

Feedback-driven self-assembly of symmetry-breaking optical metamaterials in solution

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1. Experimental Method and Characterization

Materials. Cetyltrimethylammonium bromide (CTAB), tetrachloroauric acid (HAuCl_4), silver nitrate (AgNO_3), sodium borohydride, sodium hydroxide (NaOH), ascorbic acid, mercaptopropyltrimethoxysilane (MPS), octadecyltrimethoxysilane (ODS), disodium chromoglycate (DSCG), hydrochloric acid, chloroform (99%), anhydrous ethanol (EtOH) were purchased from Aldrich and used without further purification. Ultrapure (Nanopure system) filtered water (H_2O) with a resistivity $18.2 \text{ M}\Omega \text{ cm}$ was used in all experiments.

Synthesis of gold nanorods. Gold nanorods were prepared by using a slightly modified seeded-growth method as reported in literatures¹. To prepare a seed solution, 5 mL CTAB solution (0.20 M) was mixed with HAuCl_4 solution (5.0 mL, 0.51mM). Upon vigorous stirring, 0.6 mL of 0.01 M ice-cold aqueous solution of NaBH_4 was added. The mixture turns into brownish yellow and was stirred for 2 min. The stirring was stopped and the seed solution was used by aging 5 mins at room temperature. To grow gold nanorods, 0.255mL of 4mM AgNO_3 was prepared and mixed with 5 mL of 0.2M CTAB, this solution kept at room temperature for 10min, aqueous solution of HAuCl_4 (1.8 mg in 5ml H_2O) was then added to it. After 3 min, 70 μL of 0.0788 M aqueous solution of ascorbic acid was added to the mixture and hand-stirred until it becomes colorless. The final step was the addition of 16 μL of the seed solution to the growth solution at 30 °C. After a gentle mixing, the gold nanorods start growing, and a brownish red solution is obtained within 20 mins. The mixture kept still for at least 6 hours to attain the final nanorods.

Synthesis of symmetry-breaking dimers by interfacial self-assembly

The assembly involves two processes: the control of the hydrophobation of gold nanorods² and the interfacial-preferential binding. Typically, 1ml of the previously prepared gold nanorods was centrifuged by disposal of excess CTAB and washed with a solution of water/chloroform at a 2:1 loading volume ratio by

extraction. After discarding the chloroform layer, the gold nanorod suspension was quickly added to a 3 to 5 μL MPS solution in ethanol (1mM) and the mixture was set to stir for 30 min. During the stirring, gold nanorod particles were incubated by adding 1 ml of an ODS chloroform solution (1:1000 (v/v)) and 10 μL NaOH (1M) to the mixture. Surface functionalization was achieved by hydrolysis of methoxy groups and condensation of the resulting silanetriols with surface Si-OH groups. By gentle sonication, the mixture was stirred for at least 2 hrs, a slight turbidity was observed indicating that the interface was started accumulating gold nanorods by surface hydrophobation. Dimer assembly was subsequently performed by dropwise introduction of DSCG solution with a concentration of 500 μM when the nanorods stabilized at water-chloroform interface (light red color observed at the interlayer). Because only the nanorods with patchy surface can stay at the interface, dimers were formed electrostatically at the interface by the interaction between negatively charged DSCG molecules and positively charged CTAB bilayer left on the rods³. At the same time, a shift along the longitudinal side is created due to the hydrophobation of lateral nanorod surface deprived of CTAB. After assembly, the solution near the interlayer was taken out and purified with ultrafiltration centrifugal nanosep devices containing membranes of 0.035 μm and 0.45 μm . The purification process was repeated three times in order to get rid of excess monomers and large clusters. The final product of symmetry-breaking gold nanorod dimers was washed and dispersed in aqueous solution. The structures of molecules used in the synthesis are shown in Fig. S2.

Self-gauged selective structural homogenization

200 μL as-assembled symmetry-breaking gold nanorod dimer solution was put into a quartz cuvette with an open window of 2mm and path length of 10mm. The sample irradiated by Femtosecond laser (laser pulse duration: $\tau_p \sim 100\text{fs}$) with chosen scanning range of wavelength λ (930-760nm) at low laser fluence (0.875 kWcm^{-2} average power density). The laser beam was also back-scattered with diffusing glass chips to illuminate the entire colloidal solution. Since the laser beam linewidth is the $\lambda \pm 10\text{ nm}$, each scanned wavelength was used for 1 mins at

an interval of 10nm. All of the reaction processes were monitored by UV-vis spectroscopy by sampling the reaction mixture every 4 mins. Finally, the products of homogeneous dimer structures are obtained via centrifuge process with ultrafiltration centrifugal nanosep devices as discussed.

