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Characterization of (Bio)functionalized Surface Modifications

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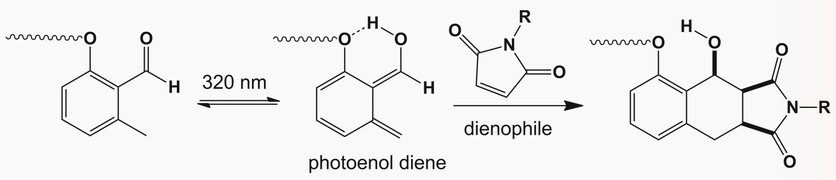
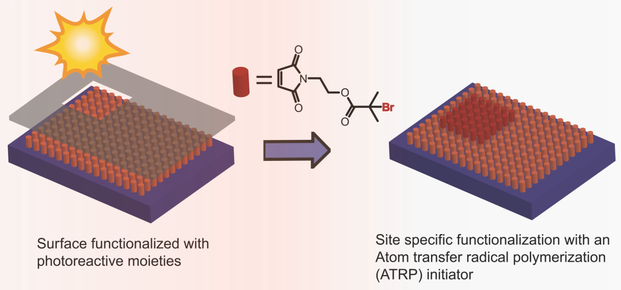
Introduction

We herein present a novel light-triggered approach to spatially functionalize silica surfaces with different chemical functionalities. Therefore pretreated silicon wafers were silanized with an 2-formyl-3-methylphenoxy (FMP) silane. Under irradiation this FMP moiety generates *in-situ* a diene which is able to react with suitable dienophiles by forming a stable cycloadduct. This highly efficient conjugation method can be performed under mild and catalyst-free conditions. The promising potential of this reaction could be useful in the fields of cell biology or tissue engineering.



Mechanism of light -triggered cycloaddition



With the use of shadow-masks µ-structured surface patterns are possible

Experimental

XPS

ThermoFisher Scientific K-Alpha Spectrometer

- Micro-focused mono-AlKα X-ray source
- Charge compensation with low energy electrons and Ar^+ -ions

ToF-SIMS

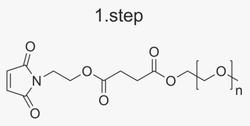
ION-TOF GmbH TOF.SIMS V Spectrometer

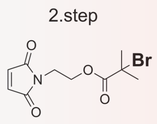
- Bi^+ bunched modus 25 keV
- Primary ion doses $<10^{11}$ ions/cm^2
- Manipulator stage scan mode

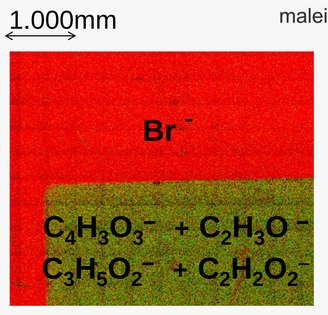
Time-of-Flight Secondary Ion Mass Spectrometry

Site-specific immobilization

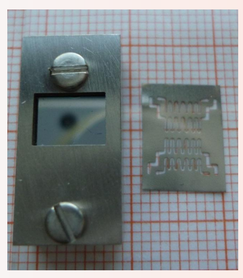
- Sequential immobilization of polyethylene glycol (1.step) and bromine containing species (2.step)
- Firstly immobilized PEG-compound is identified by several negative secondary ions known from references and literature
- Both isotopes of bromine negative secondary ions are straightforwardly detectable
- An overlay image of both fits perfectly







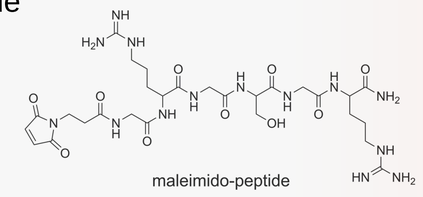
Overlay image of PEG (green) and bromine (red) containing sites

