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14. ABSTRACT
The goal of this project was to use DNA and protein as templates to assemble nanoparticles and functional molecules for photonic and electronic applications such as plasmon-enhanced fluorescence and surface-enhanced Raman scattering (SERS) (Fig. 1). Towards this goal, we have utilized both genetic and materials engineering tools. We have followed the molecular biomimetic approach in the assembly of nanoparticles. We have developed protocols using involving biological attachment of nanoparticles and quantum dots onto engineered surface-binding polypeptides (GEPI), and have used directed assembly of nanoparticles and/or functional molecular units.

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Bio-inspired Organic/Inorganic Hybrid Electronic and Photonic Materials and Structures

Final Performance Report: 10/1/2006 – 9/30/2007

Agreement Number: FA9550-05-1-0063

1

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Status of Effort:

The goal of this project was to use DNA and protein as templates to assemble nanoparticles and functional molecules for photonic and electronic applications such as plasmon-enhanced fluorescence and surface-enhanced Raman scattering (SERS) (Fig. 1). Towards this goal, we have utilized both genetic and materials engineering tools. We have followed the molecular biomimetic approach in the assembly of nanoparticles. We have developed protocols using involving biological attachment of nanoparticles and quantum dots onto engineered surface-binding polypeptides (GEPI), and have used directed assembly of nanoparticles and/or functional molecular units. We have used GEPIs as molecular erector sets to assemble fluorescent quantum dots with different distances and configurations on metal surfaces. Detailed accomplishments are listed below.

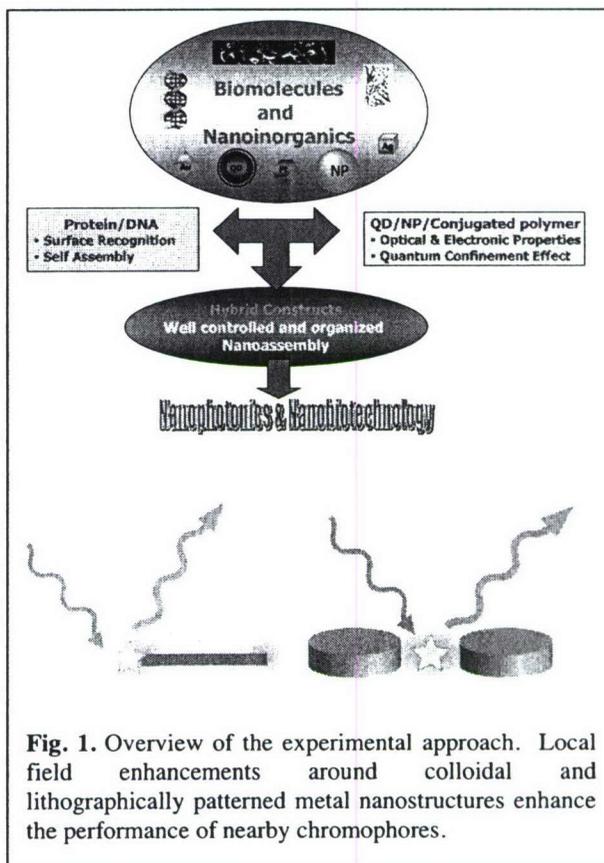
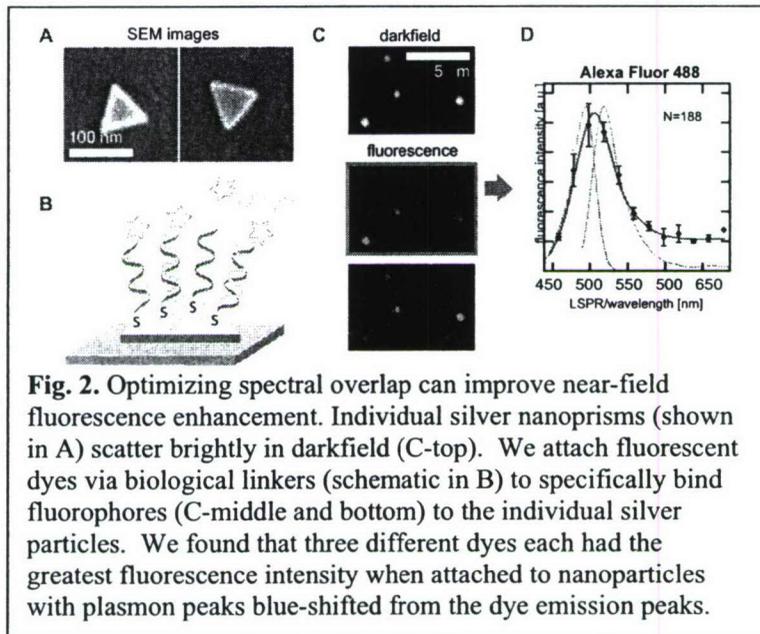


