QUEEN MARY UNIVERSITY OF LONDON

SUPRAMOLECULAR WORLD

Edited by Elham Radvar and Dominic Collis

"Self-assembly at surfaces"

Self-assembly (SA), the spontaneous organization of building blocks into ordered structures, has been used for surface modification. SA at surfaces occurs through molecule-molecule, molecule-surface interactions or both[1] (*figure 1*). The functional groups present on the surface act as a patterning platform, controlling the formation of different structures such as honeycomb network and its polygon variants; also, assembly direction depends on the presentation of these functional groups on the surface.

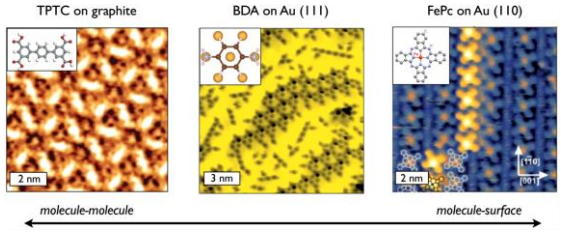


Figure 1. Left: assembly is driven by intermolecular interactions, p-terphenyl-3,5,3,5-tetracarboxylic acid (TPTC). Center: On a gold surface, 1,4-substituted benzenediamine (BDA) forms structures through both intermolecular and molecule-surface interactions. Right: iron-phthalocyanine (FePc) molecules form chains whose alignment is determined by particular 'channels' on the gold surface. (Image adapted from Whitelam., 2015)

In surface science, supramolecular assembly has introduced new studies that broadens the applications of modified surfaces to biological fields, such as bioensing, molecular recognition, and conjugation of biomolecules[2]. Substrates tyrpically used in surface-induced self-assembly include coinage metals, such as gold, silver and copper, but materials such as graphite (i.e. pencil lead), graphene and boron nitride have also been studied. However, gold has been the standard subtrate in developing self-assembling monolayers (SAMs, adsorption of organic molecules on a metal surface) due to its characteristics such as[3]:

- Gold is non-toxic to cells
- It's relatively easy to obtain films, colloids and/or nanoparticles from gold

Gold is inert metal and it does not react with O_2 in air or most chemicals, allowing only specifc reactions to take place. In biological applications, thiolates are more commonly used for surface modification, in a way that the natural thiol groups in the backbone of proteins can be coupled to gold surface due to the high affinity of thiols to gold. However, the biological molecules are sterically bulky and can affect the assembly organization on the surface[3] (*figure 2*).

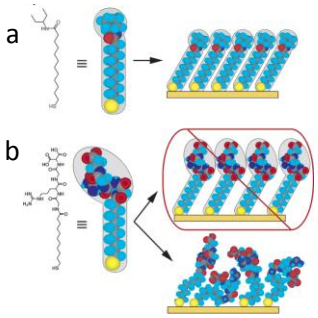


Figure 2. Schematic diagram illustrating the effects that large terminal groups have on the packing density and organization of SAMs. (a) small terminal group of amide do not distort the orientation; but, (b) peptide group at the terminal sterically infavors the secondary organization of organic layer. (adapted from Whitesides et al., 2005)

Self-assembly on metal surfaces provides a tool for molecular recognition or biochemical sensing; hence, the selectivity of biomolecules including enzymes, nucleic acids and antibodies can be utilized in molecular recognition using SAMs[4]. In a recent study, Shen at al. utilized a SAM system to develop electrochemical immunosensor to detect target molecules that cannot interact directly with surface-confined DNA probe (*figure 3*)[5].

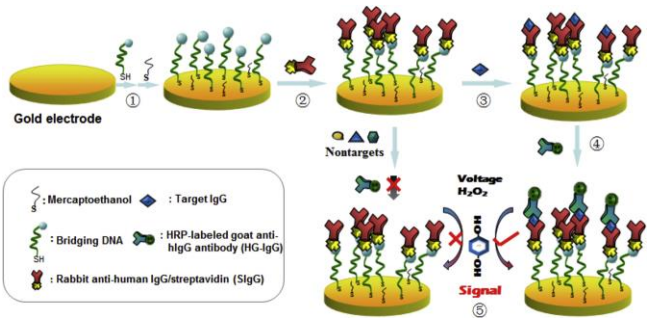


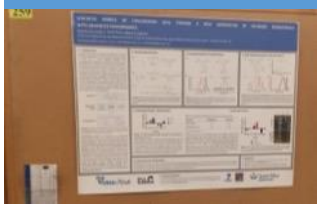
Figure 3. Schematic representation of steps of SAM preparation and sensing mechanism. (adapted from Shen at al., 2017)

The examples above show the potential of self-assembly on surfaces to produce chemically precise surfaces for developing biomedical devices, from sensors to nanoparticles for drug delivery.

