

Sub-5 nm Metal Nanogaps: Physical Properties, Fabrication Methods, and Device Applications

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Sub-5 nm metal nanogaps have attracted widespread attention in physics, chemistry, material sciences, and biology due to their physical properties, including great plasmon-enhanced effects in light–matter interactions and charge tunneling, Coulomb blockade, and the Kondo effect under an electrical stimulus. These properties especially meet the needs of many cutting-edge devices, such as sensing, optical, molecular, and electronic devices. However, fabricating sub-5 nm nanogaps is still challenging at the present, and scaled and reliable fabrication, improved addressability, and multifunction integration are desired for further applications in commercial devices. The aim of this work is to provide a comprehensive overview of sub-5 nm nanogaps and to present recent advancements in metal nanogaps, including their physical properties, fabrication methods, and device applications, with the ultimate aim to further inspire scientists and engineers in their research.

1. Introduction

Sub-5 nm metal nanogaps, a unique nanostructure, have attracted enormous attention due to their striking properties and extensive applications in physics, chemistry, material sciences, and biology. Typically, in light–matter interactions, metal nanogaps can focus the incident light to generate plasmonic-coupled electromagnetic field localization that will enhance the local electromagnetic field intensity by 2–5 orders of magnitude. Taking advantage of the plasmonic effect, sub-5 nm metal nanogaps are employed in plasmonic antennas, subwavelength waveguides, nano-optics, molecular detection, and medical treatment. The localized electromagnetic field would be enhanced significantly as the size of the nanogaps decreases toward the nanometer scale (<5 nm).^[1,2] Moreover, many phenomena have been revealed for sub-nanometer nanogaps, such as nonlocal electromagnetic effects, optical rectification, inelastic electron tunneling, and Fabry–Perot

interference.^[3–9] As the typical dimensions of molecules/nanoparticles are on the scale of a few nanometers, sub-5 nm metal nanogaps are suitable as electrodes, serving as fundamental building blocks of transistors,^[10,11] switches,^[12] and molecular electronics.^[13–15] Many of the physical phenomena, such as charge tunneling, Coulomb blockade, and the Kondo effect, occur in the single nanoparticle/molecule devices.^[16–22] Using quantum tunneling mechanics, nanogap electrodes have been adopted in the development of fast DNA sequencing technology.^[23] Due to the rich fundamental physical properties, sub-5 nm metal nanogaps can not only serve as electrodes in molecular and electronic devices, but also be applied as optical nanostructures

in optical and sensing devices by taking advantage of the high plasmonic enhancement due to light–matter interactions. Therefore, the scope of the nanogaps included in this review is broad, ranging from vacuum/air nanogaps and filled nanogaps to nanogaps based on nanoparticles.

The fabrication methods for metal nanogaps with widths greater than 10 nm are relatively mature. By contrast, the nanofabrication methods for sub-5 nm nanogaps still face challenges in achieving a controllable gap size, accurate dimensions, scalable fabrication, and reproducible features. Sub-5 nm gap fabrication has undergone significant developments in recent years, and many researchers have proposed a variety of methods to achieve sub-5 nm nanogaps. Notably, most of the methods have combined several distinct techniques throughout the fabrication process to achieve sub-5 nm metal nanogaps. Based on the key fabrication techniques employed, we can briefly classify the fabrication methods into two groups, i.e., the physical and chemical methods, as summarized in **Figure 1**. All the physical methods have employed planar nanofabrication techniques as one basic step, whereas most of the chemical methods have been developed based on metal nanoparticles.

Figure 1 shows a summary of the fabrication methods and applications for sub-5 nm metal nanogaps. The existing physical fabrication methods for sub-5 nm nanogaps include direct fabrication, controllable metal deposition, insertion of an ultrathin layer between two metal layers, and breaking-/cracking-defined nanogaps. Among the direct fabrication methods, electron-beam lithography (EBL) and focused-ion beam (FIB) milling have typically been chosen because sub-5 nm nanogaps can be directly fabricated by the high resolution electron or ion beam.^[24,25] However, a direct fabrication strategy is not an ideal option due to its low fabrication yield, low efficiency, high

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time consumption, and high cost. Therefore, various methods that utilize multiple fabrication techniques were developed to achieve features with sub-5 nm nanogaps to satisfy the needs of specific applications. Controllable metal deposition, including oblique deposition and shadow deposition, is a method frequently employed to create sub-5 nm nanogaps by controlling the deposition parameters of metal over patterns prefabricated using traditional nanofabrication techniques.^[26,27] Furthermore, in recent years, insertion of an ultrathin layer has proven to be a promising technical strategy for creating sub-5 nm nanogaps with wafer-scale throughput via atomic layer deposition (ALD) or 2D materials with a precise control of the gap width.^[28,29] Another noteworthy fabrication method for sub-5 nm nanogaps produces the so-called breaking-/cracking-defined nanogaps, formed by imposing external stimuli, such as an electric current, a mechanical force, or a strain, has been widely employed in single-molecule devices.^[22,30,31]

In contrast to physical methods, chemical fabrication methods for sub-5 nm nanogaps mostly rely on nanoparticles, including nanoparticle self-assembly, covering metal nanoparticles with ultrathin dielectric shells and embedding interior nanogaps in metal core-shell nanoparticles. The simplest nanogaps were formed by nanoparticle self-assembly. To control the gap between adjacent nanoparticles, DNA, organic molecules, or polymers were selected as spacers, and nanogaps from sub-nanometer to a few nanometers were formed between nanoparticles.^[32,33] To avoid the contamination from linker molecules, core-shell nanoparticles with dielectric (SiO₂ or Al₂O₃) shells covering on metal cores were synthesized, and the gap sizes were defined by twice the shell thickness.^[34] Core-shell nanoparticles with stable and reproducible interior nanogaps were synthesized, which could be easily tuned by controlling the thickness of the spacer between the metal core and shell.^[35,36] In addition to nanoparticle-based methods, electrochemical methods are frequently used to achieve sub-5 nm nanogaps by controlling the monitored parameters, such as the voltage, current, frequency, and time.^[37,38] The electrochemical method is a combination of physical and chemical methods, because the working electrodes are first patterned using conventional nanofabrication techniques.

Based on these striking fabrication methods, different types of sub-5 nm nanogap structures have been successfully produced and applied in optical, sensing, molecular, and electronic devices, as shown in Figure 1. Although plasmonic enhancement could appear in different metal nanogap structures under light stimuli, the field enhancement is greatly improved in sub-5 nm nanogaps, promoting their application in optical and sensing devices. In addition, the sub-5 nm nanogap enables the quantum tunneling effect to easily occur, indicating its promising application in molecular devices.

Based on the fabrication methods employed, the metal nanogap structures can be categorized into six groups according to their features, as shown in Figure 2. The nanogaps exhibited in Figure 2a–c are fabricated by physical methods, and the remaining nanogaps in panels d–f formed between two nanoparticles arise from chemical methods. As presented in Figure 2a,b, two types of nanogaps are fabricated on 2D films based on planar nanotechnologies, including simple long slit and electrode pair nanogaps, respectively. In recent years,



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3D nanogap structures have been successfully developed, as shown in Figure 2c. As illustrated in Figure 2d–f, three types of nanogaps based on nanoparticles exist, such as interparticle nanogaps, interior nanogaps in core-shell nanoparticles, and nanogap between a nanoparticle and a 2D surface.

Previously, metal nanogaps have been reviewed with different specific focuses, such as on fabrication methods based on physical^[39] or chemical methods,^[40] various applications in specific areas, including electrodes,^[41,42] molecular devices,^[43,44] or

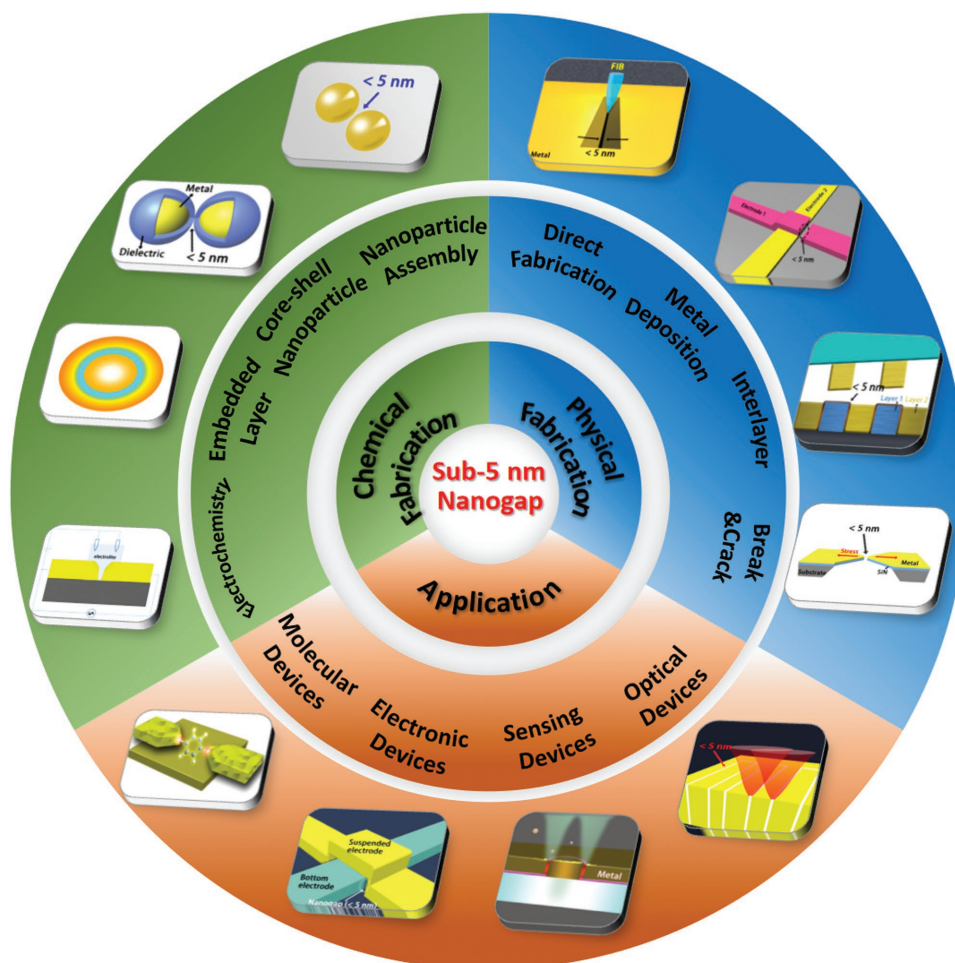


Figure 1. Summary of sub-5 nm metal nanogap fabrication methods and device applications.

plasmonic devices,^[40,45] and fabrication techniques for massive production.^[39,40] These reviews offer very good references for researchers and practitioners from a very specific perspective

or from a broad view of metal nanogaps. The sizes of the nanogaps reported in these reviews are wide, ranging from sub-nanometer to tens of nanometers, without a specific selection.

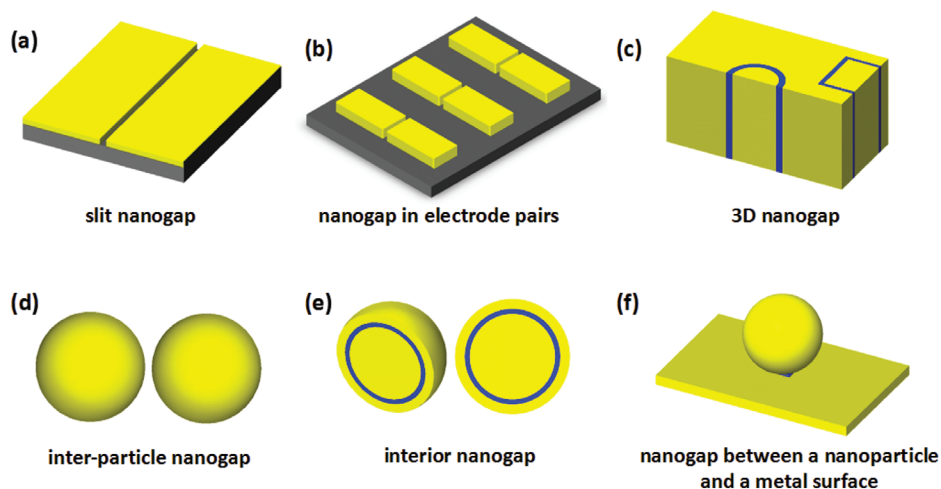


Figure 2. Schematic illustrations of different nanogap structures. a–c) The nanogap structures obtained using physical fabrication methods. d–f) The nanogap structures formed by nanoparticles synthesized using chemical fabrication methods.

Compared with the relatively mature fabrication methods for nanogaps, sub-5 nm is a critical gap size that requires special methods to achieve. Moreover, many important properties and applications can only be achieved with sub-5 nm nanogaps, and the corresponding fabrication and devices are more challenging; thus, this area deserves more attention. In this review, we focus on the sub-5 nm metal nanogaps and aim to provide a comprehensive review of sub-5 nm metal nanogaps with respect to their physical properties, fabrication methods, and device applications.

This review consists of five sections. Following the introduction, the physical properties of metal nanogaps are described briefly in Section 2. Then, various fabrication methods for sub-5 nm metal nanogaps are systematically categorized and introduced in Section 3. The fabrication methods are divided into physical and chemical methods based on the key techniques employed. In Section 4, the applications of sub-5 nm nanogaps in four typical fields are described, namely, sensing, optical, molecular, and electronic devices. Finally, the outlook for further development and potential applications of sub-5 nm nanogaps are discussed in Section 5.

2. Physical Properties of Sub-5 nm Nanogaps

Light-matter interactions generate many interesting phenomena, in which surface plasmon resonances (SPRs) induced by collective oscillation of electrons is one of the most attractive effects because it can lead to high electromagnetic field enhancement in nanomaterials and nanostructures. Among the numerous nanostructures, metal nanogaps are undoubtedly highly spotlighted because they enable high electromagnetic field confinement and enhancement at the subwavelength scale.^[40] Figure 3a presents the scheme of a simple metal nanogap, in which the local electromagnetic field in the interparticle nanogap of a Au nanoparticle dimer is extremely intense as a result of the localized SPR (LSPR).^[2] The magnitude of the localized electromagnetic field has been theoretically and experimentally demonstrated to critically depend on the size of the nanogap.^[1,46,47] Utilizing dimers in a simulation model, Le Ru and Etchegoin demonstrated that the localized field enhancement increases monotonically by 4 orders of magnitude when the gap size decreases from 10 to 1 nm.^[1] Experimentally, the electromagnetic field was enhanced by threefold or fourfold compared to that for a normal nanogap by squeezing photon through a gap (slit) of a few nanometers.^[48,49]

As the gap size decreases toward the sub-5 nm and even sub-nanometer scale, quantum mechanical effects, including non-local screening and electron tunneling, become very important and begin to influence the optical response.^[7] Figure 3b schematically illustrates the influence of these quantum mechanical effects on the plasmonic resonances of the nanogap. For gaps wider than 2 nm ($>10\delta_F$), where δ_F is the Feibelman parameter related to the surface charge positions and is usually on the angstrom scale, the plasmon resonance still corresponds to the classical regime. The plasmon behavior can be correctly described using the local Maxwell's equations. However, in the quantum mechanical regime, the classical theory cannot describe the optical response in a fairly satisfactory manner. Nonlocal

screening occurs in nanogaps of 1–2 nm and makes significant changes in the plasmon response, leading to spilling of the surface charges out of the classical boundaries.^[7–9,50] As a result of the nonlocal effect, the true electromagnetic enhancement factor is much lower than the value obtained using classical electrodynamics by adopting only the dielectric response (permittivity) of the bulk metal material,^[51] although the field enhancement continues to increase. The upper limit for the electromagnetic field enhancement can be obtained as the gap distance decreases to 1 nm.^[52–57] However, as the gap size is scaled down to the sub-nanometer, the electron tunneling effect occurs across the gap at optical frequencies, which completely modifies the behavior of the plasmonic response. The conduction electrons can tunnel through the potential barrier across the junction at optical frequencies, resulting in a blueshift of the resonance center^[32,58] and the quenching of the local field enhancement.^[59–61]

In addition to in light-material interactions, metal nanogaps have been utilized as electrodes, mostly supporting molecular devices, exhibiting notable physical features under an external electric field. In a simple setup for charge transport experiments, a voltage difference is applied to two electrodes separated by an insulating gap. A third metallic electrode is placed in the middle of the gap, which is called “island” since it is surrounded by an insulator,^[62] as presented in Figure 3c. To travel from the source to the drain, the electrons must go through the island. In the macroscopic island, the charge transport obeys Ohm's law, and the resistance is proportional to the length of the conductor. However, these laws are not valid when the electrodes are very close, down to the nanometer regime. The conduction of electrons through the insulating gaps between the source and the island and between the island and the drain is assumed to occur by quantum tunneling. In the real quantum tunneling electronics, the island could be an individual molecule, a nanocrystal, a nanotube, or a lithographically defined quantum dot, attached to metallic electrodes via tunnel barriers.^[14] The electron transport between two nanogap electrodes is dominated by single electron charging and energy level quantization. In a single electron device, the electron additional energy E_a must be greater than $100 k_B T$ to avoid thermally induced random tunneling events,^[63] in which $E_a = E_c + E_k$. As illustrated in Figure 3d, E_c and E_k are sufficiently large only when the gap size is sufficiently small, enabling the electron to go through the island and electrodes. When the gap width between two electrodes is less than 1 nm, the electron additional energy could be as large as a few electron volts, thus promising its operation at room temperature.