Transmission electron microscope (TEM) and Spectroscopic Characterizations

TEM imaging was performed with a 80 kV JOEL 1200 EX and a 200 kV JEOL 2100 Transmission electron microscope (for high resolution imaging) with a Gatan Imaging System. Over 110 particles were used for the particle statistical analysis. Solution extinction spectroscopic measurements were performed with an Agilent Cary 500 spectrometer. The Shimadzu Hewlett-Packard 8453 UV-vis spectrophotometer was employed to monitor dynamic disassembly process using 10 mm path length quartz cuvettes. A dark field spectroscopy was used for the optical confirmation of the gold nanorod assembly and it was performed with an Axiovert 200 inverted microscope setup (Carl Zeiss MicroImaging Inc., Thornwood, NY) equipped with a dark field mirror block, and a dark field objective ($100\times$, NA = 0.9). The sample was illuminated by a 100 W tungsten lamp. The dark-field scattering scheme was using a pinhole to reject out of focus excitation light and acquire spectra from specific areas of the sample⁴. The scattered light was analyzed by a Triax spectrometer (HORIBA Jobin Yvon, Edison, NJ) equipped with a liquid nitrogen cooled charge-coupled device (CCD) detector. A spectrum was obtained by measuring the signals from the single particles in the air on a TEM finder grid (Ted Pella Inc), subtracting the background signals taken nearby from the single particle signals, and normalized by the intensity of incident light.

Angle-resolved light scattering experiment

The quantification of ensemble magnetic dipole is performed in our home-built Fourier microscopy with total internal reflection (TIR) excitation measuring angle-resolved scattering pattern. The measurement has been done in an

evaporated ensemble sample on a glass slide consisting of many meta-atoms. A high numerical aperture (NA) objective lens (NA = 0.9) is used for the scattering light collection. The TIR mode illumination prevents the incident laser light entering the light-collection part directly, making excellent background suppression. The collected light passes through a Bertrand lens system to form an image in the Fourier space. A polarizer is placed before the CCD for measuring polarization-dependent patterns for further verification. The ensemble magnetic dipole radiation is quantified by taking a vertical cross section at the center of the measured radiation pattern. The details of setup and measurement are discussed in the section of Discussion 1.

2. Numerical Simulation Method

The numerical full-wave calculations are carried out to calculate the extinction and scattering spectra of synthesized gold nanorod monomer and dimer structures by using a FDTD (finite-difference time domain) package (CST Microwave Studio). The simulations use average dimension of gold nanorod from experiment, and symmetry-breaking dimers of various offsets were simulated by placing two nanorods in a parallel fashion with a gap distance of 4nm. Gold material properties are described using Johnson and Cristy data⁵ at visible frequencies. The boundary conditions were kept as open in all directions. Plane wave excitation is made with an electric field parallel to the long axis of the nanorods ($|E|=1$ V/m). The full electromagnetic spectra calculated are deduced by solving Maxwell's equation $\vec{\nabla} \times \vec{\nabla} \times \vec{E} = \omega^2 \epsilon \mu \vec{E}$. The process is repeated for a series of symmetry-breaking nanorod dimers with various offsets to compile a collective spectrum.

Effective parameter retrieval

In order to calculate the effective medium properties, we obtain polarization and magnetization densities in individual meta-atom (shifted nanorod dimers) from fullwave numerical simulations. The numerical model is created based on the experimentally measured spectra with well-matched simulation (see Fig. 2d and

e). Then we start with getting the averaged polarization density $\mathbf{P}$ and magnetization density $\mathbf{M}$ using

$$\begin{aligned}\mathbf{P} &= \frac{i}{\omega V} \int \mathbf{J}(\mathbf{r}) d^3\mathbf{r}, \\ \mathbf{M} &= \frac{1}{2V} \int \mathbf{r} \times \mathbf{J}(\mathbf{r}) d^3\mathbf{r},\end{aligned}\tag{0.1}$$

where $\mathbf{J}$ is the volume current density, and ω is the angular frequency. The integration is over the volume of a shifted nanorod dimer (V). The effective permittivity and permeability of a single shifted nanorod dimer can be obtained by

$$\begin{aligned}\varepsilon_s &= \frac{3\varepsilon_0\mathbf{E}_0 + 2\mathbf{P}}{3\varepsilon_0\mathbf{E}_0 - \mathbf{P}}, \\ \mu_s &= \frac{3\mathbf{H}_0 + 2\mathbf{M}}{3\mathbf{H}_0 - \mathbf{M}},\end{aligned}\tag{0.2}$$

where $\mathbf{E}_0$ and $\mathbf{H}_0$ is the external electric and magnetic field, respectively. Note that in order to mimic the random ensemble sample, those values are averaged among the simulated results with all dimer orientations. The effective medium properties are calculated using Maxwell-Garnett formula⁶.

