H_0^2 \ (H_0 \ll H_C)$$

$$\tau_y = \alpha\sqrt{H_C} H_0^{3/2} \ (H_0 \gg H_C)$$

where α is related to the susceptibility of fluid and volume fraction or other analogous physical parameters, H_0 and H_c are the applied magnetic field strength and the critical magnetic field strength, respectively.

8. Dual-stimuli responsive properties

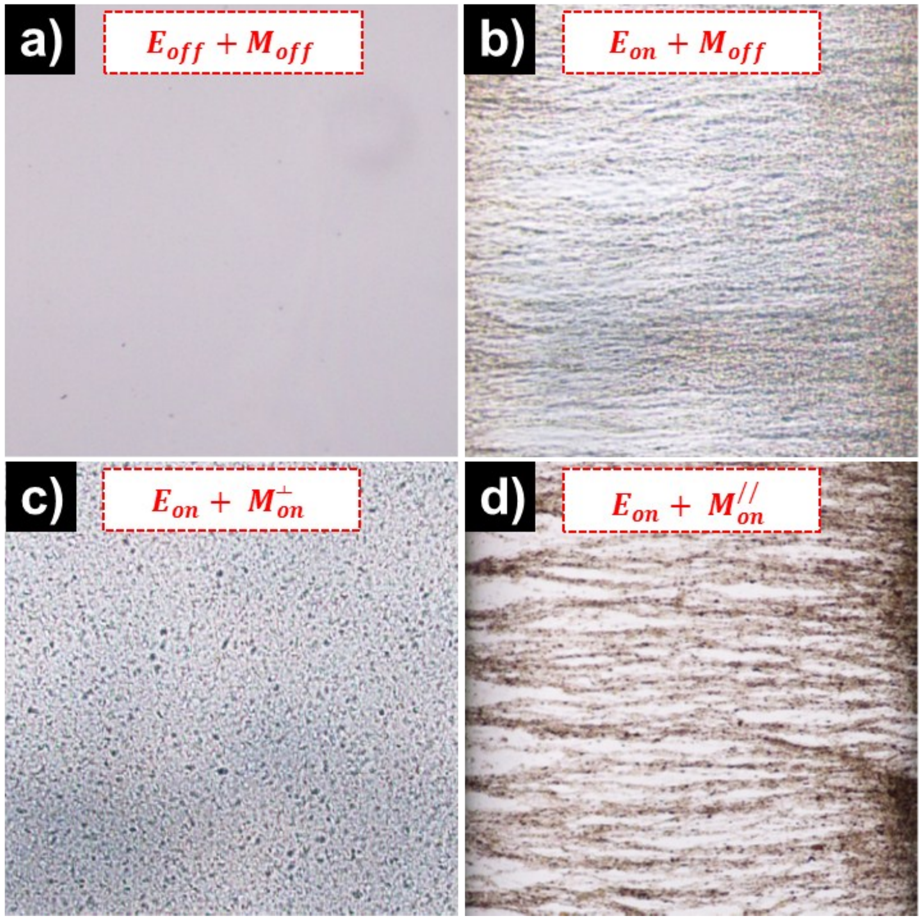

Fig. S8 Optical microscopy images of the Fe_3O_4/SiO_2/PANI-based fluid at various external fields. (a) The external field was not applied. (b) Only the electric field of 3 kV mm^{-1} was turned on. Both the electric field (3 kV mm^{-1}) and magnetic field (0.2 T) were applied simultaneously (c) with the perpendicular direction and (d) the parallel direction.

Table S2. Stimuli-responsive performance of the Fe_3O_4/SiO_2/PANI-based fluid[a]

External fields	Weight percentage[b] (wt %)	Shear stress[c] (Pa)
Electric field (3 kV mm^{-1})	5	51.7
Magnetic field (0.2 T)	5	59.7
Electric field (3 kV mm^{-1}) ⊥ Magnetic field (0.2 T)[d]	5	28.3
Electric field (3 kV mm^{-1}) // Magnetic field (0.2 T)[e]	5	90.3

[a] The experimental measurement was carried out at a standard temperature of 20 °C.
[b] Fe_3O_4/SiO_2/PANI NPs were dispersed in silicone oil [poly(methylphenylsiloxane), kinematic viscosity = 100 cSt] as an insulating medium.
[c] Shear stress was measured at a fixed shear rate of 0.1 s^{-1}.
[d] Both electric and magnetic fields were applied to the fluid simultaneously. The magnetic field was applied in the perpendicular direction to the electric field.
[e] Both electric and magnetic fields were applied to the fluid simultaneously. The magnetic field was applied in the parallel direction to the electric field.

9. Sedimentation properties

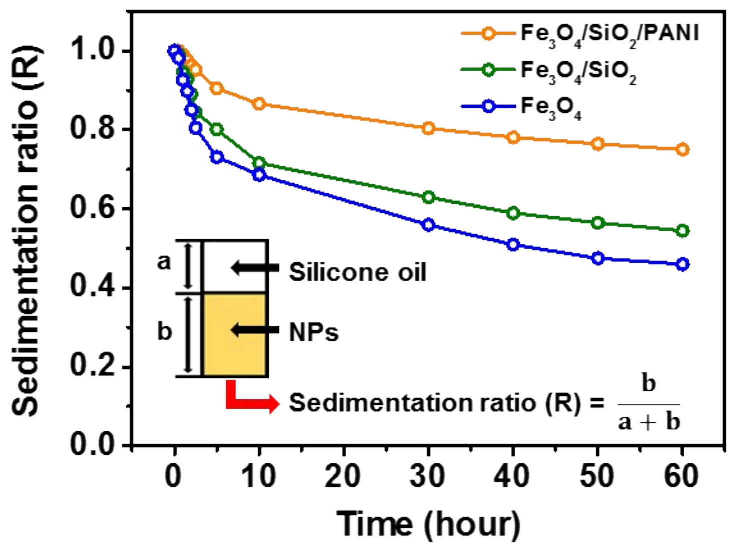

Fig. S9 Sedimentation properties of the Fe_3O_4, Fe_3O_4/SiO_2, and Fe_3O_4/SiO_2/PANI-based fluids with the concentration of 5 wt% in silicone oil [Inset: definition of sedimentation ratio].

Reference

1. H.J. Choi, M.S. Cho and J.W. Kim, *Appl. Phys. Letter*, 2001, **78**, 3806.
2. S. Lee, J. Noh, S. Hong, Y. K. Kim, *Chem. Mater*., 2016, **28**, 2624.