Electronic Supplementary Information for

Identifying Mass Transfer Influences on Au Nanoparticles Growth Process by Centrifugation

Bing-Sheng Yin,[a] Jian-Qiang Hu,*[b] Song-Yuan Ding,[a] An Wang,[a] Jason R. Anema,[a] Yi-Fan Huang,[a] Zhi-Chao Lei,[a] De-Yin Wu[a] and Zhong-Qun Tian*[a]

[a] State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China. E-mail: zqtian@xmu.edu.cn

[b] College of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China. E-mail: jqhusc@scut.edu.cn

1. Experimental Details:

Reagents: Chloroauric acid ($HAuCl_4 \cdot 4H_2O$, 99.9%), cetyltrimethylammonium bromide (CTAB, 99.0%), sodium borohydride ($NaBH_4$, 96.0%), ascorbic acid (AA, $C_6H_8O_6$, 99.7%) and ethanol (C_2H_5OH, 99.7%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). n-Dodecanethiol ($C_{12}H_{25}SH$, 98%) was purchased from Alfa Aesar. All reagents were used as received without further purification. All glassware used were washed with aqua regia and rinsed with ultrapure water. Ultrapure water (>18.0 MΩ cm) was also used to prepare all aqueous solutions.

Preparation of Au nanooctahedrons[1]. Au seeds of about 3 nm in diameter were prepared as previously described:[2] briefly, a clear solution containing 0.25 mL $HAuCl_4$ (10 mM), 9.75 mL CTAB (0.1 M) was first prepared in a flask; then 0.60 mL ice-cold $NaBH_4$ (10 mM) was rapidly injected to the mixture and kept vigorously stirring for 1 min; finally, the seed solution was acquired through storing the mixture at 28-30 °C for 2 h. 0.5 mL of the seed solution was then diluted to 50 mL. Subsequently, 0.3 mL of the diluted seed solution was introduced into 25 mL of the growth solution containing 4 mL CTAB (0.1 M), 0.1 mL $HAuCl_4$ (10 mM) and 1.5 mL AA (0.1 M). Finally, Au nanooctahedrons were obtained through leaving the mixture undisturbed at 28-30 °C overnight.

Preparation of the growth solution. 4 mL CTAB (0.1 M) and 0.5 mL $HAuCl_4$ (10 mM) were added into a 25 mL tube. The mixture was shaken and then left undisturbed at 28-30 °C for about 5 min. Finally, 1.0 mL AA (0.1 M) was added to the mixture and diluted to 25 mL.

Growth process of the Au nanooctahedrons without centrifugation. Firstly, 10 mL of the Au nanooctahedron solution was centrifuged at 8,000 rpm for 15 min and the collected precipitate was diluted to about 500 μL. Then, the concentrated Au nanooctahedrons served as single crystal seeds was quickly added into the growth solution, and left at 28-30 °C. The growth time was counted from the addition of the nanooctahedrons. 1 mL of the reaction solution were taken out after the Au seeds experienced different growth time and subsequently quickly mixed with 0.2 mL n-dodecanethiol (10 mM). The intermediate products were acquired through centrifuging and washing with ultrapure water.

Growth process of Au nanooctahedrons with centrifugation. Firstly, 10 mL of the Au nanooctahedron solution was centrifuged at 8,000 rpm for 15 min and the collected precipitate was diluted to about 500 μL. Then, the concentrated Au seed solution was quickly added into the growth solution. Next, aliquots were transferred into a centrifuge tube and grew with centrifugation for 30 min at the speed of 4,000 rpm. Final products were acquired by centrifuging, removing upper solution and washing two times with aqueous solution containing with a small amount of CTAB and n-dodecanethiol.

Characterization methods. The scanning electron microscopy (SEM) samples were fabricated by placing 2.5 μL of the concentrated sample solutions on cleaned silicon wafers and drying under vacuum, the sizes and morphologies of as-prepared samples were characterized by field-emission scanning electron microscopy (Hitachi S-4800, Japan) operated at 20 kV. UTHSCSA ImageTool (IT) software[3], explored by Wilcox et al. in San Antonio Medical Center at The University of Texas, was used to measure and analyze nanoparticles (NPs) size. With this software, the "find object" and "analyze" commands were used; the apparent area of the single Au NP was measured; the apparent area was determined as the sum of all pixels within the red frame around a certain Au NP image after the "find object" command was used. The Au NPs sizes were calculated according to the formula, $l = (A)^{1/2}$, in which the object was assumed to cover the same area as a square.

