

Magnetically tunable plasmon coupling of Au nanoshells enabled by space-free confined growth

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I. Synthesis of Au shells

Chemicals: All chemicals are used directly without further purification. Ethanol was purchased from Decon Labs. Iron chloride (III) hexahydrate, tetraethyl orthosilicate (TEOS), polyacrylic acid (PAA, MW=1800), sodium hydroxide, polyvinylpyrrolidone (PVP, MW=10000), resorcinol (R), formaldehyde (F), 2-Hydroxy-2-methylpropiophenone, polyvinyl alcohol (PVA), 2-Hydroxy-2-methylpropiophenone and Tetrakis(hydroxymethyl)phosphonium chloride (THPC) were bought from Sigma-Aldrich. Ammonium hydroxide and hydrogen peroxide (H₂O₂) were purchased from Fisher Scientific. Chloroauric (III) acid trihydrate (HAuCl₄·3H₂O) and ethylene glycol (EG) was from Acros Organics. Acrylamide (AM) and N,N'-Methylenebisacrylamide (BIS) was purchased from Fluka. Oleic acid sodium salt (NaOL) was purchased from TCI AMERICA. SYLGARD 184

silicone elastomer curing agent and SYLGARD 184 silicone elastomer base were purchased from Dow silicone corporation. Acrylamide (AM) and N,N'-Methylenebisacrylamide (BIS) were purchased from Fluka.

Synthesis of Fe₃O₄ nanoparticles: Colloidal particles of Fe₃O₄ nanoparticles with tunable size were synthesized based on our previously reported method.¹ The reaction was carried in the solution phase at elevated temperature. A stock solution was prepared by dissolving 50 mmol NaOH in 20 mL of DEG, which was heated at 120°C for 1 hour under the protection of nitrogen. The solution was kept at 70°C as a stock solution. In a typical synthesis, PAA (4 mmol) and FeCl₃ (0.4 mmol) were dissolved in DEG (17 mL), and the mixture was heated to 22°C for 30 min under the protection of nitrogen. A certain amount of stock solution was injected rapidly. The mixture was heated at 220°C for another one hour. The volumes of stock solutions were 1.7, 1.75, and 1.8 mL for the synthesis of Fe₃O₄ nanoparticles with an average diameter of 70, 125, and 150 nm, respectively. The obtained Fe₃O₄ nanoparticles were washed by deionized water several times and dispersed in 20 mL of water.

PEI modification: For PEI modification, 5mL (0.25 batch) of an aqueous solution of Fe₃O₄ nanoparticles was added into 30 mL of PEI solution (20mg/mL, Mw=800) under sonication. The mixed solution was agitated by vortex overnight. To get rid of magnetic field-induced aggregation, magnetic stirring was not suggested during PEI modification. After that, Fe₃O₄ nanoparticles were washed with water three times and then dispersed in 5 mL of water.

Au seed preparation: THPC (12 μL) and NaOH (250 μL, 2M) were added into 45 mL water. After stirring for 5 min, 2 mL of HAuCl₄ was added. The Au seeds (Aus) solution was stocked in the dark for further attachment.

Au seed attachment: To 30 mL of Au seed solution, 5 mL of Fe_3O_4 nanoparticle solutions after PEI modification was added slowly under sonication. The mixed solution was agitated for about one hour. Excess Au seed was removed by centrifugation. Au seed was attached to the surface of Fe_3O_4 nanoparticles due to the electrostatic interactions, forming $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles. They were further washed by water three times and then dispersed in 10 mL of water.

RF coating: PVP modification was first carried out before RF coating. In a typical process, a 10 mL solution of $\text{Fe}_3\text{O}_4/\text{Au}$ was added into 30 mL of PVP solution (5 mg/mL) under sonication. The solution was agitated by vortex overnight. The solution was washed by water three times to remove excess PVP. Finally, they were dispersed in 28 mL of water for RF coating. In a based-catalyzed step-growth polymerization, 20 mg R and 28 μL of F were added in sequence. 100 μL of ammonia solution (2.8%) was added into the solution. The reaction was first sonicated for 1 hour and then transferred into a 50 mL round bottom flask. The reaction was kept at 100°C for 3 hours in order to further condense RF resins and increase their cross-linking ratios. After cooling down to room temperature, the solution was washed three times by water. Then obtained $\text{Fe}_3\text{O}_4/\text{Au}@ \text{RF}$ was finally dispersed in 2 mL of water.

