Electronic Supplementary Material (ESI) for Nanoscale.

From gold nanobipyramids to nanojavelins for a precise tuning of the Plasmon resonance to the infrared wavelengths. Experimental and theoretical aspects.

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Experimental section:

General conditions:

Tetrachloroauric acid trihydrate (99,9%) and silver nitrate were purchased from Alfa Aesar, while CTAB (cetyltrimethylammonium bromide, 99%), CTAC (cetyltrimethylammonium chloride solution 25% in water), citric acid (99.5%), ascorbic acid (99%), sodium borohydride (99%), 2-methyl-8-hydroxyquinoline (MHQL, 98%), 2-naphthol (99%) and 8-hydroxyquinoline (HQL, 99%) were purchased from Aldrich. The 8-hydroxyquinoline and its 2-methyl derivative can be quickly purified by dissolution in hot toluene, and filtration on a 2 cm silica column followed by recrystallization.

A Perkin Elmer Lambda 750 was used for spectral measurements, with 1cm optic path PMMA cuvettes for bipyramids and 1mm optic path quartz cuvettes for elongated bipyramids. Regular bipyramids were diluted two times before analysis.

Preparation of gold seeds:

Typically, the seeds were prepared by reduction of $HAuCl_4$ in presence of surfactant (CTAC) at 20°C, with a quick addition of a $NaBH_4$/NaOH solution. The mixture turns from light yellow to a reddish orange indicating the formation of gold seeds. The stirring is continued during one minute to eliminate the hydrogen formed by the decomposition of $NaBH_4$, and then, the vial is tightly closed using the screw cap. The synthesized seeds are heated in a water bath regulated at 85°C during 60 minutes for aging. During this step, the seeds become more reddish, indicating an increase in size. The seed aging needs smaller precautions. A closed water bath was used for heating since the temperature is quite homogenous, and the results extremely reproducible. Without seed aging, the process gives less reproducibility and more spheres are obtained (lower yield in bipyramids). Despite the number of steps, this process is quite accessible and batches of various size particles can be obtained in short period of time.

To a mixture of 4ml $HAuCl_4$ (0.5 mM), 4 ml CTAC (95 mM) and 72µl of HNO_3 (250 mM) kept at 20°C, 100 µl of a cold and fresh $NaBH_4$ solution (containing 50 mM of $NaBH_4$ and 50 mM of NaOH) were added in a very short period of time (around 2 seconds) under vigorous stirring (1000 rpm). The mixture turned from light yellow to a reddish orange indicating the formation of the gold seeds. The suspension was stirred for one minute to eliminate the hydrogen formed through the decomposition of $NaBH_4$ and 16 µl of citric acid (1 M) were added in the solution before the seeds vials were tightly closed using the screw cap. The seeds vials were then heated in a water bath regulated at 80-85°C for 60 minutes for aging. During this step, the seeds became more reddish, indicating a slight increase in size. Finally, they were removed from the bath and stored at RT.

Growth of gold bipyramids using 8-hydroxyquinoline (HQL)

The growth solution was prepared by mixing 40 µl of $HAuCl_4$ (25 mM in water) and 4ml CTAB (47 mM in water). Then, 18 µl of aqueous silver nitrate (10 mM) were added, followed by 40 µl of 8-hydroxyquinoline (0.4 M in ethanol). The growth solution turned light yellow. 40 µl of gold seeds (the seed volume was selected between 5 to 1000 µl depending of the desired SPR wavelength) were introduced into the growth solution under stirring. The mixture was gently stirred for ten seconds and directly put into an oven at 40-45°C for 15 mn. 25 µl of HQL (0,4 M in ethanol) were added to the mixture and let for another 15 mn at 40-45°C.

Growth of elongated bipyramids using mixture of CTAC and CTAB

The growth solution was prepared by dissolving 3 mg of CTAB (increasing CTAB decreases the final LSPR wavelength) in 4 ml of CTAC solution (140 mM in water) and adding 40 µl of $HAuCl_4$ (25 mM in water). Then 12 µl of aqueous silver nitrate (10 mM) were added, followed by 40 µl of 8-hydroxyquinoline (0.4 M solution in ethanol). The growth solution turns light yellow.
40 µl of gold seeds (the seed volume was selected between 30 to 1000 µl depending of the desired SPR wavelength) were introduced into the growth solution. The mixture was gently stirred for ten seconds and directly put into an oven at 40-45°C for 15 mn. 30 µl of HQL (0,4 M in ethanol) were added to the mixture and let for 90 mn at 40-45°C.

Purification of the nanoparticles

The nanoparticles suspensions were centrifuged at 8000 rpm for 10 to 60 mn to ensure complete precipitation of bipyramids. This first step allowed removal of unreacted reducer, CTAB and other impurities. Then the yellowish supernatant was discarded and a 0,1% CTAC solution at pH=3 (1 mM HNO_3) were added to disperse the particles. The suspension was centrifuged at 8000 rpm for 5 to 30 mn. The supernatant is generally slightly purple, indicating that it contains mostly spheres and spheroidal particles. Finally this operation is repeated a second time, and the particles can be stored in 0,05% CTAB solution for months.

Precautions and advices concerning Au bipyramids synthesis

Usually, this synthesis will work as described in the article. However, some issues with reactants may lower yields in bipyramids.

