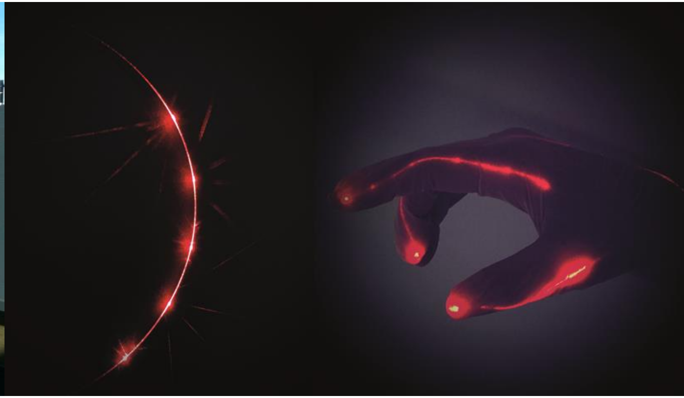
Übersicht weiterer anwendungsorientierte Aktivitäten der Wasserstoff-Forschung auf dem EnergieCampus Goslar



apl. Prof. Dr. Eike G. Hübner

Fraunhofer Heinrich Hertz Institute, HHI

Department Fiber Optical Sensor Systems

Surface Processing

Unternehmergespräch Energie

29.09.2022

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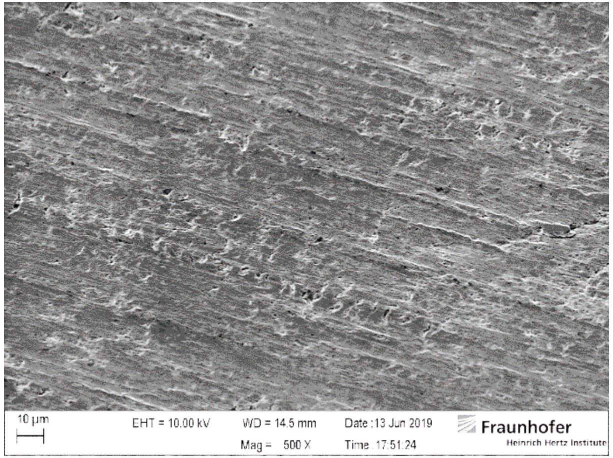
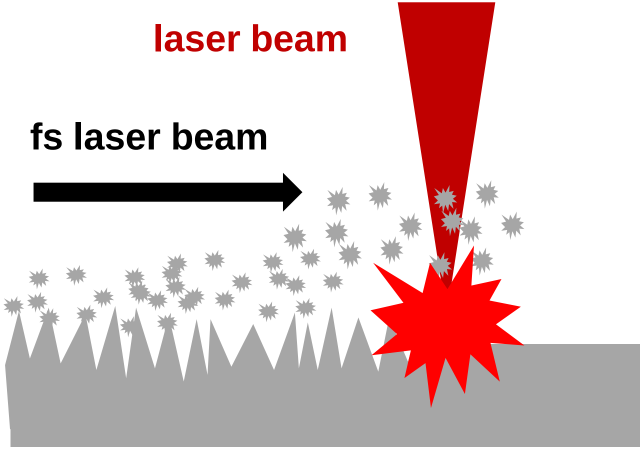
Femtosecond Laser Surface Structures

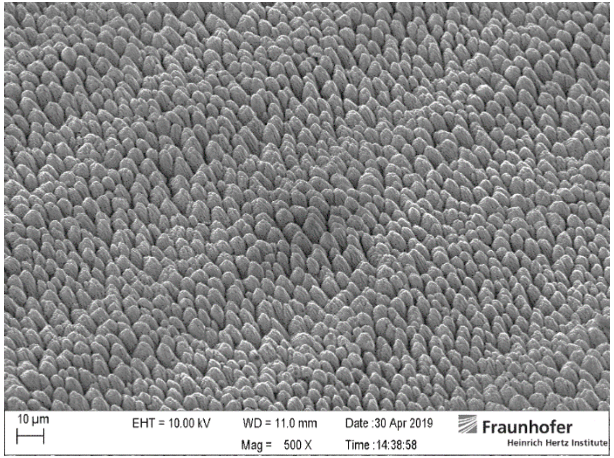
- < 0,1 mm^2 Focus spot size:
  - fs-Laser: up to 5 GW for 10^{-15} s
  - ns-Laser: 10 kW for 10^{-9} s
- Local evaporation without heating of the bulk material



pristine



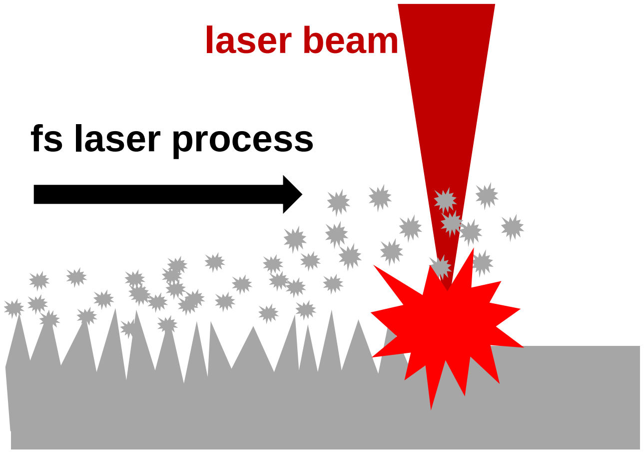
sketch of process



fs-laser structured

Femtosecond Laser Surface Structures

Structure Development



Number of laser pulses per spot on the surface[1]:

