crystals

# Supplementary Materials: Self-Assembly of Gold Nanocrystals into Discrete Coupled Plasmonic Structures

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## Solution Characterisation of Gold Nanocrystals

Gold nanoparticles with 60 nm diameter were characterised collectively in solution as well as by single particle spectroscopy. The gold nanoparticle colloidal solution showed a typical pink colour in transmission as can be seen in Figure S1a. However, when a vial of the solution was held against a black background, no light could travel straight through the vial to the observer's eye. The solution appeared in a yellow/green colour, the colour of the light scattered by the colloidal solution. A UV-Vis spectrum of the solution in Figure S1b showed a peak extinction wavelength at 525 nm. This extinction band lied in the green region of the visible spectrum, matching the colours observed in the solution.

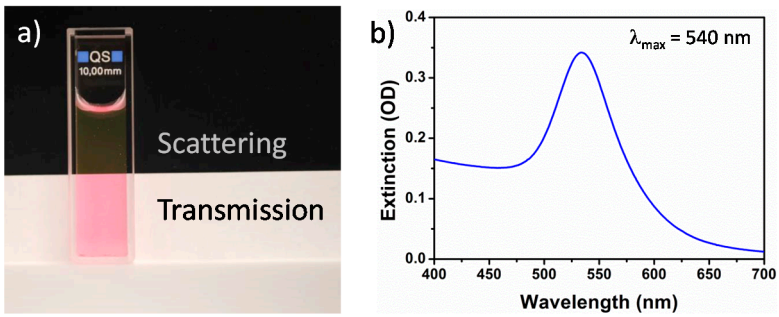


**Figure S1.** (**a**) 60 nm gold nanoparticle colloidal solution in front of a mixed background showing the difference between light scattered by and transmitted through the solution. (**b**) UV-Vis extinction spectrum of 60 nm gold nanoparticle colloidal solution.

## Characterisation of Individual Gold Nanocrystals

To study single nanocrystal, they were deposited on glass substrates and observed under darkfield illumination conditions with an optical microscope. Care was taken to deposit the nanoparticles sufficiently spaced (ideally ~5 μm) to ensure a recorded spectrum would only show contribution from a selected single nanoparticle. The experimental setup for darkfield microscopy is schematically shown in Figure S2. An optical microscope was equipped with a darkfield condenser, inserted between the light source and the sample. The darkfield condenser has a high numerical aperture and, using a central light stop and a mirror system, created a hollow cone of light which was focussed onto a point on the surface of the sample. An objective with lower numerical aperture than the darkfield condenser was located below the sample. Due to its lower numerical aperture only light that was scattered by the sample entered the objective and all light transmitted through the sample passed by the objective. The scattered light was then directed either towards a camera to form an optical image or towards a spectrograph to obtain the scattering spectrum of individual gold nanoparticles.

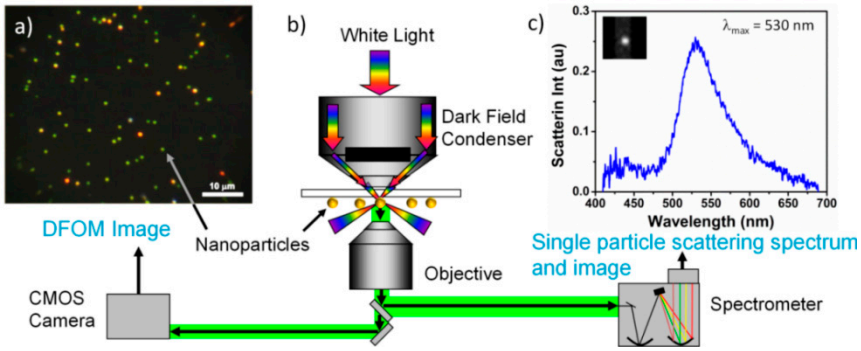


**Figure S2.** (**a**) Typical scattering image of an ensemble of gold nanocrystals; (**b**) schematic setup for darkfield imaging and spectra acquisition; (**c**) typical scattering spectrum of a single gold nanocrystal.

A typical darkfield image of deposited gold colloid is shown in Figure S2a. Only light scattered by the particles was observed, which was of green colour for most particles. The single particle spectrum shown in Figure S2c shows a scattering peak at 530 nm in the green region of the visible spectrum, matching the extinction spectrum of the bulk solution shown in Figure S1b. Looking at individual nanoparticles with darkfield microscopy also revealed that the particles from one batch of solution were, as expected from chemically synthesised nanoparticles, not entirely monodisperse and several different scattering colours were observed.

