The Structure of Gold Nanoparticles on different Substrates studied by Aberration Corrected High Resolution Transmission Electron Microscopy

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Introduction

The interface between metallic nanoparticles and their substrate determines the function as catalysts. The efficiency of catalytic reactions depend also on the size of particles [1]. Therefore the structure-properties-relationship and morphology have to be unravelled by structural investigation at the atomic level.

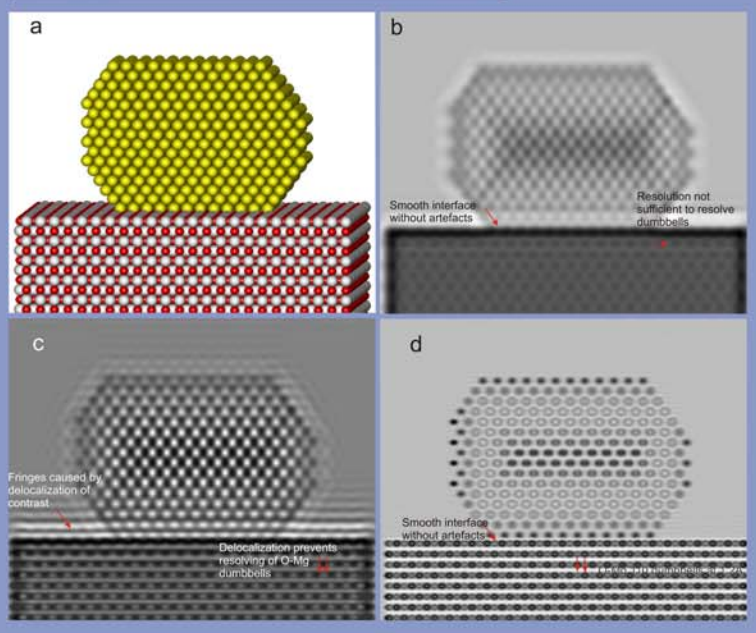
The resolution limiting imperfections have been overcome by the use of corrector elements (C_S-corrector) [2] attached to the microscope column as additional lenses [2,3]. The latest generation of aberration corrected transmission electron microscopes (TEM) offers now for the first time the look into the sub-Ångström region without artefacts such as contrast delocalization. They are ideal tools to study Au nanoparticles on metal oxides

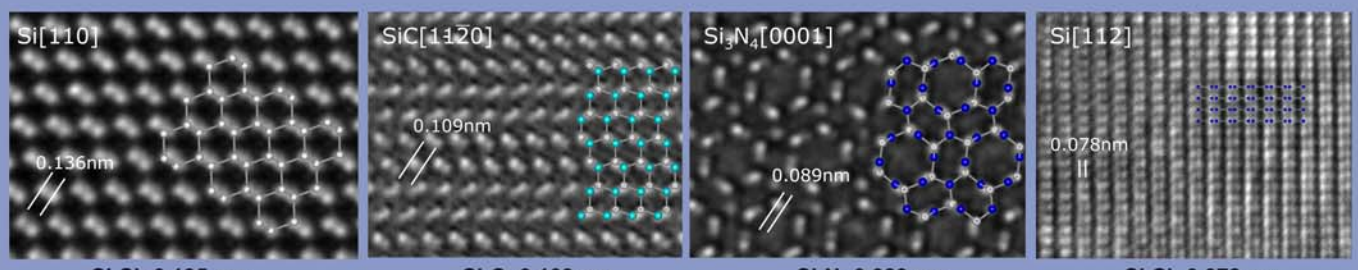
Experimental

The nanoparticles have been deposited on the substrates (Si, MgO, Al_2O_3, TiO_2 using dip coating of metal-salt loaded micelles ($AuCl_4$). Oxygen plasma removed the organic compounds and reduced the metal-salt into solid metals [4].

Cross-section TEM samples were prepared using mechanical grinding, dimpling and polishing followed by low angle, low energy argon ion etching. The TEM investigations were carried out using an objective-lens corrected FEI Titan 80-300 TEM operating at 300kV. HRTEM image calculations were done by the multislice program Musli [5].

