3D Halos Assembled from Fe₃O₄/Au NPs with Enhanced Catalytic and Optical Properties

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Experimental Section

Chemicals

The following chemicals were used as obtained: iron(III) chloride (FeCl₃·6H₂O, 98%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), diethylene glycol (DEG, 99%, Sigma-Aldrich), octyl ether (99%, TCI), sodium oleate (97%, Sigma-Aldrich), hydroxylammonium chloride (99%, Sigma-Aldrich), gold (III) chloride trihydrate (HAuCl₄·3H₂O, >49%, Sigma-Aldrich), sodium borohydride (NaBH₄, 98%, Sigma-Aldrich), cetyltrimethylammonium bromide (95%, Sigma-Aldrich), cetyltrimethylammonium bromide (99%, Sigma-Aldrich), cetyltrimethylammonium bromide (100.4%, molecular biology grade, CalBioChem), polyvinylpyrrolidone (PVP, MW = 55,000, 99.9%, Sigma-Aldrich), hexane (99.9%, Sigma-Aldrich), hexane (99.9%, Sigma-Aldrich), methanol (absolute for analysis, 99%, Sigma-Aldrich), acetone and ethanol (absolute for analysis, ACS, 99.9%, Merck). All materials were used without further purification.

Synthesis of iron-oleate complex: In a typical synthesis of the iron-oleate complex, 10.8 g of iron chloride (FeCl₃·6H₂O, 98%, Sigma-Aldrich) and 36.5 g of sodium oleate were dissolved in a mixed solvent composed of 40 mL ethanol, 40 mL deionized water and 80 mL hexane. The resulting solution was heated to 60 °C and kept at that temperature for four hours. The dark red-black iron oleate precursors were dissolved in 100 mL hexane, washed 3 times with warm DI water (~50 °C) and then separated in a separatory funnel. After washing, hexane was removed by evaporation, resulting in an iron-oleate complex in a waxy solid form.

Synthesis of iron oxide nanoparticles (NPs):¹ The following represents a typical synthesis of monodisperse 7 nm iron oxide NPs. Iron-oleate complex (4.8 g) synthesized as described above and 0.76 g oleic acid (90%, Sigma-Aldrich) were dissolved in 6 g octyl ether at room temperature. The mixture was heated to 110 °C and maintained for 60 min under Ar protection. The reaction mixture was heated to 295 °C with a constant heating rate of 3 °C min⁻¹ and then held 30 min. When the reaction temperature reached 295 °C, an obvious reaction occurred, and the initial transparent solution became turbid and brownish black. The colloidal solution was washed 5 times using isopropyl alcohol/hexane (1:1 v/v) by sedimentation and re-dispersed using centrifugation (5000 rpm for 10 min). Finally, the Fe₃O₄ NPs were

weighed and re-dispersed in hexane at the desired nanoparticle concentration.

Synthesis of Au NPs (~15 nm): Typically, an aqueous solution of HAuCl₄ (1 mM, 500 mL) was heated to reflux while stirring, and then 50 mL of a 38.8 mM trisodium citrate solution were added quickly, resulting in a color change from pale yellow to deep red. After the color change, the solution was refluxed for an additional 15 min and then cooled to room temperature.

Synthesis of Au NPs (~40 nm): Typically, Au seeds were synthesized by adding 0.6 mL ice-cold NaBH₄ aqueous solution (10 mM) to a 7.8 mL aqueous solution containing HAuCl₄ (0.25 mM) and CTAB (100 mM, 99%, Sigma-Aldrich), producing a brownish solution. The seed solution was kept undisturbed for 1 h at 37 °C to ensure complete decomposition of NaBH₄. Then, 0.8 mL HAuCl₄ (10 mM), 6.4 mL CTAB (100 mM, 99%, Sigma-Aldrich) and 31.2 mL H₂O were mixed uniformly to form the growth solution. Then a 3.8 mL ascorbic acid (AA, 100 mM) aqueous solution was added, and the growth solution turned colorless. Next, a 0.02 mL seed solution was diluted to 0.2 mL with water and added to the growth solution. The resulting solution was mixed by gentle inversion for 10 s and then left undisturbed overnight (20 h) at 27 °C.

Synthesis of Au NPs (~90 nm):² Typically, a vigorously stirred 0.1 mg/mL HAuCl₄ solution was heated to boiling. This was followed by rapid addition of sodium citrate (0.1 mg/mL), accompanied by a color change from pale yellow to red. The solution containing Au seeds was boiled for 15 min and then stirred at room temperature for another 15 min. A typical synthesis for 90 nm Au NPs was carried out as follows. Eight mL preformed Au seeds were added to 17 mL water, followed by quick addition of 40 μ L 40 mg/ml HAuCl₄. The mixture was vigorously stirred at room temperature. Then, 70 μ L of hydroxylamine hydrochloride (66.2 mM) were added to the mixture, and the reaction was completed within 15 min. The resulting gold colloids were stored at 4 °C in the dark.

