

Wet Chemical Synthesis of Soluble Gold Nanogaps

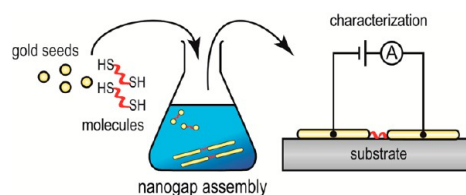
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CONSPECTUS

A central challenge in molecular electronics is to create electrode pairs separated by only a few nanometers that can accommodate a single molecule of interest to be optically or electrically characterized while residing in the gap. Current techniques for nanogap fabrication are largely based on top-down approaches and often rely on subsequent deposition of molecules into the nanogap. In such an approach, the molecule may bridge the gap differently with each experiment due to variations at the metal–molecule interface. Conversely, chemists can readily synthesize gold nanorods (AuNRs) in aqueous solution. Through controlled end-to-end assembly of the AuNRs into dimers or chains, facilitated via target molecules, they can be used as electrical contacts. In this way, the preparation of AuNR–molecule–AuNR junctions by wet chemical methods may afford a large number of identical devices with little variation in the interface between molecule and electrode (AuNR).



In this Account, we highlight recent progress in using chemically synthesized AuNRs as building blocks for molecular electronic applications. We outline the general synthesis and properties of AuNRs and describe the aqueous growth of dimeric AuNR structures from an insulating molecule linked to AuNR precursors (gold seeds). Conjugated, electronically active molecules are typically not soluble under the conditions required for the bottom-up growth of AuNRs. Therefore, we present a strategy that utilizes host–guest chemistry in order to make such π -systems compatible with the AuNR growth procedure. In order to electrically characterize the AuNR–molecule–AuNR constructs, we must transfer them onto a substrate and contact external electrodes. We discuss the implications of using electron-beam lithography for making this contact. In addition, we introduce a novel fabrication approach in which we can grow AuNR nanogap electrodes *in situ* on prepatterned substrates, thus circumventing post-processing steps that potentially damage the nanogap environment. Due to the inherent optical properties of AuNRs, electromagnetic field enhancement in the nanogaps lets us spectroscopically characterize the molecules via surface-enhanced Raman scattering. We discuss the incorporation of oligopeptides functionalized with acetylene units having uniquely identifiable vibrational modes. This acetylene moiety allows chemical reactions to be performed in the gaps via click chemistry, and the oligopeptide linking platform opens for integration of larger biological components.

1. Introduction

With their facile synthesis and remarkable size-dependent properties, metallic nanoparticles have earned their place among the key components of nanoscale research.^{1–3} Gold nanorods (AuNRs), in particular, have received tremendous attention over the past decade due to their unique physical properties that originate from their inherent anisotropy.⁴ AuNRs offer great promise for application in such diverse areas as cancer treatment,⁵ medical imaging,⁶ plasmonics,⁷ and sensing,⁸ while also providing a basis for new

fundamental discoveries in various fields. A recurring theme in our research group concerns the bottom-up self-assembly of nanoscale or molecular building blocks into functional architectures for molecular electronics.^{9,10} Herein, we highlight some recent developments in controlling the molecular assembly of AuNRs into organized linear constructs, suitable for such molecular electronic systems. The focus is on the fabrication of nanometer sized gaps between adjacent particles with the prospect of using these “nanogaps” as a platform for studying electron transport through single or a few molecules.

The fabrication of electrode pairs separated by a few nanometers is one of the fundamental challenges in nanotechnology.¹¹ Nanogap electrodes are applied in research areas such as single-molecule electronics,¹² plasmonics,⁷ and spectroscopy.¹³ The goal of single-molecule electronics is to utilize single molecules as electrical components by understanding how electron transport through molecules is governed by the chemical structure of a molecule in order to tailor its specific function. Molecules are typically deposited by evaporation or from solution in order to bridge a nanogap between an electrode pair. The contact is mediated by chemical anchoring groups ensuring a connection between the metal electrode and the target molecule. A challenge regarding this approach is that molecules may bridge the gap differently with each experimental realization due to variations at the metal–molecule interface, leading to large differences in the device properties.¹⁴ In plasmonics and spectroscopy, the nanogaps between metal nanostructures can greatly enhance the signal of molecules due to an elevated electromagnetic field, so-called “hot-spots”.¹⁵ This field enhancement permits detection at the single-molecule level and is interesting with respect to studying the activity of (bio)molecules, for monitoring chemical reactions directly in a nanogap, and for sensing applications. Despite being beyond the capabilities of current microfabrication techniques,¹¹ nanogaps are successfully prepared in research laboratories via alternative top-down methods such as the mechanical controllable break junction,¹⁶ scanning-probe techniques,¹⁷ shadow mask evaporation,¹⁸ and electromigration.^{19,20} Common shortcomings of these techniques are low throughput, time consumption, and the requirement for expensive and complicated experimental setups. In contrast, bottom-up approaches for the fabrication of nanogaps have the potential to be more cost-effective and provide parallel fabrication schemes for the production of multiple devices ($\sim 10^{23}$) in only a few synthetic steps.^{21,22} Research in this direction has typically focused on the integration of colloid nanoparticles into devices, where precise control of placement and orientation is required.^{23,24} For example, Dadosh and co-workers²³ explored solution-based dimerization of 10 nm gold particles with dithiol end-capped conjugated molecules, electrostatically trapping them in lithographically defined electrode gaps, which permitted electrical characterization of the molecules. Later work from the same group used the plasmonic properties of self-assembled silver particles as hot spots to spectroscopically characterize single molecules.²⁵ In our group, we demonstrated the fabrication of segments of gold

