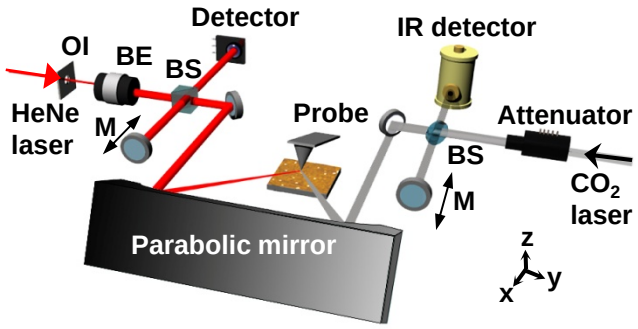
Figure 1. Schematics of the experimental setup showing optical beam paths of the s-SNOM for visible (left side of tip) and IR frequencies (right side of tip). M = mirror, OI = optical isolator, BE = beam expander, and BS = beam splitter.



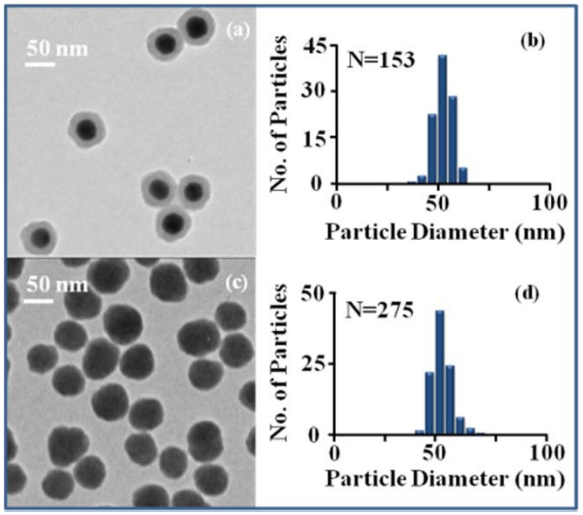


Figure 2. Transmission electron microscope (TEM) images and size statistics for monodisperse nanoparticles. (a-b) Silica-capped Au core nanoparticles, showing uniformity of shape and thickness of the silica capping layer and (c-d) pure silica nanoparticles. N is the number of particles measured.

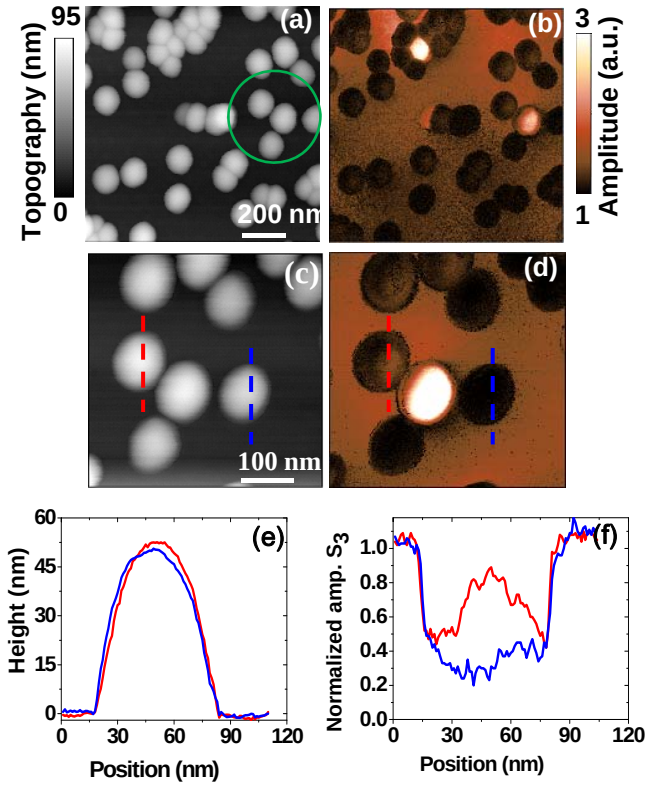


Figure 3. Near-field images of a mixture of 3 types of nanoparticles: silica, silica-capped Au and Au nanoparticles on a Si substrate. (a) AFM topographic image of the mixture. (b) third harmonic s_3 near-field amplitude image. High resolution zoom in scan results of the 3 particle types shown in green circle in (a) in a 500 nm x 500 nm area, (c) topography and (d) near-field amplitude third harmonic s_3. (e) Line profiles of the topography of nanoparticles (red and blue broken lines) showing similar height of the two particles. (f) Different optical signal line profiles for the two particles shown in in red and blue dashed lines. Amplitude signal line profiles shown in (f) are normalized to the signal of a Si substrate.