Seed-mediated growth of Au nanoshells: In a typical process, 500 μL of PVP (50mg/mL, $M_w=40000$), 100 μL of NaOL (10 mM), 20 μL of HAuCl_4 (0.25 M) and 50 μL of H_2O_2 were added into 7.5 mL of deionized water in sequence. Then, 25 μL of $\text{Fe}_3\text{O}_4/\text{Au}@ \text{RF}$ solution was added. The reaction occurred at room temperature for 30 min. The product was washed by deionized water three times and dispersed in deionized water for characterization.

Etching RF shells: The solutions of $\text{Fe}_3\text{O}_4@ \text{Au}@ \text{RF}$ nanoparticles were first dispersed in 2 M of NaOH solutions. To improve dispersibility of colloidal particles, the reaction occurred under the presence of 0.5 M PVP. After incubating at 80°C overnight, $\text{Fe}_3\text{O}_4@ \text{Au}$ nanoparticles were

washed by DI water for three times. The removal of RF also led to a blueshift from 730 nm to 685 nm in the plasmon band of Au shells synthesized with 70-nm cores (**Figure S8g**). Against a bright background, the perceived color in the colloidal dispersion was complementary to the plasmonic extinction. Therefore, the color turned from green to light blue (left two panels in the inset of **Figure S8g**). Interestingly, against a dark background, both the solutions before and after removing RF shells appeared red (right two panels in **Figure S8g**), which is ascribed to their strong scattering of red light between 622 and 770 nm.

Characterization: Extinction spectra were measured by Ocean Optics HR2000 spectrometer. TEM images were taken on Tecnai 12 transmission electron microscope at 120 kV. Dark-field optical macroscopic images were taken using A Zeiss AXIO Imager optical microscope. The SEM images were taken on ThermoFisher Scientific (formerly FEI/Philips) NNS450 scanning electron microscope with a back-scattering electron detector. The elemental mapping was performed at 50 kV.

II. Fabrication of plasmonic films

Preparation of PVA-Au composite films: PDMS film served as a transparent substrate for the PVA-plasmonic composite films. Silicone elastomer curing agent and silicone elastomer base were thoroughly mixed with a mass ratio of 1 to 10. The mixture was placed at ambient conditions for 2 hours to remove the air bubble inside the viscous solution. Then, it was cured at 60°C for two hours. 10% PVA solution was first prepared by dissolving PVA into deionized water under sonication. Then a certain amount of PVA solution was added into the Au shell solution with a final concentration of about 0.005 mg/mL. The obtained mixture solution was spin-casted on a PDMS substrate. To form a uniform thin PVA film, the PDMS substrate was first treated by plasma for 20 min. The casted film was dried in a vacuum at room temperature.

Preparation of anti-counterfeiting films: 2-Hydroxy-2-methylpropiophenone serves as a photoinitiator. AM is monomer and BIS is the cross-linking agent. In a typical process, 250 mg of AM, 14 mg of BIS and 3 μ L of 2-Hydroxy-2-methylpropiophenone were added in 1 mL of DEG. Au shell was first precipitated by centrifugation and then dispersed in the DEG solution. The mixture solution was sandwiched between glass slides and then was exposed to UV light (254 nm) for 1 min. A photomask with a pre-designed pattern was placed atop the sample, followed by applying a magnetic field (B_1). After the first UV exposure, 1D plasmonic chains with parallel alignment to external fields were fixed in the uncovered areas. The photomask was then removed, and a second UV exposure was applied to polymerize the remaining parts of the film under a horizontal magnetic field (B_2). The magnetic alignment was achieved by placing the mixture into the center of two identical permanent magnets. The field strength was measured to be 25 mT (250 G).

III. Analyzing Optical properties of Au nanoshells by finite element method

Calculating optical cross-section of single Au nanoshell: The computation of optical cross-section and efficiency is achieved based on the finite element method (Comsol Multiphysics). A sphere with core-shell-shell geometry is modeled to mimic the $\text{Fe}_3\text{O}_4@\text{Au}@\text{RF}$ nanostructures. The refractive index of RF is identified as 1.5. The domain of Au is defined by the built-in “Au” materials. Their physical properties, like the wavelength-dependent complex refractive index, have been fully described in the material library of Comsol Multiphysics. For the Fe_3O_4 domain, their refractive index is also wavelength-dependent and has a complex value with the real part determining the scattering properties and imaginary part determining the absorption of Fe_3O_4 material. To analyze the size-dependent opportunities of Au shell (**Figure. 1**), the thickness of Au and RF shell is 25 nm and 20 nm, respectively. Instead, the diameter of the magnetic core increases

from 20 to 30, 50, 70, 80, 90, 100, 125, and 150 nm. Their scattering (σ_{sca}), absorption (σ_{abs}) and extinction (σ_{ext}) cross-sections are calculated by solving the Maxwell equations in Comsol Multiphysics. The optical coefficients (Q) of Au shell, like scattering and absorption coefficient, were calculated by dividing the corresponding optical cross-sections by the physical cross-sections of the Au shell. The correlation between them can be expressed as $\sigma = Q\pi r^2$, where r is the radius of the Au shell.

