

Supporting Information

Investigation of Au-Hg Amalgam Formation on Substrate-Immobilized Individual Au Nanorods

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Influence of NaBH_4 and Hg(II) exposure on Au nanorod optical properties, SEM images and statistical size analysis of nanorods exposed to Hg(II) solutions, detailed EDX analysis, theoretical calculations.

Influence of NaBH₄ and Hg(II) exposure on Au nanorod optical properties

The effect of exposure to NaBH₄ was investigated in order to exclude any contribution from the reducing agent during mercury exposure. The λ_{\max} shift of the nanorod scattering band was measured against time and averaged over 10 different nanorods (see Figure S1, black squares). Initially (2 min) a red shift occurred, followed by a blue shift back to the initial wavelength. After 5 min small blue shift of the λ_{\max} were measured until after 20 min no further spectral changes were detected. Therefore nanorod samples were immersed for 10 min in reducing agent solution prior to addition of mercury aliquot. In a similar manner the effect of immersion time on the spectral response of nanorods exposed to mercury was tested by adding 100 nM HgCl₂ and monitoring the spectral changes of 10 nanorods over time (see Figure S1, red circles). A strong blue shift occurred within the first 5 min after which the λ_{\max} reached a plateau and no further spectral changes were detected after 10 min. Therefore in all darkfield microscopy experiments substrates were immersed in NaBH₄/HgCl₂ solutions for 10 min before spectral examination.

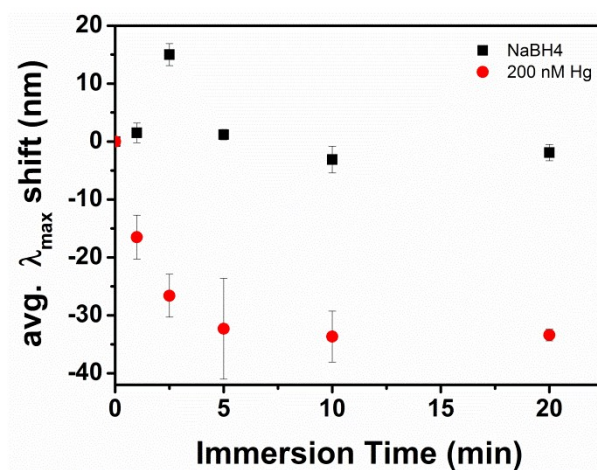


Figure S1. λ_{\max} shift of nanorod scattering band over time averaged over 10 nanorods immersed in NaBH₄ (10 mM, H₂O, black squares) and after addition of 100 nM HgCl₂.

SEM imaging and size analysis of nanorods exposed to Hg(II) solutions

The shape evolution of Au nanorods exposed to Hg was monitored with SEM imaging in the concentration range from 50 nM to 10 μ M. For each sample a statistical analysis of the present nanorod dimensions was performed on 300 nanorods. Figure S2 shows representative SEM images and nanorod length and width histograms for all analyzed samples. At 500 nM Hg(II) concentration coalescence of nanorods was observed until at 10 μ M Hg(II) concentration complete spherical reshaping was observed for all deposited nanorods. The histograms of nanorod dimensions for every Hg(II) exposure show the shape evolution from AR = 2.9 to AR = 1.1.