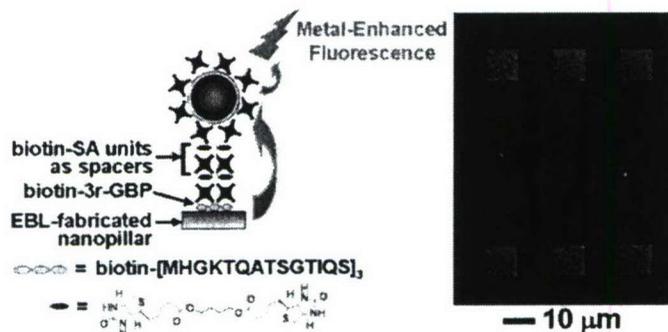
Fig. 1. Overview of the experimental approach. Local field enhancements around colloidal and lithographically patterned metal nanostructures enhance the performance of nearby chromophores.

Accomplishments/New Findings:

- 1) We demonstrated the attachment of fluorescent chromophores to metal nanostructures prepared by both bottom-up colloidal synthesis and top-down lithography. Proteins, peptides, DNA, and functionalized organic small molecules were demonstrated as bifunctional linkers for mediating the metal-dye distances, as described the published manuscripts.
- 2) We demonstrated that the hybrid chromophore-metal nanostructures could exhibit a range of unique photonic activity, including: Up to ~8-fold enhancement of fluorescence intensity due to near-field antenna effects on the excitation and emission of the molecules, as described in the published manuscripts (Fig. 2).
- 3) We have developed a protein-enabled strategy to fabricate tunable QD arrays where up to 15-fold increase in surface-plasmon-enhanced photoluminescence has been achieved. This approach permits a comprehensive control both laterally (via lithographically defined gold nanoarrays) and vertically (via QD-metal distance) of the collectively behaving QD-NP assemblies by way of biomolecular recognition. Specifically, we demonstrated the spectral tuning of plasmon resonant metal nanoarrays and the self-assembly of protein-functionalized QDs in a step-wise fashion with a concomitant incremental increase in separation from the metal surface through biotin-streptavidin spacer units (Fig. 3, 4)



Biomolecule-mediated fabrication of tunable QD arrays (Fig. 3)



Complementary to DNA-based systems for plasmonic applications, we demonstrate here a protein-based method to construct tunable QD nanoarrays with surface-plasmon-enhanced photoluminescence. In view of optimizing the fluorescence enhancement, there are several key features that make our approach potentially suitable for investigating resonance phenomena in hybrid nanostructures. One advantage is the capability to independently tailor fluorophores (via colloidal synthesis of QDs), plasmonic template (via lithographic patterning) as well as the emitter-metal distance (via step-wise self-assembly). This opens up different combinations of ways to create optimally integrated systems for a target application. Another advantage is the possibility to engineer hybrid nanoassemblies such

