

Supplementary information for: In situ tuning of nanorods' plasmon through oxidative etching with KCN

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1 Bulk Results

Figure S1 shows the behavior of the same nanorods dispersed in 100 μM KCN. It is possible to observe a clear blue shift of the longitudinal plasmon resonance, towards the transverse peak at around 530 nm. As stated in the main text, we attribute the blue shift of the peak to a shortening of the long axis of the rods. This is because the CTAB is more efficient in protecting the sides than the tips of the particles. It is also possible to note an asymptotic blue-shift of the plasmon. We attribute this to a complete reaction of the KCN with the gold atoms. If more KCN was added to the vial, the blue-shift would have continued.

The spectra were acquired in an UV-Vis spectrometer. The first spectrum was acquired with the rods dispersed in water, before adding KCN into the vial. Later a solution such that the final concentration was 100 μM was added and a set of automatic spectra was recorded at a fixed interval of time. The peak position was extracted by fitting a double lorentzian, one with a fixed central wavelength (the transverse resonance) and a second one for the longitudinal plasmon.

2 SEM Images

Figure S2 shows the SEM images of the rods. In S2a an example of the rods after synthesis and before being etched. Figures S2b and S2c are after 2 minutes in 20 μM KCN and the difference on the shape of the particles when they are separated from each other and in contact is notable. Figures S2d and S2e were taken after 4 minutes in KCN. The histograms in Figures S2f-h show the analysis of the aspect ratio, the longitudinal and the transverse axis respectively for each of the cases. The changes observed for the axis are inside the standard distribution of each parameter. Table 2 summarizes the averaged values found after analyzing approximately 300 particles. However the small shift in the average is consistent with the optical results, yielding an etching rate of 0.5 nm/min.

	L (nm)	Sdv (nm)	R (nm)	Sdv (nm)
0min	51	5	24	3
2min	50	5	23	3
4min	49	5	22	2

Table 1: Summary of the results obtained for 300 different particles while imaging them with an SEM.

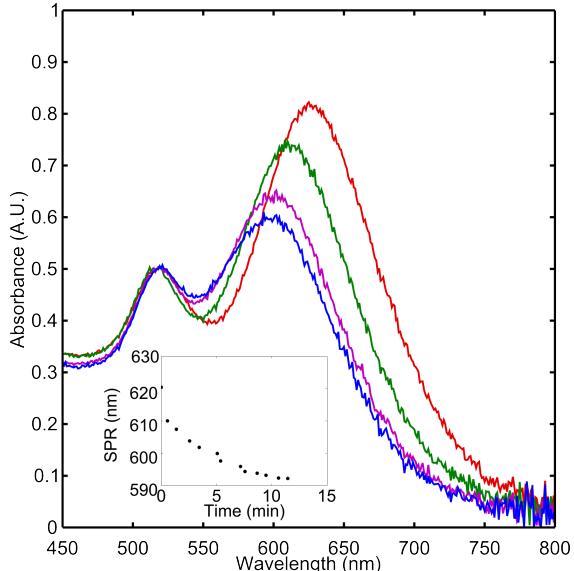


Figure S 1: Extinction spectra of a bulk suspension of gold nanorods dispersed in 100 μM KCN. The curves are displayed at 2 minutes intervals. The inset shows the peak position as a function of time. The curves were normalized to the transverse peak for clarity.

3 Background Spectrum

Figure 3 shows the typical background when exciting with a 532 nm laser. The peak at 650 nm is Raman scattering from water. Normally this background can be well subtracted from the spectra acquired on particles. For less intense curves however, it is possible to observe shoulder appearing at this particular wavelength. We conclude that it is due to a non complete subtraction of the background.

