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FOCUS REVIEW

Metal nanoarchitecture fabrication using DNA as a biotemplate

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Among the many important biopolymers, DNA has been a key component in material sciences and nanotechnology. We have focused on the fabrication of metal nanoarchitectures using DNA as a template due to its intrinsic properties and advantages, such as a well-ordered structure, rich chemical functionality and programmable base-pairing interactions, as well as the availability of multiple enzymes for DNA manipulation. In this review, various methods for the fabrication of DNA-templated metal nanoarchitecture are introduced. The methods include DNA-mediated metal nanoparticle formation, DNA-templated conductive nanowire fabrication by metal depositions, sequence-selective metal deposition onto DNA for elaborate nanowire fabrication and DNA brushes as templates for use on solid substrates. DNA sequence-selective binding of metal ions and metal complexes and subsequent reduction to metals are fundamental issues for the fabrication of metal nanoarchitectures. The resultant metal nanoparticles and their assemblies can be used as functional nanomaterials in applications such as catalysts, conducting nanowires, optical nanomaterials and especially in metamaterials. This biopolymer-templating method can be applied not only to metal deposition but also to the assembly of functional molecules.
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INTRODUCTION

Thanks to the recent developments in nanotechnology there have been a number of important advances in the fields such as electronics, optics, informatics, chemistry, biology and medicine. Nanotechnology was first mentioned in a lecture by Richard Feynman in 1959 and has been expanded markedly to date through the aid of new nanoimaging techniques such as atomic force microscopy (AFM) and electron microscopy. Top-down microfabrication technology such as lithography has contributed to the miniaturization and further integration of electronic substrates. On the other hand, bottom-up technology has been mainly applied to the fabrication and subsequent assembly of fine particles of a few nanometers to several tens of nanometers in size, providing semiconductors or metal nanoparticles with unique optical or photonic properties. For example, semiconductor nanoparticles, called Qdots, emit strong fluorescence and noble metal nanoparticles (for example, gold, silver and so on) show surface plasmon resonance. Such unique properties on the nanostructures of semiconductors and metals have opened up new fields of research. In particular, metal nanostructures have attracted a great deal of attention due to their applications to optical or photonic devices and sensors based on surface plasmon resonance[1–4] and, of course, nanoelectrodes.[5–7]

How to prepare more complex and extensive nanoarchitechtures is one of the most important issues in terms of broadening the range of practical applications. In general, top-down-type technology can provide freely designed two-dimensional structures down to several tens of nanometers in size. However, further miniaturization and three-dimensionalization remain challenges. Bottom-up type technology can produce structures of nanometer scale, although significant issues remain in terms of the fabrication and integration of complex structures. Bottom-up systems are prevalent in nature, especially in living bodies. It is a marvelous thing that bottom-up systems work in the production of sophisticated organic nanostructures and their assemblies *in vivo*. That is, bottom-up fabrication in a living system has managed to overcome the abovementioned issues. RNA and proteins are representatives of this type of fabrication. RNA is a biopolymer composed of four kinds of nucleotides and transcribed from a DNA template. When synthesized, RNAs form various structures according to their sequences and have essential roles in gene coding, decoding, regulation and expression. Proteins are translated from mRNA templates and have an amino-acid sequence as their primary structure. When synthesized, proteins form secondary and tertiary structures, such as alpha helices and beta sheets, according to their sequences. Further, more advanced functional organizations are constructed through assemblies with proteins or RNAs (quaternary structures). These elaborate biomaterials are constructed under extremely complicated conditions with various molecules and produce even longer DNA or proteins with high sequence accuracy, while organic syntheses of oligoDNA or peptides by chemists require relatively high concentration of substances (in the mM to M order) and a pure reaction solution free from impurities. These ideal fabrications in a living body are performed at controlled reaction site based on molecular recognition, templating and self-organization.

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Toward the mimicking of these good reaction sites using synthetic polymers, much attention has been paid to molecular imprinting methods, but it still remains challenging.[8,9] Therefore, bio-templated and, particularly, DNA-templated synthesis has been studied as a primary choice due to its controllability by sequence and simplicity in handling.[10]