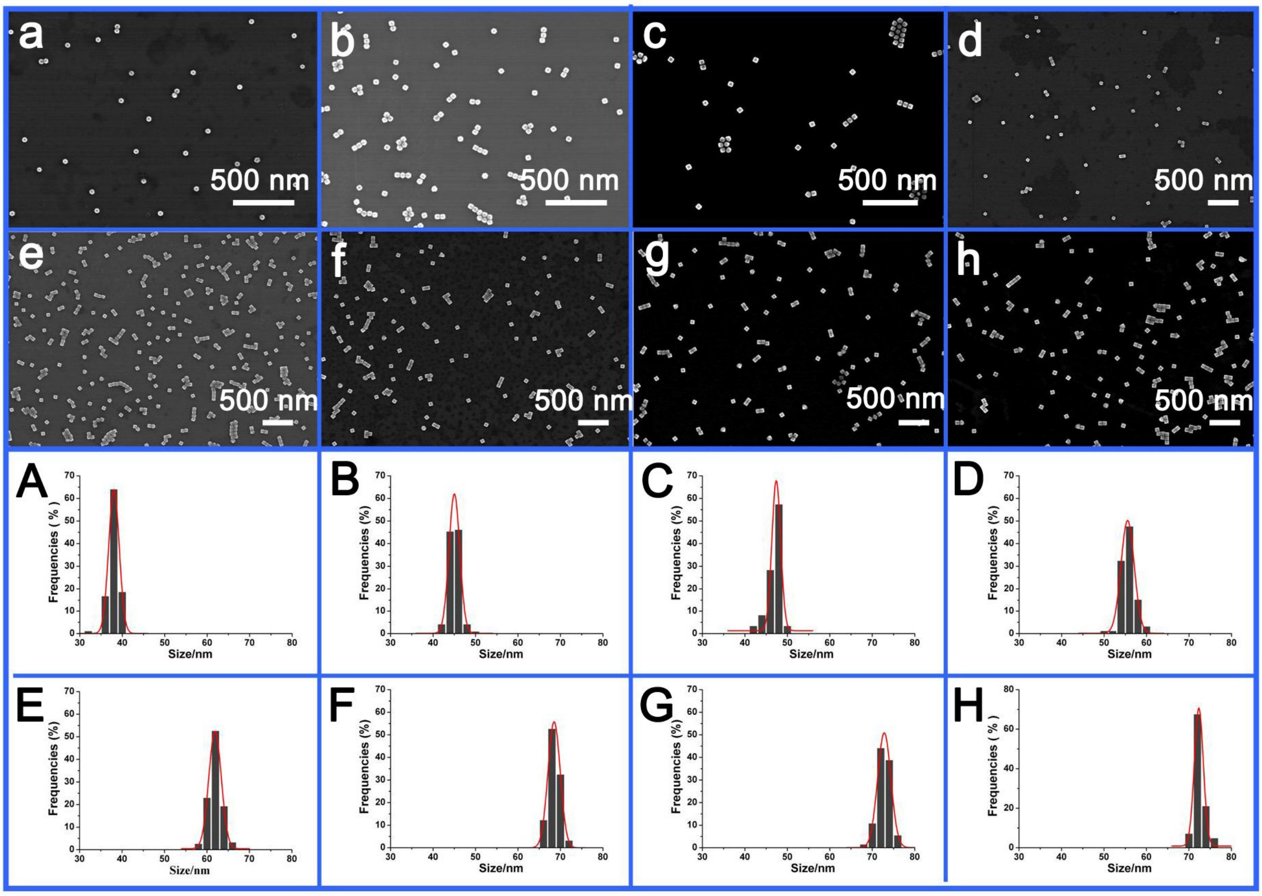

Fig. S1. SEM images of Au NPs obtained by n-dodecanethiol termination of growth in the absence of centrifugation after (a) 150, (b) 300, (c) 450, (d) 600, (e) 900, (f) 1200, (g) 1800 and (h) 2400 s, respectively, and (A-H) their corresponding sizes histogram plots.