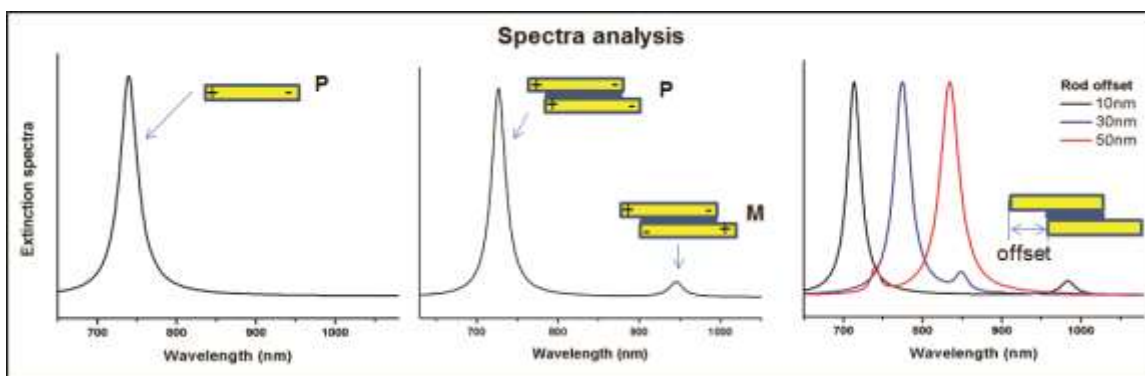


Figure S1. Breaking symmetries on gold nanorod dimers. Simulated extinction spectra indicating the degree of symmetry-breaking defines optical modes of the structure. P indicates electric dipole mode and M is magnetic mode.



Figure S2. Graphic illustration of surface molecular structures and assembly process during the synthesis of symmetry-breaking gold nanorod dimers. The surface molecules are: cetyltrimethylammonium bromide (CTAB), mercaptopropyltrimethoxysilane (MPS), octadecyltrimethoxysilane (ODS) and disodium chromoglycate (DSCG). The electrostatic interaction is between CTAB (positive charged) and DSCG (negative charged).

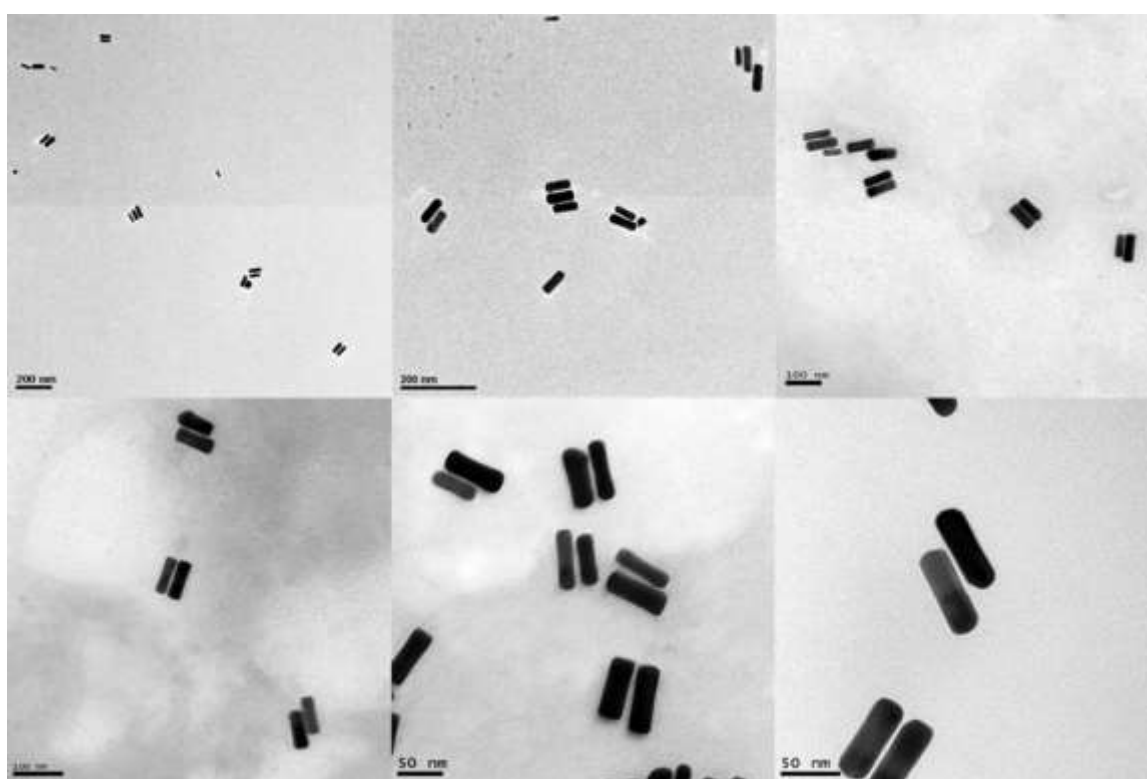


Figure S3. Typical random-taken TEM images of pure chemically assembled symmetry-breaking gold nanorod dimers at different magnifications showing dispersed gold nanorod dimers with inhomogeneous offsets.

