Supplementary information

Reshaping anisotropic gold nanoparticles through oxidative etching: the role of the surfactant and nanoparticle surface curvature

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Materials

All chemicals were purchased from Sigma-Aldrich and were used as received. All synthesis were carried out in Milli-Q water.

Gold nanorods:

6.4 mg sodium borohydride ($NaBH_4$) was disolved in 10 mL ice-cold water right before use. 25 μL of 100 mM $HAuCl_4$ was added into 10 mL 0.1 M CTABr solution. While vigorously

stirring the mixture, 0.6 mL ice-cold $NaBH_4$ solution was injected, resulting in the color of the mixture changing from golden to brownish yellow. Continuing vigorous stirring for 60 seconds, the solution was left at room temperature for 2 hours. Later this solution was used as seeds.

25 µL of 100 mM $HAuCl_4$ was mixed with 5 mL 0.1 M CTABr solution. After adding various amounts of 20 mM $AgNO_3$, 27.5 µL of 100 mM ascorbic acid was added into the growth solution, leading to a color change from golden yellow to colorless. The final step was to add various amount of the seed solution into the growth solution. Leaving the solution at 28 ºC, the color of these solutions gradually changed within 60 minutes. For different amount of $AgNO_3$ and seeds solution added into the growth solution, the dimensions of nanorods thus their SPRs were different.

Gold bipyramids:

Seed solution was prepared exactly as described in literature[20]. Briefly, 0.3 mL of ice-cold freshly prepared 100 mM $NaBH_4$ solution was added drop by drop into 10 mL $HAuCl_4$ (0.125 mM) and CTABr (100 mM, 10 ml) under vigorous stirring at room temperature. The solution turned into brownish yellow. Stirring was stopped after 30 s and the seeds solution was left in 40 ºC water bath for 7 days in the dark.
Instead of using hydroquinone to reduce gold, we used ascorbic acid. Briefly, 400 µL of $AgNO_3$ (4 mM) was added into 10 mL $HAuCl_4$ (1 mM) and CTABr (100 mM). Following injection of 75 µL of ascorbic acid (100 mM) into the growth solution under vigorous stirring, 75 µL of seed solution was added. The solution was further stirred for 60 s and was left in 40 ºC water bath in the dark overnight. Due to the different reducing agent used during synthesis, the resulted suspension was a mixture of small gold nanorods (~30%) and large gold bipyramids (~70%) of very different volumes. Bipyramids were further separated and purified by centrifuging.

Gold prisms:

The synthesis of gold prisms was strictly following the protocol described in literature[14]. Briefly, gold nanoparticle seeds were prepared by injecting 0.25 mL of ice-cold 100 mM $NaBH_4$ into premixed solution that contained 0.25 mL of 10 mM $HAuCl_4$, 0.25 mL of 10 mM sodium citrate and 9 mL Milli-Q water under vigorous stirring. Stirring was continued for another 60 seconds after addition og $NaBH_4$. The resulting solution was aged for 2 hours before use. Three growth solutions were prepared. The first two solutions (1 and 2) prepared by mixing 125 µL of 10 mM $HAuCl_4$, 25 µL of 100 mM NaOH, 25 µL of 100 mM ascorbic acid, and 4.5 mL of 50 mM CTABr solution. The third growth solution (3), prepared by mixing 0.42 mL of 10 mM $HAuCl_4$, 83 µL of 100 mM NaOH, 83 µL of 100 mM ascorbic acid, and 15 mL of 50 mM CTABr solution. Finally, KI solution was added in the previously prepared growth solutions to reach a

final iodide concentration of 50 µM. The final step was adding 0.5 mL of seed solution to the growth solution 1. After gentle shaking, 0.5 mL of the growth solution 1 was immediately added to 2. Following gentle shaking, the entire solution 2 was mixed with 3. After mixing, the final solution was left still overnight.After the suspension turned into deep magenta-purple, it was further purified by Al_2O_3 filters of 100 nm pore size, leaving gold nanoprisms attached onto the filters. Gold prisms were later collected by sonicating the used Al_2O_3 filters in 10 mM CTABr solution for 30 minutes.

Etching in solutions

Briefly, 1.5 mL of a suspension of each GNP sample was centrifuged and was washed twice with 500 µM CTABr or 50 mM CTACl solution into about 20 µL by removing the supernatant. For etching experiments, 1.5 mL etchant solution was added into 20 µL GNP suspension.

Etching on Si substrates

Briefly, 0.2 mL of a suspension of NRs (118±10 nm × 33±4 nm, 100 mM CTABr) was firstly diluted to 1mL using MilliQ water, then was centrifuged into about 20 µL by removing the supernatant. Afterwards, it was further diluted to 1.5 mL with MilliQ water, resluting a final CTABr concentration of about 270 µM. 50 µL of such solution was drop-casted on a Si chip (5 mm × 5 mm) and was dried. Later on, the sample was washed with MilliQ water for several times and finally was dried in Nitrogen flow. After a SEM measurement, the sample was immersed into a etching solution containing 10 mM CTABr, 30 mM H_2O_2 and 30 mM HCl for an hour. Another SEM measurement was carried out after etching, shown in Fig. S3.

