Controlling Colloidal Superparticle Growth Through Solvophobic Interactions

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1. Chemicals
Iron(III) chloride hexahydrate (FeCl₃·6H₂O 98%), oleic acid (OA, 90%), 1-Octadecene (ODE, 90%), 1-Tetradecene (TDE, 92%), gold(III) chloride (AuCl₃, 99.99%), sodium borohydride (NaBH₄, 99%), Rhodamine 6G (R6G, 99%), Hexadecyltrimethylammounim bromide (CTAB, 99%), Triocylphosphine Oxide (TOPO, 99%), Octadecylamine (ODA, 97%), polyvinylpyrrolidone (PVP, MW=55,000), Gelatin (from porcine skin, type A), ethylene glycol (EG, 99%) were purchased from Aldrich. Cadmium oxide (CdO, 99.998%), selenium (Se, 99.99%), dodecyltrimethylammonium bromide (DTAB, 97%), dodecyl dimethylammonium bromide (DDAB, 99%) and 1-dodecanethiol (98%) were purchased from Alfa Aesar. Sodium oleate (95%) was purchased from TCL. All the other solvents were purchased from Fisher Scientific International Inc. Water used in the experiments was Nanopure water made by Barnstead Nanopure Diamond system.

2. Nanoparticle synthesis
Fe₃O₄ nanoparticles were prepared according to the literature method (S1). Two samples were synthesized. The first sample has nanoparticles with a diameter of 5.8 nm and a standard deviation of 3.7%, and the second one has particles of 8.9 nm in diameter with a standard deviation of 3.2%.

CdSe nanocrystals were synthesized based on a modified literature method (S2). Briefly, CdO powder (0.256 g, 2.00 mmol) and stearic acid (4.55g, 16.0 mmol) were mixed in a 250-ml three-neck flask. The mixture was heated to 240 °C under argon flow and kept at that temperature until a colorless solution was formed. After the solution was cooled to room temperature, octadecylamine (18.0 g) and triocylphosphine oxide (18.0 g) were added into the reaction flask. The reaction system was re-heated to 280 °C under argon flow, and a Se TBP solution (0.900 mM, 10.0 mL) was swiftly injected into the system. The temperature was naturally dropped to 270 °C and maintained. The particle size was monitored by UV-Vis spectroscopy on a Shimadzu UV 1700 spectrophotometer, and the reaction was stopped when the nanoparticles reached a desired size. The nanoparticles
were extracted from the reaction solution using a hexane/methanol (1:1) mixture, and the extraction was performed three more times. The purified CdSe nanoparticles were dispersed in chloroform as a stock solution. TEM shows that the resulting nanoparticles have a 6.3-nm diameter with a standard deviation of 4.5%.

Gold nanocrystals were synthesized according to the literature procedure (S3). The resulting nanoparticles have a diameter of 5.4 nm with a standard deviation of 4.1%.

3. Synthesis of supercrystalline colloidal superparticles from Fe₃O₄ nanoparticles

In a typical synthesis, DTAB (20.0 mg, 65.0 μmol) was dissolved in Nanopure water (1.0 mL) to form a solution. A chloroform solution of 5.8-nm Fe₃O₄ nanoparticles (28 μM, 1.0 mL) was thoroughly mixed with the DTAB solution by a vortex mixer. Afterwards, the chloroform was removed from the mixture by bubbling Ar at 40 °C. A clear, dark nanoparticle-micelle aqueous solution was obtained (S4).

This Fe₃O₄ nanoparticle-micelle aqueous solution was injected into a three-neck flask with a PVP ethylene glycol solution (2.0 mM, 5.0 mL) under vigorous stirring. The mixture solution was further stirred at room temperature for 10 min and then heated to 80 °C under Ar flow at 10 °C/min. After aging at 80 °C for 6 h, the solution was cooled to room temperature. The resulting colloidal superparticles were separated by centrifuge (500g, 15 min). The black precipitate was re-dispersed into ethanol and the superparticles were further purified twice by centrifugation. The superparticles have a diameter of 190 nm with a standard deviation of 15% and a yield of 70%. During the synthesis, serial quantitative aliquots (~50 μL) were taken for kinetic studies on superparticle formation, and samples were characterized by using TEM.