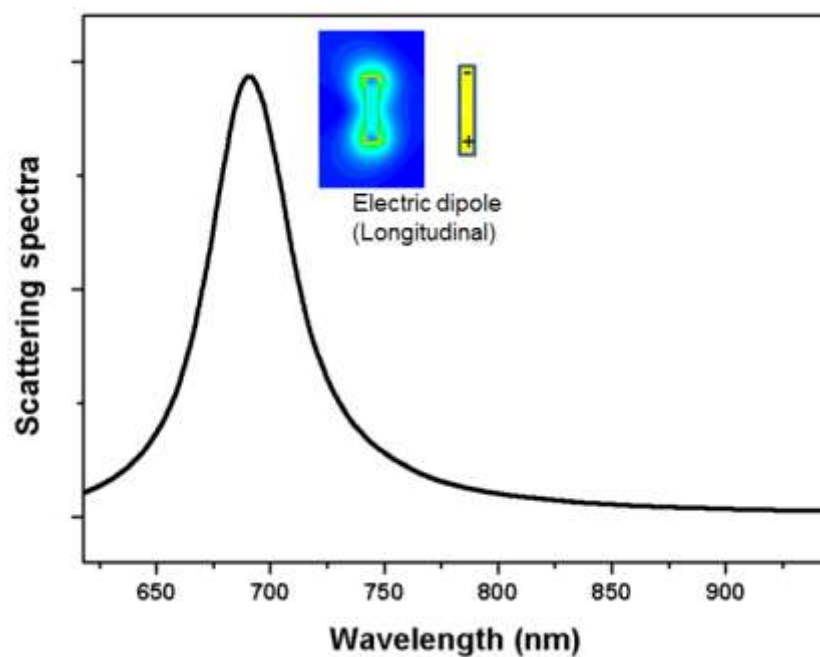


Figure S4. Far-field scattering simulations of single gold nanorod shown in Fig. 2c. The inset panels shows in plane electric field for longitudinal electric dipole.

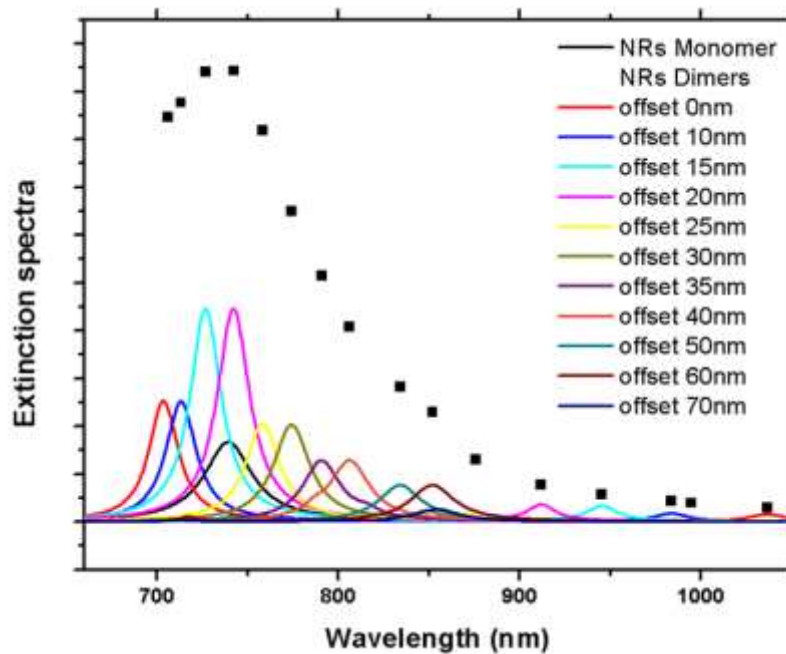


Figure S5. Simulated spectra of pure chemically assembled symmetry-breaking gold nanorod dimers. The curves in different color indicate the simulated spectra of dimers with different offsets. Each dimer population in solution was evaluated from experiment shown in Fig. 3b. The black dots reveal the collective spectra responses showing a broad and asymmetric response.

