

Highlights in Polymer and Colloid Chemistry

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Probing the Diffuse Layer of Modified Electrodes by Direct Force Measurements

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The diffuse double layer corresponds to the cloud of counterions forming around a charged surface in contact with electrolyte solution. The overlap of diffuse layers leads to repulsive forces between like-charged surfaces and has thus important consequences for the stabilization of colloidal suspensions. Diffuse layers were first described by electrochemists at the charged water-electrode interface. Despite the importance of the diffuse layer concept many questions remain still open.

In recent years new analytical tools became available, which allow the diffuse layer properties to be probed in a complementary way to classical electrochemical techniques. One of these techniques is the atomic force microscope (AFM), where the diffuse layer properties are derived from the forces acting on a probe surface.^[1] The figure on the left shows the setup we used to measure the interaction forces between a colloidal particle attached to the end of an AFM-cantilever and a gold electrode modified by a thiol-layer. Such modified electrodes provide versatile, well-defined model systems

as their layer thickness and terminating functional groups can be easily varied.

The right-hand figure shows the interaction force between a silica particle and an electrode modified by 11-mercapto-1-undecanol as function of separation distance. The interaction can be tuned from attractive to repulsive by varying the potential applied to the electrode. The solid lines show fits to the Poisson-Boltzmann equation, which was used to determine the diffuse layer potential of the electrode. Its dependence on the applied potential can be described quantitatively by a model based on capacitors in series.^[2] The approach outlined here provides new possibilities in studying the diffuse layer properties: Besides the influence of the thiol-length and chemical termination of the layer we studied the effect of ion adsorption and could demonstrate that the adhesion of particles to electrodes can be tuned over a wide range.

The present approach is complementary to many classical electrochemical techniques and allows electrode properties to be determined with high lateral resolution, which is important for heterogeneous or nanostructured electrodes.

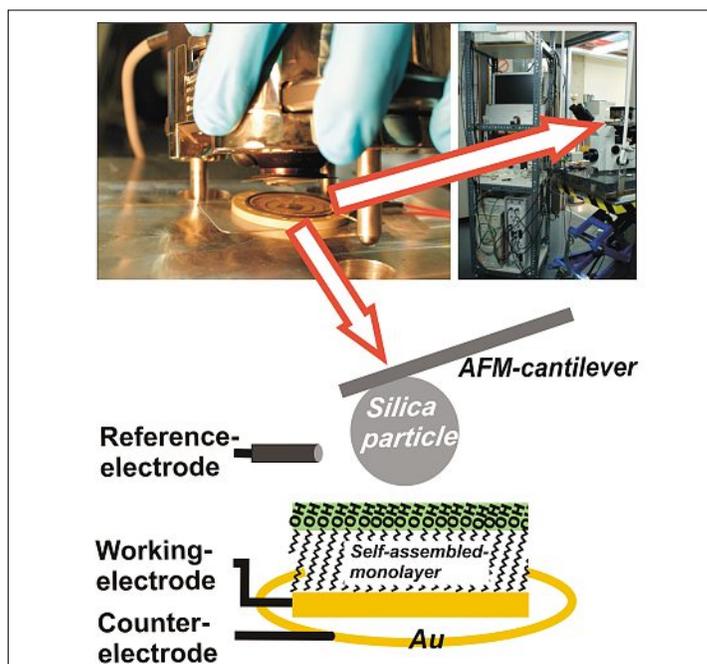
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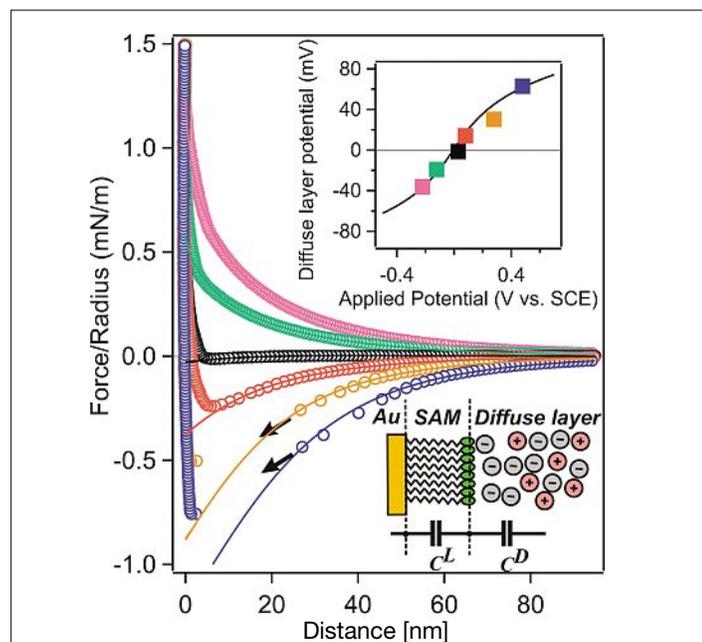
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[1] D. J. Fermin, *Chimia* **2006**, *60*, 789.

[2] S. Rentsch, H. Siegenthaler, G. Papastavrou, *Langmuir* **2007**, *23*, 9083.



The set-up with an atomic force microscope and a potentiostat. The scheme represents the colloidal probe and the modified electrode in detail.



Force versus distance profiles in dependence of the externally applied potential. The inserts show the electrode potentials obtained from the fits and the underlying model, respectively.

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