Supporting Information

pH Regulated Synthesis of Monodisperse Penta-twinned Gold Nanoparticles with High Yield

Xing Zhang, Reese Gallagher, Dong He, and Gang Chen*

AUTHOR INFORMATION

Corresponding Author

* Gang Chen - Department of Chemistry, University of Central Florida, Orlando, FL 32816 (USA); Email: gang.chen@ucf.edu

Authors

Xing Zhang - Department of Chemistry, University of Central Florida, Orlando, FL 32816 (USA)

Reese Gallagher - Department of Chemistry, University of Central Florida, Orlando, FL 32816 (USA)

Dong He – Department of Chemistry, University of Central Florida, Orlando, FL 32816 (USA); and State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, Jilin 130012 (China)

Table of Contents

Part I. Note for all the procedures	3
Part II. Supplementary Figures and Tables	4
Figure S1.	4
Figure S2.	5
Table S1	6
Table S2	7
Figure S3.	8
Figure S4	9
Figure S5	10
Table S3	11
Figure S6.	
Figure S7	13
Table S4	14
Figure S8	15
Figure S9	
Table S5	17

Part I. Note for all the procedures

All glassware was absolutely pristine. Any used glassware was washed with concentrated aqua regia (volume ratio of HCl: HNO_3 is 3:1) including stir bars. Before each synthesis, the glassware was washed with ultrapure water and dried via compressed air.

Reference pH solution: A reference solution was made to test the initial pH value of the growth solution for various amounts of acid or base added. The reason for using a reference as opposed to measuring the growth solution itself was to ensure that the growth solution came into contact with as little contamination as possible so as not to affect the seed-mediated synthesis. For the reference solution the same amount of 0.1 M CTAB, 0.1 M HAuCl₄, 10 mM AgNO₃ and reductants was used as in the growth solution (here note: seeds were not used). At different amounts of acid or base the pH was measured (see corresponding tables for amounts and values). All measurements were made using a Thermo Scientific Orion Star A211 that was calibrated before use.

List of abbreviation:

LSPR – localized surface plasmon resonance FWHM – full width at half maximum TEM – transmission electron microscopy UV-Vis - ultraviolet–visible CTAB - hexadecyltrimethylammonium bromide

Part II. Supplementary Figures and Tables

How to measure the size of bipyramid and decahedron



Figure S1. Schematic representation of the size measurement of bipyramid and decahedron.

The length of bipyramid is defined as the distance between its two apexes along the longitudinal axis, while its width is defined as the length of the projection of the pyramid base on the substrate. The length of decahedron is defined as its edge length.



Figure S2. TEM image of the product with starfish shape prepared from ascorbic acid at pH 6.39 by adding 150 μ L of NaHCO₃ (0.2 mol·L⁻¹) to the growth solution.

LSPR (nm)	FWHM (nm)	Length (nm)	Width (nm)	Aspect ratios	^[a] HCl (µL)	рН
601	63	47.1±3.4	28.0±2.3	1.69±0.14	300	0.31
636	60	56.7±3.7	28.2±1.6	2.01±0.13	225	0.42
695	66	63.5±4.4	27.0±2.0	2.36±0.14	175	0.53
727	60	67.5±4.1	27.7±2.0	2.44±0.13	150	0.61
750	59	68.6±4.2	26.8±1.8	2.57±0.14	100	0.76
773	60	71.2±4.3	26.9±1.8	2.65±0.17	60	0.98
809	60	78.3±3.7	26.0±1.9	3.01±0.19	20	1.45
835	68	78.9±3.6	24.0±2.4	3.32±0.32	10	1.73

Table S1. LSPR, FWHM, dimensions, and aspect ratios of the penta-twinned nanoparticles prepared from ascorbic acid at different pH.

[a] The concentration of HCl solution is 12.7 mol·L $^{\cdot 1}$

LSPR (nm)	FWHM (nm)	Length (nm)	Width (nm)	Aspect ratios	^[b] NaHCO ₃ (µL)	рН
570	^[d] 57	37.4±3.0	26.1±1.8	1.44±0.13	40	3.11
605	^[d] 62	52.1±4.7	30.1±1.8	1.74±0.17	60	3.42
640	77	56.8±4.7	28.8±1.5	1.97±0.15	80	4.37
665	81	65.4±4.0	29.5±1.1	2.22±0.12	85	5.27
705	99	68.3±4.2	28.0±1.1	2.44±0.16	88	5.39
745	86	77.8±3.8	27.8±2.0	2.81±0.19	90	5.45
780	54	77.8±2.0	26.8±1.2	2.91±0.14	95	5.60
800	71	82.9±3.2	26.9±2.3	3.11±0.32	110	5.88
/	/	/	/	/	120	5.96
/	/	/	/	/	140	6.18
/	/	/	/	/	160	6.34
^[c] 575	93	/	46.4±3.5	/	200	6.55

 $\label{eq:s2.LSPR, FWHM, dimensions, and aspect ratios of the penta-twinned nanoparticles prepared from hydroquinone at different pH.^{[a]}$

[a] Some sample data are not available because of the irregular shape of the product or because the product is a mixture.

[b] The concentration of NaHCO $_3$ solution is 0.2 mol·L⁻¹.

[c] Decahedra were formed at this reaction condition.

[d] The data are derived from the curve fitting results.



Figure S3. FWHM of the LSPR peaks of the penta-twinned nanoparticles synthesized from different reductants vs the pH values of the growth solution.



Figure S4. UV-Vis spectra of penta-twinned nanoparticles prepared from resorcinol at different pH: 6.94 (black), 7.71 (red), 8.15 (green), 8.57 (blue), 9.05 (cyan), 9.19 (magenta), 9.52 (yellow), and 9.73 (dark yellow).