that the QDs are sandwiched in the local EM fields of bottom nanopatterned metal support and top metal nanoparticle by using the template-directed self-assembly scheme described above. Finally, the unique benefit of genetically engineered polypeptides such as bio-3RGBP1 is their biomolecular recognition for an inorganic compound – potentially specific in terms of its elemental composition, crystallographic orientation and morphology. Using side-by-side gold and platinum patterns on SiO₂/Si substrate, we have demonstrated previously the specific adsorption of bio-3RGBP1 onto just gold regions and not onto platinum nor SiO₂/Si regions. This suggests the prospect of potentially using multiple genetically engineered polypeptides (for example, gold-, silver- and platinum-binding peptides) to selectively anchor multiple emitters (for example, red-, green- and blue-emitting QDs) onto plasmonic architectures in a nanoscale proximity to realize simultaneous resonance phenomena – a subject of future projects. A synergetic combination of inorganic nanostructures, peptide-mediated assembly, and lithographic patterning should enable the precise control necessary to produce highly integrated multifunctional hybrid nanoassemblies for a diverse range of nanobiotechnological applications.

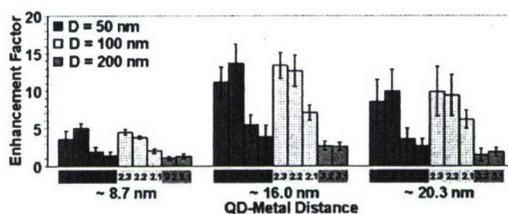
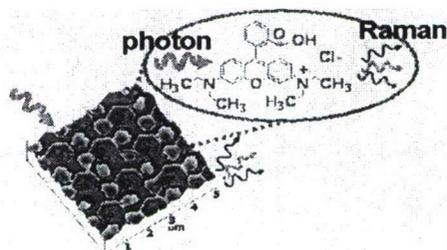


Fig. 4. Enhancement factors of the QD nanoarrays. To ensure a reliable normalization, the distance-effect was taken into account; QDs are attached onto either gold nanopillars or planar gold substrates using the same linkers and their PL intensities were measured. Enhancement factors were calculated by dividing the PL intensity from QDs in a particular pattern by that from QDs in an unpatterned area.

4) A simple, inexpensive, parallel approach has been developed for scalable large-area fabrication of 2-D periodic arrays of plasmon resonant structures. This method allows engineering of plasmon modes through precise tailoring of the structural parameters of metal nanostructures for reproducible Raman enhancement. Significant increase in the Raman scattering activity of chromophores attached to new nanostructured substrates have been observed (Fig. 5, 6).



We have developed an inherently parallel nanofabrication technique that is simple, inexpensive, compatible with a variety of materials, and easily scalable for large-area formation of 2-D

periodic arrays of plasmon resonant structures by combining the strengths of both NSL and GLAD. Specifically, our approach benefits simultaneously from the ability of GLAD to manipulate the morphology of thin films into desired spatial forms on 10-nm scale as well as the attributes of NSL such as generation of ordered arrays, nanoscale resolution, and flexibility to control the nanoparticle size, shape and interparticle spacings. By carefully planning the fabrication process, regular arrays of composite binary patterns and 3-D multi-component surface structures have been successfully achieved, which are difficult – if not impossible – to be achieved by conventional techniques based on electron beam lithography, etching and lift-off. With a view on near-field applications, we have demonstrated the use of our technique to produce a novel class of SERS-substrates in which the plasmon modes can be engineered to give reproducible Raman enhancements. Unique topographic characteristics of plasmon resonant structure with void-like geometries, in particular honeycomb structures, support trapped surface plasmons that can couple strongly to incident light and produce large Raman enhancements. Engineering of plasmon modes through precise tailoring of the structural parameters of metal nanostructures is likely to impact the progress in the fields of surface-enhanced spectroscopy, metal-enhanced fluorescence, and plasmonic devices.