Single electron transport occurs in the molecular devices based on sub-5 nm nanogaps, indicating the possibility of measuring some intrinsic physical properties, such as Coulomb blockade and the Kondo effect, which are determined by a combination of the classical Coulomb charging, electronic level spacing, spin, and vibrational modes.^[16–22] Figure 3e presents a representative figure of the Coulomb blockade effect for a single C_{60} transistor, in which conductance was suppressed near zero bias voltage, followed by step-like current jumps at higher voltages.^[17] At low bias, an electron does not have sufficient energy to tunnel into a molecule; therefore, the current is blocked through the Coulomb blockade effect. The dark triangular regions correspond to the conductance gap, and

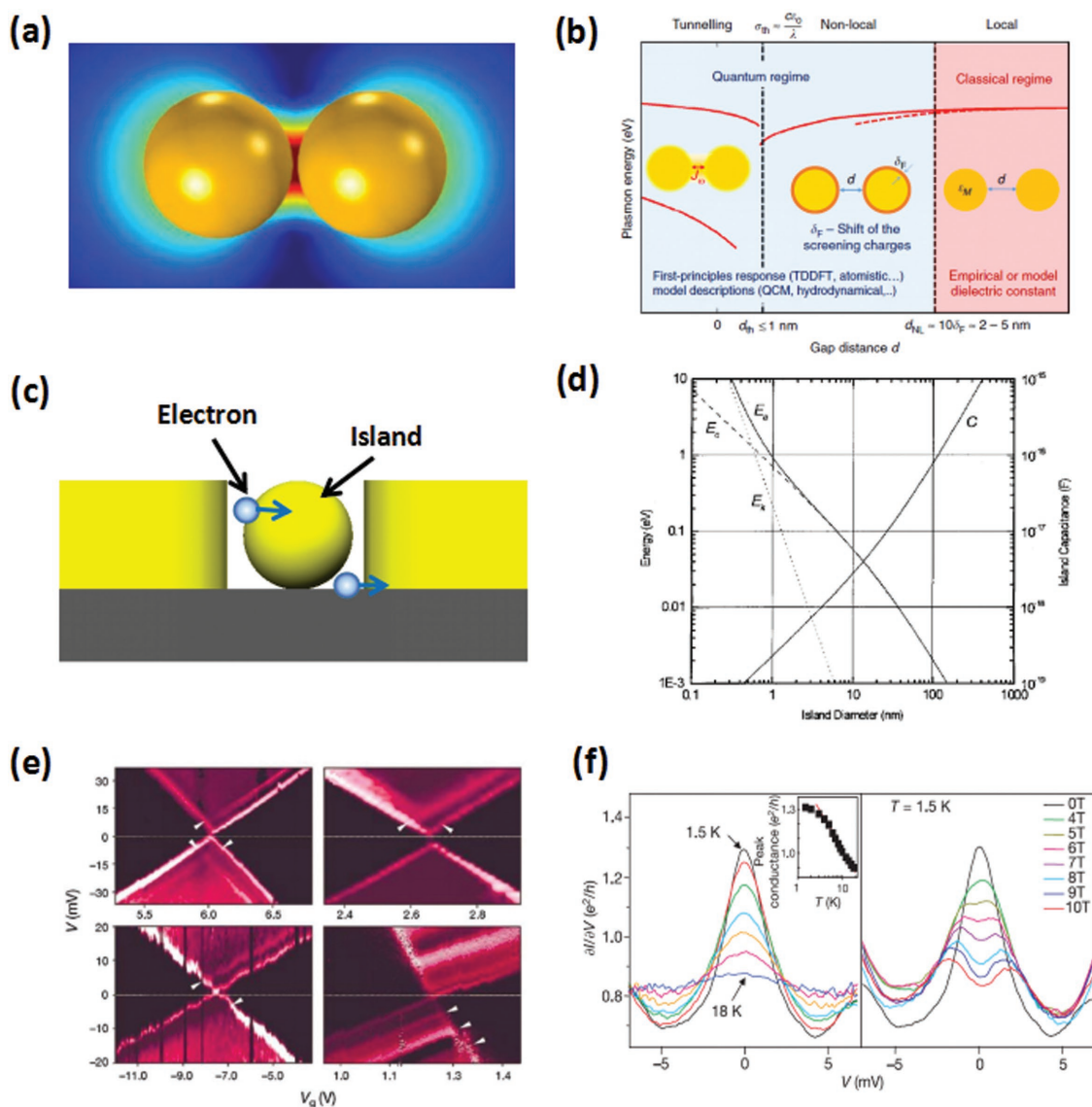


Figure 3. a) Finite-element simulations of the electromagnetic field enhancement distribution for a Au nanosphere dimer with a gap size of 2 nm in water that has an excitation line at 645 nm. Reproduced with permission.^[2] Copyright 2016, Macmillan Publishers Limited. b) The impact of quantum mechanical effects on plasmonic resonances. Sketch of the different regimes for the plasmon resonances of a sphere dimer in vacuum identified as a function of the gap distance d . Reproduced with permission.^[7] Copyright 2016, Nature Publishing Group. c) Illustration of a simple setup of charge transport experiments. d) The calculated single electron addition energy E_a (solid line) and its components, charging energy E_c (dashed line), and electron kinetic energy E_k (dotted line) as a function of the island diameter. Reproduced with permission.^[63] Copyright 1999, IEEE. e) Different conductance plots as a function of the bias voltage and the gate voltage obtained from four different single-molecule devices. Reproduced with permission.^[17] Copyright 2000, Nature Publishing Group. f) (left) The temperature dependence of the Kondo peak. The inset shows the $V = 0$ conductance as a function of temperature. (right) Magnetic-field dependence of the Kondo peak. Reproduced with permission.^[22] Copyright 2002, Nature Publishing Group.

the bright lines represent peaks in the differential conductance. Suppressing a certain gate voltage, the electron can easily tunnel through the blockade with a low bias. These transport features clearly indicate that the conduction in this device is dominated by the Coulomb blockade effect. Figure 3f shows the logarithmic temperature dependence of the differential conductance $\partial I/\partial V$ peak between 3 and 20 K, in which the logarithmic temperature dependence and magnetic-field splitting are attributed to the Kondo effect. The Kondo effect gives rise to the formation of an entangled, many-body state arising

from the interaction of a single magnetic impurity and a sea of conduction electrons.^[64] When a magnetic impurity is inserted between electrodes, an electron can jump from the magnetic impurity to an electrode. During this time, another electron from the Fermi sea must jump to the impurity to replace the remaining one. The coherent superposition of such cotunneling events results in the screening of the local spin of the impurity, thereby producing Kondo resonance, in which a transport channel appears at zero bias and a conductance peak will be observed at zero bias.^[30] Kondo effects have been

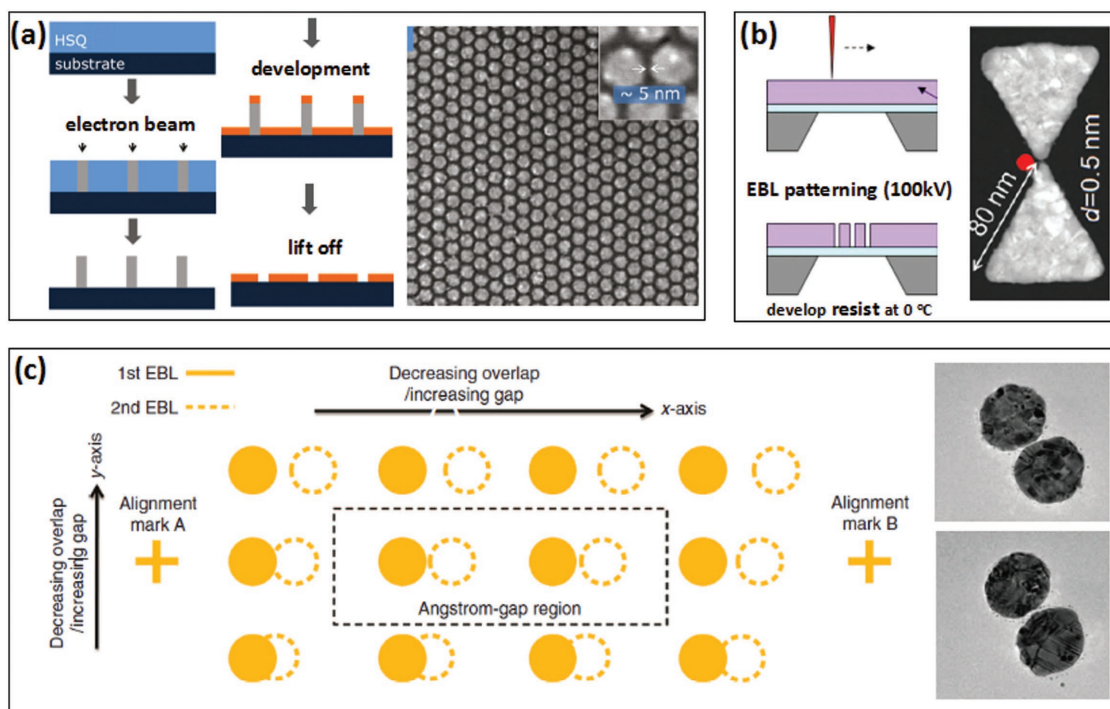


Figure 4. a) Lift-off process using HSQ to fabricate dense metal structures separated by small gaps and scanning electron microscopy (SEM) image showing a large array of gold nanodisks. Reproduced with permission.^[24] Copyright 2011, American Chemical Society. b) (left) Schematic process for fabricating Au nanostructures on a Si_3N_4 membrane. Reproduced with permission.^[69] Copyright 2010, American Vacuum Society. (right) High-angle annular dark field scanning TEM (HAADF-STEM) image of nanoprism dimers fabricated on a Si_3N_4 membrane. Reproduced with permission.^[71] Copyright 2012, American Chemical Society. c) Schematic of the two-step EBL process for fabrication. Solid objects represent the patterns in the first step. Dashed objects represent the patterns in the second EBL step, aligned with the first EBL pattern using a procedure that corrects the offset position (error = 10 nm) and rotational angle (error = 1 mrad). TEM images of nanodisk dimers formed on a TEM membrane using two-step EBL. Reproduced with permission.^[59] Copyright 2014, Macmillan Publishers Limited.

observed for quantum dots,^[16,19] nanotubes,^[65] as well as a wide variety of molecules.^[21,22,66]

The striking physical properties described above depend solely on the sub-5 nm gap structures. Therefore, the fabrication methods are undoubtedly important in the study of these physical properties and the related device applications. In the following section, the various fabrication methods will be introduced in two groups, physical and chemical methods.

3. Fabrication Methods for Sub-5 nm Nanogaps

3.1. Physical Fabrication Methods

3.1.1. Direct Fabrication Methods

Direct fabrication methods refer to direct fabrication of sub-5 nm metal nanogaps using a single technology under special conditions, such as EBL and FIB milling. However, these nanopatterning technologies are still unable to deliver a nanostructure with a resolution of a few nanometers' scale. To overcome this obstacle, special processing steps were introduced to realize a sub-5 nm nanogap.

EBL has an ultimate resolution that can be below 10 nm. However, the final size of the transferred pattern depends on the combined properties of the resist and developer. Directly

fabricating sub-5 nm metal nanogaps via EBL remains a challenge due to the proximity effect originating from backscattered electrons;^[67] thus, the formation of sub-5 nm nanostructures requires special conditions and experimental methods.

In 2002, Liu et al. fabricated electrode pairs using an automated proximity effect correction algorithm based on the self-consistent exposure equalization technique.^[68] To fabricate nanogap arrays over large areas, Duan et al. developed a method based on a lift-off process based on high-resolution EBL with a negative-tone hydrogen silsesquioxane (HSQ) resist,^[24] and a large array of gold nanodisks with ≈ 5 nm gaps were successfully obtained. As presented in Figure 4a, negative-tone HSQ was selected because the HSQ process required less electron-beam exposure and resulted in resist structures that are mechanically and thermally stable compared with a positive resist (e.g., poly(methyl methacrylate) or PMMA).

In addition, a substrate with lower density and atomic number could greatly reduce the range and intensity of the proximity effect, respectively. In 2010, Koh et al. patterned triangle dimers with sub-1 nm gaps on electron-transparent 30 nm thick silicon nitride (Si_3N_4) transmission electron microscope (TEM) windows using high-resolution EBL.^[69,70] As shown in Figure 4b, the Si_3N_4 substrate is essentially transparent to the electron beam, and thus, nanoprism dimers separated by gaps as small as 0.5 nm have been achieved by EBL patterning (100 kV) as well due to the small proximity effect.^[71]

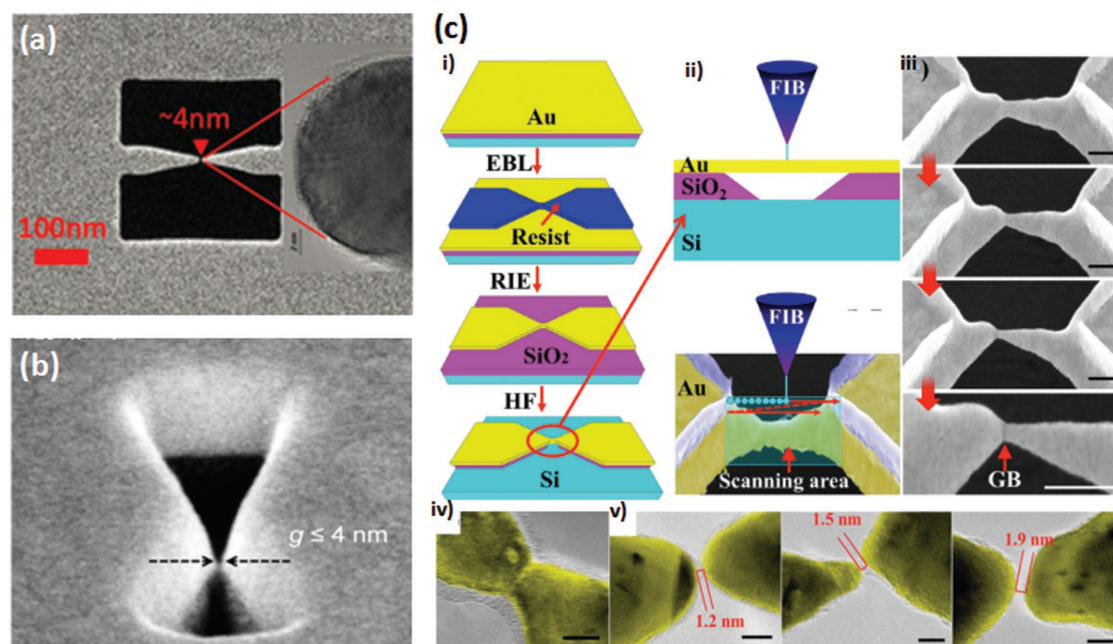


Figure 5. a) Two gold antennas separated by 4 nm, machined in 100 nm thick gold using a He-ion beam. The inset shows a TEM image of a gold tip. Reproduced with permission.^[73] Copyright 2013, Cambridge University Press. b) Top view images of a fabricated 3D gap-plasmon antenna milled by a Ga-ion beam. Reproduced with permission.^[49] Copyright 2015, American Chemical Society. c) i,ii) The fabrication scheme of a single GB junction. iii) SEM images of the same Au wire after a series of FIB milling, through which a single GB junction was formed. The scale bar is 100 nm. iv) TEM images of the fabricated single GB junction. v) TEM images of fabricated nanogap electrodes with a 1–2 nm gap width. The scale bar is 5 nm. Reproduced with permission.^[25] Copyright 2015, WILEY-VCH Verlag GmbH & Co.

