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Nanostructures Enabled by On-Wire Lithography (OWL)

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Abstract

Nanostructures fabricated by a novel technique, termed On-Wire-Lithography (OWL), can be combined with organic and biological molecules to create systems with emergent and highly functional properties. OWL is a template-based, electrochemical process for forming gapped cylindrical structures on a solid support, with feature sizes (both gap and segment length) that can be controlled on the sub-100 nm length scale. Structures prepared by this method have provided valuable insight into the plasmonic properties of noble metal nanomaterials and have formed the basis for novel molecular electronic, encoding, and biological detection devices.

Introduction

The development of new materials with structural dimensions that can be controlled precisely on the sub-100 nm scale remains a major area of current research. These nanomaterials have garnered attention for various applications including coatings (1–2), catalysis (3), photovoltaics (4), sensing (5), diagnostics (6), and therapeutics (7–8). These applications are made possible because of the new properties that emerge as the critical dimensions of a given structure are reduced below the wavelength of light. Indeed, as research advances in this field, scientists have attained the ability to control the shape of metals (8), semiconductors (9), binary materials (10), and polymers (11), to include spheres (12), cubes (13), prisms (14), platonic solids (15), and cages (16) or other hollow structures (17). Extensive studies of these materials have demonstrated that their assembly, interactions with light, and electrochemical properties are often intimately related to their shape and size (18). As these relationships are increasingly understood, there is a push towards developing high-throughput synthetic methods capable of synthesizing or fabricating nanomaterials with predictable and desirable properties. This *Frontier* is devoted to the description of a new method, termed On-Wire Lithography (OWL), for forming gapped metallic nanowires and nanodisks comprised of cylindrical segments where feature size (gap and segment length) can be controlled down to the sub-20 nm and, in certain cases, sub-5 nm length scale.

Several high-throughput methods now exist for preparing multisegmented, cylindrical rods with at least one dimension on the sub-100 nm length scale. The vapor-liquid-solid (VLS) technique has been utilized to prepare a variety of nanowire materials using a spherical nanoparticle catalyst (19). Structures made by the VLS method include single and multicomponent wires consisting of a variety of materials including insulators,

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semiconductors, and metals (20). While materials prepared by the VLS technique are being explored in a variety of important contexts, including electronics (21) and sensing (22), VLS offers only limited control over architecture and dimension.

In 1970 Possin reported a method for the electrochemical synthesis of metal nanowires within the pores of a mica template (23). Using this method, wire structures of tin, zinc, and other metals with diameters as small as 40 nm were produced. Expanding this technique, Martin and Moskovits independently experimented with the use of anodic aluminum oxide (AAO) as a template for metal nanowire preparation (24–26). Conducting polymers, metals, and semiconductors were all deposited electrochemically within the AAO templates and subsequently isolated by dissolving the template. Natan *et. al.* then described a method by which “metallic barcodes” could be produced by alternating metal plating solutions during electrochemical deposition within the AAO templates to fabricate striped nanowires (27). Indeed, this templated, electrochemical method provided better control of composition and segment length compared to other multisegmented nanowire synthesis protocols.

OWL also relies on templated synthesis but utilizes new innovations enabling superior control of architecture along the long axis of the metal rod (28–29). In the OWL process (Figure 1), metals, semiconductors, or polymers are deposited electrochemically within the linear pores of the AAO. The number of Coulombs passed from the counter to working electrode is directly related to the length of the resulting nanowire segment. Using calibration curves specific to each material, segments of known lengths can be prepared, with the width of the nanowire determined by the size of the pores in the AAO template. In addition, by altering the metal electrolyte solution, it is possible to synthesize segmented nanowires. After wire synthesis and subsequent dissolution of the AAO template and wire release, an oxide (e.g. SiO₂) or metal backing is deposited on the wire by plasma-enhanced chemical vapor deposition (PE-CVD) or thermal evaporation, respectively. Etching chemistries can then be employed to selectively dissolve certain segments, while the backing maintains spacing between domains. This method provides access to myriad architectures, including segmented disk arrays of dimers, trimers, tetramers, pentamers or nanogapped wires (30) with a precisely controlled intersegment spacing as small as 2.5 nm (31).

Optical Properties of OWL-Generated Nanowires

The interaction of nanomaterials with light is important for sensing and electronic applications and is also interesting in the context of fundamental investigations. The surface plasmon resonance (SPR) of noble metal anisotropic nanostructures can be tuned from the visible to the near-infrared (NIR) regions of the electromagnetic spectrum (32–33) by controlling particle dimensions. The SPR excitation is a consequence of the collective oscillation of the conduction electrons of a noble metal nanostructure upon irradiation with light of an appropriate wavelength (34). This process generates locally amplified electromagnetic (EM) fields at the surface of the nanostructure, and the EM intensities of those “hot spots” are larger than the intensity of the incident optical excitation field (35–36). Structures generated by OWL provide a unique platform to interrogate the relationship between the dimensions of noble metal nanomaterials and their SPRs. Surface enhanced Raman scattering (SERS) is a phenomenon that involves the enhancement of Raman scattering from a molecule adsorbed on the surface of a noble metal nanostructure with an active plasmon resonance (37–39). When the SPR is in resonance with the wavelength of the illumination source, the local EM field intensity that a molecule experiences can be enhanced by factors as large as 10⁸ in OWL-generated structures (40). SERS greatly increases the sensitivity of Raman spectroscopy and is therefore a powerful tool for chemical sensing (41), biological imaging (42), and biomedical diagnostics (43–44). However, the relationship between SERS enhancement and the structure of the noble metal