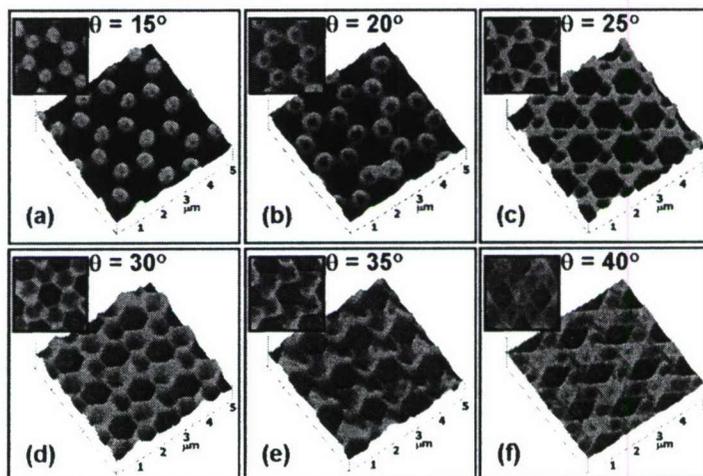


Fig. 6. Evolution of pattern formation in the deposited structures when the sample is tilted at a fixed angle ($\theta \neq 0$) with respect to the propagation vector of metal vapor flux and rotated simultaneously. AFM images depict how the mask geometry (i.e., shape, size, and spacing) at six representative θ values determine the morphology of resulting structures. For all structures, 100 nm of gold is deposited through a monolayer of 1.5- μm -diameter silica beads on Si substrate while the sample is being rotated at 35 rpm. With increasing θ values, the thickness of surface structures decreases as the line-of-sight metal deposition through the projected interstices of colloidal masks is blocked to a larger extent.

Personnel Supported:

Melvin Zin (Jen)

Tuguy Kacar (Sarikaya)

Abhishek Kulkarni, Postdoc (Ginger)

Affiliated Personnel not receiving direct salary support:

Alex Jen, Professor

Mehmet Sarikaya, Professor

David S. Ginger, Assistant Professor

Hong Ma, Research Scientist/Research Assistant Professor, Jen

Kirsty Leung, Ph. D. Student, Jen

Andrea M. Munro, Ph.D. Student, Ginger

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Keiko Munechika, Ph.D. Student, Ginger

Joseph Wei, Ph.D. student, Ginger

David Coffey, Ph.D. student, Ginger

Publications acknowledging AFOSR funding since 1 Oct 2006:

1. M. T. Zin, A. M. Munro, M. Gungormus, H. Ma, C. Tamerler, D. S. Ginger, M. Sarikaya, and A. K.-Y. Jen, "Peptide-Mediated Formation of Well-Controlled Quantum Dot Arrays with Tunable Photoluminescence Properties", *J. Mater. Chem.* **17(9)**, 866 (2007).
2. H. Ma, M. T. Zin, M. H. Zareie, M. S. Kang, S. H. Kang, K. S. Kim, B. W. Reed, C. Tamerler, M. Sarikaya, and A. K.-Y. Jen, "Assembly of Nanomaterials through Highly Ordered Self-Assembled Monolayers and Peptide-Organic Hybrid Conjugates as Templates", *J. Nanosci. Nanotech.* **7(8)**, 2549-2566 (2007).
3. Zin, M. T., Leong, K., Wong, N. Y., Ma, H., Jen, A. K.-Y., "Plasmon Resonant Structures with Unique Topographic Characteristics and Tunable Optical Properties for Surface-Enhanced Raman Scattering", *Nanotech.* **2007**, 18, 455301.
4. Xu, Q. M., Ma, H., Tucker, N., Bardecker, J. A., Jen, A. K.-Y., "Controlled Assembly of Large π -Conjugated n-Type Molecules on Au(111)", *Nanotech.* **2007**, 18, 335302.
5. Kang, M. S., Ma, H., Yip, H. L., Jen, A. K.-Y., "Direct Surface Functionalization of Indium Tin Oxide via Electrochemically-induced Assembly", *J. Mater. Chem.* **2007**, 17, 3489-3492.
6. M. T. Zin, H. Ma, M. S. Kang, S. H. Kang, K. S. Kim, M. H. Zareie, K. Leong, M. Sarikaya, and A. K.-Y. Jen, "Controlled Self-Assembly of Nanomaterials through Highly Ordered Self-Assembled Monolayers and Genetically Engineered Polypeptides", *Poly. Mater. Sci. Eng.* **95**, 1071 (2006).
7. M. T. Zin, H. Ma, A. M. Munro, D. S. Ginger, M. Gungormus, K. Leong, C. Tamerler, M. Sarikaya, and A. K.-Y. Jen, "Well-Controlled Arrays of Core-Shell Quantum Dots with Tunable Photoluminescence Properties", *Poly. Mater. Sci. Eng.* **95**, 1002 (2006).
8. T. Kacar, M. T. Zin, B. Wilson, S. Sepheri, A. K.-Y. Jen, H. Ma, C. Tamerler, and M. Sarikaya, "Template Directed Self Immobilization of Alkaline Phosphatase on Micropatterned Surfaces via Genetically Fused Metal Binding Peptide", submitted.
9. M. T. Zin, K. Leong, H. Ma, N. Y. Wong, M. Sarikaya, and A. K.-Y. Jen, "Peptide-Mediated Fabrication of Tunable Quantum Dot Arrays with Surface-Plasmon-Enhanced Fluorescence", *J. Mater. Chem.* 2007, submitted.
10. Y. Chen, K. Munechika, and D. S. Ginger, "Dependence of fluorescence intensity on the spectral overlap between fluorophores and plasmon resonant single silver nanoparticles," *Nano Letters* **7**, 690 (Mar 14, 2007).
11. K. Munechika, J. M. Smith, Y. Chen, and D. S. Ginger, "Plasmon linewidths of single silver nanoprisms as a function of particle size and plasmon peak position," *J. Phys. Chem. C* in press (2007).