Sodium borohydride is well known for its instability in water, especially in dilute conditions. During storage, sodium borohydride also reacts slowly with water if not stored in inert atmosphere. We observed that already opened (several months) sodium borohydride was less effective for AuBP synthesis. Moreover, preparation of dilute solutions of $NaBH_4$ involves weighting very small quantities of solid $NaBH_4$ which tends to absorb water and aggregate quickly, resulting in bad weighting precision. An effective way to work with $NaBH_4$ is to make a concentrated (4 or 5 M) stock solution of $NaBH_4$ in water with an equimolar amount of NaOH (if the solution is cloudy, centrifuge or filter to get a clear solution). Such a solution can be stored in a fridge for more than one month, and used to prepare dilute solutions when needed without any issue in the synthesis. This way, reproducibility and yields are improved.

25% solution of CTAC (cetyltrimethylammonium chloride) in water are normally perfectly adapted for this synthesis. However, solid CTAC or some liquid solution of CTAC may not have the expected behavior (low yield of bipyramids, seed solution becoming pink) described in this paper. Normally, even without heating the seeds for one hour, some bipyramids can be obtained (but with low yield) and during heating the seeds turn slowly from a brown orange to a red orange. A pink or deep red coloration during heating and a low yield of bipyramids indicates a problem with CTAC purity.
In this case, purification of solid dry CTAC can be done by recrystallization in acetone/ethanol 60:1 (solutions of CTAC or wet CTAC are preceded by a cryo-desiccation step to remove water). After purification, addition of 2-5%mol of fatty primary amine hydrochloride (such as cetylamine hydrochloride, stearylamine hydrochloride or oleylamine hydrochloride) can be added to the CTAC. Those amine salts act as potent growth slowing agents during the seed preparation step and therefore, improve yield significantly.

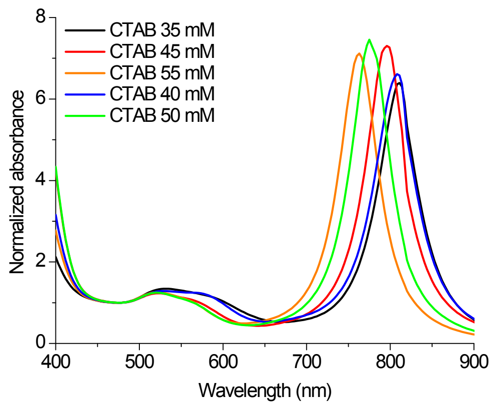

Figure S1: Absorption spectra of the bipyramids versus the surfactant concentration (normalized spectra at 480 nm). Due to the strong interactions of CTAB with the gold surface, variations in the concentration led to noticeable shifts in the LSPR although the changes were observed only for a short range of wavelength.

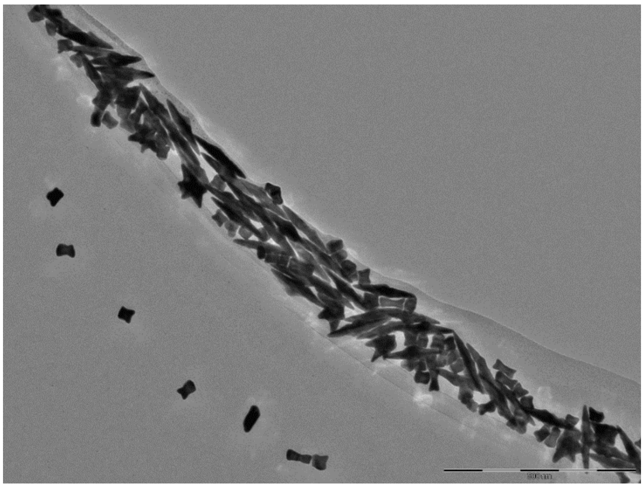

Figure S2: TEM image of nanojavelin prepared with low concentration of CTAC/CTAB mixture shwing low yield and heterogeneity.

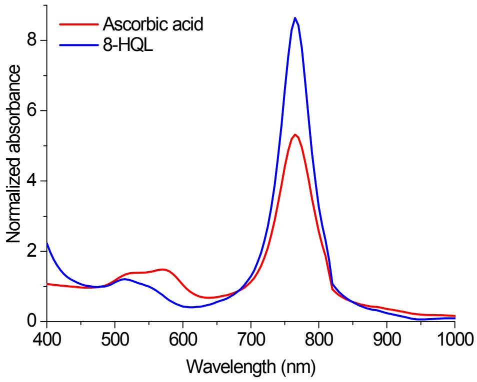

Figure S3 : Comparison between 8-HQL and ascorbic acid in the synthesis. For ascorbic acid, Geitner *et Al.*[35] growth protocol was used since no bipyramids were obtained with our growth conditions.

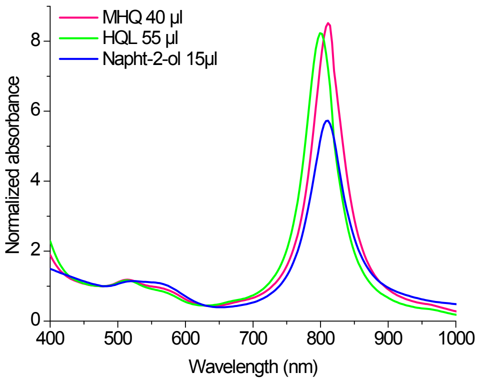

Figure S4 : Comparison between 8-HQL and MHQ and 2-naphthol using 0,4 M solution of each reducer. The optimal volume for each reducer was used.