Plasmonic Activity of Freestanding and Purified 3D-FEBID Architectures

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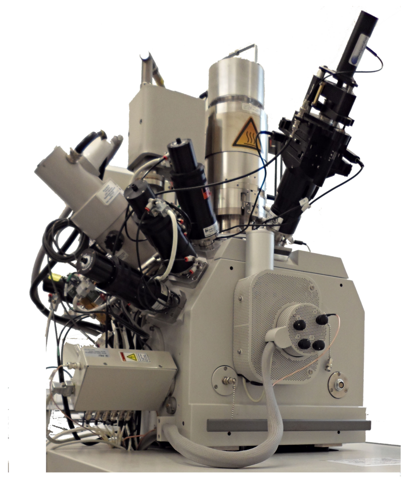
Introduction & Basic Principle

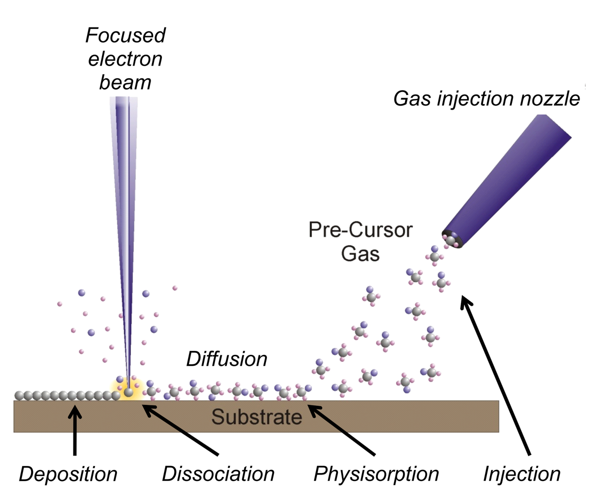
Metal-strucutres with particle sizes smaller than the wavelength of light exhibit interesting optical effects. During the last decade plasmonic activity was investigated in numerous studies and interesting applications were demonstrated. This development goes along with proper fabrication methods on the nanoscale.

While lithography and wet chemical synthesis are suitable to create structures on that scale it is a challenging task to meet all upcoming requirements for novel plasmonic investigations. In high demand beside the small sizes are the shape, material purity, crystallinity, accurate positioning on any surface material and morphology as well as the capability to fabricate complex and freestanding 3-dimensional geometries.

One technique, which meets all these requirements, is Focused Electron Beam Induced Deposition (**FEBID**) as demonstrated in this study.



Focused Electron Beam Induced Deposition (FEBID) uses the highly localized decomposition of surface adsorbed precursor molecules via electrons to fabricate functional nanostructures.

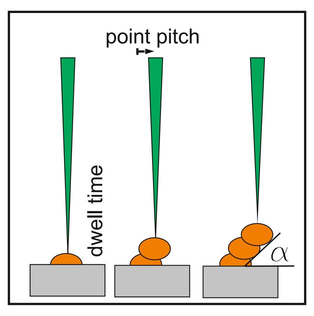


In this study we show:

- direct-write 3D-nanoprinting via FEBID
- material purification to achieve pure gold structures
- plasmonic activity of 2-dimensional disks in comparison to electron beam lithography (EBL) reference disks
- plasmonic activity for freestanding 3D structures

By that, this opens entirely new capabilities for on-demand fabrication of 3D architectures for resonant optics.