nanomaterial remains difficult to experimentally quantify and optimize, because of the challenge facing researchers in synthesizing or fabricating Raman-active structures with sub-5 nm control of architectural features and surface roughness. Important advances in this regard have been made with Nanosphere Lithography, but the architectures available through this method are limited (41,45).

Two mechanisms are frequently offered to explain the high field enhancement of SERS by noble metal nanostructures: EM and chemical enhancement. EM enhancement involves the increase in the EM field at hot spots as a result of SPR excitation. Chemical enhancement arises from nanometer changes in morphology of the Raman enhancing nanostructures that induce SERS by charge transfer excitation from the metal to the Raman-active molecules (40) and is often attributed to the metal assisted charge transfer from the HOMO to the LUMO of the Raman probe. Conventional techniques for nanostructure fabrication, such as VLS or AAO templating, cannot achieve this level of architectural control over anisotropic noble metals to quantitatively explore SERS. In particular, size, shape, wavelength, and surface roughness are all known to affect SERS, but limitations in the shapes of SERS active materials that can be fabricated, has precluded the development of accurate, quantitative models that thoroughly explain the effects of nanostructure geometry on SERS. Therefore, there is a need for more high-throughput fabrication methods with the requisite control and precision to produce identical anisotropic noble metal structures, whose uniformity enables quantitative and reproducible measurement of SERS that will enable the design of functional sensors and electronic devices.

SERS is often described as a near-field phenomenon that occurs when the Raman molecules are in close proximity to a nanostructure's surface (34,46–47). Theoretical calculations have predicted that the enhanced EM fields decay rapidly as a function of distance from the surface, however, a shortage of experimental evidence has prevented the validation of these theoretical results with all relevant parameters considered (particle size, shape, composition, dielectric material, molecule type, etc.). Investigations conducted by introducing shells of high dielectric materials between the Raman molecules and the surfaces of the noble metal particles (48–49), result in an even more rapid decay of EM fields away from the nanostructure surface (34). As a consequence, conventional nanofabrication and synthesis techniques are not ideal for interrogating the relationship between the enhanced EM fields as a function of distance from the surface. Additionally, it has been shown that SERS enhancement is greater within the gap of two noble metal structures rather than solely on the edge of one, but few methods exist for varying this gap systematically on the nanoscale. Several groups have reported the decay of SERS intensity for functionalized noble metal particles separated by spacings of a few nanometers, but these studies are influenced by experimental uncertainty in the interparticle separation, particle shape, and surface roughness of the nanostructure (48,50). The architectural control of metallic structures on the nanometer length scale enabled by OWL can be utilized to create uniform, noble metal, cylindrical nanostructures that are appropriate for investigating the contributions of EM enhancement on SERS. Because rods with controlled gap size or multiple Au disk pairs and related structures of varying geometries can be synthesized on a single array using OWL, the necessary internal controls can be added along the nanowire to directly compare the relative Raman intensity contribution of different architectures in a single experiment.

Although previous experimental and theoretical work suggested that SERS enhancement is largest for Au disk pairs with the smallest gap (35,51), a more thorough investigation of EM field enhancement was warranted. Accordingly, a series of Au disk pairs were prepared with a systematic variation in gap size and disk thickness using OWL to determine the effect of gap length on SERS enhancement. Interestingly, Au features composed of 120 nm thick disk dimers functionalized with methylene blue (MB) having a 30 nm gap spacing, rather than

smaller gaps, produced the maximum SERS enhancement, with over 100 times the enhancement provided by a single disk, upon excitation at the Au resonance with 633nm light (30). This disagreement between experiment and theory illustrated the need for further investigation of these structures and the development of more sophisticated theoretical models that explain these anomalous results. The discrete-dipole approximation (DDA) was employed to model the optical properties of the Au disk pairs. In this method, the particle is represented as a cubic array of point dipoles, where the polarization of $\vec{P}_j$ each dipole arises in response to the total electromagnetic field at that site in the array according to (52):

$$\vec{P}_j = \alpha_j \left[\vec{E}_j^{inc} - \sum_{k=j}^N A_{jk} \vec{P}_k \right]$$

Here α is the polarizability, $\vec{E}_j^{inc}$ is the incident field, and A_{jk} is the interaction matrix. Using this method, it was determined that this non-zero optimum gap size for a specified excitation wavelength results from the red-shifting of the dipole plasmon wavelength caused by surface roughness of the disks (53). In addition, the observed SERS enhancement factor of ≈ 100 times for a disk pair separated by 30 nm, compared to isolated disks, agrees well with the DDA calculations (53), providing a quantitative model of the EM enhancement for a well-defined metal nanostructure.

