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Final Report: Chemical Sciences: Transient Nanopatterns by Biocatalytic Self-Assembly

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5c. PROGRAM ELEMENT NUMBER
611102

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Research Foundation CUNY - Advanced Sc
85 Saint Nicolas Terrace

New York, NY 10031 -1246

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14. ABSTRACT

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Rein Ulijn
UU	UU	UU	UU		19b. TELEPHONE NUMBER 212-413-3380

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as of 15-Oct-2021

Agency Code: 21XD

Proposal Number: 69180CH **Agreement Number: W911NF-16-1-0113**
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Principal: N

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Phone Number: 2124133380
Principal: Y

Organization: **Research Foundation CUNY - Advanced Science Research Center**
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Country: USA

DUNS Number: 831361857 EIN:
Report Date: 30-Apr-2021 Date Received: 05-Jun-2021
Final Report for Period Beginning 01-Jul-2016 and Ending 31-Jan-2021
Title: Chemical Sciences: Transient Nanopatterns by Biocatalytic Self-Assembly
Begin Performance Period: 01-Jul-2016 **End Performance Period:** 31-Jan-2021
Report Term: 0-Other

Submitted By: Rein Ulijn Email: Rein.Ulijn@asrc.cuny.edu
Phone: (212) 413-3380

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STEM Degrees: 3 **STEM Participants:** 3

Major Goals: It was the overall aim of this research program to develop transient nanoscale patterns that change their chemical information content and functionality over time with nanoscale resolution. To achieve this, we combined pioneering work from Riedo's Lab (thermochemical nanolithography–TCNL) , and Ulijn's Lab (biocatalytic self-assembly).

A major goal was to provide fundamental understanding and take concrete steps towards laboratory-based mimicry of fabrication approaches used by living systems. We achieved this by exploiting similar mechanisms used by living systems (catalytic amplification, self-assembly, structural confinement) but harness them as new tools for nanoscale fabrication, in non-biological contexts.

Accomplishments: The objective of this collaborative grant between the labs of Rein Ulijn (CUNY) and Elisa Riedo (NYU) was to combine revolutionary nanoscale patterning with catalytic self-assembly to obtain spatio-temporal control of nanostructure formation and breakdown and consequent dynamic control of functionality. By using thermochemical scanning probe lithography (tSPL) we were able to precisely tune the film 3D topographical landscape simultaneously with surface chemistry. This provided control over positioning and concentration of surface-immobilized enzymes [1,2]. Furthermore, by making use of competing enzyme-catalyzed assembly and dis-assembly reactions, we could demonstrate the transient formation of nanoscale fibers that have programmable chemical content and (electronic) functionality, as well as time programmable assembly - disassembly behavior. We studied fundamental aspects of biocatalytic assembly at solid-liquid interfaces by using both synthetic and biological surfaces and particles. Finally, we developed a versatile and modular chemical method to incorporate fluorescent dyes into peptide nanostructures, which allowed us to visualize in real-time the formation and breakdown of nanostructures with super-resolution (STED) fluorescent microscopy. More recently, we demonstrated the possibility to apply tSPL for the production of high performing 2D materials-based field effect transistors (FETs) fabricated on flexible materials without the need of masks, or markers, and in ambient conditions. Also, we have developed innovative methodologies for the time- and cost-effective scaling up of tSPL in combination with a biocompatible polymer, and we have replicated the exact topography of the bone tissue microenvironment with unprecedented sub-15 nm resolution over millimeter scale areas creating new possibilities for biomedical research and applications.

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The project resulted in 15 publications, one patent and training opportunities for several postdocs, graduate and undergraduate researchers as detailed in the uploaded report.

A pdf is attached with more details.

Training Opportunities: Training opportunities provided to students and postdocs include:
- experimental training in nano fabrication, surface analysis, imaging provided at CUNY ASRC and NYU. Training is provided by core facility directors and students eventually run these instruments and acquire data independently.
- mentoring opportunities for all postdocs and graduate students through Sumer research programs at NYU and CUNY
- all students and postdocs regularly participated in national and international conferences and workshops through presentation of posters and contributed talks. Examples in crude MRS, ACS, APS.

Results Dissemination: Dissemination of research results through regular interaction with groups of high school children to CUNY ASRC as part of our Illumination Space science exhibits. Postdocs and Grad students are involved in hosting students at these events.

Ulijn participated in a summer program for high school students through the World Science Festival in NYC and created an online course for gifted high school students across the world.

Given the broad impact of the project on different research area, students and postdocs worked on diverse research topics and areas and even interdisciplinary fields. Students and postdocs were encouraged to work in diverse groups and to build a research group consisting of people from different backgrounds. Relating with people from different areas and disciplines often brought up new perspectives and new ideas.

Part of the dissemination activity of the project was devoted to the Diversity, Equity and Inclusion (DEI) initiative organized by Riedo (Chair of the Committee) in the Chemical and Biochemical department at Tandon. This activity is aimed at giving voice to racial and gender diversity problematics and addresses issues such as sexual harassment and work-life balance issues within STEM career path development, and how they will prepare themselves for key career-based transitions.

Honors and Awards: Ulijn was awarded a Vannevar Bush Faculty Fellowship from ONR (2021).
Ulijn was elected co-Chair of the editorial board of ChemSystemsChem (Wiley) (2020).
Ulijn was elected to World Science University Faculty for the World Science Festival's global science scholar program (2020).
Ulijn awarded Batsheva de Rothschild Fellowship, personal travel fellowship to support lecture tour and University visits in Israel (Tel Aviv, Weizmann Institute, Ben Gurion, Hebrew University) (2020).
AFOSR DURIP (Rein Ulijn Co-PI) Dual Source Single Crystal X-ray Diffractometer for the Characterization of Small Molecules and Materials, $399,000 (PI Share-$0), 7/15/20-7/14/21
Ulijn (in his role chair) received sponsorship from ARO for the Gordon Research Conference on Systems Chemistry (June 2020). The conference was postponed to 2022 due to COVID.
Riedo was invited speaker at the Faraday Discussions on "Nanolithography of Biointerfaces" (ARO UK office program managers among the participants, Hollie Pietsch CCDC Atlantic).
Riedo became Editorial Board Member of Nature 2D Materials and Applications
Riedo Invited Speaker at the 2021 TMS Meeting
Riedo Invited Speaker at the 2020 Fall MRS Meeting
Riedo Invited Speaker at the Workshop on 2D and Quantum Materials at the 2020 CFN/NSLS-II Brookhaven Meeting
Riedo's work on tSPL selected to appear in the National Nanotechnology Initiative (NNI) Supplement to the President's 2020 Budget (which also serves as the annual report to Congress for the NNI).
ARO Materials Science (Elisa Riedo, Single PI) Novel properties of pressure activated 2D materials, $569,887, 08/01/20-07/31/23
Post-Doc Zanut received the NYU Provost Fellowship.
Ph.D. Xiangyu Liu won a Conference Award for the World Congress on Micro and Nano Manufacturing.