3D-Nanoprinting



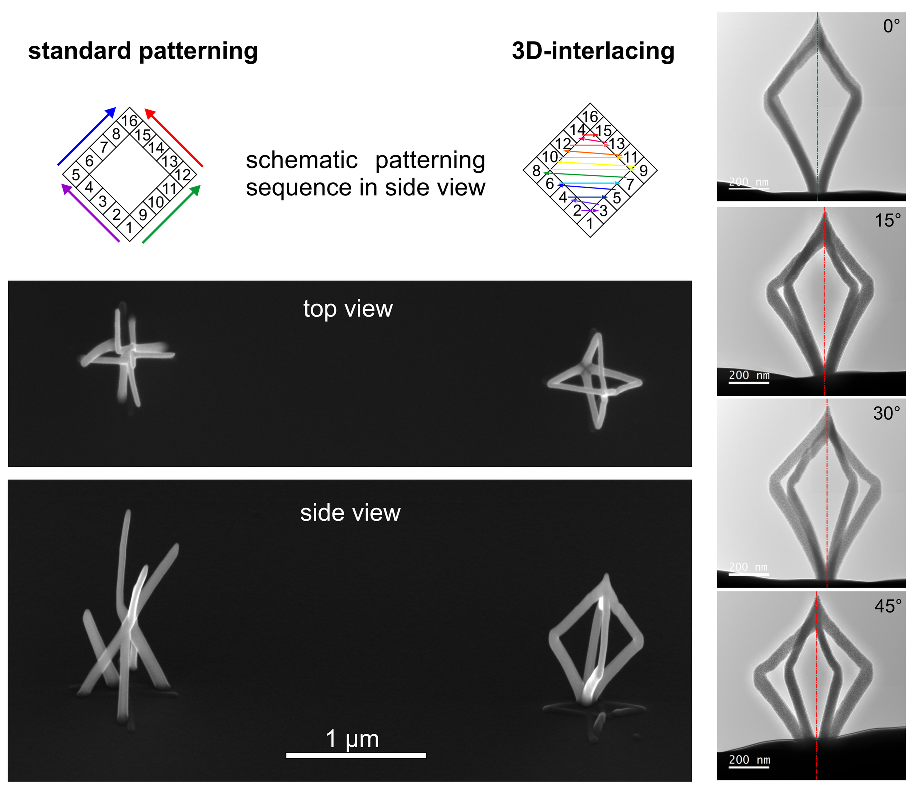
Simple freestanding 3-dimensional nanostructures can be fabricated with FEBID in one single step by using suitable pulse durations (dwell times, DT) and pixel distances (point pitch, PoP).

More complex 3D-geometries require a more detailed understanding of

- precursor dynamics[1] (molecule adsorption, diffusion,...)
- beam parameter (primary energy, beam current,...)
- patterning strategy ("3D interlacing")

With that, defined nano-architectures[2] can be fabricated reliably and structure deformation or unwanted co-deposition, disabeling complex structures in the past, are avoided.

For the deposition of complex multi-branch structures we introduced an alternating point sequence (3D interlacing), enabling the fabrication of tetragonal-bi-pyramids for plasmonic characterizations.



Material Purification

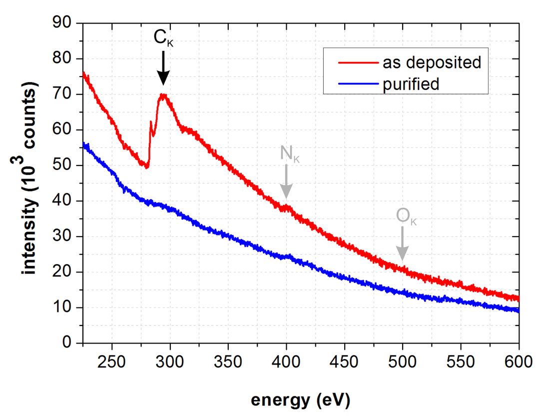
FEBID deposits notoriously contain very high carbon content, compromising the intended functionality like plasmonic activity.

Gold/Carbon deposits from

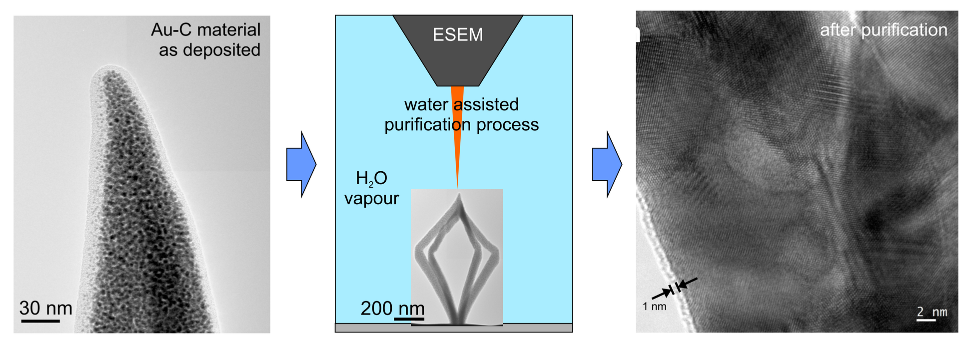
- $Me_2Au(acac)$ (acetylacetonate- dimethyl-gold(III))
- as deposited carbon content is higher than 90 at.%

Purification step for Au-C deposits successfully introduced via an e-beam assisted H_2O purification in an environmental SEM (ESEM)[3]

- completely removal of carbon
- deposition shrinkage
- good shape retention
- pore and crack-free morphology