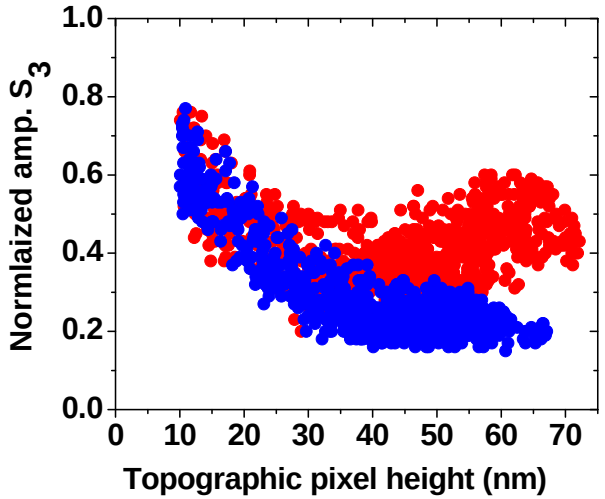


Figure 4. Pixel-by-pixel correlation of measured near-field third harmonic signal contrast as a function of the topographic pixel height at 633 nm wavelength recorded for two samples, pure silica (blue data points) and silica-capped AuNPs (red data points) adsorbed on a Si substrate. Signal values on Si substrate are used to normalize all optical data.

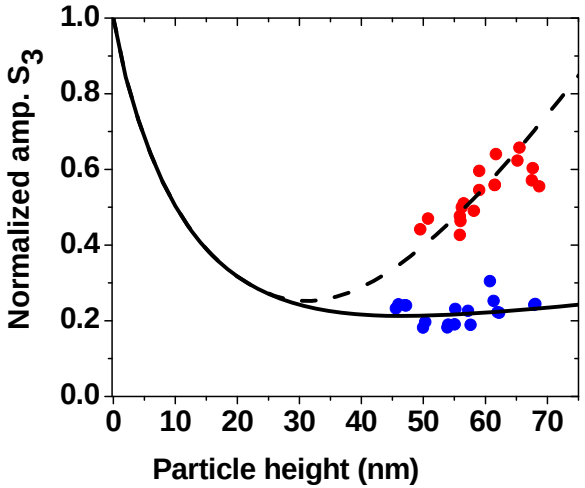
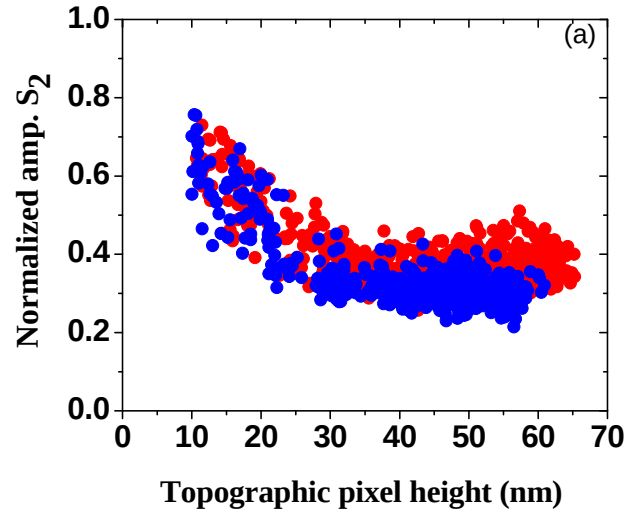


Figure 5. Calculated results of the normalized optical signals for silica-capped AuNPs (dashed line) and silica nanoparticles (solid line) as a function of particle height. Superimposed on the theoretical curves are experimental signal average values of pixels near the center of particles.