Subsequent work focused on developing a quantitative theoretical model for SERS enhancement using OWL-generated disk pairs as enhancing elements and determining the maximum distance a chromophore could be separated from a Raman enhancing structure and still experience Raman enhancement (54). A Au disk pair with a 30nm gap and excitable plasmon resonance at 633 nm was prepared by OWL and placed adjacent to plasmon-inactive Ni segments. The Ni was modified with Raman active phthalic acid, which binds selectively to Ni but not Au. With this architecture (Figure 2), the Au SPR is excited by the incident 633 nm light and enhancement is experienced by molecules within a critical distance of the Au disk pair (54). The previously suggested maximum decay length of EM fields for a traditional localized SPR based detection system is roughly 5–15 nm (55). To test the upper limit of distance from which EM field enhancement could be observed in this system, the Au disk pair was separated from the Ni rod by 120 nm. Surprisingly, enhancement of the Raman probes on the non-plasmonic Ni was still observed at such a large separation.

The enhancement from a Au rod adjacent to a Ni rod was also measured to determine whether this long-range SERS enhancement was generalizable to Au structures other than disk dimers. Interestingly, this unprecedented long-range SERS was also confirmed with a 1.5 μm Au wire having separations up to 78 ± 8 nm from a 2.0 μm Ni nanowire. This discovery of such long range enhancement further warranted a more thorough study involving the systematic interrogation of the relationship between segment length, gap-size, excitation wavelength, and SERS intensity to develop a more comprehensive theoretical model based on DDA calculations of SERS-active nanowires. Accordingly, a series of 360 nm diameter gapped Au nanorods were prepared by OWL with varying Au segment lengths and similar gap sizes (~ 20 nm) (56). These structures were functionalized with MB, and the SERS enhancement was determined at an excitation wavelength of 633 nm. The SERS intensity was found to be a periodic function of segment length, with maxima occurring when the Au segment lengths were multiples of 560 nm. This value is roughly equivalent to the 600 nm period of the surface plasmon polaritons for 360 nm diameter Au rods having an infinite length under 633 nm excitation. DDA calculations confirmed that the electric field strength within the gap is a periodic function of segment length, rather than a monotonically

decreasing function, as previously suggested. Additionally, all maxima in field strength correspond to odd-order plasmon multipole modes of each segment because excitation of even modes is symmetry forbidden. These results led to a new model to understand Raman scattering and enhancement within nanogaps on long Au segments. One can now create gapped structures long enough to address and probe electrically while maintaining the spectroscopic enhancement within a molecular scale gap essential to sensing applications. These results demonstrate that OWL can be used to probe the nature of the EM enhancement mechanism of SERS and to develop predictive models for the SERS of noble metal nanostructures. These observations may enable the design of functional nanosystems where the optical properties can be predicted prior to fabrication.

Surface Plasmon-Mediated Energy Transfer in Hetero-Gap Au-Ag Nanowires

The study of energy transfer between different noble metals via SPR is rare (57–58). While such information could lead to new functional devices, the inability to produce nanostructures containing different compositions with precise control over the distance between the different materials has hindered the investigation of EM enhancement. Since OWL allows one to bring together different metals with controlled interdomain spacing, it provides a means to explore energy-transfer in bimetallic nanostructures. For example, a series of nanostructures consisting of a Au nanodisk pair and a Ag nanowire separated by a well-defined nanoscale gap (120nm) were prepared using the OWL fabrication process (59). With *p*-mercapto benzoic acid (pMBA) as the Raman reporter, this structure could be used to investigate SPR-mediated energy transfer from Au to Ag because the SPR mode of the Au nanodisk pair was excited by the 633 nm incident radiation while the Ag rod was only weakly excited. Upon irradiation of the wire, energy transfer from the Au nanodisk pair to the Ag nanowire across the 120 nm gap was indicated by the 15-fold SERS enhancement of the pMBA transitions in the Raman spectrum. Importantly, the Raman intensity depends nonlinearly on the incident laser intensity, suggesting energy transfer via an enhanced nonlinear polarization mechanism. These results are supported by EM theory calculations that show that only a non-linear transfer mechanism can account for the 15 fold observed Raman enhancement: the SPR excitation of the Au nanodisk pair induces high EM field density which triggers the higher energy plasmon resonance excitations in the Ag rod, resulting in larger Raman scattering than occurs with isolated Ag segments. It should be noted that the nonlinear induced polarization mechanism could be related to recently reported SPR-enhanced optical Kerr effects for Au and Cu nanoparticles (60–61). These results suggest strategies for energy conversion, where energy can be transferred from a nanostructured plasmonically active material that interacts with light to a material capable of catalyzing new chemical processes. This new understanding of the relationship between nanorod structure and SERS, formulated through a series of systematic investigations, can be used to develop a variety of devices for biological and chemical sensing applications.

