Efficient and facile synthesis of gold nanorods with finely tunable plasmonic peaks from visible to near-IR range

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EXPERIMENTAL SECTION

Seed-mediated GNRs synthesis by using 1,2,4- trihydroxybenzene as a reductant

The seeds solution for GNRs growth was prepared as follows: 0.125 mL of $HAuCl_4$ solution (0.01 M) was added to 5 mL of CTAB (0.10 M), the solution was mixed by inversion. Then 0.3 mL of fresh $NaBH_4$ solution (0.01 M) was injected into the Au(III)-CTAB solution under vigorous stirring for 2 min. The solution color changed from yellow to pale brown-yellow color. The seeds solution was aged at room temperature for 1 h before use. To prepare the growth solution, 40 µL of silver nitrate (0.02 M) and 0.3 mL of $HAuCl_4$ (0.01 M) solutions were added into 7.125 mL of CTAB solution (0.1M). Then 40 µL of 1,2,4-trihydroxybenzene (0.1 M) aqueous solution was added, and the solution was mixed by hand-stirred until the color changed from yellow to reddish purple. Finally, a certain amount of seeds solution was injected into the growth solution. The resultant mixture was mixed by hand-stirred and left undisturbed at 30 °C for 12 h for GNRs growth.

Length and width statistical analysis

All samples were analysed over 100 particles. And corresponding length and width distributions were shown in Figure S8. Aspect ratios were calculated using the size of length dividing width, and the LSPR was plotted as a function of aspect ratio.

RESULTS AND DISCUSSION

Forming dogbone-like GNRs using trihydroxybenzene as reducer

In the case of using reducers of trihydroxybenzene, GNRs have dogbone shape. Similar dogbone-like GNRs were also reported when using ascorbic acid as the reducing agent. several literatures[1, 2] proposed the mechanism. One explanation is that with the overgrowth of GNRs, the {111} phase at the end of the rods break out of the CTAB shell to enlarge into the dogbone shape.[2] Another explanation is that the growth of GNRs involves preferential deposition of silver-containing species.

Therefore, once all available silver is used up, further growth of the rods will be unconstrained by the passivated sheath, causing a transition from the cylindrical rod to the dogbone morphology.[1] When we attempted to prepare GNRs by adding seeds to the growth solution, we found that GNRs with the dogbone morphology can be easily obtained with a small number of seeds**.** However, silver concentration seems to have little effect on the formation of the dogbone morphology. Therefore, we attributed the dogbone morphology to the overgrowth of GNRs (Figure S11) with the {111} phase at the end of the rods breaks out of the CTAB.

References:

1. Xu, X.; Cortie, M. B., Shape Change and Color Gamut in Gold Nanorods, Dumbbells, and Dog Bones. *Advanced Functional Materials* **2006,** 16, (16), 2170-2176.
2. Gou, L.; Murphy, C. J., Fine-Tuning the Shape of Gold Nanorods. *Chemistry of Materials* **2005,** 17, (14), 3668-3672.

Figures

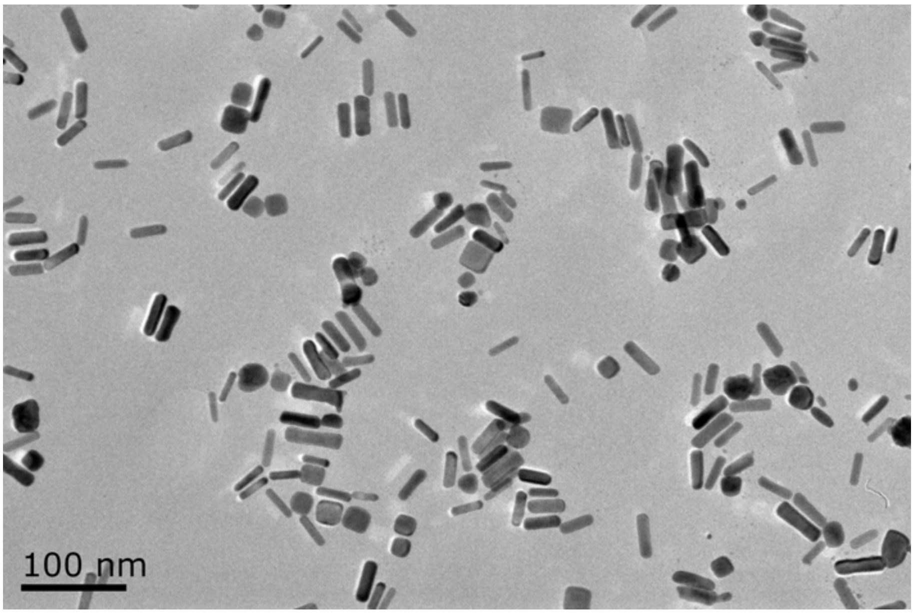


Figure S1. TEM image of ascorbic acid-reduced GNRs via the one-pot method. GNRs preparation condition: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [$AgNO_3$] = 0.11 mM, [ascorbic acid] = 0.6 mM, and [$NaBH_4$] = 0.00066 mM in a total volume of 7.6 mL.

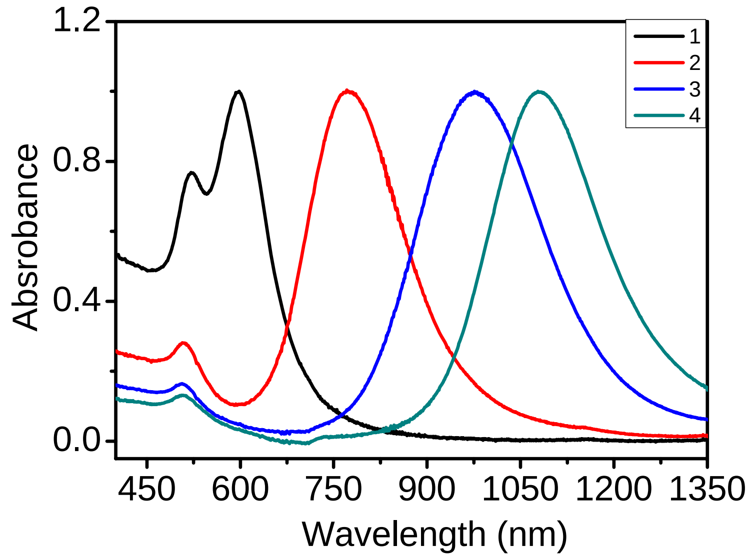


Figure S2. VIS-NIR spectra of hydroquinone-reduced GNRs at different $AgNO_3$ concentrations: (1) 0.08, (2) 0.16, (3) 0.21, and (4) 0.37 mM. GNR preparation conditions: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [hydroquinone] = 5.26 mM, and [$NaBH_4$] = 0.0017 mM in a total volume of 7.6 mL.