In 2014, Zhu and Crozier proposed a two-step EBL process to decrease overlap and achieve metallic dimers separated by angstrom-scale gaps.^[59] As illustrated in Figure 4c, the designed pattern ranges from dimers with overlapping features (overlapped by 40 nm) on the lower left corner to dimers with large gap widths (40 nm) on the upper right corner. In this way, the gap width as the distance between the two closest points on two disks can be tuned from ≈ 2 Å to 5.8 nm.

FIB milling has been demonstrated to be a convenient technique for directly fabricating nanopatterns. However, fabrication of sub-5 nm nanogaps via FIB milling still faces challenges due to the low resolution (>10 nm) of the Ga-ion beam. Milling-based He-ion lithography (HIL) has been reported as another resist-free milling technique for the fabrication of nanostructures, and with even higher and better precision compared with Ga⁺ FIB milling.^[48,72] Carl Zeiss Company reported a 4 nm nanogap on a suspended Au film obtained using HIL, as presented in Figure 5a.^[73] However, due to the lighter ions of HIL, the milling speed is lower than that of Ga-ion milling, resulting in low fabrication efficiency and a high cost. To improve the Ga⁺ FIB resolution limit, a proximal milling technique was proposed by Kim et al. in 2015.^[49] In this method, the distances between two triangular milling patterns that were intentionally off-designed were precisely controlled, giving rise to a 3D plasmon antenna with 4 nm gap, as shown in Figure 5b.

Recently, Cui et al. have developed a method to produce 1–2 nm Au gap electrodes through the breaking of a single grain boundary (GB) junction of a Au nanobridge utilizing Ga⁺ FIB milling.^[25] As shown in Figure 5c, a suspended Au bridge is first fabricated on a SiO₂/Si substrate using EBL and reactive-

ion etching (RIE), followed by hydrofluoric (HF) etching. Then, traditional Ga⁺ FIB milling is performed on the suspended Au. The reduced raster scanning strategy of FIB milling is used for the milling of the Au wires in a designated area. By controlling the ion dose during the FIB milling process, the original Au wires can be milled into a bowtie-shaped structure with a neck at the nanometer scale, where a single GB is always located. Finally, a nanogap of 1–2 nm in width is formed at the location of the GB by performing the FIB reduced raster scanning process carefully on the single GB junction.

Technically, FIB milling has potential for integrated circuit (IC) construction. However, the FIB process requires delicate operation, and mass production cannot be achieved, limiting further commercial application. One potential drawback of FIB-fabricated electrodes is that the implanted Ga⁺ ions on the surface of the electrodes may change the transport properties of the molecular device.

In addition to utilizing ion beams to mill patterns on metal films, high-energy electron beam can also be used for direct fabrication of nanogaps. In a TEM, metals can be reshaped using electron beams, in particular, gold and platinum, which have been demonstrated for the controlled manufacturing of electrodes with nanometer-sized gaps.^[74,75] Metal films ranging 10–50 nm are deposited on Si₃N₄ membrane substrates by standard thermal evaporation procedures, and then bridge-shaped nanopatterns are obtained using EBL. Employing an electron beam, a sub-nanometer gap is successfully achieved, as presented in Figure 6a. Two-terminal and three-terminal electrodes have been fabricated successfully. Although a 1–2 nm nanogap can be controllably fabricated via TEM milling, the

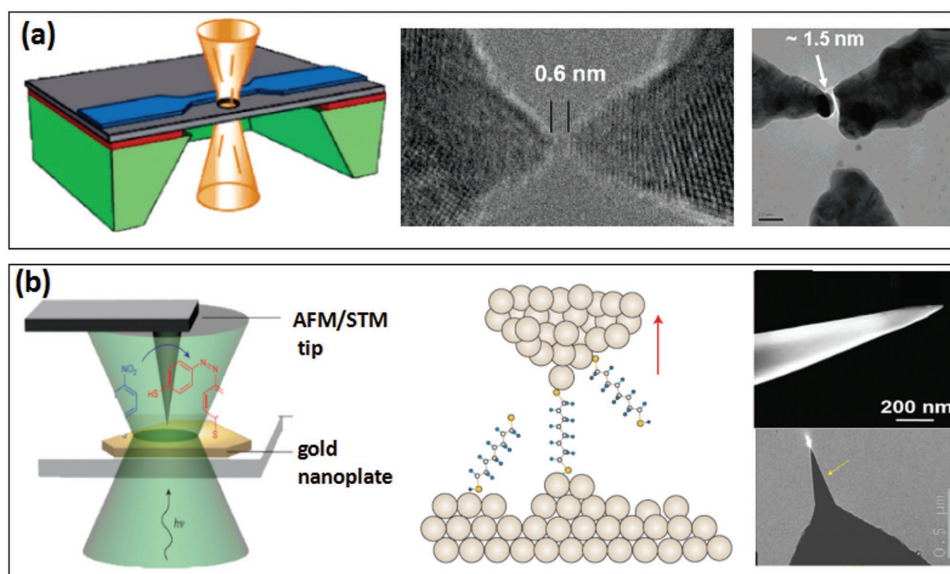


Figure 6. a) Scheme of the TEM milling process. High-resolution transmission electron microscopy (HRTEM) images after the formation of a gap in the lower part of the bridge. Reproduced with permission.^[74] Copyright 2005, American Chemical Society. TEM milling of a three-terminal device for molecular detection. Reproduced with permission.^[75] Copyright 2007, American Chemical Society. b) Scheme of the TERS experimental setup. Reproduced with permission.^[83] Copyright 2012, Macmillan Publishers Limited. Scheme of the STM molecular junction setup. Reproduced with permission.^[82] Copyright 2006, Nature Publishing Group. (top) SEM image of an electrochemically etched Au tip. Reproduced with permission.^[84] Copyright 2004, American Institute of Physics. (bottom) TEM image of a polyethylene-coated tip. Reproduced with permission.^[77] Copyright 2010, Macmillan Publishers Limited.

obtained device can only be constructed in vacuum on a dielectric layer substrate, and the yield is considerably low.

Except the above direct fabrication methods, the tip-based approach can also be used to construct a nanogap, thus producing a “tip-based nanogap,” which is formed by modifying the tip of a SPM system, typically by a scanning tunneling microscopy (STM)^[76–78] or an atomic force microscopy (AFM),^[79–81] as presented in Figure 6b. The scanning probe microscopy (SPM) tip acts as the top electrode and is gently brought into direct contact with the molecules, whose movement can be precisely controlled by a piezoelectric transducer, enabling the control of the nanogap in the sub-nanometer regime. The molecules are dispersed on a conducting substrate, acting as the bottom electrode, while an external circuit is used to measure the current–voltage characteristics. The disadvantage of this type of tip-based nanogap is that it is difficult to couple it with commercial devices, hindering its practical application. Tip-based nanogaps have been widely used to measure the charge transport properties of a very small number of molecules.^[82] In addition to studying the transport properties of molecules, tip-based nanogaps have been frequently utilized in tip-enhanced Raman spectroscopy (TERS), in which a nanogap is constructed experimentally by using an SPM system to control the approach of a gold tip to a gold nanoparticle or a gold film.^[83,84] A dual AFM tip configuration was realized by orienting two gold nanoparticle-terminated AFM tips tip-to-tip.^[54] The most obvious advancement arising from this arrangement is the background-free broadband spectroscopic characterization of the tip–tip plasmonic nanocavity throughout the sub-nanometer regime.

3.1.2. Controlled Metal Deposition

Although sub-5 nm nanogaps have been successfully obtained using EBL, FIB milling, and TEM milling, these techniques are demanding and time consuming and have low throughput. Therefore, some simple and scalable fabrication methods have been widely proposed over the past ten years. Among these, controllable metal deposition has been proven to be a feasible way to achieve metal nanogaps over large areas by precisely controlling the deposition parameters, such as the deposition time and angle, on patterns fabricated using traditional nanofabrication techniques, such as EBL, FIB milling, and RIE.

A straightforward single-step fabrication method for patterning various antennas over large areas has been reported.^[26,85,86] As presented in Figure 7a, upon normal incidence deposition, the evaporated metal layer not only grows vertically but also slightly expands horizontally due to surface diffusion. When the metallic layer extends above the photoresist layer, an elongated nanogap is formed. Nanogap channels and complex 3D nanostructures have been successfully fabricated. Although this method is simple to operate, the gap width cannot be as small as 5 nm or smaller due to the uncontrollable expansion length of the metal layer.

Shadow deposition was introduced to form sub-5 nm gaps, in which the size and shape of the metal pattern are determined not only by the resist mask dimensions, but also by the angle of incidence and the deposition thickness.^[87–90] As shown in Figure 7b, glancing angle deposition (GLAD) was achieved by flipping the substrate to the opposite direction. At a certain thickness, sub-5 nm nanogaps were formed over mm²

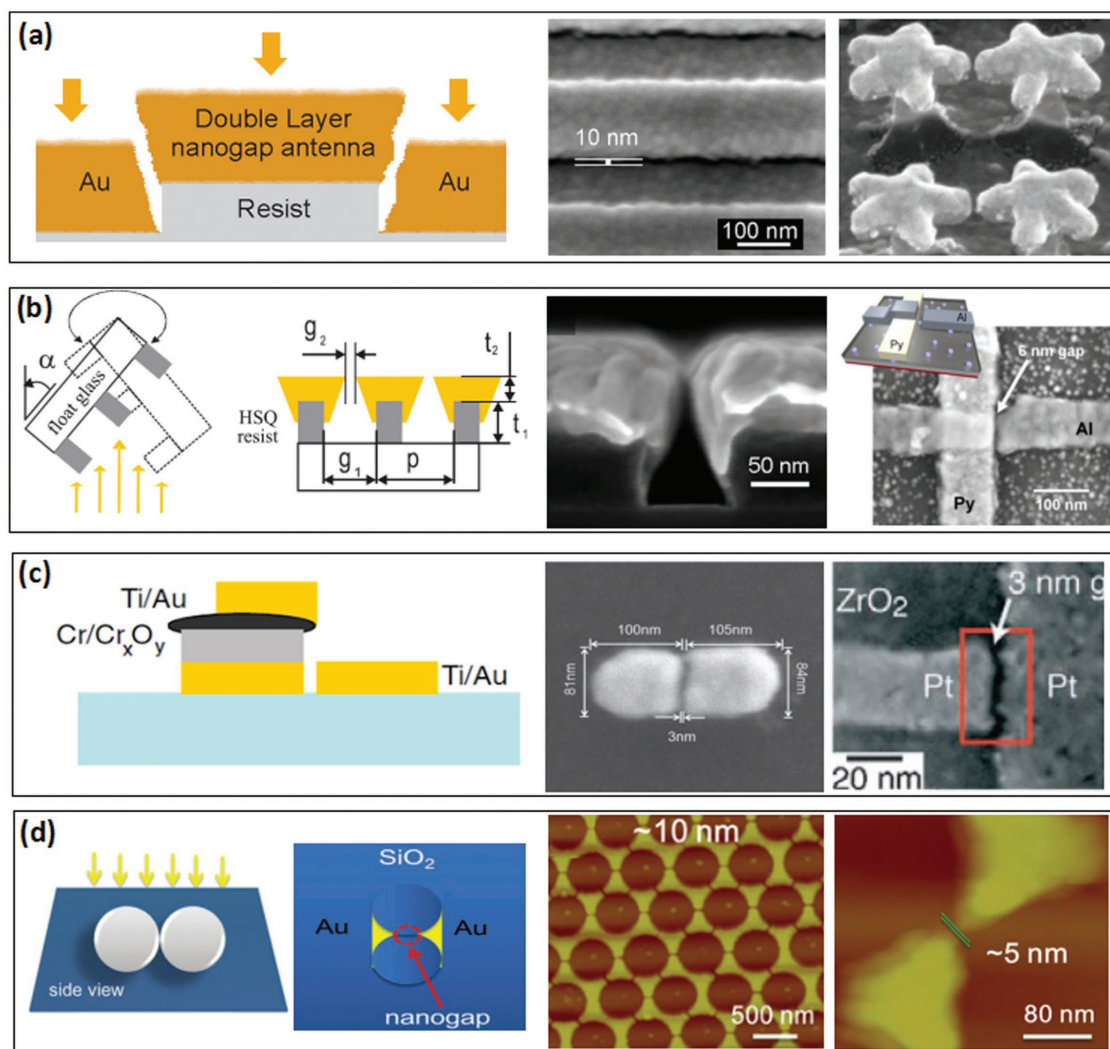


Figure 7. a) Diagram of the directly evaporated cross-section of a double-layer pattern with a nanogap channel for a metal layer thickness greater than the resist layer thickness. SEM images of a cleaved 120 nm thick gold metal double layer structure. Reproduced with permission.^[26] Copyright 2014, American Chemical Society. Magnified view of 3D nanostar dimers with a 6 nm interparticle spacing. Reproduced with permission.^[86] Copyright 2014, WILEY-VCH Verlag GmbH & Co. b) Scheme of the glancing angle deposition process. The metal is evaporated iteratively from the two sides of the surface. Reproduced with permission.^[89] Copyright 2011, American Institute of Physics. The cross-section of a 1D grating with ≈ 10 nm gaps. Reproduced with permission.^[90] Copyright 2013, American Chemical Society. SEM image of electrodes with a 6 nm nanogap. Schematic 3D view of the gap resulting from the shadowing effect (inset). Reproduced with permission.^[91] Copyright 2014, AIP Publishing LLC. c) Schematic diagram of the fabrication process of a sub-5 nm gap using sacrificial layers. SEM image of a dimer structure in the fabricated array. Reproduced with permission.^[93] Copyright 2011, WILEY-VCH Verlag GmbH & Co. SEM image of a Pt electrode pair with a 3 nm gap. Reproduced with permission.^[27] Copyright 2007, WILEY-VCH Verlag GmbH & Co. d) The illustration of fabrication of nanogap structures by nanosphere lithography: O_2 plasma treatment and liftoff of polystyrene nanospheres to form a nanogap. AFM image of ≈ 10 nm nanogap arrays and a nanogap of ≈ 5 nm. Reproduced with permission.^[98] Copyright 2016, WILEY-VCH Verlag GmbH & Co.

areas.^[89,90] By employing shadow-edge deposition, ≈ 5 nm gap electrodes have been fabricated for single electron transistor (SET) devices.^[91] Theiss et al. fabricated arrays of plasmonic nanoparticles with separations on the order of 1 nm using the angle evaporation technique, a freestanding ZEP mask.^[92]

In addition to resist masks defined by lithography techniques, sacrificial layers are used as another type of mask for controllable metal deposition.^[93] As illustrated in Figure 7c, a chromium layer was oxidized and then expanded laterally on the order of several nanometers, resulting in it overhanging the edge of the silver layer. The silver layer served as the spacer

layer to form an undercut structure beneath the chromium layer. Then, the right part of the dimer was realized by a second evaporation process. Finally, a nanogap was formed by wet etching the silver and chromium layers, together with the gold layer on top. Pairs of nanoparticles separated by a controllable gap size that can be as small as 3 nm were fabricated using this method.^[93,94] In addition to chromium layers, Al and Al_2O_3 layers are also employed as spacer layers to form 3 nm gap electrode pairs.^[27] To obtain the narrowest gaps, 5 nm of SiO_2 was added between the platinum and aluminum films to aid the subsequent removal of the thin Al film.

