Supporting Information for

Asymmetric Hetero-assembly of Colloidal Nanoparticles through "Crash Reaction" in a Centrifugal Field

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Experimental Details

Materials: All the chemicals were A. R. grade, bought from Beijing Chemical Reagent Co., Inc., and used as received without further purification.

1. Synthesis of Au NPs

Gold nanoparticles were synthesized in two steps by seed-mediated method using cetyltrimethylammonium chloride (CTAC) as surfactant.

Preparation of Au Seeds

Seed solution was prepared by vigorous mixing of 10 ml of $HAuCl_4$ (2.5×10^{-4}M) aqueous CTAC (0.1 M) solution with 0.4 ml $NaBH_4$ (0.02 M).

Preparation of the growth solution

The growth solution was prepared by adding 10 ml of HAuCl4 (10 mM), 400 µl of NaBr (0.01 M) and 4 ml of ascorbic acid (0.1 M) to 400 ml of aqueous CTAC (0.1 M) solution.

The growth of Au NPs

The seed solution was aged for 60 minutes and diluted 10 times before adding it to the growth solution. To this colorless growth solution, depending on the size of particles required, 60 µl and 2mL of diluted seed solution was added under vigorous agitation and left undisturbed one week.

Functionalization of gold nanoparticles

For surface modification, the Au NPs were firstly centrifuged and concentrated by 10 times, then 10µl p-ATP (100µM) and 5µl MPA (100µM) were added in 1ml of 50nm and 20 nm Au NP solution, respectively. Then 0.43ml of EG was added to 20 nm Au NP solution.

2. Crash reaction in the tube

(1) Density gradient preparation

All separation experiments were performed using a Beckman Optima L-100XP ultracentrifuge. Typically the separation layer step gradient was made using 40%, 50%, 60%, 70%, and 80% (by volume) solutions of Ethylene glycol（EG）in water. For instance, a volume ratio of EG: H_2O = 6:4 was used to make the 60% solution. A step gradient was created directly in Beckman centrifuge tubes (polyallomer) by adding layers to the tube with decreasing density (i.e., lower EG concentration). To make a (40% + 50% + 60% + 70% + 80%) gradient, 1.8 mL of 80% solutions of EG in H_2O was first added to the centrifuge tube, then 1.8 mL 70% solutions of EG in H_2O was slowly layered above the 80% layer. The subsequent layers were made following the same procedure and resulted in a density gradient along the centrifuge tube.

(2) Asymmetric hetero-assembly of colloidal nanoparticles in a centrifugal field

Highly concentrated 60nm Au nanoparticle solution was put on top of the gradient and 20 nm NPs were in 30% ethylene glycol (EG) solution layer. A buffer layer was placed between two Au NP layers to prevent spontaneously assembly of the NPs with opposite charges. Then the tubes were centrifuged at 10,000 rpm for 10 minutes (a photograph of the ultracentrifuge tube after separation is shown in Fig. 2A). Fractions (200 µL each) were obtained by orderly manual extraction along the centrifuge tube after ultracentrifugation.

(3) Asymmetric hetero-assembly of colloidal nanoparticles in a centrifugal field by introducing a water/oil interface

Only 40% EG solution was replaced by 35% CCl4 in cyclohexane, others remain unchanged.

3. Characterization of nanocrystals

Transmission electron microscopy (TEM): A transmission electron microscope (Hitachi H-800, operated at 200 kV) was used to evaluate Au NPs size and morphology. Fractions obtained by gradient separation were directly dried on carbon film supported on copper grids. The optical properties of samples were characterized by UV-vis absorbance spectroscopy (UV-2501PC, Shimadzu, working in the range 300 – 1100 nm).

Calculations

1. Calculation of sedimentation rate

Particle density (ρ_p) depends on both the sizes(r) and the hydration layer thickness (t). For the big Au nanoparticles, TEM shows that r is about 30 nm,. The hydration layer thickness (t) can be assumed to be about 3nm (double layer of CTAC molecule) . The density (ρ_p) of the Au nanoparticle is given by formula:

$$\rho_p = \frac{\rho_{Au} V_{Au} + \rho_{\mathrm{H_2O}}(V_{\mathrm{p}} - V_{\mathrm{Au}})}{V_p} \qquad \text{(I)}$$

where V_{p} denotes the volume of the particle and V_{Au} is the volume of the Au particle without its hydration layer. The density of Au (ρ_{Au}) and the hydration layer ($\rho_{\mathrm{H_2O}}$) are 19.32×10^3 kg/m^3 and 1×10^3 kg/m^3, respectively.