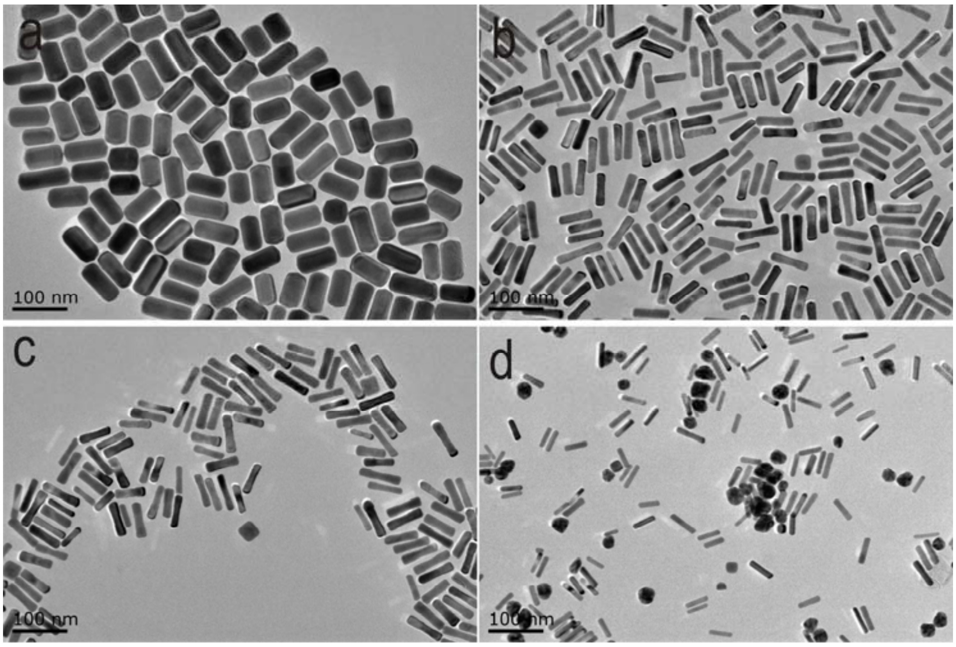


Figure S3. TEM images of 1,2,3-trihydroxybenzene-reduced GNRs at different $AgNO_3$ concentration. GNR preparation conditions: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [1,2,3-tridydroxybenzene] = 0.36 mM, and [$NaBH_4$] = 0.0039 mM in a total volume of 7.6 mL. The $AgNO_3$ concentrations are (a) 0.052, (b) 0.11, (c) 0.16, and (d) 0.33 mM.

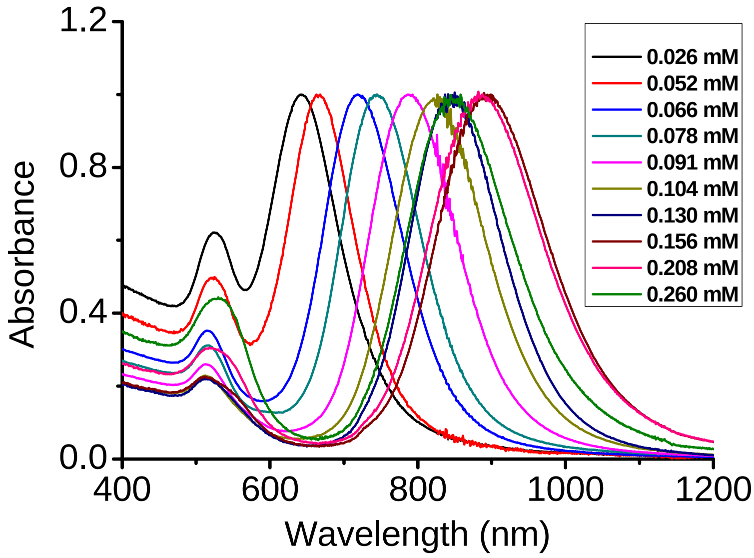


Figure S4. VIS-NIR spectra of 1,2,3-trihydroxybenzene-reduced GNRs at different $AgNO_3$ concentration. GNRs preparation conditions: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [1,2,3-tridydroxybenzene] = 0.36 mM, and [$NaBH_4$] = 0.0039 mM in a total volume of 7.6 mL.