DNA is an anionic polymer with excellent recognition ability that forms a double-stranded helical structure with quite rigid mechanical properties by Watson–Crick base pairing (A and T or G and C of different chains form complementary base pairs by specific hydrogen bonding). This double-helix formation, called hybridization, is reversible under high temperature and is highly sequence-specific. Because of the benefits of these characteristics, there are a huge number of reports on nanostructure fabrication using DNA hybridization. Mirkin *et al.*[11] demonstrated that two kinds of DNA-modified gold nanoparticles (AuNPs), which have complementary sequences, could form ordered assemblies through hybridization. Shultz and colleagues reported that DNA-attached AuNPs could be set on a complementary DNA at a predetermined distance.[12] DNA origami is a most impressive example of DNA nanotechnology first reported by Rothemund.[13] In this method, long single-stranded DNA from the M13mp18 phage genome is used as a scaffold and folded into a predetermined nanostructure through hybridization with the aid of a number of appropriately designed short DNAs, called staple strands. Further, controlled bottom-up integration of metal nanoparticles was performed by the use of DNA origami or DNA assemblies as programmable scaffolds.[14–16] Nanoarchitecture fabrications based on DNA hybridization are promising approaches and many well-summarized review papers already exist.[17–21]

On the other hand, DNA has other potential uses apart from hybridization in nanoarchitecture fabrications, such as specific binding to molecules, the formation of long rigid structures of easily controllable length, catalytic activities and chirality. Thus, in this review, we describe the recent advances in the fabrication of metal nanoarchitectures using DNA as a biotemplate with particular focus on the following topics: (1) DNA-mediated synthesis of metal nanoparticles; (2) metal depositions on DNAs for conductive nanowire; (3) sequence-selective metallization on DNA; and (4) DNA brushes as novel templates for metal nanoarchitectures to afford another approach to programmable assembly.

DNA-MEDIATED SYNTHESIS OF METAL NANOPARTICLES

DNA possess the ability to bind specifically to metal ions via several different modes of interaction dependent on nucleotide composition.[22] Thus, the use of DNA as templates for the syntheses of inorganic nanoparticles to control size and morphology has been an active area of research. Petty and co-workers prepared Ag nanoclusters with a narrow size distribution by utilizing a specific DNA–Ag ion interaction.[23,24] The strong interaction of Ag ions to DNA enabled stoichiometrically controlled complex formation and subsequent chemical reduction with $NaBH_4$ provided size-controlled Ag nanoclusters showing strong fluorescence. The fluorescence of the Ag nanoclusters could be tuned by the sequence of the oligonculeotides used as templates.[25,26] It is noteworthy that the plasmonic absorption of the prepared Ag nanoclusters with short oligonucleotides (short oligonucleotide-encapsulated Ag nanoclusters) showed induced circular dichroism.[23] On the other hand, Kotlyar *et al.*[27] reported a large circular dichroism response for silver nanoparticles (AgNPs) grown on the double-stranded long DNA of poly(dG)/poly(dC) as a chiral template of a helix structure at the surface plasmon frequency of AgNPs, suggesting that the chiral DNA template induced the growth of nanoparticles with chirality (Figure 1a).

As some DNA shows catalytic activity in reactions with nucleic acid substrates, known as deoxyribozyme (DNAzyme), DNA-catalyzed or DNA-modulated synthesis is another focus of the work on active templates.[28] Berti *et al.*[29] utilized the photo-harvesting property of DNA to reduce Ag ions bound to DNA chains. Ultraviolet irradiation of the DNA–Ag ion complexes provided an AgNP plasmon