Advances of C_S corrected imaging



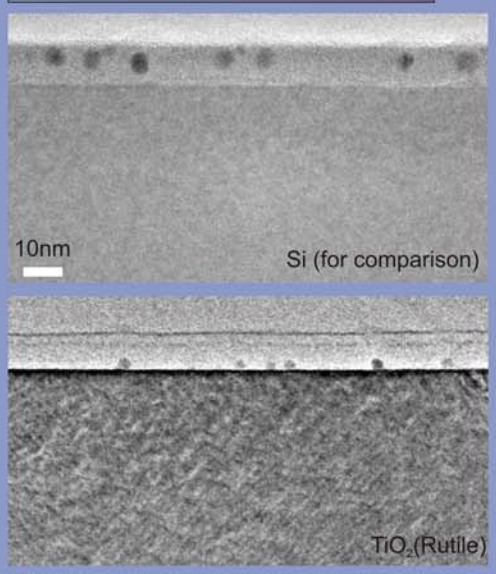


Si-Si: 0.135 nm **Si-C: 0.109 nm** **Si-N: 0.089 nm** **Si-Si: 0.078 nm**

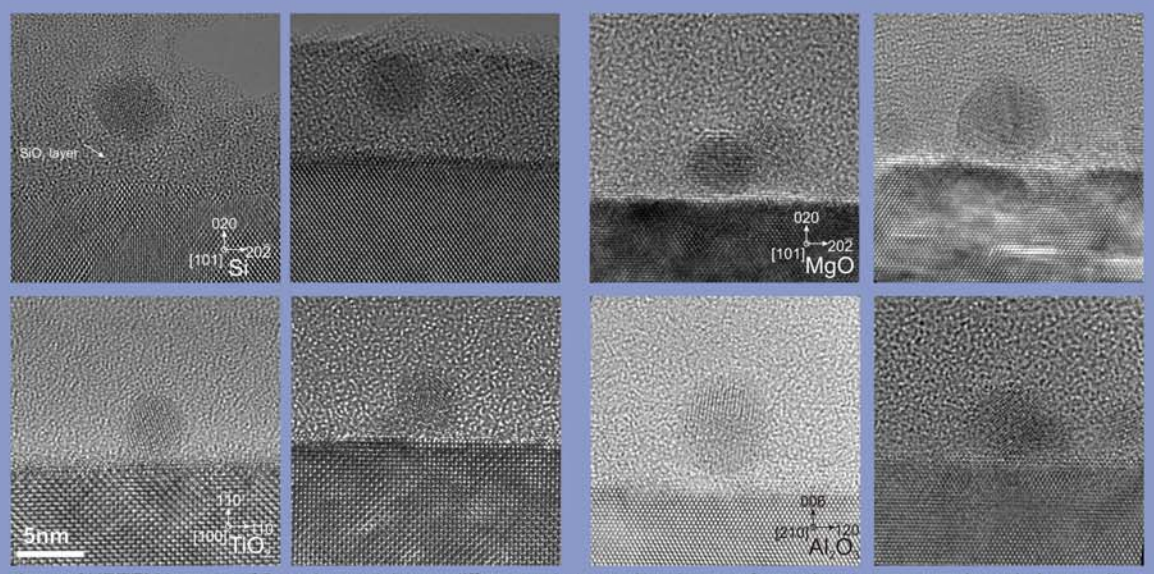
Upper set of images: This series of experimental HRTEM images of different standard samples show the possibilities of Cs-correction. They are obtained on the Titan machine of Ulm. For the first time it is possible to directly resolve interatomic distances down to 0.078 nm.

The **left** set of images shows the theoretical possibilities of a C_S-corrector on a 300kV TEM.
(a) A model of an Au particle on [110] MgO is shown.
Figures b-d show calculated HRTEM images applying gun and lens parameters of different types of 300kV TEMs using the program Musli [4]
(b) LaB_6-TEM with C_S=1.4mm at Scherzer-focus, the point-resolution is about 2.1Å, the information limit is about 1.8Å. There are no disturbing delocalization artefacts as e.g. in (c) but resolution is not sufficient to resolve the atomic structure.
(c) Uncorrected FEG-TEM with C_S=1.4mm. The point-resolution is still about 2.1Å as in the case of a LaB_6 gun, but the information limit is enhanced to about 1.0Å resulting in high delocalizations of contrast. This produces especially artefacts on non-symmetric structures like interfaces.
(d) Cs-corrected FEG-TEM with negative C_S of -5µm at Scherzer-focus. Information-limit and point-resolution are both at 0.8Å. The oxygen columns of MgO with a distance of 1.2Å to Mg can be resolved.