nanowires separated by 1–3 nm gaps via lipid templated self-assembly of gold nanoparticles,²⁶ which made it possible to insert electronically active oligo(phenylene vinylene) (OPV) molecules into the gaps and measure the I – V response of the network.²⁷ A similar approach was later demonstrated by Liao et al.²⁸ who fabricated two-dimensional nanoparticle arrays exposed to redox-active molecules enabling cyclic conductance switching of the molecular junctions.

Herein, we account for recent progress toward utilizing chemical fabrication and self-assembly of nanogaps using colloidal anisotropic metallic nanoparticles. Gold nanorods are readily synthesized in aqueous solution, and controlled end-to-end assembly of the AuNRs into dimers or chains, facilitated via target molecules, allow them to be employed as electrical contacts. The ultimate goal of preformation of the AuNR–molecule–AuNR junctions already in solution is to increase reproducibility of the individual junctions compared with the top-down approaches discussed above and in this way afford a large number of identical copies of single-molecule devices in solution before depositing the structures onto substrates for electrical characterization.

2. Nanorod Synthesis

The synthesis of AuNRs follows a wet-chemical, seed-mediated growth approach first introduced by Jana et al.^{29,30} The AuNRs are grown from seed particles in the presence of the surfactant cetyltrimethylammonium bromide (CTAB). CTAB has larger affinity for the {110} and {100} side facets of the evolving AuNRs, causing gold reduction to occur predominantly on the accessible {111} end facets, which leads to anisotropic crystal growth (Figure 1A). CTAB covers the resulting AuNRs in the form of a bilayer oriented normal to the surface.³¹

Furthermore, the addition of Ag(I) ions to the growth solution has been shown to produce single-crystalline {100}-oriented nanorods, presumably through selective underpotential deposition (UPD) of Ag onto the gold {110} facets.³²

The dimensions of the AuNRs are tunable; they can be prepared in lengths between 50–600 nm, with typical diameters ranging from 10–20 nm, and possess unique optical properties due to their inherent anisotropy. Coherent oscillations of delocalized surface electrons (plasmons) can be induced upon interaction with light. When in resonance, these surface plasmons oscillate along both the long and short axes of the AuNRs giving rise to distinct absorption

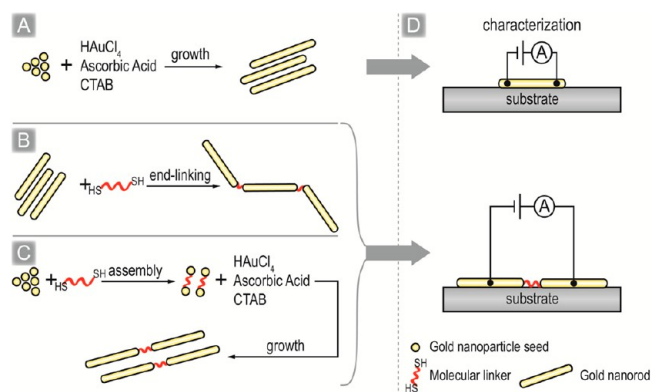


FIGURE 1. Schematic illustrations of AuNR synthesis and strategies for end-to-end assembly. (A) Gold nanoparticle seeds subjected to growth conditions favoring anisotropic growth of nanorods. (B) End-to-end linking of pregrown AuNRs via reaction with a molecular linker. (C) Assembly of the seed precursors prior to growth resulting in end-linked structures. (D) Deposition of AuNR assemblies on substrates for optical and electrical characterization.