Synthesis of Au nanorods (Au NRs):³ Au NRs were synthesized by a two-step seed-mediated growth method. First, according to the previous method, the seed solution was synthesized by adding HAuCl₄ (0.01 M, 0.25 mL) to the solution of CTAB (0.1 M, 10 mL). A freshly prepared, ice-cold NaBH₄ solution (0.01 M, 0.6 mL) was then added to the mixture and stirred for 2 h. Then, to grow Au NRs, HAuCl₄ (0.01 M, 4 mL) was incubated with AgNO₃ (0.01 M, 0.8 mL), CTAB solution (0.1 M, 80 mL), and HCl (1.0

M, 1.6 mL), followed by the addition of ascorbic acid (0.1 M, 0.64 mL). Finally, the seed solution (192 μ L) was injected into the growth solution, gently mixed for 30s, and left undisturbed at 27 ~ 30 °C for 6 h to obtain the desired Au NRs.

Synthesis of multi-shaped Au NP mixtures (~40 nm): Typically, Au seeds were synthesized by adding 0.6 mL ice-cold NaBH₄ aqueous solution (10 mM) to a 7.8 mL aqueous solution containing HAuCl₄ (0.25 mM) and CTAB (100 mM) (100.4%, molecular biology grade, CalBioChem), producing a brownish solution. The seed solution was kept undisturbed for 1 h at 25 °C to ensure complete decomposition of NaBH₄ remaining in the solution. The growth solution containing 0.8 mL HAuCl₄ (10 mM), 6.4 mL CTAB (100 mM) (100.4%, molecular biology grade, CalBioChem) and 31.2 mL H₂O was mixed uniformly. Then a 3.8 mL ascorbic acid (AA) aqueous solution (100 mM) was added, and the growth solution turned colorless. Next, a 0.02 mL seed solution was diluted to 0.2 mL with water and also added to the growth solution. The resulting mixture was mixed by gentle inversion for 10 s and then left undisturbed overnight (19h).

Materials Characterization

Morphology of the samples was characterized with a transmission electron microscope (TEM) system (JEOL Model JEM-2010F) operating at 200 kV. UV-Vis measurements were performed with a Cary Bio-100 UV/Vis spectrometer (Varian) for Au nanoparticles. Magnetic studies of two compounds were performed on the Quantum Design MPMS-XL SQUID magnetometer. The hysteresis measurements were carried out at 10 K with applied magnetic fields varying up to 7 T.

We analyze the self-assembled mechanism from energy or entropy aspects.

As we know, entropy-driven self-assembly minimizes the system free energy (Helmholtz free energy, F), expressed in terms of energetic (U) and entropic (S) components as⁴

$$F = U - TS. \tag{1-1}$$

The free energy change ΔF upon self-assembly provides the driving force for ordering and results from corresponding changes in the system internal energy and entropy,

$$\Delta F = \Delta U - T \Delta S. \tag{1-2}$$

Usually, the internal energy change of the assembling system is broken down approximately into core (e.g., building block) and ligand contributions,⁵

$$\Delta U \approx \delta U_{cores} + \delta U_{ligands},\tag{1-3}$$

and the entropy follows:

In

$$\Delta S \approx \delta S_{cores} + \delta S_{ligands}.$$
 (1-4)

Energetic interactions between core (i.e., building block (Fe₃O₄ NPs)) are described by the set of van der Waals interactions,⁶

$$\delta U_{cores} \approx \delta U_{vdW} \approx \delta U_{London} + \delta U_{Keesom} + \delta U_{Debye}.$$
(1-5)

 δU_{London} : London dispersion attraction; δU_{Keesom} : dipole-induced dipole interactions; δU_{Debye} : dipoledipole interactions. Here, London dispersion force is the weakest intermolecular force. For hard core-NPs, $\delta U_{London} \approx 0$. This elastic resistance to chain (ligands) deformation balances the attractive London dispersion interaction between aliphatic chains (e.g., oleic acid (OA)): ⁷

$$\delta U_{ligands} \approx \delta U_{elastic} + \delta U_{London} \approx \delta U_{elastic} + 0 \approx \delta U_{elastic}.$$
 (1-6)

Meanwhile, the core (building block (NPs)) entropy has configurational, translational, and rotational terms,⁸

$$\delta S_{cores} \approx \delta S_{conf} + \delta S_{trans} + \delta S_{rot}.$$
(1-7)