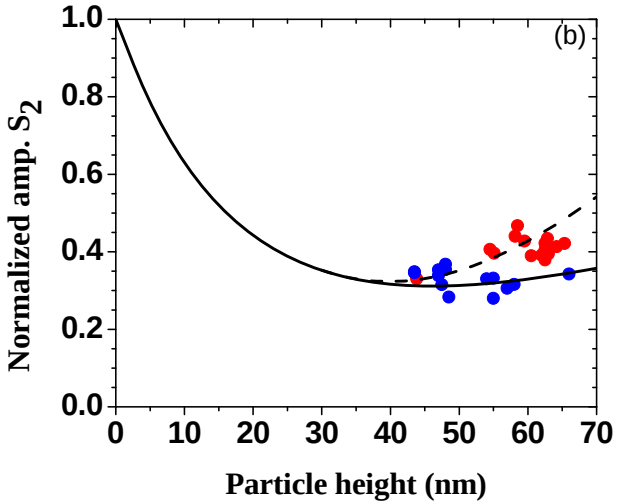


Figure 6. (a) Pixel-by-pixel correlation of measured near-field second harmonic signal s_2 as a function of the topographic pixel height at λ=10.7 μm wavelength recorded for two samples, silica (blue data points) and silica-capped AuNPs (red data points) adsorbed on a Si substrate. (b) Calculated results of the normalized optical signals for silica-capped AuNPs (dashed line) and silica nanoparticles (solid line) as a function of particle height. Superimposed on the theoretical curves are shown experimental signal average values of pixels near the center of particles.

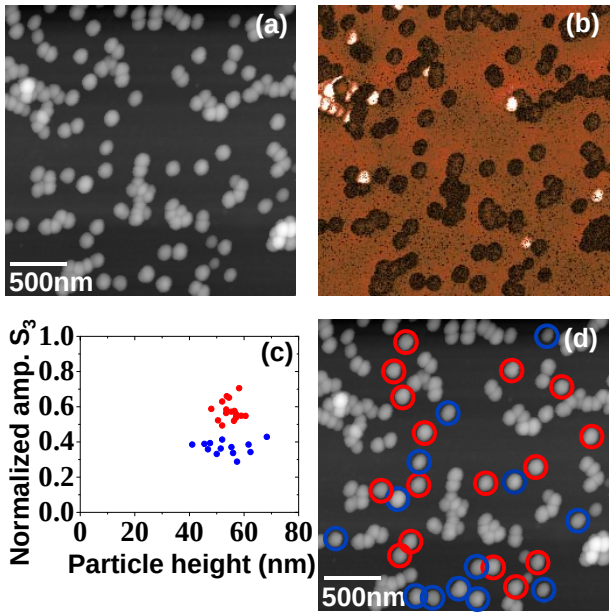
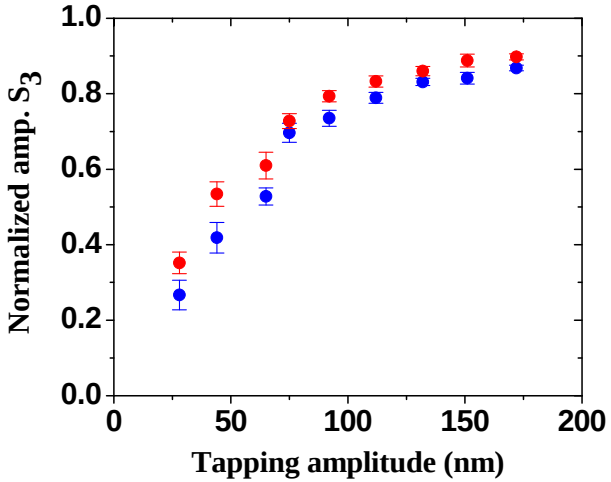
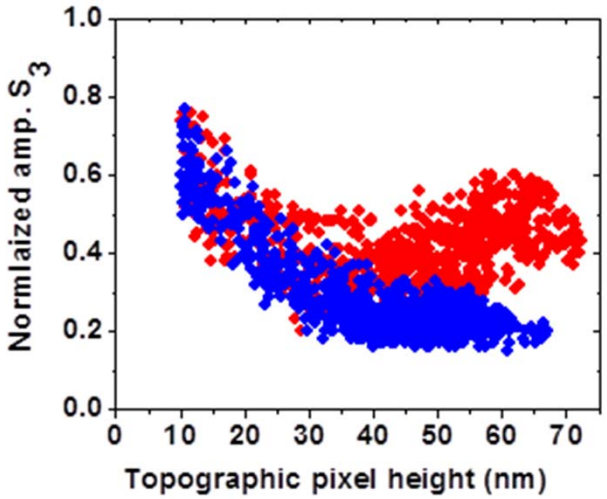


Figure 7. Identification of particles based on their near-field amplitude contrast. (a) Topography of a mixed sample and (b) near-field amplitude contrast. (c) Experimental signal, averaged near the center of particles: red (capped) and blue (uncapped). (d) Particles labeled according to their material contrast as capped (red) and uncapped (blue).

Figure 8. Third harmonic near-field amplitude signals versus tapping amplitude measured at λ=633 nm. Red dots represent data points on silica-capped Au and blue dots on pure silica nanoparticles. Signal values on Si substrate are used to normalize all optical data.




Normlaized amp. S_3
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
Topographic pixel height (nm)