Laser-basierte Nanopartikelsynthese und Ihre Herausforderungen für die RFA

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TECHNICAL CHEMISTRY I
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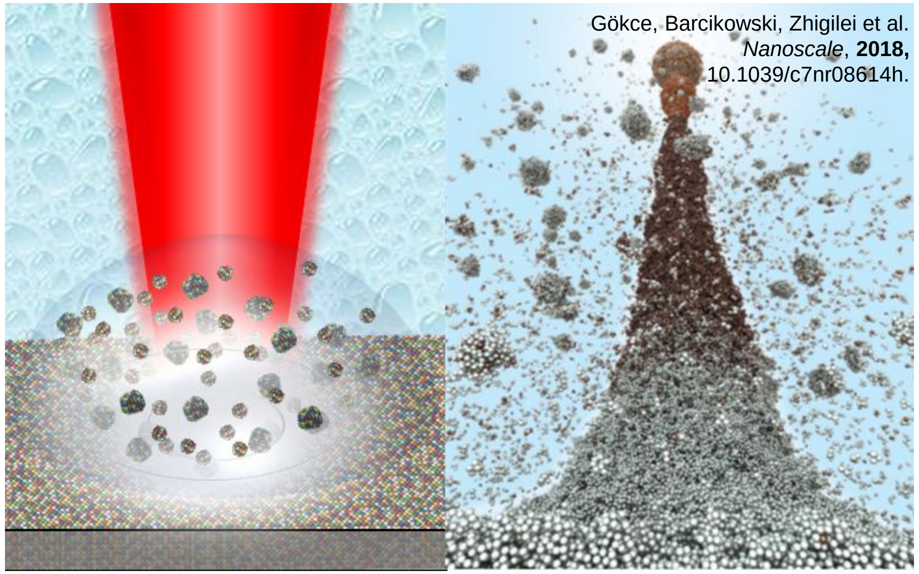
NETZ
CENIDE
UNIVERSITÄT DUISBURG ESSEN
Offen im Denken
DFG Deutsche Forschungsgemeinschaft
German Research Foundation
Bundesministerium für Bildung und Forschung

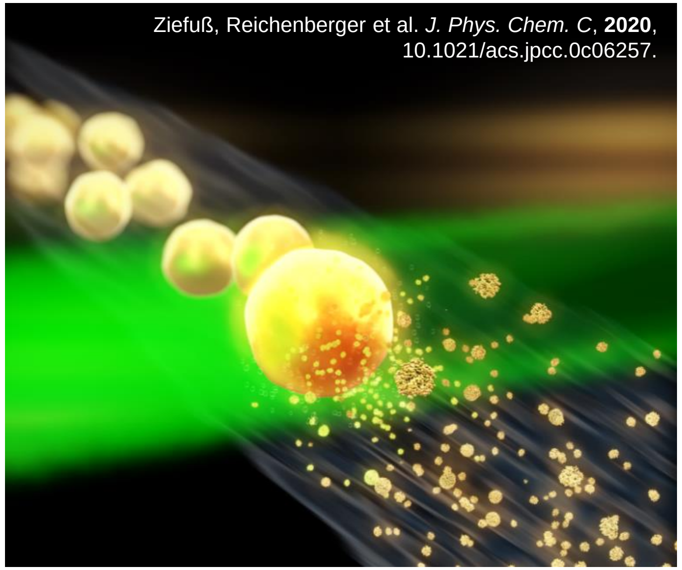
Im Herzen Europas

Laser Synthesis and Processing of Colloids (LSPC)

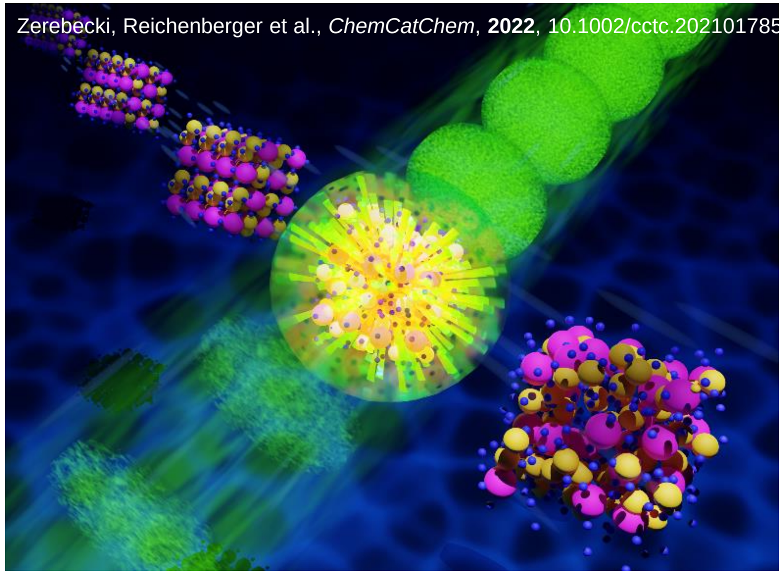
Laser ablation in liquid (LAL)



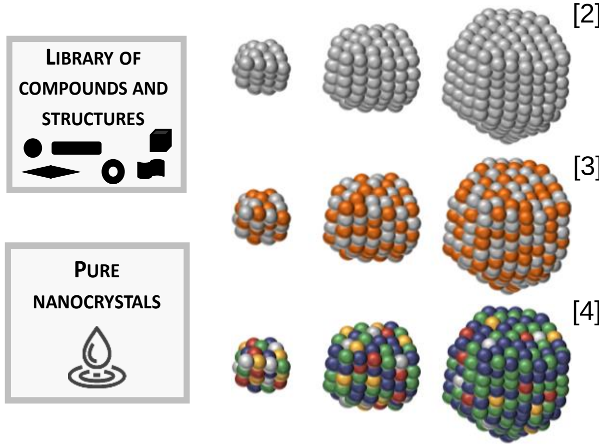
Laser fragmentation in liquid (LFL)



Laser defect-engineering and surface doping in liquid

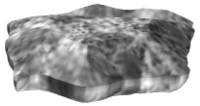


Laser-based Synthesis[1]



Support material

Oxide

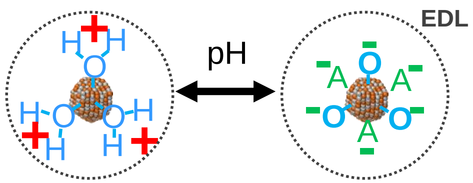


Carbon / Graphene

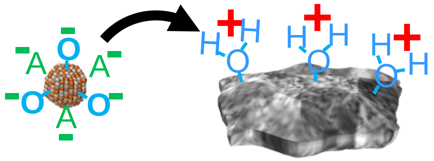
… others

Colloidal deposition

pH-dependence of zetapotential



Electrostatic attraction[5]



[1] V. Amendola, D. Amans, Y. Ishikawa, N. Koshizaki, S. Scirè, G. Compagnini, S. Reichenberger, S. Barcikowski, *Chem. - A Eur. J.* **2020**, *26*, 9206–9242.

[2] Dong, W., Reichenberger, S., Chu, S., Weide, P., Ruland, H., Barcikowski, S., Wagener, P., & Muhler, M. (2015). *Journal of Catalysis*, *330*, 497–506

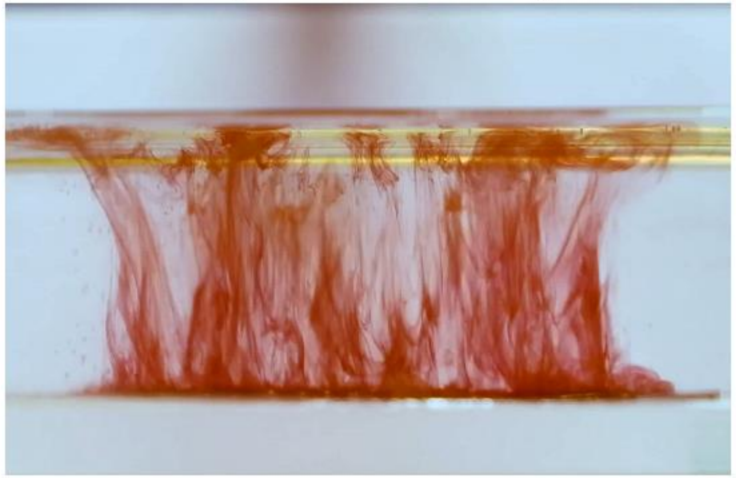
[3] Schade, O. R., Stein, F., Reichenberger, S., Gaur, A., Saraçi, E., Barcikowski, S., Grunwaldt, J. D. (2020), Adv. Synth. Catal. 2020, 362, 5681-5696

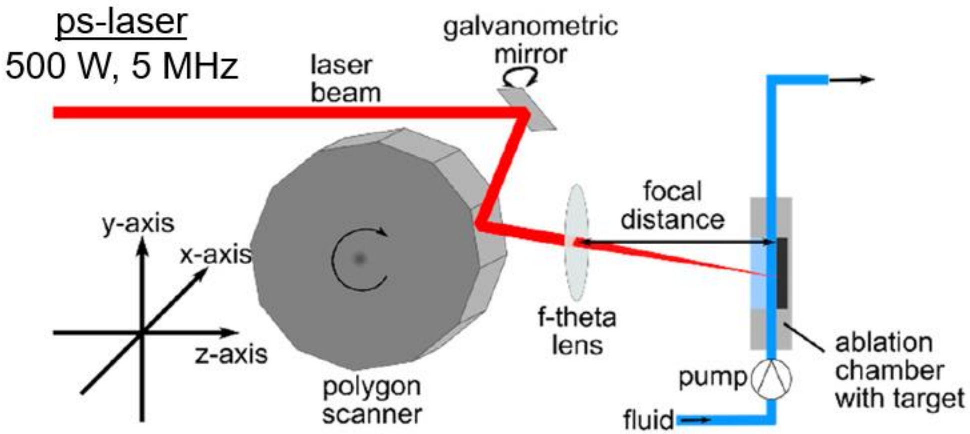
[4] Waag, F., Li, Y., Ziefuß, A. R., Bertin, E., Kamp, M., Duppel, V., Marzun, G., Kienle, L., Barcikowski, S., Gökce, B. (2019) *RSC Advances*, *9*(32), 18547–18558.

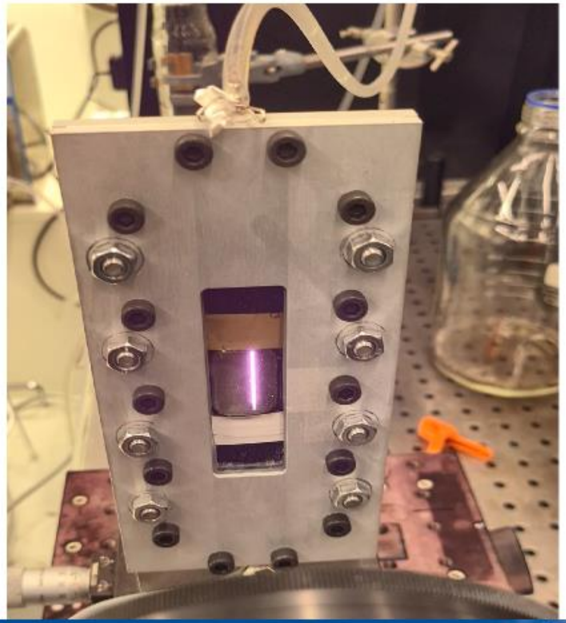
[5] Marzun, G., Streich, C., Jendrzej, S., Barcikowski, S., Wagener, P. (2014), *Langmuir*, *30*(40), 11928–11936.

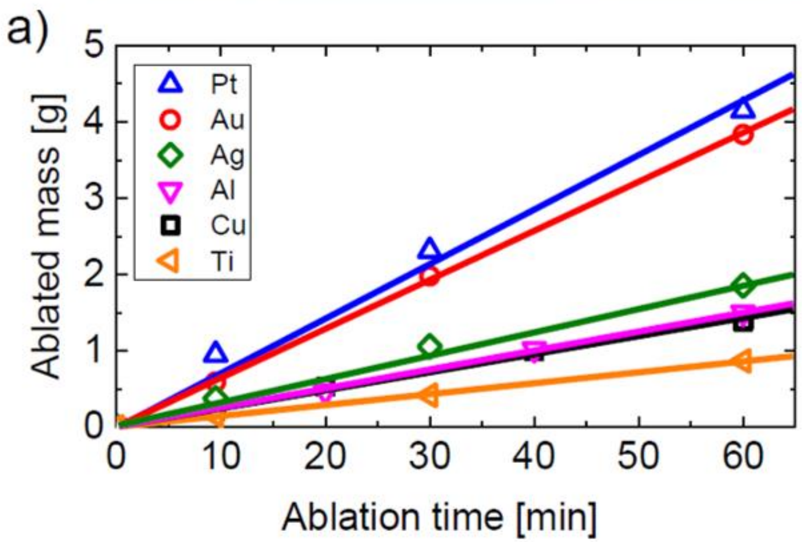
Scalability and kg-scale synthesis of het. catalysts

Scale up of laser power

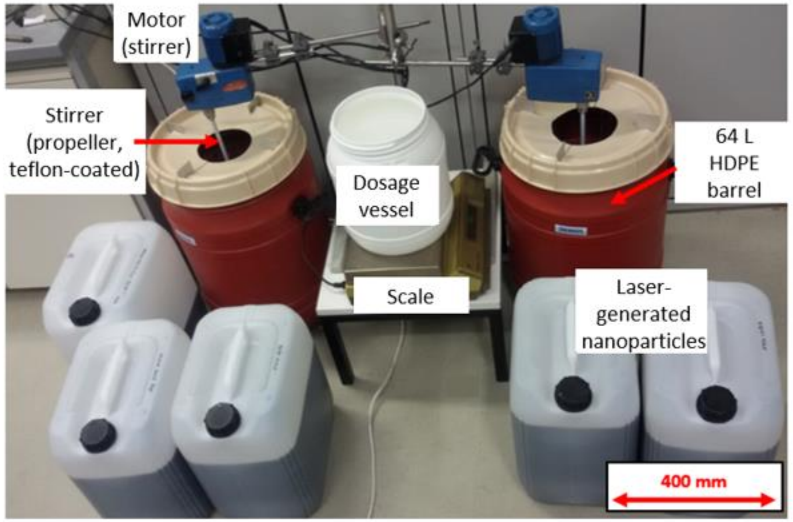








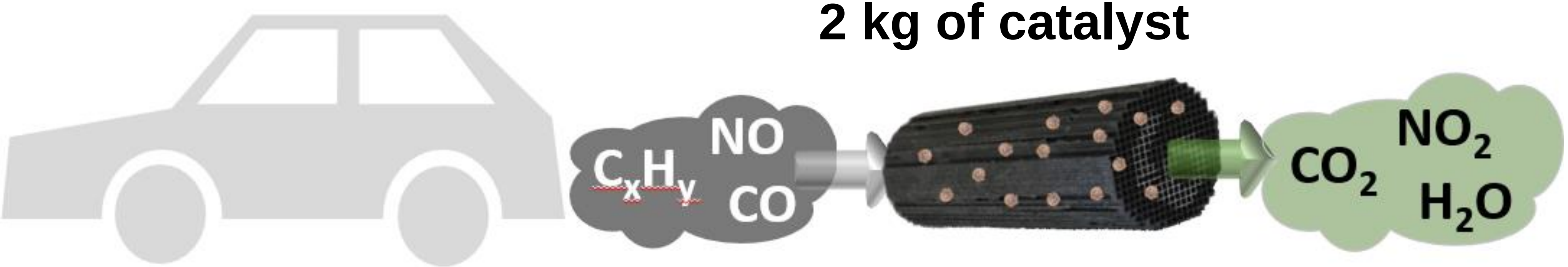
Streubel, R., Barcikowski, S., & Gökce, B. (2016). *Optics letters*, *41*(7), 1486-1489.

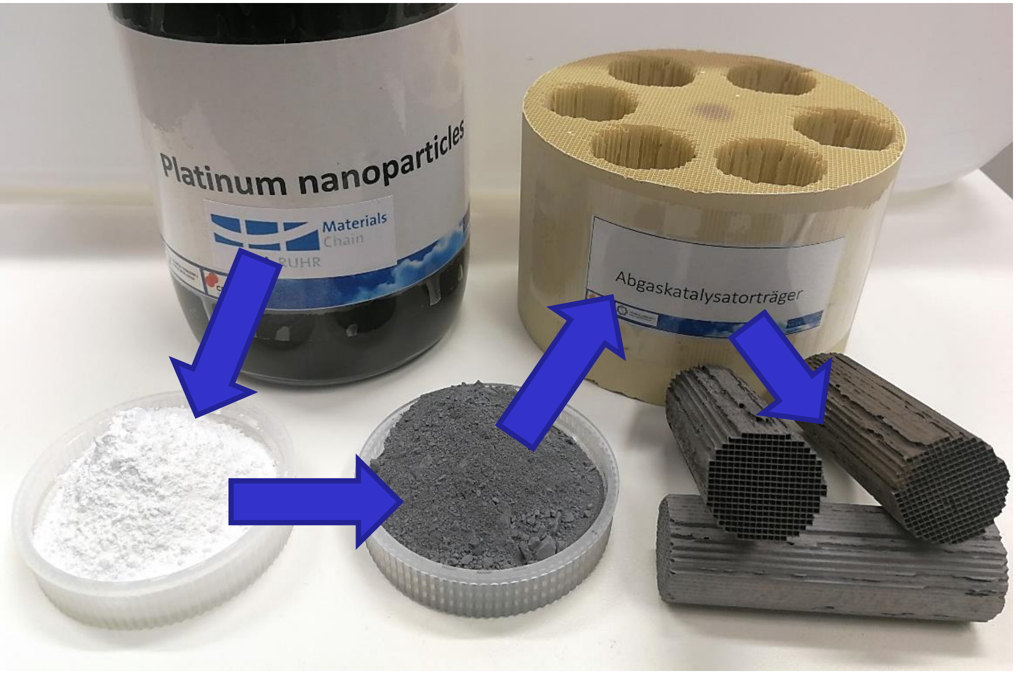


Dittrich, S., Kohsakowski, S., Wittek, B., Hengst, C., Gökce, B., Barcikowski, S., Reichenberger S., (2020) *Nanomaterials*, 10, 1582

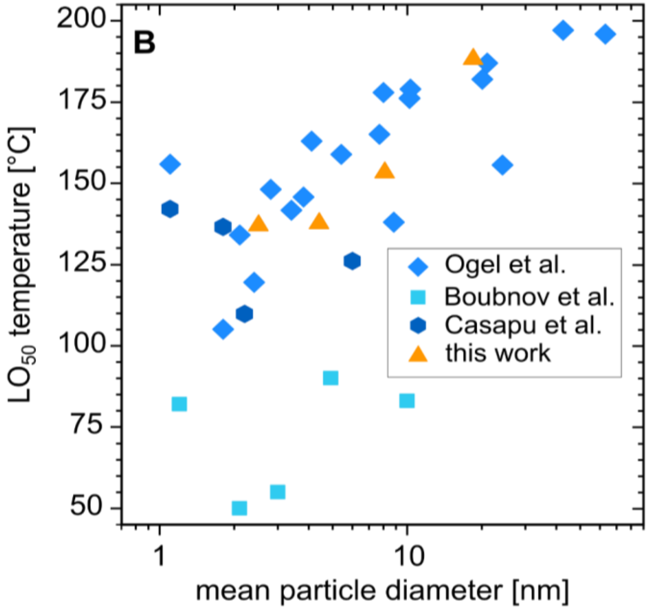
Laser-generated benchmark catalysts: exhaust gas treatment

