The Final Technical Report (DE-FG02-07ER45935), Office of Basic Energy Sciences, Materials Sciences and Engineering Division, Program Manager: Michael A. Markowitz

"Programmed Nanomaterial Assemblies in Large Scales: Applications of Synthetic and Genetically-Engineered Peptides to Bridge Nano-Assemblies and Macro-Assemblies"

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I-(i) Large-scale & reconfigurable 3D structures of precise nanoparticle assemblies in self-assembled collagen peptide grids

The ability to control self-assembly of complex 3D architectures from functional building blocks could allow further development of complex device configurations. Here our goal is to develop peptide-based assembly technology enabling the precise 3D superlattice assembly of Au nanoparticles in defined 3D shapes in large scale (from μm^3 to mm^3), higher yield, and higher reproducibility. In this work, nanoscale peptides and

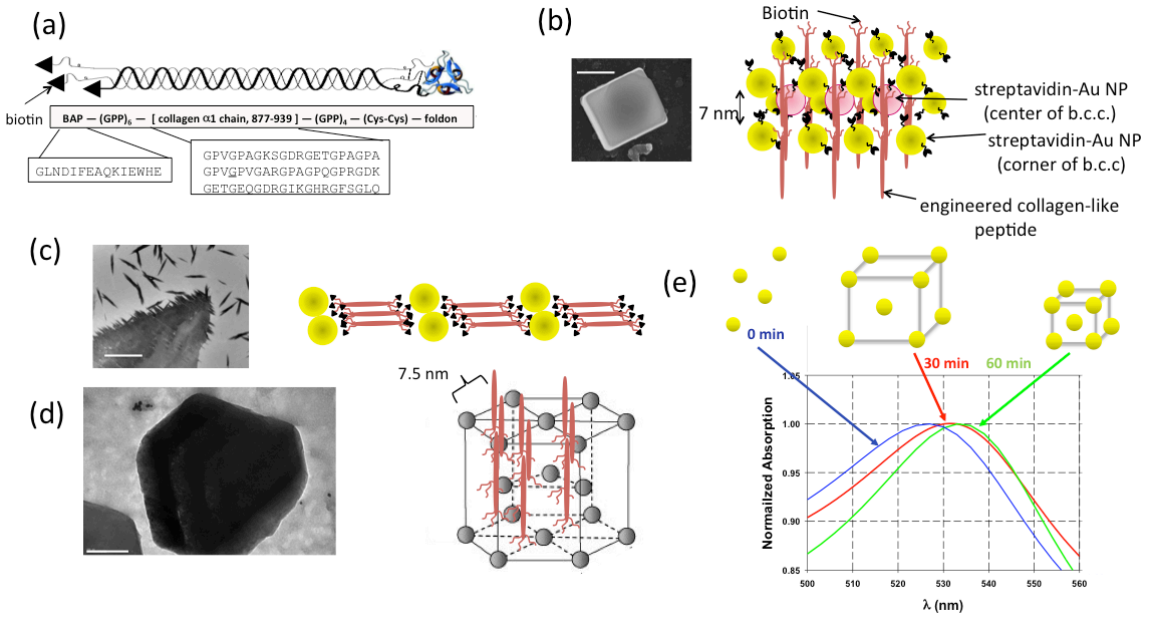

Figure 1. (a) Illustrated structure and sequence of the genetically-engineered triple helix peptide. Biotin is displayed at N-terminus to bind streptavidin-functionalized NP joints. (b) The 3D superlattice structure of the biotinylated triple helix peptides and streptavidin-functionalized Au NPs (ϕ = 10 nm) assembled by the streptavidin-biotin interaction and lateral peptide-peptide association through the collagen motif. The interparticle distance is 7 nm (edge-to-edge). (left) SEM image of the 3D superlattice. Scale bar = 2 μm. (c) Reconfiguration of (b) as the conformation change of peptide is triggered by pH change (pH = 4). Scale bar = 2 μm. (d) Reconfiguration of (b) as the conformation change of peptide is triggered by NP size change (ϕ = 30 nm). Scale bar = 600 nm. (e) Reconfiguration of NP alignment in (b) with assembly time monitored by UV/Vis absorption spectra. The interparticle distance of Au NPs agrees with the simulated absorption peak position of Au NP assembly. [P. Kaur, Y. Maeda, A.C. Mutter, T. Matsunaga, Y. Xu, H. Matsui, *Angew. Chem. Intl. Ed.,* **49**, 8375, (2010)]