N = 1 – 10 → 10 – 25 → 25 – 50 → 50 – 100 → **100 – 250** → >> 1000

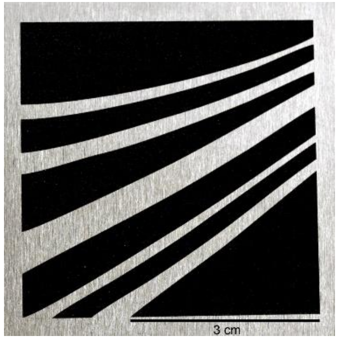
LIPSS → ripples → grooves → cones → **cones** (10 µm) → **?**

surface enlargement

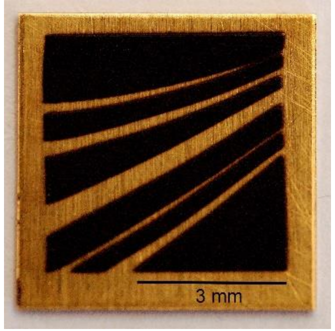
[1] for J ~ 1 J/cm² @1 - 10 kHz
See e.g. B. N. Nayak, M. C. Gupta, *Opt. Laser. Eng.* **2010**, *48*, 966 - 973.
DOI: 10.1016/j.optlaseng.2010.05.009

Femtosecond Laser Surface Structures

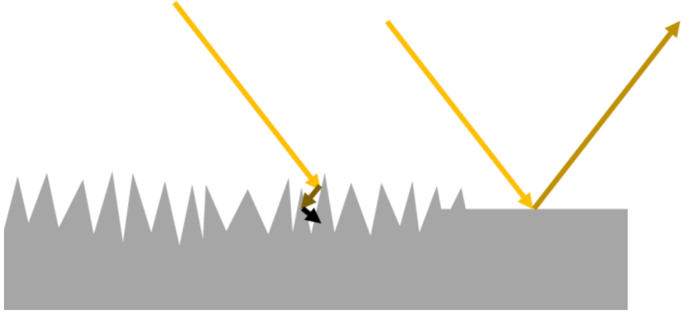
Black Metals – Black Gold



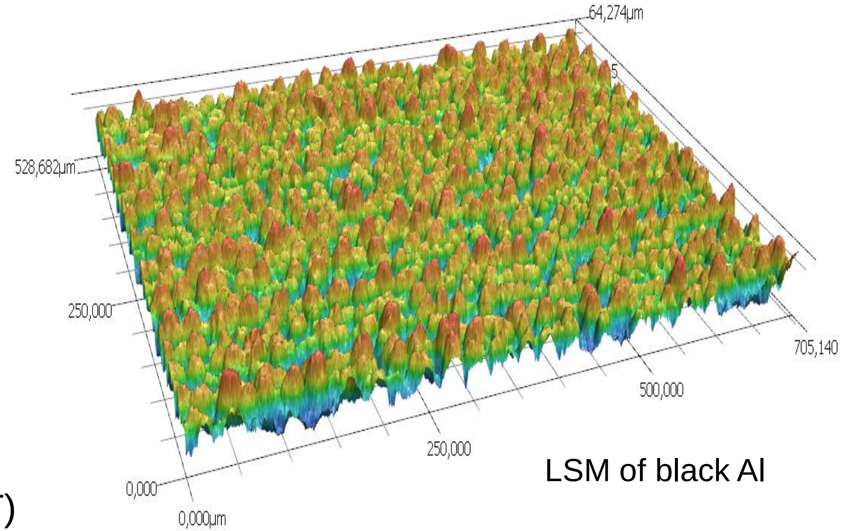
aluminum



gold



Microcones act as light trap



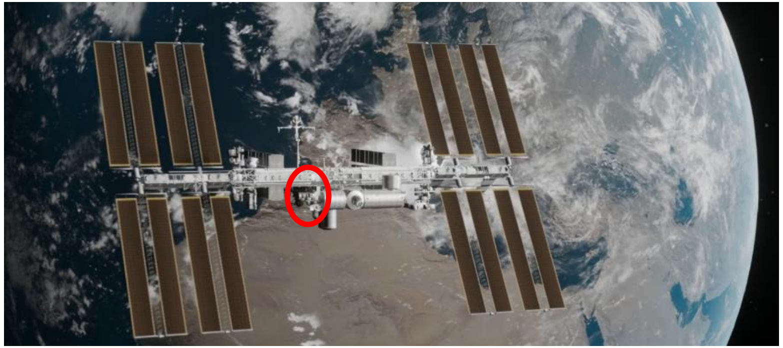
LSM of black Al

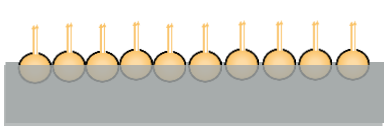
- Jewellery
  - Motifs on plates, rings, …
- Absorptivity required → **surface chemistry**!
  - N pulses[1] ~ 250
  - **Surface enlargement: ~ 10x – 20x** (LSM/BET)