Protocol Activity Status:

Technology Transfer: Ulijn: Virtual seminar at Soldier Center, US Army Future Command, Natick MA (May 2020).
Riedo: Provisional Patent Application: “Biomimetic Tissue And Method Of Use Thereof”, NYU and NYSCF (2021)
Riedo: new collaboration with Thomas J. Kiel, Armaments Center, CCDC U.S. Army Futures Command Picatinny Arsenal
Riedo: ongoing partnership with SwissLitho and IBM for commercialized tSPL.
Visit by Wendy Mills and Dawanne Poree to CUNY ASRC (October 2018).
Visit by Rajesh Naik (AFoSR) to CUNY ASRC as part of 5-year review (February 2019).
Visit by Thomas J. Kiel, U.S. Army Futures Command Picatinny Arsenal to NYU Tandon Engineering (May 2019)
Riedo participated in a virtual meeting with Dr. Daniel Cole, Dr. Dan Magagnosc, and Dr. Matt Guziewski from ARL to discuss possible interactions and collaborations.

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Participant: Rein Ulijn
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
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Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Project Contribution:
National Academy Member: N

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Project Contribution:
National Academy Member: N

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Project Contribution:

National Academy Member: N

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Project Contribution:
National Academy Member: N

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National Academy Member: N

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Project Contribution:
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National Academy Member: N

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Person Months Worked: 3.00 **Funding Support:**
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ARTICLES:

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Volume: 27 Issue: 31 First Page #: 315302
Date Submitted: 8/30/18 12:00AM Date Published: 8/1/16 4:00PM
Publication Location:
Article Title: Thermochemical scanning probe lithography of protein gradients at the nanoscale
Authors: E Albisetti, K M Carroll, X Lu, J E Curtis, D Petti, R Bertacco, E Riedo
Keywords: scanning probe lithography, biofunctionalization, nanopatterning, protein gradient,extracellular matrix, surface functionalization
Abstract: Patterning nanoscale protein gradients is crucial for studying a variety of cellular processesin vitro. Despite the recent development in nano-fabrication technology, combining nanometricresolution and ?ne control of protein concentrations is still an open challenge. Here, wedemonstrate the use of thermochemical scanning probe lithography (tc-SPL)for de?ning micro-and nano-sized patterns with precisely controlled protein concentration. First, tc-SPL isperformed by scanning a heatable atomic force microscopy tip on a polymeric substrate, forlocally exposing reactive amino groups on the surface, then the substrate is functionalized withstreptavidin and laminin proteins. We show, by ?uorescence microscopy on the patternedgradients, that it is possible to precisely tune the concentration of the immobilized proteins byvarying the patterning parameters during tc-SPL. This paves the way to the use of tc-SPL forde?ning protein gradients at the nanoscale, to be used as chemical cues e.g. for st
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Applied Materials & Interfaces
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsami.6b13162
Volume: 9 Issue: 4 First Page #: 3266
Date Submitted: 8/21/18 12:00AM Date Published: 1/1/17 8:00PM
Publication Location:
Article Title: Biocatalytic Self-Assembly Using Reversible and Irreversible Enzyme Immobilization
Authors: M. P. Conte, K. H. A. Lau, R. V. Ulijn
Keywords: bioinspired materials; biointerfaces; hydrogel; polydopamine; polyphenol; protein; supramolecular chemistry; surface functionalization
Abstract: Biocatalytic control of molecular self-assembly provides an effective approach for developing smart biomaterials, allowing versatile enzyme-mediated tuning of material structure and properties as well as enabling biomedical applications. We functionalized surfaces with bioinspired polydopamine and polyphenol coatings to study the effects of enzyme surface localization and surface release on the self-assembly process. We show how these coatings could be conveniently used to release enzymes for bulk gelation as well as to irreversibly immobilize enzymes for localizing the self-assembly to the surface. The results provide insights to the mode of action of biocatalytic self-assembly relevant to nanofabrication and enzyme-responsive materials.
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Publication Identifier Type: DOI Publication Identifier: 10.1039/C7NR04624C
Volume: Issue: First Page #:
Date Submitted: 8/30/18 12:00AM Date Published:
Publication Location:
Article Title: Pathway-dependent gold nanoparticle formation by biocatalytic self-assembly
Authors: Jugal Kishore Sahoo, Sangita Roy, Nadeem Javid, Krystyna Duncan, Lynsey Aitken, Rein V. Ulijn
Keywords: biocatalytic, self-assembly, nanoparticles, template, dynamic
Abstract: We report on the use of non-equillibrium biocatalytic self-assembly and gelation to guide the reductive synthesis of gold nanoparticles. We show that biocatalytic rates simultaneously dictate supramolecular order and presentation of reductive phenols which in turn results in size control of nanoparticles that are formed.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1038/s41557-018-0047-2
Volume: 10 Issue: 7 First Page #: 696
Date Submitted: 8/21/18 12:00AM Date Published: 4/1/18 4:00AM
Publication Location:
Article Title: Amino-acid-encoded biocatalytic self-assembly enables the formation of transient conducting nanostructures
Authors: Mohit Kumar, Nicole L. Ing, Vishal Narang, Nadeesha K. Wijerathne, Allon I. Hochbaum, Rein V. Ulijn
Keywords: peptide, supramolecular materials, biocatalytic self-assembly
Abstract: Aqueous compatible supramolecular materials hold promise for applications in environmental remediation, energy harvesting and biomedicine. One remaining challenge is to actively select a target structure from a multitude of possible options, in response to chemical signals, while maintaining constant, physiological conditions. Here, we demonstrate the use of amino acids to actively decorate a self-assembling core molecule in situ, thereby controlling its amphiphilicity and consequent mode of assembly. The core molecule is the organic semiconductor naphthalene diimide, functionalized with D- and L- tyrosine methyl esters as competing reactive sites. In the presence of ?-chymotrypsin and a selected encoding amino acid, kinetic competition between ester hydrolysis and amidation results in covalent or non-covalent amino acid incorporation, and variable supramolecular self-assembly pathways. Taking advantage of the semiconducting nature of the naphthalene diimide core, electronic wires coul
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Journal: Communication Physics of Nature Research
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 6/5/21 12:00AM Date Published:
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Article Title: Nanoscale spin-wave circuits based on engineered reconfigurable spin-textures
Authors: Edoardo Albisetti, Daniela Petti, Giacomo Sala, Raffaele Silvani, Silvia Tacchi, Simone Finizio, Sebastia
Keywords: reconfigurable spin-textures, spin-wave, Nanoscale
Abstract: The development of a scalable and cost-effective nanofabrication method is of key importance for future advances in nanoelectronics. Thermalscanning probe lithography (t-SPL) is a growing nanopatterning method with potential for parallelization, offering unique capabilities that make it an attractive candidate for industrial nanomanufacturing. Here, we demonstrate the possibility to apply t-SPL for the fabrication ofgraphene devices. In particular, we use t-SPL to produce high performing graphene-based field effect transistors (FETs). The here described t-SPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active regionof the device. The electrical measurements on the t-SPL fabricated FETs indicate a symmetric conductance at the Dirac point and a low specific contact resistance without the use of any contact engineering strategy.
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Date Submitted: 11/14/18 12:00AM Date Published: 1/1/18 10:00AM
Publication Location:
Article Title: Biocatalytic Self-Assembly on Magnetic Nanoparticles
Authors: Maria P. Conte, Jugal Kishore Sahoo, Yousef M. Abul-Haija, K. H. Aaron Lau, Rein V. Ulijn
Keywords: biocatalysts, molecular self-assembly, magnetic nanoparticles
Abstract: Combining (bio)catalysis and molecular self-assembly provides an effective approach for the production and processing of self-assembled materials by exploiting catalysis to direct the assembly kinetics and hence controlling the formation of ordered nanostructures. Applications of (bio)catalytic self-assembly in biologically interfacing systems and in nanofabrication have recently been reported. Inspired by self-assembly in biological cells, efforts to confine catalysts on flat or patterned surfaces to exert spatial control over molecular gelator generation and nanostructure self-assembly have also emerged. Building on our previous work in the area, we demonstrate in this report the use of enzymes immobilized onto magnetic nanoparticles (NPs) to spatially localize the initiation of peptide self-assembly into nanofibers around NPs. The concept is generalized for both an equilibrium biocatalytic system that forms stable hydrogels and a nonequilibrium system that normally has a preset life
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Volume: 56 Issue: 46 First Page #: 14511
Date Submitted: 11/14/18 12:00AM Date Published: 11/1/17 4:00AM
Publication Location:
Article Title: Switchable Hydrolase Based on Reversible Formation of Supramolecular Catalytic Site Using a Self-Assembling Peptide
Authors: Chunqiu Zhang, Ramim Shafi, Ayala Lampel, Douglas MacPherson, Charalampos G. Pappas, Vishal Na
Keywords: peptide catalysis stimuli-responsive
Abstract: The reversible regulation of catalytic activity isafeature found in natural enzymes whichisnot commonlyobserved in artificial catalytic systems.Here,wefabricate anartificial hydrolase with pH-switchable activity,achieved byintroducing acatalytic histidine residue at the terminus ofapH-responsive peptide.The peptide exhibits aconformationaltransition from random coil to b-sheet by changing the pHfrom acidic to alkaline.The b-sheet self-assembles to form longfibrils with the hydrophobic edge and histidine residuesextending in an ordered arrayasthe catalytic microenviron-ment, which shows significant esterase activity.Catalyticactivity can be reversible switched by pH-induced assembly/disassembly of the fibrils into random coils.Athigherconcentrations, the peptide forms ahydrogel whichisalsocatalytically active and maintains its reversible (de-)activation.
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Volume: 32 Issue: 51 First Page #: 13600
Date Submitted: 11/14/18 12:00AM Date Published: 12/1/16 10:00AM
Publication Location:
Article Title: Understanding How Charged Nanoparticles Electrostatically Assemble and Distribute in 1-D
Authors: Keith M. Carroll, Heiko Wolf, Armin Knoll, Jennifer E. Curtis, Yadong Zhang, Seth R. Marder, Elisa Ried
Keywords: Nanoparticles
Abstract: The effects of increasing the driving forces for a 1-D assembly of nanoparticles onto a surface are investigated with experimental results and models. Modifications, which take into account not only the particle–particle interactions but also particle–surface interactions, to previously established extended random sequential adsorption simulations are tested and verified. Both data and model are compared against the heterogeneous random sequential adsorption simulations, and finally, a connection between the two models is suggested. The experiments and models show that increasing the particle–surface interaction leads to narrower particle distribution; this narrowing is attributed to the surface interactions compensating against the particle–particle interactions. The long-term advantage of this work is that the assembly of nanoparticles in solution is now understood as controlled not only by particle–particle interactions but also by particle–surface interactions. Both particle–partic
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Volume: 113 Issue: 16 First Page #: 162401
Date Submitted: 8/30/19 12:00AM Date Published: 10/1/18 4:00AM
Publication Location:
Article Title: Stabilization and control of topological magnetic solitons via magnetic nanopatterning of exchange bias systems
Authors: Edoardo Albisetti, Annalisa Calò, Martin Spieser, Armin W. Knoll, Elisa Riedo, Daniela Petti
Keywords: topological spin textures, nano devices
Abstract: Stabilizing and manipulating topological magnetic quasiparticles in thin films is of great interest for potential applications in data storage and information processing. Here, we present a strategy for stabilizing magnetic vortices and Bloch lines with controlled position, vorticity, and chirality in a continuous exchange bias system. By tailoring vectorially the unidirectional anisotropy of the system at the nanoscale, via thermally assisted magnetic scanning probe lithography, we show experimentally and via micromagnetic simulations the non-volatile creation of vortex-antivortex pairs. In addition, we demonstrate the deterministic stabilization of cross and circular Bloch lines within patterned N└eel magnetic domain walls. This work enables the implementation of complex functionalities based on the control of tailored topological spin-textures in spintronic and magnonic nanodevices.
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Journal: Nature Electronics
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1038/ s41928-018-0191-0
Volume: 2 Issue: First Page #: 17
Date Submitted: 8/30/19 12:00AM Date Published: 1/1/19 5:00AM
Publication Location:
Article Title: Patterning metal contacts on monolayer MoS2 with vanishing Schottky barriers using thermal nano lithography
Authors: X. Zheng, A. Calò, E. Albisetti, X. Liu, A.S.M. Alharbi, G. Arefe, X.i Liu, M. Spieser, W.J. Yoo, T. Taniguc
Keywords: 2D materials, nano lithography
Abstract: Two-dimensional semiconductors, such as molybdenum disulfide (MoS2), exhibit a variety of properties that could be useful inthe development of novel electronic devices. However, nanopatterning metal electrodes on such atomic layers, which is typically achieved using electron beam lithography, is currently problematic, leading to non-ohmic contacts and high Schottky barriers.Here, we show that thermal scanning probe lithography can be used to pattern metal electrodes with high reproducibility,sub-10-nm resolution, and high throughput (105 ?m2 h?1 per single probe). The approach, which offers simultaneous in situ imaging and patterning, does not require a vacuum, high energy, or charged beams, in contrast to electron beam lithography. Using this technique, we pattern metal electrodes in direct contact with monolayer MoS2 for top-gate and back-gate field-effect transistors.
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Date Submitted: 6/5/21 12:00AM Date Published: 2/1/21 5:00AM
Publication Location:
Article Title: Cost and Time Effective Lithography of Reusable Millimeter Size Bone Tissue Replicas With Sub? 15 nm Feature Size on A Biocompatible Polymer
Authors: Xiangyu Liu, Alessandra Zanut, Martina Sladkova?Faure, Liyuan Xie, Marcus Weck, Xiaorui Zheng, Elis
Keywords: bone tissue regeneration scanning probe lithography
Abstract: The development of a scalable and cost-effective nanofabrication method is of key importance for future advances in nanoelectronics. Thermalscanning probe lithography (t-SPL) is a growing nanopatterning method with potential for parallelization, offering unique capabilities that make it an attractive candidate for industrial nanomanufacturing. Here, we demonstrate the possibility to apply t-SPL for the fabrication ofgraphene devices. In particular, we use t-SPL to produce high performing graphene-based field effect transistors (FETs). The here described t-SPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active regionof the device. The electrical measurements on the t-SPL fabricated FETs indicate a symmetric conductance at the Dirac point and a low specific contact resistance without the use of any contact engineering strategy.
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Volume: 9 Issue: 1 First Page #: 011107
Date Submitted: 6/5/21 12:00AM Date Published: 1/1/21 5:00AM
Publication Location:
Article Title: Nanofabrication of graphene field-effect transistors by thermal scanning probe lithography
Authors: Xiangyu Liu, Zhujun Huang, Xiaorui Zheng, Davood Shahrjerdi, Elisa Riedo
Keywords: nanofabrication graphene field-effect transistor scanning probe lithography
Abstract: The development of a scalable and cost-effective nanofabrication method is of key importance for future advances in nanoelectronics. Thermalscanning probe lithography (t-SPL) is a growing nanopatterning method with potential for parallelization, offering unique capabilities that make it an attractive candidate for industrial nanomanufacturing. Here, we demonstrate the possibility to apply t-SPL for the fabrication ofgraphene devices. In particular, we use t-SPL to produce high performing graphene-based field effect transistors (FETs). The here described t-SPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active regionof the device. The electrical measurements on the t-SPL fabricated FETs indicate a symmetric conductance at the Dirac point and a low specific contact resistance without the use of any contact engineering strategy.
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Article Title: In Situ, Noncovalent Labeling and Stimulated Emission Depletion-Based Super-Resolution Imaging of Supramolecular Peptide Nanostructures
Authors: Mohit Kumar, Jiye Son, Richard H. Huang, Deborah Sementa, Magdelene Lee, Stephen O'Brien, Rein \
Keywords: Nanostructures peptides STED superresolution microscopy
Abstract: The development of a scalable and cost-effective nanofabrication method is of key importance for future advances in nanoelectronics. Thermalscanning probe lithography (t-SPL) is a growing nanopatterning method with potential for parallelization, offering unique capabilities that make it an attractive candidate for industrial nanomanufacturing. Here, we demonstrate the possibility to apply t-SPL for the fabrication ofgraphene devices. In particular, we use t-SPL to produce high performing graphene-based field effect transistors (FETs). The here described t-SPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active regionof the device. The electrical measurements on the t-SPL fabricated FETs indicate a symmetric conductance at the Dirac point and a low specific contact resistance without the use of any contact engineering strategy.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
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Article Title: Inhibiting cancer metabolism by aromatic carbohydrate amphiphiles that act as antagonists of the glucose transporter GLUT1
Authors: Alexandra Brito, Patrícia M. R. Pereira, Diana Soares da Costa, Rui L. Reis, Rein V. Ulijn, Jason S. Lew
Keywords: aromatic peptide Amphiphiles antagonist self-assembly cancer
Abstract: The development of a scalable and cost-effective nanofabrication method is of key importance for future advances in nanoelectronics. Thermalscanning probe lithography (t-SPL) is a growing nanopatterning method with potential for parallelization, offering unique capabilities that make it an attractive candidate for industrial nanomanufacturing. Here, we demonstrate the possibility to apply t-SPL for the fabrication ofgraphene devices. In particular, we use t-SPL to produce high performing graphene-based field effect transistors (FETs). The here described t-SPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active regionof the device. The electrical measurements on the t-SPL fabricated FETs indicate a symmetric conductance at the Dirac point and a low specific contact resistance without the use of any contact engineering strategy.
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WEBSITES:

URL: ulijnlab.com
Date Received: 21-Aug-2018
Title: ulijn group website
Description: research group website

RPPR Final Report
as of 15-Oct-2021

Partners

,

Dr. Giuseppe De Peppo, New York Stem Cell foundation (New York)Dr. Ricardo Pires, University of Minho (Portuga

I certify that the information in the report is complete and accurate:
Signature: rein Ulijn
Signature Date: 6/5/21 12:31PM

Major accomplishments

Summary

The objective of this collaborative grant between the labs of Rein Ulijn (CUNY) and Elisa Riedo (NYU) was to combine revolutionary nanoscale patterning with catalytic self-assembly to obtain spatio-temporal control of nanostructure formation and breakdown and consequent dynamic control of functionality. By using thermochemical scanning probe lithography (tSPL) we were able to precisely tune the film 3D topographical landscape simultaneously with surface chemistry. This provided control over positioning and concentration of surface-immobilized enzymes [1,2]. Furthermore, by making use of competing enzyme-catalyzed assembly and dis-assembly reactions, we could demonstrate the transient formation of nanoscale fibers that have programmable chemical content and (electronic) functionality, as well as time programmable assembly - disassembly behavior [3-8]. We studied fundamental aspects of biocatalytic assembly at solid-liquid interfaces by using both synthetic and biological surfaces and particles [9-11]. Finally, we developed a versatile and modular chemical method to incorporate fluorescent dyes into peptide nanostructures, which allowed us to visualize in real-time the formation and breakdown of nanostructures with super-resolution (STED) fluorescent microscopy [12]. More recently, we demonstrated the possibility to apply tSPL for the production of high performing 2D materials-based field effect transistors (FETs) fabricated on flexible materials without the need of masks, or markers, and in ambient conditions [13, 14]. Also, we have developed innovative methodologies for the time- and cost-effective scaling up of tSPL in combination with a biocompatible polymer, and we have replicated the exact topography of the bone tissue microenvironment with unprecedented sub-15 nm resolution over millimeter scale areas creating new possibilities for biomedical research and applications [15]. The grant partially supported one postdoctoral research fellow, and one graduate student.