bands that can vary from the visible to the near-infrared part of the spectrum by tuning the size of the AuNRs. Plasmon excitation in nanorods leads to an amplified electromagnetic field due to charge up-concentration at the metal–dielectric interface. This amplification is orders of magnitudes larger in nanogaps between dimers of metal NRs and can be exploited to study single molecules via the effect known as surface-enhanced Raman scattering (SERS). For details on AuNR synthesis, growth mechanisms, and optical properties, we refer to recent reviews.^{33–35}

In the following, we describe solution-based self-assembly of AuNRs using linker molecules and present a strategy to address the challenges associated with the metal–molecule interface. Next, the assembly of AuNRs using biorecognition motifs and the incorporation of uniquely identifiable chemical handles potentially allowing for in-gap click chemistry is discussed. Finally, the deposition and assembly of AuNRs onto surfaces is presented with strategies for *in situ* growth of nanogaps directly on electrically addressable substrates.

3. Solution-Based Assembly of AuNRs into Electronic Nanogap Devices

Directed assembly of AuNRs has been realized using a wealth of different strategies into both three-^{36,37} and two-dimensional^{38,39} superstructures as well as one-dimensional linear constructs. Most research has focused on the assembly of low aspect ratio (<5) AuNRs by adding molecular linkers to pregrown AuNRs (Figure 1B). For example, in work by the group of Thomas, both α,ω -alkanedithiols and

aromatic dithiols have been used to covalently assemble AuNRs into nanochains via Au–S bonds and study the effects of plasmonic coupling between AuNRs in close proximity.⁴⁰ Following similar assembly strategies, the same group investigated the effect of SERS at the nanorod edges and in dimer junctions and showed large SERS enhancement of molecules in the nanometer sized junctions compared with that for molecules residing at the edges of the AuNRs.⁴¹ Tetrakis(4-sulfonatophenyl)porphyrin was used as the linking agent by Zhang and co-workers to create a “plasmon ruler” by controlling the interparticle distance through tuning of the linker concentration.⁴²

Other linear assembly strategies exploit intermolecular interactions of molecules grafted to the end facets of the AuNRs. Coordination chemistry directed end linking of AuNRs has been demonstrated via metal complexation of thiol-terminated terpyridine derivatives,^{43,44} with the average interparticle distances matching the calculated sizes of the linking complexes (~2–3 nm). An elegant example of controlling the AuNR orientation was realized by Zhong et al.,⁴⁵ who utilized bifunctional poly(ethylene glycol) molecules to selectively bind to either the side or the end facets. In this way, AuNRs were selectively controlled into either end-to-end, end-to-side, or side-to-side configurations with the end-to-end oriented AuNRs exhibiting the largest SERS enhancement compared with the other configurations. Nie et al.⁴⁶ selectively functionalized the ends of AuNRs with hydrophobic polystyrene polymers; upon variation of the solvent composition, the AuNRs were assembled into end-oriented rings, side-to-side aggregated bundles, or 3D nanospheres. Careful tuning of the water contents of a DMF/H₂O mixture even permitted control over the nanogap sizes between adjacent AuNRs from ~6 to 12 nm.

End linking of AuNRs with different aspect ratios has been demonstrated in the absence of linking agents in water by control of the amount of stabilizing CTAB surfactant.⁴⁷ Removal of CTAB from the AuNR surface occurs primarily at the end facets, which presumably exposes the alkyl parts of the surfactant resulting in a hydrophobically driven end assembly.⁴⁷

In 2009, we developed a new approach for AuNR end linking.²¹ Instead of assembling the AuNRs after growth (Figure 1B), it was demonstrated that end-to-end linked gold nanorods can be grown directly from chemically linked seeds (Figure 1C). Self-assembling citrate-stabilized AuNP seeds using a water-soluble dithiol-functionalized poly(ethylene glycol) (HS-PEG-SH) linker and exposing the

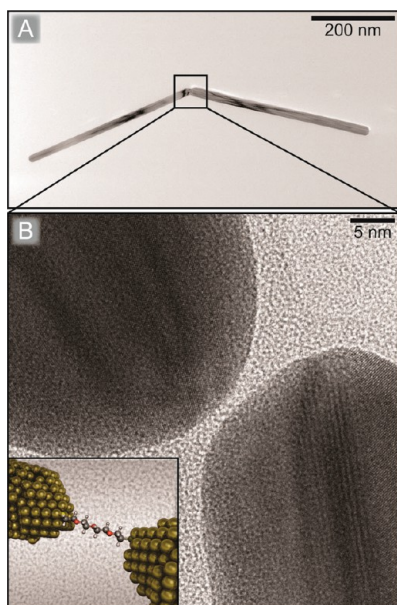


FIGURE 2. TEM images of (A) a gold nanorod dimer grown following the scheme in Figure 1C and (B) the nanogap between the nanorods. Inset: Illustration of the linker molecule bridging the gap.

assembled seeds to growth conditions favoring anisotropic growth resulted in dimeric nanorods (Figure 2A) with a 1–3 nm gap, a size perfectly suited for molecular electronic or plasmonic applications (Figure 2B). The yield of the grown dimers was up to 55% per batch compared with AuNR batches grown in the absence of linking agent (see Supporting Information, Figure S1).