12. A. M. Munro, J. A. Bardecker, M. S. Liu, Y.-J. Cheng, Y. Niu, I. J.-L. Plante, A. K.-Y. Jen, and D. S. Ginger, "Electroluminescence from Colloidal CdSe Quantum Dots: Ligand Effects and Light-Emitting Diodes," *Microchimica Acta*, DOI: 10.1007/s00604 (2007).

Interactions/Transitions during Award Period (2006-2007):

(invited lectures)

1. "Material and Interface Engineering for Highly Efficient Polymer Light-Emitting Diodes", Frontier of Optics Conference, OMD Symposium, Optical Society of America, San Jose, CA, 9/07.
2. "Bioengineered-Inorganic Nanosystems for Nanophotonics and Bionanotechnology", The Second International Molecular Biomimetics Workshop, Friday Harbor, San Juan Island, WA, 9/07.
3. "Molecular Design and Self-Assembly for Unprecedented Electro-optic Activities", The SPIE Meeting, The International Society of Optical Engineering, San Diego, CA 8/07.
4. "New Paradigm for Ultrahigh E-O Properties through Supramolecular Self-Assembly and Novel Lattice Hardening", The Molecular Electronics and Bioelectronics Conference, Japan Applied Physics Society, Tokyo, Japan, 3/07.
5. "Exceptional Electro-optic Properties from Molecular Design and Supramolecular Self-Assembly", The 2007 Taiwan Polymer Society Meeting, Taipei, Taiwan, 1/07.
6. "Supramolecular Self-Assembly and Lattice-Hardening for Electro-optic Coefficients Beyond 450 pm/V", International Molecular Photonics Symposium, San Juan Island, WA, 8/07.
7. "Molecular Design, Self-Assembly, and Interface Engineering for Molecular and Organic Electronics", IBM Tom Watson Laboratory, Yorktown Heights, NY, 9/07.
8. "Material and Interface Engineering for Highly Efficient Polymer Light-Emitting Diodes", IEEE/LEOS Summer Topical Conference, Portland, OR, 7/07.
9. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Wuhan University, Hubei, China, 6/07.
10. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Beijing University, China, 7/07.
11. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Tsing Hua, University, Beijing, China, 7/07.
12. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Institute of Chemistry, The Chinese Academy of Sciences, Beijing, China, 7/07.
13. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", RIKEN, Tokyo, Japan, 3/07.
14. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Photonics West Meeting, San Jose, CA, 1/07.
15. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Hannam University, Korea, 2/07.
16. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Seoul National University, Seoul, Korea, 2/07.

