

SUPPORTING INFORMATION

Experimental determination and analysis of gold nanorods settlement in differential centrifugal sedimentation

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S1. Synthesis of GNRs

S1.1. Chemicals

Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium borohydride (NaBH_4), silver nitrate (AgNO_3), sulphuric acid (H_2SO_4), L-ascorbic acid (AA), cetyltrimethylammonium chloride (CTAC) and cetyltrimethylammonium bromide (CTAB) were purchased from Alfa and used as received. Sucrose was purchased from Alfa Aesar Co., Ltd. (Tianjin, China). Standard nanoparticle of silicon dioxide (SiO_2 , with diameter of 164nm) was purchased from Putian Tongchuang Biotech Co., Ltd. Double deionized water (18 M Ω -cm) was produced by D-Q5 pure/ultrapure water machine (Merck Millipore, Germany) and used in all the preparations.

S1.2 Synthesis of the GNRs with equal volume

GNRs were synthesized by a seed-mediated method¹. Firstly, 7.5 mL of CTAB (0.1M) aqueous solution was mixed with 100 μL of HAuCl_4 (24 mM) and diluted with deionized water to 9.4 mL. Then, 0.6 mL of ice-cooled NaBH_4 (0.01 M) was added into the above solution under rigorous magnetic stirring. After 3 min, the stirring was stopped and the seed solution was kept statically at 30°C prior to any further experimentation. The seeds can be used within 2-5 h after preparation.

The growth solution for the GNRs was prepared by mixing CTAB (0.1 M, 100 mL), HAuCl_4 (25.5 mM, 1.96 mL), AgNO_3 (0.01 M, 0.45 mL, 0.6ML, 0.75 mL, and 1.0 mL for different aspect ratio), H_2SO_4 (0.1M, 2 mL) and L-ascorbic acid (0.1 M, 0.8 mL). Then 240 μL of the seed solution was added to the above growth solution to initiate the growth of the GNRs. After 12 h, GNRs with equal volume were obtained.

S1.3 Synthesis of the GNRs with equal diameter

The growth solution of the GNRs was prepared by mixing CTAB (0.1M, 100mL), HAuCl₄ (25.5mL, 1.96mL), AgNO₃ (0.01M, 1.4 mL) and L-ascorbic acid (0.1M, 0.55mL) following the above procedure. Then 120 μ L of seed solution was added to the above growth solution to initiate the growth. After 12 h, 55 μ L of 0.1M AA was added twice at an interval of 30min and the GNRs with longitudinal surface plasmon resonance (LSPR) at 750 nm were obtained. In order to produce GNRs with LSPR at 712, 675, 640 nm and 600 nm, H₂O₂ (10 M, 150 μ L) and H₂SO₄ (1 M, 125 μ L) were added to aliquots of the above solution at 65°C for 15, 30, 45 and 60 min, respectively.

Table S1. Aspect ratio of the calculated GNRs

v-GNR $\lambda_{\text{LSPR}}/\text{nm}$	630	680	740	800
β	2.21	2.73	3.37	4

d-GNR $\lambda_{\text{LSPR}}/\text{nm}$	600	640	675	712	750
β	1.89	2.32	2.68	3.07	3.47

Note: v-GNR is the GNRs with equal volume while d-GNR is those with equal diameter

S2. Measurement on sedimentation coefficient

A UV-vis spectrophotometer (Lambda 650, PerkinElmer) was used to record all GNR absorbance spectra.

DCS was performed on a DC24000 UHR Disc Centrifuge particle size analyzer (CPS Instruments, Inc., USA) operated at 24000 rpm, and pre-filled with 14.4mL of sucrose solution in a gradient of 8%–24% (averaged density between the injection point and detector is 1.06 g cm⁻³), which was formed by batched injection (1.5 mL \times 9) of the sucrose solution in the order of higher to lower density. 1 mL of evaporation-proof fluid, n-dodecane (density 0.75 g cm⁻³) was introduced into the rotating chamber after the centrifugal field was established. Particle suspensions were injected through the central point of the disc, and the settled particles were optically detected by the light intensity change. The settling time of the particles could therefore be recorded and correlated to the size and shape of the particles. The rheological properties of the fluid (density, viscosity) were calibrated by the use of 164 nm SiO₂ certified reference materials.

S3. Quantitative calculation of sedimentation coefficient by other models

He *et al* have derived an orientation averaged sedimentation coefficient

expression (Eq. S1) in vertical direction assuming that using Brownian ellipsoidal particles replace of GNRs who is experiencing force balance in a Stokes flow ².

$$s = \frac{\beta\pi d_c^2}{12\eta} (\rho_p - \rho_f) \frac{\Omega_{\parallel} + \Omega_{\perp}}{\Omega_{\parallel}\Omega_{\perp}} \quad (S1)$$

By aid of substitutions:

$$\Omega_{\parallel} = 4\pi \frac{\beta^2 - 1}{(2\beta^2 - 1)/(\beta^2 - 1)^{1/2} \ln \left[\beta + (\beta^2 - 1)^{\frac{1}{2}} \right] - \beta} \quad (S2)$$

$$\Omega_{\perp} = 8\pi \frac{\beta^2 - 1}{(2\beta^2 - 3)/(\beta^2 - 1)^{1/2} \ln \left[\beta + (\beta^2 - 1)^{\frac{1}{2}} \right] + \beta} \quad (S3)$$

Leith ³ and Sommerfeld ⁴ have studied out the drag coefficient for rod-like particles as stated in Eq. 6 and Eq. 7.

$$C_D = \frac{8}{Re} \frac{1}{\sqrt{\Phi_{\perp}}} + \frac{16}{Re} \frac{1}{\sqrt{\Phi}} \quad (6)$$

$$C_D = \frac{8}{Re} \frac{1}{\sqrt{\Phi_{\parallel}}} + \frac{16}{Re} \frac{1}{\sqrt{\Phi}} \quad (7)$$

Finally, the sedimentation coefficient of GNRs can be calculated according to Eq.5 and its definition, which was expressed as Eq. S4 by employing the drag coefficient from Leith, and which was expressed as Eq. S5 by employing the drag coefficient from Sommerfeld.

$$s = \frac{d_c^2 (\rho_p - \rho_f)}{4\eta} \times \frac{\left(\frac{\pi}{4}\beta - \frac{\pi}{12}\right) \left(\frac{3}{2}\beta - \frac{1}{2}\right)^{\frac{2}{3}}}{4 \left(1 + 2\beta^{\frac{1}{2}}\right) \times \left[\frac{\pi}{4} + (\beta - 1)\right]} \quad (S4)$$

$$s = \frac{d_c^2 (\rho_p - \rho_f)}{\eta} \times \frac{\left(\frac{3}{2}\beta - \frac{1}{2}\right)^{\frac{2}{3}} \left(\frac{\pi}{4}\beta - \frac{\pi}{12}\right)}{(\pi + 4\beta - 4) (2^2 \sqrt{\beta} + 2 \sqrt{\left(2 - \frac{4}{\pi}\right)\beta - 1 + \frac{4}{\pi}})} \quad (S5)$$

Reference

1. B. Nikoobakht and M. A. El-Sayed, Chem Mater., 2003, 15, 1957-1962.
2. B. Xiong, J. Cheng, Y. Qiao, R. Zhou, Y. He and E. S. Yeung, J Chromatogr A., 2011, 1218, 3823-3829.
3. D. Leith, Aerosol Sci Tech, 1987, 6, 153-161.
4. A. Holzer and M. Sommerfeld, Powder Technol, 2008, 184, 361-365.