ligand-functionalized Au nanoparticle joints were self-assembled into micron scale 3D cube-shaped crystals, creating a physical framework for the proposed biomimetic assembly strategy.[1] In this approach we took advantage of the naturally robust assembly of collagen-like triple helix peptides and used them as nanowire building blocks for the 3D crystal generation. Using streptavidin-functionalized Au nanoparticles and the α1 chain of type I wild type collagen specifically modified with a biotin moiety *in vivo* (Figure 1-a), we created micro-sized 3D superlattice cubes with peptide nanowires as grids and Au NPs as joints (Figures 1-b, left). SAXS spectra indicate that Au NPs are arranged in b.c.c structure in the collagen peptide frameworks. High resolution TEM image of the assembly of stained collagen-like peptide resolves the stripe pattern with the gap of 20 nm (data not shown), indicating that each peptide is staggered with the 20 nm displacement to assemble the peptide framework as shown in Figure 1-b (right). The similar pattern was observed in wild-type collagen and other low molecular-weight triple helix peptide assemblies.[2,3] This gap size is consistent with the interparticle distance of Au NPs observed in SAXS spectra. The reconfiguration of the 3D directed assembly was observed by lowering pH (<4.0) and the dynamic conformational transformation of peptide with pH triggers the disassembly of the hybrid NP-peptide cube, following the reassembly of reconfigured peptides into different shapes such as rod and rhombus after several days (Figure 1-c). The conformation change of peptide could also be induced by changing the size of Au NPs, resulting in the transformation of superlattice structure to close-packed hexagonal poles (Figure 1-d). The evolution for dynamic reconfigurability was also observed by absorption peak shifts. One the basis of the comparison between the spectral simulation and the red shift of Au NP absorption peak in Figure 1-e, the aggregation of Au NPs in the peptide frameworks starts at 30 minutes and the inter-particle distance is shortened with assembly time. The assembly time of 1 hour yields the interparticle distance of 11 nm (edge-to-edge distance), and at 2 hours of assembly time the interparticle distance becomes 7 nm (edge-to-edge distance). After 3 hours some superlattices further pack Au NPs closer while the monodispersity of structure is also lost at this point.

I-(ii) Binary QD-Au NP 3D superlattices assembled with collagen-like peptides and energy transfer between QD and Au NP in 3D peptide frameworks

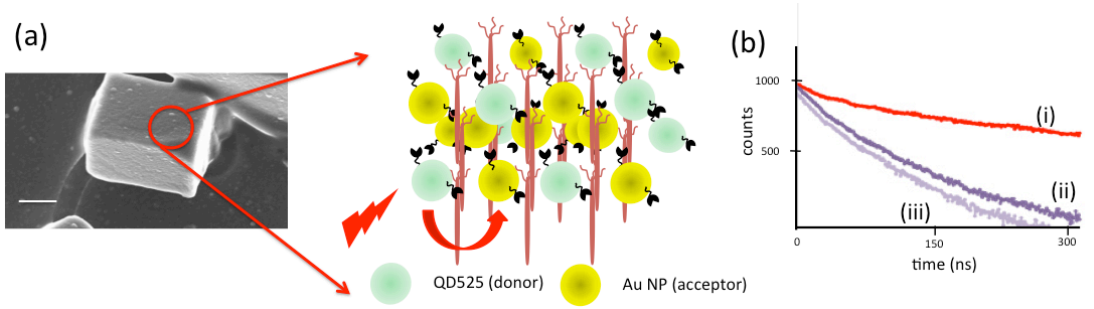

Figure 2. (a) (left) SEM image of binary QD-Au NP superlattices in 3D peptide frameworks. (right) Scheme of energy transfer between QD (donor) and AU NP (acceptor). Scale bar = 1 μm. (b) Fluorescence lifetime measurements (excitation at 525 nm) of (i) random aggregations of QDs and Au NPs, (ii) QD-Au NP superlattices after 25 min of assembly with the peptide, (iii) QD-Au NP superlattices after 60 min of assembly with the peptide. [K. Fabijanic, H. Krishnamoorthy, V. Menon, H. Matsui (2013)]

Recently, in collaboration with Vinod Menon (CUNY-Queens College), we studied the energy transfer between donor and acceptor NPs assembled in the 3D peptide framework by analyzing the emission lifetime of donor. When CdSe QDs and Au NPs in a diameter of 10 nm, both functionalized by streptavidin, were co-assembled with the biotinylated collagen-like peptide, 3D cubic superlattices were formed (Figure 2-a) in the similar condition that Au NP-peptide superlattices were assembled in Sec. II-(i). As shown in Figure 2-b, when Au NPs and QDs were assembled in the ordered 3D superstructure with the peptide framework, fluorescence (FL) lifetime was quenched significantly as compared to the random aggregation of QDs and Au NPs (4.7 ns -> 2.7 ns). This comparison indicates that the energy transfer from CdSe QD (donor) to Au NP (acceptor) becomes very efficient when they are assembled into ordered 3D superlattices. The interparticle distance becomes shorter as the assembly time becomes longer (Figure 4-e), and thus it is consistent that the FL lifetime becomes shorter (2.0 ns) as the assembly time is extended to 60 min. This observation supports the hypothesis that the peptide superlattice is applicable as a framework to assemble multiple QDs within the distance of electronic coupling and the 3D superlattices with various interparticle distances can be extracted at different assembly time. Therefore, this assembly methodology serves as a powerful toolbox for the future photovoltaic device fabrication.