17. "Material and Interface Engineering for Highly Efficient Polymer Light-Emitting Diodes", Hannam University, Korea, 2/07.
18. "Material and Interface Engineering for Highly Efficient Polymer Light-Emitting Diodes", The Electronics and Telecommunications Research Institute (ETRI), Daejeon, Korea, 2/07
19. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Institute of Chemistry, Academia Sinica, Taiwan, 1/07.
20. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Department of Applied Chemistry, National Chiao-Tung University, Taiwan, 12/06.
21. "Material and Interface Engineering for Highly Efficient Polymer Light-Emitting Diodes", The Symposium on Organic Electroluminescence, The Polymers Society of Japan, Tokyo, Japan, 10/06.
22. "Exceptional Photonic and Optoelectronic Properties from Molecular Design and Supramolecular Self-Assembly", Colloquium, Department of Materials Science & Engineering, University of Wisconsin, Madison, WI, 10/06.
23. "Exceptional Electro-optic Properties through Molecular Design and Supramolecular Self-Assembly", Optics East, The international Society of Optical Engineering, Boston, MA, 10/06.
24. WRF presentation, Seattle, WA, 10/06
25. Purdue University, Chemistry Department Seminar, Oct. 31, 2007.
26. American Vacuum Society 54th International Symposium, Seattle, WA, Oct. 14-19 2007

Patent Disclosures:

Jen, A. K.-Y., Zin, M. T., Ma, H., Leong, K., "Ordered arrays of plasmon resonant structures with unique topographic characteristics and tunable optical properties for ultra-sensitive surface-enhanced sensing", patent disclosure, 2007.

Honors/Awards:

During Award Period:

- AAAS Fellow, American Association for the Advancement of Science (Alex Jen)
- SPIE Fellow, The International Society of Optical Engineering (Alex Jen)
- OSA Fellow, The Optical Society of America (Alex Jen)
- 2007 Faculty of Research Innovation Award, College of Engineering, University of Washington (Alex Jen)
- Changjiang Endowed Chair Professor, Wuhan University, Ministry of Education, China (Alex Jen)
- Camille Dreyfus Teacher-Scholar Award (David Ginger)
- Alfred P. Sloan Foundation Fellowship (David Ginger)
- Research Corporation Cottrell Scholar (David Ginger)
- Materials Research Society Graduate Student Award (David Coffey, Fall 2006 Meeting)

Lifetime:

Alex K.-Y. Jen

- Endowed Visiting Professorship, Chinese University, Hong Kong.

- Boeing-Johnson Endowed Chair, University of Washington.
- Industrial Fellow, Materials Research Center, Northwestern University.
- Founder's Award, ROI Technology.
- Outstanding Achievement Award, Advanced Materials Laboratory, EniChem America Inc.
- National Research Council Lectureship, Taiwan.
- Outstanding Achievement Award, President, EniChem America Inc.
- Rohm & Hass Research Fellowship, University of Pennsylvania.

David S. Ginger

- Camille Dreyfus Teacher-Scholar Award (2007)
- Alfred P. Sloan Foundation Fellowship (2007)
- Research Corporation Cottrell Scholar (2006)
- Presidential Early Career Award for Scientists and Engineers, DoD 2004
- National Science Foundation CAREER Award 2005
- National Institutes of Health Postdoctoral Fellowship, 2001-2003
- DuPont Postdoctoral Fellowship, 2001-2003
- Marshall Scholarship, 1997-2000, (British Government)
- Materials Research Society Graduate Student Gold Award, Nov. 2000
- National Science Foundation Graduate Research Fellowship, 1999-2001
- American Chemical Society Charles D. Coryell Award, 1997 (Division of Nuclear Chemistry)

Mehmet Sarikaya

- Director, NSF-funded Materials Research Science & Engineering Center