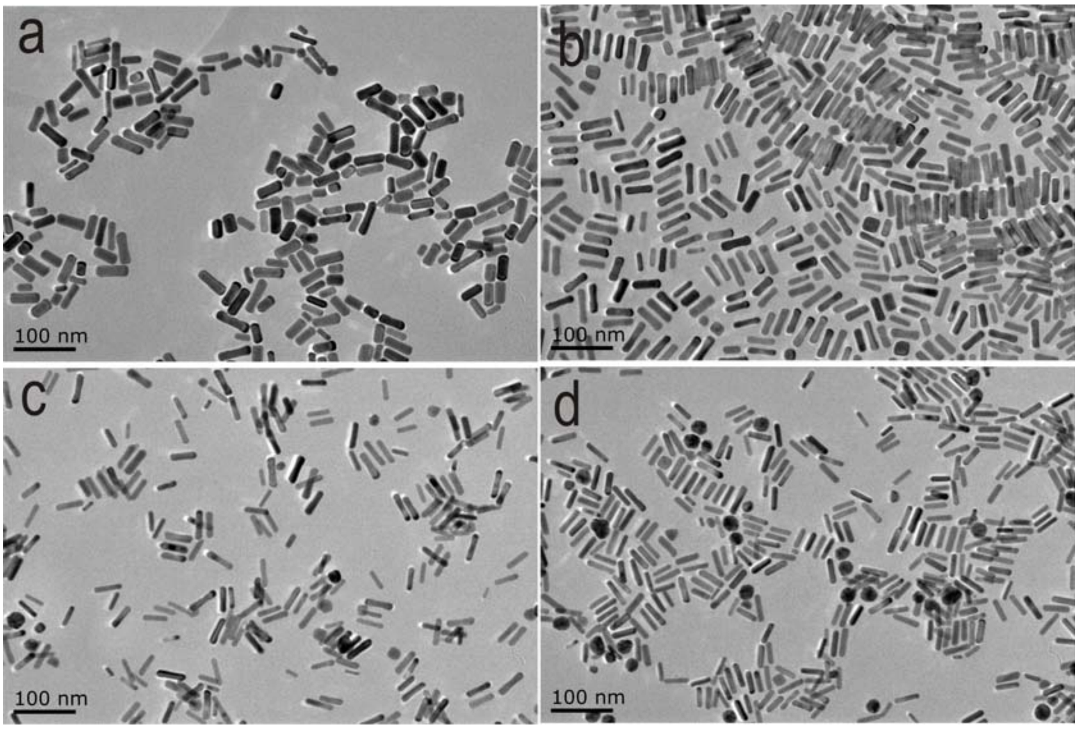


Figure S5. TEM images of 1,2,4-trihydroxybenzene-reduced GNRs at different $AgNO_3$ concentration. GNRs preparation conditions: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [1,2,4-tridydroxybenzene] = 0.8 mM, and [$NaBH_4$] = 0.00067 mM in a total volume of 7.6 mL. The $AgNO_3$ concentrations are (a) 0.027, (b) 0.055, (c) 0.11, and (d) 0.135 mM.