I-(iii) Catalytic peptides discovered by new hydrogel-based combinatorial phage display approach and their enzyme-mimicking 2D assembly

Efficient catalysis in water is a fundamental molecular process of all living systems that may be exploited in green chemistry, biotechnology and medicine. The *de novo* design and discovery of molecular catalysts mimicking enzyme has been a longstanding challenge. One of specific aims in our previous DOE proposal is to find catalytic peptides that can grow semiconductor spacers between 3D QD superlattices in the peptide framework at room temperature for the effective QD-based solar cell fabrication. Since there is no combinatory approach to build the library of catalytic peptides for material growth and chemical reactions, we decided to build one for this specific aim. Herein, we describe a new methodology that enables the selection of catalytic oligopeptides from sequence libraries based on their catalytic turnover (Figure 3).[4] This approach is accomplished by *catalytic gelation*: by exposing vast peptide libraries, obtained through phage display, to precursors that catalytically convert to powerful gelators of reactants. When the phage display library is exposed to these precursors, phages that present catalytic sequences facilitate amide condensation and consequent localized gelation on

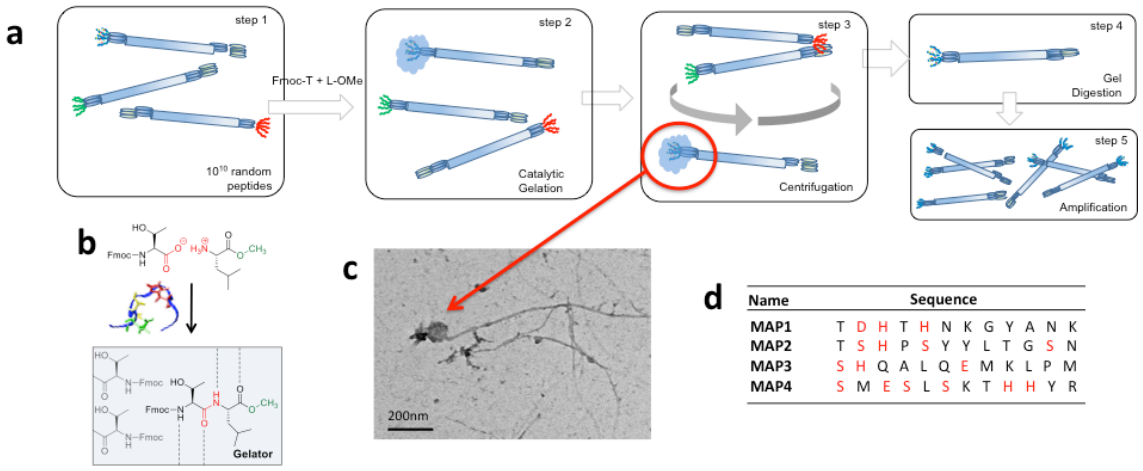

Figure 3. Gelation-driven discovery process of phage particles displaying catalytic peptides. (a) The phage *sequence library* covers a vast (10^9) peptide sequence space (step 1). Once the soluble precursors, Fmoc-T and L-OMe, are added, *catalytic gelation* of the amide condensation product, Fmoc-TL-OMe, generates localized gel aggregates (step 2). The gelation facilitates separation of catalytic peptides from non-catalytic phage particles *via* centrifugation (step 3). *Gel digestion* by subtilisin, which hydrolyses the terminal methyl ester, is then performed on the catalytic peptides (step 4). Finally, the catalytic peptides undergo a process of *amplification* in *E. coli* host and decoding to reveal the peptide sequences (step 5). (B) Catalytic condensation of amino acid derivatives to form gelators locally assembled on phages. (C) TEM image showing a globular nucleus of the product gel associated with the tip of the phage filament in the early stage of gelation. (d) The sequences of catalytic peptide for protease activity (MAP) identified with possible catalytic residues highlighted. [Z. Wei, Y. Maeda, H. Matsui, *Angew. Chem. Intl. Ed.,* ***50,*** 10585 (2011), Y. Maeda, L. Birchall, D. Cannon, T. Tuttle, R.V. Ulijn, H. Matsui, (2013)]

the phages (Figure 3-c). This panning process yields a number of peptides that mimic protease and they are able to generate amide bonds (Figure 3-d). The isolated peptides can also spontaneously access conformations that conceivably facilitate charge-relay between amino acids, similar to the catalytic mechanisms evolved by certain hydrolase enzymes but with minimal complexity. We believe that the methodology described here adds a dynamic element to the toolbox already available for the design of future bioinspired technologies and design of artificial life. These minimal catalytic peptides may support one of various original pathways in the evolution of more active, more specialized enzymes and the discovery of such precursors to enzymes may hold important information to our understanding of the origins of life.