Nanosphere lithography (NSL), developed first by Van Duyne and co-workers,^[95–97] has been demonstrated to be a facile, inexpensive, and reproducible fabrication method for the production of large-area ordered nanostructures. However, for most of the NSL approaches, the gap sizes are dependent on the diameter of the colloidal spheres. In other words, changing the size of the gold nanotriangles, especially decreasing the gap size, is difficult. In 2017, Ji et al. developed a method based on NSL to produce electrodes with sub-5 nm nanogaps over a large area.^[98] As illustrated in Figure 7d, O₂ plasma treatment was utilized to etch a close-packed monolayer of polystyrene nanospheres. The etching process aimed at shrinking the connecting part between two adjacent nanospheres, giving rise to a mask for producing narrow gaps. With different etching times, the length of the gaps can be tuned from 10 to 5 nm. Except the dimer nanostructures, other types of nanostructures with sub-5 nm gaps were also developed by combining NSL with other fabrication techniques. A method for templated, high-throughput fabrication of a periodic array of ring-shaped nanocavities with a sub-5 nm gap was achieved by combining NSL with straightforward batch processing steps, ALD, and ion milling.^[99] As presented in Figure 7, controllable metal deposition is a promising candidate for fabricating scalable sub-5 nm nanogaps for functional devices. However, further shrinking the gap size to smaller than 3 nm using this method is difficult due to the diffusion length of metal atoms, which coalesce from each side of the gap.

3.1.3. Insertion of an Ultrathin Layer between Two Metal Layers

A sandwich-structured nanogap was obtained by inserting an ultrathin layer between two metal layers, as illustrated in Figure 8a. For many cases, this ultrathin layer was left in between the metal layers, as it does not impede the application of this nanogap. Of course, this ultrathin layer has to be removed to form a vacuum/air gap for application as electrodes. Thin film deposition techniques, such as physical/chemical vapor deposition and ALD, can provide a level of nanometric precision. Taking advantage of this feature of thin film deposition, nanoscale gap structures for which the critical dimensions are independent of lithography control have been successfully obtained.^[100,101] Miyazaki and Kurokawa produced Au/SiO₂/Au multilayers processed with FIB to the normal direction, in which a thin dielectric sheet was inserted between two noble metal slabs.^[101] Instead of using the ALD layer, sub-nanometer-thick 2D materials (e.g., graphene) are also good candidates for spacers with angstrom precision between two metal layers. However, a major limitation of this nanogap is that the orientation of the nanogap is lateral rather than upward, which is problematic for optical device applications because coupling with normally incident light into and out of the in-plane nanogap is difficult, and the illumination and collection of the light are shadowed by the metallic cover layers.

In order to fabricate easily sub-5 nm gaps by inserting an ultrathin layer, a new method called atomic layer lithography was developed, in which ALD was the key technique and used to define the nanogaps between predefined nanopattern and deposited metal film, giving angstrom-scale lateral resolution along the entire contour of structures. Compared with EBL and

FIB, the key strength of atomic layer lithography is that the critical dimension and the gap width are decoupled from the pattern size and density. In recent years, various nanostructures with different sub-5 nm nanogaps have been fabricated by this technique with good robustness and scalability.^[102–105] As illustrated in Figure 8b, a conventional optical lithography defines firstly the initial metal pattern, and then the top and vertical sidewall surfaces are conformably covered by the ultrathin alumina layer using ALD. After the deposition of a second metallic layer, anisotropic ion milling is performed to create metallic sidewalls spaced by the exposed alumina layer. Using this method, high aspect-ratio coaxial nanocavities with gaps as small as 2 nm are fabricated.^[103] Vertically oriented sub-5 nm air nanogaps could be obtained by removing the alumina layer with a buffered oxide etchant.^[106]

In addition to ion milling, another low-cost technique has been employed, using adhesive tape to remove the second layer metal to form nanometer-sized gaps.^[28,107–109] As illustrated in the top panel of Figure 8c, after patterning the vertical sidewall first, nanogaps are exposed by partially peeling off the second metal layer that coated on the ALD layer. Large-scale arrays of sub-5 nm annular gaps are formed in Ag films over Si wafers.^[28] If the second metal layer is a continuous film, then the three-layered nanopattern (i.e., the first predesigned nanopattern of the ALD layer and the second metal coating) will be peeled off together from the substrate. A periodic metal–dielectric–metal (MDM) nanostructure in which each pair of nanometer gaps was connected using planar ALD layers was massively fabricated using atomic layer lithography.^[108] Furthermore, 3D split-wedge antennas with gaps as small as 1 nm were also produced over an entire wafer by combining template stripping and atomic layer lithography.^[109] This peeling-off strategy is promising for realizing nanopatterns with ALD-defined gaps over large areas and can increase the fabrication quality and yield.

Besides the above fabrication technique, ultramicrotome sectioning or the so-called “nanoskiving” technique was introduced to create sub-5 nm nanogaps.^[29,110,111] First, Au/Al/Au sandwich film deposited on a patterned epoxy substrate was embedded in epoxy. Then, a 150 nm thick slab was fabricated using ultramicrotome sectioning, as illustrated in Figure 8d. A nanogap would be formed after the removal of the aluminum template and epoxy. The gap size can be tuned from 2 to 8 nm by controlling the thickness of the Al sacrifice layer. 3D nanogap arrays were obtained through a unique stacking procedure, followed by removing the Al interlayer and epoxy, respectively.^[111] By replacing the template layer with graphene, the gap size in a Au/graphene/Au sandwich structure could be controlled at the angstrom scale.^[29]

The insertion of an ultrathin layer method has several advantages. 1) The width of the nanogap can be precisely controlled with a resolution of angstroms by the ALD technique. 2) Nanogap structures can be fabricated over a large area, even on a wafer scale. 3) Various 2D or 3D nanostructures can be fabricated easily, meeting the requirements for different application regimes.

Strictly speaking, most of these nanogaps fabricated by inserting an ultrathin layer should be nanospaces rather than real nanogaps, as the space between the two metal layers is

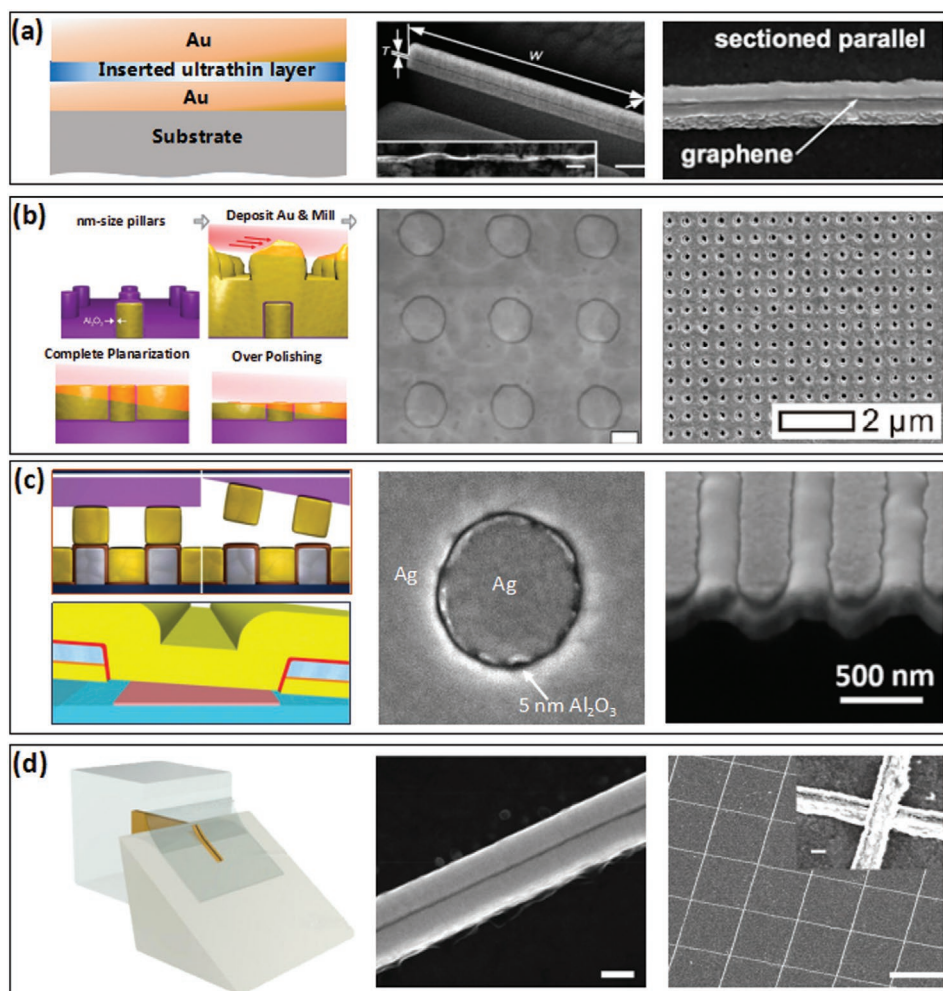


Figure 8. a) A simple schematic of the MDM nanogap. SEM image of a fabricated nanosheet plasmon cavity. Scale bar, 500 nm. Inset: TEM image of the cross-section for $T = 3.3$ nm. Scale bar, 20 nm. Reproduced with permission.^[101] Copyright 2006, The American Physical Society. SEM image of a sub-nanometer graphene-templated gap between gold nanowires. Reproduced with permission.^[29] Copyright 2015, American Chemical Society. b) Schematic of the fabrication of a coaxial nanocavity array using glancing angle ion polishing. SEM image of the planarized patterned Au surface planarized. Scale bar: 150 nm. Reproduced with permission.^[103] Copyright 2016, American Chemical Society. SEM image of a nanogap array of hole patterns. Reproduced with permission.^[106] Copyright 2010, American Chemical Society. c) (top) Removal of excess metal top layer the using an adhesive tape. And, the SEM image of a 5 nm wide annular gap in a 200 nm thick Ag film. Reproduced with permission.^[28] Copyright 2013, Macmillan Publishers Limited. (bottom) Peeling off procedure to fabricate MDM structure. Cross-sectional SEM images of a corrugated MDM structure with a 5 nm gap. Reproduced with permission.^[108] Copyright 2017, WILEY-VCH Verlag GmbH & Co. d) Scheme for fabricating graphene-templated gaps between gold nanowires using ultramicrotomy. Reproduced with permission.^[29] Copyright 2015, American Chemical Society. SEM image of a 1D gold nanogap with an 8 nm width and a 3D nanogap grid array. Inset: magnified images. Scale bar, 100 nm. Reproduced with permission.^[111] Copyright 2016, WILEY-VCH Verlag GmbH & Co.

filled by a dielectric layer. Compared with air nanogaps, the applications of this type of nanogaps are mainly limited to the field of plasmonic optical devices. To expand its applications to molecular and electronic devices, removal of the inserted layer using an etching process is needed to form an air gap, consequently, the cost is increased.

3.1.4. Breaking- or Cracking-Defined Nanogaps

As discussed in the previous section, one significant application of metal nanogaps is as electrodes in nanometer-sized electrical devices. A type of air nanogaps, called a breaking- or cracking-defined nanogap, has been demonstrated to be

suitable as and beneficial for electrodes in molecular electronics due to its unique advantages. Sub-5 nm breaking-/cracking-defined nanogaps are ideally suited for investigating molecular transport because they enable a few or even single molecules to be contacted in a relatively simple way. Based on the intrinsic mechanisms underlying the fabrication process, the breaking-/cracking-defined nanogaps can be categorized into three groups: electromigration break nanogaps, mechanical controllable break (MCB) nanogaps, and strain-induced crack nanogaps, as shown in **Figure 9**.

Electromigration break nanogap has been proposed to be well suited for fabricating nanogap electrodes and molecular-based devices. Electromigration break nanogaps were first developed by Park et al. in 1999.^[112] A metal wire/bridge with certain

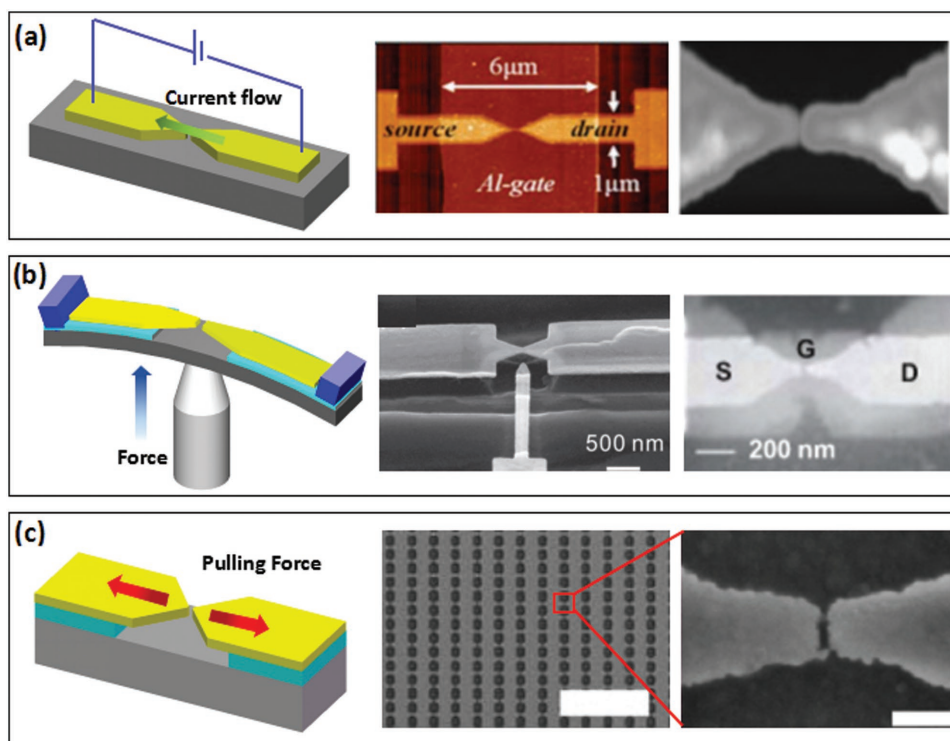


Figure 9. a) Schematic of the electromigration fabrication procedure. AFM image of a SET device fabricated by electromigration break. Reproduced with permission.^[121] Copyright 2007, American Institute of Physics. Magnified AFM image of electrodes with a gap of 1–2 nm wide. Reproduced with permission.^[22] Copyright 2002, Nature Publishing Group. b) Schematic of the MCB apparatus. Side gating with a nanogap metal electrode. Reproduced with permission.^[30] Copyright 2013, WILEY-VCH Verlag GmbH & Co. SEM images of a gated mechanically controllable break junction. Reproduced with permission.^[125] Copyright 2010, IOP Publishing Ltd. c) Schematic illustrating the fabrication of a nanogap electrode using strain-induced crack. SEM images of fabricated arrays of crack-defined break junctions. Magnified SEM image of one sub-3 nm nanogap. Reproduced with permission.^[31] Copyright 2018, Springer Nature.

constraints is typically defined using lithography techniques. As illustrated in Figure 9a, under an applied electric field, the metal atoms obtain additional kinetic energy that causes their physical movement from a high-density area so as to give rise to a nanoscale gap in the neck of the nanowire/bridge.^[27] Due to the atom flux, the structural defects increase, accelerating the melting-induced breaking at the metal bridge.^[113] In the early stage, most of the gap sizes are larger than hundreds of nanometers, resulting in them being unsuitable for single-molecule investigation. Therefore, a feedback-controlled electromigration technique was recently developed that actively adjusts the applied voltage in response to the changing conductance of the weak link to controllably create nanoscale junctions.^[114,115] Following the electromigration process, different types of nanogaps have been successfully fabricated.^[116–120] Henderson et al. introduced sandwich-type electrodes on the basis of depositing a gold layer directly on an oxidized aluminum gate, similar to three-terminal devices.^[121] Thus, the gap size can be simply controlled by changing the magnitude of the applied voltage, and the gap width of electromigration break nanogaps can be controlled to as small as 1 nm.^[22,112,116,120] In 2009, Prins et al. made nanogaps with few-atom contacts using feedback-controlled electromigration.^[122]

The fabrication of MCB nanogaps is generally considered as a mechanical way to create atomic-sized quantum point contacts from a much bulkier and hence manufacturable entity.^[30,123–126]

A schematic of a common MCB setup is shown in Figure 9b. A small piece of a metallic wire with a notch normally produced near the middle is fixed on a flexible substrate, called a bending beam. The bending substrate is normally fixed at both the ends by counter supports. A vertical movement of the push rod, which can be precisely controlled by a piezoelectric actuator or motor, can load a force on the bending beam. As the beam is bent, the metal wire starts to elongate, which results in the reduction of the cross-section at the notch and finally a complete fracture of the metal wire. After breaking of the metal wire, two clean facing nanoelectrodes are generated. The distance between the electrodes for both the opened and closed directions is controlled by the bending or relaxing of the substrate, respectively. In 2013, Xiang et al. proposed a design of a MCB nanogap by adding a side-gate electrode near the source-drain electrode.^[30] In this configuration, the gate electrode remains unchanged when one tries to break the metal wire and to obtain a large gap size by deeply bending the substrate.