In our assembly system, the NP is a hard (building block) core, so the configurational, translational, and rotational rearrangement of the NPs in the system would ignore local $e \square$ ects, i.e.

$$\delta S_{cores} \approx \delta S_{conf} + \delta S_{trans} + \delta S_{rot} \approx 0 \tag{1-7}$$

Here, we used (1-3), (1-4), (1-5), (1-6) and (1-7) into (1-2):

$$\Delta F = \Delta U - T\Delta S \approx (\delta U_{cores} + \delta U_{ligands}) - T(\delta S_{cores} + \delta S_{ligands}),$$

$$\approx (\delta U_{vdW} + (\delta U_{elastic} + \delta U_{London})) - T(0 + \delta S_{ligands})$$

$$\approx \delta U_{vdW} + (\delta U_{elastic} + \delta U_{London}) - T\delta S_{ligands} \approx \delta U_{vdW} + \delta U_{ligands} - T\delta S_{ligands}$$
(1-8)

sum,
$$\Delta F \approx \delta U_{vdW} + \Delta F_{ligands}$$
 (1-8)

$$\Delta F_{ligands} \approx \delta U_{ligands} - T\delta S_{ligands} \approx \delta U_{elastic} + 0 - T\delta S_{ligands} \approx \delta U_{elastic} - T\delta S_{ligands}$$
(1-9)

Therefore, there is a balance of the elastic repulsive force ($\Delta F_{ligands} \approx \delta U_{elastic}$ - $T\delta S_{ligands}$) contributed by the ligands (OA) and van der Waals attractive forces (δU_{vdW}) and hydrophobic attraction of the hydrophobic groups in the formation of 3D halos. ^{9,10,11} Calculation of the number of Fe₃O₄ NPs (N_{particles})



For one Fe₃O₄ NP, the radius is *r*. The density, mass and volume are ρ , m_1 and V_1 . The mass of one Fe₃O₄ NP (m_1) was calculated as

$$m_1 = \rho \bullet V_1 \tag{1}$$

$$V_1 = \frac{4}{3}\pi r^3$$
 (2)

$$m_1 = \rho \bullet V_1 = \rho \bullet \frac{4}{3}\pi r^3 \tag{3}$$

The number of Fe₃O₄ NPs (N_{particles}) was calculated as

$$N_{particles} = \frac{m_{Total}}{m_1} = \frac{m_{Total}}{\rho \bullet V_1} = \frac{m_{Total}}{\rho \bullet \frac{4}{3}\pi r^3}$$
(4)

where ρ =5.17 g/cm³, d=2*r*=7±0.5 nm, and m_{Total} is the total mass that was weighed in the experiment: m_{Total} =5 mg and $N_{particles}$ =5.387 x 10¹⁵ in 5 mg total mass.

Calculation of the number of OA molecules (N_{OA})

For OA molecules, N_A is Avogadro constant ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$), *n* is the number of mole, M_{OA} is the molecular weight, and m is total mass. The number of OA molecules (N_{OA}) was calculated as

$$N_{OA} = n \bullet N_A \tag{1}$$

$$n = \frac{m}{M_{OA}} \tag{2}$$

$$m = \rho \bullet V \tag{3}$$

The number of OA molecules (N_{OA}) was calculated as

$$N_{OA} = n \bullet N_A = \frac{m}{M_{OA}} \bullet N_A = \frac{\rho \bullet V}{M_{OA}} \bullet N_A$$
(4)

where ρ =0.887 g/cm³, M_{OA} = 282.46 g/mol, and the oleic acid content of the purchased material was 90% (OA, 90%, Sigma-Aldrich),

 $V_{OA} = 10 \ \mu L, N_{OA} = 1.702 \ \text{x} \ 10^{19}.$ $V_{OA} = 30 \ \mu L, N_{OA} = 5.106 \ \text{x} \ 10^{19}.$

*V*_{*OA*}= 40 μL, *N*_{*OA*}=6.808 x 10¹⁹.

Calculation of the number of OA molecules stabilized on the surface of one Fe₃O₄ NP (N_{θ})

$$N_0 = \frac{N_{OA}}{N_{particles}}$$

 $V_{OA} = 10 \ \mu L, N_0 = 3.159 \ x \ 10^3.$

 $V_{0A} = 30 \ \mu L, N_0 = 9.478 \ x \ 10^3.$

 $V_{0A} = 40 \ \mu L, N_0 = 1.264 \mathrm{x} \ 10^4.$



Figure S1 TEM images of (a) Fe₃O₄ NPs and (b) Fe₃O₄ NP micelles.

Note: Hydrophobic van der Waals interactions between the hydrocarbon chains of the ligands (oleic acid) and the hydrocarbon chains of the surfactant (CTAB) caused these NP micelles to disperse in aqueous solution.^{12, 13}



Figure S2 Scheme for the formation of micelles: a) OA-ligated NPs; b) NP micelles.