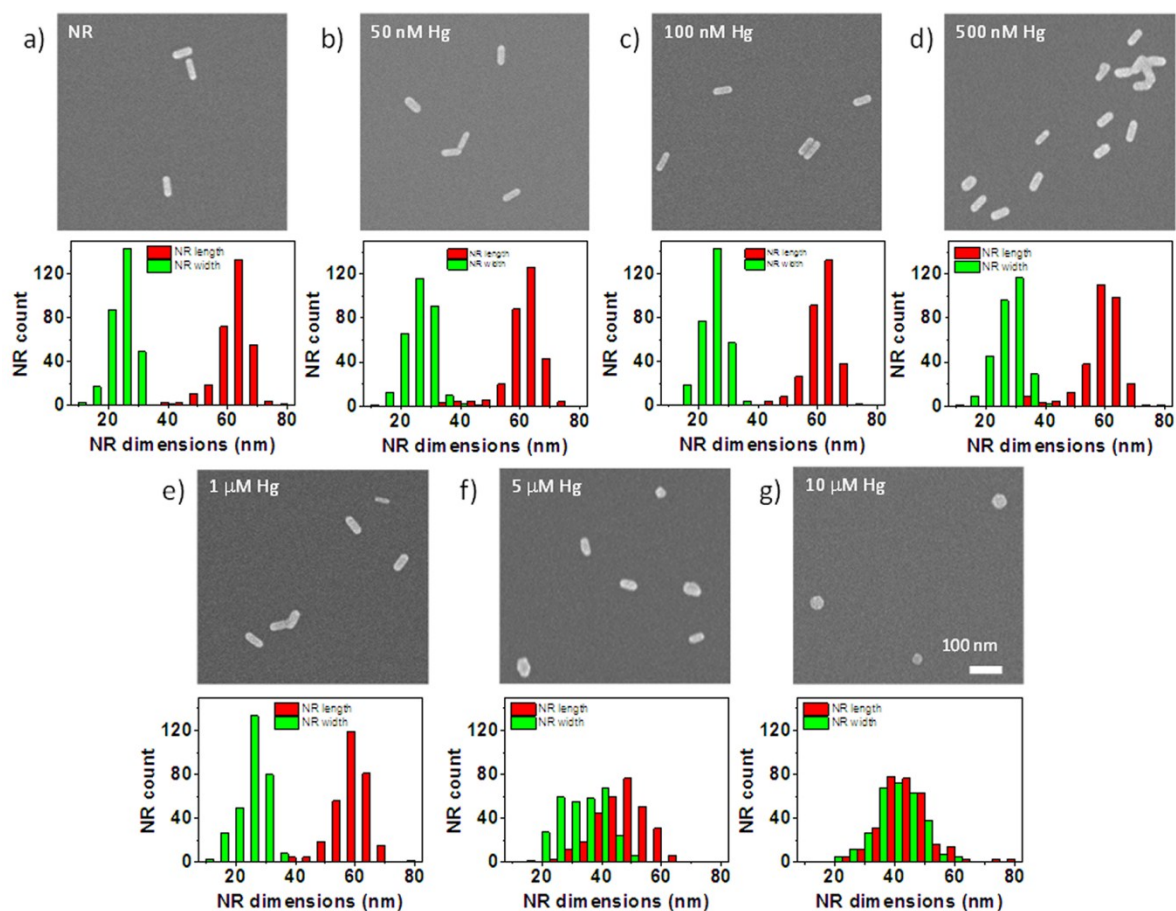


Figure S2. SEM images of nanorods a) as deposited and after immersion in Hg(II) solutions b) 50 nM, c) 100nM, d) 500 nM, e) 1 μ M, f) 5 μ M and g) 10 μ M Hg(II). Corresponding length (red) and width (green) analysis averaged over 300 nanorods.

Correlated measurements were taken of Au nanorods deposited on a TEM carbon grid before and after exposure to 0.01 M NaBH₄, 5 μM Hg(II) solutions. As can be seen this Hg concentration is accompanied with nanorods morphological transition to spherical shapes (Figure S3).

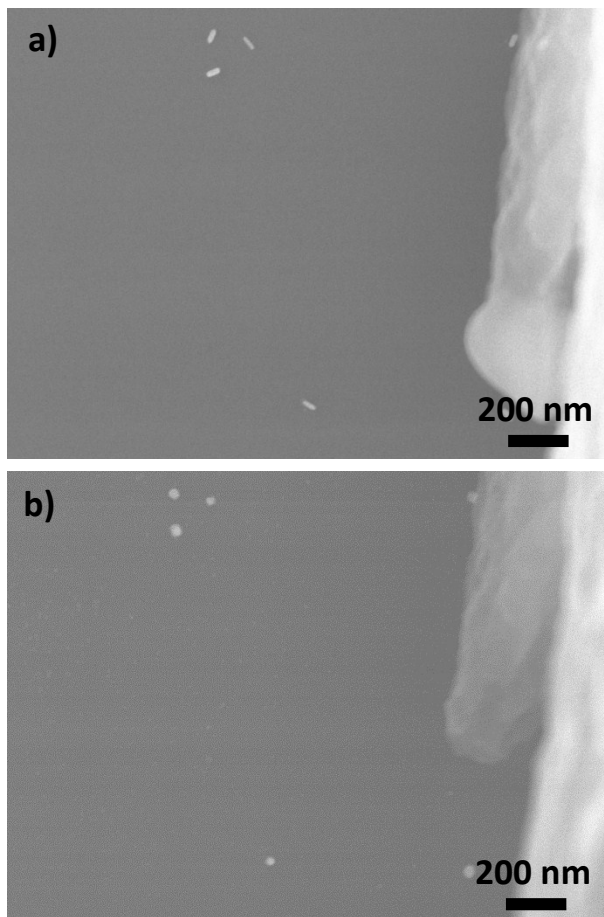


Figure S3. SEM images of Au nanorods deposited on TEM carbon grids before (a) and after (b) exposure to 5 μM Hg(II) solution.

Optical and electron microscopy analysis correlation. It should be pointed out that only qualitative correlation between optical and electron microscopy analysis is possible. The density of nanorods deposited on glass substrates (optical analysis) was kept low in order to ensure minimum aggregation and light collection from isolated particles. In contrast, for SEM analysis the density of nanorods on the SiO₂ substrate was purposely increased in order to perform statistical analysis. Since for Hg solutions of equal concentrations the magnitude of the morphological effects caused by Hg depends on the density of deposited nanorods, only

qualitative correlation between results obtained by optical and electron microscopy analysis can be considered accurate.