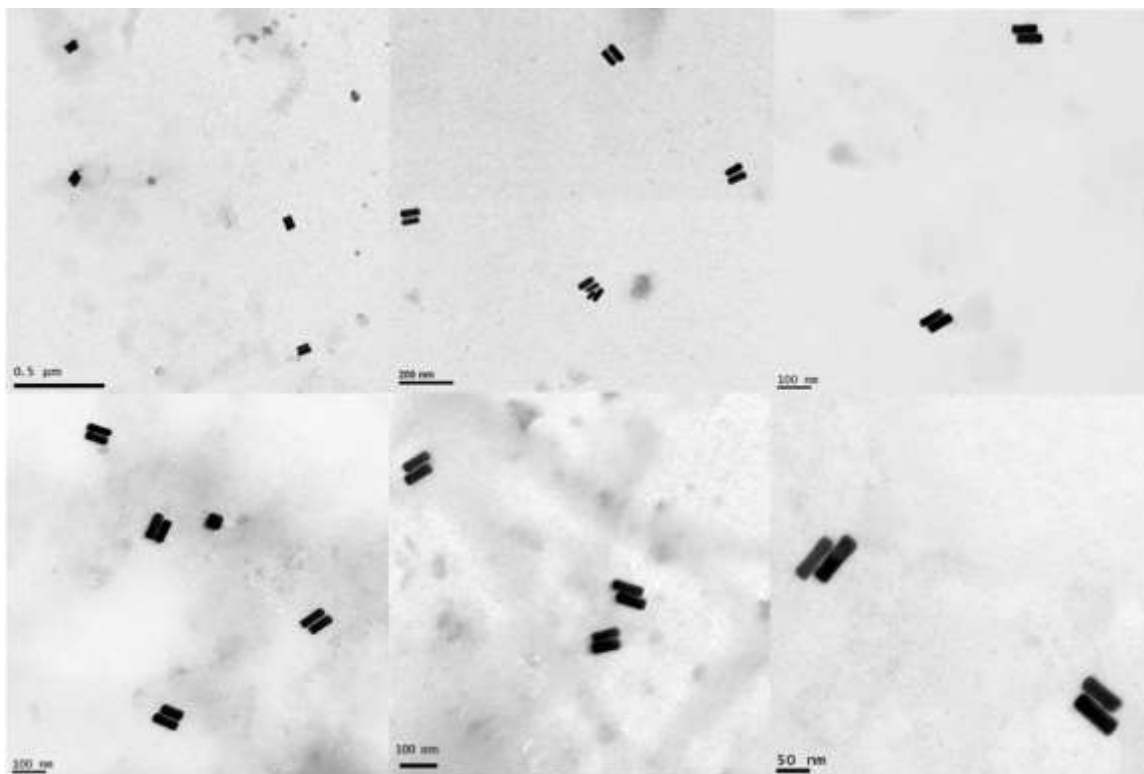


Figure S6. Typical random-taken TEM images of symmetry-breaking gold nanorod dimers after self-gauged selective assembly at different magnifications showing relative homogeneous metamaterial structures with a uniform longitudinal offset. .

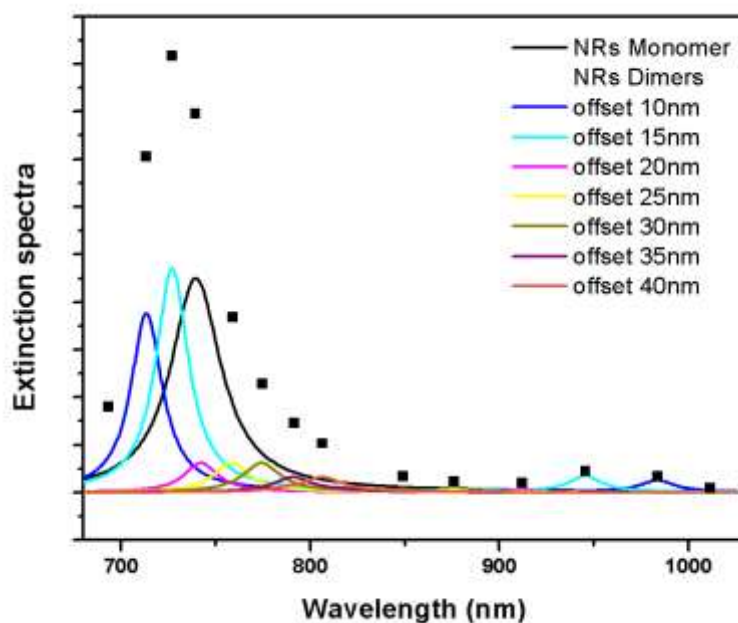


Figure S7. Simulated spectra for symmetry-breaking gold nanodimer metamaterial after self-gauged selective assembly. The curves in different color indicate the simulated spectra of dimers at the offsets and populations evaluated from experiment shown in Fig. 3d. The black dots reveal the collective spectra responses with clear evidence that the peak around 740 nm is attributed to longitudinal electric response and the peak around 960 nm is attributed a magnetic response.

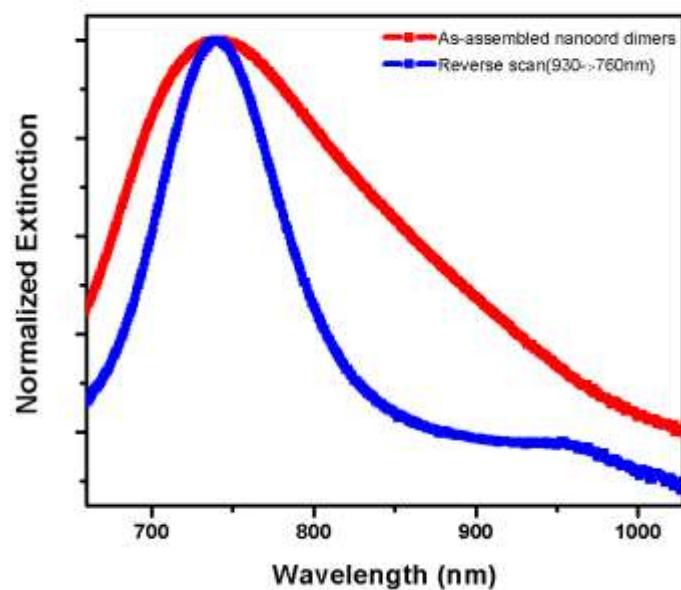


Figure S8. Extinction spectra recorded by reversing the scan windows during plasmon mediated self-selection process. As comparing to the spectrum of as-assembled dimers (red), the longitudinal electric resonance peak after self-gauged assembly narrows down and changes from asymmetric to symmetric and finally centered $\sim 740\text{nm}$. Besides, the magnetic feature emerges at wavelength $\sim 960\text{ nm}$ indicating the realization of offset homogenization (from red to blue), which is consistent with the results shown in Fig. 3e in the manuscript.