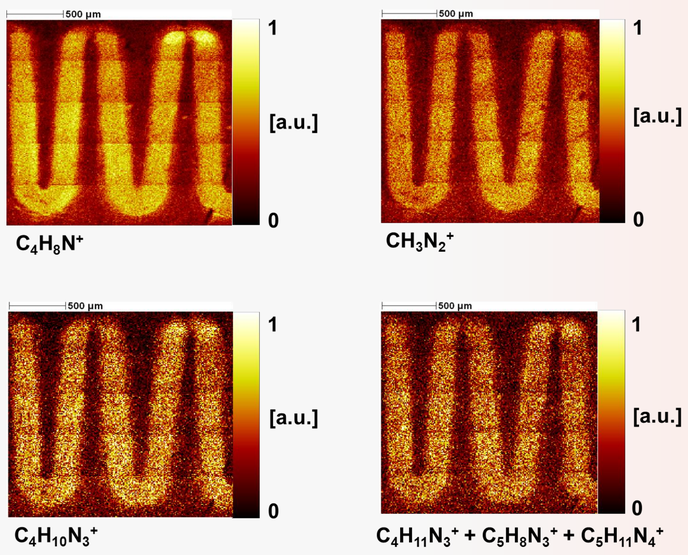


Sample Holder with shadow mask and µ-structure mask

Peptide immobilization

- Functionalization with maleimido-peptide compound
- From reference measurements $C_4H_8N^+$ is identified as a peptide characteristic positive secondary ion
- Various nitrogen-rich positive secondary ion images represent arginine sequences of peptide

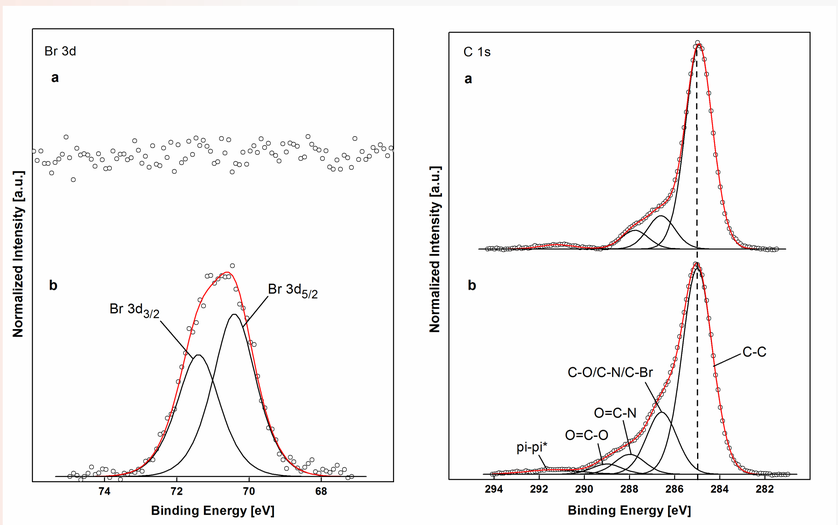




SIMS images of nitrogen-rich (+)secondary ions

X-ray Photoelectron Spectroscopy (XPS)

Analysis of silanization step (a) and model reaction with bromine-containing maleimide derivative (ATRP – Initiator) (b)



C 1s and Br 3d spectra of silanized photoactive unit **a** and after the reaction with a bromine-containing maleimide derivative **b**

C 1s

- Spectrum after silanization (**a**) can be deconvoluted into 4 components at 285.0 eV (C-C/C-H), 286.5 eV (C-O/C-N), 287.9 eV (C=O) and 291.1 eV (π-π*)
- After photoreaction (**b**) an additional characteristic component at 289.0 eV (O-C=O) proves the cycloaddition of the maleimide compound

Br 3d

- The Br 3d spectrum after silanization step indicates the absence of bromine
- Clear visible peak of bromine at 70.2 eV (bromine bond to quaternary carbon) after photoreaction

→ Both Br 3d and C 1s spectra demonstrate successful silanization and photoreaction

Conclusions

The characterization of surface-immobilized FMP moieties and of the subsequent grafting products was successfully demonstrated with XPS. In the case of peptide µ-structured samples, ToF-SIMS is the method of choice to resolve the surface patterns. Both surface analysis techniques revealed detailed information about the chemical composition of modified surfaces and contribute significantly to the successful verification of key synthetic steps.

Acknowledgement

This study was carried out with the support of the Karlsruhe Nano Micro Facility (KNMF), a Helmholtz Research Infrastructure at KIT.

Reference

T. Paulöhrl, G. Delaittre, V. Winkler, A. Welle, M. Bruns, H.G. Börner, A. M. Greiner, M. Bastmeyer, C. Barner-Kowollik, Adding Spatial Control to Click Chemistry: Phototriggered Diels–Alder Surface (Bio)functionalization at Ambient Temperature, *Angew. Chem. Int. Ed.*, 51 (2012) 1071–1074.