Although electromigration and mechanical break nanogaps are particularly suitable for generating sharp electrode tips with sub-5 nm gaps, they can only be fabricated as discrete devices, and large-scale fabrication and the stability of the nanogap are still problematic. Some researchers have also tried to fabricate electrode arrays over large areas;^[120,127] however, the size and topography of these nanogaps cannot be precisely controlled. Therefore, fabricating sub-5 nm electronic nanogaps over large

areas remains challenging because of difficulties in ensuring dimensions and electrode separations in an accurate and reliable manner.

The production of strain-induced crack nanogap is an effective method for fabricating nanostructures in a cost-efficient manner. Different from electromigration and mechanical break nanogaps that are initiated under external stimuli, the strain-induced crack nanogaps are formed as a result of releasing the internal stress of a thin brittle film layer, as illustrated in Figure 9c. Different nanopatterns with sub-5 nm gaps were created in Si_3N_4 by making use of the cracking effect.^[128] However, Si_3N_4 is an insulator, hindering its application as electrodes in devices. Dubois et al. reported crack-defined electrodes with sub-5 nm nanogaps in a thin electrically conductive film over a large area, obtained using TiN.^[129] However, TiN is brittle, and its conductivity is much lower than that of metal, limiting its application in electronic devices. Recently, their group introduced a true parallel fabrication method for gold break junctions with sub-3 nm gaps on the wafer scale by relying on a self-breaking mechanism based on controlled crack formation in notched bridge structures.^[31] The fabrication densities were reported to be as high as 7 million junctions cm^{-2} , with fabrication yields for sub-3 nm junctions of $\approx 7\%$. This strategy advanced the development of crack-induced nanogap a large step forward. However, the relatively low production yields are still an urgent challenge to overcome in the future. Compared with the electromigration and mechanical break nanogaps, the most obvious advantage of this parallel fabrication method for crack-defined nanogaps is a 10^5 -fold improvement in fabrication throughput at comparable fabrication yields.

3.2. Chemical Fabrication Methods

3.2.1. Nanoparticle Self-Assembly

Among the chemical fabrication methods used to achieve sub-5 nm nanogaps, the self-assembly of metal nanoparticles presents one of the simplest methods. The interparticle capillary force due to solvent evaporation promotes metallic nanoparticle packing that provides good conditions for the formation of nanogaps.^[32,130,131] As presented in Figure 10a, Au dimers with different gap sizes can be formed during solvent evaporation.^[32] In these studies, the size of the gold nanoparticle is small because of the requirement of high surface activity of the Au nanoparticles. Recently, Si et al. demonstrated that high-density sub-1 nm gaps can be easily fabricated from Au nanoparticle monolayers by taking advantage of the oil-water interfacial self-assembly of large-sized Au nanoparticles (30–120 nm) without any assistance from molecular ligands.^[132] Larger Au nanoparticles possess a lower surface charge that decreases the repulsive force between the adjacent nanoparticles at the oil-water interface, thus, the obtained large-area nanoparticle monolayer generates a high density of sub-1 nm gaps, as shown in Figure 10b. Besides nanogaps formed on the 2D surface, 1D linear metal nanogap chain was also created by a striking methods.^[133] In this process, the gold nanoparticles were internalized and self-assembled linearly inside silica nanotubes grown on an anodic aluminum oxide (AAO) template by capillary force using a repeated wet-dry process on a rocking

platform placed in a vacuum chamber. After dissolving the AAO template, single-line or a double-line nanoparticles with sub-1 nm gaps were formed in silica nanopeapods. However, the size of these nanogaps formed by solvent evaporation is randomly distributed and uncontrollable.

To control the gap size between nanoparticles and promote the production yield, polymers and organic molecules have been chosen as linkers to form nanogaps between nanoparticles.^[56,134–137] Cha et al. developed a method called masked desilanization, which can change the distance between nanoparticles from 0.7 to 1.6 nm using a series of alkanedithiol linkers, $\text{SH}(\text{CH}_2)_n\text{SH}$ ($n = 2\text{--}10$; abbreviated as C_n hereafter).^[61] Figure 10c illustrates isolated dimers linked by 1,8-octanedithiol with controllable gap sizes dispersed on a glass slide. As shown in Figure 10d, a nanogap ranging from 0.4 to 1.3 nm was formed by silver nanocubes through self-assembly separated by a self-assembled monolayer (SAM) of different organic molecules.^[33] In particular, DNA would be another ideal candidate employed as a linker between two nanoparticles to realize sub-5 nm nanogap.^[138–142] Further, ordered nanogap arrays over a large area were fabricated by assembling gold nanocubes onto a gold film decorated with DNA-binding patterns prefabricated using EBL.^[143] After drying in air, a 4.6 nm gap was formed between the nanocubes and substrates, as presented in Figure 10e. As shown in Figure 10f, a high-yield synthetic method was proposed by Lee and co-workers for preparing surface-enhanced Raman spectroscopy (SERS)-active dimeric gold/silver core-shell nanodumbbells (GSNDs) tethered with a single DNA molecule.^[139] By changing the thickness of the silver shell, the gap size could be tuned from 4.8 to <1 nm. Later, they developed a method for producing Au trimer structures with two ≈ 1 nm interparticle gaps using single dye-labeled DNA in each gap with varying interparticle distances and symmetries.^[141] Besides organic molecules, polymers, and DNA, 2D materials have also been employed as sub-nanometer-sized gaps to form a nanoparticle-on-layered-material configuration, which has been adopted for plasmonic applications.^[144,145]

It follows that by choosing the proper linkers, the gap size between two nanoparticles can be easily tuned from sub-nanometer to a few nanometers, which is a major advantage of this self-assembly method. However, the contamination and impurity signals that could interfere with distinguishing the information from target molecules is still an existing drawback.

3.2.2. Covering Metal Nanoparticles with an Ultrathin Shell

To avoid the contamination from linker molecules, core-shell nanoparticles with dielectric shells were introduced. Directly covering ultrathin dielectric shells on the surface of metal nanoparticles undoubtedly provides a shortcut access to separating adjacent nanoparticle and forming nanogap structures.^[46,146] In 2010, Li et al. developed a type of Au nanoparticles, coated with an ultrathin (1–5 nm) optically transparent shell of silica sodium using the citrate reduction method or alumina using ALD.^[46] Without the use of a special process, sub-5 nm nanogaps can be easily formed between adjacent nanoparticles, as shown in Figure 11a. Based on these core-shell nanoparticles composed of plasmonic Au or Ag cores with ultrathin and

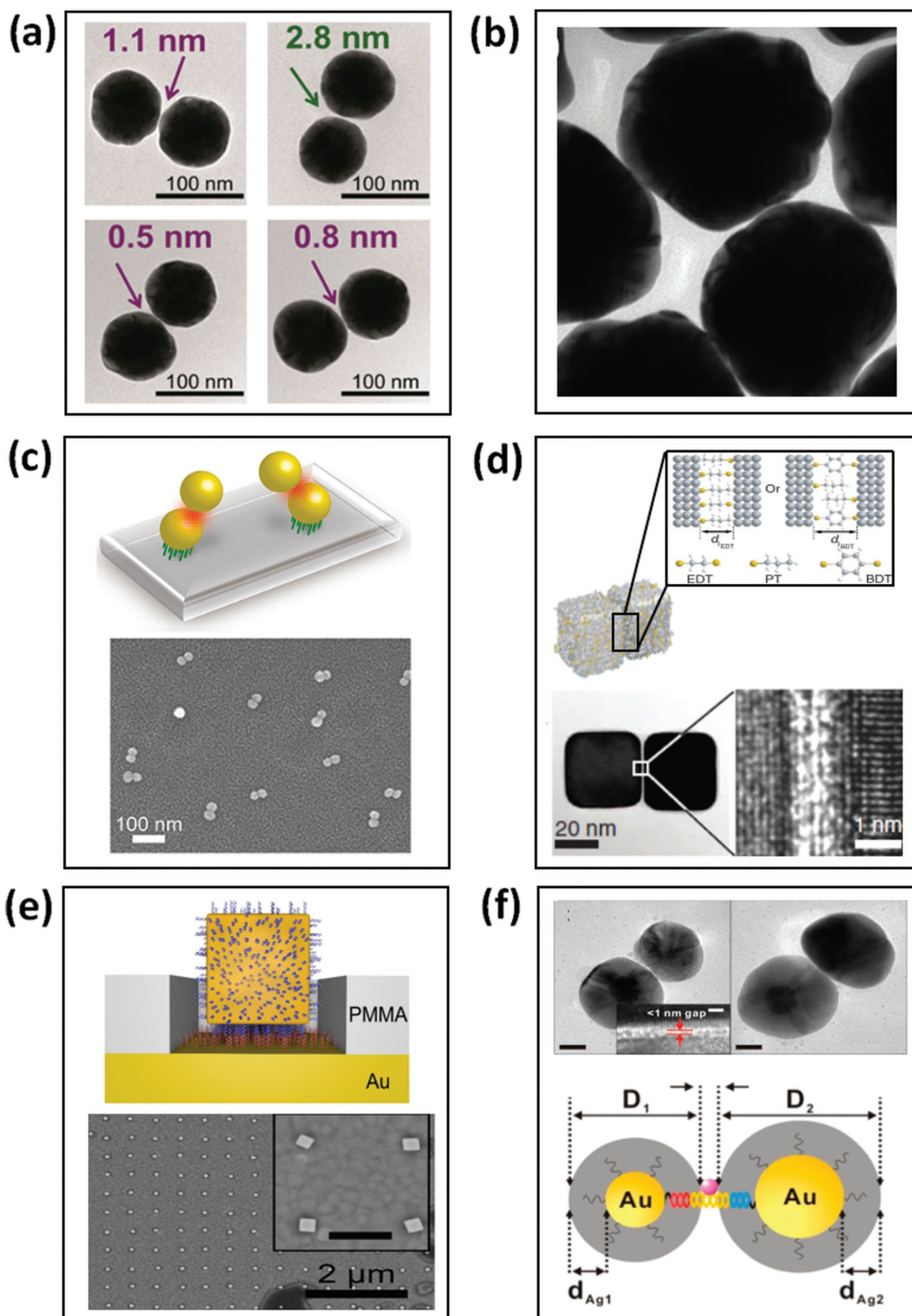


Figure 10. Various nanogap configurations formed by nanoparticle self-assembly. a) TEM images of randomly self-assembled gold dimers with gap sizes as small as 0.5 nm. Reproduced with permission.^[32] Copyright 2015, American Chemical Society. b) TEM image of Au nanoparticle monolayers with an interparticle distance of 0.5 nm for Au nanoparticles self-assembled at the oil–water interface. Reproduced with permission.^[132] Copyright 2016, WILEY-VCH Verlag GmbH & Co. c) A scheme for stepwise dimer assembly using masked desilization (top). A representative SEM image

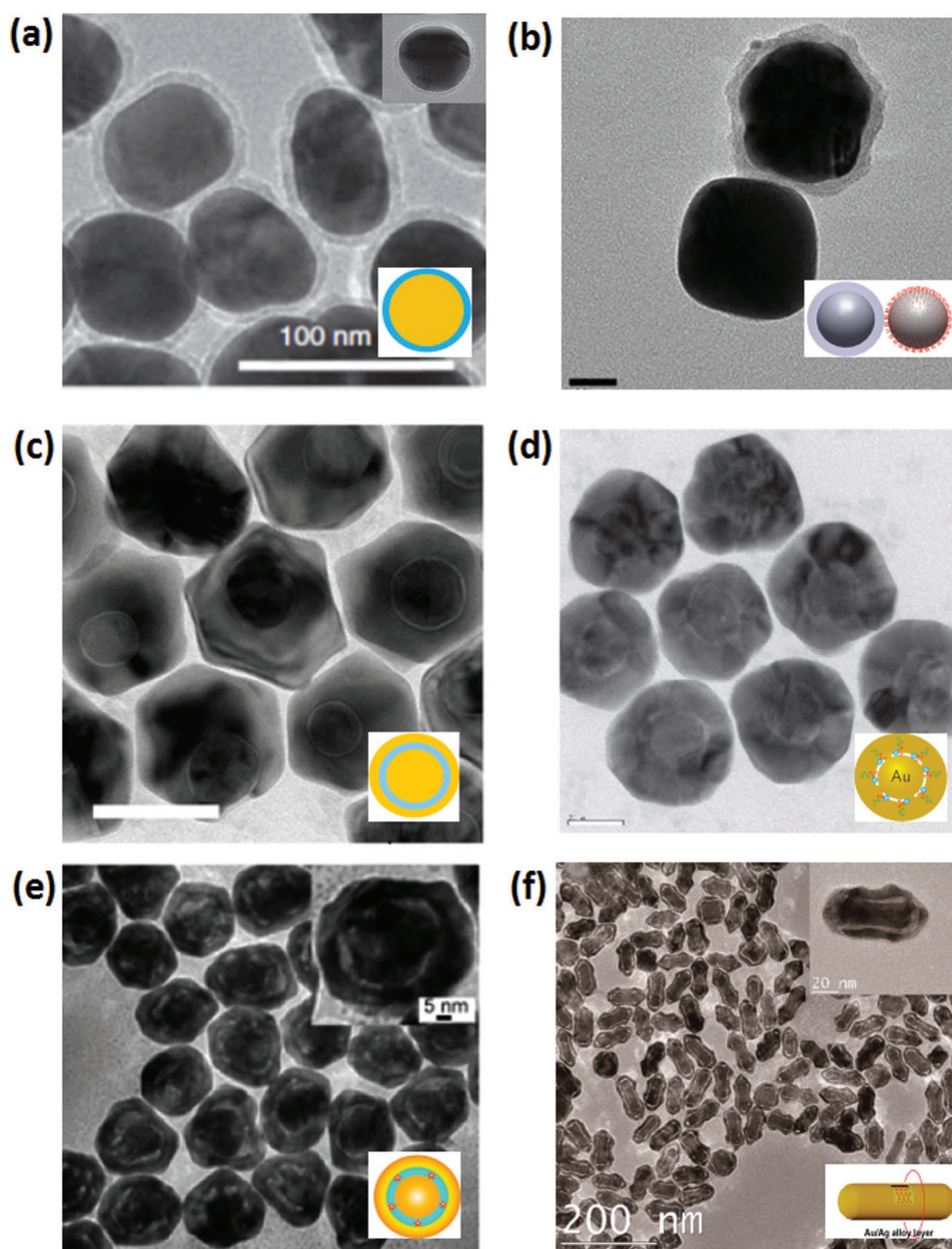


Figure 11. a) HRTEM image of Au@SiO₂ NPs with 4 nm shells. Inset: TEM image of Au@SiO₂ NPs with 2 nm shells. Reproduced with permission.^[34] Copyright 2012, Nature America, Inc. b) TEM image of electrostatically assembled particles with opposite charges, one of which is covered with a silica shell. Reproduced with permission.^[147] Copyright 2014, American Chemical Society. c) TEM image of core-shell nanoparticles with a 0.72 nm thick 1,4-BDT spacer layer. Inset: geometrical illustration of nanomatryoshkas. Reproduced with permission.^[148] Copyright 2015, American Chemical Society. d) TEM images of intermediate gold nanobridged nanogap particles with a 1 nm gap. Inset: scheme for Au NNPs obtained using DNA-modified gold nanoparticles as templates. Reproduced with permission.^[152] Copyright 2011, Macmillan Publishers Limited. e) TEM images of the corresponding Au NNPs with an interior nanogap of 5 nm. Inset: scheme of the synthesized nanogapped Au nanoparticles. Reproduced with permission.^[150] Copyright 2014, American Chemical Society. f) HAADF-STEM images of Au@CA+Mpy@Ag NPs with an ≈ 3.3 nm gap. Inset: scheme of core-shell plasmonic nanorods with Raman reporters loaded in the nanogap. Reproduced with permission.^[36] Copyright 2017, American Chemical Society.