Plasmonic Focusing in Rod Sheath Structures

The OWL method enables the exploration of exotic SERS active architectures that would be difficult to make by other nanowire fabrication methods. For example, a Au-polypyrrole (PPy) rod was created within the pores of the AAO template. When dried under vacuum, the PPy rods shrink in diameter, thereby generating a crescent shaped vacancy within the AAO pore. Subsequent Au electrodeposition was performed within the AAO template filling the vacancy created within the pore by the shrinking polymer (Figure 3) (62). Dissolving the PPy segment yielded the resulting architectures, termed rod-sheath heteronanostructures, whose SERS enhancing properties were investigated. It was discovered that these structures were able to generate increased SERS response at the rod-sheath interface when compared

to the terminal end of the rod or sheath. Further analysis using DDA calculations confirmed that a plasmonic focusing event occurs at the junction such that the SERS response at the interface is roughly 4 times greater than that of either end of the rod-sheath heteronanostructure. The DDA modeling suggests that the SERS enhancement is periodic in nature with respect to the length of both the rod and sheath. This interesting result provides further insight into SERS focusing systems for applications in plasmonic waveguide and lithography technologies.

Nanodisk Codes

The optical properties of OWL-generated structures were also utilized in the context of detection and encoding applications. Previously, Raman-chromophore labeled nanoparticles (20), striped nanorods (27,63–64), and fluorophore modified beads (65–68) have been investigated as unique nanoscale labels for encoding applications. Among these systems, striped nanorods are particularly interesting because they allow for massive encoding based upon the length and location of individual chemical blocks within the structures (27). However, several major obstacles prevent their widespread adoption in additional encoding applications. The high degree of overlap between common fluorescent labels, quenching properties of the metal blocks that comprise the structures, and difficulty in resolving differences in metal reflectivity all limit the overall utility of these structures.

In an attempt to address some of these limitations, OWL was used to synthesize dispersible, segmented nanorod structures with fixed diameters and well-defined metal block sizes along the long-axis of the nanostructure. “Nanodisk codes” (NDCs) were produced by immobilizing Raman enhancing Au disk pairs in a linear array (Figure 4) (69). Information is encoded by the presence or absence of Raman-dye labeled Au disk dimers in five positions along the array, which can be read utilizing confocal Raman spectroscopy. These structures represent a binary code where the presence of a dimer at a specific position represents a 1 and the absence represents a 0. For example, the code 11011 was created by intentionally omitting the third disk pair in a five bit array. Because of symmetry considerations, only 13 unique disk codes could be prepared from the 5-bit design.

The NDCs were also utilized in the context of DNA sensing. NDC codes 11011 and 10101 were functionalized with different DNA sequences complementary to their respective target strands. Once functionalized, the solutions of NDCs were mixed together and subsequently added to a solution of DNA target strands and fluorophore labeled DNA reporter strands. Cy5 and TAMRA were designated to be reporter molecules for NDC₁₁₀₁₁ and for NDC₁₀₁₀₁, respectively. Using this approach, the code of the array as well as the presence of the dye produces a readout signal that could be identified with Raman spectroscopy. Subsequent experiments indicated that the limit of detection for target DNA using this architecture was 5 pM. The limit for target strand detection was further reduced to 100 fM by using Au nanoparticles modified with the appropriate Raman-labeled DNA reporter strand. This increase in sensitivity was made possible by having multiple Raman reporters present on the nanoparticle for a single DNA binding event. Both the high Raman enhancement and the ability to embed information by controlling the inter-dimer spacing suggests a variety of applications in the context of point-of-care diagnostic or cryptographic platforms.

Nanotrap Detection Systems

An alternative DNA detection scheme was devised by combining the ability to electronically address the gapped Au rods and the advantageous SERS enhancement of these structures (70). Gapped Au wires were synthesized (Au-gap-Au, 3 μ m-50 nm-3 μ m) following the OWL protocol (Figure 5). The wires were dispersed on a surface, and Au microelectrodes

were then attached to the OWL generated structure using conventional lithography techniques. The SiO₂ surface was subsequently functionalized using 3-aminopropyltrimethoxy silane followed by reaction with succinimidyl 4-(p-maleimidophenyl) butyrate. This chemistry provides an anchor molecule for the DNA capture strand (5' CGC GGA TAT TTC TGT TGA CTC GCG AGA GGA AAA AAA SH 3') complementary to the fluorophore-labeled DNA target (5' TCC TCT CGC GAG TCA ACA GAA ATA TCC GCG AAA AAA Cy5 3') in solution. Target DNA was then passed through a microfluidic channel containing the device. By applying an AC field to the device, the ionic DNA was concentrated within the gap and subsequently captured by the complementary DNA on the exposed SiO₂ in the gap. Raman spectroscopy was able to detect an analyte signal for concentrations as low as 230 fM, over 20 times that of a comparable Raman detection system having no applied field (69) and twice the reported sensitivity of tip-enhanced Raman spectroscopy (48).