The HS-PEG-SH linking molecule is electrically insulating due to the nature of its poly(ethylene glycol) backbone. However, solution deposition of conducting molecular wires into the gap of surface-immobilized AuNR dimers is an alternative option currently being pursued (*vide infra*). The AuNRs grown in the study were approximately 500 nm in length, making them ideally suited for contacting to external macroscopic electrodes.

With the strategy of direct growth of AuNR dimers sandwiching a molecule, the next step in producing molecular electronics is to incorporate conjugated π -systems that exhibit interesting electrical properties into the nanogap. Thiol end-capped OPVs show exciting electrical properties¹⁴ but are typically not soluble under the aqueous reaction conditions required for AuNR growth. The possibility to encapsulate OPVs in cyclodextrins (CDs), to make the OPVs water soluble and thus compatible with the presented strategy, was investigated in our laboratories.²² Fluorescence-titration experiments showed that OPV and CD form a water-soluble inclusion complex with a 1:3 stoichiometry (see Figure 3A,B).

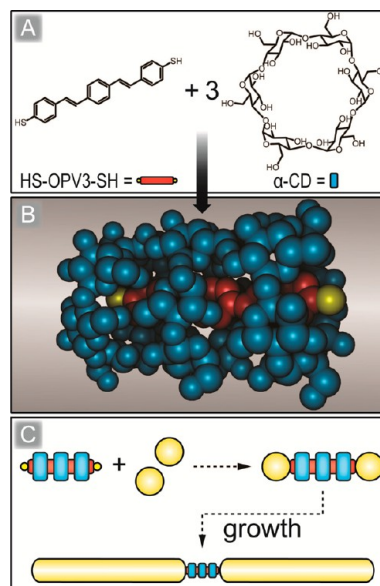


FIGURE 3. Strategy for incorporating π -conjugated molecular wires into the AuNR junctions prepared in aqueous solution. (A,B) Thiol end-capped OPV3 forms a water-soluble inclusion complex with α -CDs with a 1:3 stoichiometry. (C) Strategy for attaching gold seeds to the inclusion complex via Au–S bonding and growth into AuNRs.

As a water-soluble host, the CDs serve the purpose of bringing the OPV molecule into aqueous solution, making it accessible for gold-seed attachment followed by growth into AuNRs (Figure 3C). In addition, the CD host provides a structurally and dielectrically well-defined environment. Structurally, the OPV/CD inclusion complex will be preorganized in a way likely to limit the number of possible binding motifs between sulfur and gold. This confinement may provide a more reproducible molecule–metal interface compared with molecules randomly deposited into a pre-fabricated nanogap.

A complementary approach was explored by Wijaya and Hamad-Schifferly,⁴⁸ who developed a customizable ligand-exchange procedure to replace the CTAB layer on the AuNRs with alkanethiols, rendering the nanorod hydrophobic and thus soluble in organic solvents. The group proceeded to functionalize the ligand exchanged AuNRs with a variety of different molecules.

In order to enable electrical characterization, the assembled AuNR systems must be transferred from solution onto a suitable substrate on which a metal–metal contact can be established by electrode deposition using, for example, electron-beam (e-beam) lithography (Figure 4A,B). Contacting individual AuNRs typically results in resistances of 100–500 Ω , which is in good agreement with the bulk resistivity of gold, suggesting that the CTAB bilayer covering