of the assembled sub-nanometer gold dimers linked by 1,8-octanedithiol on a glass slide (bottom). Reproduced with permission.^[61] Copyright 2014, American Chemical Society. d) A high-resolution TEM image of a silver cubic junction ranging from 0.4 to 1.3 nm bridged by a self-assembled molecule monolayer. Reproduced with permission.^[33] Copyright 2014, AAAS. e) Schematic of a DNA-functionalized gold cube assembled onto a gold substrate through DNA hybridization (top). SEM image of a typical gold cube periodic array separated from a gold film by a 4.6 nm gap, and a zoomed-in SEM image showing only 4 gold cubes (bottom). Reproduced with permission.^[143] Copyright 2015, American Chemical Society. f) Schematic (top) and TEM images of gold/silver nanodumbbell structures with a sub-1 nm gap (bottom) tethered with a single DNA. Reproduced with permission.^[139] Copyright 2012, American Chemical Society.

chemically and electrically inert shells (for example, SiO_2 or Al_2O_3), an important variant of SERS was introduced, called shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).^[35,46,137] However, the minimal gap size between adjacent nanoparticles is limited by twice the shell thickness, which cannot be smaller than 2 nm. In 2014, Zohar and Haran proposed a method to form a dimer composed of a silica-shell silver-core particle (SNP@SiO_2) and a bare silver particle,^[147] as shown in Figure 11b. SNP@SiO_2 with a silica shell as thin as 1 nm, whose surface is negatively charged, was synthesized utilizing a special procedure. After mixing SNP@SiO_2 with bare silver particles positively charged by citrate ions, dimers were created via electrostatic assembly, as illustrated in the inset of Figure 11b. However, this nanogap is filled by dielectric shells rather than being an air gap, which may be a limitation for ultrasensitive detection applications because the target molecules cannot enter the gap area where the strongest enhancement of the local field occurs.

3.2.3. Embedding an Interior Nanogap into Core–Shell Nanoparticles

In recent years, core–shell nanoparticles with interior nanogaps have attracted increasing attention due to their unique chemical and physical properties, as the gap size can be easily tuned by controlling the thickness of the spacer between metal core and shell, consequently controlling the extent of the coupling and induced near-field enhancement between the core and shell. As exhibited in Figure 11c–f, dielectric layers,^[35,148] DNA,^[149] small organic molecules,^[36,145] and polymers^[151,152] have been employed as spacers to form interior nanogaps. Although dielectric spacers are easily coated on metal cores, their thickness is normally on the scale of tens of nanometers.^[35,148] Using a SAM of 1,4-benzenedithiol (1,4-BDT) molecules as well as of 4-methylbenzenethiol (4-MBT) as a spacer, the nanogap could be shrunk into a sub-nanometer scale.^[148] Lim et al. synthesized core–shell nanoparticles with interior nanogaps in high yield using DNA-modified Au nanoparticles as seeds, with subsequent addition of polymer, reductant, and precursor.^[152] Well-defined, hollow, 1 nm interior gaps between a gold core and a gold shell are clearly seen in Figure 11d. Taking advantage of nanoparticle templated self-assembly of amphiphilic block copolymers and localized metal precursor reduction by redox-active polymer brushes, Song and co-workers synthesized core–shell nanogapped nanoparticles (NNPs) with an interior gap tuned within 5 nm.^[150] As shown in Figure 11f, core–shell plasmonic nanorods with enclosed nanogaps were successfully prepared based on coordination interactions and galvanic replacement.^[36] The size (length and width) and morphology of the core–shell plasmonic nanorods as well as the nanogap size depend on the concentration of the coordination complexes formed between Ag^+ ions and 4-mercaptopyridine.

The advantages of core–shell nanoparticles are obvious:^[152] 1) the molecular layer is sandwiched between the core and shell, and will not be influenced by the outer environment; 2) the shell surface is totally free and can be accessed by target molecules without worrying about dynamic replacement; and 3) the nanoparticle is simultaneously used as an internal standard and enhancing substrate, without affecting the spatial distribution of

target molecules. Certainly, interior nanogaps also have obvious drawbacks that the contamination and impurity signals from the molecule layer will affect distinguishing the information from target molecules.

Above all, as described in Sections 3.2.1–3.2.3, the chemical method based on metal nanoparticles for fabricating sub-5 nm nanogap has shown some obvious advantages, such as precise control of the gap size, a simple fabrication process, mass production formed in solution, and low cost, which are very good features for practical applications. In addition to the important advantages of the fabrication methods based on nanoparticles, the main disadvantages can be described as follows. 1) The discrepancy in the surface morphology of each nanoparticle results in the low controllability and repeatability in forming uniform gap sizes over a large area. 2) Periodic array and inaccessibility for the nanogap between nanoparticles are problematic, limiting their practical application in single-molecule devices. 3) Due to the existence of linker molecules or surfactants, a risk of chemical contamination exists for nanogap samples, impeding their application in biological or environmental detection.

3.2.4. Electrochemical Deposition

In addition to the nanogaps formed based on nanoparticles, nanogap electrodes can also be fabricated using the electrochemical methods, such as electrodeposition or electrodis-solution.^[153,154] The working principle of the electrochemical deposition method is sophisticated. Figure 12a illustrates a standard electrochemical cell for the plating process.^[37] The working electrodes were formed using photolithography or EBL followed by a conventional evaporation and lift-off process. By electrodepositing metal atoms onto a specific face of the working electrodes, the gap between two facing electrodes can be sequentially narrowed, and a precise tunable width can be achieved. As presented in Figure 12b–d, by controlling the electrochemical processing parameters, the gap between two electrodes can be precisely tuned to within a few nanometers.^[153,155–158] Ah et al. developed a simple and reproducible method to fabricate multifingered nanogap electrodes of a few nanometers in separation.^[38] Electrodes were obtained by utilizing surface-catalyzed chemical deposition following a traditional EBL step. Noticeably, 200×100 integrated nanogaps with separations of a few nanometers could be realized at the same time, as shown in Figure 12d. Electrochemical methods have been proven to be simple, controllable, and device-compatible approaches for rapidly fabricating nanogap electrodes. However, the rough surface and morphology of metal nanostructures deposited by electrochemical methods are unsatisfactory and problematic. Particularly, as the nanogaps are prepared in solution, obstacles to coupling with other IC processes to form complex devices exist.

4. Device Applications

Due to their rich underlying physical mechanisms, sub-5 nm nanogaps have exhibited superiority in many application fields, such as sensing, optical, molecular, and electronic

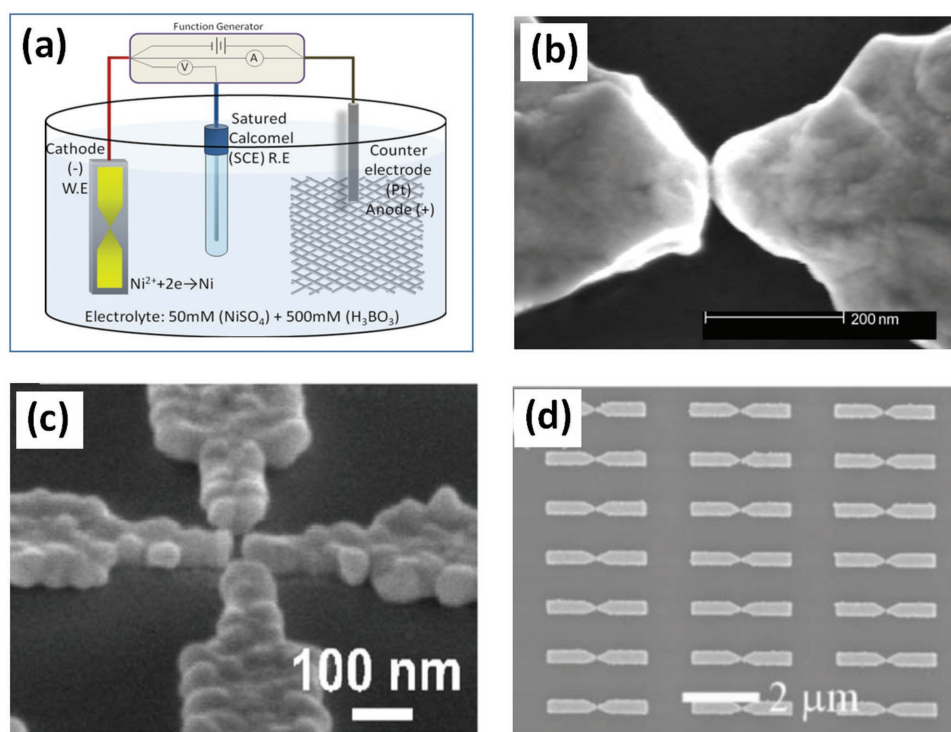


Figure 12. a) Schematic diagram of the electrochemical cell for the preparation of samples. The sample is placed in the cathode, and the voltage is referenced to a saturated calomel KCl electrode. Reproduced with permission.^[37] Copyright 2010, IOP Publishing Ltd. b) SEM images of an ≈ 1 nm nanogap electrode couple prepared at 3 kHz. Reproduced with permission.^[158] Copyright 2005, Wiley-VCH Verlag GmbH & Co. c) SEM images of four electrodes with sub-5 nm gaps. Reproduced with permission.^[157] Copyright 2007, American Institute of Physics. d) Field emission SEM (FESEM) image of an array of nanogaps with ≈ 2 nm separations after surface-catalyzed chemical deposition. Reproduced with permission.^[38] Copyright 2006, American Institute of Physics.

devices. Due to the extremely enhanced local electromagnetic field induced by the plasmonic coupling effect in the nanogap zone, sub-5 nm nanogaps are utilized in sensing devices and optical devices. Sensing devices are mainly based on various spectroscopic techniques, such as SERS, surface-enhanced infrared absorption (SERIA), and surface-enhanced photoluminescence (PL). Optical devices, with detection ranges from the far-infrared to the visible, have been employed for terahertz (THz) devices, and second-harmonic generation (SHG) devices. On the other hand, molecular devices and electronic devices have been proposed by taking advantage of the quantum tunneling effect in sub-5 nm nanogaps. Molecular devices can not only examine the intrinsic physical phenomena, such as charge tunneling, Coulomb blockade, and the Kondo effect, but also be used for DNA sequencing, molecular magnets, thermotunneling devices, etc. Electronic devices, without any molecule in the nanogap, have demonstrated their potential application in nano-electromechanical (NEM) switches and nonvolatile memory, with greatly enhanced performance for sub-5 nm nanogap electrodes.

4.1. Sensing Devices

In the past decades, SERS has been demonstrated to be a good detection technique in chemistry, in environment, and

in medicine. The ultrahigh SERS sensitivity, even down to the single-molecule level, is determined by the strongly enhanced electromagnetic field due to the excitation of SPR in nanostructures. To enable single-molecule detection, a Raman enhancement factor of $\approx 10^7$ is required.^[56,159,160] To date, many remarkable results of SERS based on sub-5 nm nanogaps have been reported, reflecting the fact that sub-5 nm nanogaps with significant enhancement in the local electromagnetic field are ideal candidates for application in ultrasensitive detection of various molecules and even single molecules. As shown in **Figure 13a**, a 2 nm gap 3D split-wedge SERS antenna was fabricated using atomic layer lithography, exhibiting Raman enhancement factors exceeding 10^7 .^[109] Furthermore, DNA interior gapped Au core-shell nanoparticles also exhibited the strongest and most reproducible SERS signals with time, and a sensitivity as high as 10×10^{-15} M concentrations and enhancement factors greater than 1.0×10^8 were demonstrated for this type of interior nanogap,^[37] as shown in **Figure 13b**. In addition, interior gapped core-shell nanoparticles have proven to be a good sensing platform for drug delivery.^[150] Besides SERS, plasmonic metal nanogaps have also been employed in SERIA spectroscopy.^[105,108,161,162] As presented in **Figure 13c**, Dong et al. produced a bowtie-shaped Au structure with a sub-3 nm gap for SERIA spectroscopy to quantitatively analyze chemical components.^[163] The percentages of mixed 4-nitrothiophenol (4-NTP) and 4-methoxythiophenol (4-MTP) composites were successfully identified. As shown in **Figure 13d**, Au nanoparticle

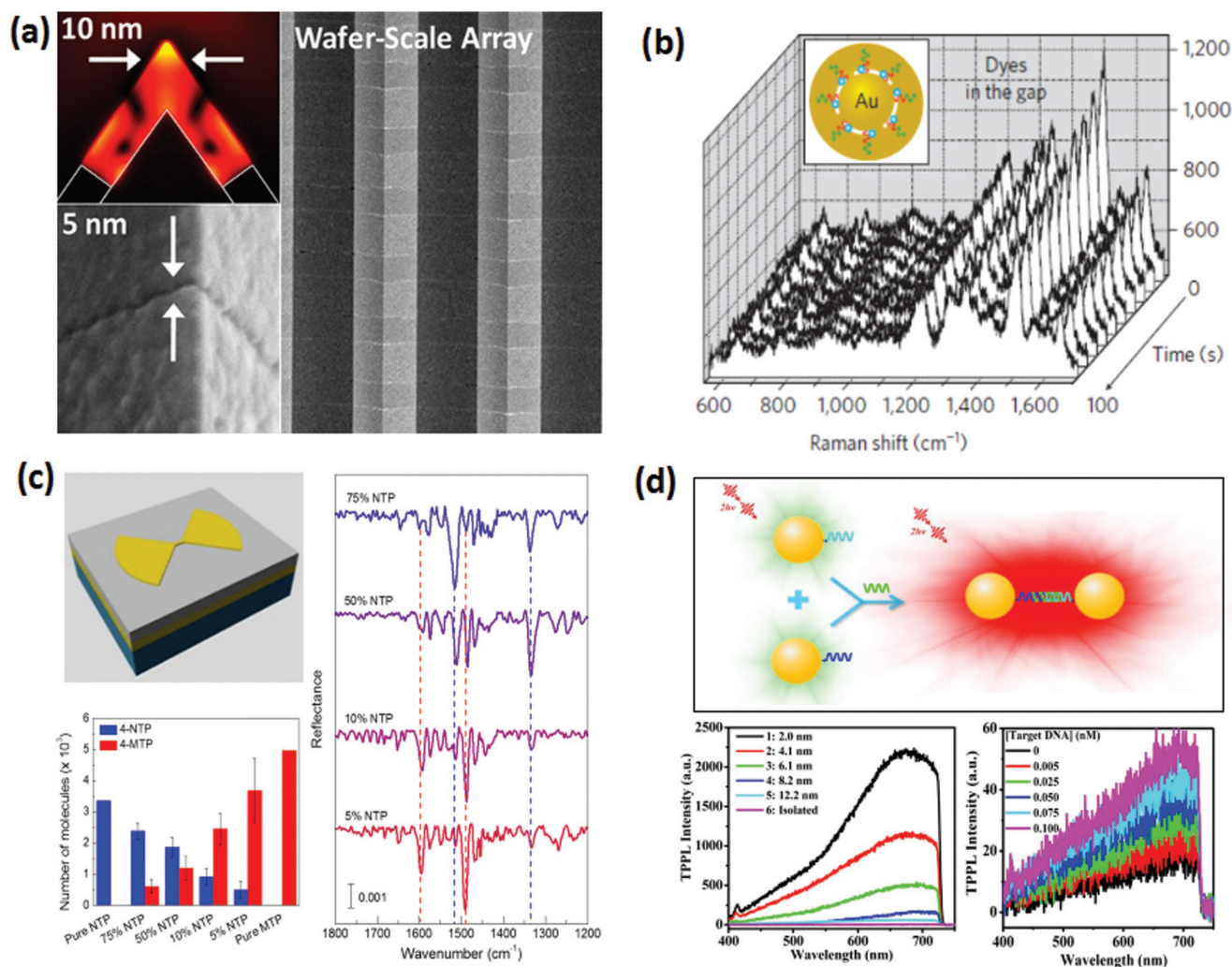


Figure 13. Typical sensing devices based on a sub-5 nm nanogap. a) Electric field distribution inside the center of a SERS device. SEM images of arrays of split-wedge antennas with a 5 nm nanogap on a silver wedge tip. Reproduced with permission.^[109] Copyright 2016, American Chemical Society. b) Time-dependent SERS profiles of core-shell nanoparticles with a 1 nm gap. Reproduced with permission.^[152] Copyright 2011, Macmillan Publishers Limited. c) Scheme of a SERIA device. Number of 4-NTP (blue) and 4-MTP (red) molecules on the Au surface in a 3 nm gap after functionalization in mixed solutions of various molar percentages. Reproduced with permission.^[163] Copyright 2017, American Chemical Society. d) Scheme of the two-photon sensing platform for detection of target ssDNA. TPPL spectra of Au NP-dsDNA assembly with five different gap sizes in the presence of different concentrations of target single sequence DNA (ssDNA). Reproduced with permission.^[164] Copyright 2014, American Chemical Society.