Analyzing the coupling between Au nanoshells within plasmonic chains: The optical cross-sections of plasmonic chains were also calculated by the finite element method. In geometry, a 1D chain containing Au shells with well-controlled interparticle separation and orientation was first created in the Comsol Multiphysics. Then, the σ_{ext} was calculated and normalized to a number of Au shells in the 1D chains.

1. Ge, J.; Hu, Y.; Biasini, M.; Beyermann, W. P.; Yin, Y. Superparamagnetic magnetite colloidal nanocrystal clusters. *Angew. Chem. Int. Ed.* **2007**, 46, 4342-4345.

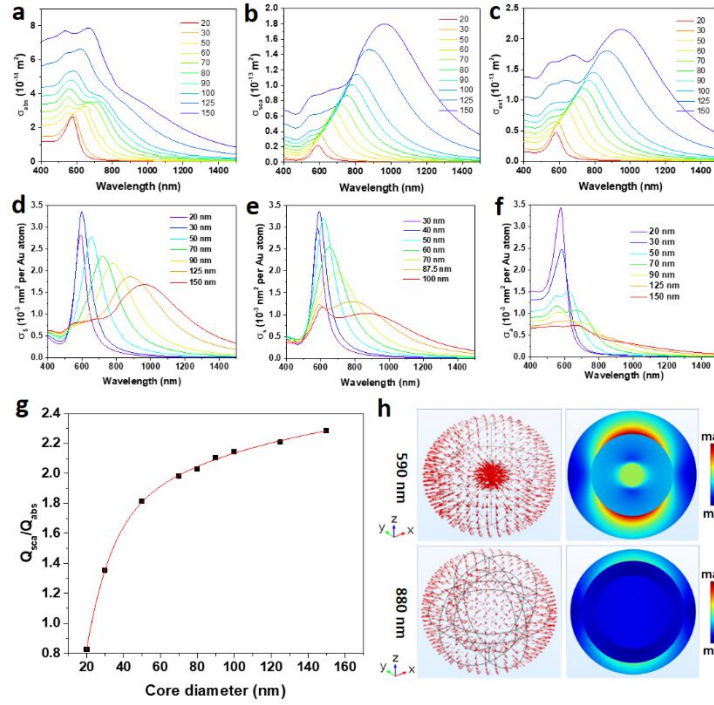


Figure S1. (a-c) Concept design. Simulated absorption (a), scattering (b), and extinction (c) cross-sections of Au nanoshells. The thickness of Au nanoshells is 25 nm. The core size increases from 20 to 150 nm. (d, e) Simulated atomic scattering cross sections of (d) Au nanoshells and (e) solid Au nanoparticles with different diameters. The Au nanoshells of 25 nm thickness were used for simulations. (f) Simulated atomic absorption cross-sections of Au nanoshells. (g) Merit figure of scattering of Au nanoshells. (h) Near-field electric field distribution (right) and Poynting vectors (left) of Au nanoshells excited at the resonant wavelength as indicated.

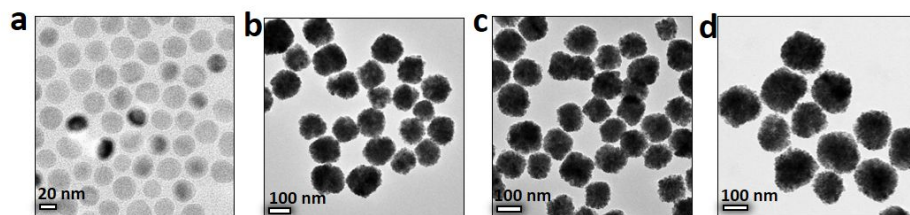


Figure S2. TEM images of Fe₃O₄ nanoparticles of (a) 20 nm, (b) 70 nm, (c) 125 nm and (d) 150 nm.