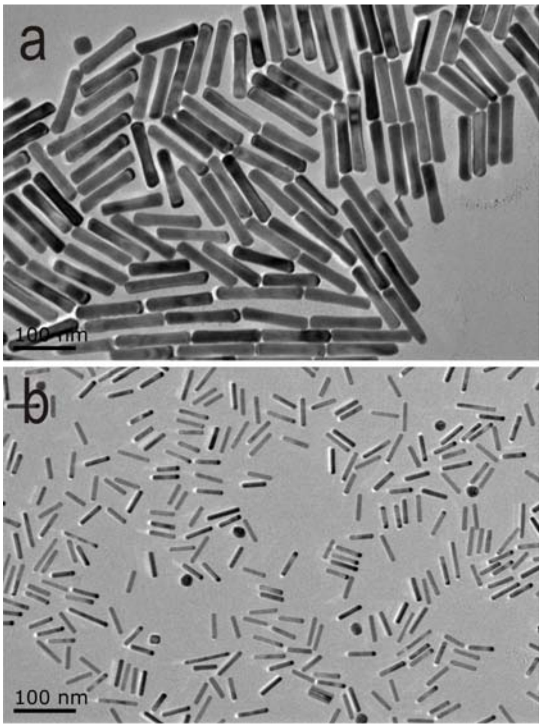


Figure S6. TEM images of hydroquinone-reduced GNRs with (a) 0.00033 mM and (b) 0.0017 mM $NaBH_4$. Other additive concentrations: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [hydroquinone] = 5.26 mM, [$AgNO_3$] = 0.21 mM, in a total volume of 7.6 mL.

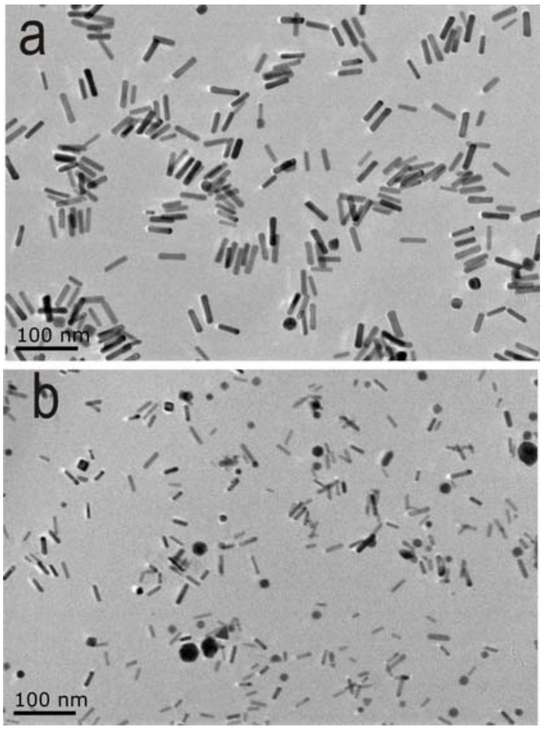
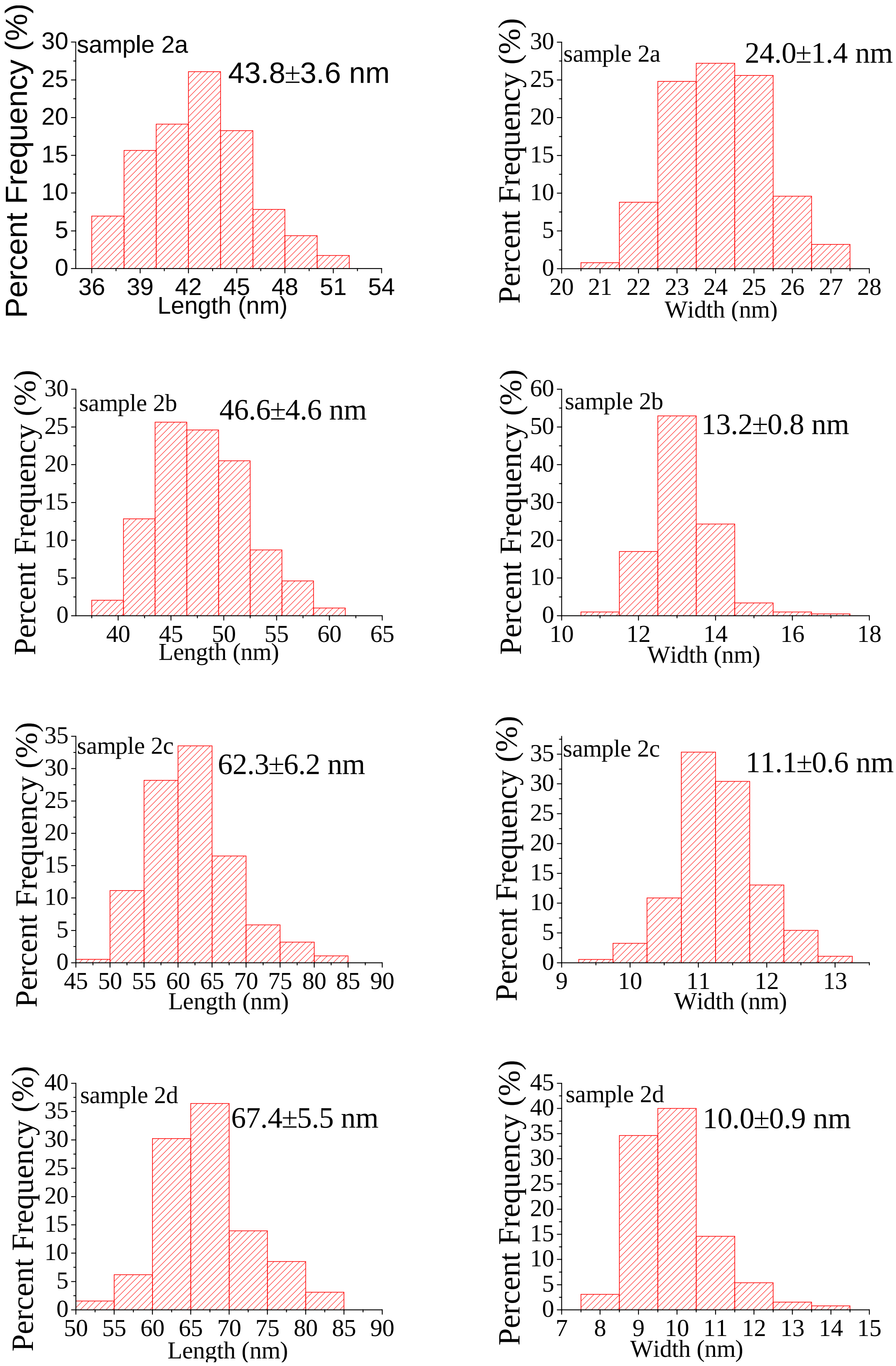