2 kg of catalyst

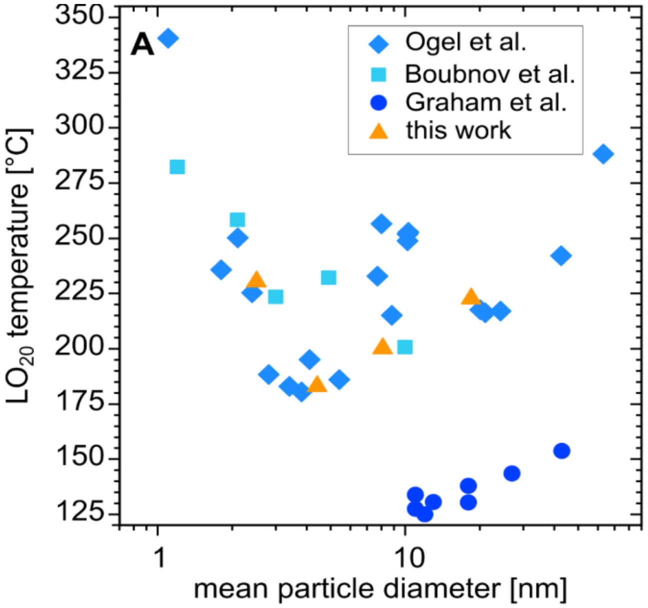




CO conversion



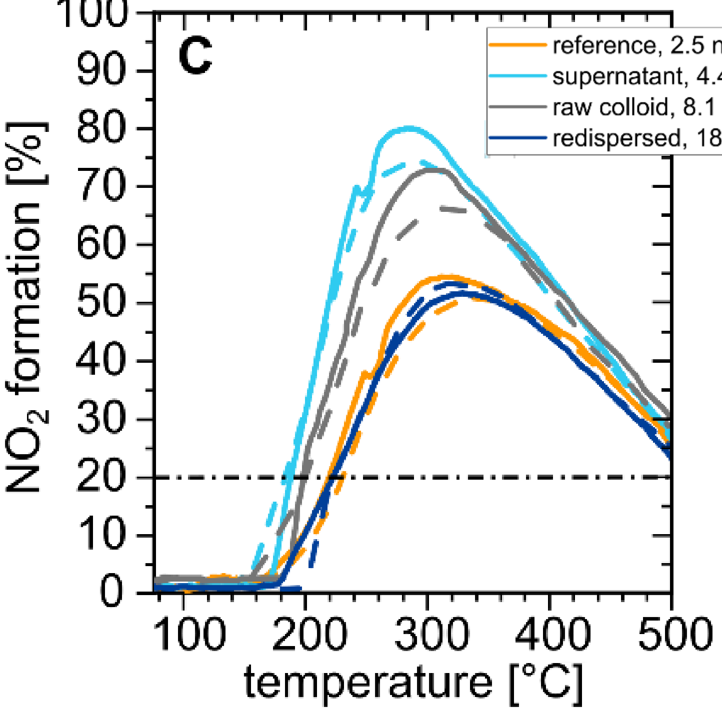
NO conversion



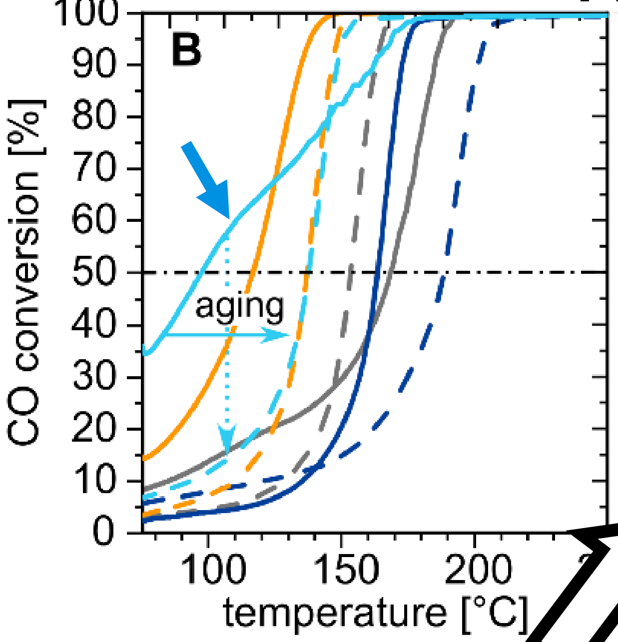
S. Dittrich, S. Kohsakowski, B. Wittek, C. Hengst, B. Gökce, S. Barcikowski, S. Reichenberger, *Nanomaterials* **2020**, *10*, 1–16.

Features of laser-generated catalysts

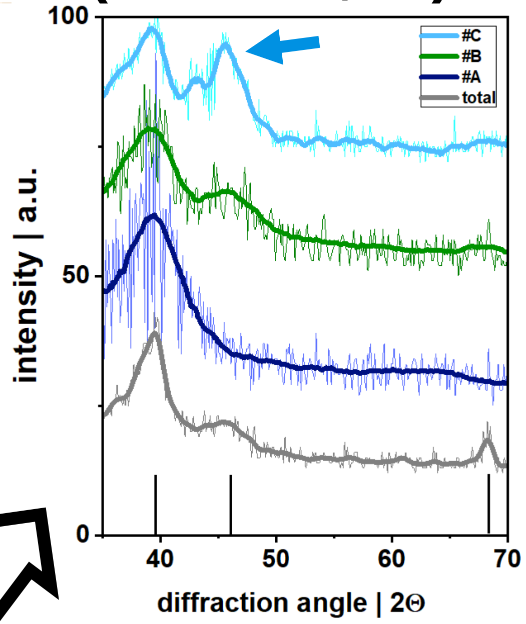
NO conversion

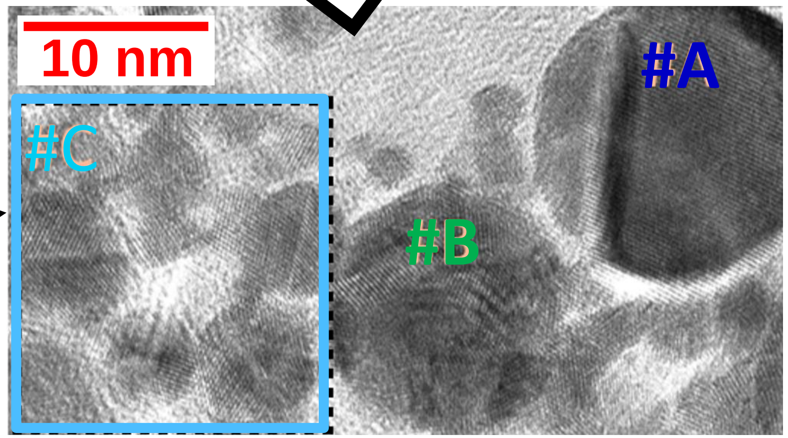


CO conversion



FFT (HR-TEM; Pt)





NO: active and stable catalysts!

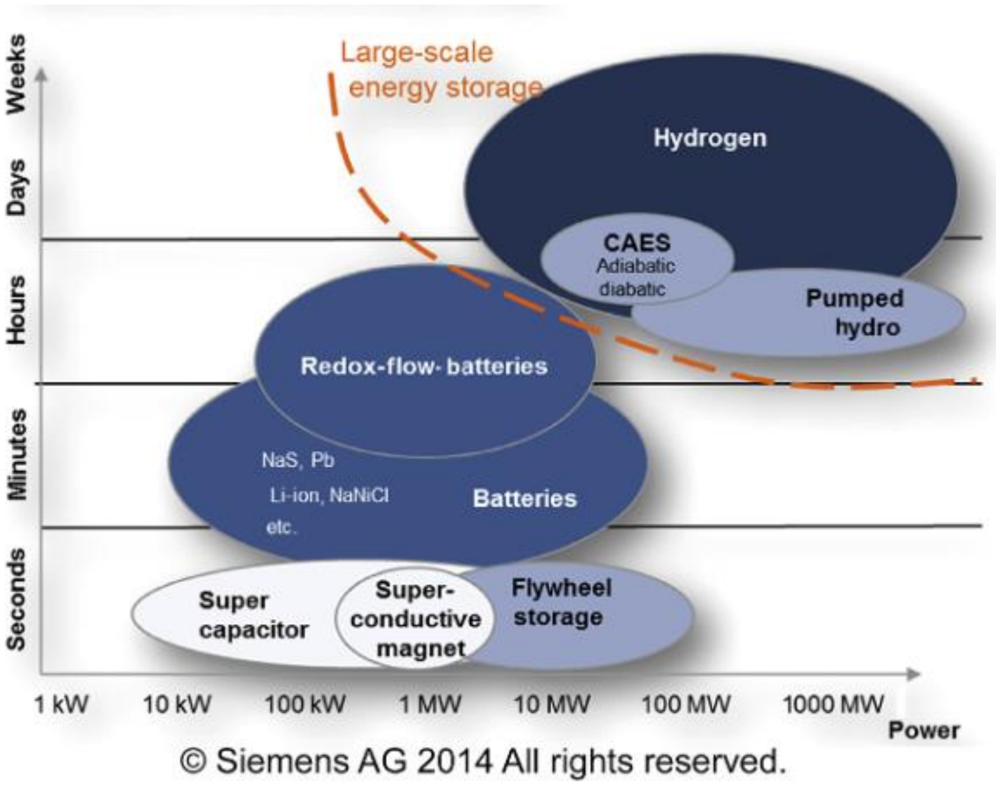
CO: dynamic active sites with low temp. activity (higher order facets & defects for NP < 5 nm)

S. Reichenberger, G. Marzun, M. Muhler, S. Barcikowski, *ChemCatChem* **2019**, *11*, 4489–4518.

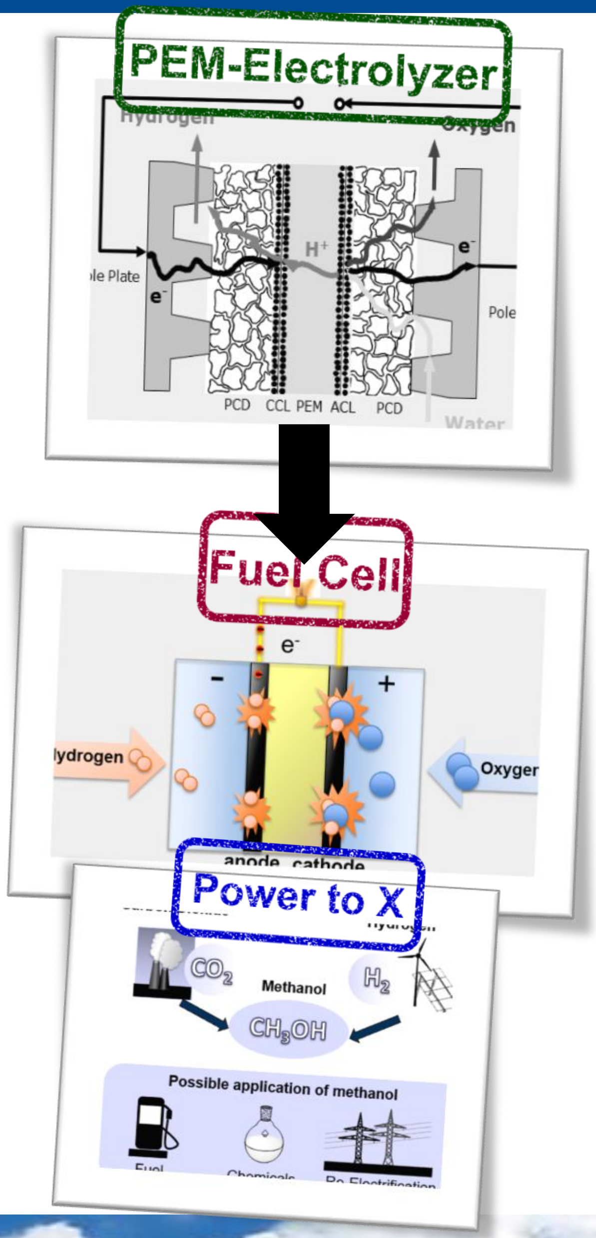
S. Dittrich, S. Kohsakowski, B. Wittek, C. Hengst, B. Gökce, S. Barcikowski, S. Reichenberger, *Nanomaterials* **2020**, *10*, 1–16.

Nanoparticle design

The Noble Metal-Challenge of Hydrogen-based Technologies



R. Wolf, Electrochemical Energy Storage for Renewable Sources and Grid Balancing, Chapter 9: Large-Scale Hydrogen Energy Storage, 2015, Elsevier, https://doi.org/10.1016/B978-0-444-62616-5.00009-7

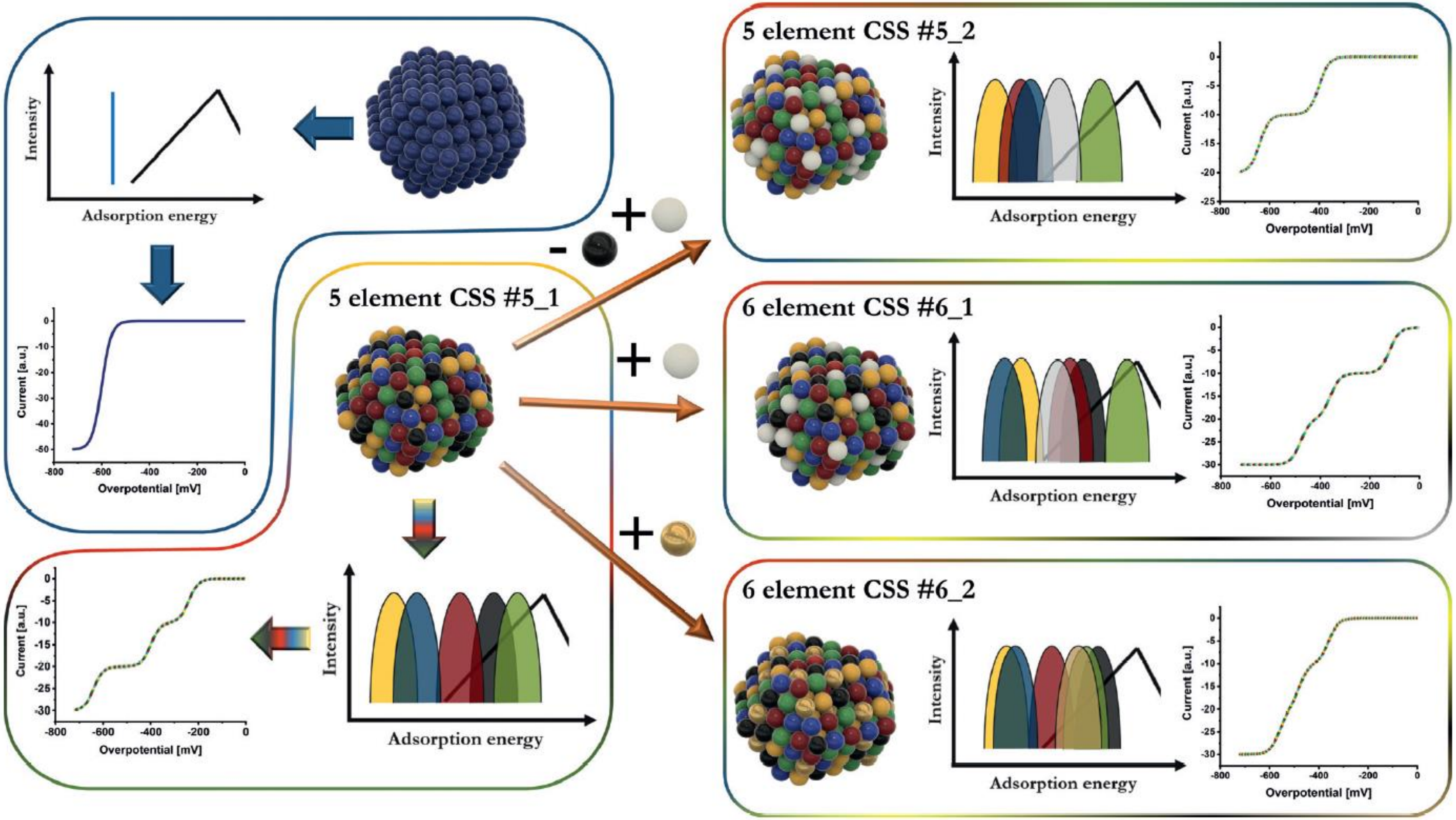


Challenge: Demand for expensive catalysts

→ Iridiumoxide (Oxygen evolution reaction)

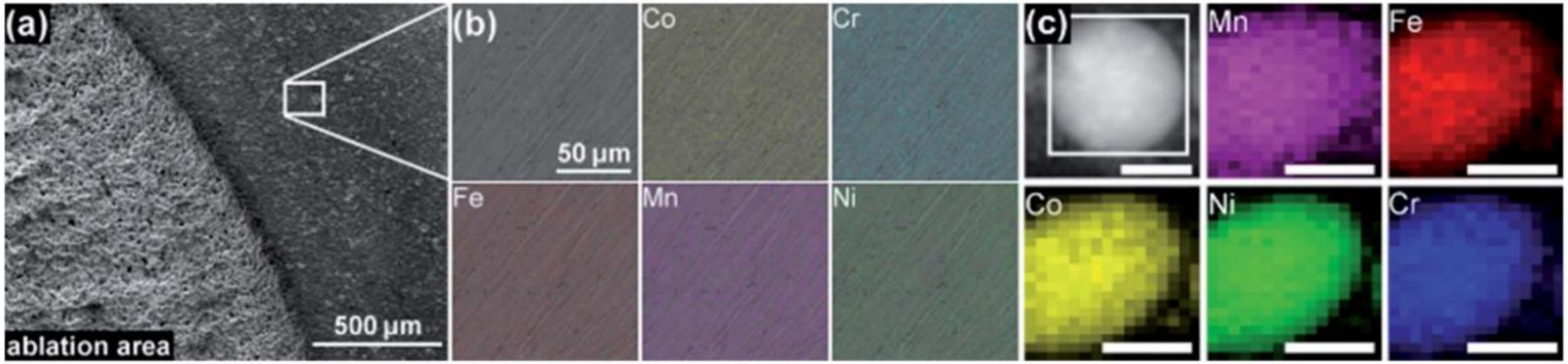
→ Platinum (Oxyen reduction reaction)