To investigate the origin of the various colours, correlated darkfield spectroscopy and SEM analysis was performed, which allowed a reliable association of a particle's properties such as size and shape to its scattering properties. For this purpose ITO coated glass substrates were employed, which ensured sufficient conductivity for SEM imaging and sufficient transparency for darkfield microscopy. Additionally, the substrates were covered in etched alignment marks to allow unambiguous identification of single nanostructures in optical and electron microscopy. Figure S3 shows a set of typical gold nanostructures found in a gold nanoparticle solution (60 nm diameter) with associated optical signatures that they produced. The majority of the particles (88% occurrence) were like s01 spherical or near-spherical with a measured peak plasmon resonance wavelength between 526 nm and 536 nm. A tetrahedron (s02) was found to exhibit the same resonance wavelength (534 nm) with, however, a slightly broader full width half maximum (FWHM). Apart from the tetrahedron, a general trend could be observed: the greater the deviations of a nanostructure's shape from a perfect spherical shape the stronger the red shift of the peak plasmon resonance wavelength compared to the resonance wavelength of a spherical particle. Hexagons like s03 (9% occurrence) were found to scatter in the range from 554–572 nm and triangles like s04 (2% occurrence) from 583 nm to 606 nm.

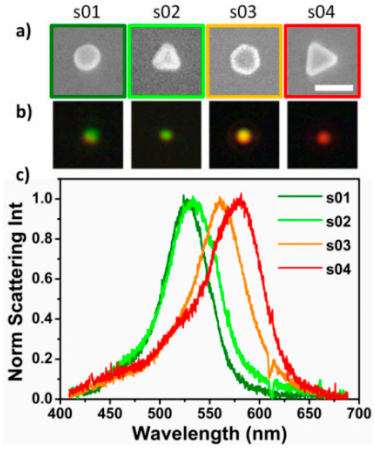


**Figure S3.** (**a**,**b**) Correlated darkfield scattering images—SEM images of various nanoparticle shapes found in a batch of 60 nm gold nanoparticle colloidal solution (scale bar 100 nm); (**c**) corresponding scattering spectra.

## SEMs of Gold Nanostructures

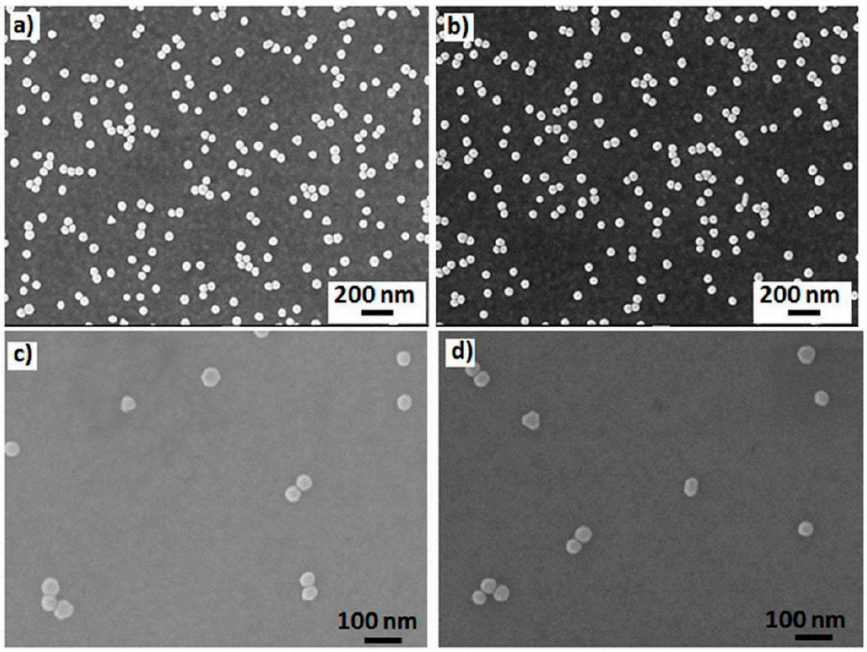


**Figure S4.** (**a**,**b**) SEM images of high concentration n-mers deposited on SiO2; (**c**,**d**) SEM images of low concentration n-mers deposited on SiO2.