Figure S7. TEM images of 1,2,4-trihydroxybenzene-reduced GNRs at (a) 0.00066 and (b) 0.0040 mM $NaBH_4$. Concentrations of other additives: [CTAB] = 0.1 M, [$HAuCl_4$] = 0.40 mM, [1,2,4-trihydroxybenzene] = 0.80 mM, and [$AgNO_3$] = 0.11 mM in a total volume of 7.6 mL.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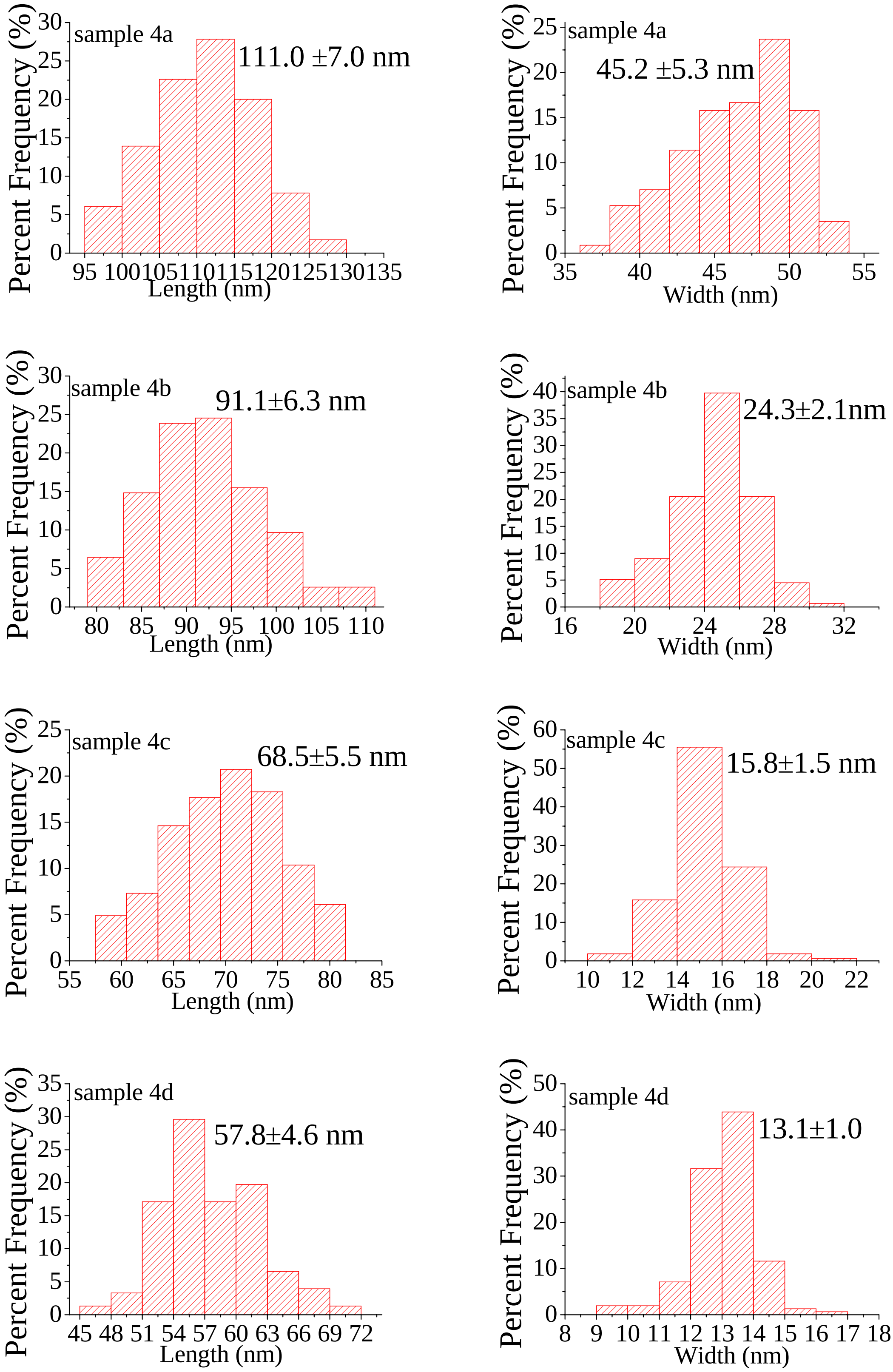
Percent Frequency (%)
Length (nm)
sample 2a
24.0±1.4 nm
Percent Frequency (%)
Width (nm)
sample 2b
46.6±4.6 nm
Percent Frequency (%)
Length (nm)
sample 2b
13.2±0.8 nm
Percent Frequency (%)
Width (nm)
sample 2c
62.3±6.2 nm
Percent Frequency (%)
Length (nm)
sample 2c
11.1±0.6 nm
Percent Frequency (%)
Width (nm)
sample 2d
67.4±5.5 nm
Percent Frequency (%)
Length (nm)
sample 2d
10.0±0.9 nm
Percent Frequency (%)
Width (nm)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Length (nm)
95 100 105 110 115 120 125 130 135
sample 4a
45.2 ±5.3 nm
Percent Frequency (%)
Width (nm)
sample 4b
91.1±6.3 nm