Discovering New Active Sites for Noble Metal-free Electrocatalysts

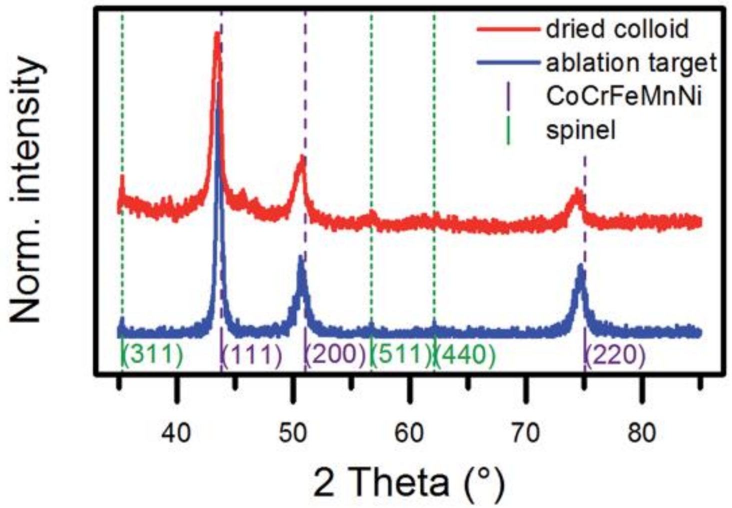


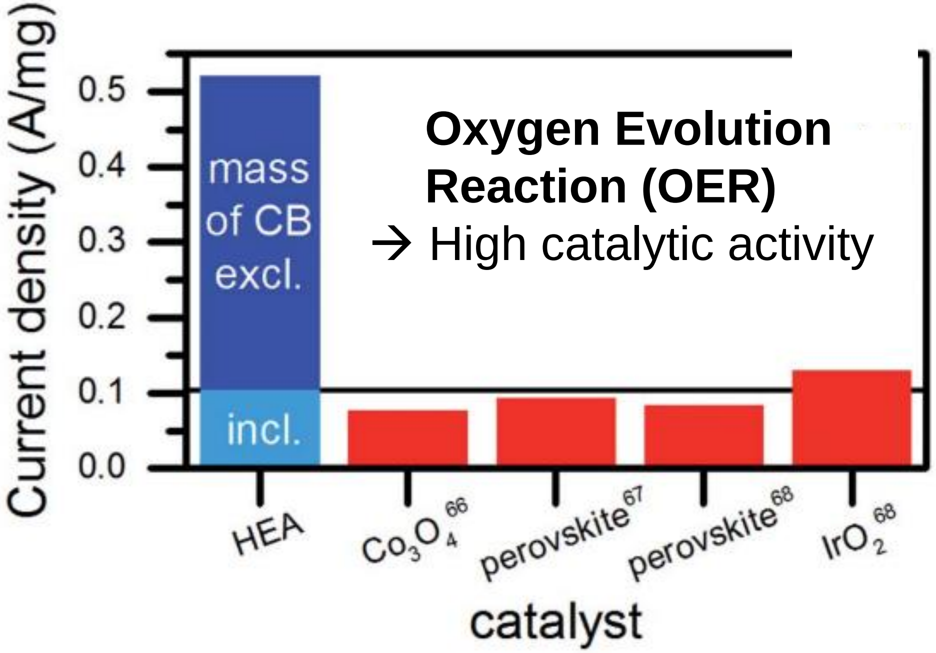
A. Ludwig & W. Schuhmann, *Angew. Chemie Int. Ed.*, 2020, 59, 14, 5844–5850

Laser-based Synthesis of Active HEA-based Electrocatalysts



Crystalline Alloy Nanoparticles

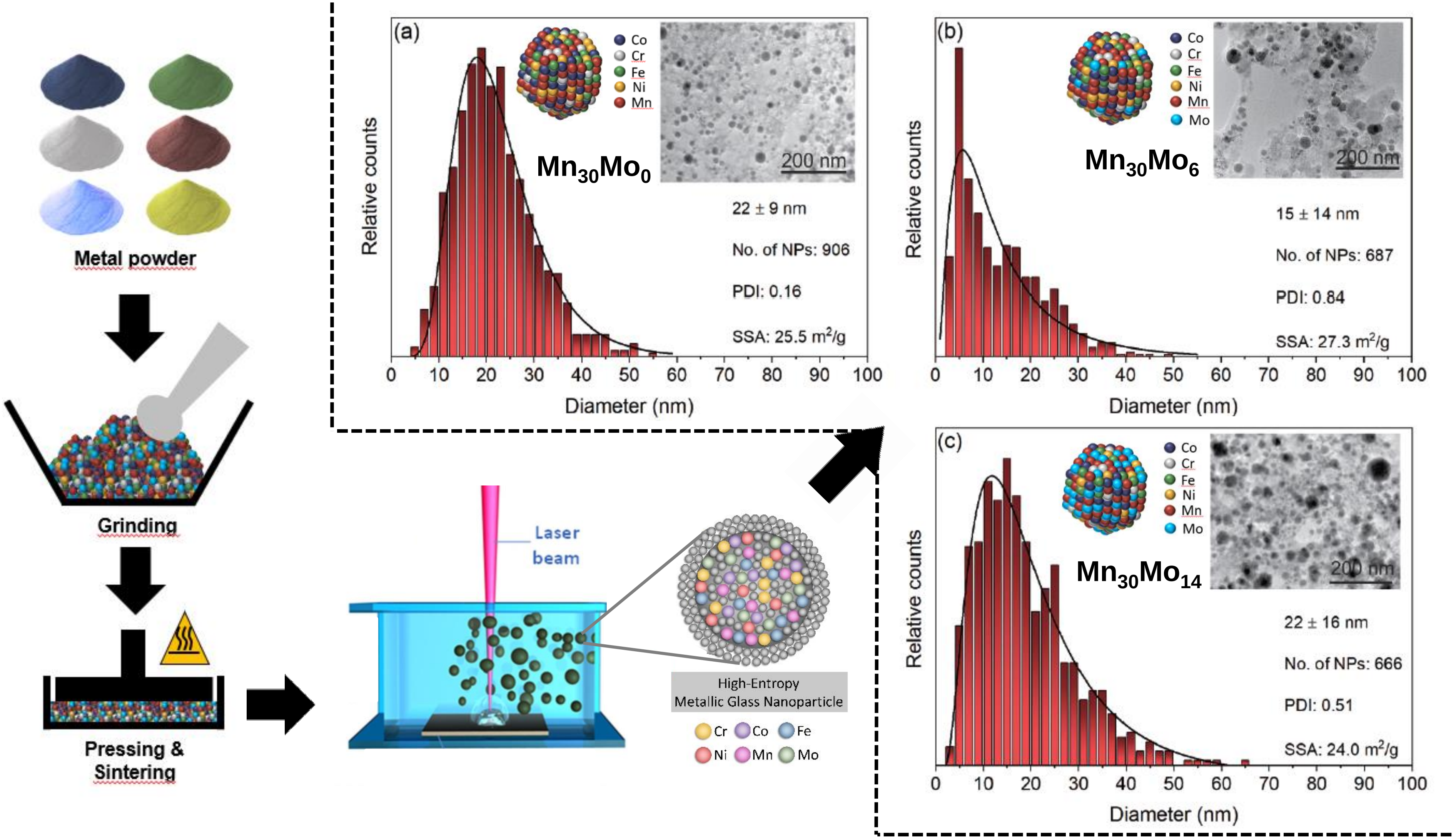




Oxygen Evolution Reaction (OER)
→ High catalytic activity

F. Waag, Y. Li, A. R. Ziefuß, E. Bertin, M. Kamp, V. Duppel, G. Marzun, L. Kienle, S. Barcikowski, and B. Gökce, *RSC Adv.*, **2019**, 9, 32, 18547–18558, doi: 10.1039/c9ra03254a.

Laser-based Synthesis of HEA Composition Series: Addition of Mo to $Co_{17.5} Cr_{17.5} Fe_{17.5} Ni_{17.5}Mn_{30}$



J. Johny, Y. Li, M. Kamp, O. Prymak, S. Liang, T. Krekeler, M. Ritter, L. Kienle, C. Rehbock, S. Barcikowski, and S. Reichenberger, "*Laser-generated high entropy metallic glass nanoparticles as bifunctional electrocatalysts*," *Nano Res.*, 2021, https://doi.org/10.1007/s12274-021-3804-2

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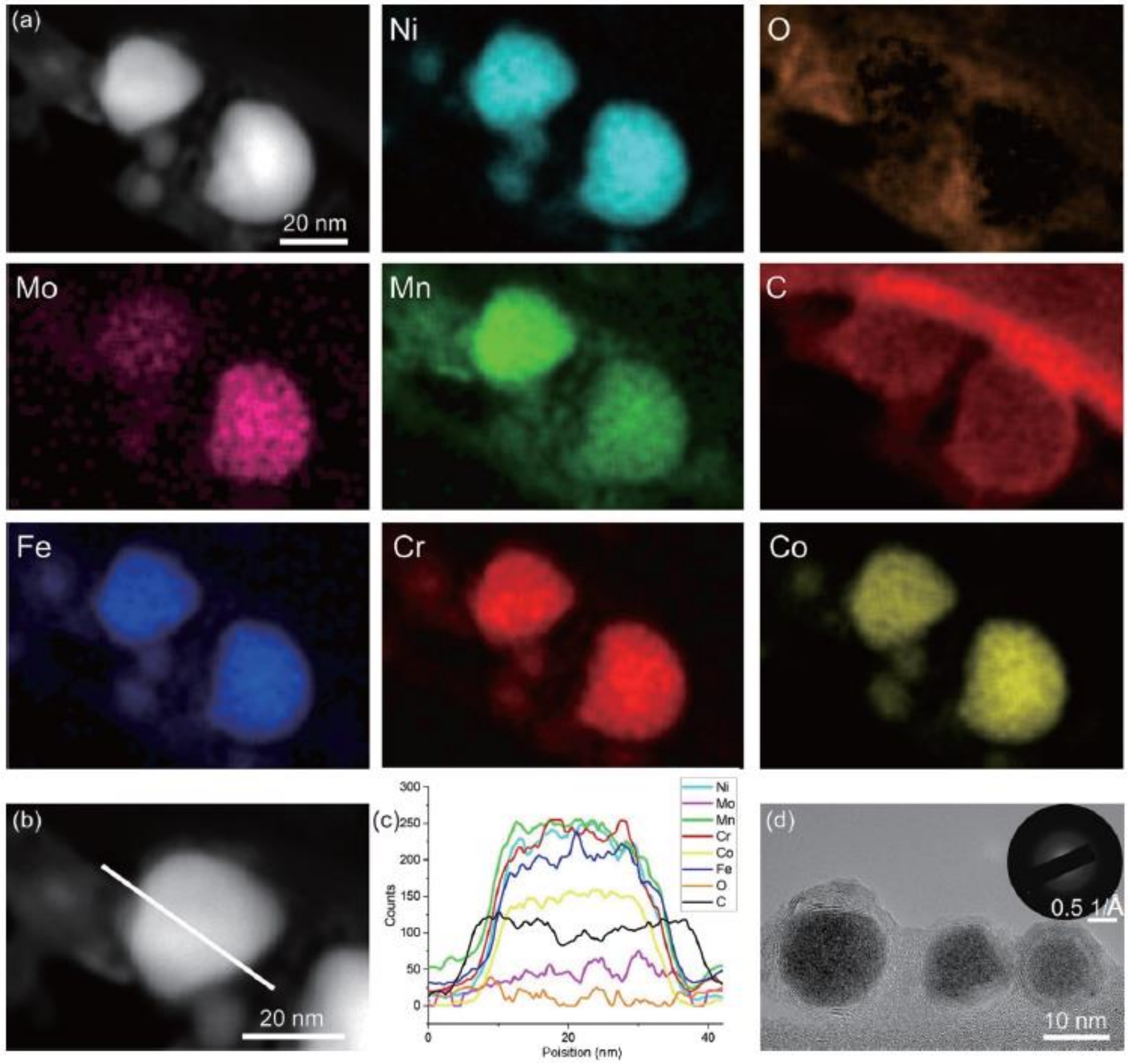
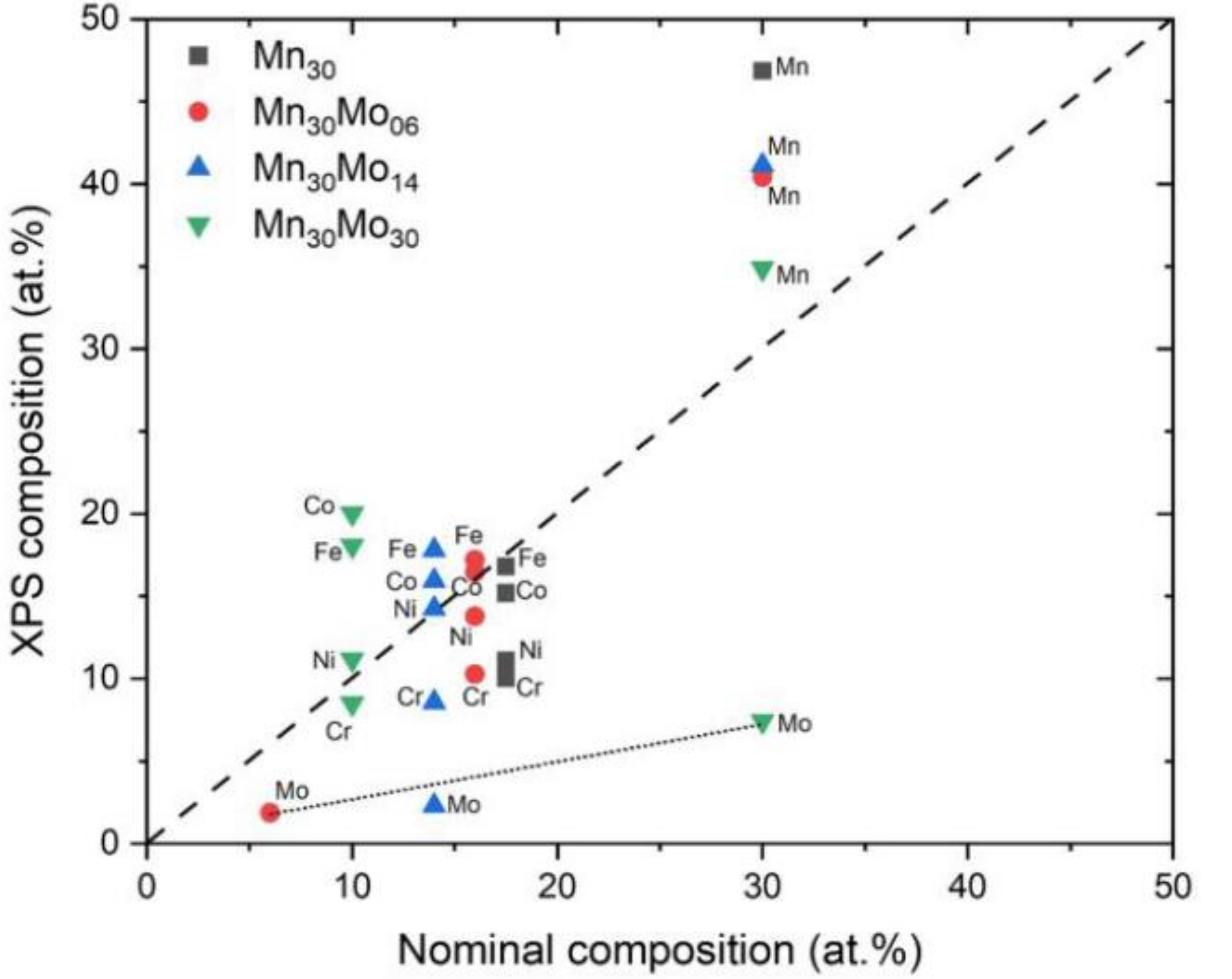


<u>Mn-enriched / Mo depleted surface</u>

→ Linear increase of Mo content in the nanoparticle surface



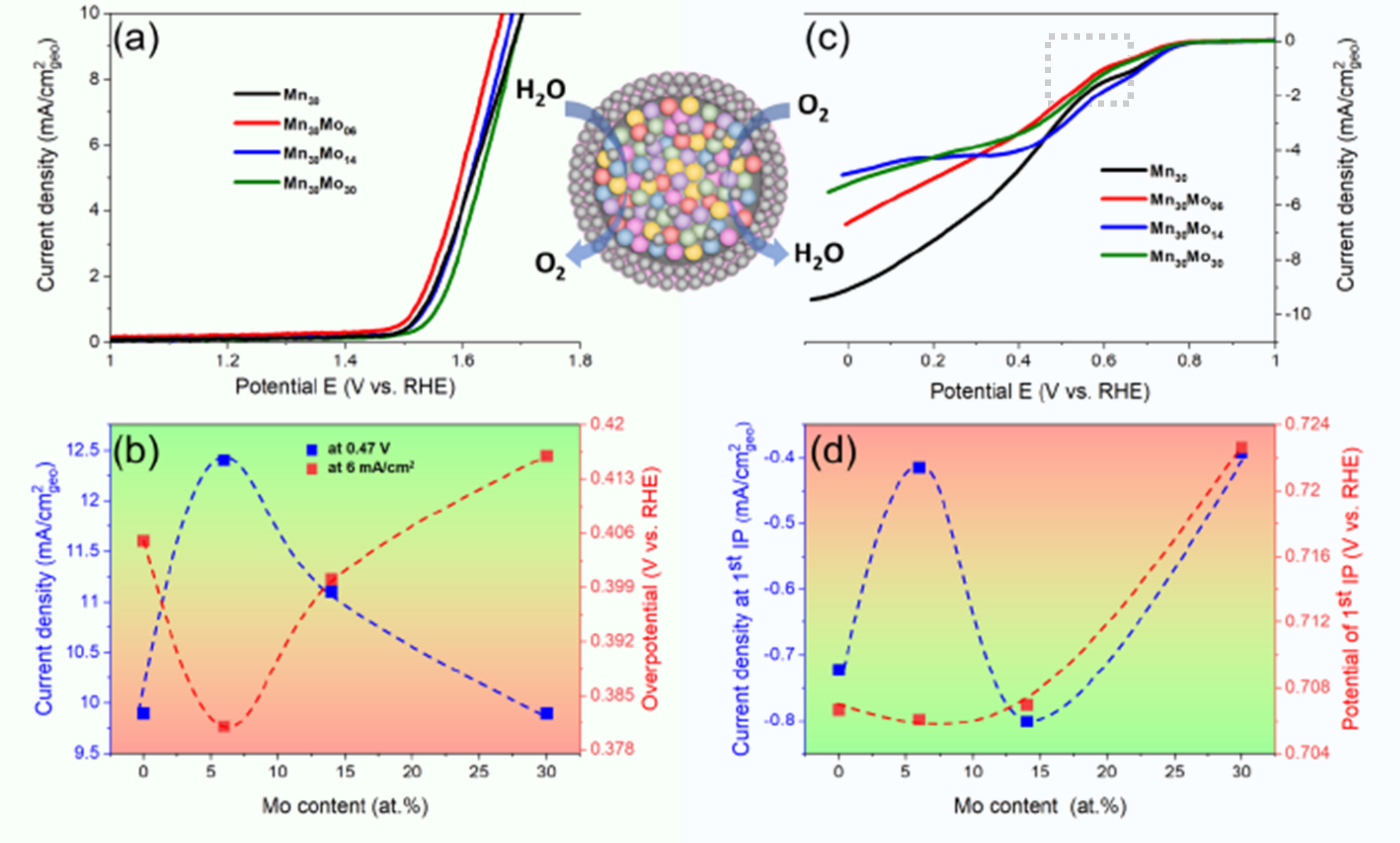
J. Johny, Y. Li, M. Kamp, O. Prymak, S. Liang, T. Krekeler, M. Ritter, L. Kienle, C. Rehbock, S. Barcikowski, and S. Reichenberger, "*Laser-generated high entropy metallic glass nanoparticles as bifunctional electrocatalysts*," *Nano Res.*, 2021, https://doi.org/10.1007/s12274-021-3804-2