While selected catalytic peptides in the library are very specific to the target reaction, the catalytic activity is 100 times lower as compared to enzymes, probably due to the lack of structured catalytic pocket. To increase the activity, we added a short amyloid peptide sequence to one of the catalytic peptides, SMESLSKTHHYR, to form artificial β-sheet catalytic pockets resembling enzymes (Figure 4-a). As the protease-like peptide was conjugated with the amyloid sequence of FFKLVFF,[5] the modified peptides were assembled into anti-parallel β-sheet and the catalytic activity of the peptide assembly was increased 100 % in ester hydrolysis as compared to the monomeric form (data not

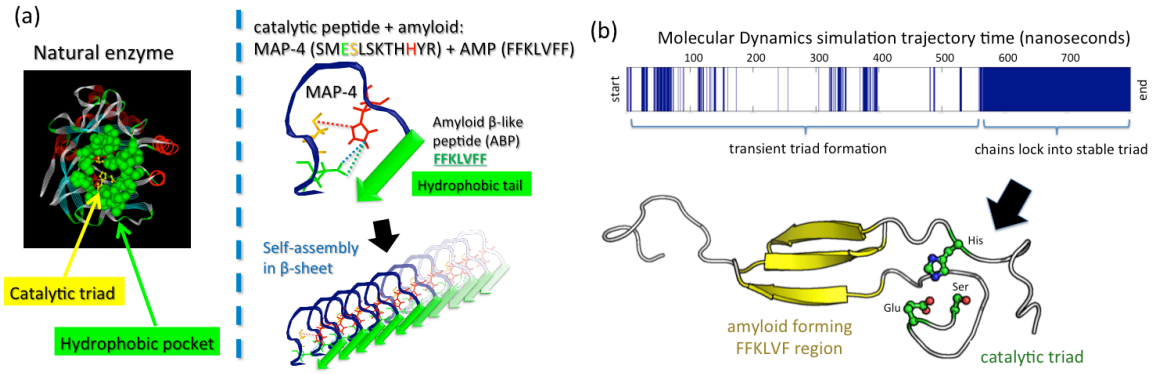

Figure 4. (a) Catalytic MAP-4 peptide in Figure 6-(d) is conjugated with the amyloid-like ABP peptide (right) to form the artificial catalytic pocket resembling enzyme (left). By assembling the MAP-4 peptides into the antiparallel β-sheet, the catalytic activity of MAP-4 increases 100 % as compared to the monomeric MAP-4 peptide in ester hydrolysis (data not shown). (b) The dynamic molecular modeling shows that the antiparallel β-sheet assembly of the MAP-4 peptide (bottom) aids forming the catalytic triad more frequent as compare to the monomeric MAP-4, and then this triad conformation stays locked after 500 ns in the simulation (top). The stable triad formation in the MAP-4 β-sheet assembly is consistent with the observed higher catalytic activity. [Krysmann, M. J.; Castelletto, V.; Hamley, I.W., *Soft Matter*, ***3***, 1401 (2007), Y. Maeda, Y. Ikezoe, D. Pike, V. Nanda, H. Matsui, (2013)]

shown). In collaboration with Vikas Nanda (Rutgers/*UMDNJ*), the molecular dynamic simulation reveals the origin of the high catalytic activity; When the local interaction of peptide was optimized by *AMBER molecular dynamics simulation package* and the unit cell geometry of anti-parallel β-sheet assembly was optimized by *protCAD,* the modeling showed that the triads were folded into the catalytic configuration within a few hundred nanoseconds, and subsequently stayed locked in this highly active configuration (Figure 4-b) – consistent with the experimental studies.

Another application of this phage display library is to discover enzyme-mimicking peptides that can catalyze room-temperature growth of oxide semiconductors.[4] Biomimetic material growth is a potential path to break through room-temperature inorganic nanocrystal synthesis because biocatalytic function of peptides exhibits high growth efficiency of materials in accurate structures at low temperature. Recently, several promising peptides and proteins were demonstrated to catalyze the growth of semiconductors.[6-8] However, a successful discovery of the catalytic peptide sequences is strongly dependent on trial-and-error processes because the panning process is based on the binding affinity, not the catalytic activity.[9] Thus, the development of the systematic methodology with combinatorial selection is desirable for future materials science. Our combinatorial phage display library approach directly screens peptides that catalyze the target material growth. The unique feature of this technique is the panning process of peptides; Precursors are carefully chosen so that the only nanocrystal grown on the phage is the target product *via* catalytic reactions. Our methodology provides a simple and convenient route to discover biomineralizing peptides for ZnO nanocrystal growth at room temperature and one of these peptides induces non-classical crystallization process conventional ZnO synthetic methods cannot match at room temperature.[4] The broad impact is highly expected from this outcome because this novel combinatorial screening technology can be applied to discover a wide range of catalyses for room-temperature material growth.