Purification of freestanding 3D-structures



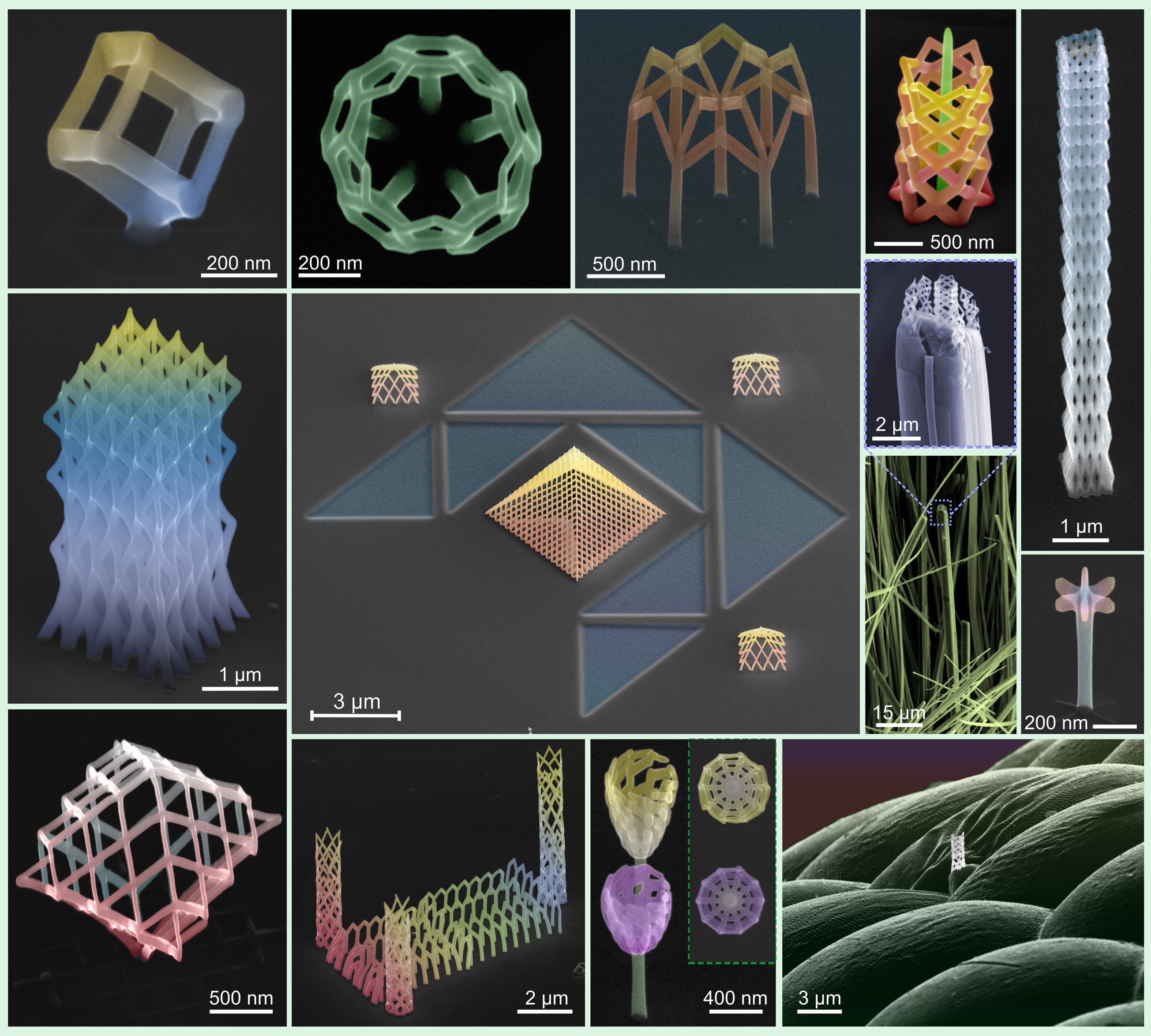
By changing the purification from 2-dimensional to freestanding 3-dimensional structures, the process parameter (electron dose, purification current, dwell time,...) have to be adapted slightly. The purified structures are

- highly compact
- highly crystalline gold
- minimal surface contamination
- suitable for plasmonic characterization

3D-Nanoprinting Examples

Some expamles to demonstrate the capability of the 3D-Nanoprinting via Focused Electron Beam Induced Deposition (FEBID):