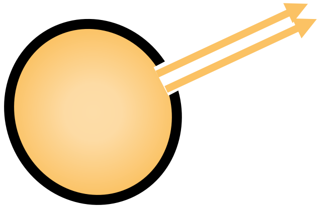
[1] for J ~ 2.5 J/cm² @10 kHz at air

Femtosecond Laser Surface Structures

Maximized Thermal Emissivity







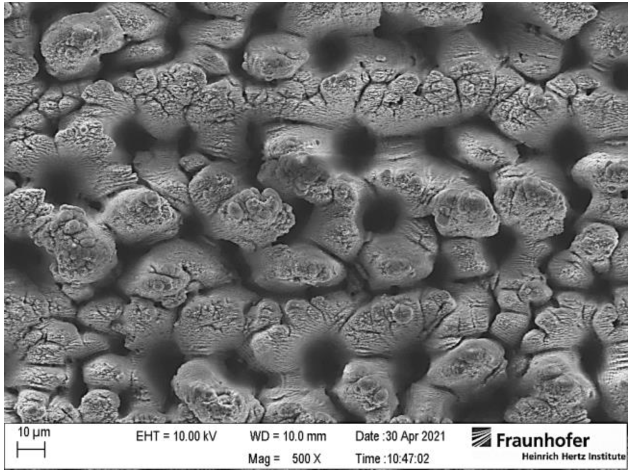
Cavity with a hole – Black Body Emitter

N pulses ~ 800[1]

Surface enlargement: ~ 20x/100x (LSM/BET)

- On the outside of the ISS from Dec. 2022
- Thermal emissivity on Al/Fe/Ti >90%
- Temperature stable
  - ➢ tested for Fe up to 650 °C

Thermographic image (100 °C)



Titanium

[1] for J ~ 4 J/cm² @10 kHz
ISS Model: **NASA Visualization Technology Applications and Development** (VTAD)
Projects: **BLAST** (ESA), **BLAST-EMA** (ESA), **STEER** (ESA)

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Femtosecond Laser Surface Structures

Liquid Organic Hydrogen Carriers (LOHC)

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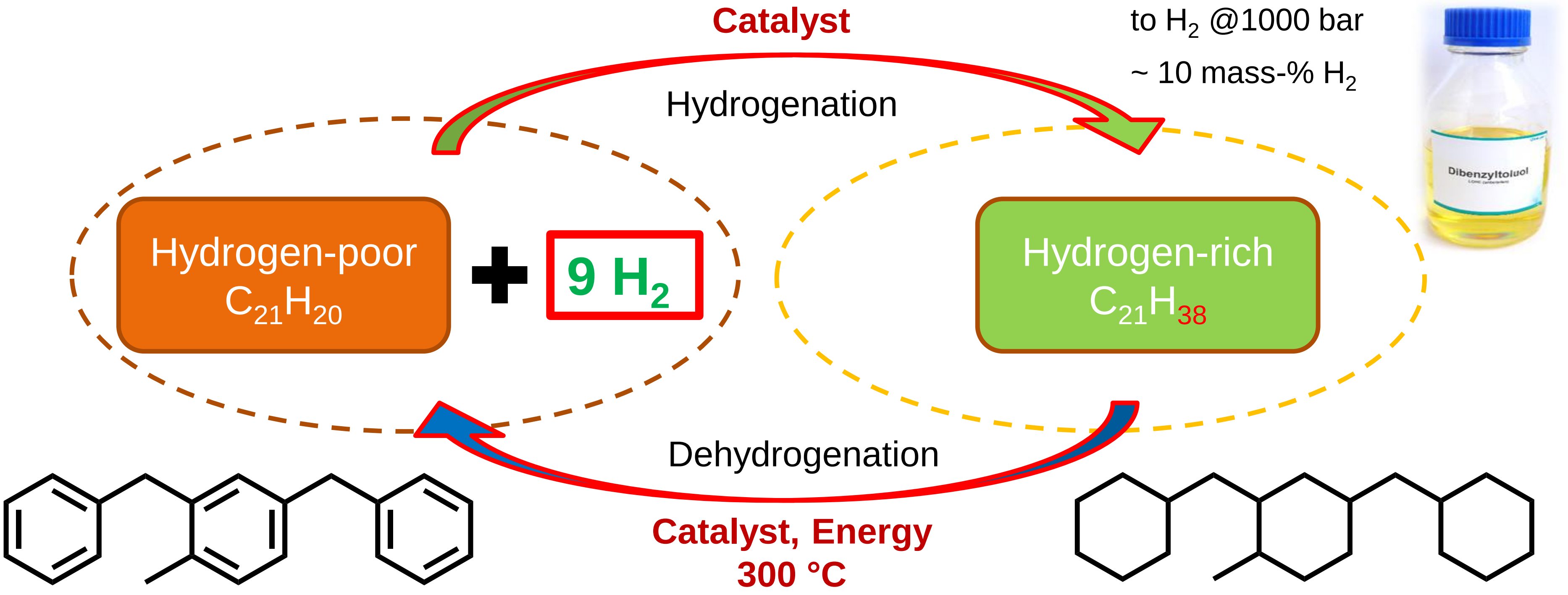
Gefördert durch
Bayerisches Staatsministerium für Wirtschaft, Landesentwicklung und Energie

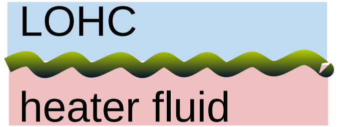
Storage density approx. eq. to H_2 @1000 bar
~ 10 mass-% H_2



