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Direct-write, cell-like materials

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Problem

The success of biological systems rests upon the ability to direct biochemical reactions using asymmetric recognition and catalysis under strict compartmentalization. In order to better understand, mimic, and ultimately improve upon evolutionarily optimized cellular behaviors requires development of new materials and manufacturing approaches. Thus efforts to engineer directional propulsion of bioinspired nanomachines such as catalytic nanomotors requires asymmetric placement of a catalytic entity (e.g., platinum). Alternatively, placement of catalysts within asymmetric 3D compartments could facilitate directional 'cell-like' reactions and prove useful for systems ranging from micropumps to microfluidic chemical reactors and energy converters. However, this presents a materials fabrication challenge. In other words, *how can we fabricate micro-scale structures that incorporate both hard (e.g., catalysts) and soft (e.g., membranes hydrogels) within a user-defined 3D framework at the scale of individual cells?* In this work we investigate multiphoton lithography (MPL) to create arbitrary 3D bimolecular and multicomponent assemblies for development of autonomous, cell-like materials.

Asymmetry and compartmentalization are key features of biological systems

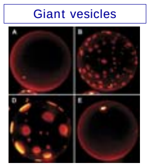
Compartmentalization and directed energy flow underpin cellular behavior

Features of cellular behavior mimicked in synthetic systems.

Dynamic emulsions

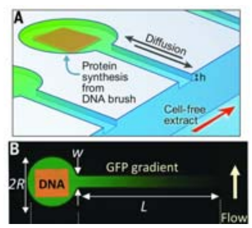
Zarzar et al, *Nature* 518, 520–524 (2015)

Giant vesicles



Parikh group; *eLife* 2014;3:e03695

Directed, on chip, biochemical reactions



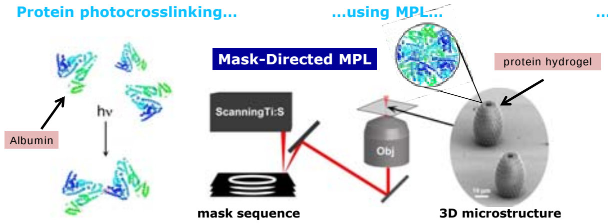
Karzbrun et al., *Science*, 345 (6198): 829-832

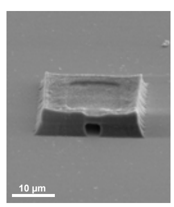
Can multiple cell-like functionalities be assembled in 3D compartmentalized microenvironments?

Approach

Multicomponent 3D assemblies can be achieved using Multiphoton Lithography (MPL)

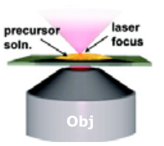
Protein photocrosslinking… **…using MPL…** **…to fabricate hollowed, hydrogel chambers.**





MPL Photo-Crosslinking of Proteins occurs via photoexcitation of a sensitizer to generate reactive intermediates that activate oxidizable residues (e.g., Tyr-radicals) to produce inter-protein crosslinks. MPL confines this process to the focal point of a focused light source. Translation of this reactive voxel within a protein solution allows fabrication of 3D objects with nearly arbitrary features.

MPL for patterning of platinum and palladium catalysts



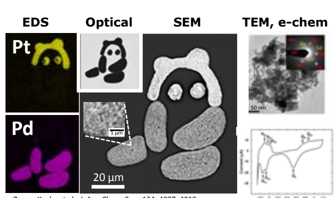
Pt(II) and Pd(II) in aqueous solution are photoreduced at the beam waist of a focused femtosecond laser (Ti:S centered at 750 nm) using a sensitizing agent (trisoxalatoferrate(III) anion) which generates a strong reducing agent to form metallic Pt and Pd according to the following reactions

Multiphoton Photoreduction of Fe(III) → Fe(II)

$h\nu + 2[Fe(C_2O_4)_3]^{3-} \rightarrow 2[Fe(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2\uparrow$

Reduction of Pt(II) → Pt

$[PtCl_4]^{2-} + 2[Fe(C_2O_4)_2]^{2-} \rightarrow Pt\downarrow + 2[Fe(C_2O_4)_2]^{-} + 4Cl^{-}$



Zarzar, Kaehr et al., *J. Am. Chem. Soc.*, 134, 4007–4010.