Addition of Mo to $Co_{17.5}$ $Cr_{17.5}$ $Fe_{17.5}$ $Ni_{17.5}Mn_{30}$: Bifunctionality of HEA Nanoparticles in Alkaline OER and ORR Reaction

Oxygen Evolution Reaction

Oxygen Reduction Reaction

Relevant for Fuel Cell



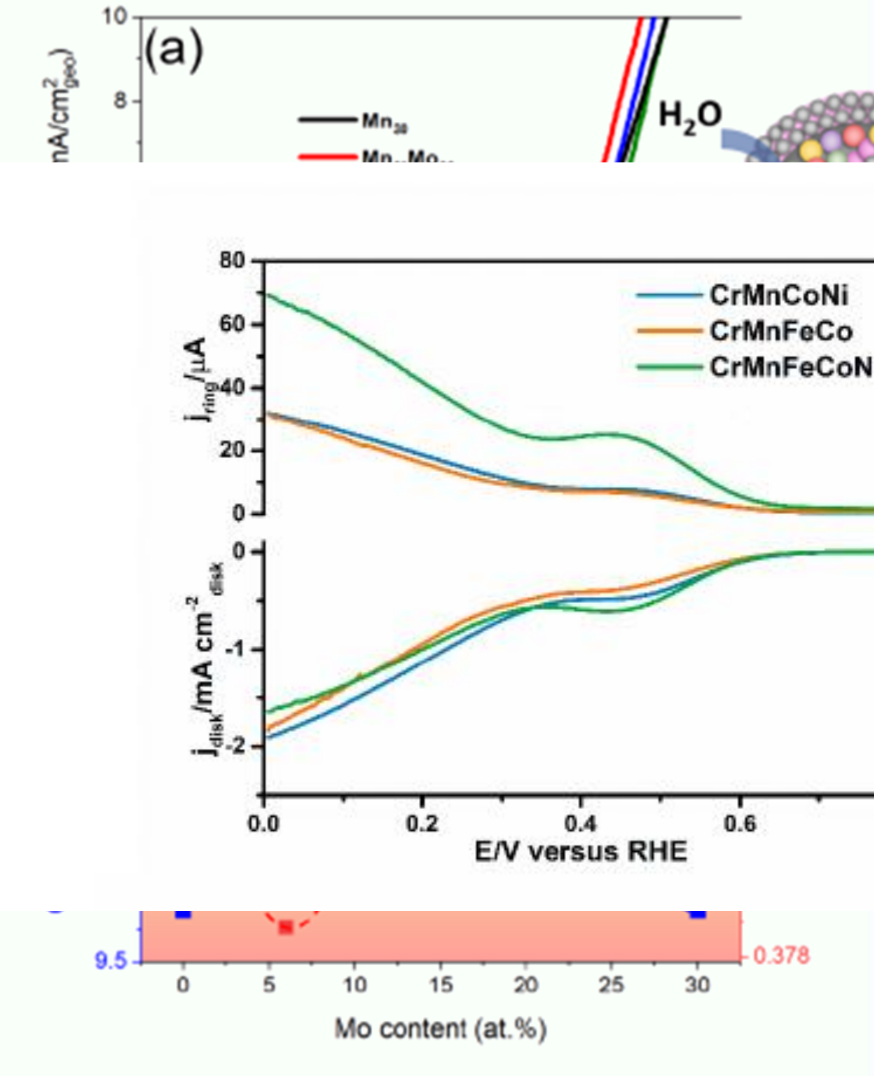
Relevant for Electrolyseurs

J. Johny, Y. Li, M. Kamp, O. Prymak, S. Liang, T. Krekeler, M. Ritter, L. Kienle, C. Rehbock, S. Barcikowski, and S. Reichenberger, *Nano Res.*, 2021, https://doi.org/10.1007/s12274-021-3804-2

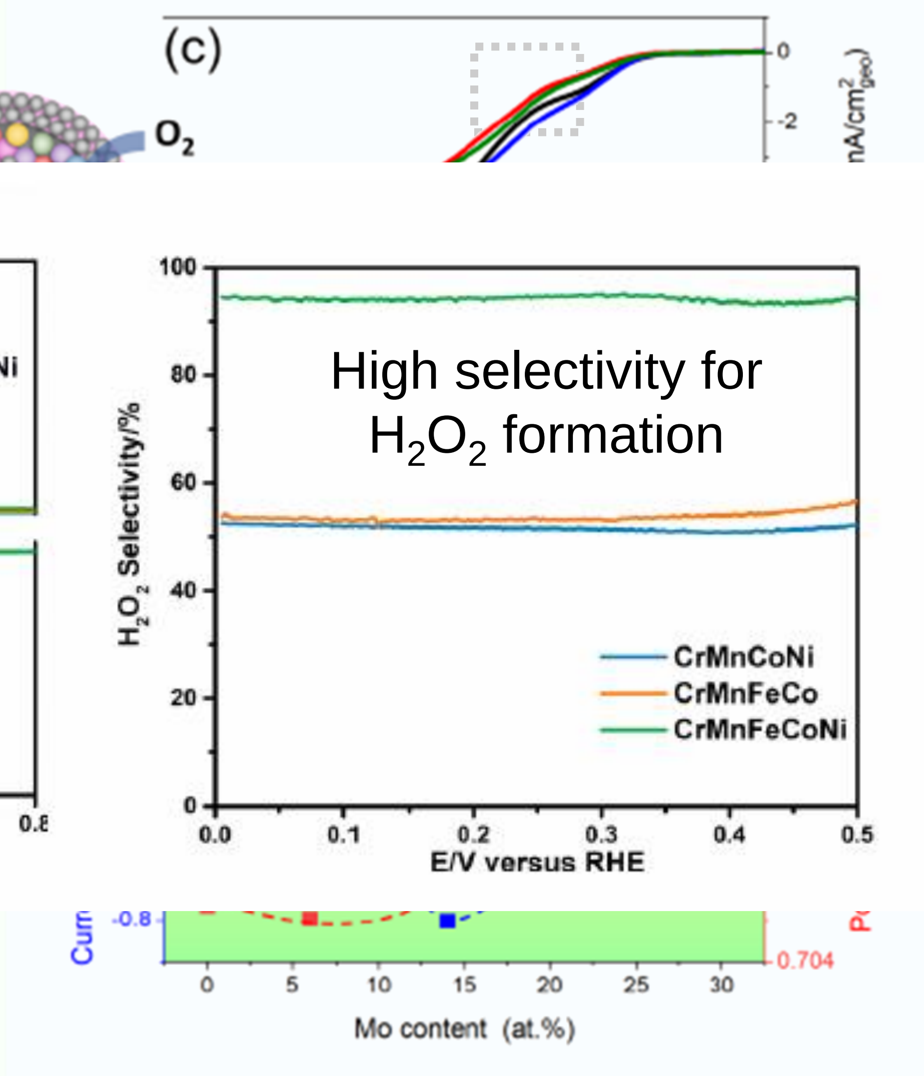
Addition of Mo to $Co_{17.5}$ $Cr_{17.5}$ $Fe_{17.5}$ $Ni_{17.5}Mn_{30}$: Bifunctionality of HEA Nanoparticles in Alkaline OER and ORR Reaction

Relevant for Fuel Cell

Oxygen Evolution Reaction



Oxygen Reduction Reaction



Relevant for Electrolyseurs

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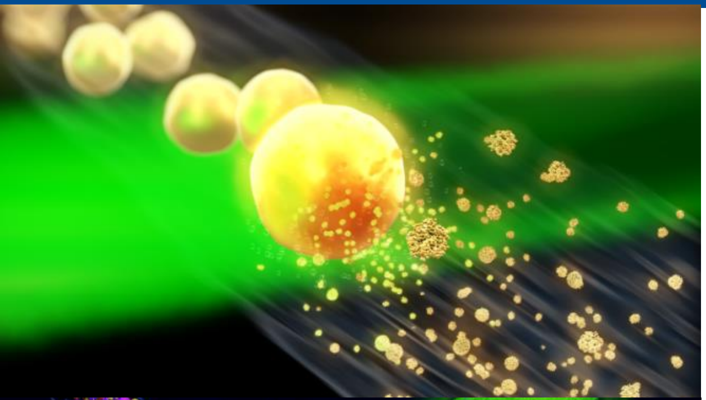
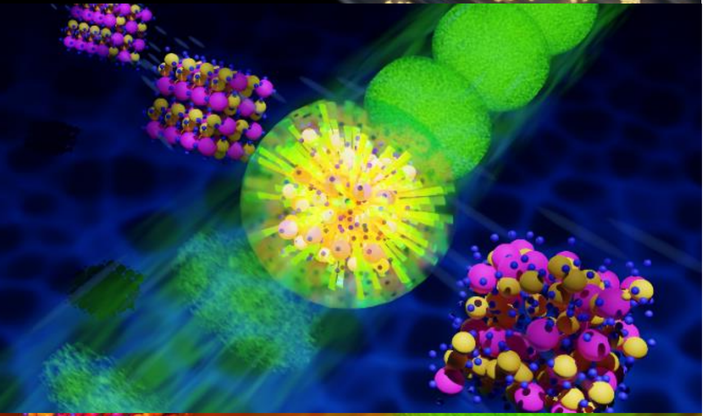
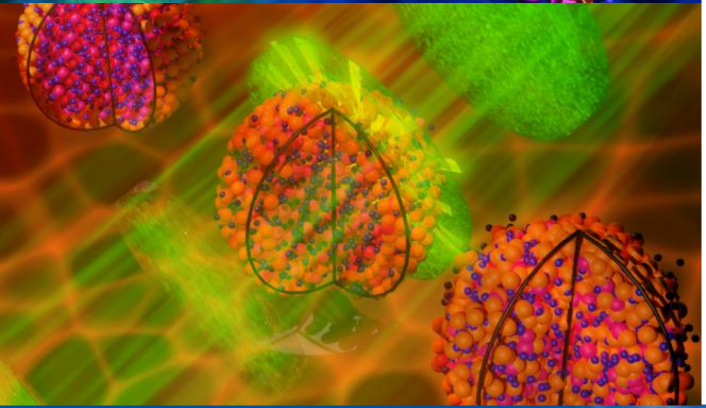
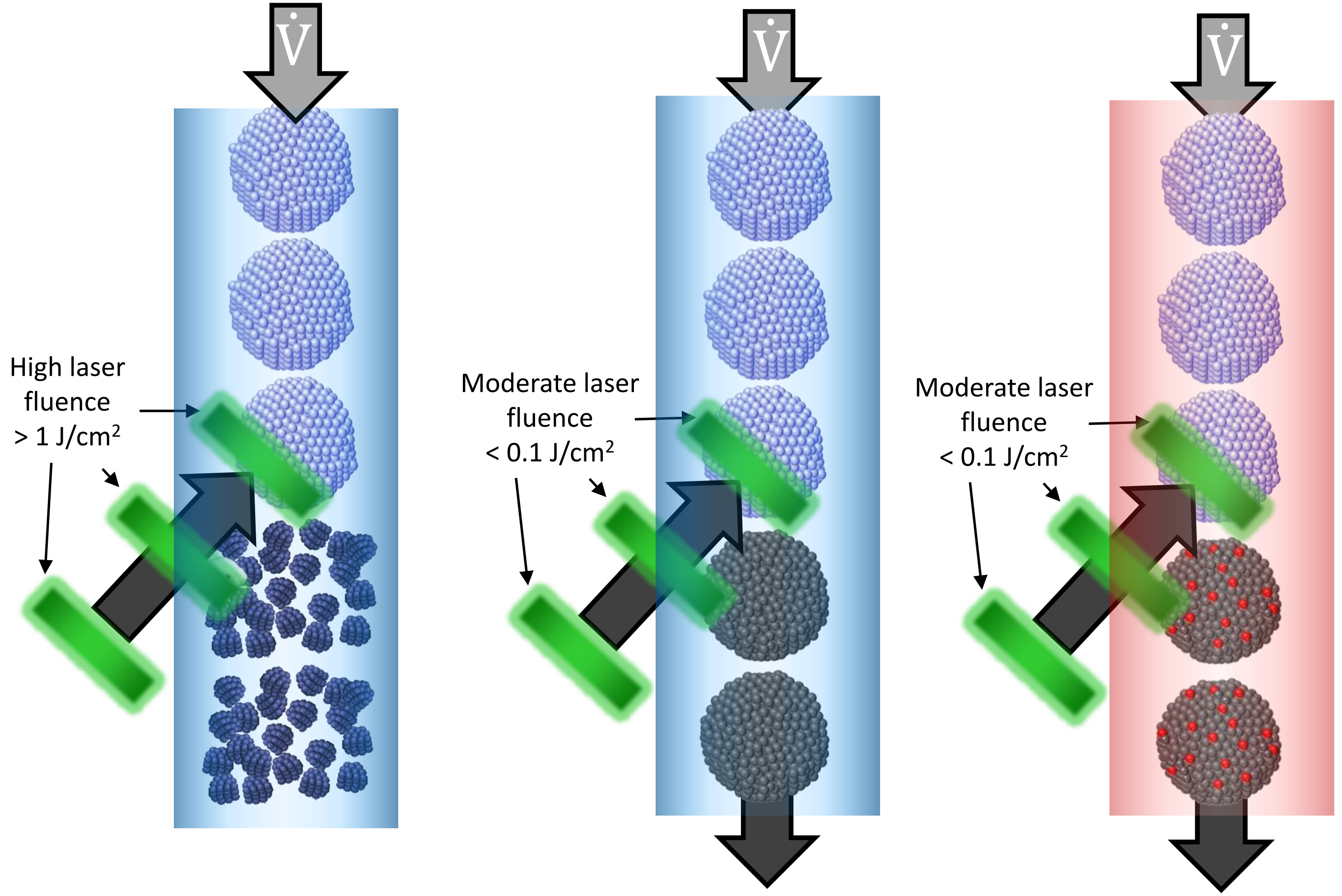
Laser Post-Processing in Liquid



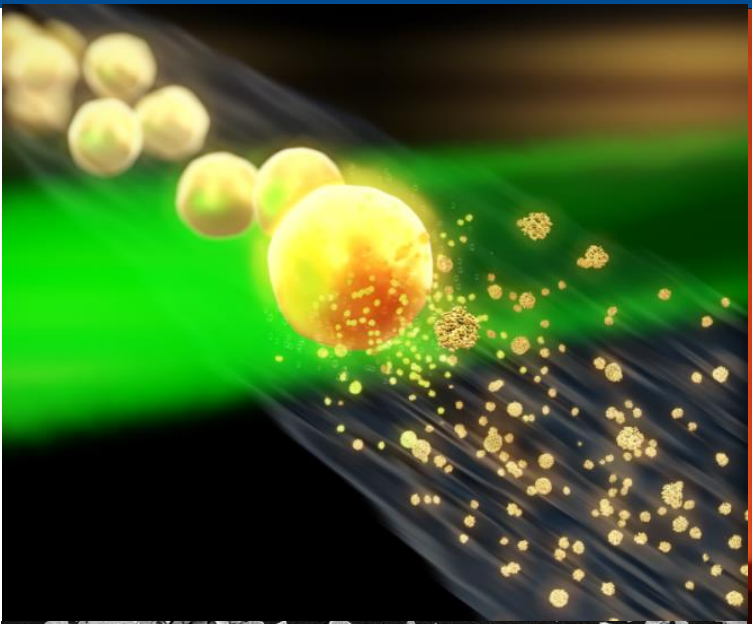


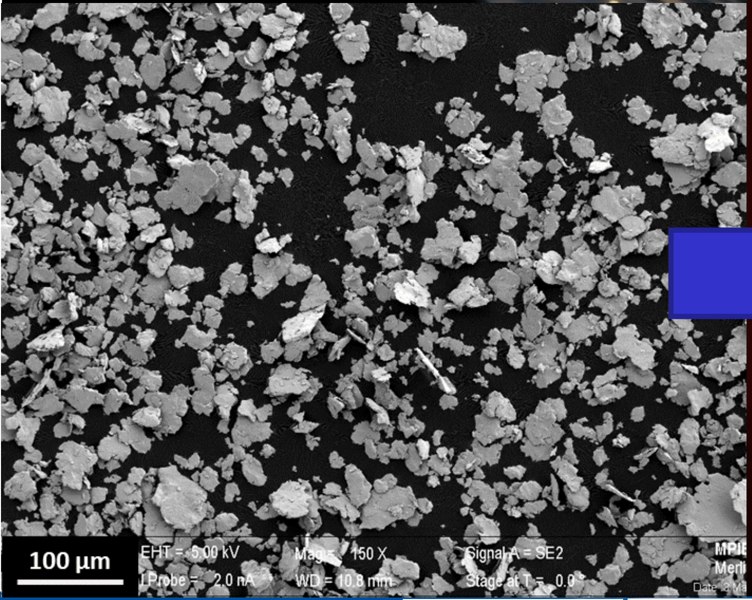


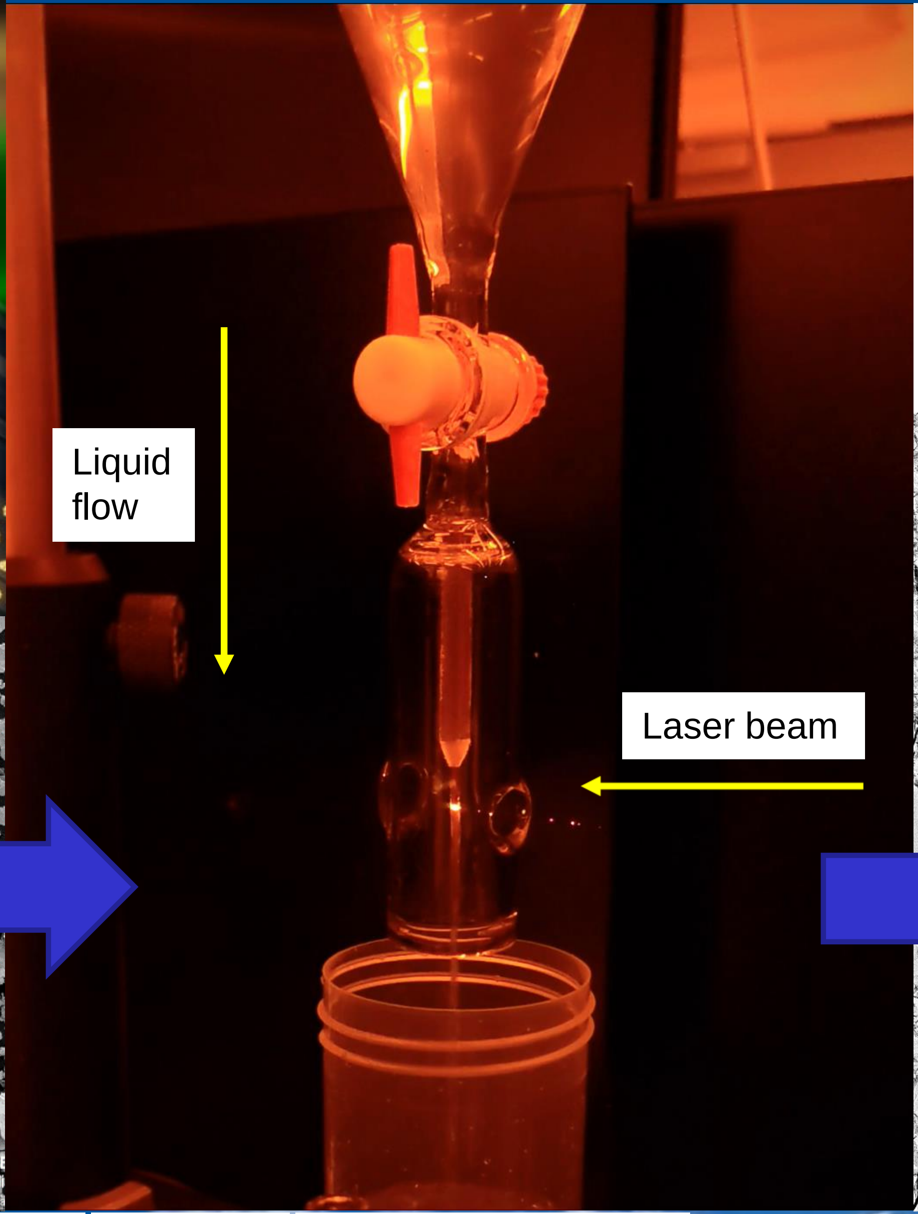
Laser Fragmentation | **Laser Defect Engineering** | **Laser-induced Doping**