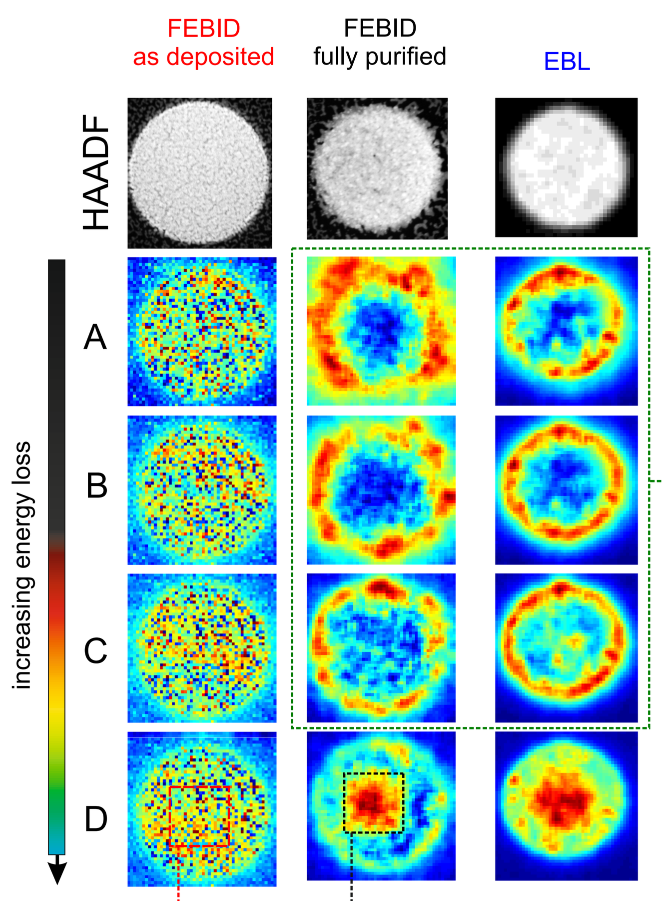
- precise structuring on the lower nanoscale
- direct writing of complex freestanding architectures
- fabrication on almost every surface material and morphology



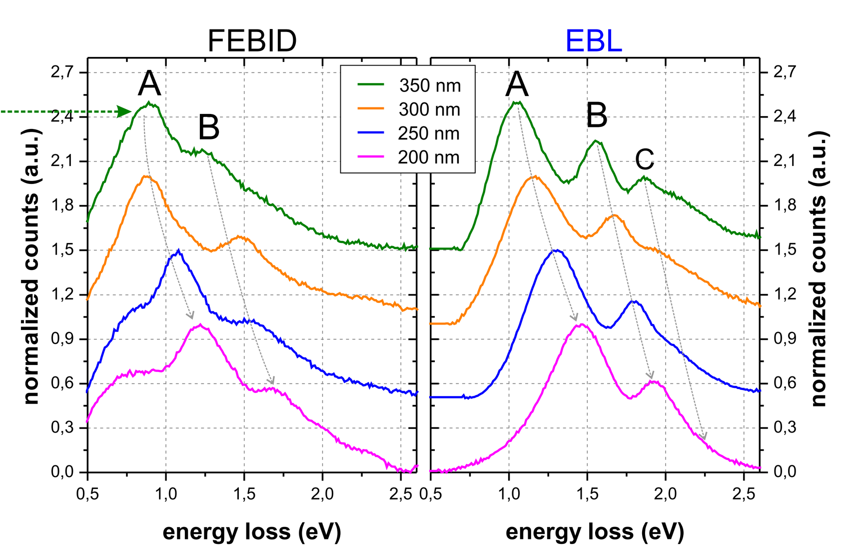
Plasmonic Activity in 2D

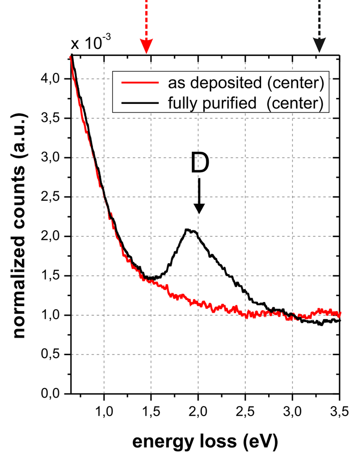
Gold disks were fabricated on a Si_3N_4 TEM grid via

- FEBID (as deposited)
- FEBID (after a full purification step)
- Electron beam lithography



To investigate influence of disk sizes, these were fabricated with diameters ranging from 200 to 350 nm.





Plasmonic characterization is enabled with scanning transmission electron microscopy (**STEM**) based electron energy loss spectroscopy (**EELS**)[4].

While EEL-maps of as deposited discs show no plasmonic behaviour, fully purified disks clearly show plasmonic activity.

By comparison to identical EBL disks, dipole, quadrupole and hexapole edge modes can be assigned.

Breathing mode[5] of purified disks is visible even in the raw data.