The report for the new phage display library methodology and the discovery of catalytic peptide for oxide semiconductor growth was published in *Angewandte Chem. Intl. Ed.* (50, 10585-10588 (2011)), and this paper was selected as a highlight paper in

2011. The report for the protease-mimicking peptides is currently under review in *Nature Chemistry*.

I-(iv) New autonomous motors of metal-organic frameworks (MOFs) powered by reorganization of self-assembled peptides at interfaces

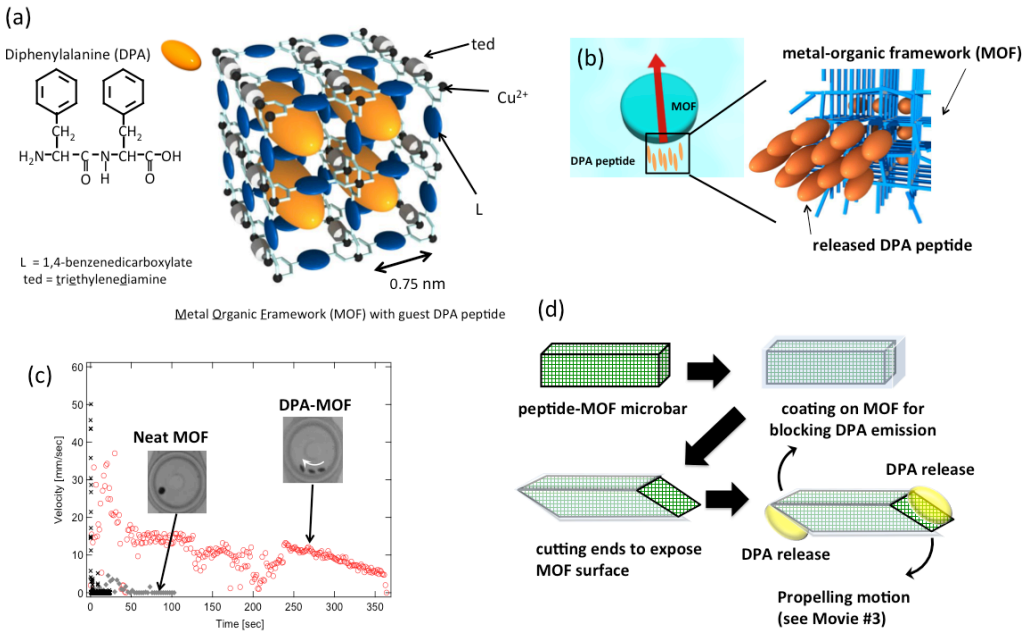

Figure 5. (a) Chemical structures of DPA peptide and MOFs. (b) Mechanism of DPA-MOF motion: after releasing DPA peptides from the MOF, the re- assembly of DPA peptides creates a hydrophobic domain at the end of the MOF particle. Because this domain lowers the surface tension of the MOF on the released side, the MOF particle moves in the direction of the red arrow as a result of the surface tension gradient with no energy input. (c) While the MOF does not move in aqueous solution (grey), when the DPA peptides are incorporated in the MOF it can sustain the swimming motion for longer than 6 min as the released peptides are re-assembled at the interface (red). (also see Movies #1 and #2) (d) Design of a bar-shaped peptide-MOF motor system to generate propelling motion. (See Movie #3) [Y. Ikezoe, G. Washino, T. Uemura, S. Kitagawa, H. Matsui, *Nature Mater.*, **11**, 1081-1085 (2012)]

In collaboration with Takashi Uemura and Susumu Kitagawa in Kyoto University, we developed a new bioinspired autonomous motor system, metal-organic framework (MOF) encapsulating diphenylalanine (DPA) peptides in its MOF pores (Figure 5-a).[10] The MOF, comprised of metal ions and bridging organic ligands, has recently emerged as an important family of nanoscale porous materials because of their unique structural and functional properties.[11] In this system, release of the stored peptides from the MOF and their subsequent reconfiguration into hydrophobic assemblies at the interface creates a non-equilibrium condition by generating a large surface tension gradient, the driving force of the autonomous motion. MOF is a perfect peptide storage for the motor because of its capability to assemble molecules in the highly ordered pore array of the coordination framework and release guest molecules in a isotropic direction *via* bond-