dimers with gap sizes well tuned from 2.0 to 12.2 nm by DNA were employed in the two-photon photoluminescence (TPPL) enhancement measurements.^[164] The largest TPPL enhancement factors of 265 was achieved at the shortest available separation distance of 2.0 nm for 41 nm Au NP-double sequence DNA (dsDNA) assemblies. Moreover, a limit of detection of 2.9×10^{-12} M was realized on target DNA, demonstrating the high sensitivity and excellent selectivity of this TPPL method. This method could potentially be applied to DNA detection inside cells or even to in vivo detection.

4.2. Optical Devices

Working as deep-subwavelength apertures, plasmonic nanogaps have been employed in various optical devices

because they can squeeze electromagnetic waves into a small volume, leading to a high field enhancement.^[29,109] In recent years, MDM nanogaps have emerged as versatile platforms for THz science and applications, such as detectors, switches, and resonators. As shown in **Figure 14a**, a wafer-scale array of annular nanogaps was fabricated using atomic layer lithography, which can confine THz waves in sub-5 nm metallic gaps and be used to detect refractive index changes caused by only a 1 nm thick ($\sim \lambda/10^6$) dielectric overlayer.^[102] The maximum field ($|E_x|$) enhancement factor at the resonance frequency of 0.45 THz reaches 1250 for the 2 nm gap devices. Although the 2 nm gaps expose only 0.008% of the gold surface, the absolute transmission amplitude ($|E_x|$) of the input pulse measured through the sample was as high as 10%.

By controlling the gap size, i.e., the period of patterns, the working range of optical devices could be extended from the

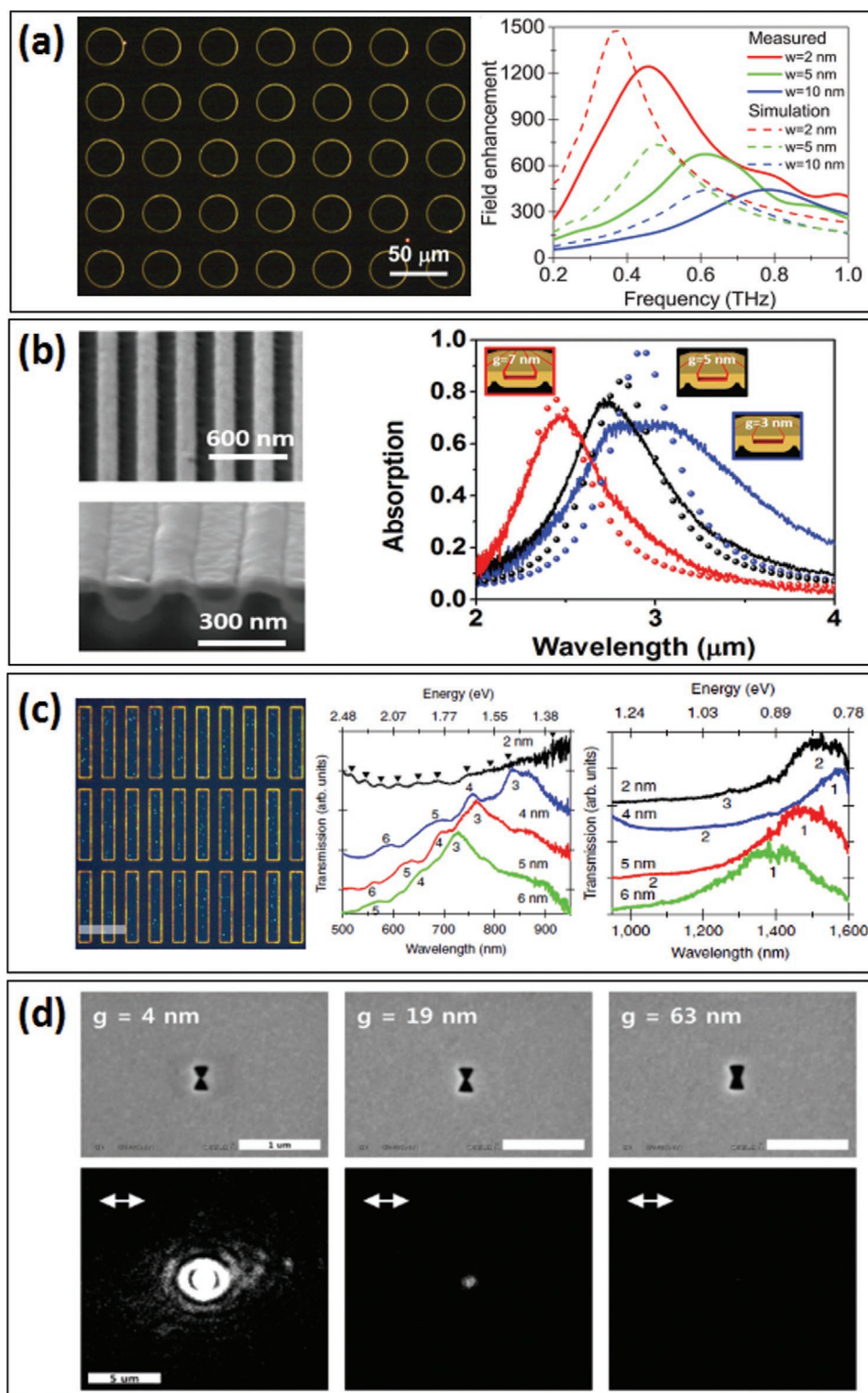


Figure 14. Typical optical devices based on a sub-5 nm nanogap. a) Top-view microscope image of a THz device based on an annular 5 nm nanogap array (left). Electric field enhancement spectra from annular nanogap samples (right). Solid lines indicate measured field spectra. Dashed lines indicate numerically simulated field spectra. Reproduced with permission.^[102] Copyright 2015, American Chemical Society. b) SEM image of a mid-IR device based on a 3 nm nanogap grating. Absorption spectra of three devices with different gap sizes from 3 to 6 nm. Reproduced with permission.^[108] Copyright 2017, WILEY-VCH Verlag GmbH & Co. c) Optical microscopy image of a visible and near-IR (NIR) device based on rectangular silver nanogaps. Measured visible and NIR transmission spectra through nanogaps with 2, 4, 5, and 6 nm widths. Reproduced with permission.^[28] Copyright 2013, Macmillan Publishers Limited. d) SEM and EMCCD images of the SHG signals generated from nonlinear optical antennas with 4, 19, and 63 nm gaps, respectively. Reproduced with permission.^[49] Copyright 2015, American Chemical Society.

THz to the mid-infrared and then to the visible range. As presented in Figure 14b, a three-layered planar MDM metamaterial superabsorber with sub-5 nm gaps was fabricated using ALD lithography, exhibiting extremely enhanced light fields in the mid-IR range.^[108] The different absorption resonances centered at 2.96, 2.74, and 2.48 μm for grating with gap sizes of $g = 7, 5,$ and 3 nm , respectively, agree reasonably well with the numerical modeling results. As shown in Figure 14c, the dispersion curves indicate that light with a free-space wavelength of 517 nm, when confined to a 2 nm Al_2O_3 gap in Ag rectangular, exhibits a plasmon wavelength $\lambda_{\text{SP}} = 29\text{ nm}$; this value corresponds to an effective refractive index of 17.8, the highest index yet reported in the visible spectral range.^[28]

In addition, the nonlinearity of an electromagnetic wave can be realized by utilizing a deep-subwavelength gap to induce a large electric field. Figure 14d shows that the SHG measurement was performed on a 3D nanodibolo structure with different gap sizes from 4 to 63 nm.^[49] Strong SHG signals were detected in the 4 nm gap by an electron-multiplication charge-coupled device (EMCCD), which were 1000 times brighter than the signal for the nanoantenna with a 63 nm gap.

We can see from the above reports that the metal nanogap nanostructure plays a very important role in deep-subwavelength optical devices, and their working wavelengths cover a wide range from the THz to the visible. In particular, the sub-5 nm nanogap greatly enhanced the optical properties and hence became a perfect candidate for nanogap-based optical devices.

4.3. Molecular Devices

Utilizing quantum tunneling, sub-5 nm metal nanogaps serving as electrodes have been demonstrated to be a good platform to investigate the fundamental charge transport features in molecules, which play a large part both in basic science and technological applications.^[14,64] Electrochemical deposition, mechanical break, and electromigration break methods have been widely employed to fabricate sub-5 nm metal nanogaps, which are frequently used as electrodes to trap single molecules, nanoparticles, and quantum dots, in molecular electronics, especially transistors. Based on the expected utilization of the charge transport of molecules, molecular devices could be used for switching devices, thermoelectricity devices, and electrical biosensing devices.

As shown in Figure 15a, two-way photoswitching and the corresponding charge transport characteristics of a single photochromic molecule were systemically investigated in a MCB nanogap system at low temperatures.^[165] Notably, the side chains and end groups of the sulfur-free diarylethene molecules are both crucial to understanding the charge transport mechanism of reversible photoswitching molecular junctions. The conductance of all four types of molecules increased after transitioning from the open to the closed state. This nanogap structure led to a relatively large conductance signal ratio, e.g., a high ratio between the single-molecule conductance in the closed form and that in the open form.

Probing thermal transport properties is not only useful for understanding the fundamental properties of molecule, but

also essential for future practical applications in electronic devices and for developing high-efficiency energy conversion devices.^[166,167] As shown in Figure 15b, extremely large temperature gradients (exceeding $1 \times 10^9\text{ K m}^{-1}$) have been realized in sub-5 nm-nanogapped molecular devices.^[168] Consequently, the direct relationship between the charge transmission characteristics and the thermoelectric properties of molecular junctions was demonstrated as a function of the gate voltage. The Seebeck coefficient of the biphenyl-4,4'-dithiol (BPDT) junction decreases monotonically with increasing V_G , demonstrating that its thermoelectric properties can indeed be tuned electrostatically by $\approx 35\%$. By contrast, a negative sign of the Seebeck coefficient was observed in the C_{60} junction, which started to increase when V_G was greater than 0 V. These results not only demonstrated the direct relationship between the charge transmission characteristics and the thermoelectric properties of molecular junctions, but also suggest a method to adjust the thermoelectric properties of molecular junctions. Thus far, the investigation of the thermoelectric properties of molecular junctions is still at an early stage, opening a new research area in molecular devices.

For the detection of a few biomolecules or even single biomolecules, the devices must have very small feature sizes, typically a few nanometers, be compact, and provide a sufficient level of sensitivity. Therefore, nanogap devices in electrical biosensing have become an extensively developed field and have attracted increasing attention in recent years.^[168] In the early stage, by monitoring a potential difference across these electrodes, nanogap electrodes were only used to detect molecules while it passed through the nanogap, as shown in Figure 15c.^[169] Recently, with the progress in drug and medical treatment, the ability to decode the information of the complete genomes (DNA), transcriptomes (RNA), and proteomes (all proteins) at an atomic level and via quantum tunneling is crucial for molecular devices.^[23] Benefiting from the advanced fabrication techniques, nanogaps with widths of 1–2 nm have been successfully obtained, enabling the differentiation of single nucleobases and amino acids based on the measurement of their electron transport properties.^[170,171] As shown in Figure 15d, the demonstration by Tsutsui et al. indicated that single nucleotides can be identified statistically through the electron transmissivity related to their highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap, based on the observations of temporal changes in the two-probe tunneling current, I , associated with trapping of nucleotides.^[170] Positive peaks can clearly be seen in the I - t curves acquired for thymidine 5'-monophosphate (TMP), cytidine 5'-monophosphate (CMP), and guanosine 5'-monophosphate (GMP) at $V_b = 0.75\text{ V}$. The positive value of the current peak is attributed to the electron tunneling during molecule trapping. The corresponding I_p histograms have single peaks, suggesting effective transverse field effects that restrict the molecular conformational freedom. The peak I_p values reveal a single-molecule conductivity order of $\text{GMP} > \text{CMP} > \text{TMP}$. This result can be interpreted qualitatively as reflecting the order of differences in the DNA base HOMO–LUMO gaps of guanine, cytosine, and thymine. As presented in Figure 15e, using a sub-5 nm gap molecular device, single-molecule electrical resequencing of DNA and RNA can be achieved using a hybrid method of identifying single-base