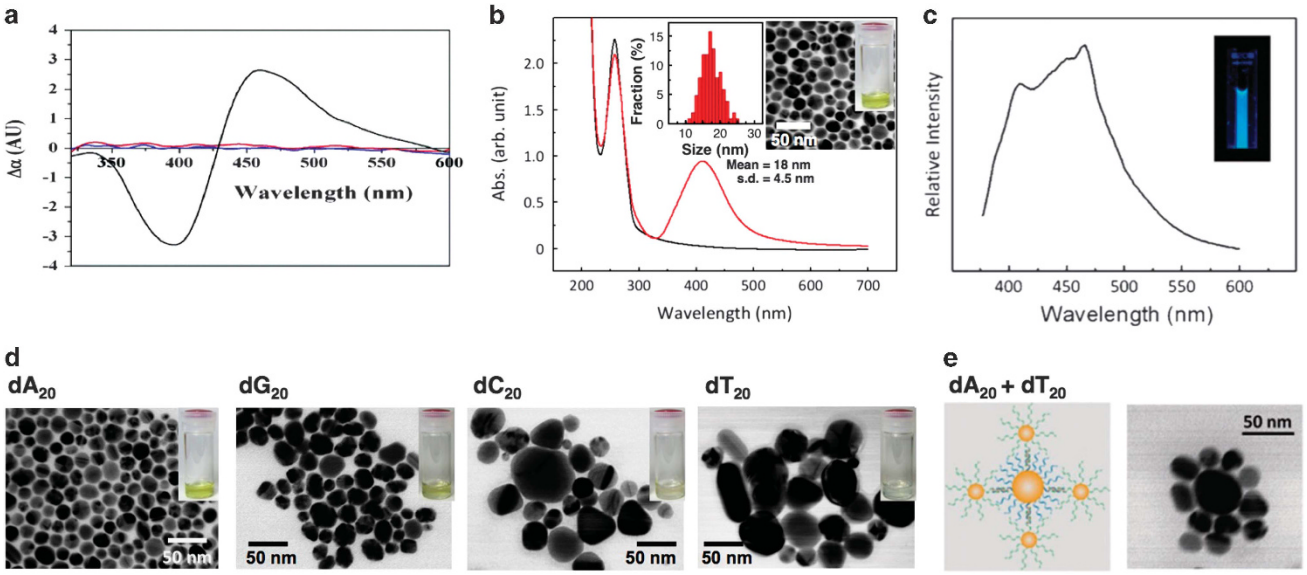

Figure 1 (**a**) Circular dichroism spectra measured of gold nanoparticles (AgNPs) grown on the DNA (black), grown in solution without DNA (red) and adsorbed to the DNA (blue).[27] (**b**) Absorption spectra of the suspension before (black) and after (red) ultraviolet irradiation for 5 min. Inset shows the size distribution, transmission electron microscopy (TEM) image and photograph of the dA_{20}-AgNP solution. (**c**) Fluorescence spectrum and photograph of the dA_{20}-AgNP dispersion under excitation by light at 360 nm. (**d**) TEM images of AgNPs prepared with dA_{20}, dG_{20}, dC_{20} or dT_{20}. (**e**) Illustration (left) and TEM image (right) of the DNA hybridization-directed assembly between the dA_{20}-AgNP and the dT_{20}-AgNP.[30] **a** was adapted with permission from Shemer *et al.*[27] Copyright (2006) American Chemical Society. **b**–**e** were adapted from ref. 30 with permission from the Royal Society of Chemistry.

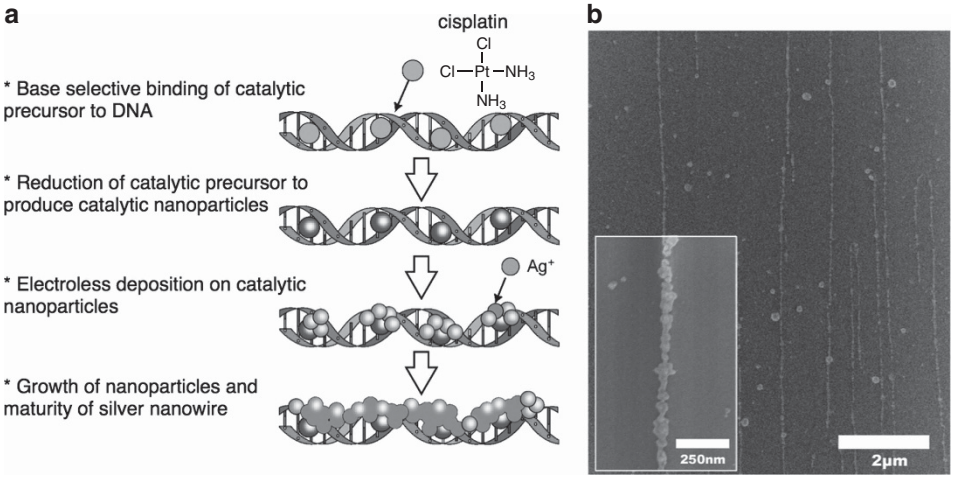

Figure 2 (**a**) A scheme for the fabrication of silver nanowires by base-selective electroless deposition on the stretched DNA molecule. (**b**) Scanning electron microscopy images of the DNAs after silver electroless deposition. A full color version of this figure is available at *Polymer Journal* online.

