Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for: *In situ* tuning of gold nanorod plasmon through oxidative cyanide etching

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Solution Results

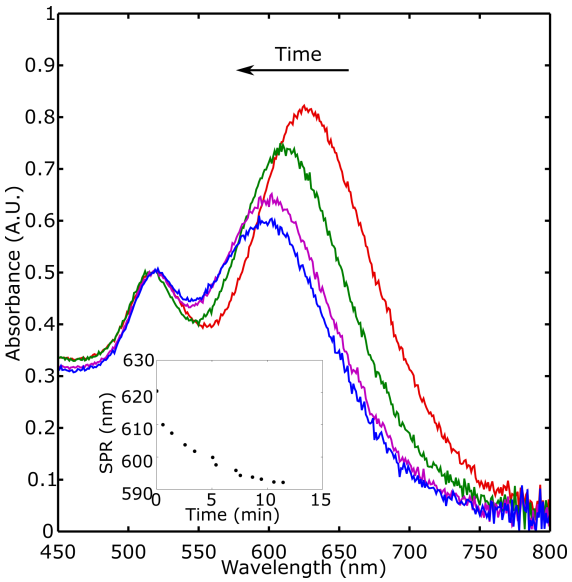

Figure S 1: Extinction spectra of a bulk suspension of gold nanorods dispersed in 100 μM KCN. The curves are displayed at 2 minutes intervals. The inset shows the peak position as a function of time. The curves were normalized to the transverse peak for clarity.

Figure S1 shows the behavior of nanorods dispersed in 100 μM KCN. The same sample than for the single-particle experiments was used. We 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. The blue shift does not seem stabilized for the last spectrum. We attribute this to a complete consumption of KCN by excess gold metal in our sample. If more KCN had been added, the blue-shift would probably 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 cuvette. 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.

SEM Images

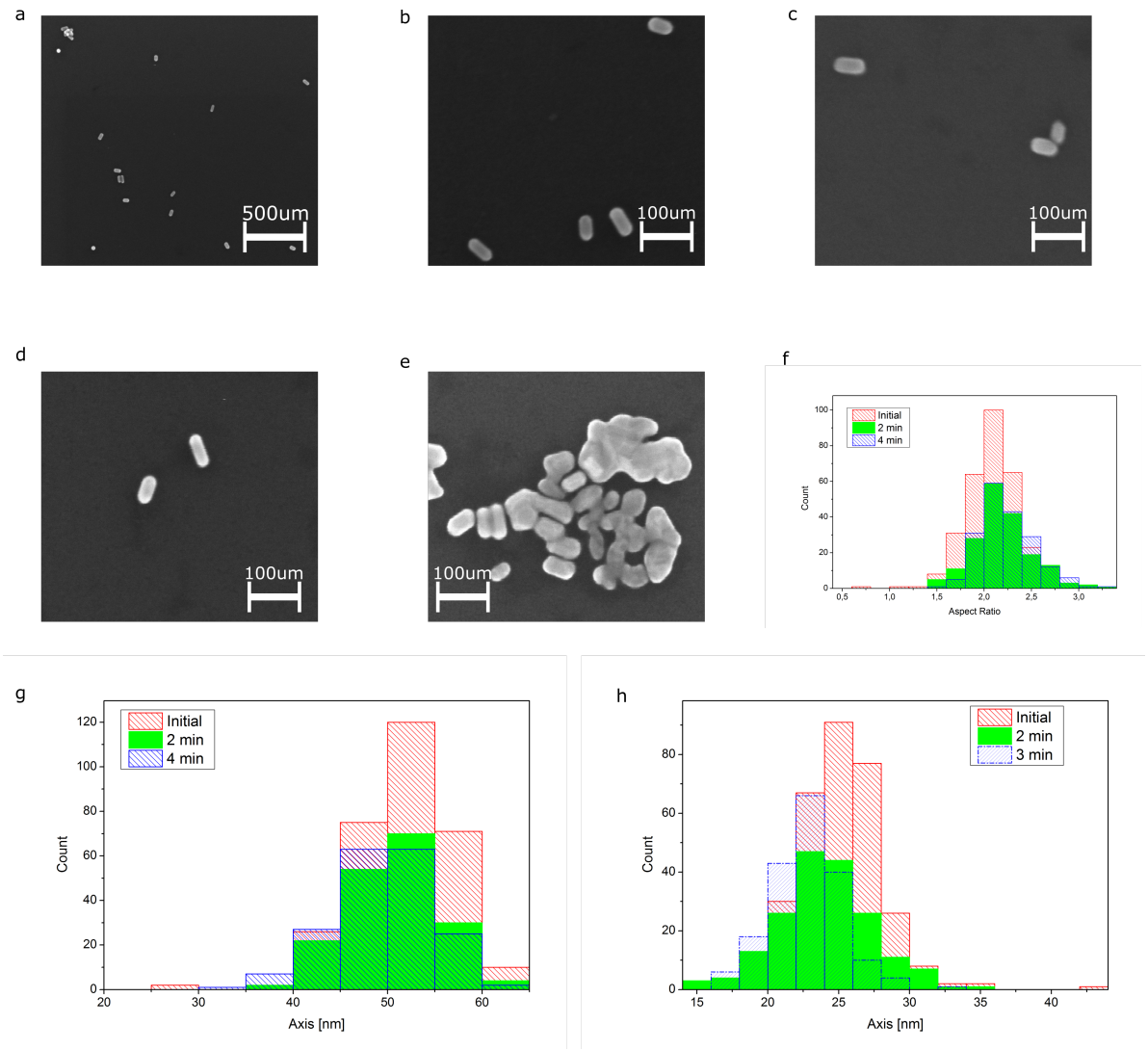

Figure S 2: SEM images of the rods a-b) after synthesis, at different magnifications c) after 2 minutes in 20 μM KCN. d) after 4 minutes in KCN and e) when they were forming clusters. f-h) Histograms of the aspect ratio (f), longitudinal(g) and transverse axis(h) before, after 2 and after 4 minutes in KCN. The distribution of values is too broad to visualize a shift in aspect ratio. Statistics on the values, however, show a slight increase and the data is summarized in table 1.