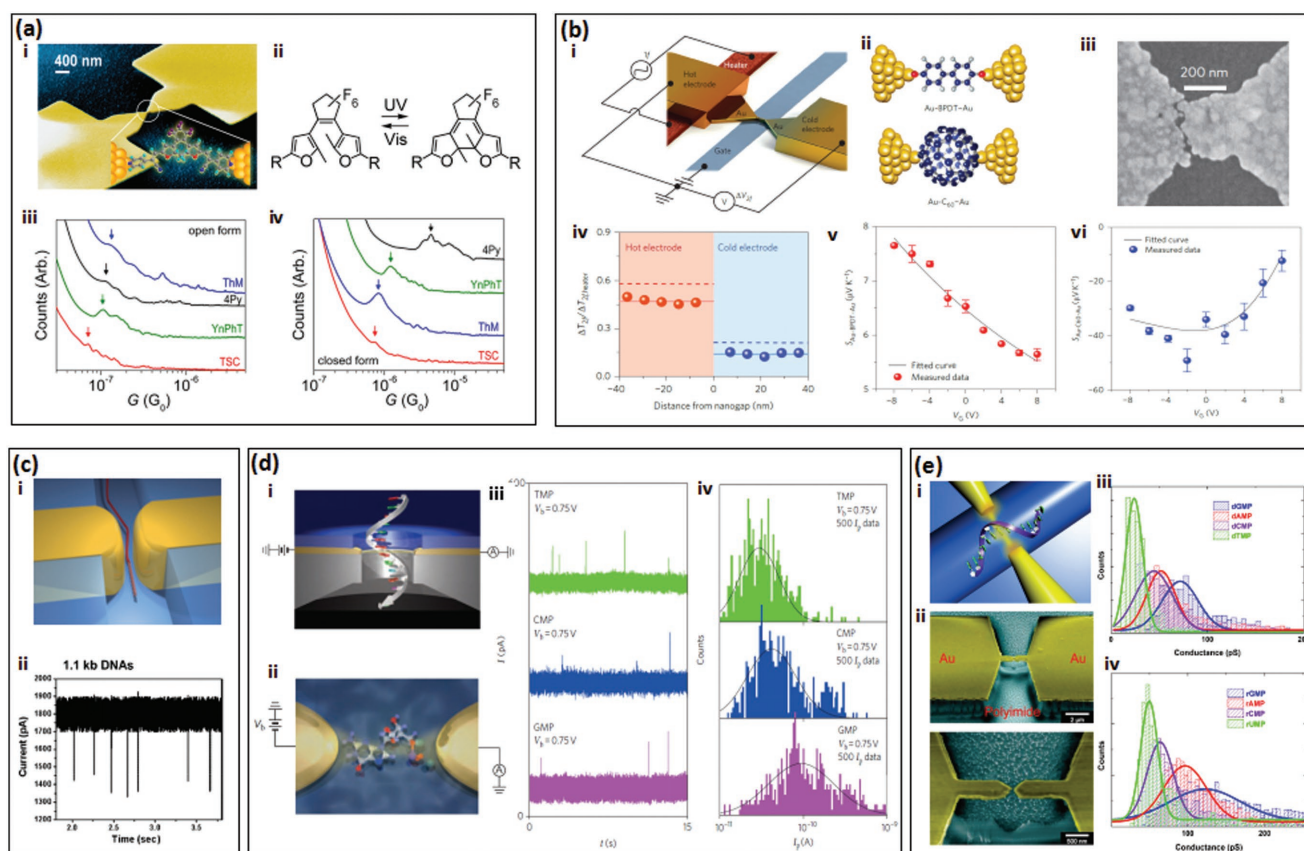


Figure 15. Typical molecular devices based on sub-5 nm nanogaps. a) i) Scheme of a photoswitching based on a Au-4Py-Au junction with a mean stretching length of ≈ 8.7 Å. ii) Sketches of open (left) and closed (right) forms of difuryl ethenes; R indicates the extended side chains and end groups. Conductance histograms of photochromic molecular junctions for iii) open and iv) closed forms of four molecules. Reproduced with permission.^[165] Copyright 2012, American Chemical Society. b) Schematics of a i,ii) molecular device for thermoelectrical measurement. iii) Magnified SEM image of an ≈ 1 nm nanogap. iv) Normalized temperature profile in the vicinity of the nanogap measured using scanning thermal microscopy (SThM) (circles) and calculated by thermal modeling (dotted line). The red and blue solid lines are fits to the measured temperature data on the hot and cold electrodes, respectively. Seebeck coefficient of the v) BPDT and vi) C_{60} junction as a function of V_G . Reproduced with permission.^[168] Copyright 2014, Macmillan Publishers Limited. c) Scheme and electrical measurement of a molecular device for DNA detecting. Reproduced with permission.^[169] Copyright 2008, American Chemical Society. d) DNA sequencing results obtained using a molecule device. Schematic of i) the DNA sequencing method and ii) tunnel current measurement of single-nucleotide molecules. iii) Partial $I-t$ curves, and iv) the corresponding I_p histograms of TMP (green), CMP (blue), and GMP (purple). Reproduced with permission.^[170] Copyright 2010, Macmillan Publishers Limited. e) DNA and RNA sequencing results obtained using a nanogap molecular device. i) Schematic diagram of single-molecule electrical sequencing of DNA and RNA. ii) A magnified SEM image of the Au bridge before and after mechanical breakage. iii) Conductance histograms of four deoxynucleoside monophosphates of DNA and iv) four nucleoside monophosphates of RNA. The blue, red, purple, and green lines indicate the single-molecule conductance values of GMP, adenosine 5'-monophosphate (AMP), CMP, and TMP, respectively. Reproduced with permission.^[171] Copyright 2010, Nature Publishing Group.

molecules via tunneling currents and random sequencing.^[171] Moreover, the complete sequence of 5'-UGAGGUA-3' from the let-7 microRNA family was identified by creating a composite of overlapping fragment sequences.

For both molecular devices and sensing devices, the trapping efficiency is an important factor in their practical application. Taking advantage of the sub-5 nm nanogap, low energy consumption trapping devices with high efficiency were achieved using an ultralow bias voltage or laser power.^[172,173]

4.4. Electronic Devices

Without filling a molecule in the nanogap, empty (metal-air-metal) nanogaps can be used in NEM switches, which are

core components in ultralow-power-integrated circuits, NEM resonators, and nonvolatile memory (NVM). However, the unacceptably high operating voltage (4–20 V) poses a major obstacle in the practical use of the NEM switch, especially in low-power-integrated circuits. Obtaining a NEM switch with an operation voltage below 1 V is still a challenge, because of the difficulties in fabricating electrodes within a sub-5 nm gap.^[174,175]

Figure 16a illustrates a switching device with a two-terminal “pipe clip” structure consisting of a fixed bottom electrode and a freely suspended top electrode.^[12] The TEM image clearly shows a small air gap of ≈ 4 nm formed on the side edges of the bottom electrode after removing the sacrificial layer. Taking advantage of the extremely small air gap and movable electrode, an operating voltage down to sub-1 V was obtained. The current curve rises abruptly at an applied voltage of 400 mV. As

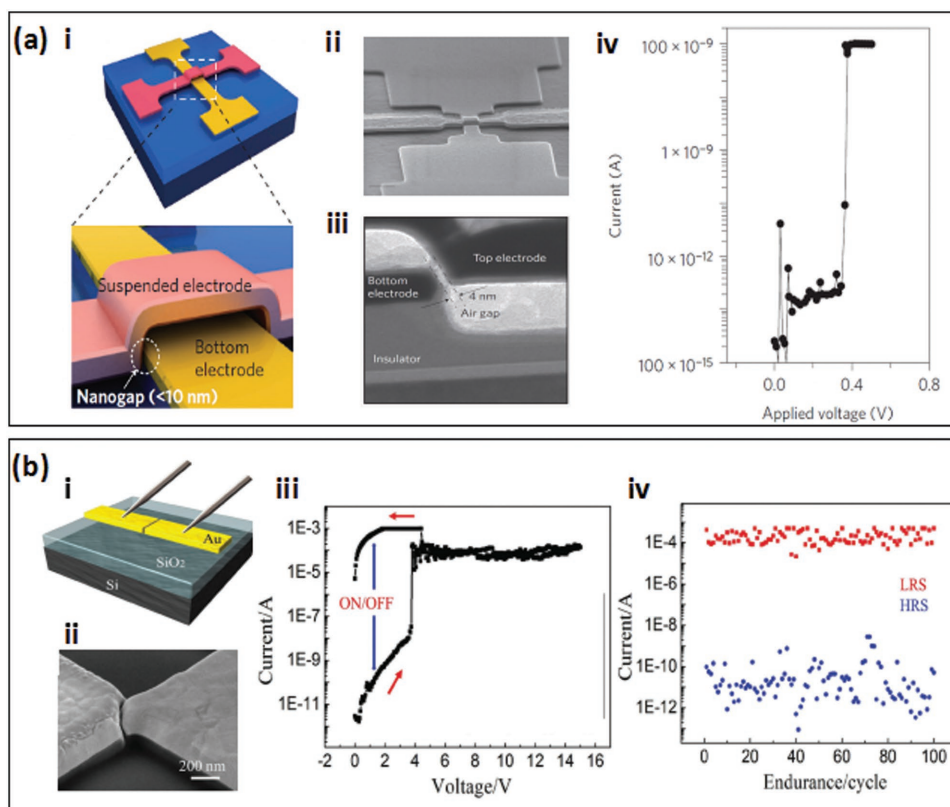


Figure 16. Two types of electronic devices based on a sub-5 nm nanogap. a) Two-terminal NEM switch device. i) Device schematic. An extremely small nanogap is built in the side edges of the bottom electrode. ii) Related SEM images after fabrication. iii) Magnified cross-sectional TEM image of the contact point with a 4 nm thick air gap after removing the sacrificial layer. iv) The I - V characteristics show a two-terminal switching behavior. Reproduced with permission.^[172] Copyright 2013, Macmillan Publishers Limited. b) Resistive random access memory. i) Device schematic. ii) SEM image of nanogap electrodes fabricated with FIB milling. iii) I - V curve of nanogap electrodes with an initial high resistive state obtained by sweeping from 0 to 15 V and from 15 to 0 V. iv) Repetitive resistive switching characteristics of nanogap electrodes. Reproduced with permission.^[176] Copyright 2016, WILEY-VCH Verlag GmbH & Co.

shown in Figure 16b, sub-5 nm nanogap electrodes for resistive random access memory (RRAM) were fabricated by combining ALD lithography and chemical etching.^[176] The air nanogap was formed after Al_2O_3 removal from between the first and second Au layers by chemical etching. Then, nanogap electrodes with a smaller aspect ratio were fabricated by UV lithography, followed by FIB milling. The ON/OFF ratio of about 10^4 was measured under a READ voltage of 0.5 V, thus demonstrating the nondestructive memory property. As shown in Figure 16, such nanogap-based electronic devices have an obvious feature of the gap size defining the operation voltage. Hence, a sub-5 nm nanogap can optimally decrease the operation voltage to greatly improve the functional properties of electronic devices.

5. Conclusions and Outlook

In this review, we have addressed the physical properties, fabrication methods, and device application variants for sub-5 nm metal nanogaps. Interesting physical properties emerge from the sub-5 nm nanogaps under the stimuli of light or electric fields, such as ultrastrong plasmon resonance and quantum tunneling, coinciding with the growing demand for exploring

cutting-edge devices, including sensing, optical, molecular, and electronic devices. Here, we provide this review that comprehensively covers the subject of sub-5 nm nanogaps and present recent advancements in metal nanogaps, with the ultimate aim to further inspire scientists and engineers in their research.

In Table 1, we list and compare the typical fabrication methods of sub-5 nm metal nanogaps. Each method has its own unique advantages as well as disadvantages. The nanogaps fabricated using physical methods exhibited higher controllability, reproducibility, and large-scale periodicity compared with those obtained using chemical methods. These advantages could be attributed to the advanced planar nanofabrication techniques, which in turn, would lead to high costs for this type of nanogap. However, forming sub-nanometer nanogaps using physical methods is very difficult, whereas they can be easily achieved via the chemical methods by controlling the thickness of linker molecules or the shell thickness. In addition, as shown in Table 1, only a few methods can be used to fabricate multiple nanogap devices in a parallel manner. However, the production yields of nanogaps with the desired width are still very low,^[31,38] although the fabrication densities of nanogaps have reached a high level. In the application aspect, the nanogaps fabricated by physical methods can

Table 1. Comparison of sub-5 nm metal nanogaps fabricated by different approaches.

Fabrication method		Key fabrication technique	Minimum gap size	Single/ large area	Controllability ^{a)}	Reproducibility	Addressability	Cost	Application/ functionality ^{b)}
Physical fabrication methods	Direct nanofabrication	FIB	1 nm	Single	M	M	M	H	■ ★
		TEM	Sub-nanometer	Single	M	M	H	H	■
		EBL	Sub-nanometer	Large area	H	H	M	M	■ ● ★
		SPM	Sub-nanometer	Single	H	H	L	H	■ ●
	Controllable metal deposition	Metal deposition	3 nm	Large area	M	M	L	M	■ ◆ ●
		Nanosphere lithography	5 nm	Large area	M	M	L	L	■ ●
	Insertion of ultra-thin layers	ALD	2 nm	Large area	M	M	L	M	● ★
		2D material	1 nm	Large area	L	M	L	M	● ★
	Breaking-/ cracking-defined	Electromigration	1 nm	Large area	M	L	H	M	■ ◆
		Mechanical	1 nm	Single	M	L	H	H	■
		Strain	3 nm	Large area	H	H	M	M	■ ●
Chemical fabrication methods	Nanoparticle self-assembly	Nanoparticle	Sub-nanometer	Large area	L	L	L	L	●
		Nanospacer	Sub-nanometer	Large area	H	H	L	L	●
	Covering ultrathin shell	Dielectric shell	Sub-nanometer	Large area	H	H	L	L	●
	Embedding interior nanogaps	Interior gap	1 nm	Large area	H	H	L	L	●
	Electrochemical	Electrochemical	1 nm	Large area	H	L	H	L	■

^{a)} L = low, M = medium, H = high; ^{b)} ● Sensing devices, ★ optical devices, ■ molecular devices, ◆ electronic devices.

be used in various regimes ranging from molecular electronics to sensing and optical devices, whereas the sub-5 nm nanogaps formed by nanoparticles are mostly limited to the regime of sensing and biomedicine devices based on the SERS technique. For applications in molecular and electronic devices, precisely controlling the orientation, location, and number of probe molecules is still challenging. As depicted in Table 1, only a few methods exist thus far that possess the ability to achieve good addressability, whether in locating or probing a molecule in a nanogap. Comparing physical and chemical fabrication methods, physical methods hold many advantages in device application, whereas chemical methods exhibit obvious advantages in biomedicine and sensors. The combination of current physical fabrication methods and chemical methods to improve manufacturability could be the next trend for successful batch fabrication of sub-5 nm nanogaps.

Metal nanogaps have undergone rapid development in recent years, but no mature strategies for fabricating sub-5 nm nanogaps exist thus far. Several challenges are still being encountered, such as achieving a large scale, high density, uniformity, reproducibility, precise control of the gap width, and addressability. Based on the surface topography of the working area, the nanogaps could be refined as point-to-point or face-to-face nanogaps. Compared with the face-to-face nanogap, the point-to-point nanogap is easier to realize, is less of controllability, and exhibited unstable physical properties. Therefore, face-to-face nanogaps would be an ideal configuration in the

development of nanogaps.^[49] From this point of view, a sacrificial layer obtained by ALD deposition would be a proper choice because of the precisely controlled layer thickness, wafer-scale coverage, compatibility with planar fabrication techniques, and sophisticated etching techniques.^[103,106,176] The existing challenge of this method is the risk of contamination in the gap and on the facing electrode surfaces during removal of the sacrificial layer. With the recent development of nanofabrication techniques, new fabrication strategies are expected to emerge, and the gap size is expected to continually be reduced from the nanometer down to the angstrom scale, which is desirable to eventually achieve wafer-scale throughput.

Along with innovating fabrication methods, expanding the application areas of sub-5 nm nanogaps is a growing demand of scientists. In addition to the important applications in biological devices and optical devices, the utilization of nanogaps in environmental sensors, memory devices, and energy harvesting is attracting more attention. Certainly, all these applications are possible only if reliable and controllable nanofabrication processes of sub-5 nm nanogaps are achieved and further improved. In the future, a nanogap device serving as a multifunctional platform that can simultaneously measure the transport signal, optical spectra, and mechanical responds is favorable. Highly efficient lab-on-a-chip devices are possible because the electronic detection technology can be mass-produced with high yield and then coupled to widely used spectroscopic instruments. Lesser-Rojas et al. developed a multifunctional real-time

characterization device that could measure the Raman spectra and conductance across nanogaps and simultaneously perform fluorescence imaging during protein molecule trapping.^[177] However, the reported bioelectronic signal simply indicated the appearance of a molecule. Therefore, manipulating the fundamental charge transport in a single molecule holds the key to advancing basic science and achieving multifunctional devices.

The goal for the development of sub-5 nm nanogaps is to fabricate commercial devices that will be available in the market. Commercial sub-5 nm nanogap devices are still facing challenges and are not available in the market due to their low controllability, low molecular selectivity, low substrate-to-substrate reproducibility, and high cost. At the current stage, most of the studies have been carried out on a prototype device in the laboratory environment. When transitioning from proof-of-concept experiments to electronic devices, packaging and signal measurement technologies must be considered in actual measurement systems. Hence, integration with traditional semiconductor techniques is still the orientation of metal nanogap development. We are confident that platforms with a compact size, a reduced cost, easy operation, and intuitive readout nanogap devices will eventually be commercially available, although great efforts are still needed.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

device applications, fabrication methods, physical properties, sub-5 nm metal nanogaps

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