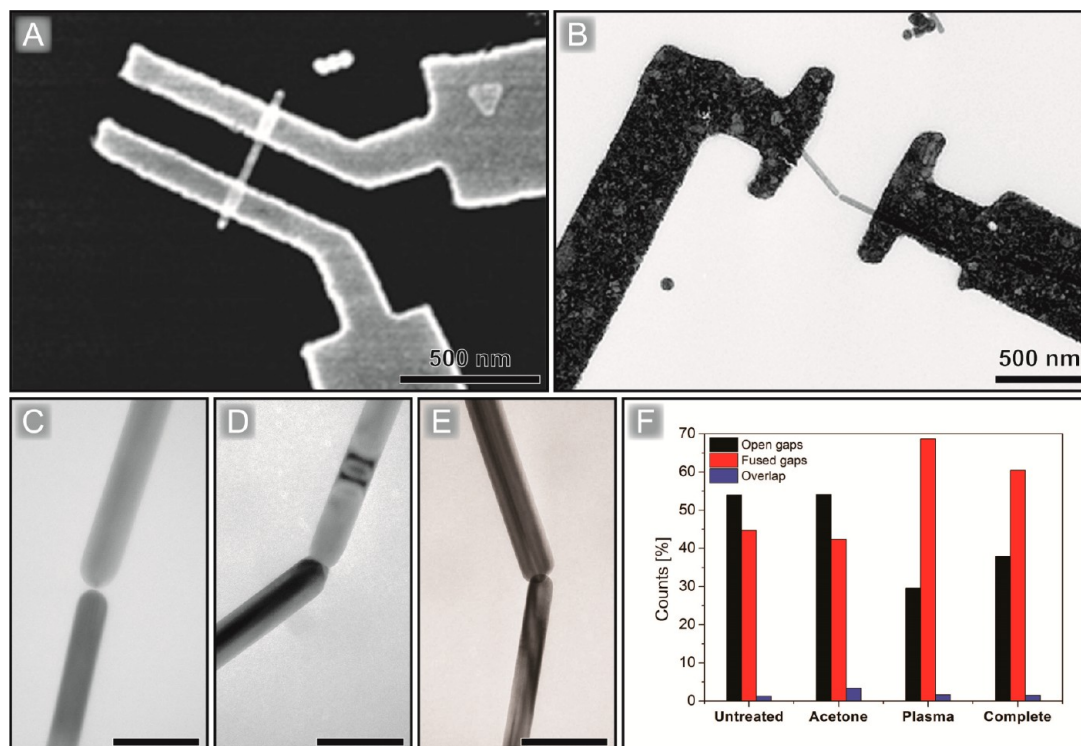


FIGURE 4. Micrographs of (A) a single AuNR and (B) a dimeric structure connected with lithographically defined electrodes. TEM images of (C) open, (D) fused, and (E) overlapping indistinguishable gaps. Scale bars are 50 nm. (F) Counts of open, closed, and overlapping gaps in samples that are untreated, immersed in acetone, ashed in O₂-plasma, and subjected to complete lithographic treatment except for plasma.

the AuNR surface does not prevent reliable electrical contact.⁴⁹ The conditions employed to contact a single AuNR may be too harsh for contacting the nanogaps between AuNR dimers. To test their robustness and stability, AuNR dimers, prepared as described in Figure 1C, were subjected to the different steps of e-beam lithography in order to examine the effect on the nanogap environment.⁴⁹ The study distinguishes between open nanogaps, fused gaps, and overlapping AuNRs, where the TEM viewing angle makes it impossible to determine whether it is a fused or open gap (Figure 4C–E). The results (Figure 4F) reveal that while some of the lithographic steps have little or no effect on the nanogaps, it is difficult to avoid reducing the overall number of viable junctions when completing the entire electrode fabrication cycle.

4. Device Integration on Planar Surfaces

For device integration, AuNRs must be deposited or grown from solution onto suitable planar surfaces, preferably with controlled positions and orientations of the individual AuNRs. Directional assembly of AuNRs can be obtained, for example, by stretching AuNR-embedded poly(vinyl alcohol) polymer films,^{50,51} via electric field-assisted deposition between lithographically defined electrodes,⁵² by electrospinning,⁵³ or by

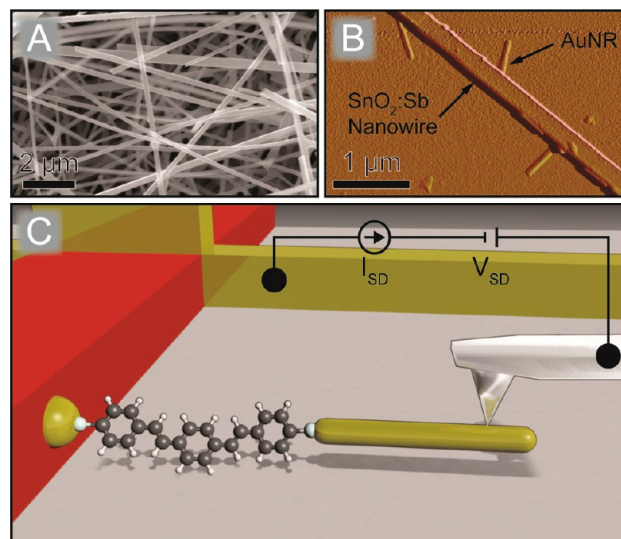


FIGURE 5. Self-assembly approach using AuNP-coated SnO₂/Sb nanowires to capture AuNRs via dithiol-functionalized OPV3. (A) SEM image of conducting SnO₂/Sb nanowires. (B) AFM image of AuNRs assembled onto a nanowire. (C) Schematic of the electrical circuit using the nanowire as one contact via evaporated metal electrodes and a conductive AFM probe as the other contact closing the circuit.