EDX analysis

An EDX spectrum of the entire 0-20 keV energy range is shown in Figure S4. For the determination of the nanorod composition the Au and Hg L series at 9.712 and 9.987 KeV respectively were chosen

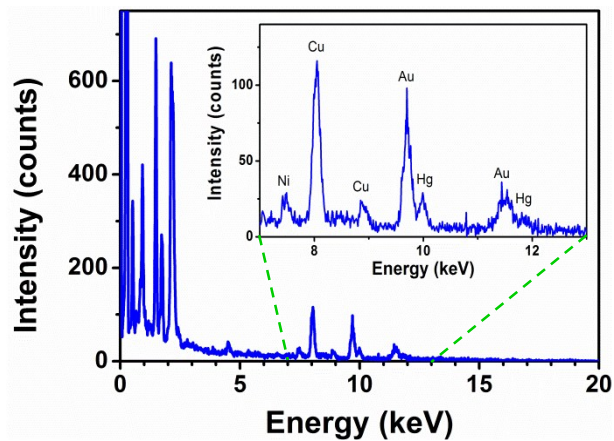


Figure S4. EDX spectrum of a single Au nanorod after exposure to 5 μ M Hg (II) solution in presence of NaBH_4 .

Supplementary theoretical calculations

Using the core-shell model presented in the manuscript one has to also take into consideration that by adding Hg shells of uniform thickness onto the Au core the dimensions of the nanorod alter somewhat: the volume of the nanorod increases and the aspect ratio decreases slightly. The effect of these changes was estimated by calculating the scattering spectra for a Au-Au core-shell nanorod with the same initial dimensions as the previously considered Au-Hg core-shell nanorod. The resulting spectra are presented in Figure S5. As the shell thickness increased and the nanorod AR decreased, the nanorod λ_{\max} experienced a slight blue shift. The intensity of the scattering peak increased due to the elongation of the long axis of the nanorod and the increase of nanorod volume. Comparison with the experimentally observed scattering spectra leads to the conclusion that this effect caused by the slight nanorod size modification can be considered minor in comparison to the changes arising from the dielectric properties of a Hg shell shown in Figure 5a.

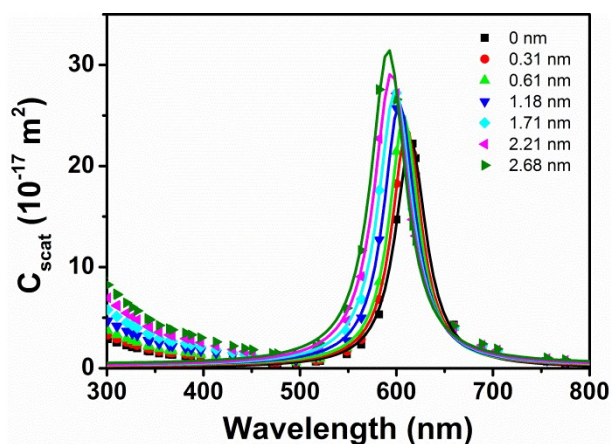


Figure S5. Calculated scattering cross sections for a Au-Au core-shell nanorod with Au core dimensions of 61 x 21 nm and increasing Au shell thicknesses from 0 to 2.68 nm corresponding to 0, 5, 10, 20, 30, 40 and 50 at% Hg composition of the nanorod.

SEM imaging of amalgamated nanorods immediately after removal from Hg(II) solution

Supplementary to the time dependent optical characterization of Au nanorods exposed to Hg(II) solutions, SEM images were taken of a sample immediately after immersion in 10 μM Hg (II) solution (see figure S6). This confirms that the shape transformation of nanorods is happening within 20 min from the beginning of the immersion of the nanorods in the Hg(II) solutions.

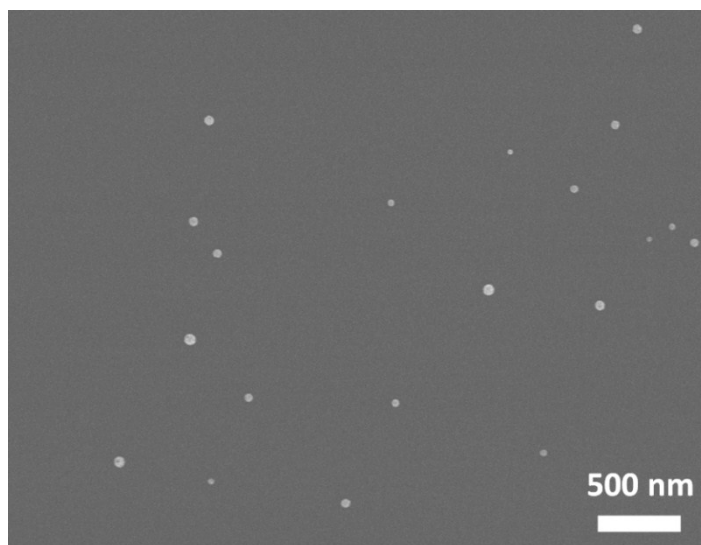


Figure S6. SEM image of Au nanorods taken immediately after immersion in 10 μM Hg (II) solution.