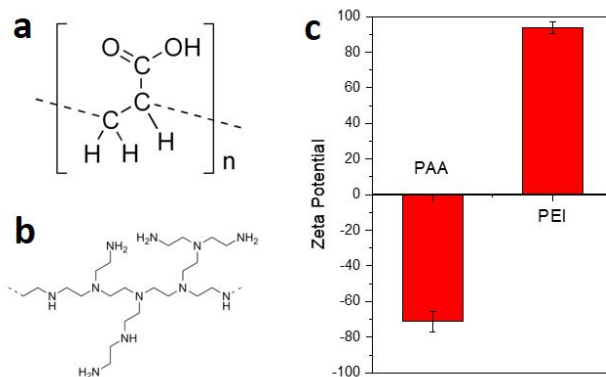


Figure S3. Chemical structures of (a) PAA and (b) branched PEI. (c) Zeta potential of magnetic nanoparticles before and after PEI modification.

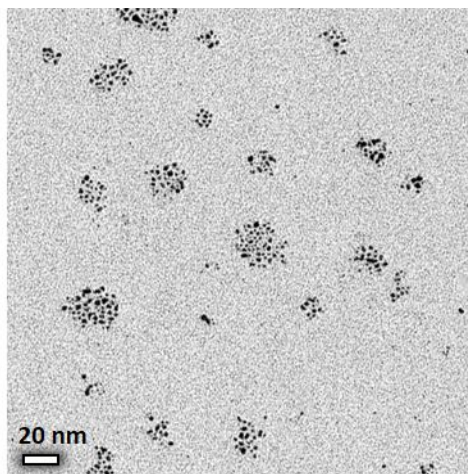


Figure S4. A TEM image of Au seeds.

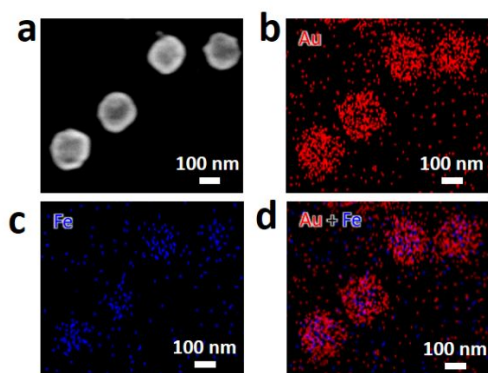


Figure S5. (a) Backscattered scanning electron microscopy of $\text{Fe}_3\text{O}_4@\text{Au}@\text{RF}$ nanospheres with 125-nm cores. The corresponding elemental mapping of (b) Au, (c) Fe, and the (d) merged images.

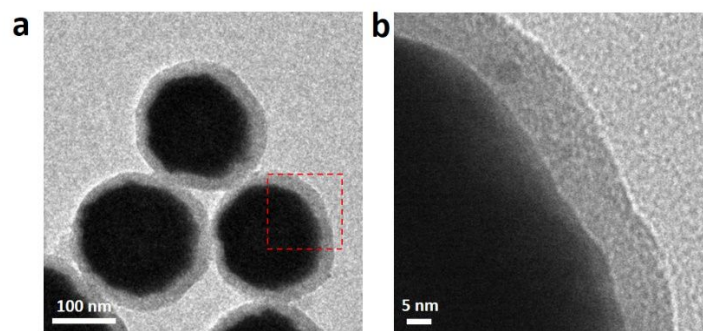


Figure S6. (a) A typical TEM and (b) High-magnification TEM images of $\text{Fe}_3\text{O}_4@\text{Au}@\text{RF}$ nanospheres using 125-nm CNCs as cores. The selective areas for high-resolution images is indicated by the dashed red box in (a).