Projects: **LOReley** (BMWi), **Zugprojekt** (state of bavaria)

Femtosecond Laser Surface Structures

Liquid Organic Hydrogen Carriers



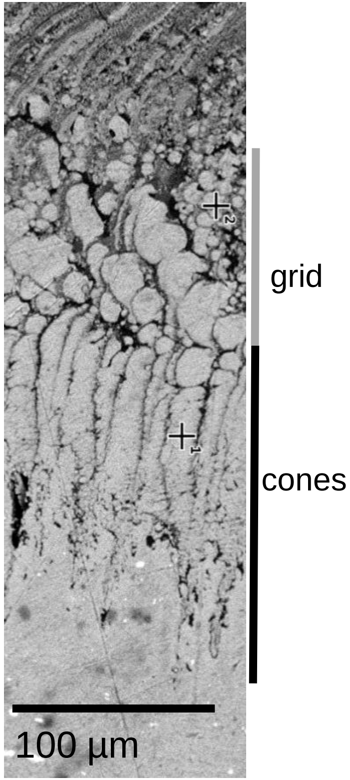
- Highly endothermic dehydrogenation reaction
  - ➢ Efficient heat transfer
- Expensive noble metals
  - ➢ Efficient catalysts (HI ERN)
- Femtosecond laser structured surfaces as catalyst carriers
  - ➢ Large surface area, stable surface structure, irregular structures

N pulses > ~ 10 x 10 000[1]

Surface enlargement: ~ 1000x (BET)

Thickness approx. 350 µm

“Micro”cones: 200 µm (height) x 20 µm



Aluminum cross-section[2]

[1] for J = 0.5 J/cm² @1 MHz
[2] cross-section: Nikolas Herz, Helmholtz Institute Erlangen-Nürnberg (HI ERN)

Projects: **LOReley** (BMWi), **Zugprojekt** (state of bavaria)

Femtosecond Laser Surface Structures

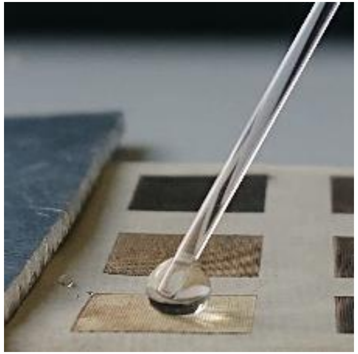
Zinc-air Batteries

GEFÖRDERT VOM
Bundesministerium
für Bildung
und Forschung

- Rechargeable zinc-air battery
- Key part: (bifunctional) gas diffusion electrode (GDE)
  - ➢ Ag/AgO (Co_3O_4) and hydrophobic binder
- Femtosecond laser structuring to optimize surface structure and wettabiliy