With OWL it is now possible to design a nanostructure based detection system that combines the aforementioned electrical approaches with the virtues of spectroscopic detection, and thus provide necessary internal assay controls (71) within a single detection platform. Indeed, a detection system containing both optical and electrical detection elements was constructed by OWL (Figure 6) (72). PPy is a hole-carrying conducting polymer, and a Au/PPy interface behaves as a diode-like Schottky barrier. Binding events on the Au side of the wire will modulate the Au Fermi level, which is detectable by changes in conductance (73–74). This property was utilized within an OWL-based detection assay. Binding can also be measured with SERS by incorporating Au disk dimers at the end of the wire. This architecture was prepared by synthesizing the Au disk dimers along the long axis of the wire and then depositing the subsequent Au and PPy rod segments. These wires were cast on a substrate, and electrode contacts were then connected to the ends of the Au and PPy wire segments using conventional lithography methods.

The sensitivity of this electro-optic detection platform was demonstrated by testing for the presence of the cancer marker telomerase. Telomerase is an enzyme that catalyzes the addition of the telomeric repeat sequence TTAGGG to the 3'-end of a DNA sequence in the presence of deoxyribonucleotide triphosphates (dNTP). Following immobilization of the thiolated DNA recognition strand (5' HS T5 AAT CCG TCG AGC AGA GTT 3') to the Au segment of the OWL-generated Au/PPy wire, the devices were exposed to different concentrations of telomerase extracted from HeLa cells (1000, 5000, and 10000 cells) through a microfluidic channel. The binding of telomerase to the recognition strand was monitored by changes in conductance along the Au/PPy wire. The electrical portion of the device could detect the telomerase binding from as few as 1000 HeLa cells. In addition to the electrical detection of telomerase binding, the enzymatic activity could also be confirmed using SERS. Raman-labeled probes (5' CCC TAA CCC TAA Cy5 3') hybridize to the DNA elongated by the telomerase, producing an enhanced Raman response within the gaps of the Au disk dimers. These results, combined with the ease of implementing these structures into functional systems may enable this new detection scheme to be integrated into future medical diagnostic devices.

Transport in OWL-Fabricated Molecular Transport Junctions

As the miniaturization of feature size in circuits continues, there is increasing exploration of the properties of molecules for performing memory and logic functions in the context of molecular electronics. The use of OWL-fabricated nanogaps as testbeds for molecular electronic devices was demonstrated by the assembly of thiolated molecular wires of different dimensions across gaps formed between two Au electrodes (75). Au rods separated by a gap of 3 nm and held together by a SiO₂ backing were prepared by the OWL method.

The gapped structures were cast onto a gold substrate prepatterned with Au microelectrodes, and then connected to the electrodes by electron-beam lithography and subsequent Cr and Au thermal deposition. The devices were immersed in a solution of α,ω -dithiol terminated oligo(phenylene ethynylene) (OPE), which is a well-known π -conjugated organic molecular wire from which a high quality self-assembled monolayer (SAM) on Au can be prepared. The two-terminal I - V characteristics were measured both before and after the device had been modified with the OPE. The empty gap exhibits no conductance, whereas the device loaded with OPE shows an I - V response characteristic of molecular conductance (Figure 7). This result suggests that the OPE spans the gap in such a way that it is chemically bonded to each side of the gapped Au nanorod.

Importantly, these new molecular transport junctions (MTJs) provide a platform to identify the intrinsic transport properties of the molecules spanning the gap. The monotonic decrease of current with temperature observed in the OPE MTJ suggested a thermally activated transport mechanism, such as thermionic emission or hopping conduction. However, hopping was excluded on the basis of the temperature-dependence of the voltage, and the transport was more consistent with thermionic emission at high temperatures, which involves thermally activated charge injection from the electrode to the OPE. However, at low temperatures (<120 K), charge transport is more consistent with tunneling. As a result, it was concluded that there are two charge transport mechanisms, depending on temperature, that were observed for the OPE MTJs based on the OWL generated nanogaps. The transition from tunneling to thermionic emission was attributed to the onset of torsional fluctuations of the OPE as temperature is increased. This study is the first such example of the transition from tunneling to thermionic emission in MTJs. These results demonstrate not only the ease by which MTJs can be fabricated with OWL-generated nanogapped wires, but also that they are sensitive probes for understanding the charge transport characteristics of molecular electronic devices. Indeed, from a molecular electronics point of view, OWL-fabricated nanostructures are remarkably simple to fabricate, stable, and scalable.