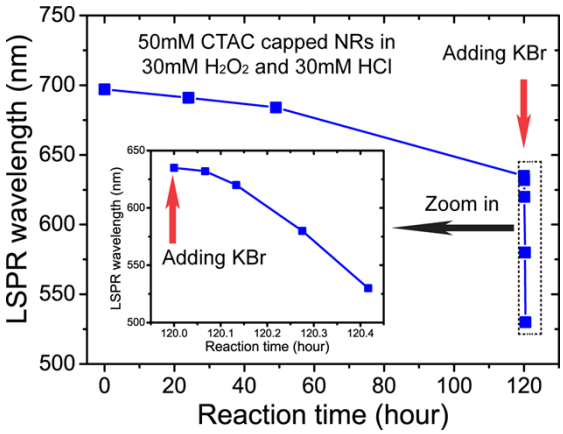

Figure S1. Accelerated etching by adding 100 mM KBr into CTACl capped NRs.

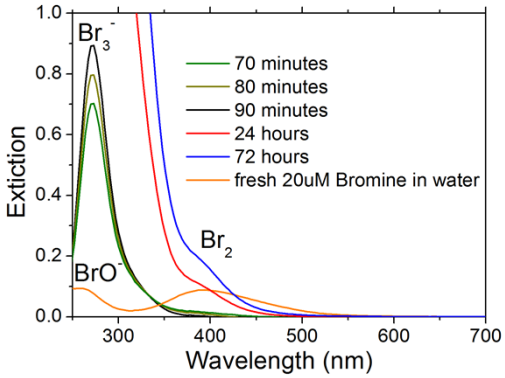

Figure S2. UV-Vis spectra of freshly prepared 20 μM Br_2 water solution (the orange line) and the aged etching solution (50 mM CTABr, 30 mM H_2O_2 and 30 mM HCl) at different time after preparation. The absorption peaks at 260 nm, 265 nm and 390 nm indicate BrO^-, Br_3^-, and Br_2, respectively.

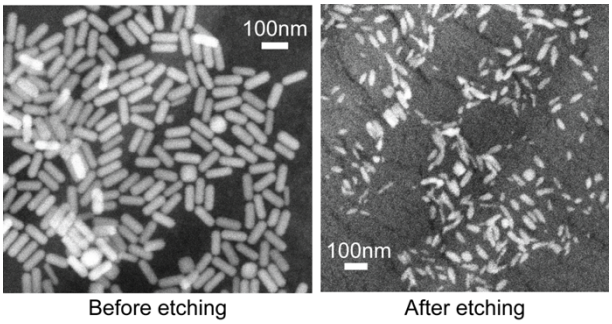

Figure S3. SEM images on large NRs (118±10 nm × 33±4 nm) on Si substrate before and after etching for an hour (10 mM CTABr, 30 mM H_2O_2 and 30 mM HCl).

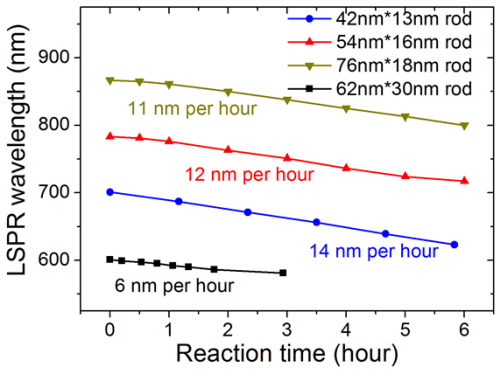

Figure S4. The LSPR shift rates of NRs under the same etching conditions scale with diameters of NRs at 10 mM CTABr concentration. The nanorods used in this experiment have dimensions

of 42±4 nm×13±3 nm, 54±6 nm×16±3 nm, 76±18 nm×18±3 nm and 62±6 nm×30±3 nm, respectively.

Time in hours	NRs length	NRs thickness	NRs length	NRs thickness	BPs length	BPs thickness
0	42±4 nm	13±3 nm	62±6 nm	30±3 nm	108±5 nm	29±3 nm
2	38.7±4.2 nm	11.8±2 nm	58.4±7.3 nm	29.1±4.4 nm	58.9±9 nm	27±6 nm
4	32±4.5 nm	9.8±2.2 nm	53±6.7 nm	27.5±3.6 nm	38.2±9.4 nm	25.8±6.5 nm

Table S1. Average dimensions measured at different time during etching of NRs (42 nm×13 nm and 62 nm×30 nm) and BPs (108 nm×29 nm) in 0.5 mM CTABr solutions.