Θ → 180°

Θ → 0°

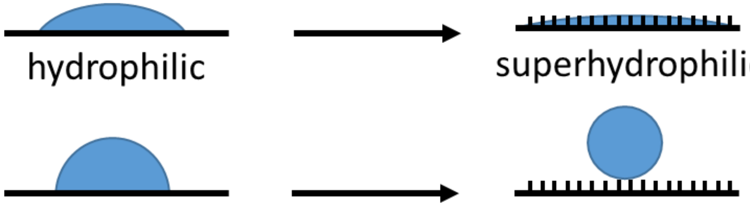


Θ → 180°

Θ → 0°

Video: Oxygen evolution

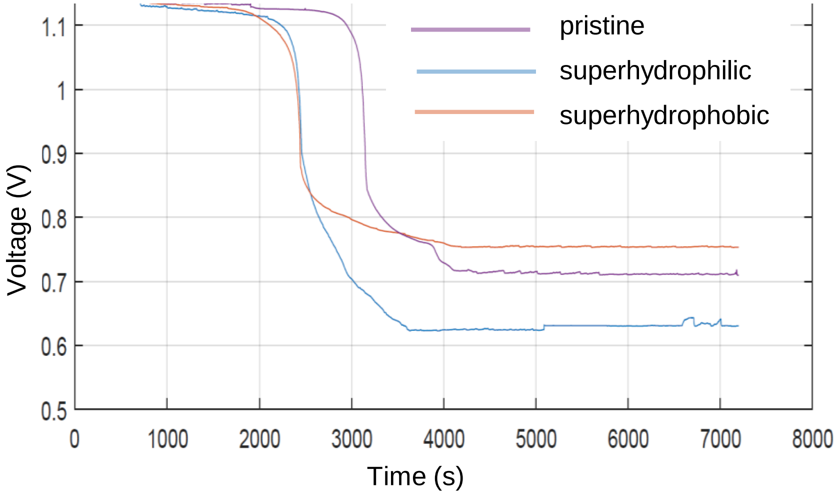
Femtosecond Laser Surface Structures

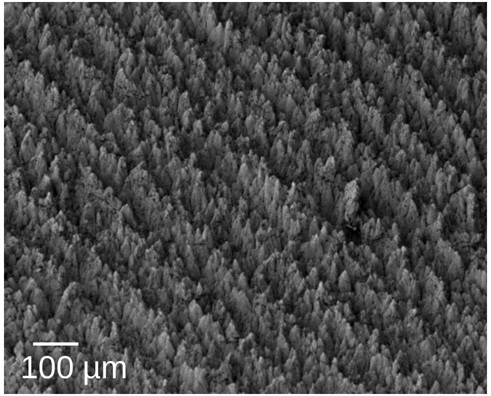


Controlling Wettability

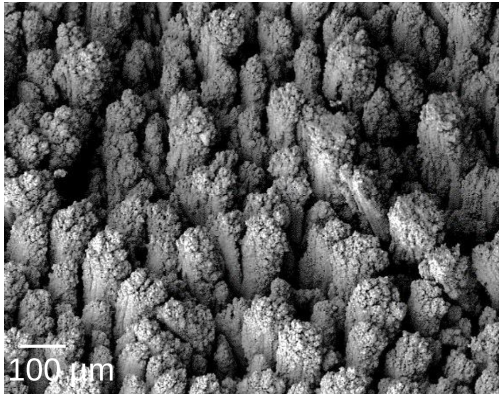
- Rechargeable zinc-air battery
- GDE water contact angle: 0° vs. 130° (pristine) vs. 180°
- Improved oxygen consumption

➢ Cell voltage - 0.1 V (0°) → + 0.05 V(180°)





Θ → 0°

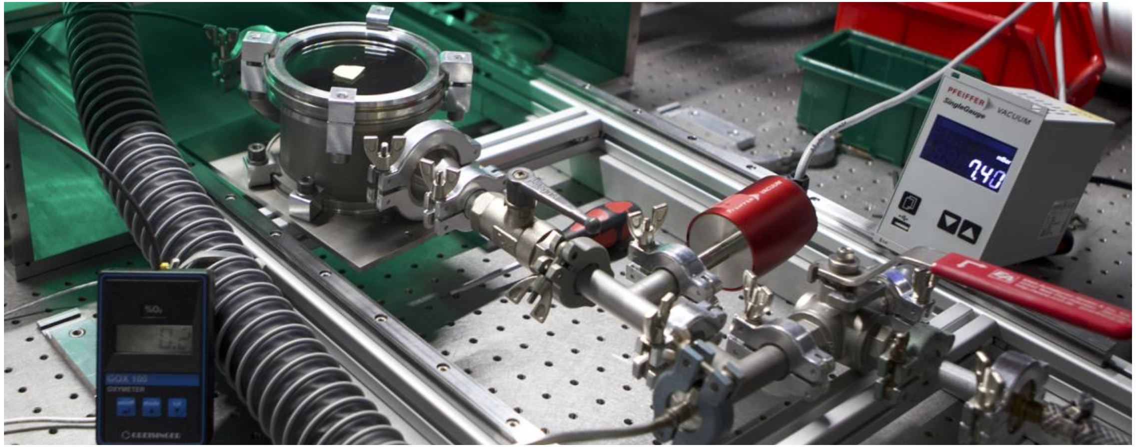


Θ → 180°

Femtosecond Laser Surface Structures

Controlling Surface Chemistry

- To control wettability
- Optimized stoichiometry for catalysts
- Ar, N_2, CO_2, O_2, Cl_2, Br_2, I_2, acetylene, …

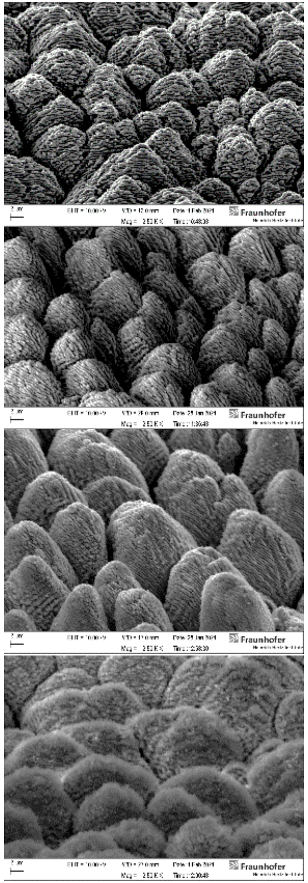


@ Argon:
2.5 atom-% O

@ CO_2:
12 atom-% O

@ Air:
36 atom-% O

@ O_2:
46 atom-% O



steel

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[1] R. Fedorov, F. Lederle, M. Li, V. Olszok, K. Wöbbeking, W. Schade, E. G. Hübner, *ChemPlusChem* **2021**, *86*, 1231 - 1242.
DOI: 10.1002/cplu.202100118

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Femtosecond Laser Surface Structures

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Bundesministerium für Wirtschaft und Energie
Gefördert durch:
Niedersächsisches Ministerium für Wissenschaft und Kultur

Electrodes for Alkaline Water Electrolysis (AEL)

- Key Factor: Overpotential reduction
  - ➢ Recent reviews define major aspects[1]:
    - Specific surface area (Tafel equation: overpotential η (V) ~ current density i (A/cm²))
    - Presence of gas bubbles on the surface of the electrode
    - Electrocatalytic materials

- Surface enlargement
  - ➢ Porosity

Superhydrophilicity

Nickel oxides

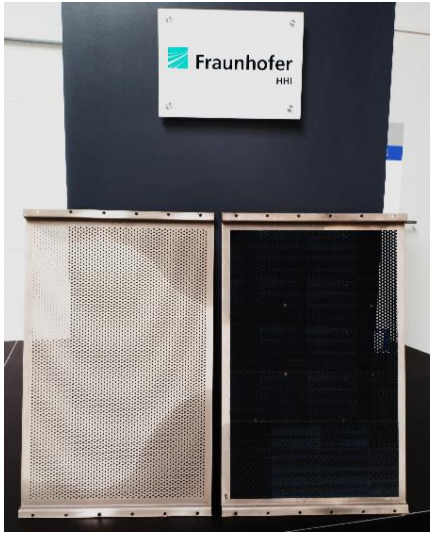
N pulses >1000 ⟷ N pulses >250 processing at oxygen/air ⟷ processing at oxygen/air