breaking of the framework. The robust self-assembling nature of peptide is also appropriate as a guest molecule to power the MOF motor because the released peptides from the MOF are re-self-assembled at the MOF-water interface in the highly ordered structure. The release of peptides triggered by partial destruction of the outer MOF surface robustly induces reorganization of peptides at the MOF-liquid interface (Figure 5-b). The chemical energy generated by this process propels the MOF to swim like bacteria towards the higher surface tension side of the gradient. In nature, biological motors convert chemical free energy to mechanical power directly by creating isothermal and non-equilibrium conditions through biochemical reactions such as the metabolism of chemicals by cells to produce products that are simultaneously exploited as energy resources. The manner for the creation of MOF motion by generating the non-equilibrium condition *via* the peptide reconfiguration inside and outside the MOF resembles the metabolization and production of resources in cells. The velocity of the DPA-MOF particle normalized by volume is 30 times faster than the one for previous chemical motor systems (Figure 5-c).[12] When this MOF motor was incorporated into a macroscopic boat where the MOF particles fit inside the boat compartment with a very narrow slit at the tail, the boat was powered to sail into the controlled direction. This type of technology could be applied to develop miniaturized robotic systems (micro-bots) that could sense target chemicals, move toward their location, and then store them inside the porous frameworks. The outcome of this work may also shed light on the fundamental mechanisms of biological motors and chemotaxis in natural systems.

The windmill motion of the peptide-MOF superlattice was also demonstrated by limiting the peptide release at the ends of bar-shaped superlattice in the opposite direction *via* masking the MOF in between (Figure 5-d). To control the propellant motion, first the entire surface of superlattice was masked by paraffin and then both ends of the bar were cut 45° angle to expose MOF surfaces to the liquid interface where DPA peptides could be released in the directions of arrows in Figure 5-d (bottom right). By this design, the bar-shaped superlattice rotated in the stable motion.

This result was published in *Nature Materials (***11**, 1081-1085 (2012)*)* and this article was also featured in the News section of Royal Society of Chemistry (RSC) (Chemistry World) in 2012.

I-(v) Biomimetic assembly of proteins into microcapsules on oil-in-water droplets with structural reinforcement via biomolecular recognition-based cross-linking of surface peptides

In nature, many bacteria are capped by monolayer of self-assembled S-layer proteins to enhance mechanical stabilization of membranes, protection against viruses, and resistance against pH changes.[13] Protein assembly on oil/water interfaces has been used to generate a variety of functional microcapsules and artificial cellular structures.[14] In this work, we mimic the S-layer proteins to reinforce the molecular interface by capping with proteins *via* molecular recognition to accomplish high mechanical stability of the assembled artificial cellular structures. Our strategy is to assemble B877B peptides, which display biotin on both N- and C-terminus of F877 collagen-like sequence (Figure 4-a), into microcapsules on the oil-in-water droplets, and resulting protein microcapsules are stabilized by capping and cross-linking the ends of peptide surfaces with streptavidin *via* biomolecular recognition (Figure 6-a).[15] This biomolecular reinforcement allows these microcapsules to maintain their structure in extreme environment conditions such as high/low pH and high temperature (Figure 6-b). Furthermore the as-prepared protein microcapsules are shown to be versatile scaffolds such as robust QD conjugation. This methodology will be useful for the development of a variety of hierarchical protein microcapsules displaying desired biological functions for various biotechnological applications.

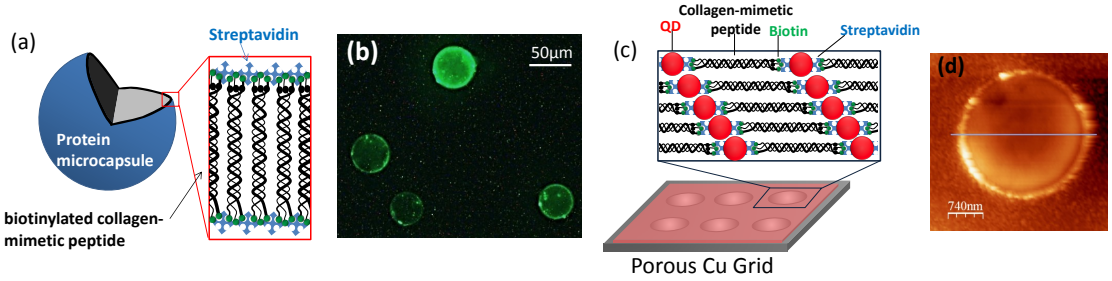

Figure 6. (a) Structure of hybrid microcapsules assembled on octane/water interface from streptavidin and collagen-like triple helical B877B peptide with the site-specific biotinylation at N- and C-terminus. (b) Fluorescence micrograph of the protein microcapsules composed of B877B peptide and Cy2-labeled streptavidin. This structure can be maintained in broad ranges of pH (2.2 – 11.5) and temperature (20 – 80 °C). (data not shown) (c) Schematic representation of the formation of peptide-QD freestanding films. QD joints reinforce the peptide films, mimicking the structure of bone tissue. (d) AFM image of the freestanding peptide-QD film formed on a pore of Cu grid. [Y. Maeda, Z. Wei, H. Matsui, *Small*, **8**, 1341-1344 (2012), Z. Wei, Y. Maeda, H. Matsui, *Soft Matter*, **8**, 6871-6875 (2012)]