Significant results up to August 2020-January 2021:

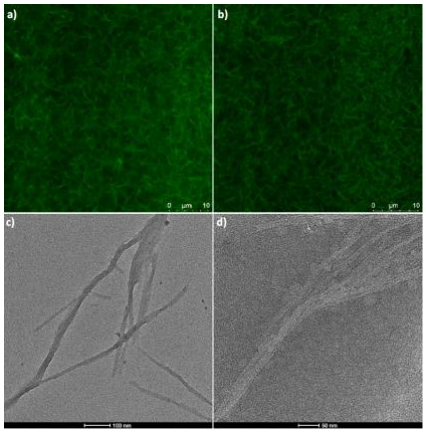
The final five months of the project were focused on completing and submitting manuscripts. Specifically, reviewers requested demonstration of the generality of the STED labeling approach and we could demonstrate labelling of arginine peptides (Table 1, entry 1), as well as nanoparticles functionalized with cationic peptides (entries 2-5) and correlate these with measured zeta potentials, as summarized in the following section. The paper was resubmitted and published in November 2020.

Table 1: Peptide sequences tested to expand the scope of Alexa-488 labeling of peptide nanostructures.

structure	sequence	Zeta potential (mV)	STED SRM imaging
1	FFALGLAGRR	10.3	yes
2	KPKGLRGDC-Au	18.1	yes
3	KKPKGLRGDC-Au	24.6	yes
4	KKKPKGLRGDC-Au	28.7	yes

Having demonstrated the nonspecific electrostatic interactions between the negatively charged sulfonate of Alexa-488 and positively charged lysines of peptides, we investigated the generality of the approach with a number of additional positively charged peptide nanostructures. We investigated if another positively charged

amino acid, arginine (R)-containing peptide nanostructures could be Alexa-488 labeled and subsequently imaged. Thus, we investigated the self-assembly of peptide **1**, which is analogous to the previously studied lysine peptide,



where the positive charge is provided by arginine (R) instead of lysine (K). We observe the formation of one-dimensional nanofibers that could also be labeled by Alexa-488 (Figure 1). Thus, we demonstrated the versatility of Alexa-488-based electrostatic fluorescent labeling of positively charged peptides containing lysine or arginine.

Figure 1: (a-b) STED SRM of peptide **1** labeled with Alexa-488 (0.5 mole % dye) and (c-d) TEM micrographs of peptide **1** without dye showing nanofiber network which could be imaged with STED SRM. Condition: 2.5 mM of **1** in 10 mM aq. phosphate buffer pH=7.4.

To further demonstrate the general utility of our approach, we tested gold nanoparticles functionalized with cationic peptide ligands, as a relevant model system for therapeutic and diagnostic applications. We synthesized **Au-1K**, **Au-2K**, and **Au-3K** (zeta potential 18.1, 24.6, and 28.7 mV, respectively) containing increasing numbers of positively charged lysines. Interestingly, all of them could be visualized by our design of electrostatic labeling with Alexa-488 (Figure 2). We observed that the resolution of STED imaging was reduced for gold nanoparticles (approximately 300 nm) compared to peptide nanofibers, which could be due to partial quenching of the dye on nanoparticles. Indeed, it should be noted that fluorescence imaging of peptides attached to gold nanoparticles is not trivial because of the general tendency of gold nanoparticles to quench the emission of fluorophore covalently conjugated on its surface. Advantageously, although it requires further investigation, we demonstrate that the electrostatic labeling design introduced here enables imaging of peptide-conjugated gold nanoparticles without complete quenching of emission. Thus, we have shown the modular nature of Alexa-488 labeling design, which can be used for fluorescent imaging of gold nanoparticles conjugated with cationic peptides.

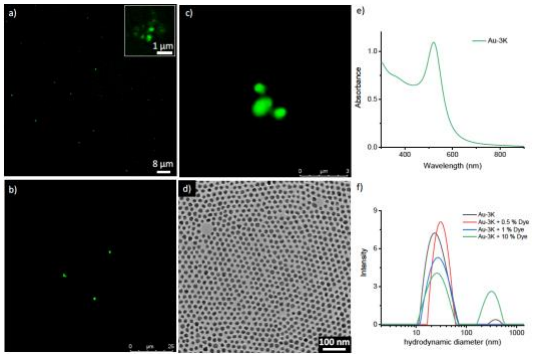


Figure 2: (a-c) STED microscopy images of peptide functionalized gold nanoparticles (**Au-3K** *i.e.* KKKPKGLRGDC-Au) labeled with Alexa-488 (0.5 mole % with respect to the concentration of ligand present of nanoparticles surface. d) TEM image; e) UV-vis absorption spectrum and f) dynamic light scattering (DLS) data of the **Au-3K** nanoparticles without and with various mole% of dye labeling. In all the cases the solvent medium was 50 mM citrate buffer at pH 7.0.

While our research capabilities were reduced during lockdown, we also wrote a comprehensive review on the topic of *Peptide-Based Systems Chemistry* for ACS Chemical Reviews which covers the new findings gained in this project positioned within the context of the recent literature. This comprehensive review, which includes 350 reference paper has been reviewed and a revision is currently in preparation.

In this funding period, we finalized experiments and published two articles related to the use of tSPL as high-resolution nanofabrication tool. In the first work we demonstrate the possibility to apply thermal scanning probe lithography for the fabrication of graphene devices. In particular, we use tSPL to produce high performing graphene-based field effect transistors (FETs). The here described tSPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active region of the device (see Fig. 3).