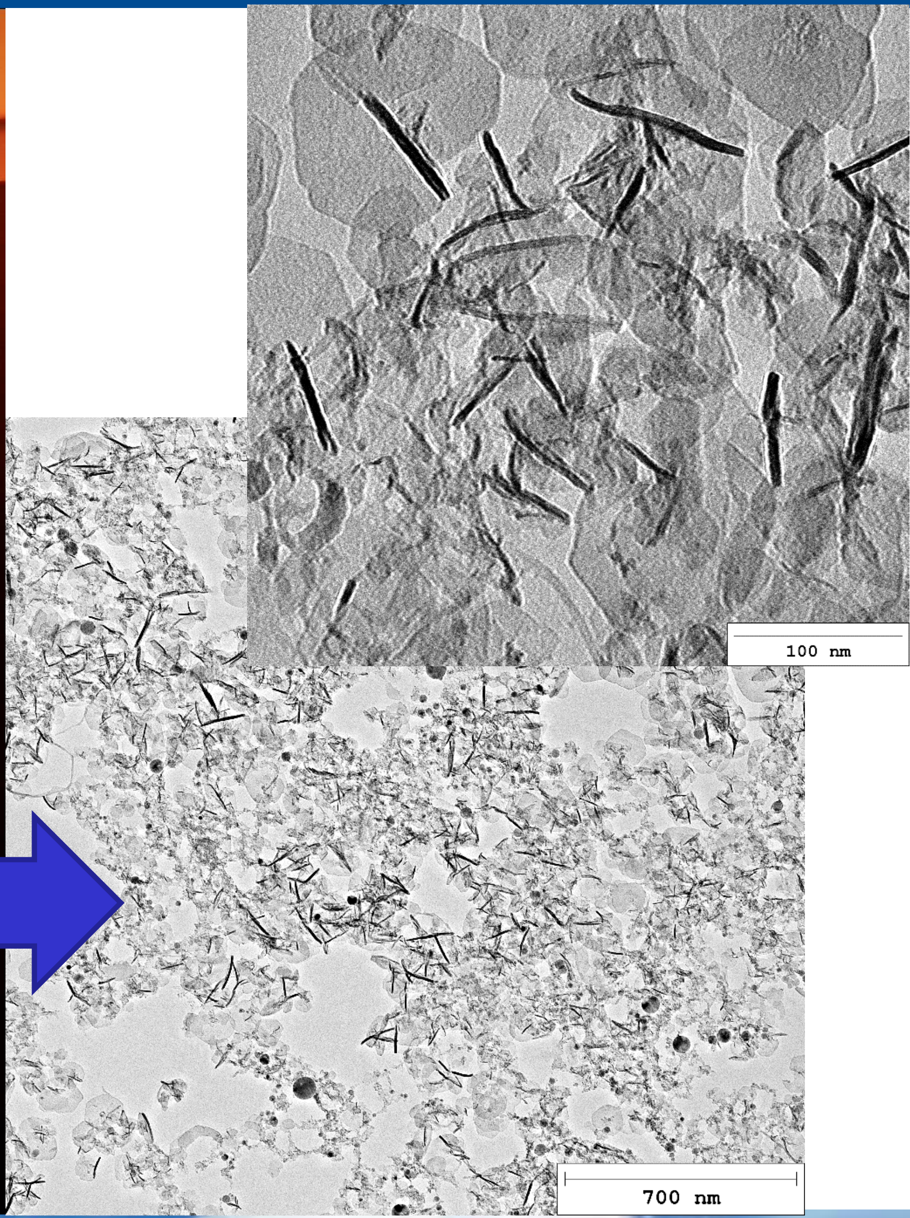


Laserfragmentation of Microparticles (here: CoFeMnNiGa)

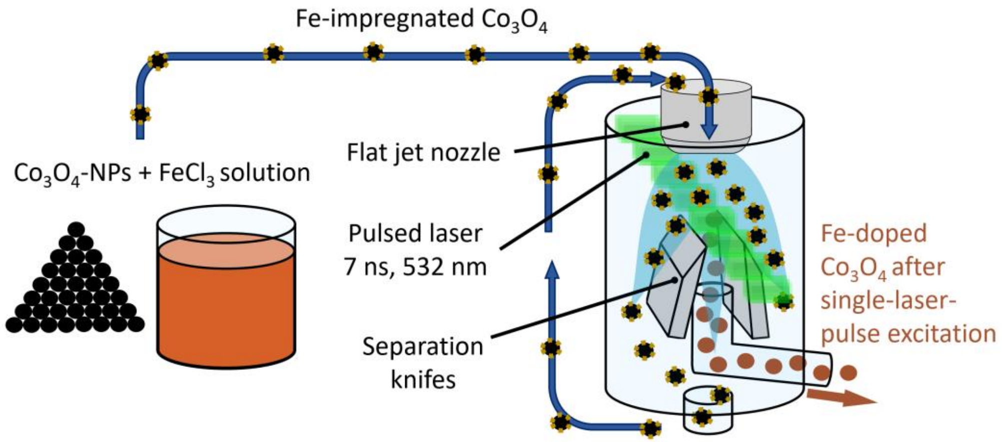


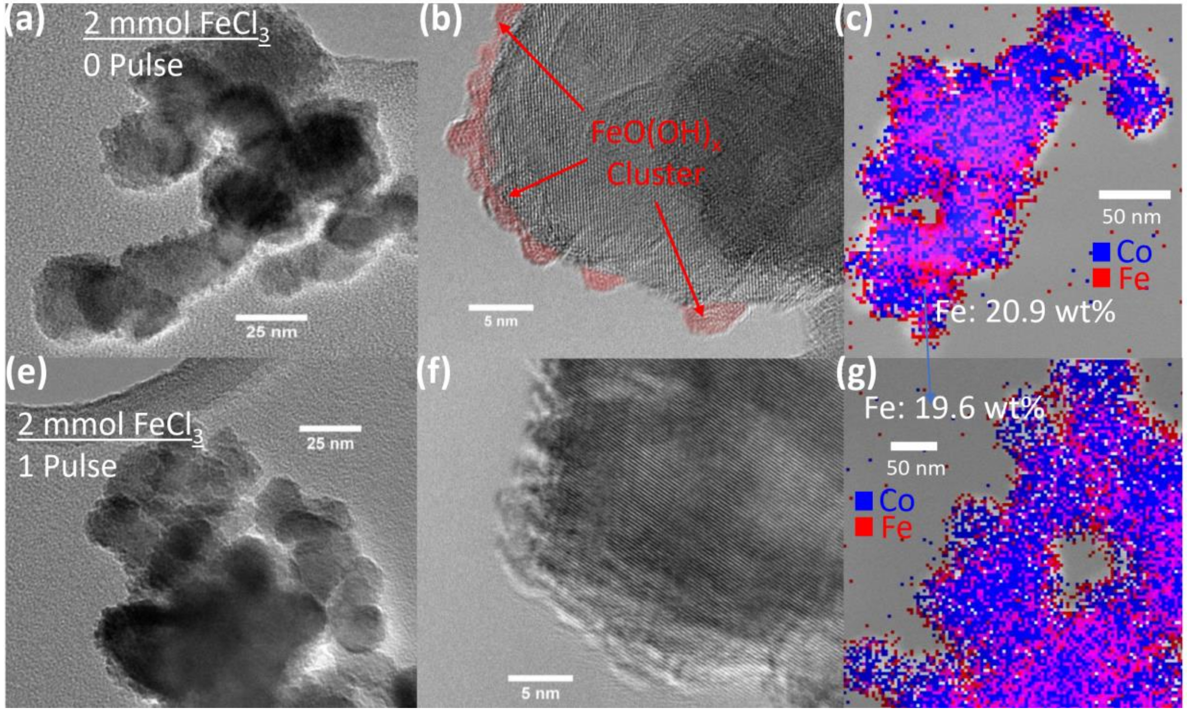


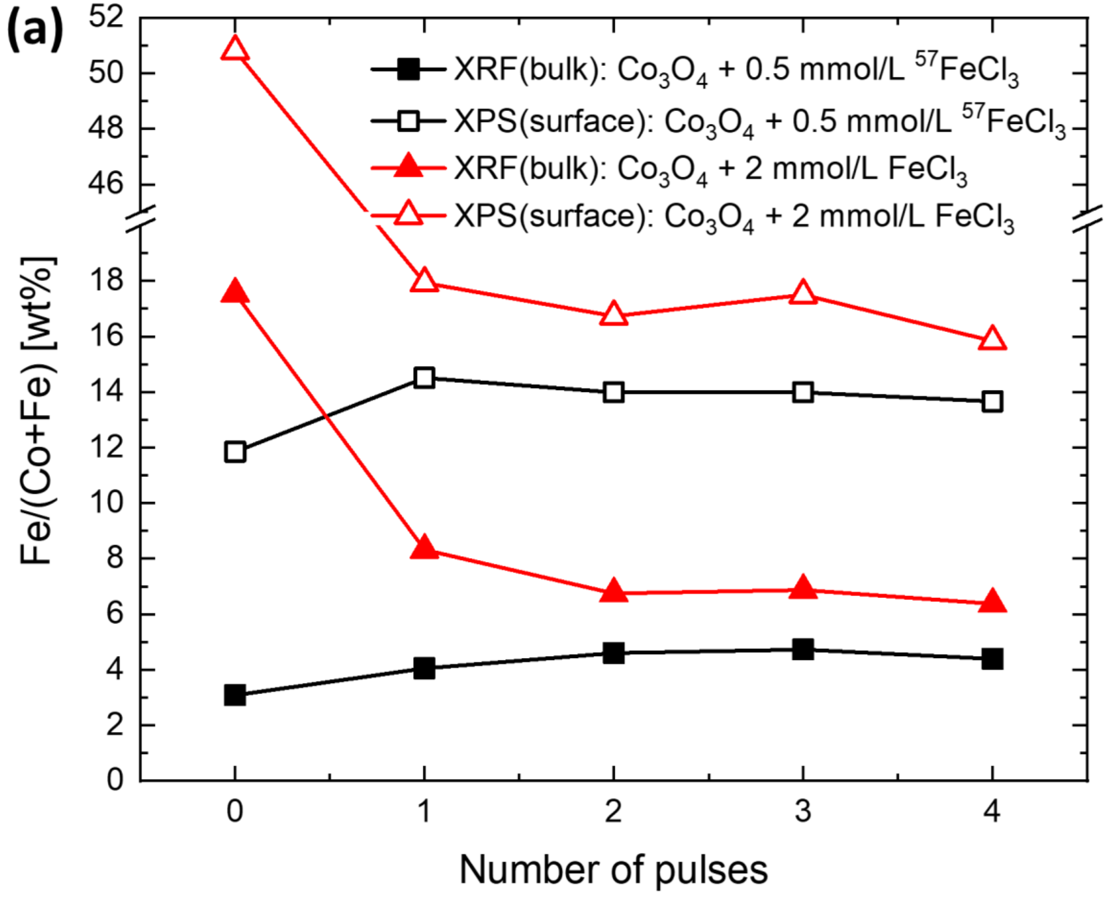




Cation doping by thermal cation diffusion initiated by repeated application of single laser pulses





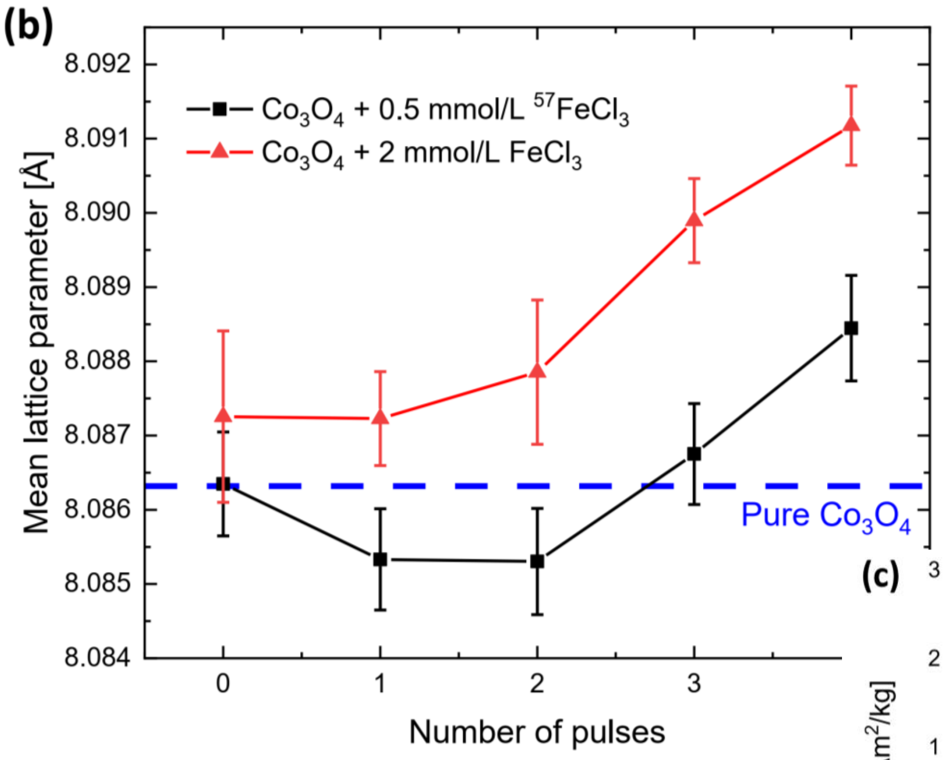


→ Adsorption of iron precursor

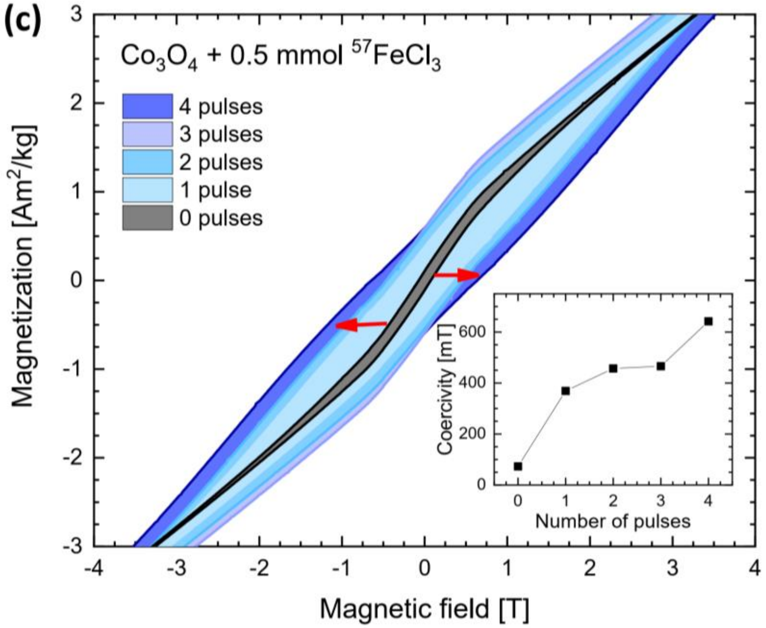
→ step-by-step (gradual) incalation of iron by thermal diffusion due to short-term heating by individual laser pulses

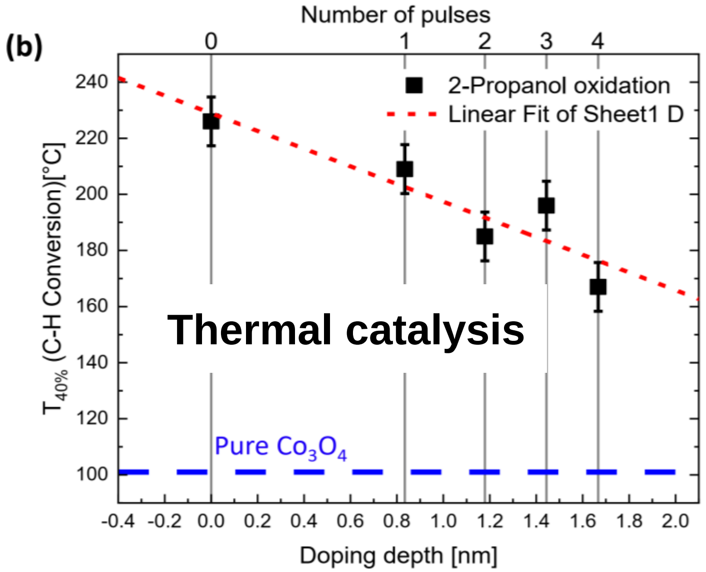
S. Zerebecki, K. Schott, S. Salamon, J. Landers, H. Wende, E. Budiyanto, H. Tüysüz, S. Barcikowski, and S. Reichenberger, J. Phys. Chem. C, vol. 126, no. 36, pp. 15144–15155, 2022, doi: 10.1021/acs.jpcc.2c01753.