[1] see e.g. M. David, C. Ocampo-Martínez, R. Sánchez-Peña, *J. Energy Storage* **2019**, *23*, 392 - 403.
DOI: 10.1016/j.est.2019.03.001

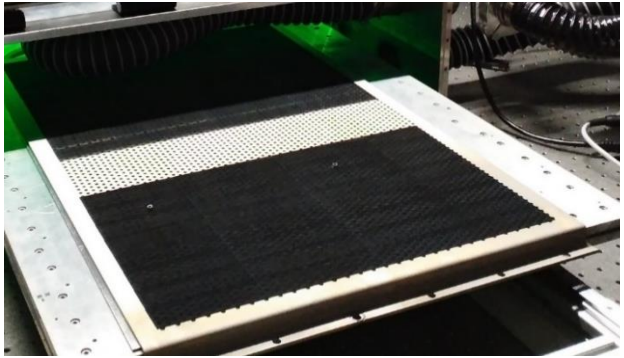
Projects: **GreenH2** (BMWi), **InnoEly** (state of lower saxony)

Femtosecond Laser Surface Structures

Large Scale Electrodes[1]

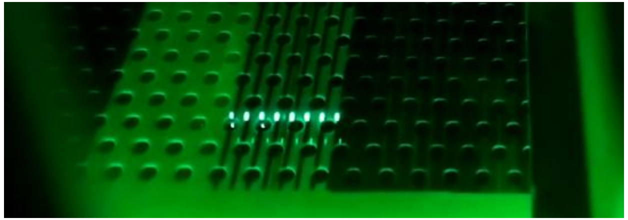


- Base material: Steel coated with approx. 300 µm nickel (MTV)
- 0.66 x 0.41 m² structured on both sides (0.54 m² per electrode)
- N pulses ~20 x 2000[2]
- Processed at air
    - ➢ Porous microcones, nickel oxides, superhydrophilic surface



processing time: ~ 150 h / electrode

8-fold beam via diffractive element



[1] C. I. Bernäcker, T. Gimpel, A. Bomm, T. Rauscher, M. Li, E. G. Hübner, W. Schade, T. Weißgärber, L. Röntzsch, *J. Power Sources*, to be submitted.

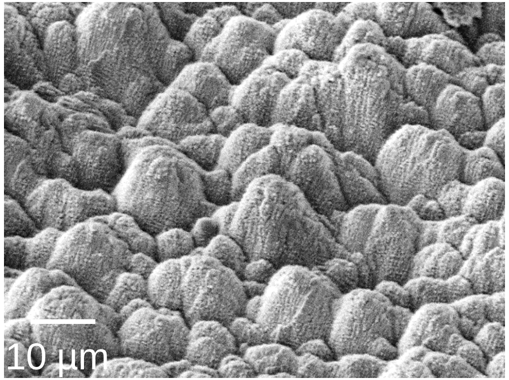
[2] for J ~ 0.1 J/cm² @ 1 MHz

Electrolyzer: Christian I. Bernäcker, IFAM Dresden

Femtosecond Laser Surface Structures

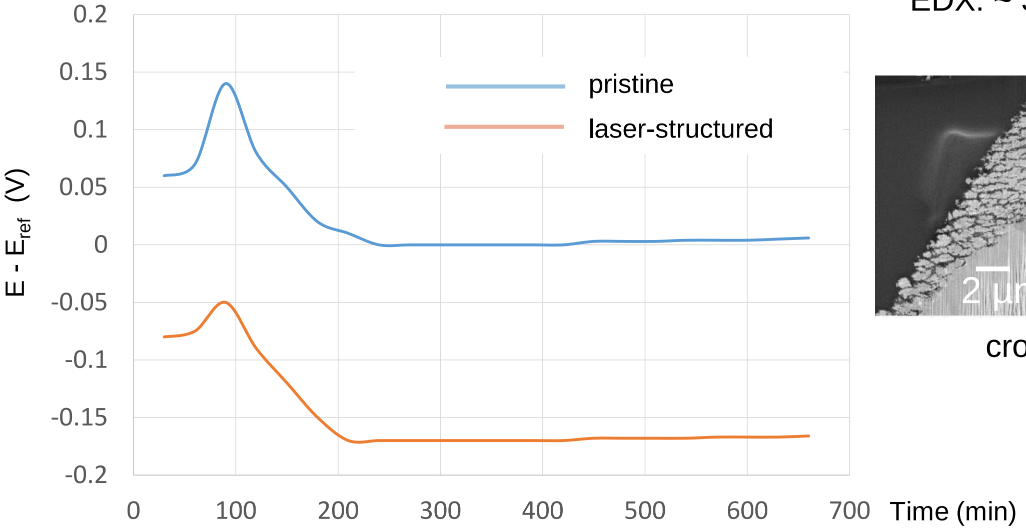
Electrodes for Alkaline Water Electrolysis (AEL)

