

## Probing the surfaces of nanostructures under reactive environments

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Nanostructures represent an interesting class of materials. Especially their surfaces which to a large extent govern the functionality of these materials are of fundamental interest. For example, the activity of heterogeneous catalysts strongly rely on the structure of these surfaces. The nature of these surfaces is a strong function of the conditions to which the nanoparticle is exposed, i.e. surrounding gases and the temperature. Detailed quantitative information of the surfaces under operating conditions is inherently difficult to access due to limitations of characterization equipment. Advances in electron microscopy such as MEMS heaters and reaction cells and fast cameras have provided new possibilities for *in situ* characterization at the atomic scale (1). Applied in combination with newly developed automated analysis techniques, strong and robust characterization of nanoparticle dynamics can be achieved. However, automated image analysis does have its pitfalls. Knowledge of imaging conditions is a necessary prerequisite in order to extract meaningful results.

In the present study, we investigate the surface structure and dynamics of gold nanoparticles under varying atmospheres. Using environmental high-resolution transmission electron microscopy, gold nanoparticles supported on cerium dioxide have been imaged under varying conditions. The data is analyzed using automated real-space peak finding algorithms and convolutional neural networks developed in-house.

Firstly, the equilibrium shape under oxidizing and reducing conditions was investigated and compared to vacuum conditions. Under vacuum, the surfaces appeared stable meaning that no change in column occupancy, see Figure 1. The figure shows both the occupancy degree of each column as well as the hopping frequency. As the samples are exposed to oxygen at 4.5 Pa, the atomic columns on both (111) and (001) facets start diffusing. When the samples are exposed to hydrogen, only the atomic columns on the (001) facet show diffusing. These observations indicate that as expected, different gas molecules interact differently with different facets. A possible explanation of the observed events is the higher desorption temperature of oxygen (> 415 K) compared to hydrogen (~120 K).

Under exposure to 4.5 Pa carbon monoxide and 300°C, surface layers start shifting in a concerted fashion, and a crystal twin parallel to the nanoparticle/support interface forms and moves dynamically resulting in at least two distinct configurations of the nanoparticle. In each configuration, the surface strain on the nanoparticle was measured using a newly developed routine, see Fig. 2 (2). In the untwinned configuration (upper pane), the lower (111) facet shows strong outwards relaxation. In the twinned configuration (lower pane), the corner sites show an outward relaxation.

These observations highlight the advantages of automated analysis and strongly suggest that the catalytically active surfaces are dynamic rather than static entities.

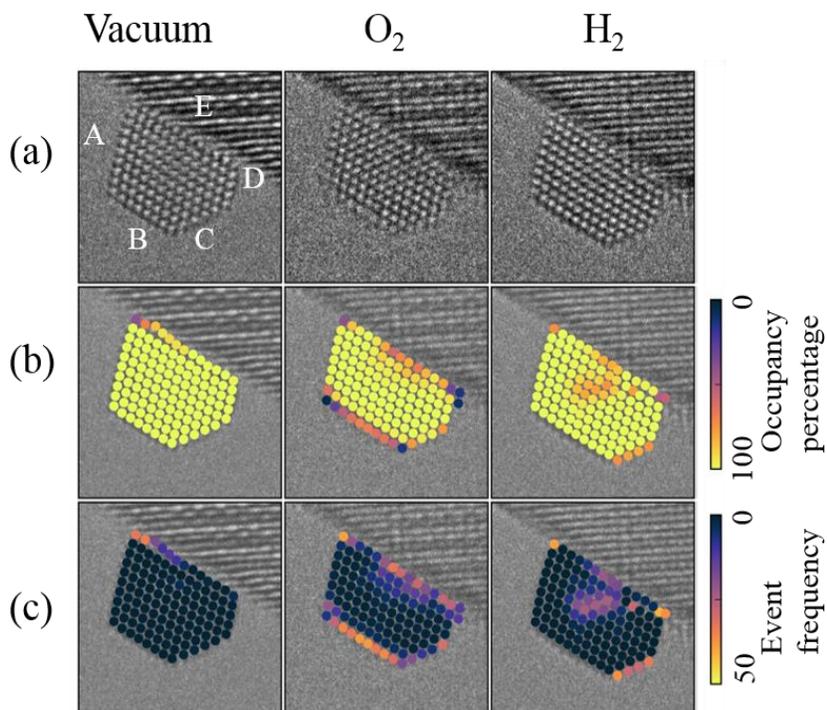


Figure 1: Quantification of occupancy and hopping frequency on the surface of a gold nanoparticle at room temperature.

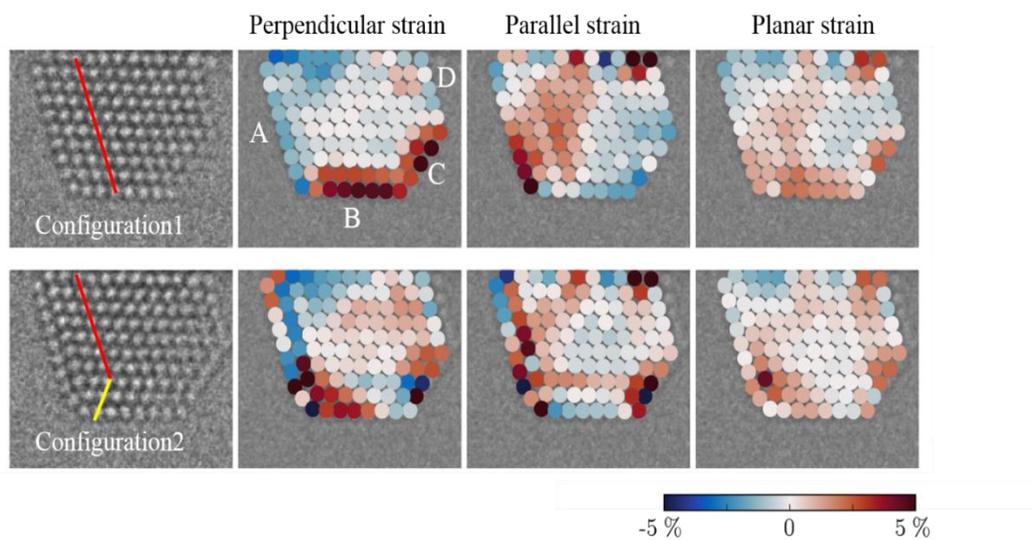


Figure 2: Surface strain on a gold nanoparticle in CO at 300°C.

1. T. W. Hansen, J. B. Wagner, Eds., *Controlled Atmosphere Transmission Electron Microscopy*, (Springer, 2016), pp. 329.
2. J. Madsen, P. Liu, J. B. Wagner, T. W. Hansen, J. Schiøtz, Accuracy of surface strain measurements from transmission electron microscopy images of nanoparticles. *Adv. Struct. Chem. Imag.* 3, 12 (2017).