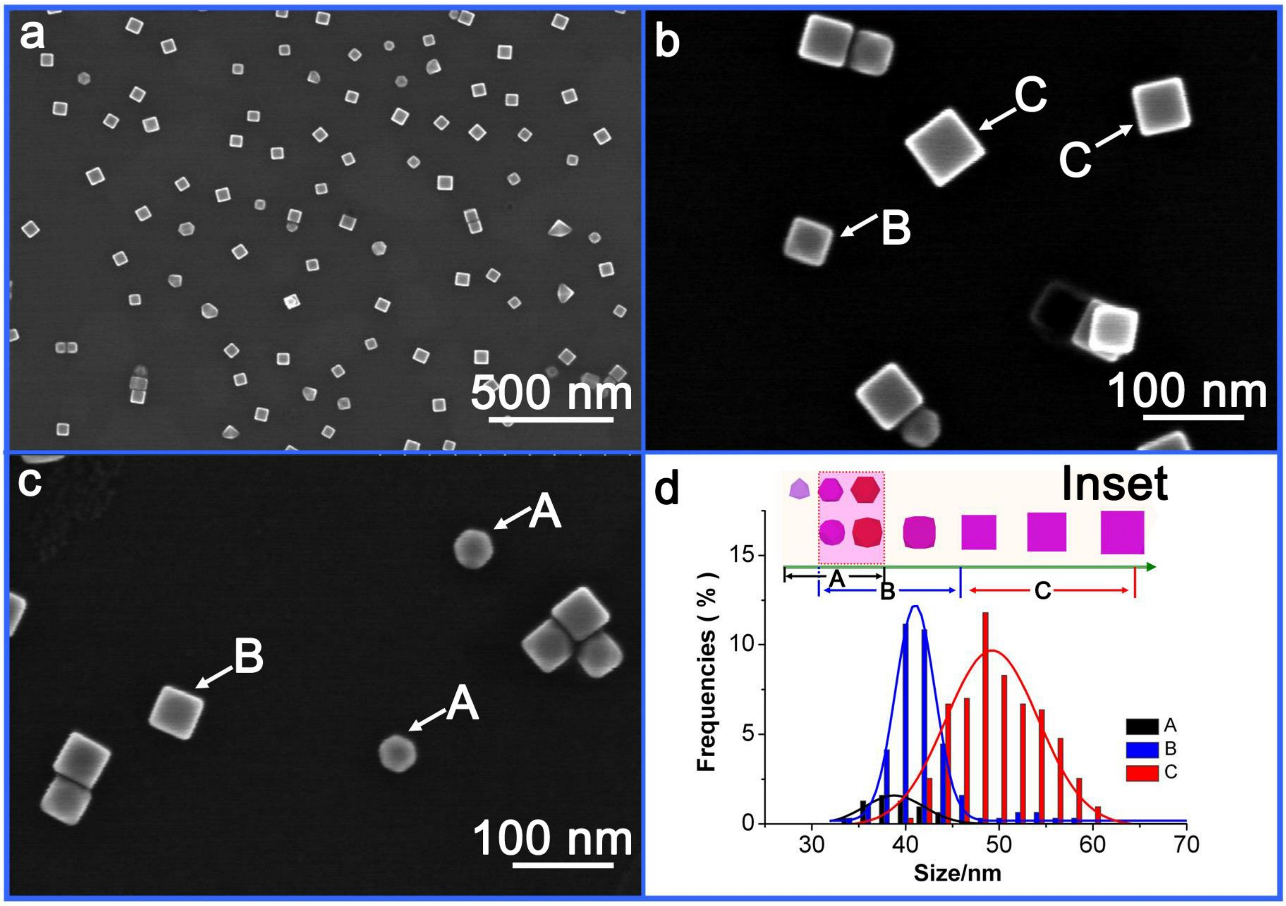

Fig. S2. (a, b and c) SEM images for size and shape analysis of Au NPs obtained after 30 min of growth while centrifuging at 4,000 rpm. (d) The histograms showing Au NPs sizes with special shapes, as the inset shows, A represents nanooctahedrons, truncated octahedrons and cuboctahedrons, B represents truncated nanocubes, and also contained of small amount of truncated octahedrons and cuboctahedrons, and C represents nanocubes. To obtain correlation between NP shape and NP size as shown in the Fig 3d, 314 NPs were counted from more than 50 high-resolution SEM images. The yield of A, B and C shapes with a size were calculated by the formula, $[Yield] = [\frac{N_i}{N}] \times 100\%$. Wherein, N and N_i are the total numbers of Au NPs with a size and the partial numbers of A, B and C shapes respectively, which can be calculated from the histogram of NPs sizes with A, B and C shapes in Fig. S2d.