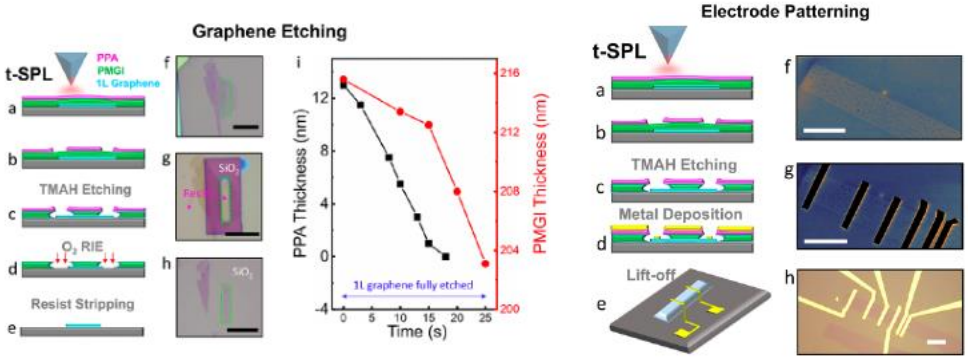


Figure 3: Left: Optimization of the t-SPL nano-patterning process for defining graphene regions. (a)–(e) Schematic illustration of the t-SPL process for patterning graphene active regions. (f) Optical microscope image of the starting graphene flake after coating with the PPA/PMGI resist. The green dotted box shows the target active region. (g) The same graphene flake after tSPL patterning and chemical etching of the PMGI layer. (h) Final rectangular graphene ribbon obtained after 25 s oxygen plasma etching. Scale bars are 10 μm. (i) Etching rates of PPA and PMGI with oxygen plasma. Each data point represents one new substrate. Right: tSPL metal electrode patterning on graphene. (a)–(e) Schematic illustrations of the tSPL patterning process for the fabrication of metal electrodes for GFETs. (f) In situ tSPL imaging of monolayer graphene (rectangular ribbon with a length and width of 80 μm and 6.7 μm, respectively) after spin-coating the PPA/PMGI resist. (g) In situ tSPL imaging of the structure, showing the patterned electrode features in the PPA layer. (h) Example of the optical image of a backgated graphene device after lift-off. The spacings between electrodes are 0.6 μm, 2.3 μm, 4.3 μm, 6.1 μm, and 8.2 μm. Scale bars are 10 μm.

In a second work, we use tSPL to replicate, with nanometer resolution, the bone microenvironment in a thermo-sensitive and biocompatible poly(methacrylate) copolymer resist - poly((tetrahydropyran-2-yl N-(2 methacryloxyethyl) carbamate)-b-(methyl 4-(3-methacryloyloxypropoxy) cinnamate)) (PMCC), spin-coated on a transparent indium tin oxide (ITO) glass. To reproduce the bone tissue topography on the PMCC resist, we use an atomic force microscopy (AFM) image of a demineralized bone tissue section as a tSPL bitmap input image (Fig. 4). The results show that the depth (4-8 nm) and the periodic D-spacing (67 nm) of the replicated collagen fibrils are within the typical values reported for the bone tissue microenvironment. The quality of this replica confirms the capability of tSPL to pattern complex 3D tissue microenvironments with high fidelity and resolution (Fig. 4). In order to scale up the size of the replica we reproduce an array of replicas starting from the same bone

input AFM images. Furthermore, we develop a probe washing procedure, based on cleaning the probe in chloroform.

Very importantly, we find that the PMCC resist supports the culture of human iMSCs similarly to standard tissue culture plasticware (TCP). The nanopatterned replicas are tested for reusability after a cell culture experiment by removing the cells and cleaning the sample, and we obtained some promising results (Fig. 5). The ability to simultaneously pattern topographical and chemical features of biological tissues creates unprecedented opportunities for the production of biomimetic materials and surfaces that control cell behavior.

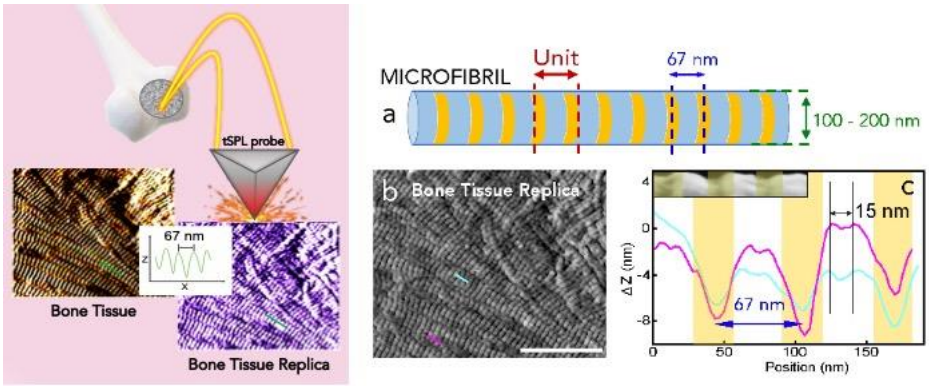


Figure 4. Left: AFM images of the bone tissue (bottom left) and the replica fabricated by tSPL (bottom right). Right: image presenting (a) a schematics of a bone microfibril; (b) a bone tissue replica fabricated by tSPL in the PMCC resist. Scale bar: 1 μm; (c) cross-sections of two segments shown in (b), highlighting the presence of ~ 20-30 nm gaps and twin-peak fibril bumps, and the characteristic 67 nm distance between the gaps, as in type I collagen microfibrils (in inset).