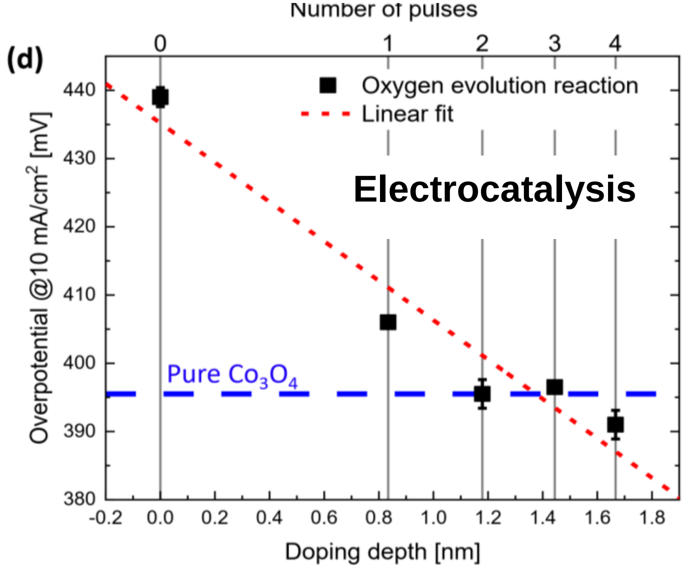
Gradual modification of physical and catalytic properties by laser doping



Doping of uncompensated Fe^{57} magnetic moments into antiferromagnetic Co_3O_4spinel







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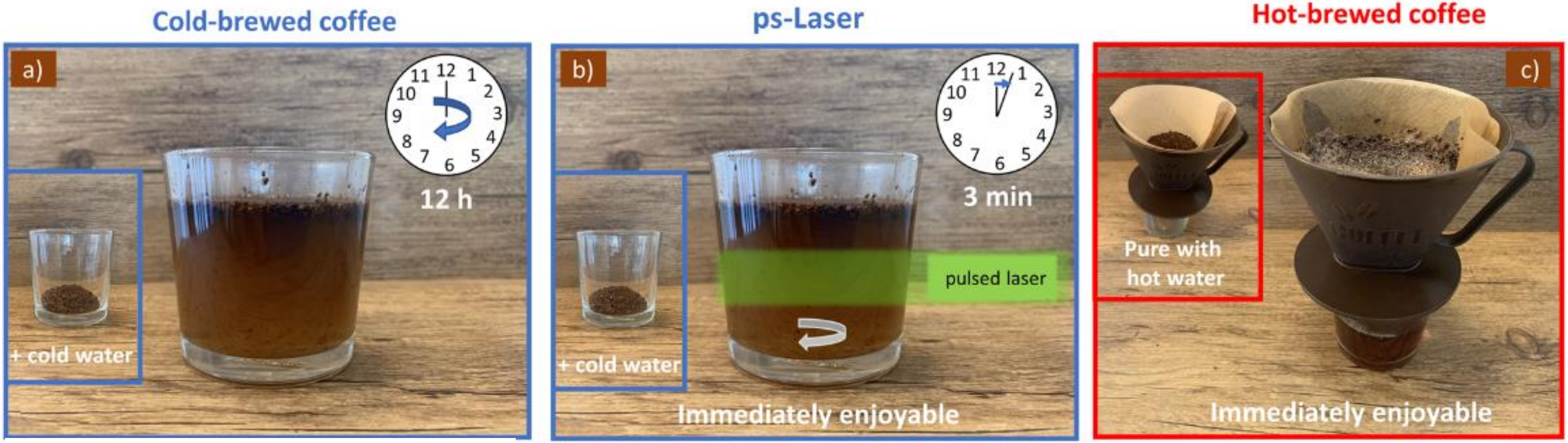
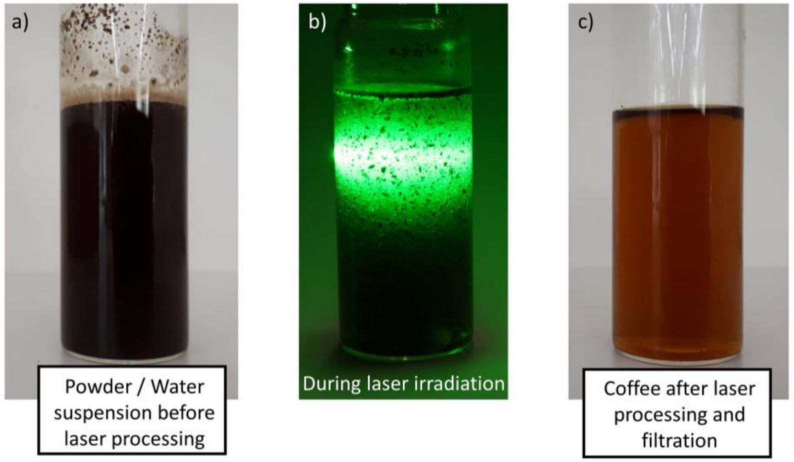
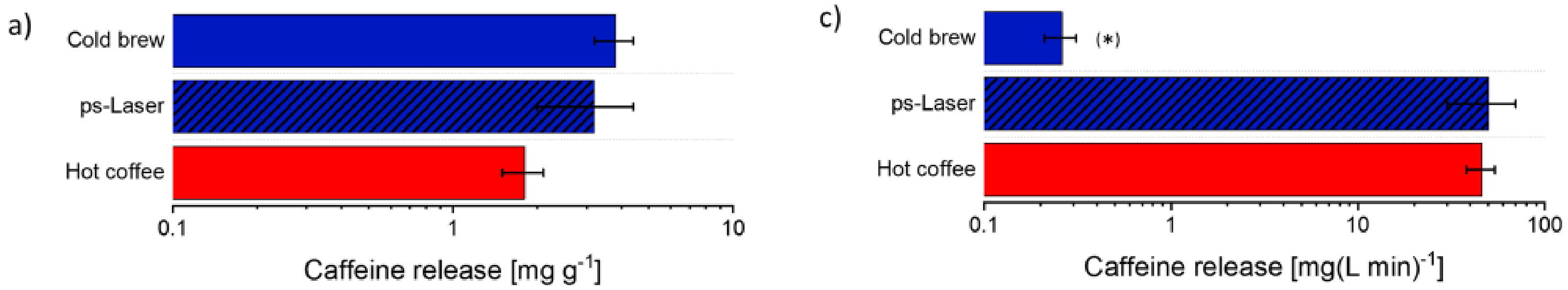
Cold brew coffee—pew, pew, pew—brewed with lasers![1]

[1] https://www.fastcompany.com/90778305/cold-brew-coffee-pew-pew-pew-brewed-with-lasers







A. R. Ziefuß, T. Hupfeld, S. W. Meckelmann, M. Meyer, O. J. Schmitz, W. Kaziur-Cegla, L. K. Tintrop, T. C. Schmidt, B. Gökce, and S. Barcikowski *npj Sci. Food*, vol. 6, no. 1, 2022, doi: 10.1038/s41538-022-00134-6.

Cold brew coffee—pew, pew, pew—brewed with lasers![1]

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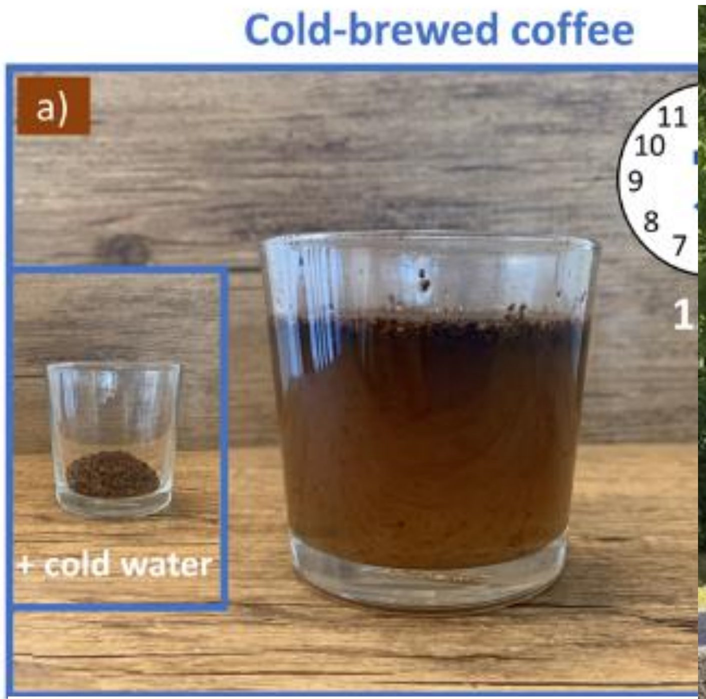
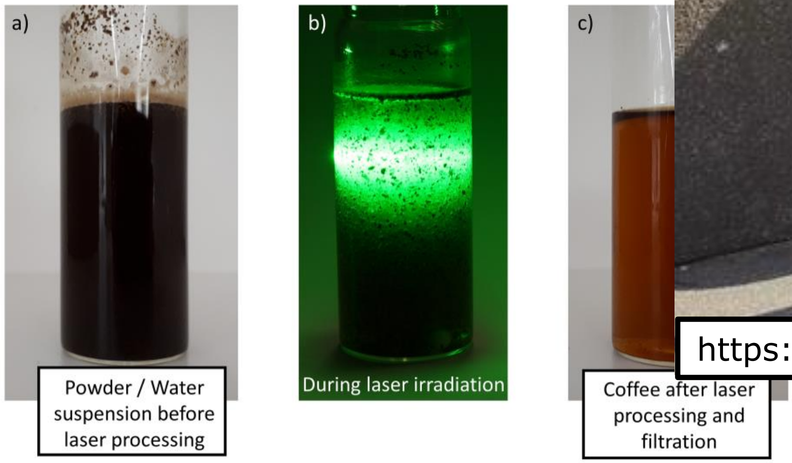
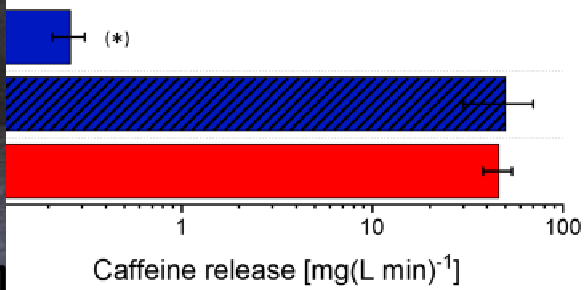


https://ndion.de/de/cold-brew-coffee-neues-laserbasiertes-verfahren/





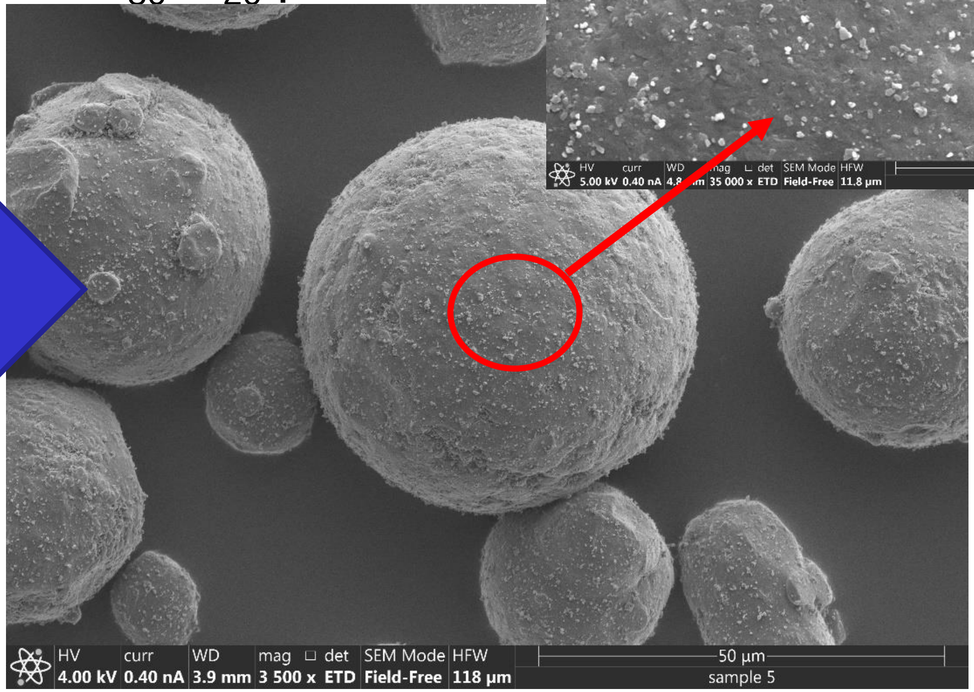
A. R. Ziefuß, T. Hupfeld, S. W. Meckelmann, M. Meyer, O. J. Schmitz, W. Kaziur-Cegla, L. K. Tintrop, T. C. Schmidt, B. Gökce, and S. Barcikowski *npj Sci. Food*, vol. 6, no. 1, 2022, doi: 10.1038/s41538-022-00134-6.

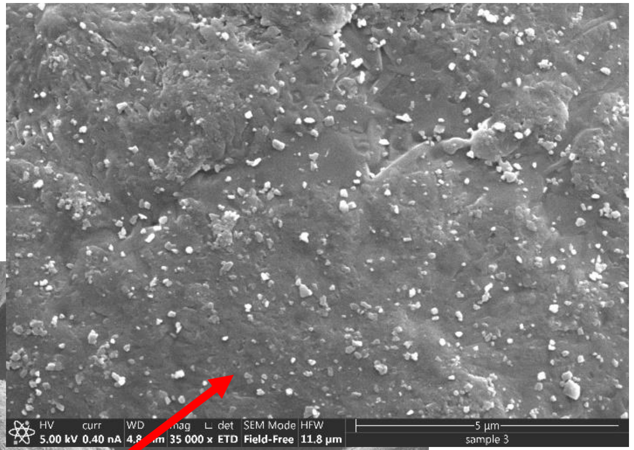
XRF measurement of nanoparticle supported metallic powders

$Fe_{80}Cr_{20}$ micropowder

Surface support by 0.8wt% ZrOx NPs (<100nm)

0.8wt%ZrOx on $Fe_{80}Cr_{20}$ powder



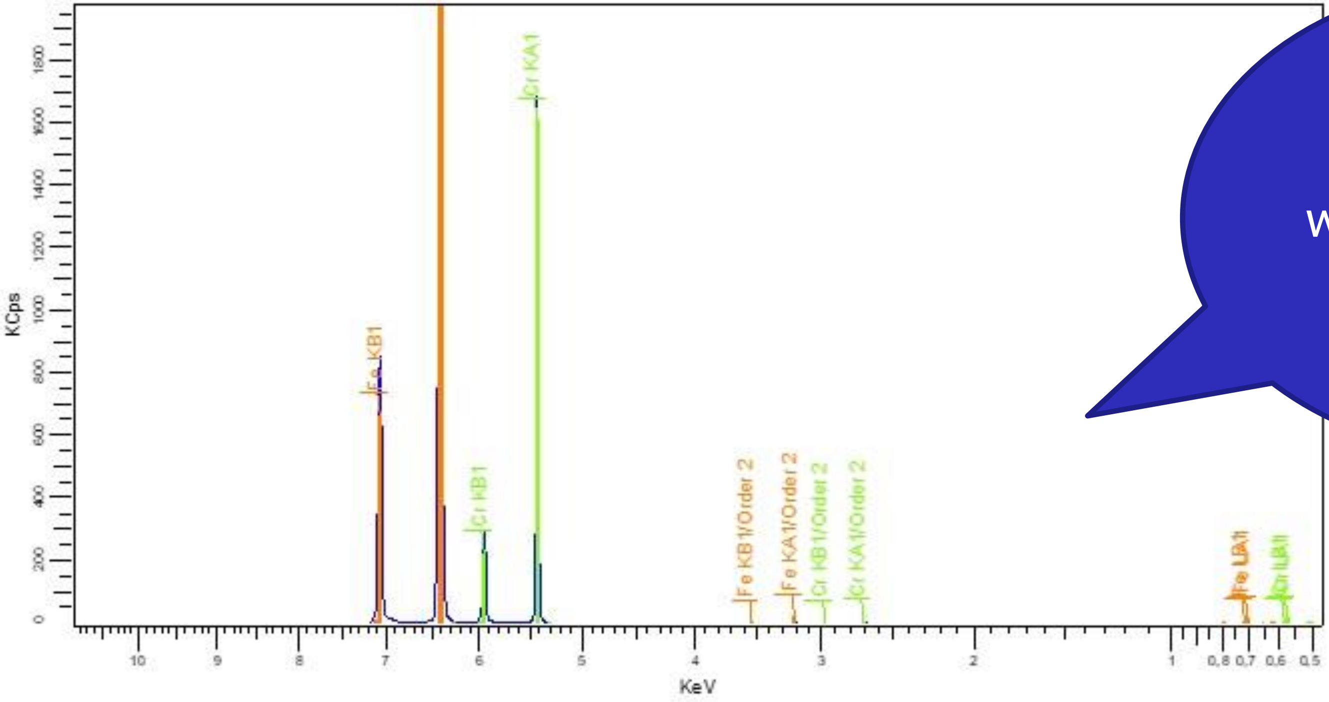


XRF measurement of nanoparticle supported metallic powders

$Fe_{80}Cr_{20}$ micropowder

ZrOx on
$_{20}$ powder

Direct powder measurement of $Fe_{80}Cr_{20}$ powder(QuantExpress)



How to decide which status (XRF1-3) and which line to use if the material composition is unknown?