Discussion. 1 Effective metamaterials properties

To prove the emerging effective metamaterial property, we have performed the angle and polarization-resolved light scattering experiment of our synthesized symmetry-breaking metamaterial ensembles [7]. As known, the radiation pattern of a magnetic dipole is characterized by $\cos^2\theta$ distribution, where θ is the angle between the dipole axis and the observation direction. However, any random distributed anisotropic/symmetry-breaking structures will have a random dipole axis regardless of the excitation polarization.

Although this orientation factor has bare influence on dipole resonance, the contrast of electric and magnetic dipole radiation would smear out in angular radiation measurement because separating the orientation factor is very difficult and the excitation power was not held constant at each incident angle. To solve this problem and make a better contrast of the magnetic property, we employed Fourier microscopy with total internal reflection (TIR) excitation measuring angle-resolved scattering pattern of symmetry-breaking metamaterials ensemble on glass substrate. The advantage of this setup is that it has a constant excitation power of illumination and gives full information of the scattering pattern [8,9].

Our home-built experimental setup is schematically sketched in Fig. S9. The ensemble sample is illuminated by a tunable laser in TIR mode. The TIR mode illumination prevents the incident laser light entering the light-collection part directly, making excellent background suppression. A high numerical aperture (NA) objective lens ($NA = 0.9$) is used for the scattering light collection. The collected light passes through a Bertrand lens system to form an image in the Fourier space. A polarizer is placed before the CCD for measuring polarization-dependent patterns for further verification. From the angular radiation pattern, we can quantify the magnetic dipole radiation of our colloidal symmetry-breaking metamaterials by taking a vertical cross section at the center of the measured radiation pattern. Due to random orientations of the dimers, it is natural to have both electric and magnetic dipole radiation even excited at the wavelength of the magnetic dipole resonance. It is reasonable to believe that the measured radiation consists of both electric and magnetic dipole radiations and the corresponded azimuth angular radiation curves of an electric dipole and a magnetic dipole on a glass substrate are

shown in Figure. 4a. We can see that the result matches reasonably well with experimental data. The slightly discrepancy comes from the measurement errors, including background noise and limited times of measurements. As shown, the direct evidence of magnetic dipole scattering from our assembled metamaterials is approximately 78% of the total radiated intensity.

By extracting the averaged polarization and magnetization density [6,10], we have successfully obtained the effective properties of our assembled aqueous symmetry-breaking metamaterials such as relative permeability and refractive index as shown in Figure. S10. As seen, the optical properties of the metamaterials are highly tunable as change of permeability and refractive index with fill fractions. For the filling fraction of 0.5 as shown, the refractive index approaches -0.8 at the magnetic dipole resonance. Further increasing fill fraction could reach a negative refractive index of -1 which is important for the applications such as perfect lens [11].

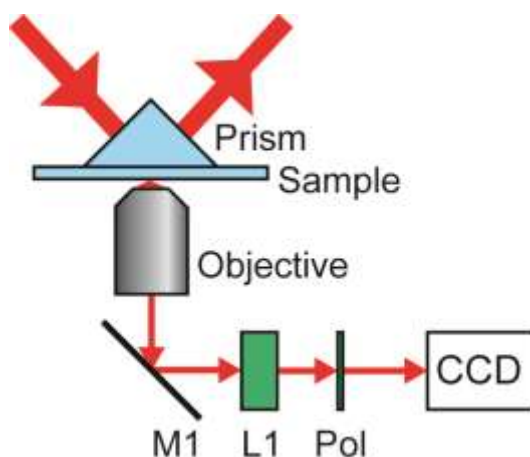


Figure S9. Experimental setup and measurement for the dipole scattering pattern.

Schematic diagram of our experimental setup is shown on the left. The measurement has been done in an evaporated ensemble sample on a glass slide consisting of many meta-atoms. A polarized laser (average power density 0.1 kW/cm^2) is illuminated to a total internal reflection mode (TIR) which prevents the laser light entering the light-collection

part directly. Scattering light was collected by a high numerical aperture objective lens (100x, NA = 0.9). The collected light passes through a Bertrand lens system to form an image in the Fourier space. M1 and L1 are reflecting mirror and Fourier lens ($f = 200\text{mm}$) respectively. A polarizer (pol) is placed before a CCD camera for polarization-dependent measurements.