Spectroscopic Tracking of Junctions Generated by Click Chemistry

Within the field of molecular electronics, several major challenges can be addressed using nanostructures prepared by the OWL method as a result of their structure, electronic addressability, and optical properties. A significant challenge in molecular electronics is the ability to spectroscopically identify molecules located within MTJs to confirm that the unique device properties are indeed the result of the molecular components. In addition, a protocol for the fabrication of uniform MTJs and versatile chemistry to immobilize different molecules within these MTJs to quickly examine their transport properties did not exist until recently (76). To address both of these issues, a fabrication method for MTJs involving the *in-situ* synthesis of molecular wires that bridged OWL-generated nanogaps was developed, whereby the assembly process was tracked spectroscopically as a result of the Raman enhancement enabled by the nanorods. The copper(I)-catalyzed 1,3-dipolar Huisgen cycloaddition reaction (click reaction) between azide and alkyne groups was utilized to generate conducting molecular wires within OWL-fabricated nanogaps to form MTJs (Figure 8). The general scheme in these studies involved first assembling a monolayer of 4-ethynyl-1-thioacetylbenzene onto the surfaces of the Au electrodes located on opposite ends of an OWL-generated nanogap. Upon exposure to 2,7-diazido-fluorene in the presence of the Cu(I) catalyst, the terminal alkyne reacts with one of the azides on the 2,7-diazido-fluorene, to form a 1,2,3-triazole. The remaining azide from the 2,7-diazido-fluorene can either form a bridge with the opposite electrode or remain unmodified so that it can further react with 2,7-diethynyl-fluorene. This cycle of reactions can be repeated until the gap is bridged by the molecular wire growing from opposing electrodes. The point at which the bridge is formed can be confirmed by the two terminal I - V curves that show conductivity.

This is only observed after the appropriate number of reaction cycles required to bridge the gap have been carried out. This process was demonstrated for 2, 5 and 7 nm nanogaps, which required 1, 2, and 3 reaction cycles, respectively. Because of the accessible functional group requirements and high yield of the click reaction, this *in situ* synthesis method could be used in a high-throughput, combinatorial fashion, to investigate how the changes in molecular structure within gaps affects the transport properties of MTJs.

In addition, SERS measurements carried out directly on the nanogaps confirmed that the click reactions proceeded within the confined gaps to form molecular wires. Because nanogaps act as Raman hot spots, the molecules within the gaps could be identified spectroscopically. For example, in a typical experiment, structures were fabricated by OWL with Au rods on either end of a sub-100 nm gap (98 ± 11 nm). For gap structures modified with 4-ethynyl-1-thioacetylbenzene, the presence of alkyne groups could be clearly identified within the gap ($\text{C}\equiv\text{C}$ symmetric stretch at 2108 cm^{-1}). When the same nanorods are reacted with azide-modified fluorene, the peak at 2108 cm^{-1} disappears, and new peaks corresponding to the triazole ring stretch appear (967 and 1010 cm^{-1}). Further reaction with alkyne modified fluorene results in the reappearance of the alkyne peak at 2108 cm^{-1} and an increase in the intensity of the triazole peak. These SERS experiments demonstrate successful reactions within the nanogaps and confirm the chemical composition of the molecules responsible for the conductivity of the MTJs. These results represent a new paradigm for the fabrication of MTJs through click chemistry in OWL-fabricated nanogaps, where the molecular composition of the material spanning the gap can be confirmed by SERS. This new method of fabricating and spectroscopically characterizing MTJs, with diverse functions and applications, will be widely utilized in the context of molecular electronics.

In-Wire Conversion of a Metal Nanorod Segment Into an Organic Semiconductor

OWL-generated nanogaps are not only enabling new characterization and assembly techniques, but new devices are also possible via the OWL process. Organic semiconductor materials have recently attracted attention as components in functional electronic memory devices. The charge transfer complexes of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with metals (MTCNQ, $\text{M}=\text{Ag}$, Cu or other metals) are of particular interest for electronic recording media because these materials can be switched reversibly between two stable states that differ substantially in conductivity. To incorporate MTCNQ into nanojunctions, a Ag section was synthesized between two Au segments prepared by the OWL process (77). Upon exposure to TCNQ under chemical vapor deposition conditions, the TCNQ reacts selectively with the Ag section to form wires of AgTCNQ (Figure 9). In contrast to the surface-only conversion of the Ag to AgTCNQ observed in bulk systems, all of the Ag in the OWL fabricated nanowire is converted to AgTCNQ because the reactant vapor can penetrate completely into the nanoscale Ag segment. In a typical experiment, a segmented rod was exposed to TCNQ vapor for 2h, which converted the Ag into needles of AgTCNQ that bridged the two Au segments. The needles were characterized by Raman spectroscopy, and the spectra were consistent with previous spectra for AgTCNQ.

The two terminal *I-V* signature was measured before and after reaction with TCNQ to further confirm its incorporation into the multisegmented nanowires and to determine the electrical properties of the Au/AgTCNQ/Au nanojunctions. Prior to exposure to TCNQ, the devices demonstrated linear, metallic conduction. Following exposure to TCNQ, a nonlinear *I-V* curve was observed at low bias ($<5\text{ V}$), which is characteristic of organic semiconductor materials, clearly demonstrating the incorporation of TCNQ into the nanowire. When a full cycle sweep at high bias ($-10\text{ V} \rightarrow 0\text{ V} \rightarrow 10\text{ V} \rightarrow 0\text{ V} \rightarrow -10\text{ V}$) was applied to the

devices, a reversible, hysteretic switching behavior was observed. As the voltage bias is swept from -10 V to 10 V, the device exhibited low impedance, however, as the bias is swept from 10 V to -10 V, it exhibited high impedance. The threshold voltage of the device is approximately ± 5 V, at which point a sudden transition in the current flow occurs. This cyclical response is typical of AgTCNQ devices, and provides further evidence of the chemical transformation within the gap. It should be noted that no further device processing is necessary following exposure to the TCNQ vapor to make these memory devices, thereby resulting in a relatively simple fabrication method for a molecular memory device.