Samples for SEM images were prepared by drop casting a suspension of gold nanorods into clean silicon wafers. An initial image of several hundreds of rods was acquired before any etching. The same samples were placed in a solution of KCN for 2 minutes and imaged again. Finally they were submersed again for 2 minutes in KCN and imaged afterwards. In

this way, even if it was not possible to track the same particles during the etching process, it was possible to reproduce the conditions in which the reshaping took place on the optical microscope.

Figure S2 shows the SEM images of the rods. In S2a,b an example of the rods after synthesis and before etching at two different magnificatins. Figures S2c and d show the rods after 2 minutes and 4 minutes in 20 μM KCN. Figure S2e was acquired after 4 minutes in KCN; the difference on the shape of the particles when they are in contact is notable. It has to be reminded however that the clusters of rods were already formed on the substrate before the etching started. Drop casting a suspension of rods tends to form conglomerates of particles rather than isolated particles as can be easily achieved by spin casting and shown in the optical experiments in the main text.

Histograms in Figures S2f-h show the analysis of the aspect ratio, the longitudinal and the transverse axes respectively for each of the cases. Table 1 summarizes the average values found after analyzing approximately 300 particles. The shift is rather small as compared to the standard deviation of the distribution of sizes.

Table 1: Summary of the results obtained for 300 different particles while imaging them with an SEM. L and D are the length and diameter respectively. Sdv is the standard deviation of the values

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

Background Spectrum

Figure S3 shows the typical background when exciting with a 532 nm laser. The peak at 650 nm is attributed to 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 a shoulder appearing at this particular wavelength. This indicates

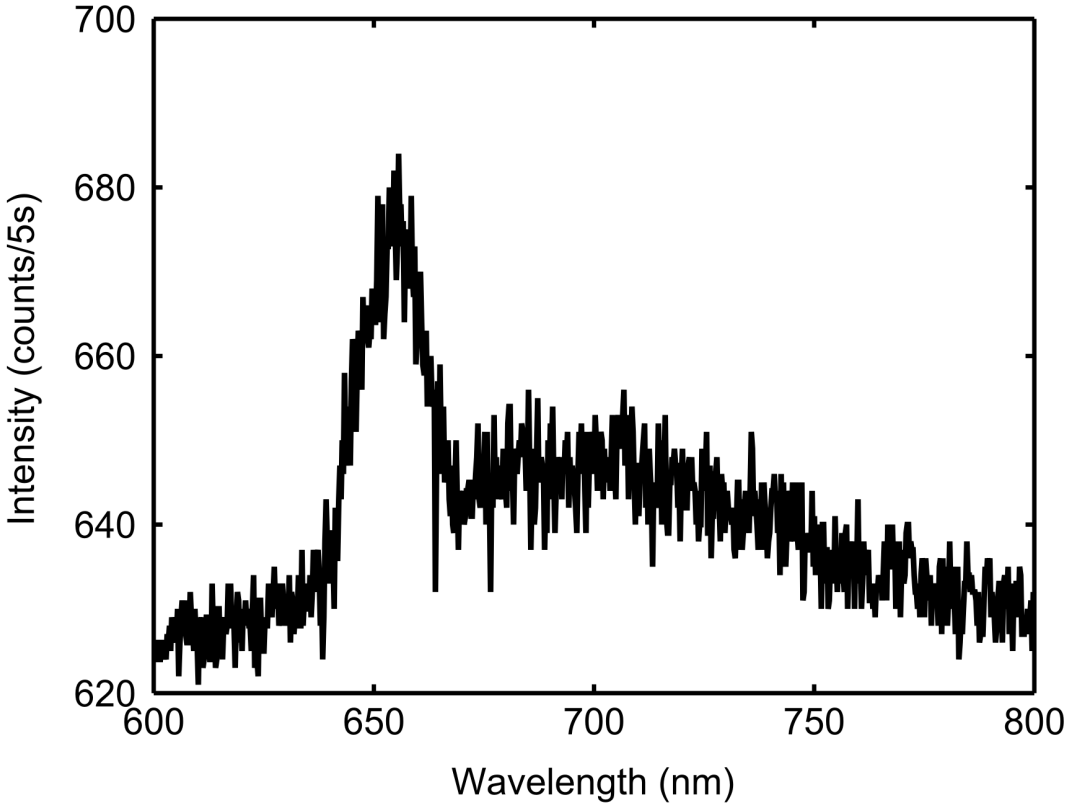

Figure S 3: Spectra from the background while exciting with a 532 nm laser. The peak appearing at 650 nm is attributed to Raman scattering from the O-H stretching modes of water.

a non-additive phenomenon that we attributed to enhanced Raman scattering close to the nanoparticles.