Supporting Information

Porosity-Controllable Magnetoplasmonic Nanoparticles and Their

Assembled Arrays

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Figure S1. (a) Wide-angle XRD diffraction patterns of Ag@Fe₃O₄ core/shell NPs and hollow Fe₃O₄ NPs after removing Ag core. (b) Magnified XRD spectra of different Ag@Fe₃O₄ samples. (c) Absorption spectra of supernatant solutions after complete etching and separating NPs and (d) dependence of absorbance of Fe³⁺ ions (at 256 nm) and particle size on OA concentration.



Figure S2. SEM images and size distribution histogram of Ag@Fe₃O₄ NPs before (a, e)

and after being etched with high concentration of oxalic acid (0.25 M) for different periods: (b, f) 5 min, (c, g) 10 min, (d, h) 12 min.

Surface	Organic materials	E _{total} (kcal·mol ⁻¹)	E _{Fe3O4} (kcal⋅mol⁻¹)	E _{organism} (kcal·mol ⁻¹)	E _{interaction} (kcal·mol ⁻¹)
(311)	OA-1	-32274.2	-32434.1	261.9129	-102.041
(311)	OA-5	-31664.4	-32434.1	856.9192	-87.246
(311)	OA-10	-30913.1	-32434.1	1578.66	-57.741
(311)	OA-15	-29931.8	-32434.1	2536.645	-34.3562
(311)	OA-20	-27973.8	-32434.1	3408.372	1051.852

Table S1. Calculated results of the molecular dynamics simulation for various number of oxalic molecule on Fe_3O_4 surface.



Figure S3. Cyclic voltammetry of 10 mM $[Fe(CN)^6]^{4-/3-}$ in 0.1 mM KCl of GCE modified with Ag@Fe₃O₄ samples.



Figure S4. TEM image of york-shell (partially etched) (a) and hollow (completely etched) (b) Ag@Fe₃O₄ NPs and extinction spectra of Ag@Fe₃O₄ NPs after treating with saturated NaCl for different periods of time (c). Inset shows photographs of colloidal solution of Ag@Fe₃O₄ NPs before and after 8-hour treatment.



Figure S5. Time-dependent UV-Vis absorption spectra for the reduction of 4NPol by NaBH₄ in the presence of the pristine (a) and Ag@Fe₃O₄ NPs etched with (b) 5 mM, (c) 10 mM, (d) 15 mM OA.



Figure S6. Raman spectra of pristine and etched Ag@Fe₃O₄ NPs. Six strong SERS peaks are attributed to the following modes: $v(C-H \text{ in-plane}) = 1283 \text{ cm}^{-1}$; v(aromatic C-H) = 1662, 1517, 1362, and 1194 cm⁻¹; and $v(C-H) = 1538 \text{ cm}^{-1}$.

Sample	OA-0	OA-5	OA-10
0D	170	167	167
2D	125	127	134

Table S2. Full width at half-maximum of different porous 0D and 2D samples.



Figure S7. Simulated extinction spectra of hexagonal arrays containing 7 and 19 particles $(n_{\text{shell}} = 2.125)$ (a) and electric field distributions corresponding to peaks and dips in the extinction spectra (b). The arrows represent the electric dipolar modes.

Computational simulations of finite-sized arrays containing 7 and 19 particles ($n_{\text{shell}} = 2.125$) were performed. In the 7-particle array, despite the curve shape fits quite well with the experimental one where a main LSPR peak exists at around 600 nm, the peak is red-shifted (585 nm \rightarrow 600 nm) compared to that of the single particle (Figure S7a). On the other hand, the 19-particle array shows additional peaks and dips in the long-wavelength range of the spectra, in which the main peak (highest intensity) is blue-shifted compared to that of the single particle (S7a). These features are attributed to the Fano resonances that are originated from the interference between narrow band plasmonic oscillation of the Ag core and broad band scattering of the Fe₃O₄ shell as well as from interference between dark subradiant mode of the center particle and bright superradiant mode caused by the collective near-field coupling of surrounding particles.^[2] In order to elucidate the character of the resonances, electric field distributions at the respective peak and dip positions are simulated (Figure S7b). At the spectral peaks (i), (ii), and (iii) in Figure S7, the electric dipole oscillations in the individual particles are originated in the same