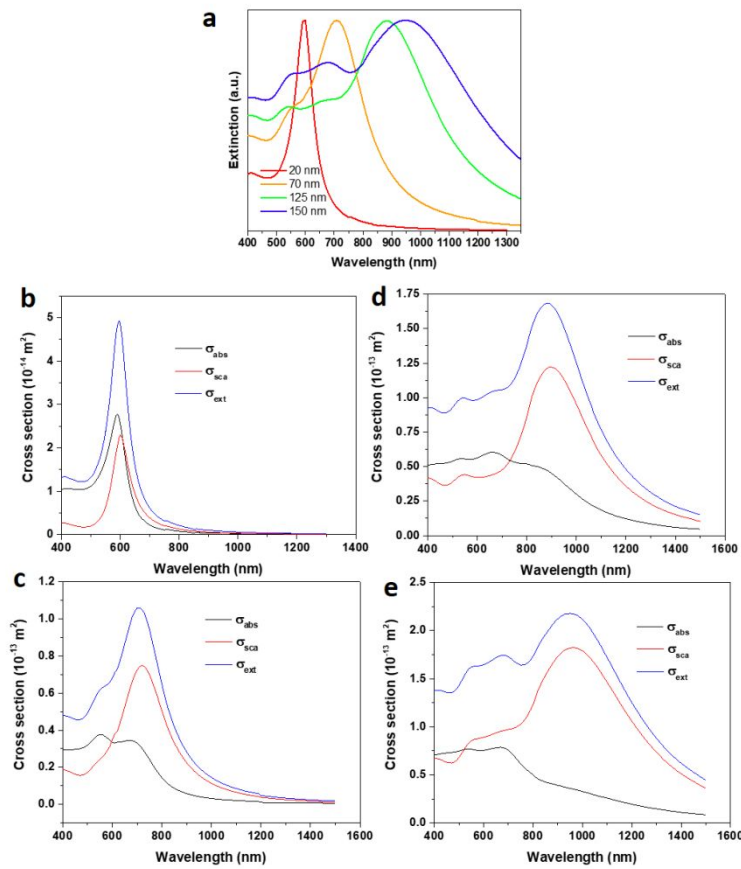


Figure S7. (a) Simulated extinction cross-sections of Au nanoshells with different core sizes. Simulated optical cross-sections of Au nanoshells with a core diameter of (b) 20 nm, (c) 70 nm, (d) 125 nm, and (e) 150 nm.

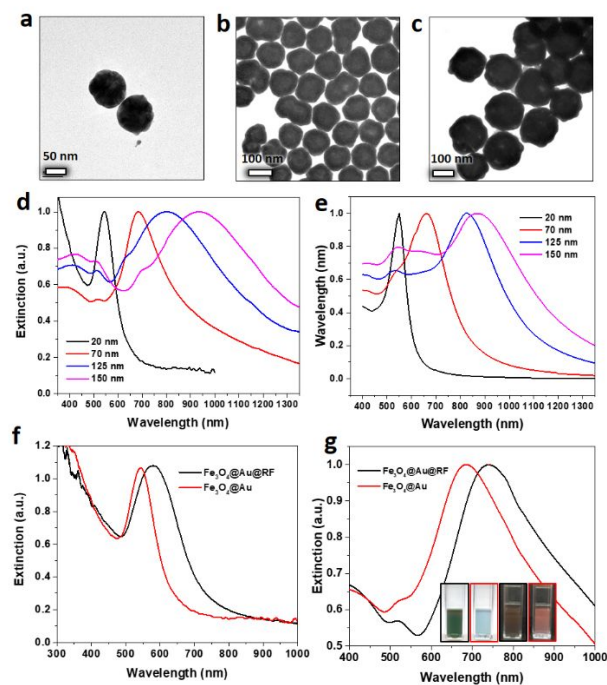


Figure S8. TEM images of $\text{Fe}_3\text{O}_4@\text{Au}$ nanoparticles prepared by etching away RF shells in NaOH solutions. Core sizes: (a) 20 nm, (b) 70 nm, and (c) 125 nm. (d) The extinction spectra of $\text{Fe}_3\text{O}_4@\text{Au}$ nanoparticles. (e) The simulated extinction spectra of $\text{Fe}_3\text{O}_4@\text{Au}$ nanoparticles. UV-Vis spectra of as-synthesized Au nanoshells before and after etching away RF: (f) 20-nm core and (g) 70-nm core. Insets in (g): solutions of $\text{Fe}_3\text{O}_4@\text{Au}@RF$ and $\text{Fe}_3\text{O}_4@\text{Au}$ with 70-nm core under bright and dark fields. Pictures highlighted by black and red frames show the solutions before and after etching away RF shells, respectively.

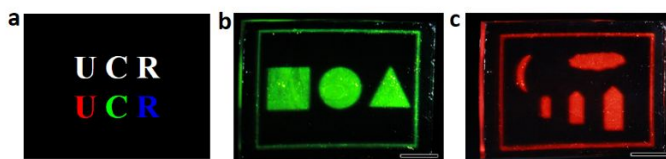


Figure S9. (a) Illustration of the “letters” projected on the transparent screens by a commercial projector. Specifically, the “UCR” in the top row is white in color. The letters “UCR” in the bottom row are red, green, and blue from left to right, respectively. (b,c) Photographs showing the projection images of PVA/Au composite films as transparent displays made of (b) 20-nm and (c) 70-nm Fe_3O_4 nanospheres as cores. Scale bars: 1 cm.