Note: These micelles were synthesized as follows: An aqueous solution of CTAB was added to OA-stabilized Fe_3O_4 NPs (OA-Fe₃O₄, **Figure S2a**) in hexane and then heated to create a water-in-oil microemulsion to from NP micelles (**Figure S2b**).



Figure S3 TEM images of the assembled products at different assembly temperatures: a) 65 °C and b) 100 °C.



Figure S4 TEM images of the assembled products at different assembly time: a) 10 min, b) 30 min, c) 1h and d) 1.5h.



Figure S5 TEM images of Au NPs: a) Au NPs (~15 nm); b) Au NPs (~40 nm); c) Au NPs (~90 nm); d) Au nanorods (length of ~ 70 nm); and e) Au NP mixture (~40 nm); f) UV/Vis spectra of Au NPs.



Figure S6 UV/Vis spectra and photographs (inset) of the catalytic properties of 3D halos with Au NRs using TMB as the substrate in the presence of H_2O_2 (pH 4.5, 25 °C).



Figure S7 The initial velocity of the reaction was measured using Fe_3O_4 NPs and 3D halos: a) concentration of TMB was 800 μ M, and H_2O_2 concentration was varied; b) concentration of H_2O_2 was 530 μ M, and TMB concentration was varied; c) and d) show double reciprocal plots with the concentration of one substrate (H_2O_2 or TMB) fixed and the other varied. Experimental conditions: 0.2 M sodium acetate (NaAc) buffer, pH 4.5, 30 °C.



Figure S8 The UV-vis spectra of 3D halos.

Table S1. The peak positions of UV and local surface plasmon resonance (SPR) of the 3D halos

3D Halos	UV Peak position (nm)	SPR Peak position (nm)
3D Halos (Au NPs~15 nm)	570~590 nm	570~590 nm
3D Halos (Au NPs~40 nm)	526 nm	526 nm
3D Halos (Au NPs mixture)	525 nm	525 nm
3D Halos (Au NRs)	530 nm	530 nm
3D Halos (Au NPs~100 nm)	560 nm	560 nm

Note: The 3D halos (Au NPs ~15 nm) show a broad SPR peak because there are about 43 Au NPs on the surface of each 3D halos. 3D Halos (Au NPs ~40 nm), 3D Halos (Au NPs mixture) and 3D Halos (Au NRs) show SPR peaks are about 530 nm. 3D Halos (Au NPs ~100 nm) show SPR peak are about 560 nm.

Optical properties of 3D Fe₃O₄-Au NPs halo structures

Herein, we further investigated the electric field distributions of the 3D halo structures with different dimensions [e.g. dimeter of Fe₃O₄ NP (d_{Fe₃O₄)/ dimeter of Au NP (d_{Au})=500/40 nm and 300/100 nm] at} different wavelengths in water. At first, we fixed the dimensions of Fe₃O₄ NP of 500 nm and varied the diameter of Au NP to 40 nm. As displayed in Figure S9, this 3D halo structure performs high electric field intensities in the visible regime while low electric field intensities in NIR regime. Furthermore, the maximum electric field intensity of 3D halo structure with $d_{Fe_3O_4}/d_{Au}$ of 500/40 nm is lower than that of structure with $d_{Fe_3O_4}/d_{Au}$ of 500/100 nm at each wavelength. We attribute these results to the larger dimensions of Au NP featuring higher extinction efficiency and longer resonant wavelength. Next, we studied the optical properties of the 3D halos structure having dFe₃O₄ and d_{Au} of 300 nm and 100 nm, respectively. We found this 3D halo structure provided high electric field intensities from the visible to the NIR regions (Figure S10). Furthermore, this structure performs much higher electric field intensities than the structure with dFe₃O₄/d_{Au} of 500/100 nm in NIR regime. Accordingly, the optical properties of the 3D halo structures could be manipulated readily by varying the dimension and shape of Fe₃O₄ and Au NPs, especially in NIR regime. Because the 3D halo structures provide high electric field intensities over broadband wavelengths, they show promising potential for use in energy harvesting, detection and biosensing-related applications.



Figure S9 Near-field electric field distributions of incident light at wavelengths of 580 nm, 650 nm, 770 nm, 840 nm, and 940 nm passing through the 3D halo structure with $d_{Fe_3O_4}/d_{Au}$ of 500/40 nm in water.



Figure S10 Near-field electric field distributions of incident light at wavelengths of 580 nm, 650 nm, 770 nm, 840 nm, and 940 nm passing through the 3D halo structure with $d_{Fe_3O_4}/d_{Au}$ of 300/100 nm in water.

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