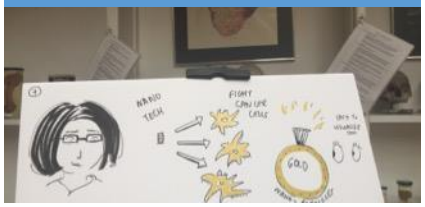
1. Whitelam, S., 2015. Examples of Molecular Self-Assembly at Surfaces. *Advanced Materials*, *27*(38), pp.5720-5725.
2. Rittikulsittichai, S., Park, C.S., Jamison, A.C., Rodriguez, D., Zenasni, O. and Lee, T.R., 2017. *Langmuir*, *33*(18), pp.4396-4406.
3. Love, J.C., Estroff, L.A., Kriebel, J.K., Nuzzo, R.G. and Whitesides, G.M., 2005. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chemical reviews*, *105*(4), pp.1103-1170.
4. Chaki, N.K. and Vijayamohanan, K., 2002. *Biosensors and Bioelectronics*, *17*(1), pp.1-12.
5. Liu, D., Luo, Q., Deng, F., Li, Z., Li, B. and Shen, Z., 2017. *Analytica Chimica Acta*, *971*, pp.26-32.

MHAtriCell activity overview 2017

Dominic's poster ISHAS, 2017

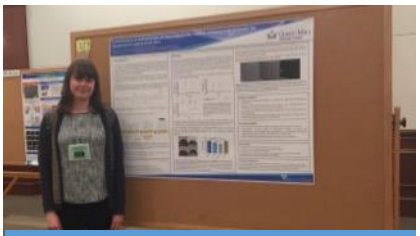


Inspiring Young Scientists, QMUL, 2017



Group at London Polymer, 2017

Elham TERMIS social run, 2017



Clare and her poster at ISHAS, 2017

SEMS Tag Rugby Team

Presentations at national and international conferences/meetings

11th International Conference on Hyaluronan, Cleveland, OH, USA, 11th – 15th June 2017

- **Poster Presentation**: Synthetic mimics of hyaluronan: toward a new generation of HA-based biomaterials with enhanced performance – Dominic Collis
- **Poster Presentation:** Supramolecular presentation of hyaluronan onto model surfaces for studying the behaviour of cancer stem cells - Clare O'Malley*/ Dominic Collis

TERMIS-EU 2017, Davos, Switzerland, 26th – 30th June 2017

- **Oral Presentation:** Multi-functional self-assembling hydrogels as biomimetic scaffolds for protein delivery and stem cell culture - Elham Radvar**/Joao Conde

Clare receiving her Travel Award at ISHAS

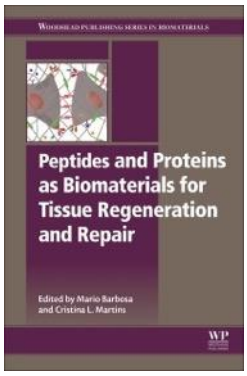
*International Society for Hyaluronan Sciences (ISHAS) Travel Award ($1500)

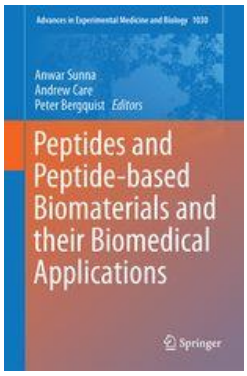
**Queen Mary Unversity of London Postgraduate Research Fund (QMPGRF) (£1000)

Our Science on display

The School of Engineering and Materials Science (SEMS) at Queen Mary has been exhibiting images produced by the students and staff on their research work. Three of the group (Left to right: Kseniya, Dominic and two of Elham's)