Percent Frequency (%)
Length (nm)
sample 4b
24.3±2.1nm
Percent Frequency (%)
Width (nm)
sample 4c
68.5±5.5 nm
Percent Frequency (%)
Length (nm)
sample 4c
15.8±1.5 nm
Percent Frequency (%)
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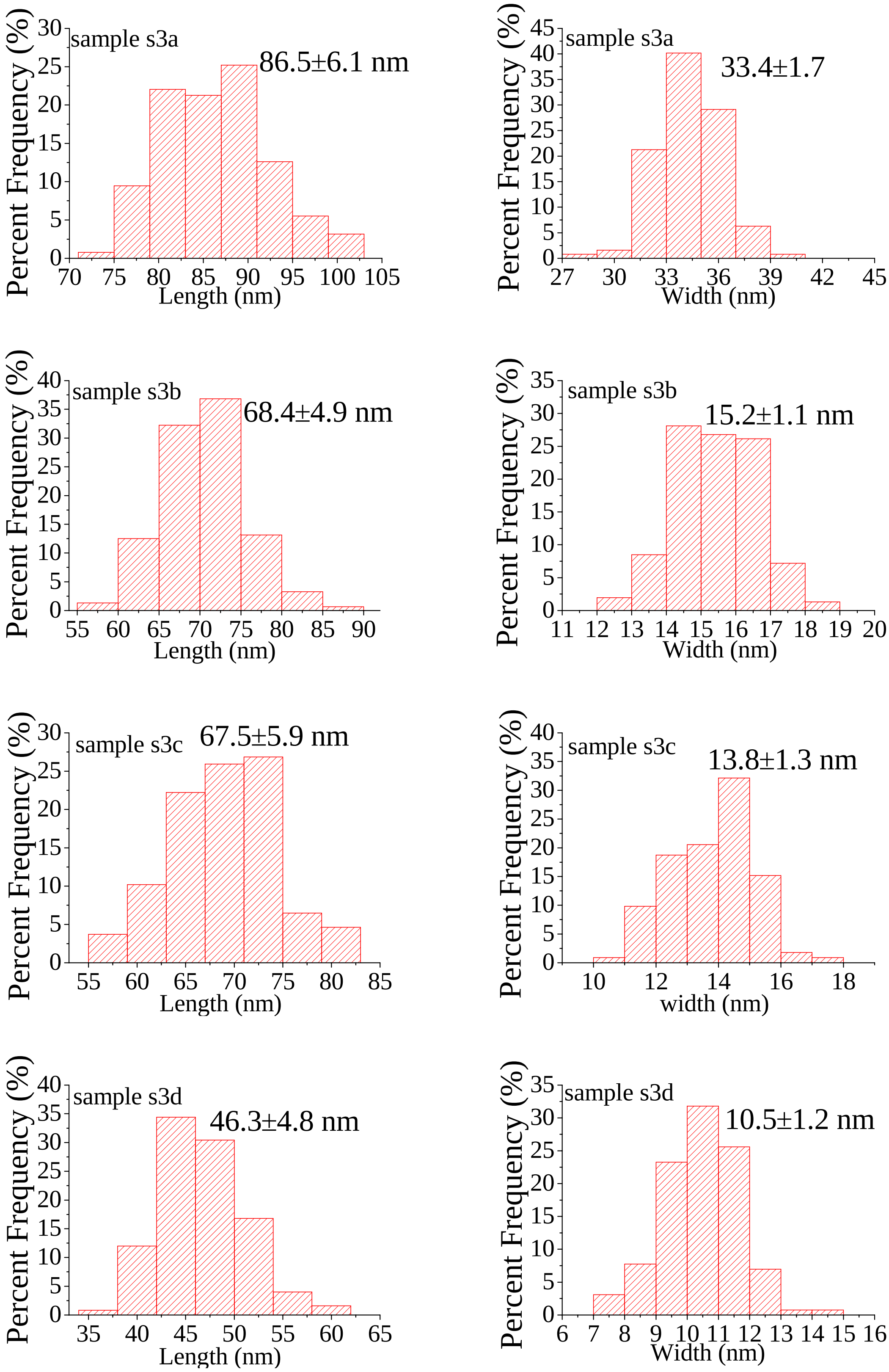
sample 4d
57.8±4.6 nm
Percent Frequency (%)
Length (nm)
sample 4d
13.1±1.0
Percent Frequency (%)
Width (nm)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Length (nm)
sample s3a
33.4±1.7
Percent Frequency (%)
Width (nm)
sample s3b
68.4±4.9 nm
Percent Frequency (%)
Length (nm)
sample s3b
15.2±1.1 nm
Percent Frequency (%)
Width (nm)
sample s3c
67.5±5.9 nm
Percent Frequency (%)
Length (nm)
sample s3c
13.8±1.3 nm
Percent Frequency (%)
width (nm)
sample s3d
46.3±4.8 nm
Percent Frequency (%)
Length (nm)
sample s3d
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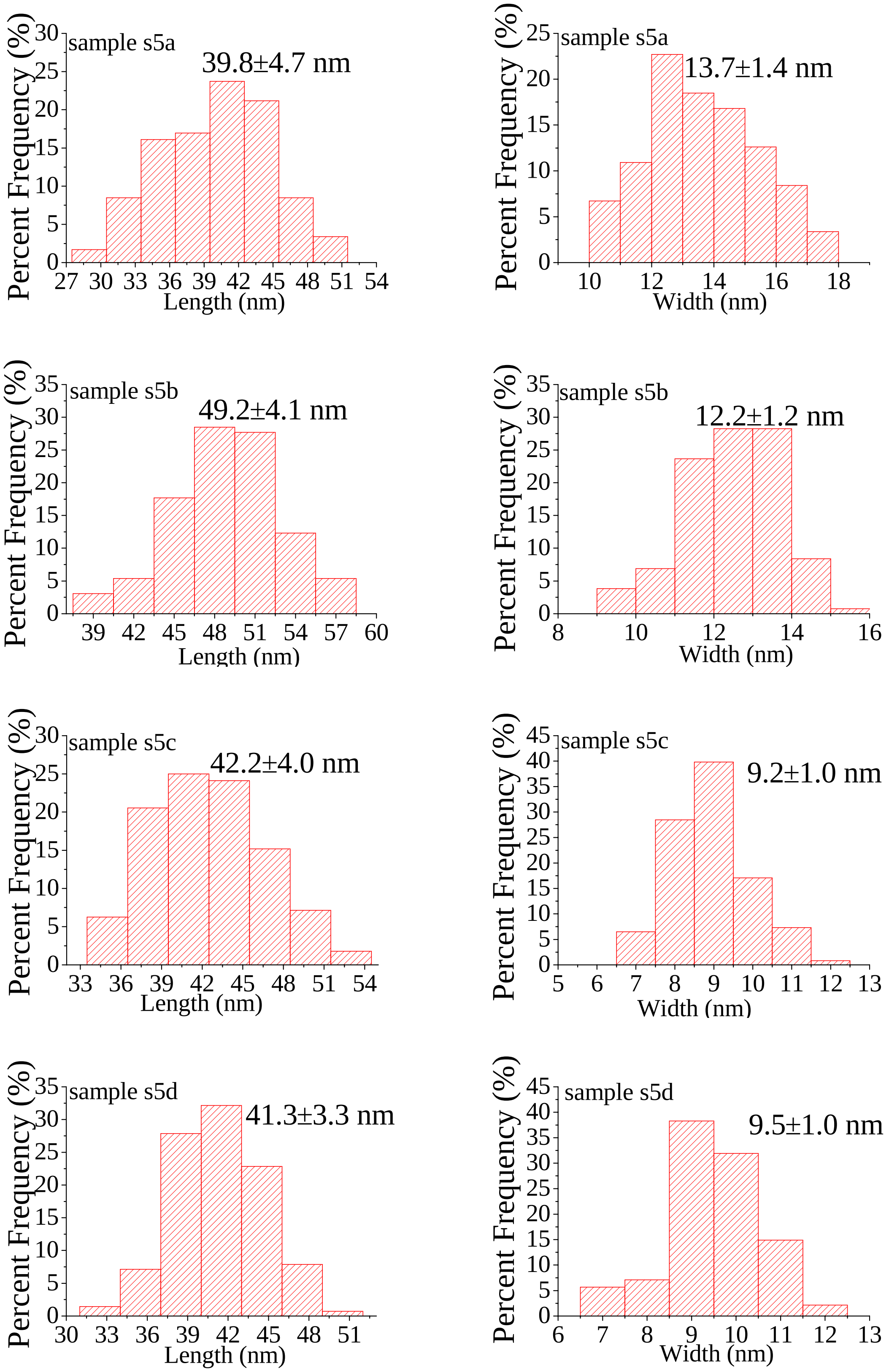
Percent Frequency (%)
Width (nm)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Width (nm)