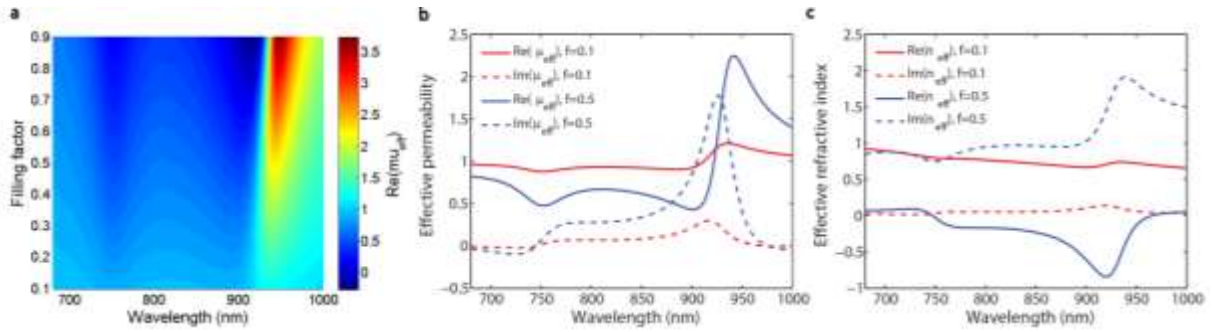


Figure. S10. Calculated effective medium properties of our self-assembled symmetry-breaking metamaterials. (a) The effective permeability (μ_{eff}) plotted as a function of fill factor and wavelength. (b) The real and imaginary components of the effective permeability at two different fill factors (blue line fill factor = 0.5, red line fill factor = 0.1). (c) The real and imaginary components of the effective refractive index at two different fill factors (blue line fill factor = 0.5, red line fill factor = 0.1).

Discussion 2. Control over the level of symmetry-breaking

To further demonstrate our concept and control over the level of symmetry breaking, we have extended our synthesis of dimers colloidal metamaterials with another uniform offset of $\sim 20\text{-}30$ nm which exhibits isotropic ensemble magnetic dipole resonance around 870 nm. Our experimental results are shown below.

The self-gauged synthesis of symmetry-breaking dimer metamaterials with controllable offsets is shown in Fig. S11. Comparing the sample that has a pronounced offset between $\sim 10\text{-}20$ nm with a longitudinal electric resonance and a magnetic resonance at $\lambda_{\text{max}} \sim 740$ nm and ~ 960 nm respectively (Fig. 3), we have extended our synthesis of shifted gold dimers with a longer offset pronounced between $\sim 20\text{-}30$ nm by our plasmon mediated self-gauged assembly with scanning wavelength range from 810 nm to 930 nm (Fig. S11). Typical random taken TEM images of sample 2 at different magnifications are also provided to illustrate the offset and structural uniformity (Fig. S12). Furthermore, we again demonstrated our uniquely developed method could overcome inhomogeneous broadening, which leads to appreciable optical magnetic functionality of our assembled metamaterials. The ensemble longitudinal electric resonance and magnetic resonance at $\lambda_{\text{max}} \sim 760$ nm and ~ 870 nm are clearly observed in sample 2 (Fig. S11c). The results are well matched with simulated ones (details in Fig. S13) indicating a good structural uniformity after our unique self-gauged assembly. As indicated, the differences in structural offsets in two samples differentiate the resonance frequencies in the measured spectra. This phenomenon is due to the level of symmetry-breaking.

Therefore, by utilizing our concept, we have demonstrated the capability of our method to precisely control over the level of symmetry breaking in the colloiddally-synthesized metamaterials.

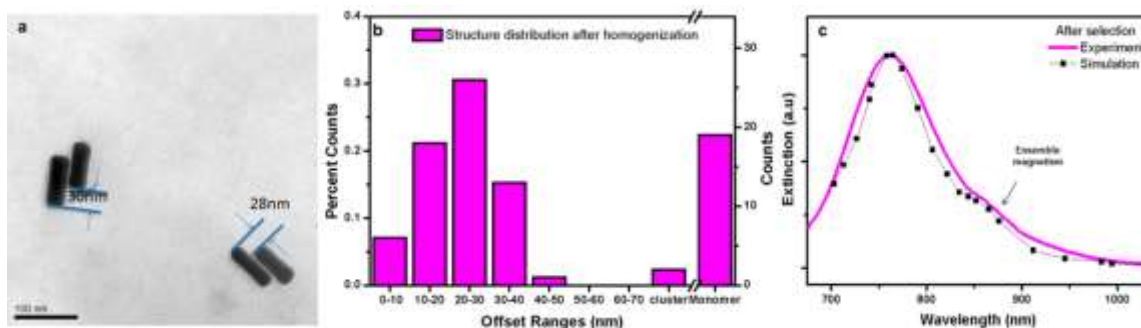


Figure S11. Control over the level of symmetry-breaking in gold nanorod dimer metamaterials by our self-gauged selective assembly. (a)-(c) TEM image, structural distribution and ensemble extinction spectra of synthesized symmetry-breaking dimer metamaterials (sample 2) with controlled longitudinal offset of ~ 20 -30 nm. A clear magnetic response emerges at about 870 nm after plasmon selection well matched with simulation.