Figure S5. TEM images of penta-twinned nanoparticles prepared from resorcinol at different pH. (a-h) the pH values of the growth solutions are 6.94, 7.71, 8.15, 8.57, 9.05, 9.19, 9.52, and 9.73, respectively. All scale bars are 100 nm.

LSPR (nm)	FWHM (nm)	Length (nm)	Width (nm)	Aspect ratios	^[b] Na ₂ CO ₃ (µL)	рН
535	^[d] 76	24.8±1.4	18.9±1.1	1.31±0.06	55	6.94
581	^[d] 60	36.3±1.6	24.8±1.3	1.46 ± 0.08	70	7.71
654	45	56.4±2.7	26.5±1.7	2.13±0.12	80	8.15
715	46	63.8±2.0	25.4±1.1	2.51±0.13	90	8.57
786	56	74.2±3.2	24.3±1.7	3.07±0.26	110	9.05
801	85	75.9±3.8	25.9±2.3	2.96±0.32	120	9.19
722	^[d] 131	/	/	/	150	9.52
^[c] 582	^[d] 113	/	40.9±3.95	/	180	9.73

Table S3. LSPR, FWHM, dimensions, and aspect ratios of the penta-twinned nanoparticles prepared from resorcinol at different pH.^[a]

[a] Some sample data are not available because of the irregular shape of the product or because the product is a mixture.

[b] The concentration of Na_2CO_3 solution is 0.2 mol·L⁻¹.

[c] Decahedra were formed at this reaction condition.

[d] The data are derived from the curve fitting results.



Figure S6. UV-Vis spectra of penta-twinned nanoparticles prepared from phloroglucinol at different pH: 6.68 (black), 7.06 (red), 7.41 (green), 7.70 (blue), 7.93 (cyan), 8.18 (yellow), 8.36 (dark yellow), and 8.49 (navy).



Figure S7. TEM images of penta-twinned nanoparticles prepared from phloroglucinol at different pH. (a-h) the pH values of the growth solutions are 6.68, 7.06, 7.41, 7.70, 7.93, 8.18, 8.36, and 8.49, respectively. All scale bars are 100 nm.

LSPR (nm)	FWHM (nm)	Length (nm)	Width (nm)	Aspect ratios	^[a] Na ₂ CO ₃ (µL)	рН
530	^[b] 90	23.8±1.1	18.6±1.2	1.28±0.07	50	6.68
563	^[b] 62	35.4±1.7	26.0±1.0	1.36±0.06	60	7.06
578	^[b] 57	40.2±2.0	26.8±0.9	1.50 ± 0.07	70	7.41
610	57	49.2±1.7	28.1±0.6	1.74 ± 0.07	80	7.70
673	42	60.9±1.4	26.4±1.5	2.31±0.11	90	7.93
761	56	68.7±2.6	24.2±1.3	2.85±0.17	110	8.18
769	82	71.1±1.7	24.8±1.9	2.88±0.22	120	8.36
778	114	71.0±2.2	25.3±1.4	2.82±0.20	130	8.49

Table S4. LSPR, FWHM, dimensions, and aspect ratios of the penta-twinned nanoparticles prepared from phloroglucinol at different pH.

[a] The concentration of Na_2CO_3 solution is 0.2 mol·L⁻¹.

[b] The data are derived from the curve fitting results.



Figure S8. UV-Vis spectra of penta-twinned nanoparticles prepared from phenol with different amount of seeds. The corresponding volume of seeds are: 1.0 mL (black), 0.75 mL (red), 0.65 mL (blue), 0.6 mL (green), 0.5 mL (cyan), 0.4 mL (magenta), 0.25 mL (olive), 0.18 mL (dark yellow), 0.125 mL (dark cyan), 0.1 mL (orange), and 0.06 mL (violet).



Figure S9. TEM images of penta-twinned nanoparticles prepared from phenol with different amount of seeds. (a-j) The volume of seeds are 1.0 mL, 0.75 mL, 0.65 mL, 0.6 mL, 0.5 mL, 0.25 mL, 0.18 mL, 0.125 mL, 0.1 mL and 0.06 mL, respectively. All scale bars are 100 nm.

LSPR (nm)	FWHM (nm)	Length (nm)	Width (nm)	Aspect ratios	Seeds (mL)
567	[b] 58	39.1±3.4	26.1±1.8	1.50±0.08	1.00
604	58	47.4±3.4	26.2±1.5	1.81 ± 0.10	0.75
642	49	53.3±2.9	25.4±1.6	2.10±0.11	0.65
667	47	57.7±3.0	25.5±1.5	2.26±0.12	0.60
710	49	67.9±3.1	26.0±1.5	2.61±0.13	0.50
786	53	95.8±2.8	32.3±2.0	2.89±0.16	0.25
822	59	106.7±3.1	34.2±2.0	3.12±0.16	0.18
858	65	130.4±3.2	39.3±2.4	3.33±0.19	0.125
880	72	144.4±4.9	43.9±4.2	3.32±0.31	0.10
945	97	174.8±5.9	46.8±3.1	3.75±0.29	0.06

Table S5. LSPR, FWHM, dimensions, and aspect ratios of the penta-twinned nanoparticles prepared from phenol with different amount of seeds.^[a]

[a] Growth conditions

Chemicals	Concentration (mM)	Volume
СТАВ	100	10 mL
HAuCl ₄	100	50 µL
AgNO ₃	10	200 µL
Na ₂ CO ₃	200	140 μL
Phenol	100	150 μL
Seeds	/	various amounts of seed s

[b] The data is derived from the curve fitting results.