sample s5b
49.2±4.1 nm
Percent Frequency (%)
Length (nm)
sample s5b
12.2±1.2 nm
Percent Frequency (%)
Width (nm)
sample s5c
42.2±4.0 nm
Percent Frequency (%)
Length (nm)
sample s5c
9.2±1.0 nm
Percent Frequency (%)
Width (nm)
sample s5d
41.3±3.3 nm
Percent Frequency (%)
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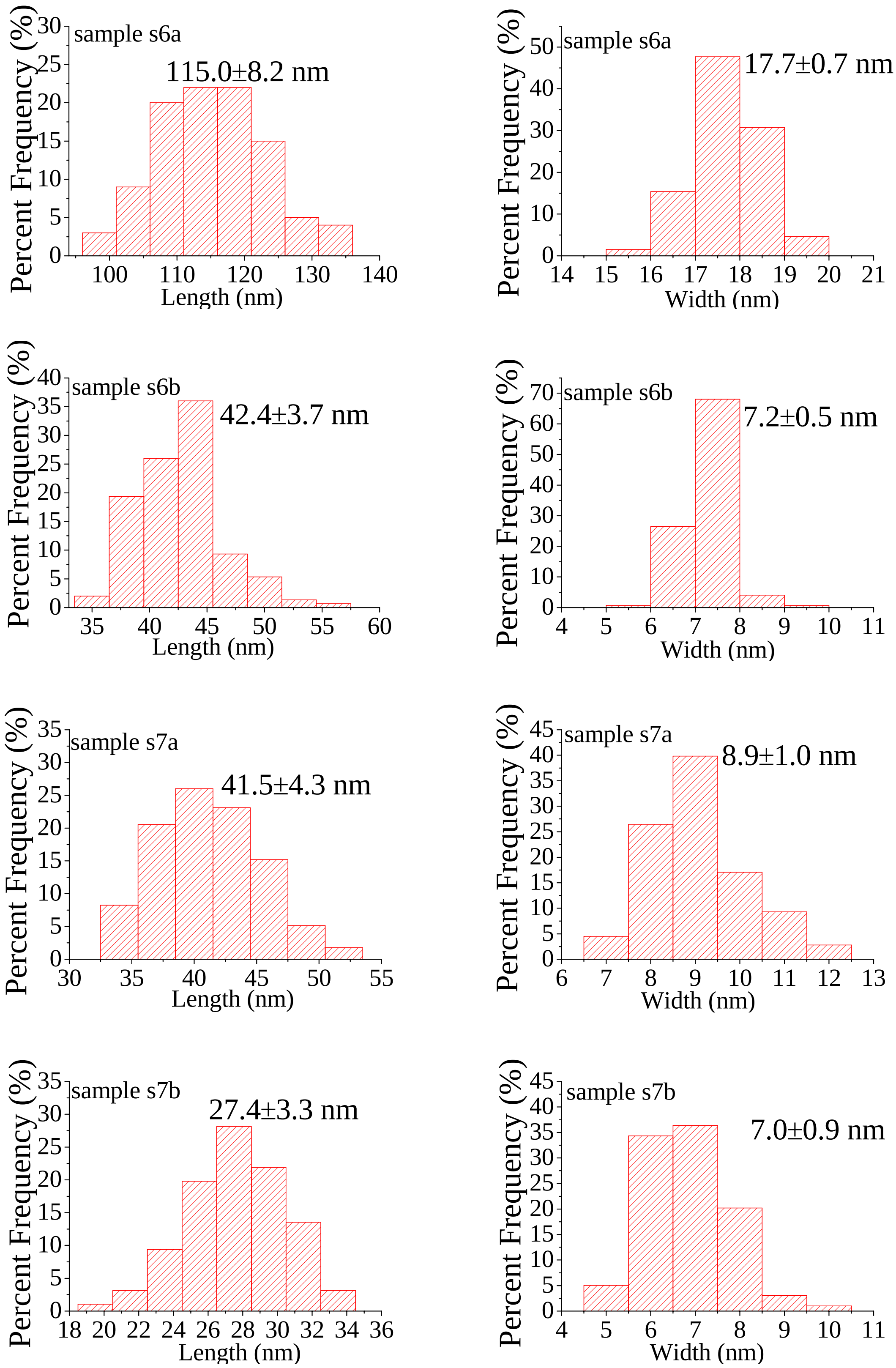
Percent Frequency (%)
Width (nm)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Length (nm)
sample s6a
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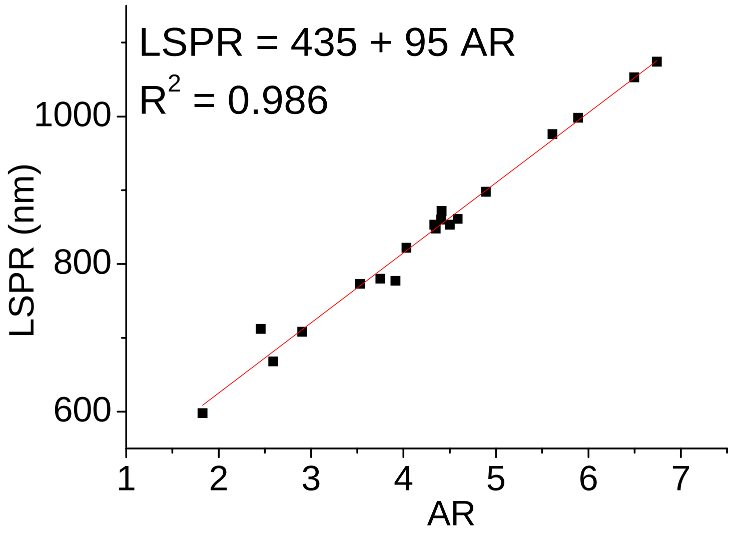
Percent Frequency (%)
Width (nm)
sample s6b
42.4±3.7 nm
Percent Frequency (%)
Length (nm)
sample s6b
7.2±0.5 nm
Percent Frequency (%)
Width (nm)
sample s7a
41.5±4.3 nm
Percent Frequency (%)
Length (nm)
sample s7a
8.9±1.0 nm
Percent Frequency (%)
Width (nm)
sample s7b
27.4±3.3 nm
Percent Frequency (%)
Length (nm)
sample s7b
7.0±0.9 nm
Percent Frequency (%)
Width (nm)