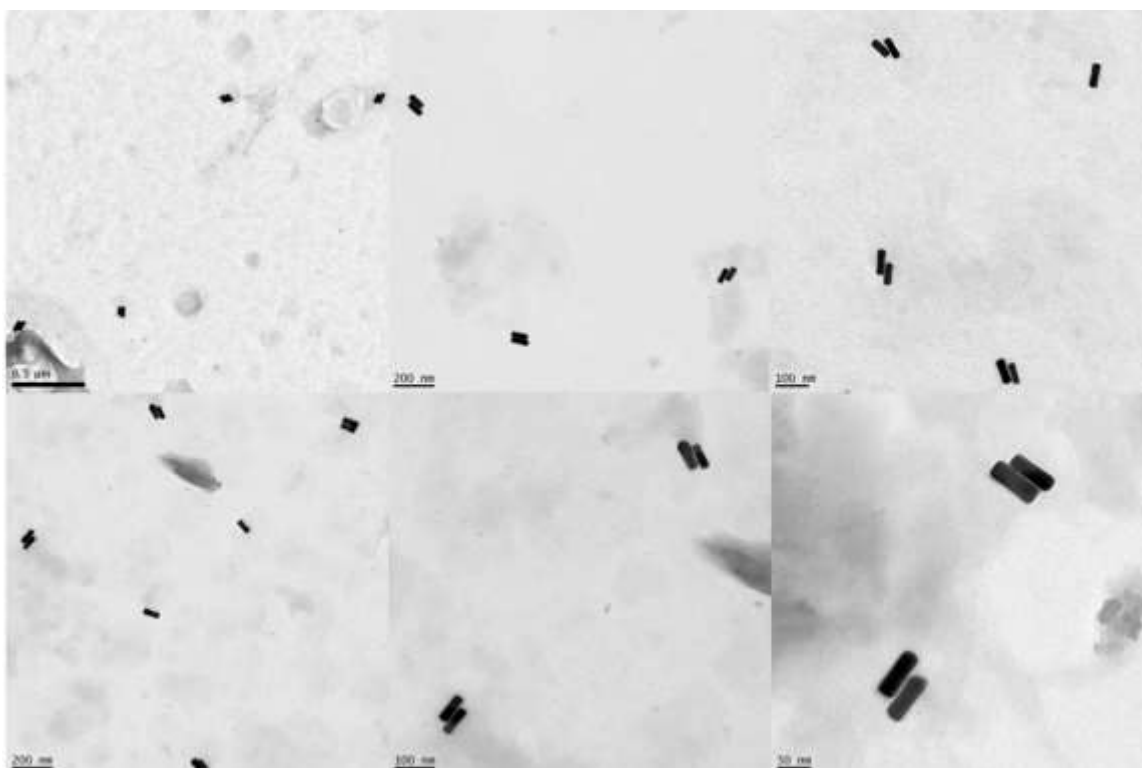


Figure S12. Typical TEM images with different magnifications taken at random places on a TEM grid showing a different level of offset (symmetry-breaking) after self-gauged assembly in sample 2 with offsets pronounced at 20-30 nm.

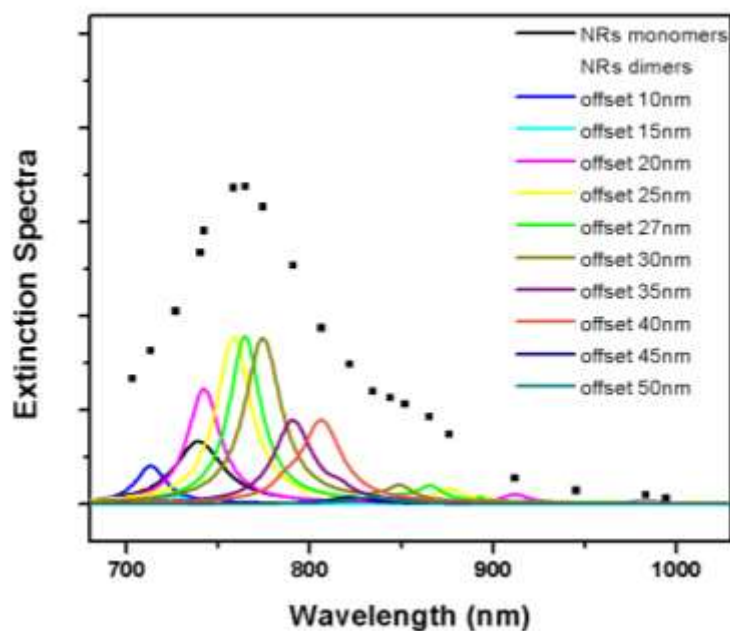


Figure S13. Simulated spectra for symmetry-breaking metamaterials (sample 2) after self-gauged selective structural reconfiguration mediated by plasmon. The color curves indicate the simulated spectra of dimers at different offsets and populations evaluated from experiment shown in Fig. S11. The black dots reveal the collective spectra responses with clear evidence that the peak around 760 nm is attributed to longitudinal electric response and the peak around 870 nm is attributed a magnetic response.

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