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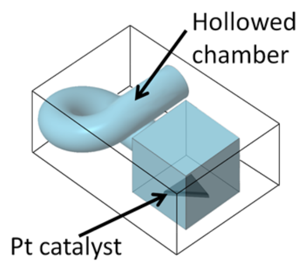
Results

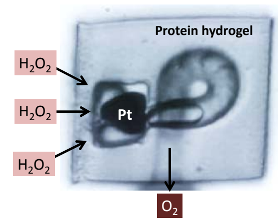
Directional catalysis in cell-like, 3D microstructures

Schematic of chamber design

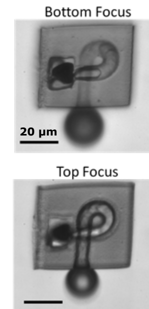


Platinum catalyzed decomposition of peroxide:
$2H_2O_2\ (aq) \rightarrow 2H_2O(l) + 2H_2O_2(g)$

Reactants diffuse across chamber walls

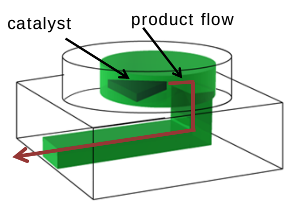


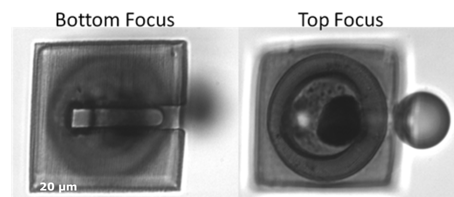
Gas products are directed through the spiral to the exit



Arbitrary placement of catalysts in 3D microenvironments

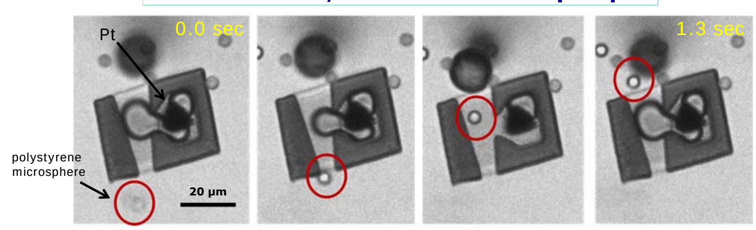
MPL allows pinpoint placement of Pt catalysts in isolated top chamber of prefabricated microstructure.





An MPL-Pt catalyst printed inside the upper chamber of a 3D microchamber designed to direct gas flow downward, underneath the catalyst.

Autonomous, directional micro-pump

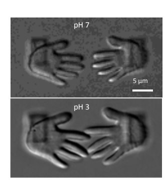


The flow of the gas products of the reaction is directed using a trapezoidal-shaped inlet/outlet structure. Bubbles preferentially exit the wider end which creates an autonomous pumping mechanism, used here to directionally pump 5 µm particles through the asymmetric tube.

Significance

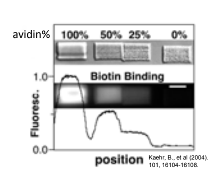
We have demonstrated the use of MPL to fabricate patterned microscale catalysts (platinum and palladium) that display excellent catalytic activity and can be integrated within 3D MPL-defined microenvironments to generate directed autonomous particle and fluid transport. This preliminary work demonstrates patterning and compartmentalization of catalytic activity at the scale of biological cells, showing that the flow of reactants and products can be strictly directed.

Mechanically-responsive hydrogels…



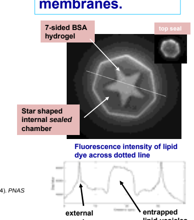
B. Kaehr and J. B. Shear, *PNAS*, 2008, 105, 8850-8854.

…comprised of active proteins…



Kaehr, B., et al (2004). *PNAS* 101, 16104-16108.

…template artificial membranes.



Compartmentalization is achieved using biological materials that can remain mechanically (left panel) active and can direct anisotropic self-assembly of additional functionalities such as lipids (right panels). These direct-write, cell-like systems provide a groundbreaking platform for the construction of living materials.