2. The Nernst-Planck equations[4]

Mass transfer, i.e., the movement of material from one location in solution to another, can be defined by the Nernst-Planck equations, written generally as[4],

$$J = -D\nabla C - \frac{zF}{RT} DC\nabla\phi + Cv \qquad \text{(S1)}$$

Where, for a certain species, J is the flux. D and ∇C are diffusion coefficient and concentration gradient of the species, respectively. F, R and T represent faraday constant, gas constant and absolute temperature, respectively. $\nabla\phi$ describes the potential gradient, z and C are charge and concentration of the species, respectively. v describe the velocity of a volume element motion in solution. The three terms on the right-hand side of eq. S1 represent the contributions of diffusion, migration and convection, respectively, to the total flux.

3. The ratio of the transient growth rate along the [100] direction relative to that along the [111] direction, $K_{([100]/[111])}$, of a Au NPs

The geometric shape of a group of cuboctahedral shapes have been described by the function of ratio, $R_{([100]/[111])}$, which is the growth rate along the [100] direction relative to that along the [111] direction.[5] Then, another $R_{([100]/[110])}$, the relative growth rate along the [100] dirction with respect to that along the [110] direction, have also been used to describe the morphologies from cube to rhombic dodecahedra.[6] Here, we defined a new function $K_{([100]/[111])}$ to describe the growth trends of a Au NPs, which is the ratio of transient growth rate along the [100] direction to that along the [111] direction.

During the growth process, there are two distinct reaction steps: the monomers were supplied to the NPs surface via mass transfer from the bulk solution, and then these monomers may react with the NPs.[7] For the surface reaction of Au monomers on the NPs, the flux, J, can be simplified as，

$$J = AkC_s \qquad \text{(S2)}$$

where, A is the surface area on the NPs, k is the rate constant of surface reaction, and C_s is the surface concentration of Au monomers. Here, the reverse reaction can be neglected in contrast to the forward reactions.

Additively, the flux of Au monomers can be also expressed through the growth rate (dX/dt) [7],

$$J = \frac{A}{V_M}\frac{dX}{dt} \qquad \text{(S3)}$$

where V_M is the molar volume of the Au.

Delimitate J in eqs. S2 and S3 , then growth rate can be expressed as:

$$\frac{dX}{dt} = V_M kC_s \qquad \text{(S4)}$$

Therefore, the ratio of the transient growth rate along the [100] direction relative to that along the [111] direction, $K_{([100]/[111])}$, of a Au NPs, can be obtained from eq. S4:

$$K_{([100]/[111])} = \frac{(\frac{dX}{dt})_{[100]}}{(\frac{dX}{dt})_{[111]}} = \frac{V_M k_{(100)} C_{s-(100)}}{V_M k_{(111)} C_{s-(111)}} = \frac{k_{(100)}}{k_{(111)}} \cdot \frac{C_{s-(100)}}{C_{s-(111)}} \qquad \text{(S5)}$$

According to eq. S5, $K_{([100]/[111])}$ is determined by the relative reaction rate constant $k_{(100)}/k_{(111)}$, and relative surface concentration $C_{(s-(100)/(111))} = C_{s-(100)} / C_{s-(111)}$. When the growth of Au NPs is surface reaction limited, the value of C_s approximately equals to the bulk concentration of Au monomers (C_b). Then $K_{([100]/[111])}$ can be further simplified as $k_{(100)}/k_{(111)}$. In other words, $K_{([100]/[111])}$ solely depends on the ratio of the rate constants of the different facets,

$$K_{([100]/[111])} \approx \frac{k_{(100)}}{k_{(111)}} \equiv K_{(s-[100]/[111])} \qquad \text{(S6)}$$

References:

1 F. R. Fan, D. Y. Liu, Y. F. Wu, S. Duan, Z. X. Xie, Z. Y. Jiang and Z. Q. Tian, *J. Am. Chem. Soc.*, 2008, **130**, 6949.

2 B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957.

3 C. D. Wilcox, S. B. Dove, W. D. McDavid and D. B. Greer, 1997, UTHSCSA Image Tool, a free image processing and analysis tool of the University of Texas Health Science Center, San Antonio, TX, USA. Available from the Internet at http://ddsdx.uthscsa.edu/dig/itdesc.html

4 A. J. Bard and L. R. Faulkner, Electrochemical methods: Fundamentals and applications (Second Edition), John Wiley & Sons, Inc., New York, 2001, 29.

5 Z. L. Wang, *J. Phys. Chem. B,* 2000, **104**, 1153.

6 H. L. Wu, C. H. Kuo, and M. H. Huang, *Langmuir,* 2010, **26**, 12307.

7 J. Embden, J. E. Sader, M. Davidson, and P. Mulvaney, *J. Phys. Chem. C,* 2009, **113**, 16342.