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Size-selected cluster deposition in liquid environments: Pd_{12} on Au films

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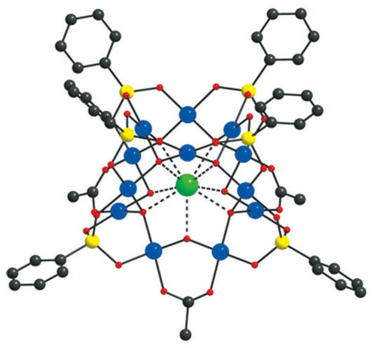
Motivation

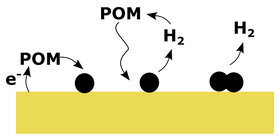
- Metal clusters with atomic size-selection promise material-efficient solutions to catalytic challenges such as water splitting or C-C coupling reactions
- Taking advantage of their high surface area and size-specific properties
- Preparation of stable and active clusters (< 100 atoms) at the solid/liquid interface demands new approaches
- Exploit intrinsic properties of POMs: Distinct number of metal atoms
- Huge variarity in kind of metal and atomic numbers of usable precursors

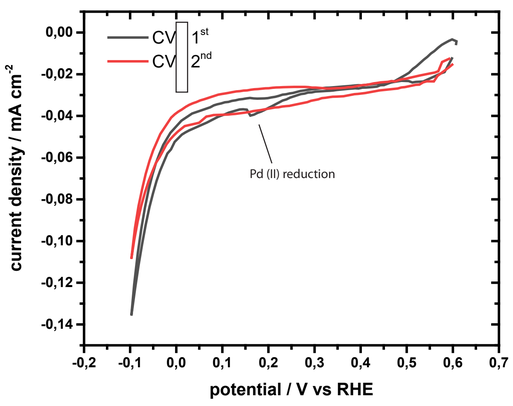


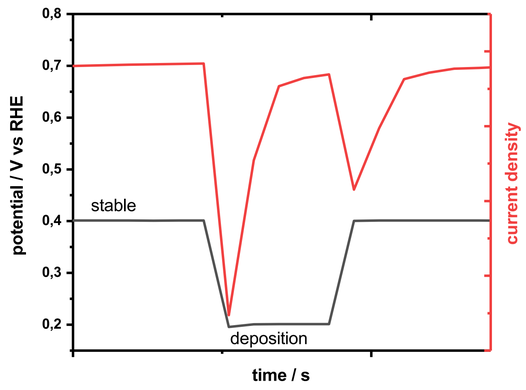
$[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_3]^{4-}$
Polyoxometalate (POM) with a discrete number of 12 Pd atoms are reduced at the solid/liquid interface. [1]

Novel preparation approach of metal clusters

- POM show no specific adsorption, but change in PZC
- POM - Pd (II) gets reduced on Au at 0.2 V vs RHE
- Concomitant hydrogen evolution on deposited Pd
- Evolved hydrogen reduces POM as well
- Pulsed deposition approach to exclude H_2 evolution
- 200 ms pulses to 0 V vs RHE result in monodisperse Pd clusters



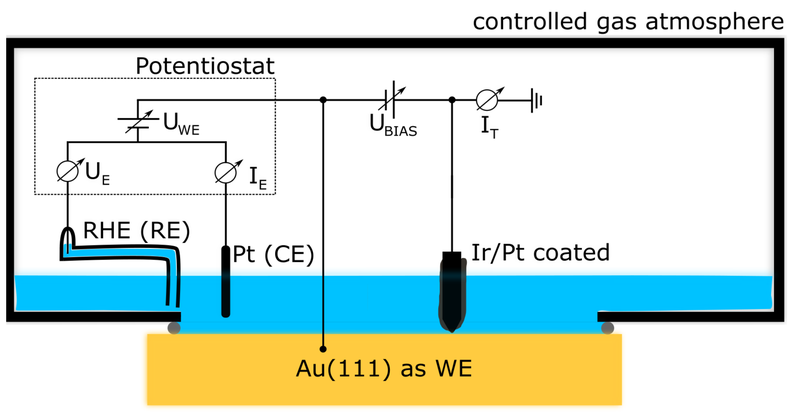




First and second cycle of Au in H_3PO_4/NaOH with Pd_{12}-POM. Deposition of Pd occurs below 0.2 V vs RHE.