The size-controlled synthesis of superparticles using different molar ratios between DTAB and nanoparticles was performed by a similar procedure to that described above. Samples of superparticles with different sizes were obtained. The size and size-distribution of these superparticles are shown in Fig. 3 of the main text.

In addition, the synthesis of colloidal superparticles using 8.9-nm Fe₃O₄ nanoparticles was carried out using a similar procedure to that described above.

4. Synthesis of supercrystalline colloidal superparticles from CdSe nanoparticles

In a typical synthesis, DTAB (20.0 mg, 65.0 μmol) was dissolved in Nanopure water (1.0 mL) to form a solution. A chloroform solution of 6.3-nm CdSe nanoparticles (28 μM, 1.0 mL) was thoroughly mixed with the DTAB solution by a vortex mixer. Afterwards, the chloroform was removed from the mixture by bubbling Ar at 40 °C. A clear nanoparticle-micelle aqueous solution was obtained. The concentration of CdSe nanoparticles in chloroform was determined by UV-Vis spectroscopy on a Shimadzu UV 1700 spectrophotometer. A molar absorptivity (ε-CdSe) of $7.9 \times 10^5$ M⁻¹•cm⁻¹ for 6.3-nm CdSe nanoparticles was used for the calculation (S5).
This CdSe nanoparticle-micelle aqueous solution was injected into a three-neck flask with a PVP ethylene glycol solution (2.0 mM, 5.0 mL) under vigorous stirring. The mixture solution was stirred for 10 min, and then heated to 80 °C under Ar flow at 10 °C/min. After aging at 80 °C for 8 h, the solution was cooled to room temperature. The resulting CdSe superparticles were separated by centrifuge (500g, 15 min). The resulting precipitate was re-dispersed into ethanol, and the superparticles were further purified twice by centrifugation.

5. Synthesis of supercrystalline colloidal superparticles from Au nanoparticles

In a typical synthesis, DTAB (20.0 mg, 65.0 μmol) was dissolved in Nanopure water (1.0 mL) to form a solution. A chloroform solution of 5.4-nm gold nanoparticles (28 μM, 1.0 mL) was thoroughly mixed with the DTAB solution by a vortex mixer. Afterward, the chloroform was removed from the mixture by bubbling Ar at 40 °C. A clear, dark red nanoparticle-micelle aqueous solution was obtained. The concentration of gold nanoparticles in chloroform was determined by UV-Vis spectroscopy on a Shimadzu UV 1700 spectrophotometer. A molar absorptivity (ε-Au) of $1.1 \times 10^7$ M$^{-1}$cm$^{-1}$ for 5.4-nm gold nanoparticles was used for the calculation (S6).

This gold nanoparticle-micelle aqueous solution was injected into a three-neck flask with a PVP ethylene glycol solution (2.0 mM, 5.0 mL) under vigorous stirring. The mixture solution was stirred for 10 min, and a gelatin aqueous solution (1.0%, 0.50 mL) was added, and then heated to 80 °C under Ar flow at 10 °C/min. After aging at 80 °C for 1 h, the solution was cooled to room temperature. The resulting gold superparticles were separated by centrifuge (500g, 15 min). The precipitate was re-dispersed into water, and the superparticles were further purified twice by centrifugation.


In a typical synthesis, DTAB (20.0 mg, 65.0 μmol) was dissolved in Nanopure water (1.0 mL) to form a solution. A chloroform solution of 5.4-nm gold nanoparticles (28 μM, 1.0 mL) was thoroughly mixed with the DTAB solution by a vortex mixer. Afterwards, the chloroform was removed from the mixture by bubbling Ar at 40 °C, yielding a clear, dark red nanoparticle-micelle aqueous solution.

An ethanol solution of rhodamine 6G (0.100 mM, 10.0 μL) was added into this nanoparticle-micelle solution, and then the mixture was injected into a three-neck flask with ethylene glycol (5.0 mL) and PVP (0.500 g, 10.0 μmol). The mixture solution was stirred for 10 min, and a gelatin aqueous solution (1.0%, 0.50 ml) was added. The mixture solution was heated to 80 °C under Ar flow. The reaction solution was aged at the same temperature for 1 h, and the solution was cooled to room temperature. The
doped superparticles were separated by centrifuge (500g, 15 min). The precipitate was re-dispersed into water, and the superparticles were further purified twice by centrifugation.