using CNTs as templates.⁵⁴ Both positional and directional control at the single AuNR level were recently demonstrated employing capillary forces.^{55,56} In another

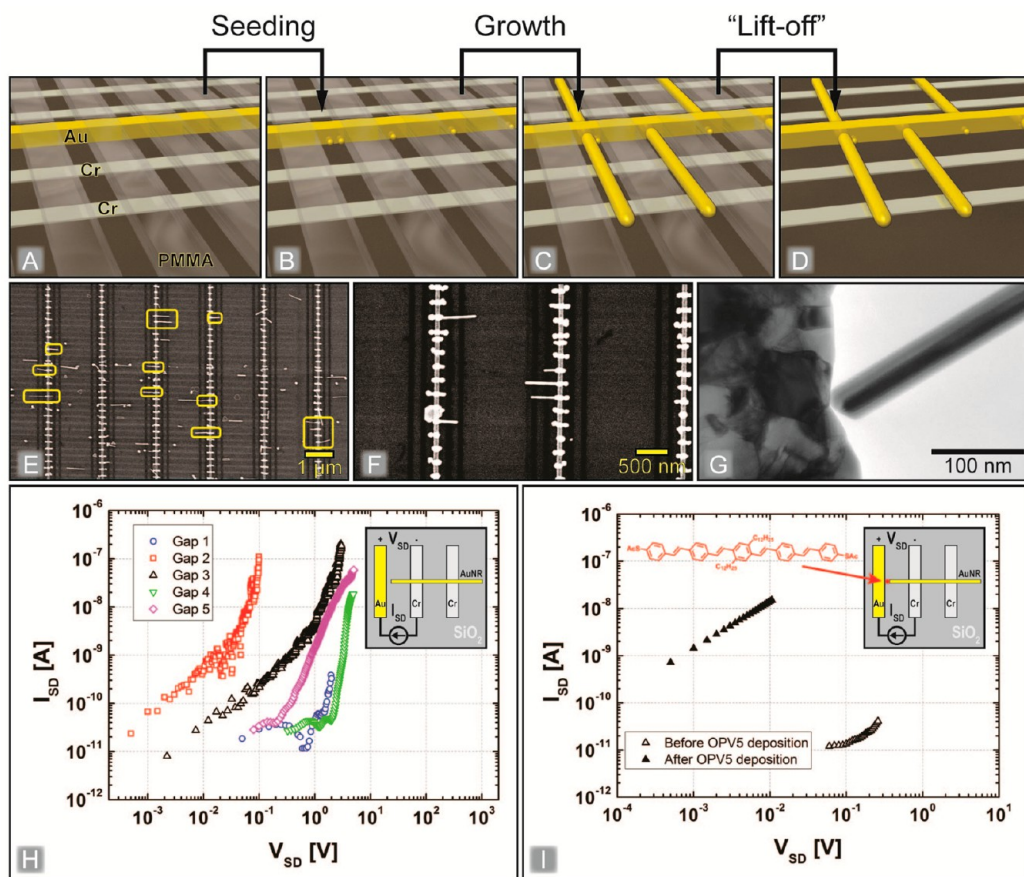


FIGURE 6. Aligned growth of AuNRs in PMMA channels and parallel fabrication of nanogaps. (A) Prefabricated chip containing five parallel electrodes (one Au wire surrounded by two Cr wires on each side) with perpendicular channels developed in PMMA. (B–D) Seeding of the chip by immersion into a seed solution, followed by growth and removal of the PMMA via “lift-off” in acetone. (E, F) AuNRs protruding from the main Au wire bridging two Cr electrodes (yellow markers). (G) TEM image of a typical ~ 1 nm gap formed between the central Au electrode and a AuNR. (H) Electrical characterization of five different gaps measured in the configuration given in the inset image. (I) I – V characteristics of a nanogap before (open markers) and after (solid markers) incubating the chip in a 1 mM solution of OPV5. The observed change in resistance of about 4 orders of magnitude suggests a successful insertion of OPV5 in the nanogap.

approach by Tang and co-workers,⁵⁷ gold nanorods were assembled onto gold nanoparticle-coated conducting SnO_2/Sb nanowires (Figure 5A) via thiol end-capped oligo(phenylene vinylene)s.