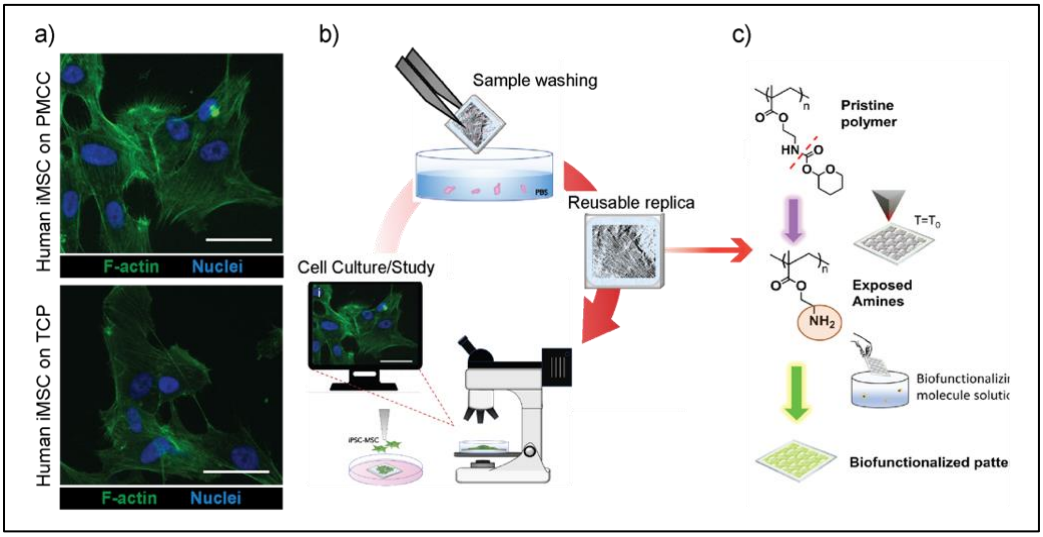
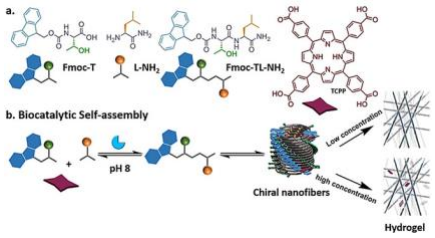


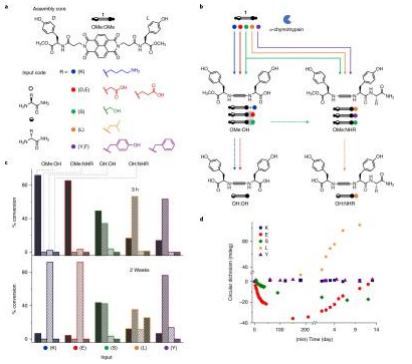
Figure 5. (a) Fluorescence micrographs of human iPSC-MP cells attached to PMCC and TCP 1 day after seeding. Scale bar 50 μm ;(b) schematic showing the reusability of the bone replica where Cell cultured on the large-scale bone tissue replicas are removed and the sample is washed and reuse for cell culture studies; (c) Schematic illustration of the tSPL patterning process and pattern biofunctionalization exploiting the PMCC carbamate block chemical structure with protected amine which are exposed by tSPL and used for the biofunctionalization. On the right the fluorescence microscopy image of an array of bone tissue replicas patterned using different probe temperatures and functionalized with Alexa 488 dye. Scale bar: 5 μm.

Summary of overall accomplishments during the project duration.

The detailed achievements in each year have been reported in our annual reports. Here we provide an overview of the most significant achievements and publications during the duration of this project.

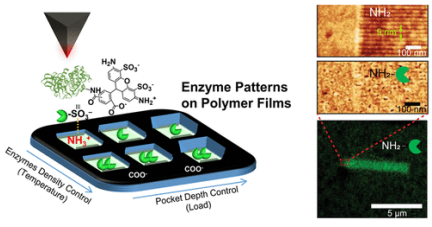


We demonstrated, in a paper published in *Chemistry European Journal*, the biocatalytic co-assembly of peptides and porphyrins in aqueous medium to generate and modulate an energy transfer hydrogel. Depending on the concentrations of porphyrin used, we observed distinct regions of self-assembly behavior: integration of the porphyrin into nanostructures to produce two-component co-assembly fibers, or heterogeneous self-aggregation. The mode of assembly directly impacts on the energy transfer efficiency of these nanostructures.



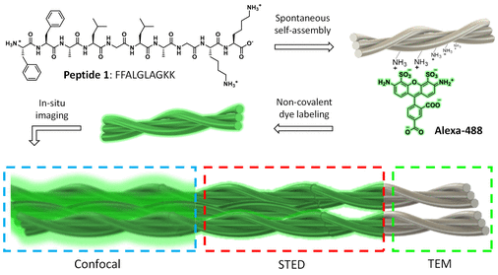
In a front cover article published in *Nature Chemistry* [7], we demonstrated the use of biocatalytic reactions to covalently or non-covalently modify a self-assembling core molecule, thereby controlling its amphiphilicity and consequent mode of assembly. Taking advantage of the semiconducting nature of the naphthalene diimide core, electronic wires could be formed and subsequently degraded, giving rise to temporally regulated electro-conductivity.

Following from this work, we focused on time-programmable, transient supramolecular naphthalimide-dipeptide nanofibers, *as reported in Chemistry European Journal*, where the lifetimes of which are predictably variable, demonstrated through variation of the self-assembly propensity of their amino acid precursors. The work shows that a thermodynamic parameter dictates kinetic lifetimes in transient fibers formed by competing biocatalytic self-assembly and disassembly of aromatic peptide amphiphiles.

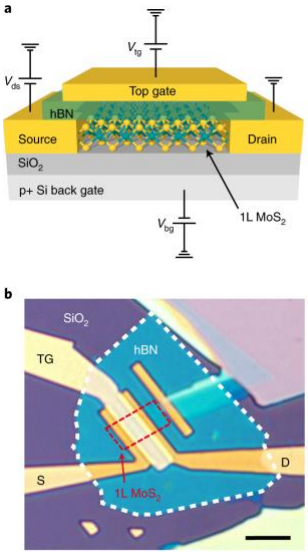


The ability to precisely control the localization of enzymes on a surface is critical for several applications including biosensing, bio-nanoreactors, and single molecule studies. Despite recent advances, fabrication of enzyme patterns with resolution at the single enzyme level is limited by the lack of lithography methods that combine high resolution, compatibility with soft, polymeric structures, ease of fabrication, and high throughput. In papers published in *ACS Advanced Materials Interfaces*, and *Faraday Discussions*, we introduced a method to generate enzyme nanopatterns (using thermolysin as a model system) on a polymer surface is demonstrated using thermochemical scanning probe lithography (tSPL). We were

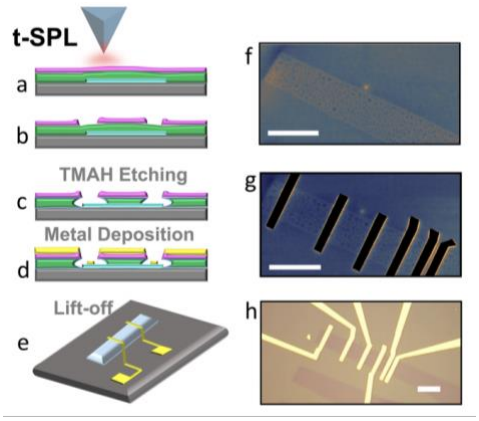
able to achieve combined single-enzyme resolution over mm^2 areas and the possibility of fabricating enzymes nanogradients.