According to the classical sedimentation theory, the sedimentation velocity of spherical colloidal particles in a given medium with density ρ_m and viscosity η_s, in a centripetal field of g', can be described as:

$$v = 2(\rho_p\text{-}\rho_s)r^2g'/(9\eta_s) \qquad \text{(II)}$$

where r denotes the radius of the Au nanoparticle coated with a solvation shell several nanometers thick. The density (ρ_m) of 30% ethylene glycol (EG) is 1.035×10^3 kg/m^3 and the viscosity (η_S) of 30% EG is 2.089×10^{-3} Pa·s. We centrifuged at 10,000 rpm, so the centripetal force field of g′ is equivalent to an acceleration of 1.7147×10^5 m/s^2. Then the sedimentation rates could be calculated to 267μm/s and 25μm/s for 60nm and 20nm Au NPs, respectively.

2. Calculation of diffusion constant

According to Stokes-Einstein equation, diffusion constant D of spherical nanoparticles could be calculated by:

$$D = k_B T/(6\pi r\eta_s) \qquad \text{(III)}$$

Where k_B is 1.38×10^{-23} J/K, the absolute temperature T is 298k, the viscosity (η_m) of 30% EG is 2.089×10^{-3} Pa·s. Then diffusion constant D of 60nm Au nanoparticles is calculated to be 3.39 μm^2/s.

3. Calculation of collision possibility

Particle concentration of original 20nm Au nanoparticle solution was about 1nM. Then, for 200µl of 10 times concentrated solution, the total amount of NP is about 1.2×10^{12}. For mathematical modeling, we divide the nanoparticle solution into several monolayers and each layer has a thickness equals the diameter to Au NP, which is 20nm. When the 200µl solution was suspended in a centrifugal tube with diameter of 14mm, the total layer number (N_l) is 6.5×10^4 and each layer contains 1.85×10^7 (N_p) nanoparticles.

Since the sedimentation velocity of 50nm NPs was 267µm/s, they would stayed in one monolayer for 7.5×10^{-5}s, thus the horizontal Brown motion distance was 15.9nm. In order to simplify the mathematical model, we could assume an NP with diameter equals to 81.8nm that collide with 20nm Au NPs and therefore the Brown motion of big NPs could be neglected. Also, we assume a uniform distribution of small NPs and thus their Brown motion could be offset.

Only when big nanoparticle appeared in the circle area with radius less than 91.8nm from the center of 20nm NPs, the collision could happen, thus the probability could be calculated by quotient value between total possible collisions area and the total area of one monolayer. The total possible collisions area could be calculated by:

$$A_c = N_p * \pi (r_{20}+d_{91.8})^2 = 1.85\times10^7 \times \pi \times (10\text{nm}+91.8\text{nm})^2 \qquad \text{(IV)}$$

The total area of one monolayer could be calculated by

$$A_t = \pi r_{tube}^2 = \pi \times 7\text{mm}^2 \qquad \text{(V)}$$

Therefore, the collision probability in one monolayer is:

$$P_l = A_c/A_t \times 100\% = 0.38\% \qquad \text{(VI)}$$

And the total collision probability is:

$$P = 1-(1-P_l)^{Nl} = 1-(1-0.38\%)^{65000} \approx 100\% \qquad \text{(VII)}$$

Supplementary Figures

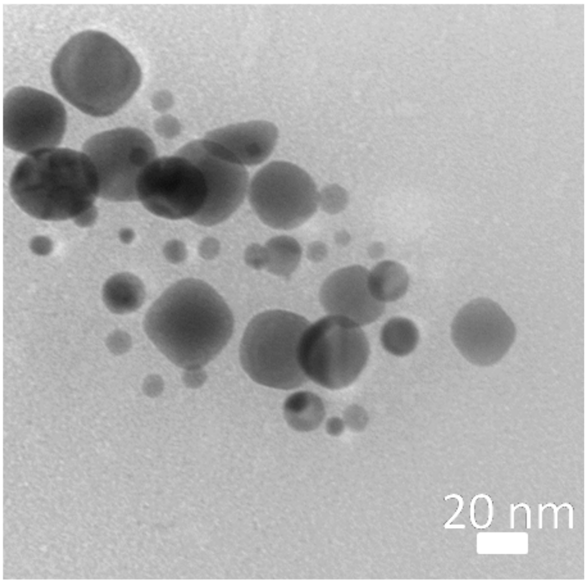


Fig. S1 TEM image of the NPs with opposite charges were mixed without EDC catalysts.