Raman spectra were obtained using a Nanoraman ADV Raman system. The specimens were prepared by drop-casting an aqueous solution of doped gold superparticles (50 μL) onto a glass slide. The laser (He-Ne, 633 nm) power was 42 mW. The collection time of the spectrum was 0.5 s.

7. TEM and SAED measurements
TEM measurements were performed on a JEOL 200X operated at 200 kV, or a JEOL 2010F TEM operated at 200 kV. SAED patterns were acquired by the 2010F TEM and operated at 200 kV with a camera length of 200 cm. The specimens were prepared as follows: a particle solution (10 μL) was dropped onto a 200-mesh copper grid, and was dried overnight at ambient conditions.

8. Small-angle XRD measurement and calculation of the lattice constant (a) of supercrystalline colloidal superparticles made from 5.8-nm Fe₃O₄ nanoparticles
Small-angle X-ray diffraction spectra were measured on a Philips MRD X'Pert System with Cu-Kα₁ radiation (λ= 1.54056 Å), operated at 45 kV and 40 mA. The sample was prepared as follows: supercrystalline Fe₃O₄ superparticles (~20mg, 190 nm in diameter) were dispersed in ethanol (0.50 mL). Then the solution was drop-casted onto a low-scattering quartz plate, and the sample was dried overnight at ambient conditions. The resulting particle film had a thickness of about 12 microns. The quartz plate coated with amorphous Fe₃O₄ superparticles (~20mg, 190 nm in diameter) was measured as the background reference.

The d spacing between superlattice planes with Miller indices {hkl} was calculated by the Bragg equation, \( \lambda = 2d \sin \theta \). The value of \( \theta \) was obtained from the small-angle XRD pattern (Figure 1e in the main text).

The table below shows the Bragg diffraction angles, d spacing and the calculated lattice constant (a), respectively.

<table>
<thead>
<tr>
<th>2θ</th>
<th>d (nm)</th>
<th>a (nm)</th>
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<tbody>
<tr>
<td>111</td>
<td>1.30</td>
<td>6.79</td>
</tr>
<tr>
<td>220</td>
<td>2.13</td>
<td>4.13</td>
</tr>
<tr>
<td>400</td>
<td>2.88</td>
<td>3.06</td>
</tr>
<tr>
<td>333</td>
<td>3.77</td>
<td>2.34</td>
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From these data the value for the lattice constant (a) was found to be 11.9 ± 0.3 nm.
9. The effect of surfactants in the synthesis of superparticles
To further prove that the solvophobic interaction between nanoparticle ligands and ethylene glycol solution is important to superparticle synthesis, we investigated the effect of surfactants. Cetyltrimethylammonium bromide (CTAB, a 16-carbon surfactant) was used to replace DTAB (a 12-carbon surfactant) in the superparticle synthesis for two reasons: (1) CTAB has a much lower solubility in ethylene glycol than DTAB (15.0 mg/mL vs. 200 mg/mL), and (2) CTAB has a stronger van der Waals interaction with the Fe$_3$O$_4$ nanoparticle ligands, i.e., oleic acid (S7).

To examine surfactant effects, a synthesis was carried out according to the typical synthesis for making Fe$_3$O$_4$ superparticles described in page S-2, but CTAB was used instead of DTAB. CTAB (22.4 mg, 65.0 μmol) was dissolved in Nanopure water (1.0 mL) by ultrasonication. A chloroform solution of 5.8-nm Fe$_3$O$_4$ nanoparticles (28 μM, 1.0 mL) was thoroughly mixed with the CTAB solution by a vortex mixer. Afterwards, the chloroform was removed from the mixture by bubbling Ar at 40 °C. A clear, dark nanoparticle-micelle aqueous solution was obtained.