(a)



(b)

Figure S8. (a) Statistical analysis of the lengths and widths of GNRs; (b) a fitting curve using LSPR as a function of AR.

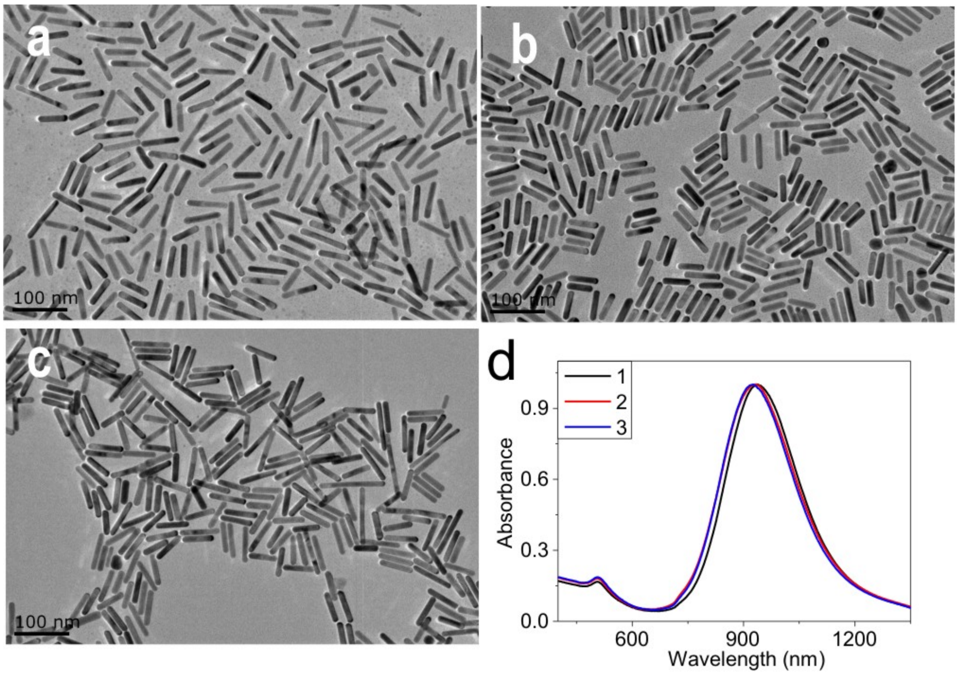


Figure S9. TEM images of GNRs initiated by three different batches of freshly prepared $NaBH_4$ solutions (a-c) and (d) corresponding LSPR spectra.

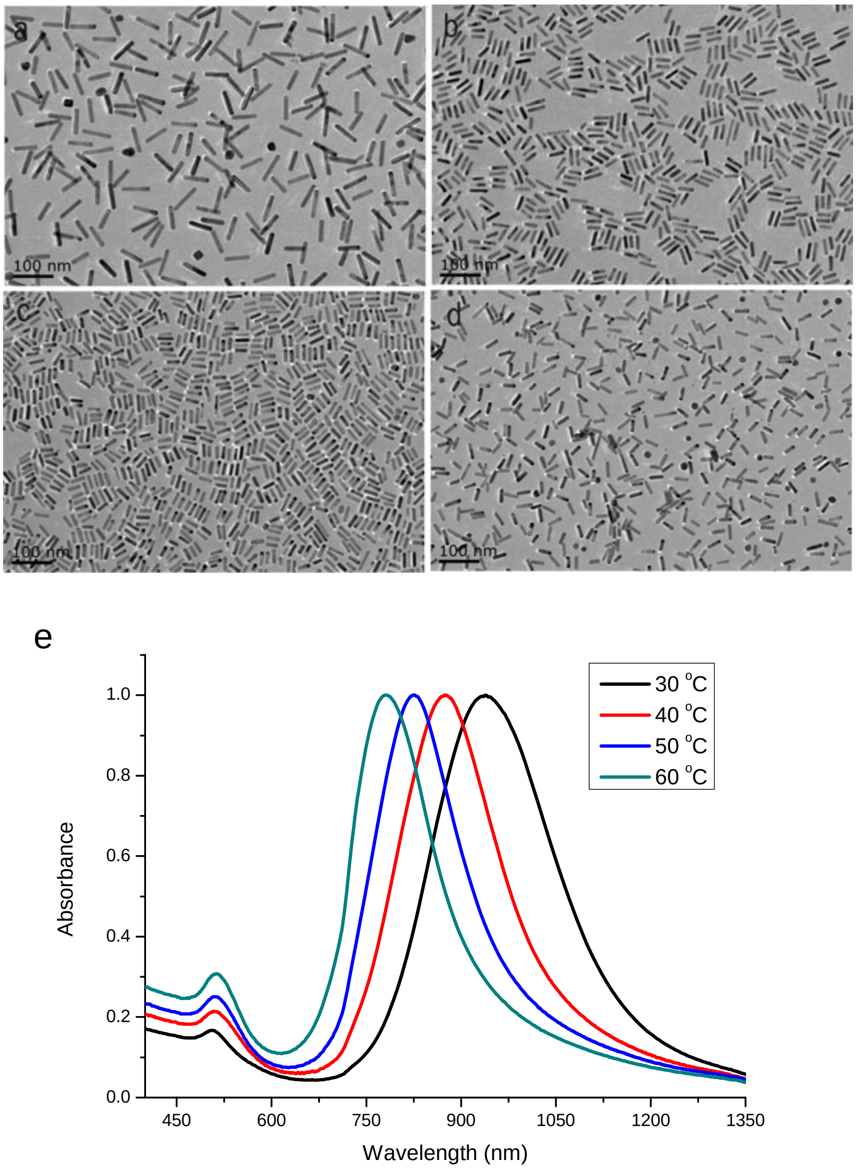


Figure S10. TEM images of GNRs produced only with different temperatures: (a) 30, (b) 40, (c) 50 and (d) 60 °C; (e) corresponding LSPR peaks of GNRs.

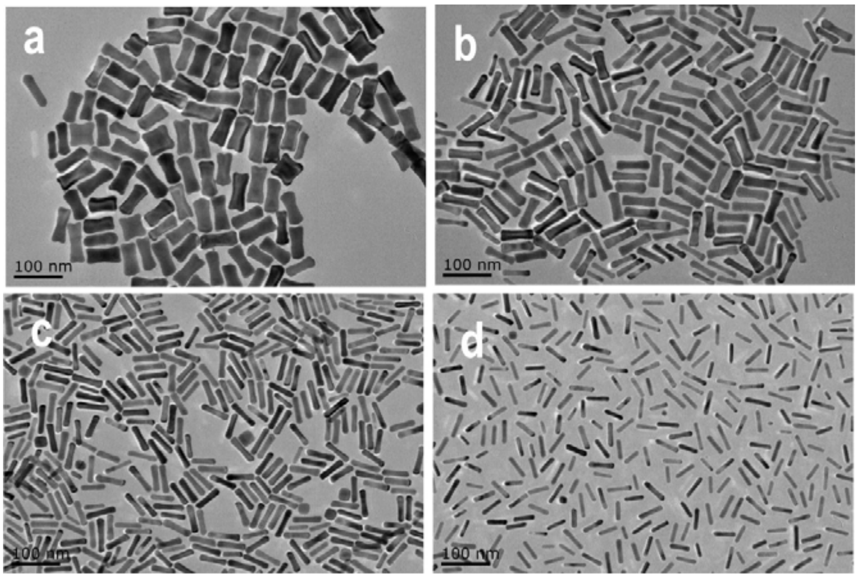


Figure S11 TEM images of 1,2,4-trihydroxybenzene-reduced GNRs with different seeds (seeds increase gradually from panels a to d)