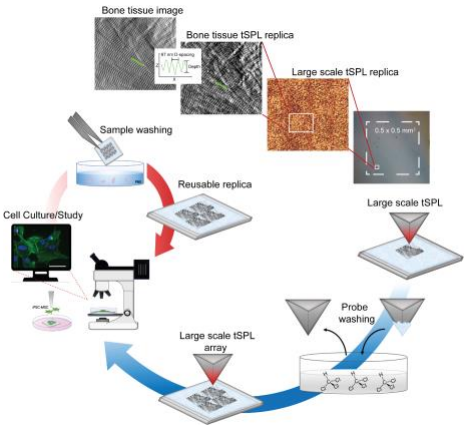
For optimum utilization of these dynamic self-assembled materials, it is important to visualize and understand their structures at the nanoscale, in solution and in real time. We demonstrate a noncovalent fluorescent labeling design for STED-based super-resolution imaging of self-assembling peptides. This is achieved by in situ, electrostatic binding of anionic sulfonates of Alexa-488 dye to the cationic sites of lysine (or arginine) residues exposed on the peptide nanostructure surface. Overall, our approach presents a general and simple method for the electrostatic fluorescent labeling of cationic peptide nanostructures for nanoscale imaging under physiological conditions and probe dynamic processes in real time and in situ.



Two-dimensional semiconductors, such as molybdenum disulfide (MoS2), exhibit a variety of properties that could be useful in the development of novel electronic devices. In this paper published on *Nature Electronics* [13], we show that thermal scanning probe lithography can be used to pattern metal electrodes with high reproducibility, sub-10 nm resolution, and high throughput. The approach, which offers simultaneous in situ imaging and patterning, does not require a vacuum, high energy, or charged beams, in contrast to electron beam lithography. Using this technique, we pattern metal electrodes in direct contact with monolayer MoS_2 for top-gate and back-gate field-effect transistors. These devices exhibit exceptional performances, including vanishing Schottky barrier heights (around 0 meV), on/off ratios of 10^{10}, no hysteresis, and subthreshold swings as low as 64 mV per decade without using negative capacitors or hetero-stacks.



As reported in *APL Materials* [14] we demonstrate the possibility to apply thermal scanning probe lithography (tSPL) for the fabrication of graphene devices. In particular, we use tSPL to produce high performing graphene-based field effect transistors (FETs). The here described tSPL process includes the fabrication of high-quality metal contacts, as well as patterning and etching of graphene to define the active region of the device. The electrical measurements on the tSPL fabricated FETs indicate a symmetric conductance at the Dirac point and a low specific contact resistance without the use of any contact engineering strategy. The entire tSPL nanofabrication process is performed without the need for masks, and in ambient conditions. Furthermore, thanks to the tSPL in situ simultaneous patterning and imaging capability, no markers are required. These features substantially decrease fabrication time and cost.



In this cover article published in *Advance Functional Materials* [15] we replicated with sub-15 nm resolution the bone tissue structure over large areas, by scaling up and adapting to cell studies thermal scanning probe lithography. By introducing cell-culture compatible reusable materials and novel writing strategies, we increase throughput and reduce cost by orders of magnitude, thus opening up unprecedented possibilities for pioneering new stem cell studies and biomedical applications.

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Honors

Ulijn was awarded a Vannevar Bush Faculty Fellowship from ONR (2021).
Ulijn was elected co-Chair of the editorial board of *ChemSystemsChem* (Wiley) (2020).
Ulijn was elected to **World Science University Faculty** for the World Science Festival's global science scholar program (2020).
Ulijn awarded **Batsheva de Rothschild Fellowship**, personal travel fellowship to support lecture tour and University visits in Israel (Tel Aviv, Weizmann Institute, Ben Gurion, Hebrew University) (2020).

AFOSR DURIP (Rein Ulijn Co-PI) *Dual Source Single Crystal X-ray Diffractometer for the Characterization of Small Molecules and Materials*, $399,000 (PI Share-$0), 7/15/20-7/14/21

Ulijn (in his role chair) received sponsorship from ARO for the Gordon Research Conference on Systems Chemistry (June 2020). The conference was postponed to 2022 due to COVID.

Riedo was invited speaker at the *Faraday Discussions* on "Nanolithography of Biointerfaces" (ARO UK office program managers among the participants, Hollie Pietsch CCDC Atlantic).
Riedo became Editorial Board Member of *Nature 2D Materials and Applications*
Riedo Invited Speaker at the 2021 TMS Meeting
Riedo Invited Speaker at the 2020 Fall MRS Meeting
Riedo Invited Speaker at the Workshop on 2D and Quantum Materials at the 2020 CFN/NSLS-II Brookhaven Meeting
Riedo's work on tSPL selected to appear in the *National Nanotechnology Initiative* (NNI) Supplement to the President's 2020 Budget (which also serves as the annual report to Congress for the NNI).

ARO Materials Science (Elisa Riedo, Single PI) *Novel properties of pressure activated 2D materials,* $569,887*,* 08/01/20-07/31/23
Grad Student Naxhije Berisha received Tow Foundation Fellowship.
Post-Doc Zanut received the NYU Provost Fellowship.
Ph.D. Xiangyu Liu won a Conference Award for the World Congress on Micro and Nano Manufacturing.

Tech Transfer

Ulijn: Virtual seminar at Soldier Center, US Army Future Command, Natick MA (May 2020).
Riedo: Provisional Patent Application: "Biomimetic Tissue And Method Of Use Thereof", NYU and NYSCF (2021)
Riedo: new collaboration with Thomas J. Kiel, Armaments Center, CCDC U.S. Army Futures Command Picatinny Arsenal
Riedo: ongoing partnership with SwissLitho and IBM for commercialized tSPL.
Visit by Wendy Mills and Dawanne Poree to CUNY ASRC (October 2018).
Visit by Rajesh Naik (AFoSR) to CUNY ASRC as part of 5-year review (February 2019).
Visit by Thomas J. Kiel, U.S. Army Futures Command Picatinny Arsenal to NYU Tandon Engineering (May 2019)
Riedo participated in a virtual meeting with Dr. Daniel Cole, Dr. Dan Magagnosc, and Dr. Matt Guziewski from ARL to discuss possible interactions and collaborations.

Students
Number of students receiving STEM degrees during the reporting period: 3
Number of undergraduate and graduate STEM participants during the reporting period: 3