Heterometallic Nanogaps for Molecular Transport Junctions

Most techniques for fabricating MTJs involve only one metal for both electrodes, but heterometallic nanogaps—where the opposing electrodes are comprised of different metals—are interesting from both a fundamental and technological standpoint. Such structures would allow researchers to more closely match the HOMO and LUMO levels of the molecules that span the gap to the work functions of the metals to optimize and adjust the device properties. In addition, the preferential assembly of certain functional groups on a particular metal could be used to manipulate the assembly of molecules within nanogaps. To this end, a heteronanogap comprised of Pt and Au electrodes was fabricated by the OWL method, and a molecular wire assembled within such a heterometallic nanogap demonstrated rectification (78).

The heterometallic nanogap was fabricated by separating Au and Pt segments of an OWL-fabricated nanorod with a 2 nm Ni segment. Following dissolution of the AAO template and deposition of the SiO₂ backing layer, the Ni was selectively removed with an HCl solution, leaving a 2 nm gap between the Au and Pt segments. The heterogapped nanowires were immersed in a solution of α,ω -dithiol substituted OPE that formed a SAM bridging the two electrodes. The presence of the molecules within the gap was confirmed by Raman spectroscopy because of the SERS hot-spot created within the gap. These gapped nanorods were inserted into a device, and the two-terminal *I-V* characteristics were measured at room temperature before and after assembly. The empty gap exhibited no conductance, whereas the nanogap loaded with the OPE showed a significant *I-V* response with rectifying behavior (Figure 10). The rectifying behavior is the result of different modes of contact between the ends of the molecules and the different electrode materials that span the heterometallic gap. The two different metal-thiol contacts induce different electronic coupling at the interface, different injection barriers, and unequal voltage drops. From the *I-V* measurements, it was determined that the Au-OPE coupling is roughly 2.5 times stronger than the Pt-OPE coupling, which led to the observed rectification. This new method of fabricating and characterizing MTJs based on heterometallic nanogaps could be used to create a wide variety of nanoelectronic devices with diverse applications and behaviors derived from the types of metals used to make the electrodes and the molecules assembled within them.

Catalytically Driven Nanorotor

While OWL-generated structures have shown utility in the context of SERS and molecular electronics, these structures can also be designed to have unique nanomechanical properties. A multitude of studies exist involving chemically powered linear motion of nanostructures (79), and there have been a variety of routes developed to make nanorotors bound to a surface (80), rotating gear-like structures (81), and self-propelled particles (82). Using the precision of OWL and the fact that one can make anisotropic structures, a nanorotor was designed that can be driven by chemical reactions that occur at catalytically active sites introduced via the synthesis technique. In this study, Au-Pt rod structures with a Au backing and a small passivating gold segment at the end of the Pt were prepared (Figure 11) (83).

The Pt surface, which is exposed to the solution at only one face of the OWL-generated wire, produced a torsional force from the catalytic decomposition of aqueous H₂O₂ forming O₂ gas. By optimizing the dimensions of the structure experimentally, a maximum velocity of 23.7 rpm was achieved. This occurred at a Pt/Au length ratio of approximately 2. This study provides an initial glimpse at how one can use OWL to rationally design nanomotors with increasingly more complex movement patterns.

Outlook

Since its inception, OWL has evolved into a versatile synthesis and nanostructure fabrication platform. Its inherent flexibility and adaptable nature have enabled novel fundamental and applied studies in molecular electronics, plasmonics, and sensing. This trend is expected to continue unabated. OWL is a highly effective method to control interparticle spacing in SERS active materials. Because of the variety of materials available for deposition into the AAO template, one can now envision strategies utilizing compositional anisotropy enabled by OWL to create unique multi-component structures for thorough studies on the effects of many parameters on SERS enhancement. Additionally, these structures have potential for integration into present technologies utilizing nanostructure-assisted field enhancement for detection.

Understanding the resonant energy transfer processes highlighted herein is also of critical importance. This process, allows lower energy photons to excite SPR modes that typically require higher energy photons. To evaluate the utility of this energy conversion process, light harvesting schemes could be developed by placing known visible light absorbers adjacent to functional materials capable of employing transferred energy for chemical or electrical processes. These architectures may provide a route to the development of systems capable of harvesting light over the visible spectrum and mitigate efficiency drops characteristic of many solar cells.

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Biographies

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Adam B. Braunschweig received his B.A. in Chemistry from Cornell University. He received his Ph.D. from the University of California, Los Angeles, working with Professor J. Fraser Stoddart in 2006. Following a postdoctoral year at the Hebrew University of Jerusalem with Prof. Itamar Willner, he joined Professor Chad A. Mirkin's laboratory at Northwestern University, where he is currently a NIH Postdoctoral Fellow.