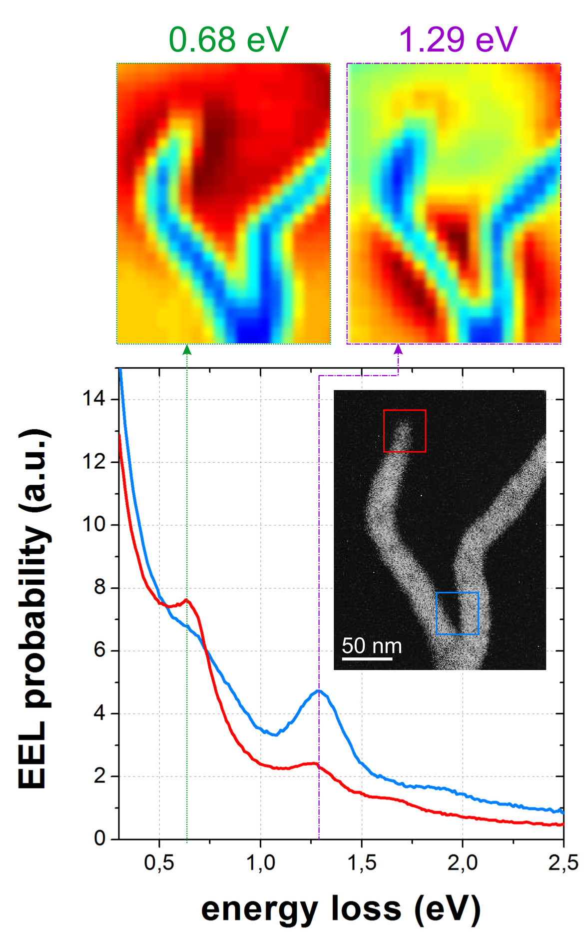
Plasmonic Activity in 3D

Plasmonic characterization via STEM-EELS reveals no plasmonic behaviour for as-deposited Au-C FEBID 3D-structures.

In contrast, after a purification step, plasmonic activity of tetragonal-bi-pyramids was achieved.

Highest surface plasmon resonance was found at the branching areas and the tip as intended by design.

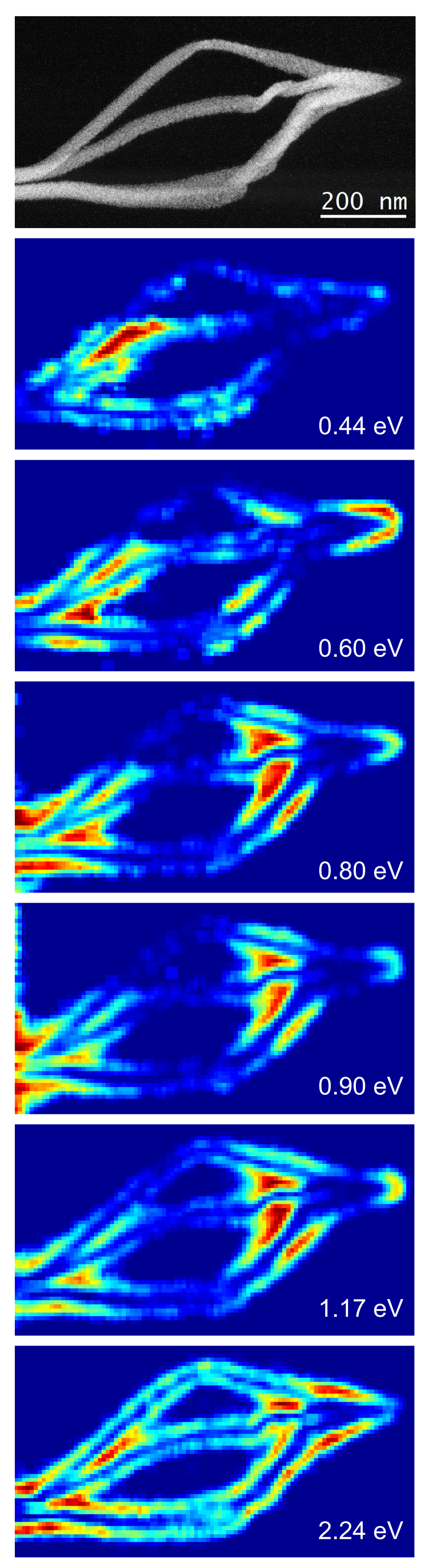
Noteworthy is also the symmetrical appearance of plasmon modes.



The achieved plasmonic activity of fully purified FEBID-3D structures can be even such strong, that the resonance peaks are visible already in the raw data.

The results clearly proof the suitability of FEBID material for plasmonic investigations.

With the on-demand 3D-printing capability of freestanding geometries on the lower nanoscale, novel possibilities and applications are now possible.



References

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