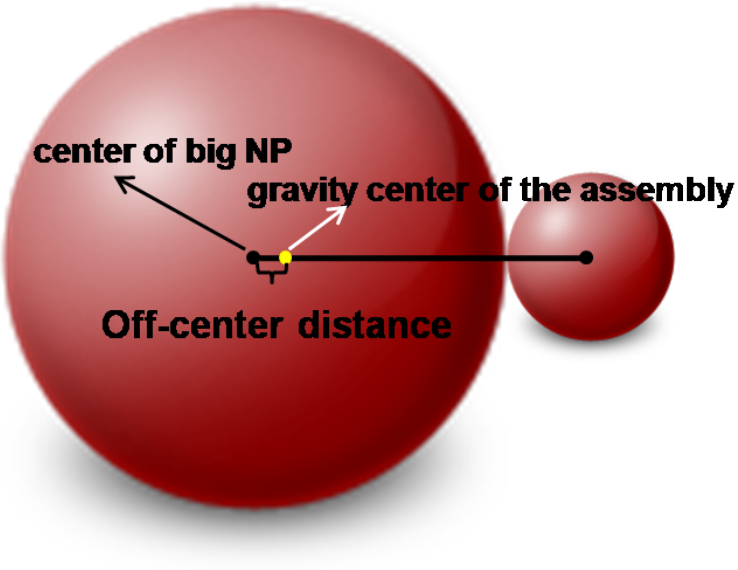


Fig. S2 Schematic illustration of the off-center distance

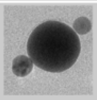
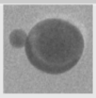
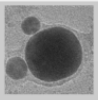
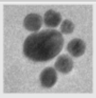
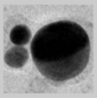
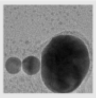
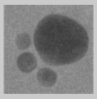
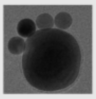
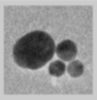
TEM	Off-center Distance(nm)	Number of Assembled NPs	Percentage （%）
	0	2	1
	1.43	79	53
	2.39	5	3
	2.49	2	1
	2.68	32	21
	3.45	10	7
	3.53	10	7
	4.4	7	5
	5	3	2

Fig. S3 Statistical data of off-center distances (from gravity center to the center of big nanoparticle) of the assemblies obtained from "crash reaction".

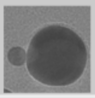
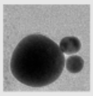
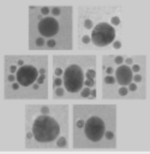
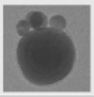
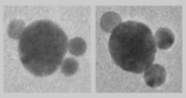
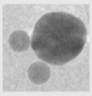
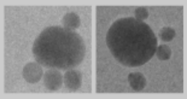
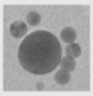
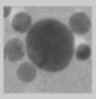
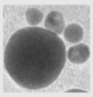
TEM	Off-center Distance(nm)	Number of Assembled NPs	Percentage （%）
	1.43	13	10.8
	2.68	10	8.3
	0	44	36.7
	3.53	14	11.7
	1.3	17	14.1
	2.39	3	2.5
	2.5	5	4.2
	2.14	3	2.5
	1.21	9	7.5
	4.4	2	1.7

Fig. S4 Statistical data of off-center distances (from gravity center to the center of big nanoparticle) of the assemblies obtained from random assembly.

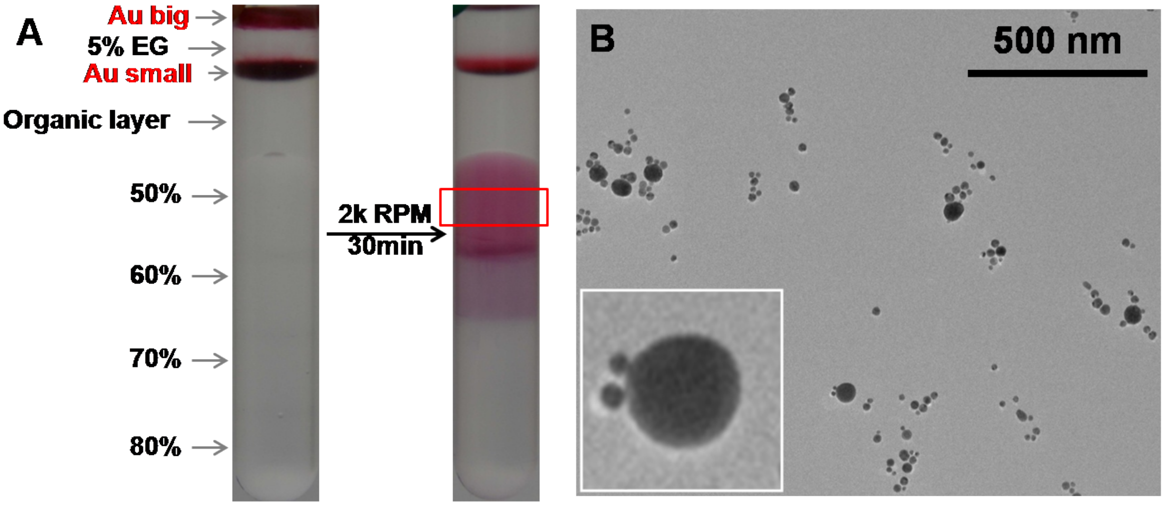


Fig. S5 Schematic illustration of "crash reaction" (A) on water/oil interfaces. (B) TEM image of as assembled superstructures passed through water/oil interfaces.