The first outcome of the software

Formula	Concentration	Status	Line 1
Cr	90,20%	XRF 2	Cr KB1-HR-Tr
Fe	9,68%	XRF 3	Fe LA1-HR-Tr
Si	605 PPM	XRF 1	Si KA1-HR-Tr
Ni	524 PPM	XRF 1	Ni KA1-HR-Tr
Cu	287 PPM	XRF 1	Cu KA1-HR-Tr

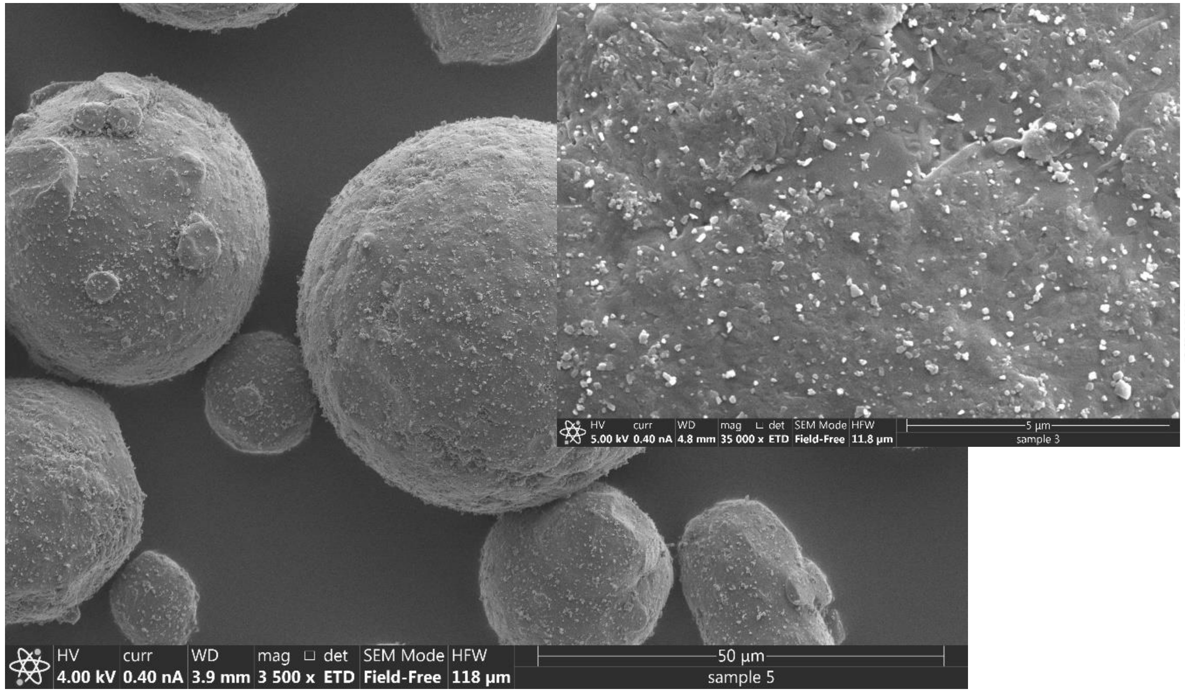
Calculates Cr with KB lines and Fe with LA lines

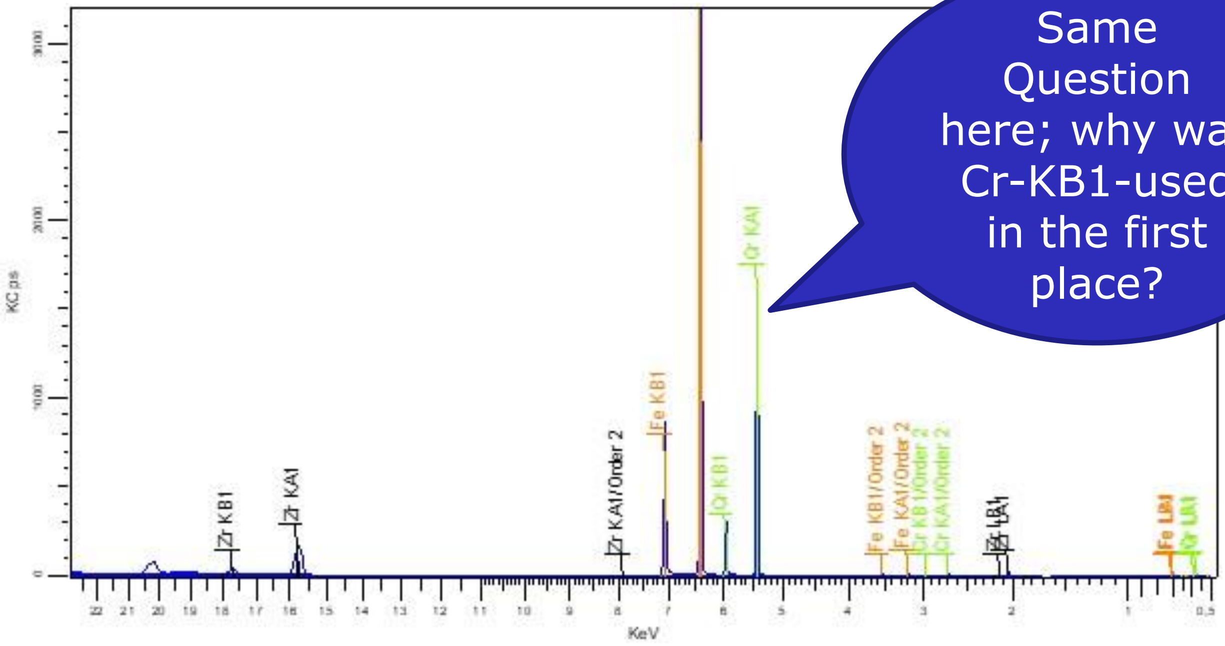
We know that $Fe_{80}Cr_{20}$ composition is around 80wt% Fe and 20wt% Cr

Formula	Concentration	Status	Line 1
Fe	78,70%	XRF 1	Fe KA1-HR-Tr
Cr	21,20%	XRF 1	Cr KA1-HR-Tr
Si	244 PPM	XRF 1	Si KA1-HR-Tr
Ni	198 PPM	XRF 1	Ni KA1-HR-Tr
Cu	113 PPM	XRF 1	Cu KA1-HR-Tr

Cr and Fe recalculated with KA lines

Direct powder measurement of 0.8 wt% ZrO_x-$Fe_{80}Cr_{20}$ powder(QuantExpress)





Same Question here; why was Cr-KB1-used in the first place?

The first outcome of the software

Formula	Concentration	Status	Line 1
Cr	91,40%	XRF 2	Cr KB1-HR-Tr
Fe	6,11%	XRF 3	Fe LA1-HR-Tr
Zr	2,01%	XRF 1	Zr KA1-HR-Tr
Si	0,29%	XRF 1	Si KA1-HR-Tr
Ni	573 PPM	XRF 1	Ni KA1-HR-Tr
Cu	359 PPM	XRF 1	Cu KA1-HR-Tr
Hf	117 PPM	XRF 1	Hf LA1-HR-Tr

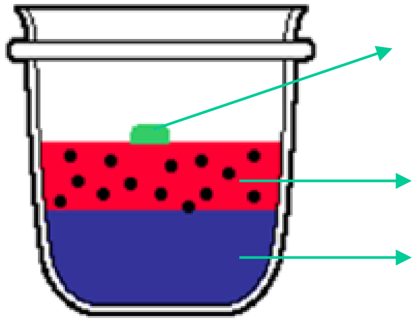
Calculates Cr with KB lines and Fe with LA lines

Recalculation with K-Alpha lines of Cr and Fe

Formula	Concentration	Status	Line 1
Fe	78,10%	XRF 1	Fe KA1-HR-Tr
Cr	20,80%	XRF 1	Cr KA1-HR-Tr
Zr	0,79%	XRF 1	Zr KA1-HR-Tr
Si	0,12%	XRF 1	Si KA1-HR-Tr
Hf	496 PPM	XRF 1	Hf LA1-HR-Tr
Ni	221 PPM	XRF 1	Ni KA1-HR-Tr
Cu	144 PPM	XRF 1	Cu KA1-HR-Tr

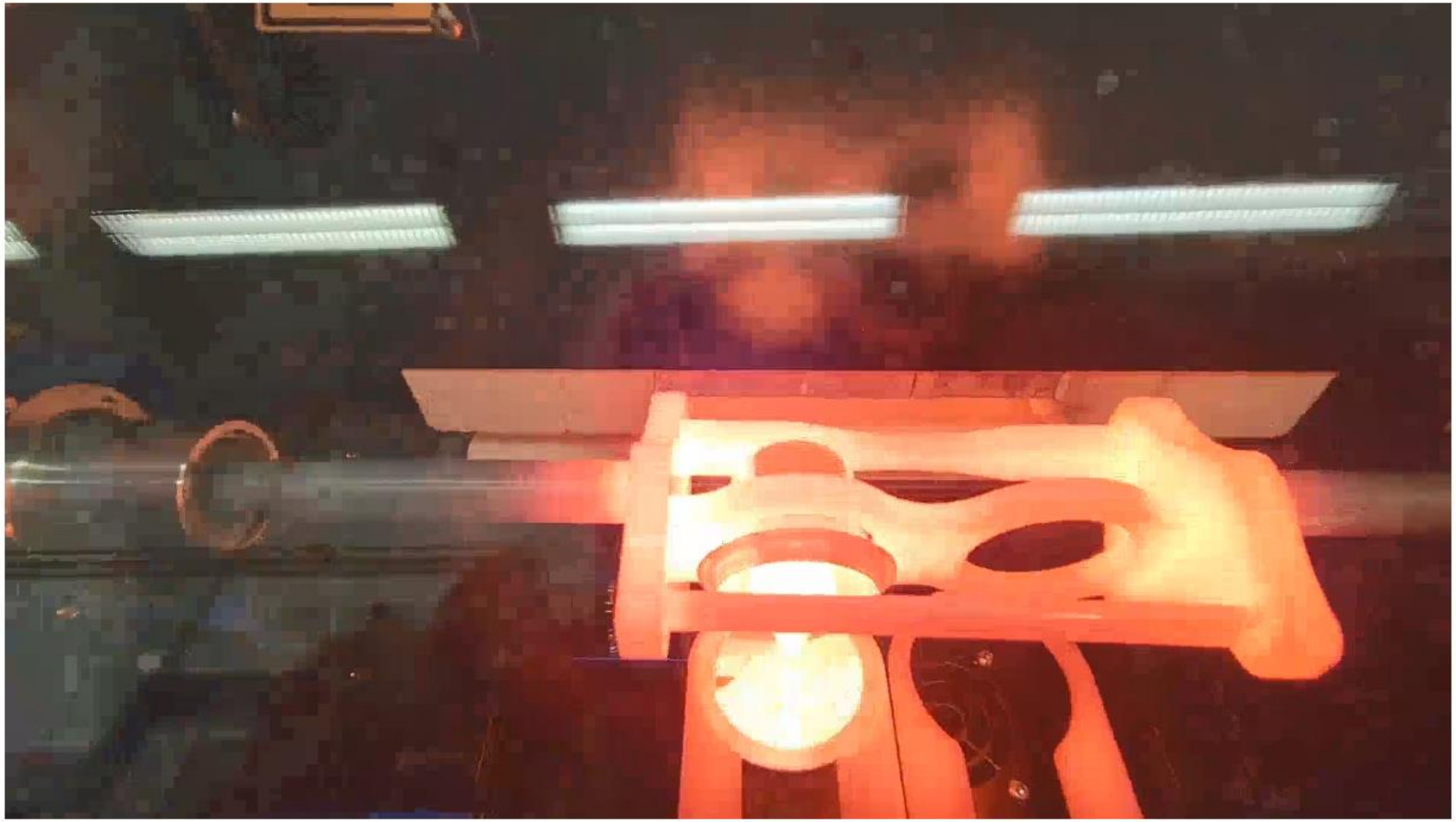
Cr and Fe recalculated with KA lines

Sample preperation for Glass bead measurements



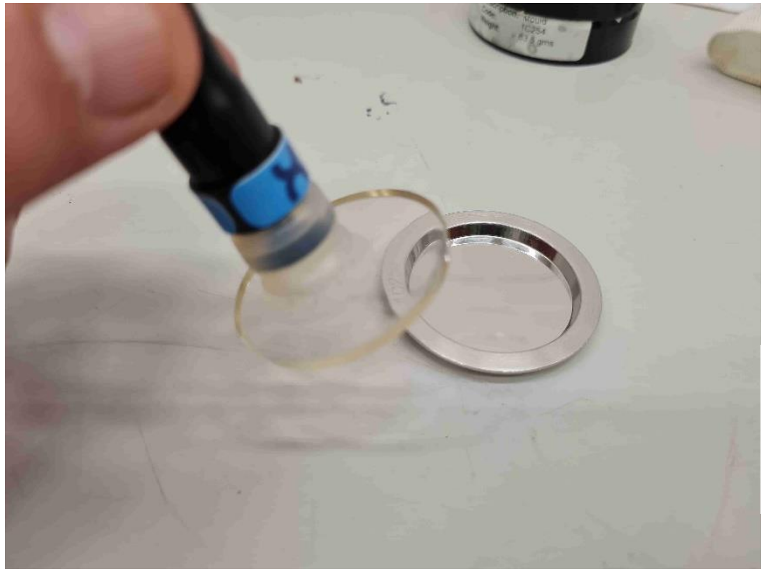
Fuser unit to produce glass beads

Glass bead production



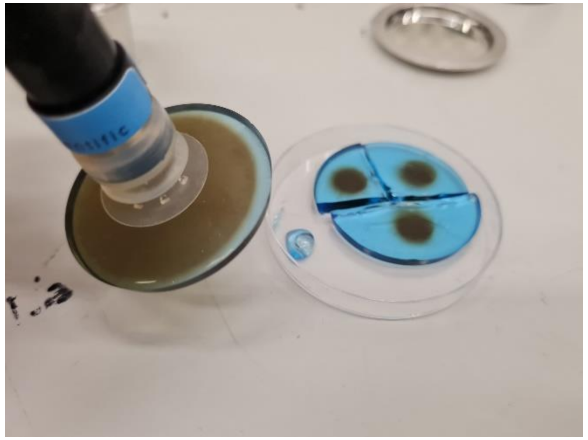
Preheating to oxidize metal powder, melting stage, shake procedure, and moulding glass bead

Glass bead handling and measurement

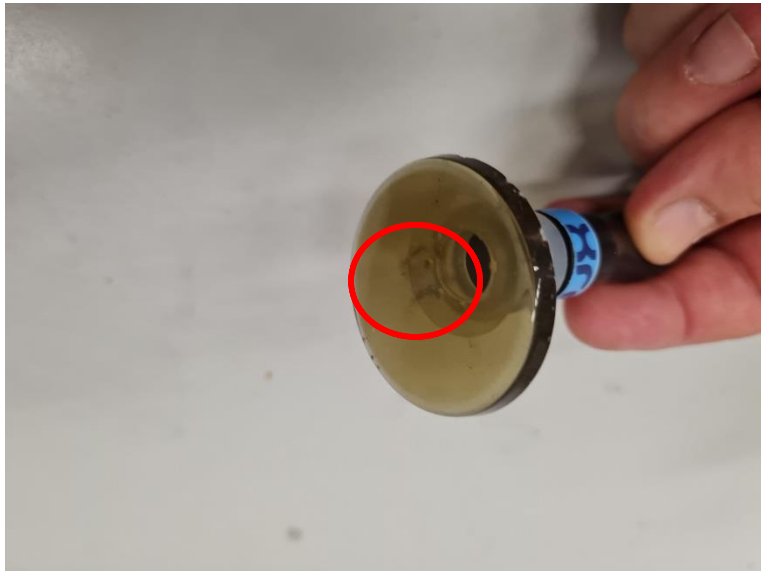


Do not touch on the surface of the glass bead and place to XRF sample holder

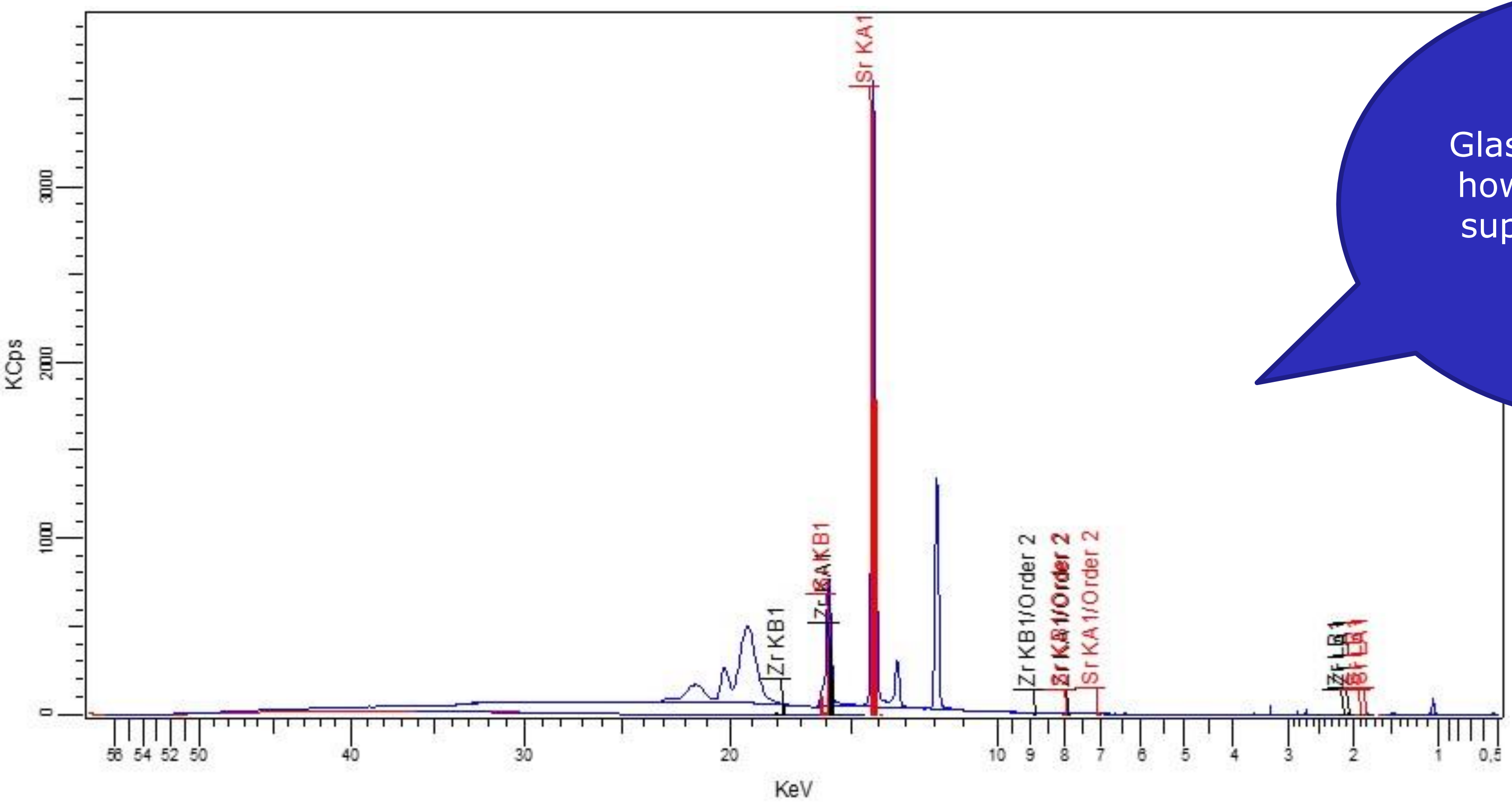
Wrong setup in fusion process forms crack



The color of glass bead changes after XRF measurement



Glass bead analysis ($Fe_{80}Cr_{20}$) (QuantExpress)



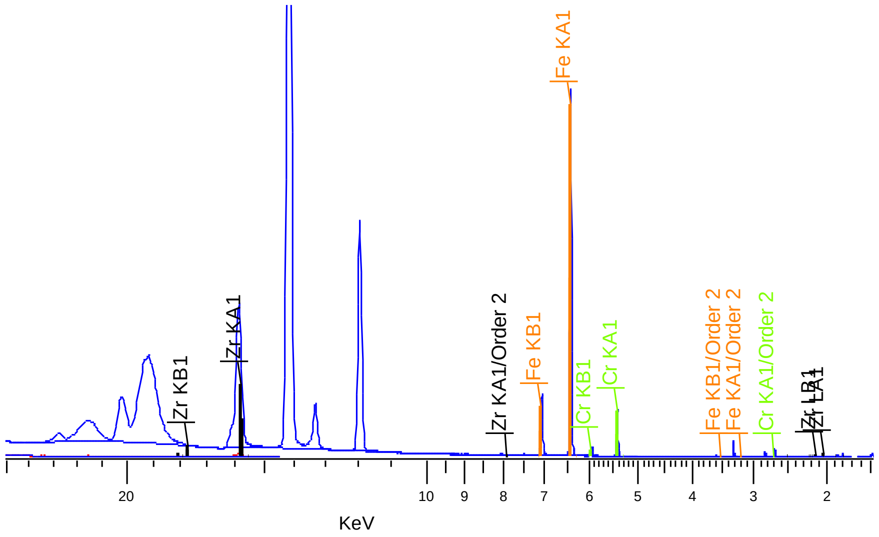
Glass forming flux includes Sr with trace Zr amount

Glass includes Zr so how to measure Zr supported $Fe_{80}Cr_{20}$ powders?