The AuNP-coated nanowires were placed in a solution of OPV molecules that assembled onto the AuNPs on the nanowires through the Au–S bond. Following transfer to a substrate, the nanowires were placed in a solution of AuNRs, which were captured by the available thiol at the other end of the OPV (Figure 5B), sandwiching the molecule in the nanogap between nanowire and nanorod. With the SnO_2/Sb nanowire as an electrical contact and a conductive AFM probe placed on the nanorod (Figure 5C), the OPV resistance was determined to be around 50 M Ω , a value in good agreement with previous reports of measurements on similar molecules.

The discussed methods for placing AuNRs onto surfaces all require the deposition of presynthesized AuNRs from

solution. An interesting alternative to this approach is to grow AuNRs directly on substrates. First demonstrated by Taub et al.⁵⁸ and later by Zamborini et al.,⁵⁹ deposition of AuNP seed precursors on surface-modified substrates followed by transfer of the substrate into a growth medium permitted the growth of AuNRs directly on the substrate. The position and direction of the resulting AuNRs were random, but some positional control was later achieved using soft lithography to print wide tracks of seed precursors onto the substrate followed by nanorod growth,⁶⁰ and local orientation alignment was obtained through a surface chemical amidation reaction.⁶¹ Recently, we obtained a high degree of alignment by assembling seeds in developed guiding channels, tens of nanometers wide, in a spin-coated layer of poly(methyl methacrylate) (PMMA) on a silicon substrate. The walls of the PMMA channels restrict the growth direction of the evolving AuNRs, resulting in parallelly aligned AuNRs

on a large scale.⁶² An additional handle for the positional control of the AuNRs was added by pre patterning the substrate with lithographically defined electrodes, placed beneath and perpendicularly to the PMMA guiding channels (Figure 6A–D).

We found that the seeds primarily assembled in the channels near the central Au wire, resulting in AuNRs protruding from the Au wire and bridging the two surrounding Cr electrodes (Figure 6E,F). A TEM study of the interface between the central Au electrode and the AuNR revealed the presence of nanogaps with an average size of 2.4 ± 1.5 nm (Figure 6G), and this interface was further characterized through electrical measurements (Figure 6H). The tunneling resistances of the nanogaps were typically measured to be on the order of 1–10 G Ω , which is expected for 1–2 nm wide gaps. In particular, the chemically prepared nanogaps were preliminary tested as a platform for molecular devices by depositing an OPV5 derivative from solution. The device displayed a change in resistance of almost 4 orders of magnitude (from 10 G Ω to 500 k Ω , Figure 6I), which may be attributed to OPV5 bridging the junction between gold electrode and AuNR. The exact gap size may be tailored by attaching conjugated molecules to the central Au electrode prior to addition of seed precursors and growth. Not only would the target molecule determine the gap size ensuring a perfect match between molecule and gap length, it would also circumvent random solution-based molecular deposition.

5. Incorporation of Biofunctionality in Nanogaps

Considerable recent attention is given to interfacing biological systems with colloidal nanoparticles and electronics,⁶³ and in this respect end linking of AuNRs can also be promoted using biorecognition systems. One of the first examples was published by Caswell et al.⁶⁴ who exploited a biotin–streptavidin pair to induce self-assembly. AuNRs modified with antigens have been assembled in the presence of antibody,⁶⁵ while oligonucleotide hybridization⁶⁶ and oligonucleotide–mercury(II) molecular recognition⁶⁷ were shown to encourage end linking. The interrod distance of end-to-end linked AuNRs was found to be 10 nm by Zhen and co-workers, in good agreement with the size of the DNA–aptamer/thrombin recognition system employed.⁶⁸ Smaller biomolecules such as the amino acid cysteine are known to promote AuNR assembly through electrostatic interactions.⁶⁹ Recently, we expanded this approach to covalently end