direction (in-phase oscillation), manifesting the excitation of the collective dipolar plasmon resonance. Notice remarkable field enhancement at the particle junctions of the peak positions (i) and (iii), indicating the dominance of the near-field dipolar coupling that induces the red-shifts. Meanwhile, negligible electric field enhancement at the particle junctions of the peak position (ii) was observed, revealing that the blue-shift is caused by the far-field coupling. These calculated results indicate that a transition occurs from near-field to far-field dipolar interaction as increasing the number of particle in the 2D arrays.^[3] Accordingly, lower intensity peaks at 640 and 730 nm in the 19-particle array ($n_{\text{shell}} = 2.125$) are assigned to collective near-field coupling that exhibits large red-shifts compared to the single particle while higher intensity peak at 590 nm in the same sample shows a blue-shift compared to the single particle that is corresponding to the experimental data. This blue shift has the same characteristics as that observed for periodic nanoparticle arrays.^[3,4]

The 19-particle array in our computational model (Figure S7) produces complex extinction spectra of Fano resonances that interfere among the center particle, the inner ring of heptamer, and additional outer ring.^[5,6] The oscillation mode of the center particle hybridizes with that of surrounding particles, which generates in-phase or out-of-phase collective modes. Indeed, at the spectral dips (v) and (vi), the electric dipole oscillations in the individual particles are oriented in different directions (out-of-phase oscillation), resulting in the destructive interference of their radiated fields (Figure S7b).^[7] Meanwhile, the resonant electric field enhancement greatly suppressed due to the destructive interaction at the dip position (iv), which is caused by the interference between dielectric shell scattering and plasmon modes of Ag cores.^[2]



Figure S8. Simulated plots of λ_{max} for 1D (a) and 2D (b) arrays (19 particles) as a function of n_{shell} .



Figure S9. Distribution of electric field intensity of Ag dimer ($r_{core}=30$ nm) particle couples without (*ai*) and with (*aii*) Fe₃O₄ shell, and with different n_{shell} (b).



Figure S10. Photographs of the 2D film before and after Pt sputtering (a). Photographs (b) and reflectance spectra (c) of the 2D film at different view angles. SEM images and photographs (inset) of 1D array before and after 4 nm Au NPs deposition (d). Pt coating was performed using magnetron sputtering with the base pressure less than 5×10^{-7} Torr and the deposition of films were performed in 7 mTorr of Ar for 30 s. The deposition of Au NPs on the 2D array was performed via layer-by-layer (LBL) process. Procedures for synthesizing negatively charged 4 nm Au^[8] and positively charged 30 nm Au NPs^[9] were reported elsewhere.



Figure S11. Extinction spectra of the 2D film before and after 30 nm Au NPs deposition.



Figure S12. Reflectance spectra of the 2D film composed of core-shell, york-shell (partially etching Ag core) and hollow (completely removing Ag core) particles: 60 nm (a) and 70 nm (b) shell thickness.



Figure S13. SEM images (a-b) and reflectance spectra (c) of the 2D films of Ag@Fe₃O₄ (a) and Ag@Fe₃O₄@SiO₂ (b) NPs. For SiO₂ coating (~14 nm), a 6 mL aqueous solution of Fe₃O₄ NPs (concentration of 25 mg/mL) is added into 40 ml ethanol followed by the addition of 2 ml ammonia (28%). The mixture was sonicated for 10 minutes. 350 μ l of tetraethyl orthosilicate (TEOS) is injected to the mixture under mechanical stirring (sonication also fine). After 4 h, the Fe₃O₄@SiO₂ core–shell NPs are collected by magnet, washed with ethanol at least 5 times, and finally dried in vacuum oven at 60 °C for 6h.

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