Supporting information

Impact of the Electron Beam on the Thermal Stability of Gold Nanorods Studied by Environmental Transmission Electron Microscopy

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Figure S1: High resolution ETEM heat treatment of a Au NR under vacuum at the temperatures shown. Already at room temperature a thin layer of amorphous carbon was observed on the surface of the gold particle. The thickness of this layer increased as the experiment progressed. The bottom row shows close-ups of the images above.



Figure S2: Energy dispersive X-ray (EDX) analysis of Au NRs performed after exposure to the electron beam. The particles were deposited on a microporous silicon nitride grid. a) Bright-field TEM image of a single Au NR indicating the presence of a thin carbon layer around it. b) Dark-field STEM image of the Au NR from (a). The zoomed-in region shows the area of the EDX line scan (blue line) consisting of 10 points (yellow squares) which were analyzed. The inset diagram shows the strength of the carbon signal along the line and in the direction indicated by the arrow. c) EDX spectra collected from three different points (yellow square) along the line (blue). The inset spectra display the zoom-in on the low-energy carbon signals whose intensities are low but sufficient to distinguish the carbon free region (leftmost spectrum) from the region close to the Au NR where carbon was present (middle and right spectra). In these three spectra it can be seen that the Si peak intensity increased as the scanning point approached the silicon nitride region on which the Au NR was resting. The microporous silicon nitride region below the Au NR in (a) can be distinguished by its different contrast from the vacuum present above the Au NR in (a).



Figure S3: Comparison of electron beam irradiated and non-irradiated 20 min plasma cleaned $(O_2 + Ar)$ Au NRs during in-situ TEM heating under vacuum. a) Au NRs imaged prior to heating at 400 °C, after 5 min and 60 min heating at 400 °C in vacuum. Self-standing Au NRs barely deformed while Au NRs that were closed to each other slightly sintered. In the area that was not irradiated with electron beam prior to and during the heating (b) Au NRs exhibited the same characteristic as the ones that were irradiated (a). This suggests that plasma cleaning transformed the CTAB layer into a protective coating which stabilized Au NRs irrespective of electron beam irradiation. The zoomed-in insets display a thin carbon layer presence around the NRs with and without the presence of the electron beam.



Figure S4: ETEM heat treatment of Au NRs under inert N_2 (100 Pa) (a) and reducing CO (100 Pa) (b) atmosphere. Each image was taken after one hour dwell time at the given temperature. No significant change in the Au NR shape was observed, while the thickness of the carbon layer seemed to increase as the experiment progressed. The growth of a carbon layer was particularly pronounced in the case of the CO experiment (b).



Figure S5: The dependence of the carbon layer thickness around the Au NRs on the temperature and gas atmosphere during the ETEM experiments. The most pronounced increase in the carbon layer thickness was observed for the experiment performed in a reducing CO atmosphere, while an oxidizing O_2 atmosphere gradually removed this layer.