Order and Orientation of Self-Assembled Long Chain Alkane Phosphate Monolayers Adsorbed on Metal Oxide Substrates

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Introduction: Long chain alkane molecules and in particular those with terminating functional groups are nowadays often employed in order to create well defined, ordered organic surfaces. The main work in this area has been performed with self-assembled thiols on gold. In view of practical applications, however, other materials such as oxidic metal surfaces are of higher interest. Ta₂O₅ and Nb₂O₅, for example, have optical transmission properties, which render them appropriate for application in a planar-waveguide-based bioaffinity sensor. TiO₂ finds direct use in implants and joint replacements. Organic modifications of these materials could be of immense importance for further (chemical) treatment.

Methods and Materials: We have used long-chain n-octadecyl phosphoric acid ester in order to modify different oxide surfaces. Films were prepared by immersion of the substrates in diluted solutions of the organic molecules in a mixture of n-heptane and propan-2-ol for an extended period.

Results: Our results show that these molecules can establish well-ordered monolayers on TiO₂, Ta₂O₅, AlOₓ and Nb₂O₅ surfaces. The resulting films are densely packed (contact angle ~112°). Figure 1 shows series of NEXAFS spectra for hexadecanethiol on gold (left, reference system) and, exemplary, for octadecylphosphoric acid ester on TiO₂ (right). The spectra were recorded at the C₁ s edge for different angles of incidence Θ. At the bottom the difference between grazing and normal incidence is shown. The observed anisotropy of the CH- and the CC-resonance is very similar in both systems indicating similar order and orientation with the alkane chains having an average tilt angle of ~30° from the surface normal.

Conclusions: Clearly, the presence of order and orientation in these organic films on metal oxide substrates is one of the parameters that will have a key role in future applications (e.g. for biosensors) and hence is at the very heart of interest. Upon appropriate ω-functionalization, alkanephosphate-based self-assembled monolayers have, for example, the potential to be used as the interface that anchors active sensing elements or as the basis of passive regions on the sensor surface, which resist the adhesion of biomolecules.

![Figure 1. Series of NEXAFS spectra for long chain alkanes adsorbed on gold and TiO₂. For details see text.](image-url)