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Fig. 1.

The on-wire lithography process. Wires are prepared by electrochemical deposition of metals within anodic aluminum oxide (AAO) templates. The template is subsequently dissolved, and the rods are then dispersed on a silicon wafer and a SiO_2 film (or another material of interest) is applied to one face of the rods by Plasma-enhanced chemical vapor deposition. Coated rods are recovered from the silicon wafer by sonication, and the sacrificial metals are then selectively etched to yield gapped wire structures.

Fig. 2.

Long range SERS enhancement. The maximum range of SERS enhancement for a Au disk pair producing optimum EM field enhancement at 633nm excitation (28) was determined by systematically adjusting the distance between a Raman-dye labeled Ni wire and a Au disk dimer made by the OWL process. SERS enhancement was observed for separations up to 120 nm. No SERS enhancement was observed on the Au wire segment in the absence of Ni because the Raman-dye attaches specifically to the Ni. Additionally, because the excitation wavelength induces no plasmonic response in the Ni segment, no SERS enhancement is observed in the absence of the Au disk pair.

Fig. 3.

Plasmonic focusing in rod-sheath structures. The rod-sheath architecture is prepared by electropolymerizing pyrrole on top of an Au wire segment within the AAO template. Upon drying, the polymer contracts, leaving crescent shaped vacancies along the length of the polypyrrole segment. Further electrodeposition of Au and subsequent etching of the PPy segment yields rod-sheath structures. These structures generate enhanced EM fields at the rod-sheath interface.

Fig. 4. Nanodisk codes. An array of binary codes can be prepared using OWL-fabricated gapped nanorods. The presence or absence of a disk pair in a specific location represent the 1's and 0's of the code, respectively, and can be "read" by SERS, based upon the Raman dye adsorbed onto the disk pairs. With a single dye, only 13 codes are possible in a 5 disk pair array because of symmetry considerations.

Fig. 5.

Nanotrap detection system. A gapped Au wire was prepared using OWL and connected to microelectrodes. The Si backing was then functionalized with a DNA capture sequence and placed within a microfluidic channel. By applying an AC current, an electric field is generated within the gap. The ionic DNA target in solution is attracted to the gap by the electric field where it is hybridized to the capture DNA strand and detected using Raman spectroscopy. The limit of detection is 230 fM.

Fig. 6.

Complementary electrical and spectroscopic detection. A Au/polypyrrole wire was synthesized adjacent to SERS enhancing Au disk pair structures allowing for two distinct detection methods in a single nanowire device. Telomerase binding was monitored electrically by measuring changes in conductance upon binding with a target DNA strand immobilized on the Au rod. The enzymatic activity was detected by SERS using a Raman-dye labeled DNA probe complementary to the TTAGGG sequence added by Telomerase to the DNA target. Telomerase extracted from as few as 1000 HeLa cells produced a detectable change in signal.

Fig. 7. OWL-fabricated molecular transport junctions. OWL was used to fabricate 3 nm gapped Au wire structures. To bridge the gap, the device was functionalized with α,ω -dithiol terminated oligo(phenylene ethynylene), and the electrical response within this molecular transport junction was characterized.

Fig. 8. Spectroscopic tracking of molecular transport junctions. Click chemistry was utilized to synthesize, *in situ*, new molecular wires within 2 nm gaps in Au wires fabricated by OWL to form molecular transport junctions. A Cu(I)-catalyzed 1,3 dipolar Huisgen cycloaddition between azide and alkyne groups of appropriately modified fluorenes formed the conducting wire to span the gap within the MTJ. These reactions could be monitored using Raman spectroscopy and gaps of 2, 5, and 7 nm were bridged using 1, 2, and 3 reaction cycles, respectively.

Fig. 9.

In-wire conversion of Ag to AgTCNQ. Using the AAO as a template, Au-Ag-Au wires were synthesized and subsequently attached to microelectrodes. The conductance was measured before and after chemical vapor deposition of TCNQ, which forms AgTCNQ. The Ag produced a linear response characteristic of metals, while the AgTCNQ curve was non-linear, suggesting a semiconducting behavior.

Fig. 10.

Heterometallic nanogaps. A Au-Pt heterometallic nanogap was prepared by OWL. Upon functionalization with OPE, molecular rectification is observed in the I - V curve. This is attributed to the stronger Au-OPE coupling compared to the Pt-OPE coupling.

Fig. 11.

A catalytically driven nanorotor. Au-Pt wires were synthesized within AAO pores. Once cast onto a substrate, a Au film was applied to one side of the wire, limiting the Pt area in contact with an aqueous solution of H₂O₂. The catalytic decomposition of H₂O₂ on the Pt resulted in rotor activation. The effect of structure on rotor performance was monitored by measuring rotation speed for different architectures as a function of H₂O₂ concentration. The maximum speed occurs at a Pt/Au segment length ratio of approximately 2.