Local measurement - Electrochemical STM

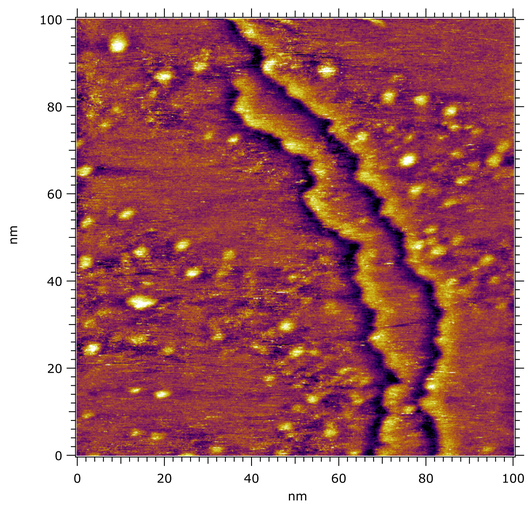
- Combines local topographic information with integral electrochemistry
- Tip as fourth electrode probing tunnel current
- Investigation of ripening processes, reactivity measurements via noise level [2]

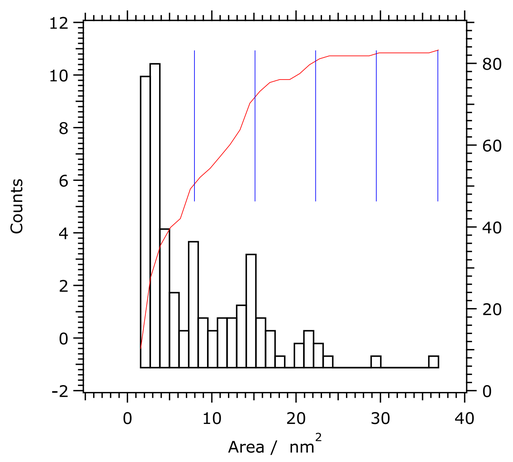


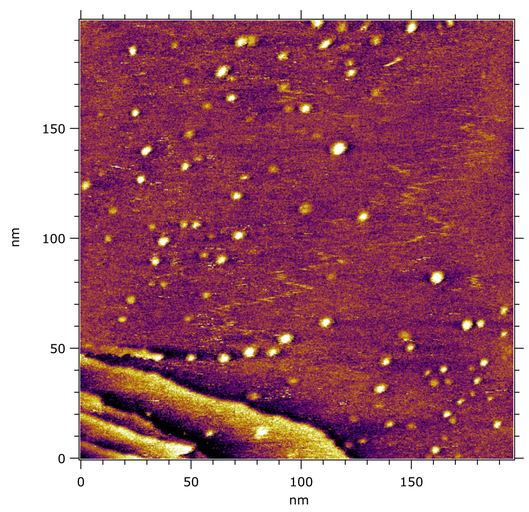
Sketch of experimental setup: Three-electrode setup combined with a STM. The immersed tip is coated.

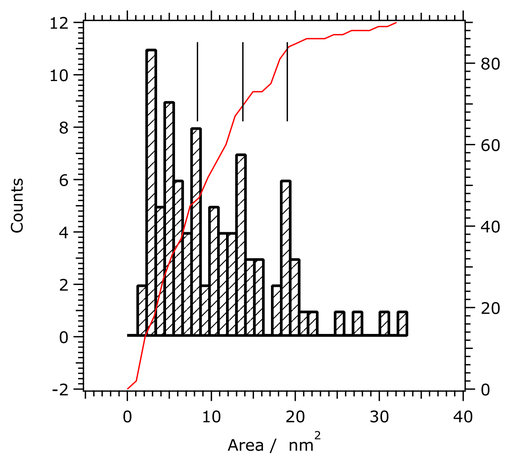
Pd_{12} clusters on Au(111)

- Immersing flame-annealed Au(111) crystal in Palladium(II)-oxo solution
- 25 x 200 ms reduction pulses to 0 V vs RHE
- Particle analysis suggests Pd_{12}, Pd_{24}, Pd_{36}, Pd_{48}, Pd_{60} cluster sizes, area in good agreement with UHV studies [3]
- Amount of pulses influences cluster coverage of surface, exact dependence still unclear
- No prefered deposition site of clusters encountered









Pd deposition on Au(111): STM with U_{tun} = 72 mV, I_{tun} = 0.9 nA. Detected particles show multiples of Pd_{12} clusters. Coverages depends on amount of reductive pulses.

Summary and Outlook

We show the successful deposition of Pd_n clusters via POM decomposition on Au(111) by means of a potential pulse. The well-defined cluster sizes promise a good understanding of the non-scalable properties.

Further studies will concern the possible ripening processes and reactivity by appropriate choice of POM precursors.

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References

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