Glass bead analysis (0.8wt% ZrO_x @ $Fe_{80}Cr_{20}$) (QuantExpress)

Digested $Fe_{80}Cr_{20}$ powder without ZrO_x NPs in glass bead

Formula	Concentration	Status	Line 1
Fe	81,00%	XRF 1	Fe KA1-HR-Tr
Cr	18,30%	XRF 1	Cr KA1-HR-Tr
Si	0,21%	XRF 1	Si KA1-HR-Tr
Ni	0,19%	XRF 1	Ni KA1-HR-Tr
Zr	0,16%	XRF 2	Zr KB1-HR-Tr
Cu	0,11%	XRF 1	Cu KA1-HR-Tr



How to measure Zr correctly by using glass bead method? Which lines (KA, KB, LB) should be take in to account?

Calibration series with varying sample content?
→ Not applicable for larger sample series
→ Other ideas?

Digested 0.8 wt% ZrO_x @ $Fe_{80}Cr_{20}$ in glass beads

Formula	Concentration	Status	Line 1
Fe	80,90%	XRF 1	Fe KA1-HR-Tr
Cr	18,40%	XRF 1	Cr KA1-HR-Tr
Zr	0,19%	XRF 2	Zr KB1-HR-Tr
Ni	0,18%	XRF 1	Ni KA1-HR-Tr
Si	0,15%	XRF 1	Si KA1-HR-Tr
Cu	0,12%	XRF 1	Cu KA1-HR-Tr

Zr is detected with K-beta lines. Let`s set measuring with K-alpha lines

Zr is detected with K-alpha lines

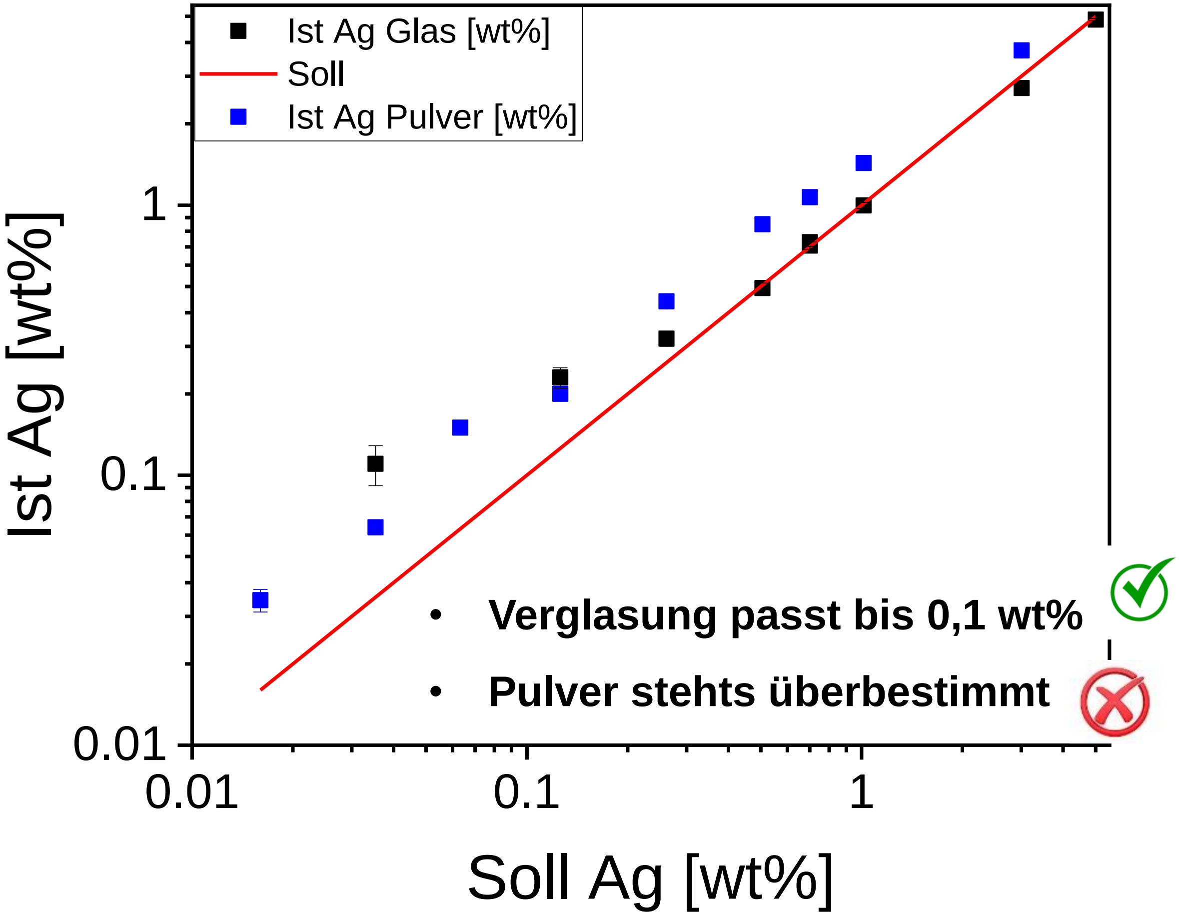
Formula	Concentration	Status	Line 1
Fe	75,40%	XRF 1	Fe KA1-HR-Tr
Cr	17,30%	XRF 1	Cr KA1-HR-Tr
Zr	6,85%	XRF 1	Zr KA1-HR-Tr
Ni	0,17%	XRF 1	Ni KA1-HR-Tr
Si	0,14%	XRF 1	Si KA1-HR-Tr
Cu	0,11%	XRF 1	Cu KA1-HR-Tr

Verwendung von Metallsalzen als potentielle Kalibrationsstandards

Kalibration: Realprobe

Ausgangsmaterial: **Ag NP auf MQP-S Mikropulver**

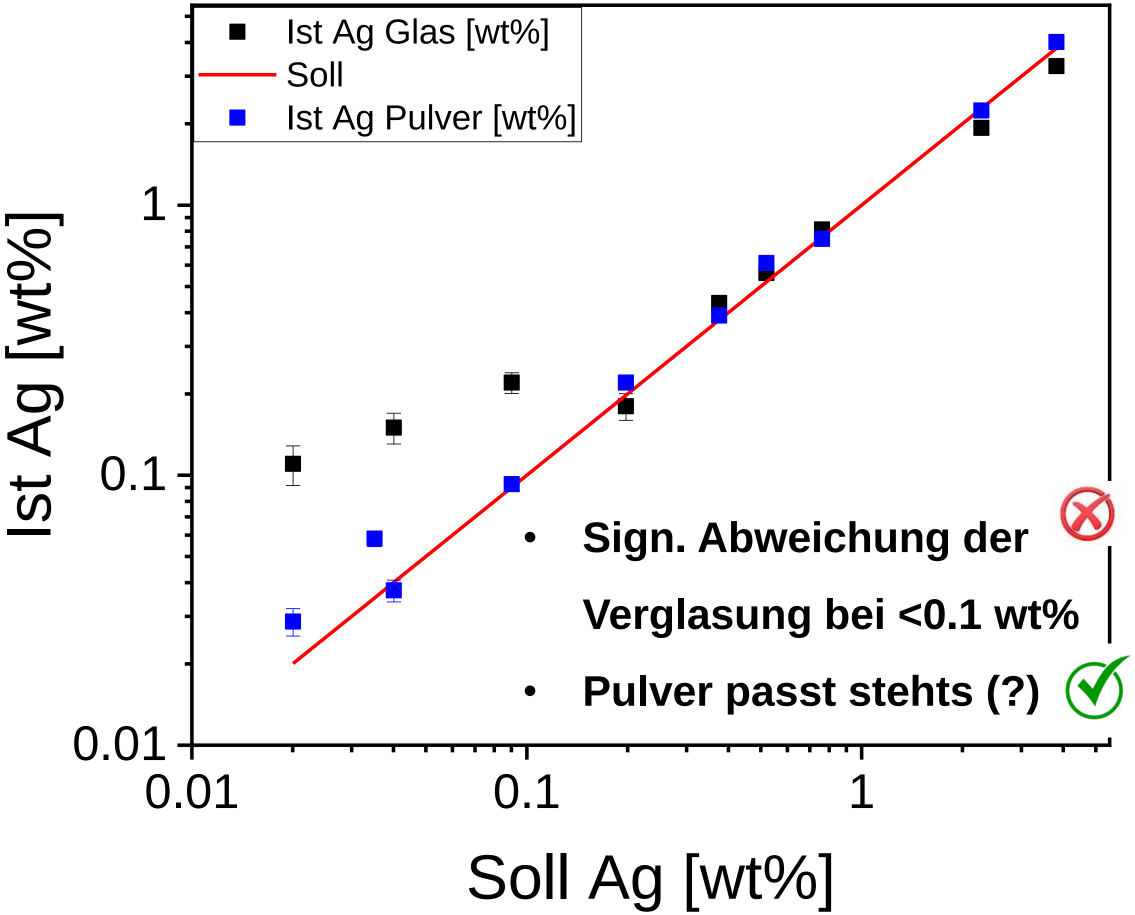
(MQP-S: magnetische Nd-Pr-Fe-Co-Ti-Zr-B Legierung)



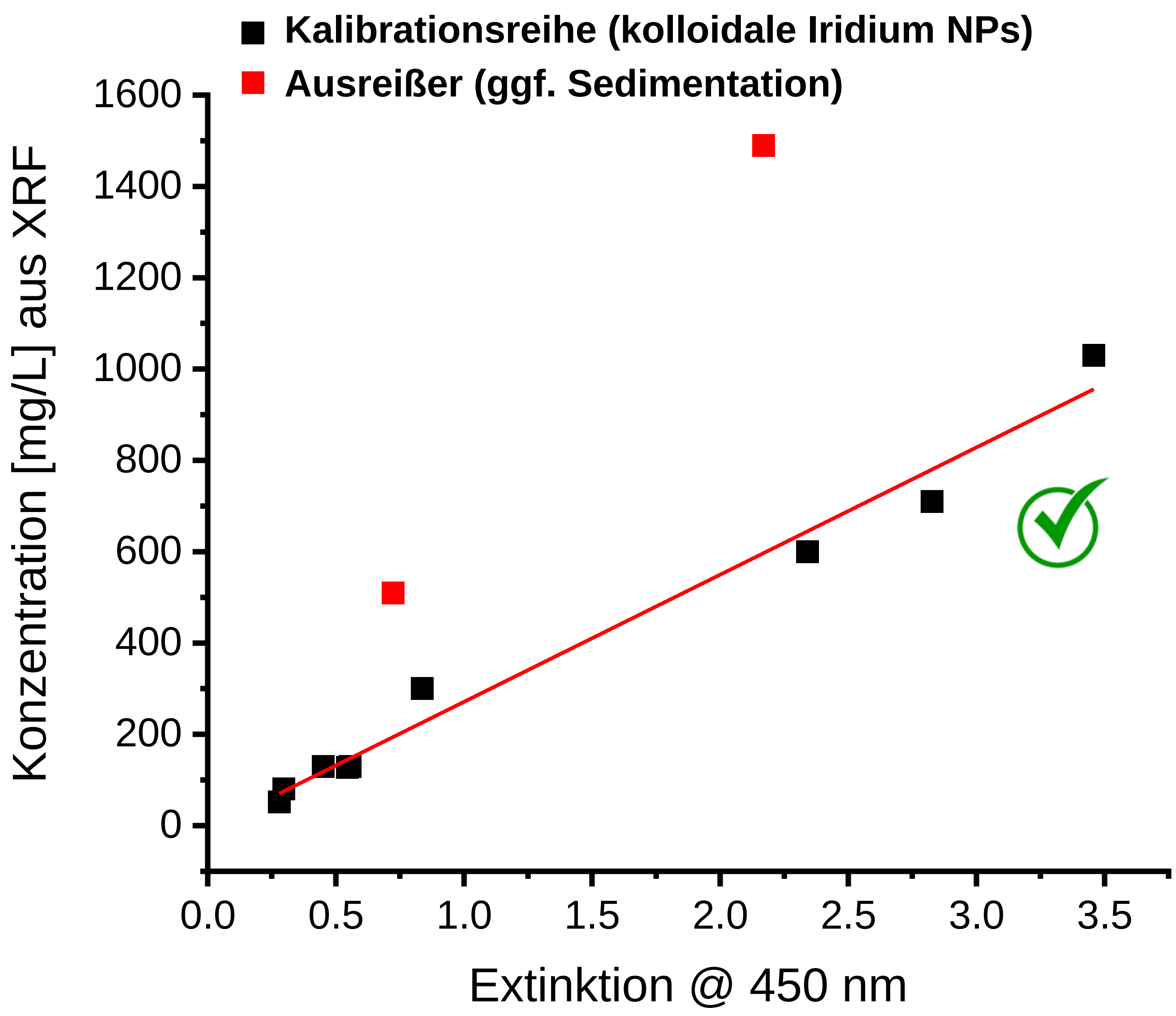
- **Verglasung passt bis 0,1 wt%**
- **Pulver stehts überbestimmt**

Kalibration: Referenz

AgCl auf MQP-S Mikropulver



- **Sign. Abweichung der Verglasung bei <0.1 wt%**
- **Pulver passt stehts (?)**



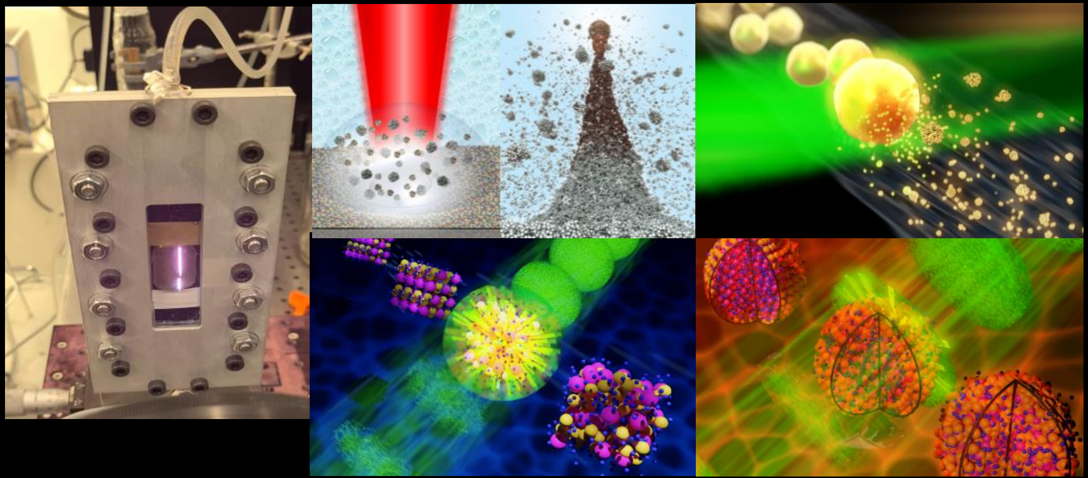
Nanopartikelkonzentration

- Alternativer Quantifizierungsansatz:

  Eintrocknen eines definierten Volumens auf Substrat (Boratglas?)
  - gleichzeitige Verwendung eines internen Metallsalzstandards
  - Oder Spiken der Probe mit Metallsalz des gleichen Elements?

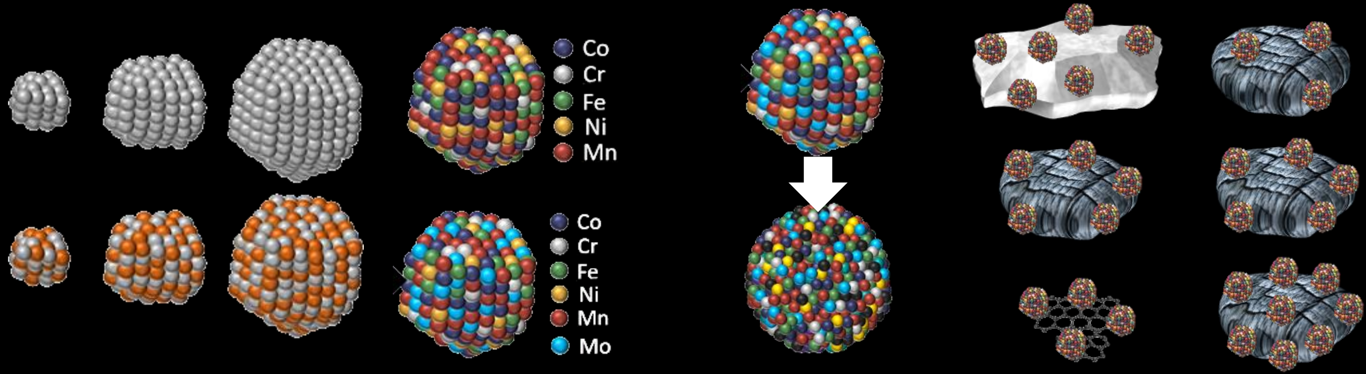
Conclusion: Laser Synthesis of Nanomaterials and Quantification with XRF

Scalable synthesis



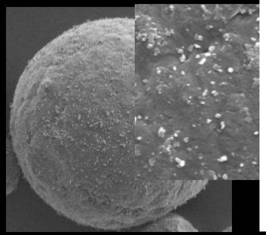
Material design

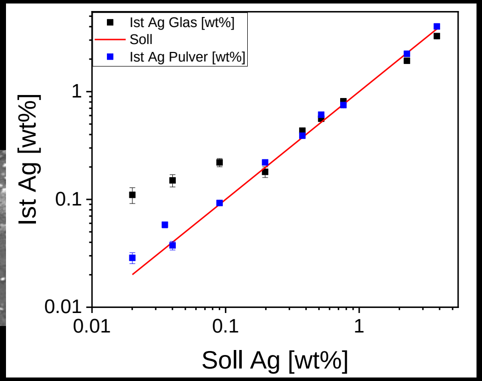
Size, Composition, crystalinity, NP loading



Succesful quantification and calibration

Formula	Concentration	Status	Line 1
Fe	78,10%	XRF 1	Fe KA1-HR-Tr
Cr	20,80%	XRF 1	Cr KA1-HR-Tr
Zr	0,79%	XRF 1	Zr KA1-HR-Tr
Si	0,12%	XRF 1	Si KA1-HR-Tr
Hf	496 PPM	XRF 1	Hf LA1-HR-Tr
Ni	221 PPM	XRF 1	Ni KA1-HR-Tr
Cu	144 PPM	XRF 1	Cu KA1-HR-Tr





Open questions: Best practice?

- How to choose the correct XRF line for the quantification when no calibration is available?
- Calibrations with metal salts transferable to nanoparticle-loaded samples?
- Usage of metal salts as internal standards?
- Spiking of samples with metal salts of quantified elements?

Nature | Engineering (currently)

Acknowledgement