This Fe$_3$O$_4$ nanoparticle-micelle aqueous solution was injected into a three-neck flask with a PVP ethylene glycol solution (2.0 mM, 5.0 mL) under vigorous stirring. The mixture solution was further stirred at room temperature for 10 min and then heated to 80 °C under Ar flow at 10 °C/min. After aging at 80 °C for 6 h, the solution was cooled to room temperature. Interestingly, no precipitate was obtained under centrifugation at 500 g for 1 h. Further centrifugation at 12,500 g for 30 min yielded some black precipitates. These black precipitates are highly dispersible in water, and TEM measurements show that these samples did not contain spherical superparticles but just monodispersed 5.8-nm Fe$_3$O$_4$ nanoparticles (fig. S3). Taken together, these results demonstrate that the CTAB nanoparticle-micelles are stable in these synthesis conditions, further suggesting that the solvophobic interaction is important to the synthesis of superparticles.

10. The function of PVP in the synthesis of single supercrystalline colloidal superparticles
To examine the function of PVP, a synthesis was carried out according to the typical synthesis for making Fe$_3$O$_4$ superparticles described in page S-2, but without PVP in the synthesis system. TEM measurements show that such syntheses did result in superparticles (Fig. 3C in the main text). But these superparticles are not stable and were easily destroyed during annealing at 80 °C for 6 h (fig. S4). To further examine the function of PVP, we varied the amount of PVP from 0.200 g to 1.50 g for different syntheses. TEM studies show that the amount of PVP in the synthesis system did not significantly affect the size or shape of the resulting superparticles.
11. NMR measurement

$^1$H-NMR analysis was used to investigate the chemical compositions of the ligands on the nanoparticle-micelles and superparticles. NMR spectra were recorded using a Varian Mercury NMR Spectrometer (300 MHz).

Fe$_3$O$_4$ nanoparticle-micelles were isolated from an aqueous solution by centrifuge (12,500 g for 30 min), and the black precipitate was washed twice with water. The resulting precipitate (100 mg) was fully digested using HCl (12.5 M, 5 mL), and then, water and excess HCl were evaporated from the solution using a rotary evaporator. The resulting yellow, oily residue was extracted using CHCl$_3$ (5 mL) under ultrasonic for 10 min. The un-dissolved part was removed using a syringe filter (0.2 µm). Afterwards, CHCl$_3$ was evaporated, and the resulting mixture was re-dissolved in CDCl$_3$ (0.8 mL) for $^1$H-NMR measurement.

For the Fe$_3$O$_4$ superparticles, purified Fe$_3$O$_4$ superparticles (100 mg) were dissolved by HCl (12.5 M, 5 mL), and then, water and excess HCl were evaporated from the solution using a rotary evaporator. The resulting yellow, oily residue was extracted using CHCl$_3$ (5 mL) under ultrasonic for 10 min. The un-dissolved part was removed using a syringe filter (0.2 µm). Afterwards, CHCl$_3$ was evaporated, and the resulting mixture was re-dissolved in CDCl$_3$ (0.8 mL) for $^1$H-NMR measurement.

![Figure S1. TEM images of (a) Fe$_3$O$_4$ nanoparticle in chloroform, and (b) Fe$_3$O$_4$ nanoparticle-micelles (the image is the same as Figure 2b in main text.)](image-url)
**Figure S2.** TEM images of Fe₃O₄ superparticles from the aliquots taken at (a) 1 min, and (b) 10 min after the nanoparticle-micelle injection in a typical synthesis.

**Figure S3.** TEM images of (a) Fe₃O₄ nanoparticle-micelles made by CTAB, and (b) Fe₃O₄ nanoparticles after the synthesis.
Figure S4. TEM images of the precipitates resulting from the synthesis without PVP after annealing at 80 °C for 6 h. (a) A low-magnification image shows large, irregularly shaped aggregates, while (b) a higher-magnification image shows that the Fe₃O₄ superparticles collapsed and fused together to form uncontrollable aggregates.
Figure S5. $^1$H NMR spectra of oleic acid (90%, purchased from Aldrich) and DTAB (99%, purchased from Alfa Aesar)
Figure S6. Zoom-in TEM images of (e) and (f) in Figure 2 of the main text.

References