Recent and upcoming publications





- S. C. Ribeiro, E. Radvar, Y. Shi, J. Borges, R. P. Pirraco, I. B. Leonor, J. F. Mano, R. L. Reis, A. Mata, H. S. Azevedo, "Nanostructured Interfacial Self-assembled Peptide-polymer Membranes for Enhanced Mineralization and Cell Adhesion", Nanoscale, (2017) DOI: 10.1039/C7NR03410E.
- J. Banerjee, H. S. Azevedo, "Crafting of Functional Biomaterials by Directed Molecular Self-Assembly of Triple Helical Peptide Building Blocks", Interface Focus, (2017).
- Y. Shi, Y. Hub, G. Ochbaum, R. Lin, R. Bitton, H. Cui, H. S. Azevedo, "Enzymatic Activation of Cell-penetrating Peptides in Self-assembled Nanostructures Triggers Fibre-to-Micelle Morphological Transition", Chem Comm, 53, (2017), 7037-7040. DOI: 10.1039/C6CC10046E
- K. Shuturminska, N. V. Tarakina, H. S. Azevedo, A. J. Bushby, A. Mata, P. Anderson, M. Al-Jawad, "Elastin-like Protein, with Statherin Derived Peptide, Controls Fluorapatite Formation and Morphology", Frontiers in Physiology, (2017). DOI: 10.3389/fphys.2017.00368
- A. Mata, H. S. Azevedo, L. Botto, N. Gavara, L. Su, "New Bioengineering Breakthroughs and Enabling Tools in Regenerative Medicine", Current Stem Cell Reports, 3 (2) (2017), 83–97. DOI: 10.1007/s40778-017-0081-9
- Y. Shi, J. Conde, H. S. Azevedo, "Empowering the potential of cell-penetrating peptides for targeted intracellular delivery via molecular self-assembly", in Peptides and Peptide-based Biomaterials and their Biomedical Applications (ISBN 978-3-319-66094-3), Eds. A. Sunna, A. Care, P. Bergquist, Advances in Experimental Medicine and Biology 1030, DOI 10.1007/978-3-319-66095-0_12, Springer International Publishing AG, (2017).
- J. Banerjee, E. Radvar, H. S. Azevedo, Self-assembled peptides for tissue regeneration and repair, in Peptides and Proteins as Biomaterials for Tissue Regeneration and Repair (ISBN: 9780081008034), Eds. M. A. Barbosa, C. L. Martins, Elsevier Woodhead, (2017).
- A. Mata, H. S. Azevedo, J. Connelly, J. Gautrot, Bioengineering complexity and tuneability in hydrogels, in Hydrogels: Design, Synthesis & Application in Drug Delivery & Regenerative Medicine (ISBN 9781498748612), Eds. T. R. R. Singh, G. Laverty, R. Donnelly, CRC Press, (2017), 298-319.
- H. S. Azevedo, Engineering hyaluronan (HA) hydrogels with bioactive and mechanical signals, in Hydrogels: Design, Synthesis & Application in Drug Delivery & Regenerative Medicine (ISBN 9781498748612), Eds. T. R. R. Singh, G. Laverty, R. Donnelly, CRC Press, (2017), 154-169.

Invited lectures:

Helena at TERMIS-EU 2017

- *10th May 2017* "Amino acids and sugars: natural building blocks to create innovative biomolecular materials", University of Strathclyde, Glasgow, UK.
- *20th June 2017* "One-step fabrication of biomaterials with inbuilt functionalities: combining macromolecules and rationally designed peptides through supramolecular approaches", Tissue Engineering and Additive Manufacturing (TEAM) Lab, Northwestern University, Chicago, USA.
- *29th June 2016* "Engineering macromolecular self-assembly of hyaluronan with peptides: from matrix design to biomedicine applications", European Chapter Meeting of the Tissue Engineering and Regenerative Medicine International Society 2017 (TERMIS-EU 2017), Davos, Switzerland.
- *30th June 2017* "Biomaterials inspired by biology: from molecules to self-assembly", EMPA, St Gallen, Switzerland.
- *10th July 2017* "Nanotechnologies for cancer therapies", CPD for science teachers, Barts Pathology Museum, London, UK.
- *14th July 2017* "Biomolecular materials for cell therapies", The Cell and Gene Therapy Catapult, Guy's Hospital, London, UK.

Project Students

Master Student

Jenny Zeng, MSc Regenerative Medicine, QMUL

Novel aromatic peptide building blocks for self-assembly with hyaluronic acid: from peptide design to biomaterials characterisation. April – August 2017.

Conferences

International events

- The 28th Annual Conference of the European Society for Biomaterials, 4 – 8th Sep 2017, Athens, Greece Link
- 12th Australian Peptide Conference, 15 - 20th Oct 2017, Peppers Noosba Resort, Australia Link
- 16th Iberian Peptide Meeting - 4th ChemBio Group Meeting, 5-7th Feb 2018, Barcelona, Spain, Link
- 35th European Peptide Symposium, August 26th – 31st, 2018, Dublin City University, Ireland. Link
- The 29th Annual Conference of the European Society for Biomaterials, 8 – 13th Sep 2018, Maastricht, The Netherlands

UK events

- Protein and Peptide Subject Group Early Stage Researcher Meeting, 14th Sep 2017, Durham University. Link
- 12th Annual Chemistry and Biology of Peptides Meeting, 15th Sep 2017, Durham University. Link
- 5th Annual Peptides Congress, 16 – 17th April 2018, London. Link
- IMAP 2018, the 8th International Meeting on Antimicrobial Peptides, Sep 2 – 4th, 2018, Edinburgh. Link

Acknowledgements

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Contacts

MHAtriCell Group
School of Engineering & Materials Science
Queen Mary University of London
Mile End Road, London E1 4NS, UK
Helena Azevedo: h.azevedo@qmul.ac.uk
Elham Radvar: e.radvar@qmul.ac.uk
Dominic William Peter Collis: d.w.p.collis@qmul.ac.uk

Left to Right: Dominic Collis, Elham Radvar, Clare O'Malley, Dr Helena S. Azevedo, Kseniya Shuturminska, Yejiao Shi, Dr Jayati Banerjee and Dr Joao Conde.