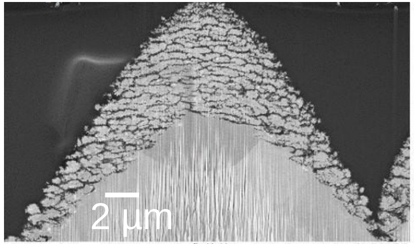
- Surface enlargement ~100x (BET)
- Operation of electrodes at realistic conditions (Fraunhofer IFAM)
- 4 Electrodes laser-structured (both sides) vs. 4 pristine electrodes



EDX: ~ 30 atom-% O

- ➢ 750 A per electrode
  300 mA/cm²
- ➢ Overpotential reduced
  by approx. 150 mV
- ➢ Process efficiency increased
  by approx. 10 %





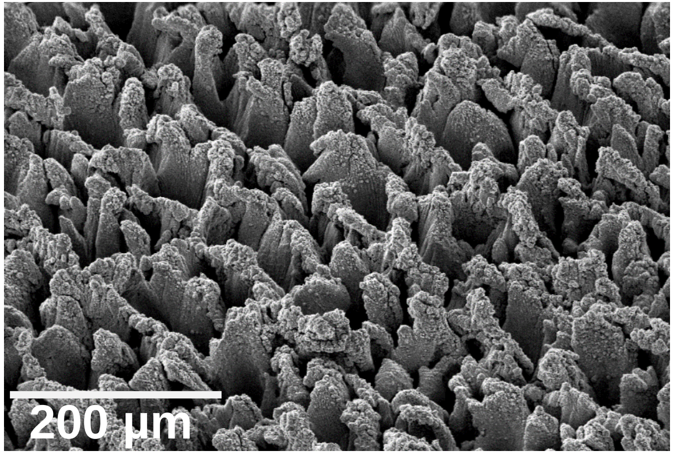
cross-section[2]

[1] C. I. Bernäcker, T. Gimpel, A. Bomm, T. Rauscher, M. Li, E. G. Hübner, W. Schade, T. Weißgärber, L. Röntzsch, *J. Power Sources*, to be submitted.
Project: **GreenH2** (BMWi)
[2] cross-section: Christian I. Bernäcker, IFAM Dresden

Fem2Nano

Self-organized Structure Formation

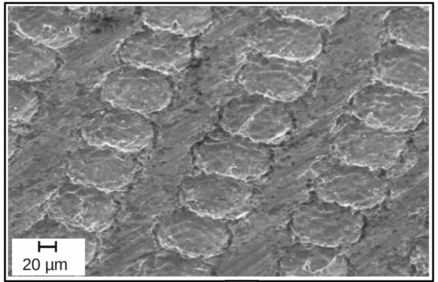
- Microcones and related structural motifs
  - ➢ By physical and chemical ablation processes
  - ➢ Initiated by energy input (laser light) on the surface



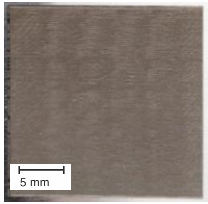
Fem2Nano

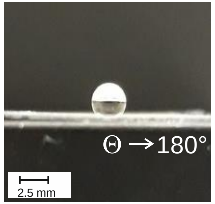
Transfer from Femtosecond to Nanosecond Laser Pulses

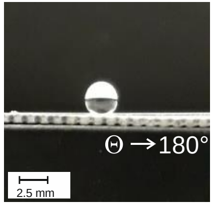
- Assisted by chemical ablation („etching“)

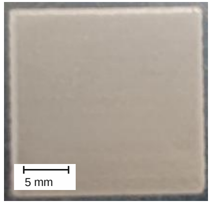


α = 77 %





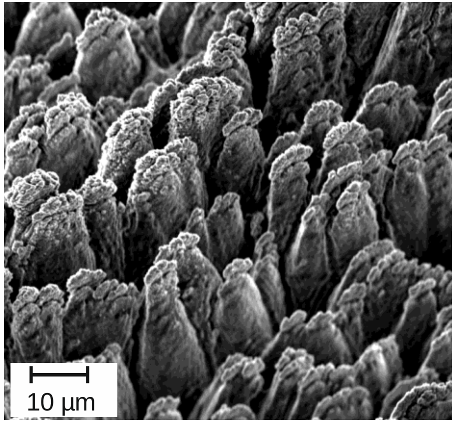




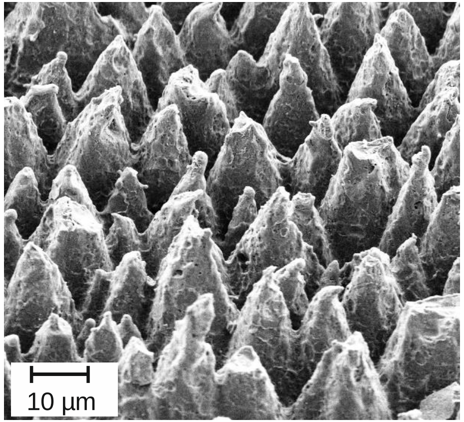
α = 56 %

Process parameters:

- τ = 60 fs
- J = 2.6 J/cm²
- N = 250 pulses
- N_2-atmosphere



vs.