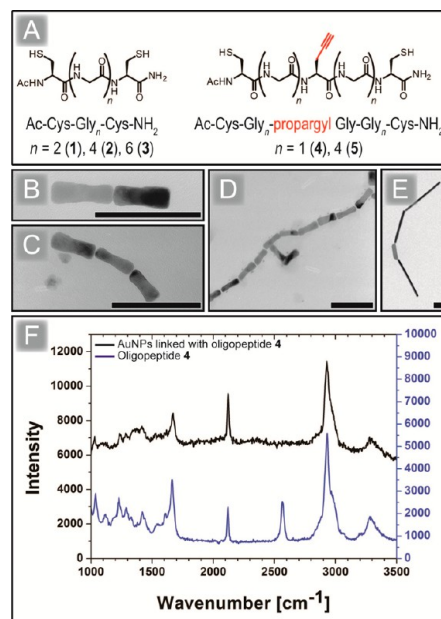


FIGURE 7. Controlled end-to-end assembly of AuNRs using dicysteine-terminated oligopeptides. (A) Chemical structures of (1–3) simple oligopeptides and (4, 5) peptides with an incorporated acetylene moiety (red). AuNRs with aspect ratios of (B–D) 3.6 and (E) 18 assembled with oligopeptide 1. Scale bars are 100 nm. (F) Raman spectrum of oligopeptide 4 showing the resonance from the acetylene functionality at 2122 cm⁻¹ and the S–H band from cysteine at 2566 cm⁻¹, and SERS spectrum of Au structures linked with oligopeptide 4 showing the acetylene mode. The loss of the S–H band indicates that the oligopeptide is linking the nanoparticles with Au–S bonds through its cysteine residues.

link AuNRs of different aspect ratios via dicysteine-terminated oligopeptides of various lengths (Figure 7), thereby controlling the gap sizes within a small range.⁴⁷ Statistically, about 50% of the AuNRs are part of end-to-end linked dimers or nanochains (see Supporting Information, Figure S2). No end-linking is observed when oligopeptides terminated with amino acids not having any thiol functionality are employed.

The development of an oligopeptide-linking platform is motivated by the high modularity of peptides. This feature enables the possibility to integrate diverse functionality into molecular nanogap junctions. We⁴⁷ incorporated a propargyl-substituted glycine into the oligopeptide backbone, which is uniquely identifiable using SERS (Figure 7F). Introduction of this acetylene functionality does not disrupt the linking process, and it is an ideal chemical handle that may be utilized further to attach novel target molecules directly in the gaps via copper-catalyzed click chemical reactions.⁷⁰ In-gap chemistry of a similar nature has been demonstrated by Chen and co-workers.⁷¹ They reported the fabrication of molecular tunnel junctions exploiting the

alkyne–azide click reaction directly within gold nanogaps fabricated using an on-wire lithography technique. SERS was employed to follow and verify the assembly process in the gaps. Connecting functional biomolecules, for example, the photosynthetic reaction center, directly to metallic nanowires using this approach is one future prospect that we are currently pursuing.

6. Outlook

Here, we have described recent strategies in the preparation of soluble self-assembled nanogap electrodes, bridged by functional organic molecules, and their incorporation into solid-state systems. The successful realization of molecule-based electronics as a potential successor to modern day microelectronics will require an exceptional level of understanding of the fundamental properties of individual and ensembles of molecules and their integration into nanogap electrode systems. The wet chemical approach presented here can potentially overcome a number of the shortcomings related to “top-down” fabrication schemes, such as scalability, reproducibility, and versatility. However, a few challenges yet remain in maturing this field; central among these is to develop and optimize the reaction conditions for obtaining true thermodynamic control of the reaction, rather than producing a kinetically controlled reaction mixture. Furthermore, the detailed nanogap geometry remains unknown with a combination of insulating CTAB molecules and electronically active linking molecules responsible for the electronic transport across the junction. The emerging insight obtained from single-molecule measurements, combined with the progress in the design and preparation of self-assembled nanoelectrodes may eventually lead to the realization of actual electronic circuitry, fabricated through wet chemical synthesis from the “bottom up”.

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Supporting Information. Statistics of linked and unlinked AuNR when grown from seed particle precursors, and relative orientation of AuNRs linked with cystein-terminated oligopeptides. This material is available free of charge via the Internet at <http://pubs.acs.org>.

BIOGRAPHICAL INFORMATION

Titoo Jain obtained his Ph.D. from the University of Copenhagen under the supervision of Profs. Nørgaard and Bjørnholm. In his thesis work, he explored the use of gold nanorods for the self-assembly of nanoscale and molecular electronics. He is currently working in the Danish chemicals industry.

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Kasper Nørgaard is Associate Professor at the Department of Chemistry and the Nano-Science Center at the University of Copenhagen. He received his Ph.D. from the university in 2005 and did postdoctoral work at the University of Nijmegen, The Netherlands. His current research activities include supramolecular chemistry, graphene, and molecular electronics.

FOOTNOTES

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The authors declare no competing financial interest.

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