5 nm Au particles on metal oxides

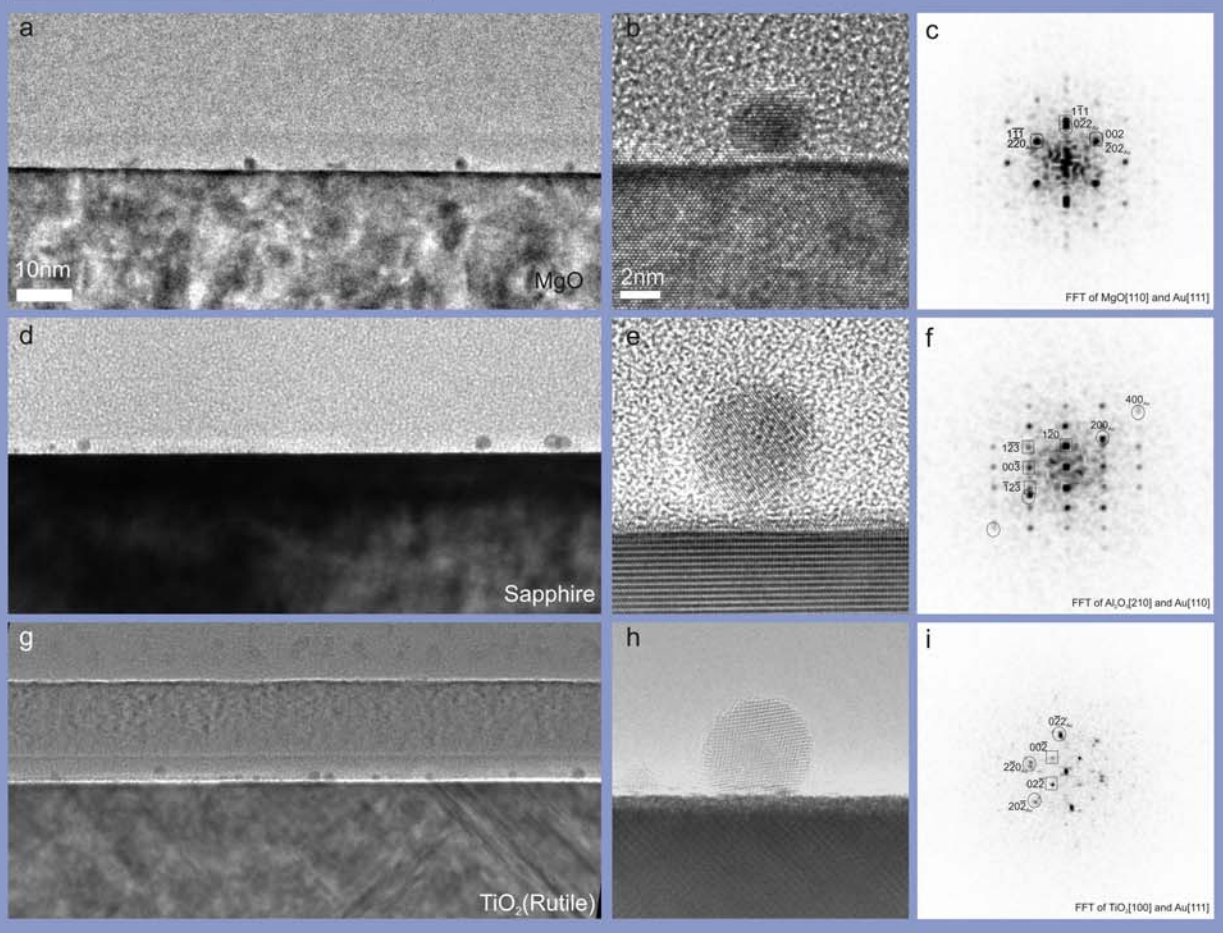


The set of figures shows overview images of 5 nm Au nanoparticles on Si, TiO_2, MgO and Sapphire



A set of HRTEM images of 5 nm Au particles on different substrates (two images for each substrate are shown). A crystalline interface between Au and Si does not exist. The natural SiO_2 that is used as diffusion barrier during formation of Au particles prevents a crystalline-crystalline interface. The interface between Au and the substrate is crystalline on MgO, Al_2O_3 and TiO_2. However, on these substrates preferred orientation relationships between 5 nm particle and substrate could not be revealed within reasonable statistics. The particles are randomly orientated and exhibit defects such as twins or stacking faults.

3 nm Au-particles on metal oxides



(a,d,g) The set of figures are overview images of 3 nm Au nanoparticles on MgO, sapphire (Al_2O_3) and rutile (TiO_2) (b,e,g). C_S-corrected HRTEM images of Au particles on MgO (b), (please compare with the image calculation above in "Advances of C_S-corrected imaging"), sapphire (e) and rutile (h). Most of the investigated nanoparticles show preferred orientation relationships to the substrates; see the diffractogramms (c,f,i) (reflections of substrates (box) and Au nanoparticles (circles) are indexed).
The following relationships could be revealed:

Au on MgO: $111_{Au} // 110_{MgO}$, $0\bar{2}2_{Au} // 1\bar{1}1_{MgO}$, $\bar{2}02_{Au} // 002_{MgO}$
Au on Al_2O_3: $110_{Au} // 210_{Al2O3}$, $002_{Au} // \bar{1}2\bar{3}_{Al2O3}$
Au on TiO_2: $111_{Au} // 100_{TiO2}$, $\bar{2}02_{Au} // 02\bar{2}_{TiO2}$

Apparently the orientation relationships of the nanoparticles are size-dependent. Only the 3 nm particles exhibit a preferred orientation relationship to the substrates, not the 5 nm particles.

Summary

Advances of C_S-Correction
HRTEM-experiments are confirming the theoretical predictions that C_S-correction can achieve sub-Ångström resolution.

Au nanoparticles on Si, TiO_2, MgO, Al_2O_3
A crystalline interface between Si and Au is prevented by SiO_2. A crystalline interface is formed on MgO, TiO_2 and Sapphire. There is a strong tendency that 5 nm nanoparticles do not have preferred orientation relationships to the metal oxides. However, most of the 3 nm nanoparticles have preferred orientation relationships to the substrates.

References
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