τ = 6 ns

J = 9.8 J/cm²

N = 512 pulses

iodine/reduced pressure

EDX [atom-%]: 97 % Al, 3 % O — 98 % Al, 2 % O

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[1] S. Rauh, K. Wöbbeking, M. Li, W. Schade, E. G. Hübner, *ChemPhysChem* **2020**, *21*, 1644 - 1652.
DOI: 10.1002/cphc.202000418

[2] K. Wöbbeking, M. Li, E. G. Hübner, W. Schade, *RSC Advances* **2019**, *9*, 37598 - 37607.
DOI: 10.1039/c9ra05918k

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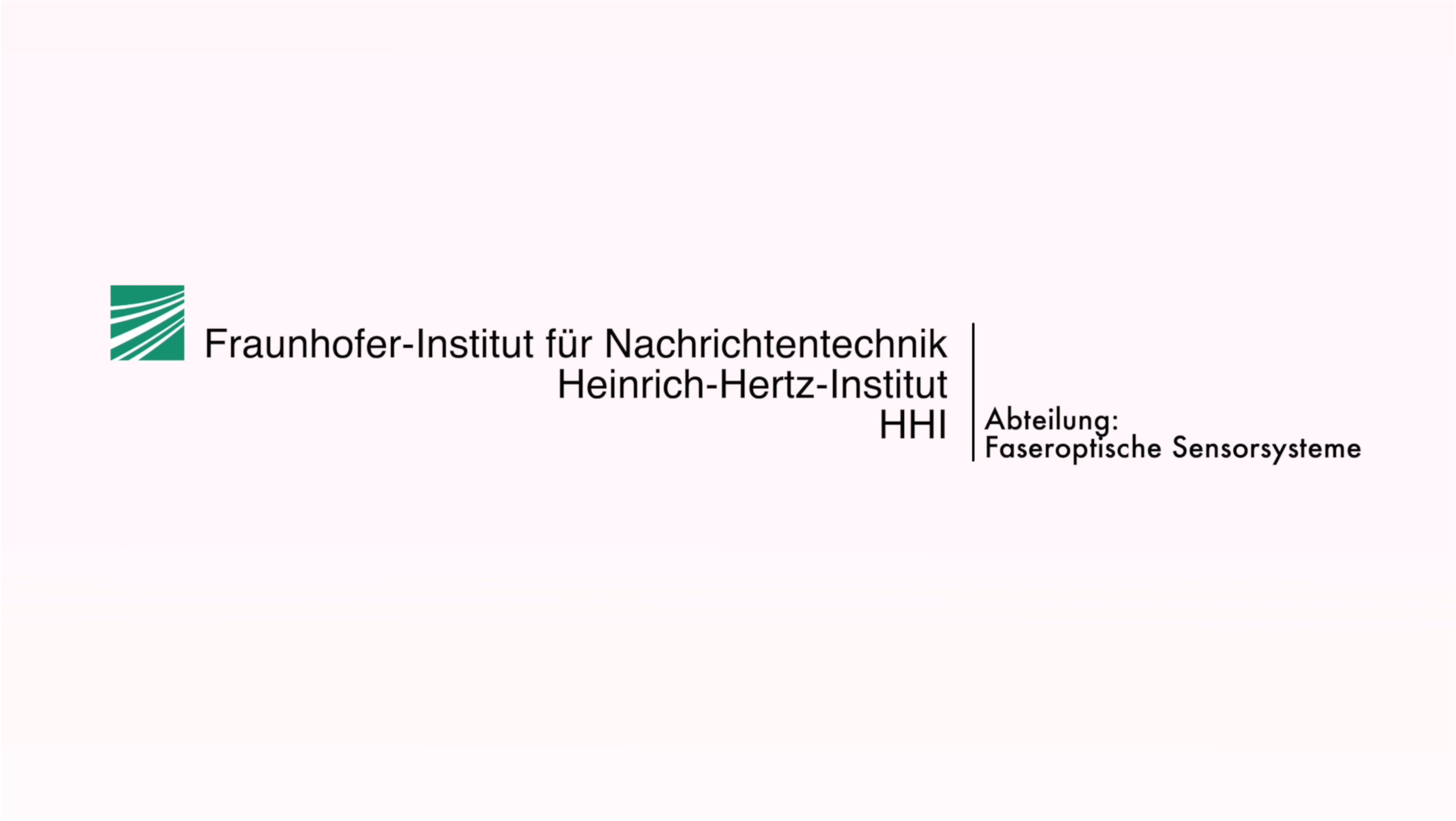
Summary



https://www.youtube.com/watch?v=i9LskwHnCEo

Acknowledgement

HI ERN Helmholtz Institute Erlangen-Nürnberg

efzn Energie-Forschungszentrum Niedersachsen

EST Forschungszentrum Energiespeichertechnologien

VARTA

covestro

Fraunhofer CAPS

Fraunhofer IFAM

TU Clausthal

AZIMUT SPACE

esa

FAU Friedrich-Alexander Universität Erlangen-Nürnberg

hydrogenious LOHC Technologies

AMPHOS Member of the TRUMPF Group

DLR Institut für Vernetzte Energiesysteme

Dr. Felix Lederle

Mingji Li

Karl Wöbbeking (Rotator)

Simon Rauh (Fem2Nano)

Rostislav Fedorov (TiN, TiC)

Hafizuddin Bin Mohd Lowin (Space)

Philipp Memmel (Ceramics)

MIOPAS

Leibniz Universität Hannover

Kelvion

ISFH