I-vi) Biomimetic fabrication of strong freestanding genetically-engineered collagen peptide films reinforced by quantum dot joints

Biomimetic assembly is an emerging technique to design novel approaches for the nanocomposite processing. An intriguing example of such strong and elastic biomaterials in nature is bone tissue consisting of collagens and hydroxyapatite particles. The bone tissue is ten to twenty times stiffer than collagen molecules while its fracture strain is much larger than the mineral crystals.[16] This excellent combination of mechanical properties is due to the building block of the collagens that can dispatch stress to the inorganic nanocrystals through complicated molecular deformation and intermolecular shear.[17] If biological molecules are assembled into freestanding films with synthetic inorganic particles as joints by mimicking the bone tissue structure, the resulting films may have superior mechanical property. In this work, we demonstrated that this biomimetic approach could produce freestanding films from the B877B triple helix peptides and the streptavidin-functionalized quantum dots (QDs) (Figure 6-c).[18] While casting only the collagen peptides on a porous substrate does not produce any freestanding films, co-assembling the streptavidin-functionalized QDs and the biotinylated collagen-mimetic peptides *via* molecular recognition enables forming strong and elastic freestanding films across the pores (Figure 9-d). The Young's modulus of the peptide-QD freestanding films is ~20 GPa, much larger than most of polymer films and previously reported freestanding NP-sheets (< 10 GPa),[19,20] and it is even close to the bone tissue in nature.[21]

This result was published in *Soft Matter* (**8**, 6871-6875 (2012)) and highlighted as a hot paper in 2012.

In summary, through our previous DOE support, we gained the broad knowledge about biomimetic material assembly from nanoscale to microscale ranges by co-assembling peptides and NPs via biomolecular recognition. We discovered:

- Genetically-engineered collagen-like peptides can be self-assembled with Au NPs to generate 3D superlattices in large volumes (> μm^3).
- The assembly of the 3D peptide-Au NP superstructures is dynamic and the inter-particle distance changes with assembly time as the reconfiguration of structure is triggered by pH change;

- QDs/NPs can be assembled with the peptide frameworks to generate 3D superlattices and these QDs/NPs can be electronically coupled for the efficient energy transfer;
- The controlled assembly of catalytic peptides mimicking the catalytic pocket of enzymes can catalyze chemical reactions with high selectivity;
- For the bacteria-mimicking swimmer fabrication, peptide-MOF superlattices can power translational and propellant motions by the reconfiguration of peptide assembly at the MOF-liquid interface;

Scientific Recognition of Researches Supported by the DOE (DE-FG02-07ER45935) for last 3 years

1. Matsui was selected as a JSPS (Japan Society for the Promotion of Science) Fellow for 2011-2012.
2. Matsui was honored to be named as an invited professor at Kyoto University in 2012.
3. Matsui was selected to attend "Global Grand Challenge Summit" (National Academy of Engineering & Royal Society of Engineering) in London in 2013.
4. Our recent publication, "New Autonomous Motors of Metal-Organic Framework (MOF) Powered by Reorganization of Self-Assembled Peptides at interfaces", in *Nature Mater*. (**11,** 1081, (2012)) was highlighted by News & Views section of Nature Materials and the News section of Royal Society of Chemistry (Chemistry World).
5. Our recent publication, "3D Self-Assembly of Peptide Nanowires into Micron-Sized Crystalline Cubes with Nanoparticle Joints", in *Angew. Chem. Intl. Ed.* (**49,** 8375, (2010)) was chosen as a hot paper in 2010.
6. A publication, "Catalytic Peptides for Inorganic Nanocrystal Synthesis Discovered by New Combinatorial Phage Display Approach" in *Angew. Chem. Intl. Ed.*, (**50**, Advance article http://dx.doi.org/10.1002/anie.201102582, (2011)), was featured as a hot paper in 2011.
7. Matsui's works funded by the DOE were recognized and he was elected as a member of Japan-America Frontiers of Engineering (National Academy of Engineering and Engineering Academy of Japan.
8. A publication, "Catalytic Peptides for Inorganic Nanocrystal Synthesis Discovered by New Combinatorial Phage Display Approach" in *Angew. Chem. Intl. Ed.*, (**50**, 10585-10588, (2011)), was featured as a hot paper in 2011.
9. A publication, "Biomimetic Fabrication of Strong Freestanding Genetically-Engineered Collagen Peptide Films Reinforced by Quantum Dot Joints" in Soft Matter (**8**, 6871-6875 (2012)), was also highlighted as a hot article in 2012.