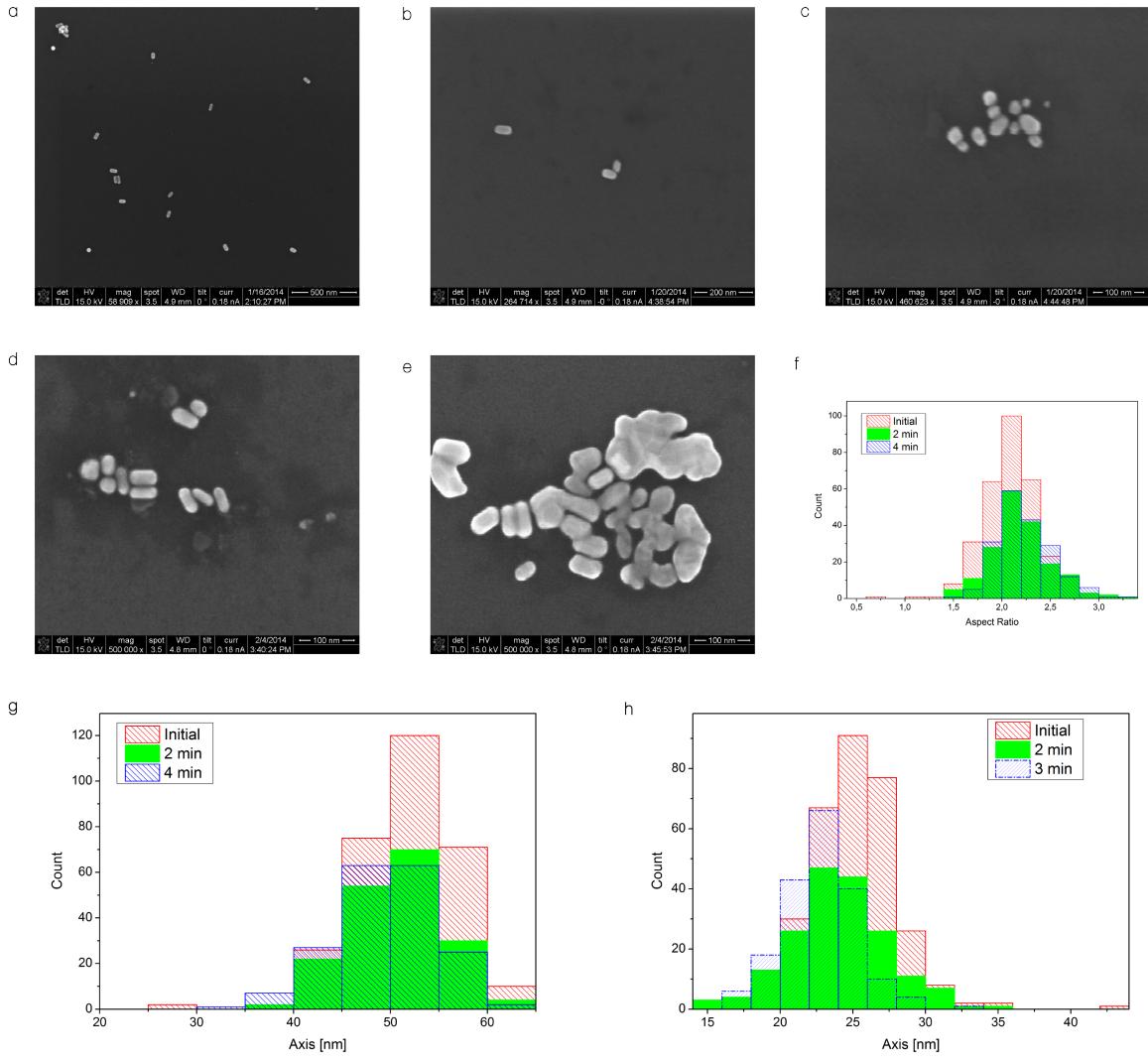


Figure S 2: SEM Images of the rods a) after synthesis, b) after 2 minutes in 20 μM KCN when particles are separated, c) or when they form clusters. d) separated particles after 4 minutes in KCN and e) when they were forming a cluster. f-h) Histograms of the aspect ratio (f), longitudinal(g) and transverse axis(h) for each of the cases (before, after 2 and after 4 minutes in KCN.)

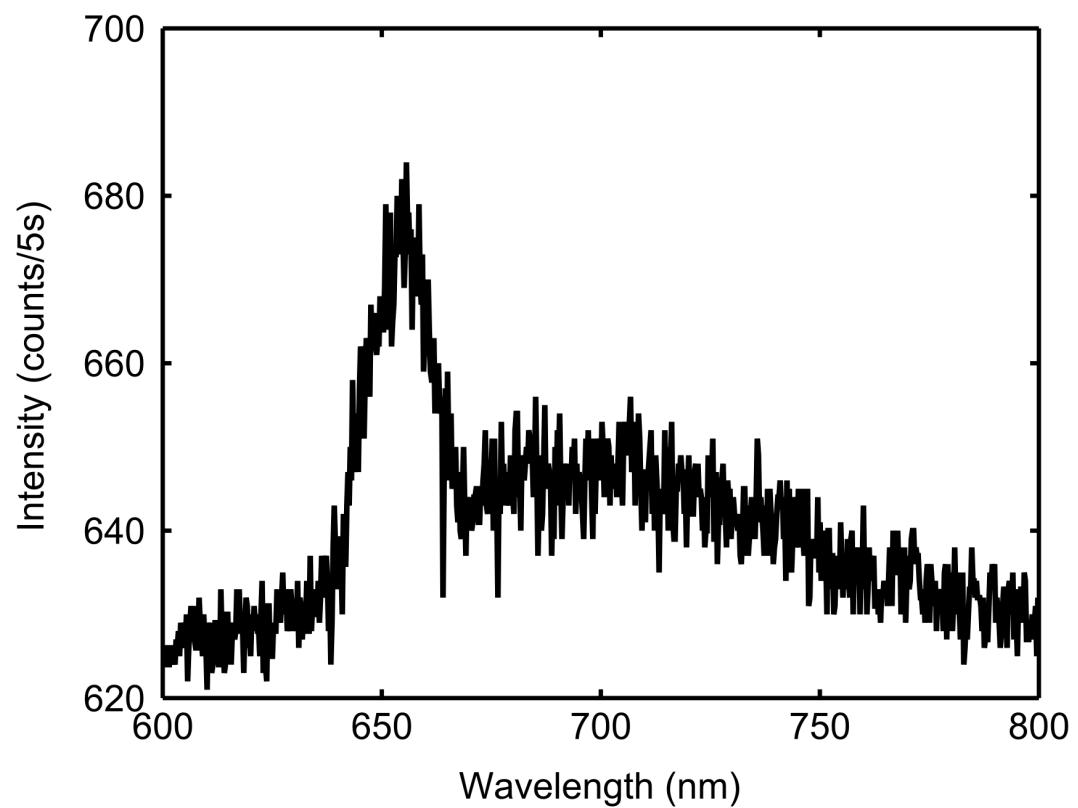


Figure S 3: Spectra from the background while exciting with a 532 nm laser. The peak appearing at 650 nm is Raman scattering from water.