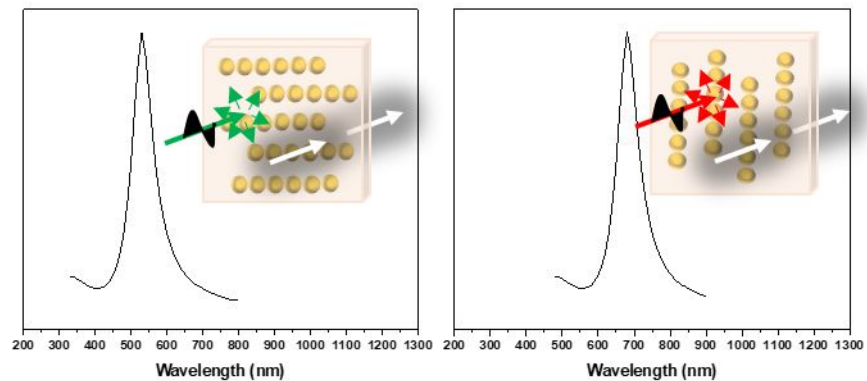


Figure S10. Schematic illustration of the active tuning of the plasmon coupling of Au shells enabled by the magnetic assembly of $\text{Fe}_3\text{O}_4@\text{Au}@\text{RF}$ nanoparticles. Specifically, changing the chain orientation relative to the light polarization will alter the plasmonic excitation of the 1D nanochains, which further leads to the changes of scattering properties of the chains.

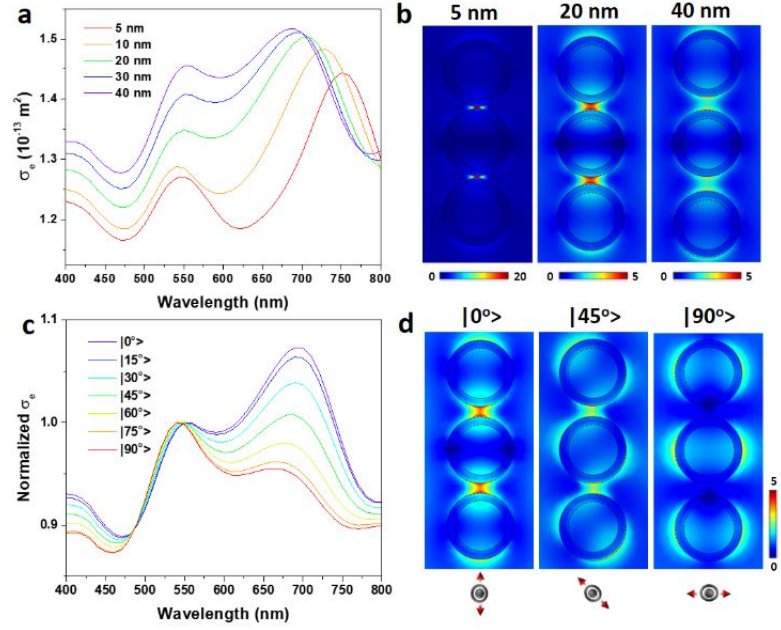


Figure S11. (a) Simulated extinction spectra of the plasmonic chain under different particle separation. (b) The localized electric field distribution at a separation of 5 nm, 20 nm, and 40 nm. The excitation wavelength from left to right is 750, 710, and 690 nm, respectively. (c) Simulated extinction spectra of the plasmonic chain under different orientations. The interparticle separation was set to be 30 nm. (d) The localized electric field distribution of plasmonic chains under orientations of 0° , 45° , and 90° .

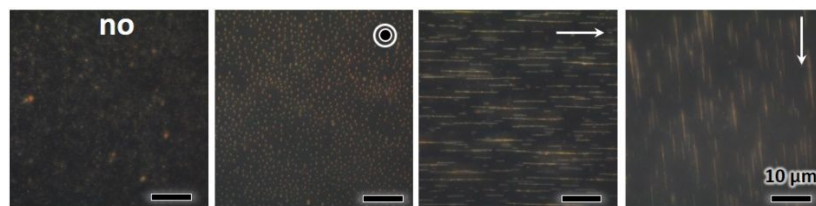


Figure S12. POM images of Fe₃O₄/Au@RF dispersions under different magnetic fields. White arrows indicate the directions of the applied magnetic fields.