A list of papers published in peer-reviewed journals by the DOE support (DE-FG02-07ER45935) for last 3 years (19 articles)

1. "Negative differential resistance in ZnO coated peptide nanotube", D. Joung, L. Anjia, H,.Matsui, S.I. Khondaker, Appl. Phys. A, **339**, in print (published online: 10.1007/s00339-013-7737-9) (2013).

   Excerpt of acknowledgement: This work for the part of electronic fabrication and measurement was supported by the US National Science Foundation under grant ECCS 0823902 (HM) and 0823973 (SIK). This work for the material synthesis and the sample preparation of the measurements was

supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DEFG-02-01ER45935 (HM). The Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12-RR003037-245476).

2. "New Autonomous Motors of Metal-Organic Framework (MOF) Powered by Reorganization of Self-Assembled Peptides at interfaces", Y. Ikezoe, G. Washino, T. Uemura, S. Kitagawa, H. Matsui, Nature Mater., **11**, 1081-1085 (2012).
   Excerpt of acknowledgement: "All of works except chemical syntheses of MOFs were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG-02- 01ER45935. Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12-RR003037-245476). Chemical syntheses of MOFs in Kyoto were supported by Grant-in-Aid for Scientific Research on Innovative Area "Emergence in Chemistry" from MEXT. H.M. acknowledges Japan Society for the Promotion of Science (JSPS) for supporting his collaboration in Kyoto University through Invitation Fellowship Program for Research in Japan. H.M was in the position of an Invited Professor at Institute for Integrated Cell-Material Sciences (iCeMS) during his sabbatical term in Kyoto University. Y.I. and H.M. thanks Prof. Raymond Tu (City College of New York) for the use and assistance of Brewster Angle microscopy".
3. "Biomimetic assembly of proteins into microcapsules on oil-in-water droplets with structural reinforcement via biomolecular recognition-based cross-linking of surface peptides", Y. Maeda, Z. Wei, H. Matsui, Small, 8, 1341-1344 (2012).
   Excerpt of acknowledgement: "This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG-02-01ER45935. Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12- RR003037-245476). The authors thank Prof. Yujia Xu for the assistance in protein expression and purification, Dr. Cliff Soll for TOF-MS, and Dr. Jorge Morales for SEM observation. Y.M. thanks Japan Society for the Promotion of Science, and the International Training Program provided through Tokyo University of Agriculture and Technology".
4. "Genetically engineered protein nanowires: Unique features in site-specific functionalization and multi-dimensional self-assembly", Y. Maeda, H. Matsui, Soft Matter, 8, 7533-7544 (2012).
   Excerpt of acknowledgement: "This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG-02-01ER45935. Y.M. thanks Japan Society for the Promotion of Science, and the International Training Program provided through Tokyo University of Agriculture and Technology. Y.M. also thanks Dr. Yasuhiro Ikezoe and Kristina Ivana Fabijanic for scientific discussions regarding the topics.
5. "One-Pot Crystalline ZnO Nanorod Growth in Mineralizing Peptide Gels", L. Anjia, Z. Wei, H. Matsui, RSC Adv, 1, 5516-5519 (2012).
   Excerpt of acknowledgement: "This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG-02-01ER45935. Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12- RR003037-245476)."
6. "Biomimetic Fabrication of Strong Freestanding Genetically-Engineered Collagen Peptide Films Reinforced by Quantum Dot Joints", Z. Wei, Y. Maeda, H. Matsui, Soft Matter, 8, 6871-6875 (2012).
   Excerpt of acknowledgement: "This work was supported the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG-02-01ER45935. Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12- RR003037-245476). Z.W. and Y.M. thank Prof. Yujia Xu for the assistance in protein expression and purification. Y. M. thanks the International Training Program provided through Tokyo University of Agriculture and Technology (TUAT) and Japan Society for the Promotion of Science (JSPS)."
7. "Effects of Divalent Metals on Nanoscopic Fiber Formation and Small Molecule

Recognition of Helical Proteins", S.K. Gunasekar, L. Anjia, H. Matsui, J.K. Montclare, Adv. Func. Mater. 22, 2154-2159 (2012).

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8. "Catalytic Peptides for Inorganic Nanocrystal Synthesis Discovered by New Combinatorial Phage Display Approach", Z. Wei, Y. Maeda, H. Matsui, *Angew. Chem. Intl. Ed.*, **50**, 10585-10588, (2011). (selected as a hot paper in 2011)

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Patent

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