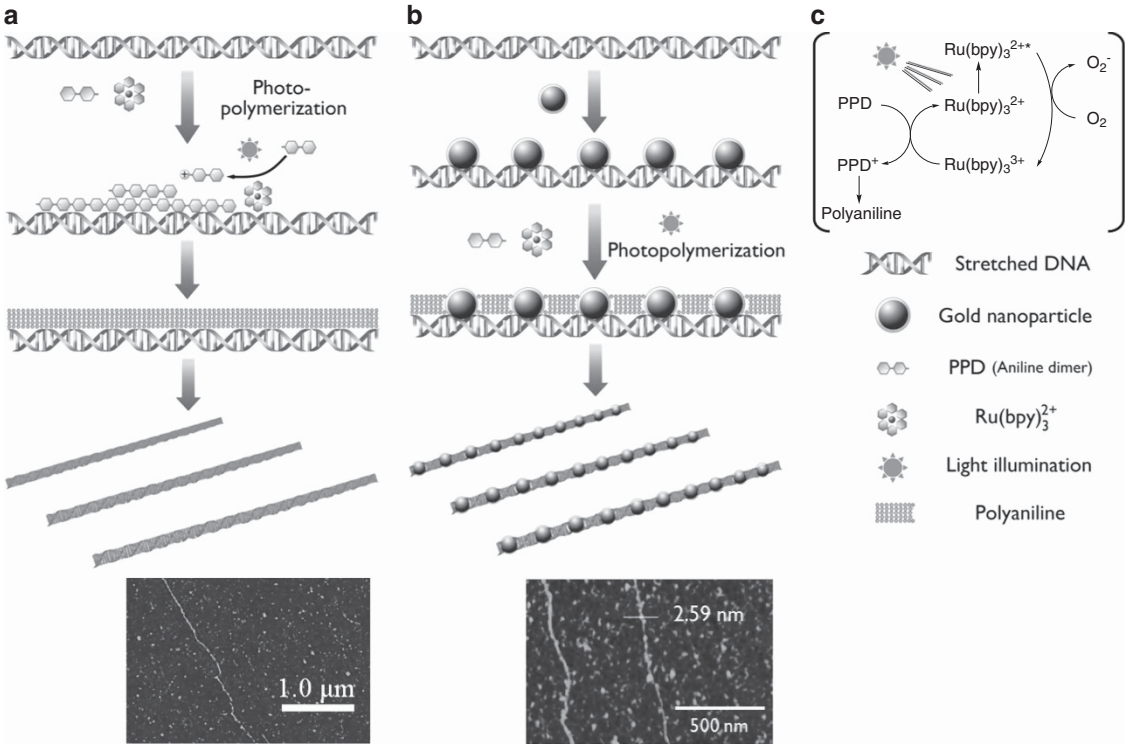

Figure 3 Schematic illustrations and typical atomic force microscopy images of the DNA-templated fabrication of polyaniline nanowires (**a**) and gold nanoparticle–polyaniline-alternated nanowires (**b**). The catalytic cycle of $Ru(bpy)_3^{2+}$-catalyzed photo-polymerization of polyaniline is shown in **c** for reference.[47] These figures were reproduced from ref. 47 with permission from the Royal Society of Chemistry. A full color version of this figure is available at *Polymer Journal* online.

absorbance peak, demonstrating AgNP formation. We have utilized DNA as a modulator for the photo-conversion of a lump of AgCl to functional AgNPs.[30–32] Although silver halides, such as AgCl, are originally photo-reactive, the photo-conversion of AgCl to AgNPs is greatly accelerated in the presence of oligoDNA (dA_{20}; 20 mer of deoxyadenosine phosphate). Prepared AgNPs were 18 nm in diameter with a relatively narrow size distribution and showed plasmonic absorption at around 400 nm in wavelength and strong fluorescence (Figure 1b and c).[30] As with previous reports, AgNPs prepared by our method also showed significant sequence dependence on particle size (Figure 1d). Encapsulated dA_{20} in AgNPs worked as a stabilizer for dispersion in water and could also be utilized as a crosslinker to immobilize dT_{20}-attached functional materials (Figure 1e). On the basis of the kinetic properties, DNA sequence dependence, and effects of solution conditions such as salt concentration and pH, we addressed the detailed mechanism of the DNA-mediated photo-transformation of AgCl to AgNPs.[32] Interestingly, Ag/AgCl nanostructures, which are intermediate products of the photo-conversion process, showed remarkable photo-catalytic activity over two orders of magnitude greater than those of previously reported systems.[31]

Moreover, DNA-encapsulated Ag/AgCl nanoparticles of ca. 40 nm in size exhibited selective photo-catalytic activity in the decomposition of dye molecules; first-order kinetics for positively charged dye molecules and zero-order kinetics for negatively charged ones.

METAL DEPOSITIONS ON DNAS FOR CONDUCTIVE NANOWIRE

Because of the long linear structure with substantial rigidity of the double helix, rich chemical functionality and programmable nature based on high-molecular recognition, DNA molecules have been studied as potential templates for the fabrication of conductive nanowires of <10 nm in width via doping to DNA,[33] electroless plating for the reduction of metal ions on DNA[34–36] and so on.[29,37–42] Braun and co-workers reported AgNP deposition on DNA, in which the DNA bridged the gap between microelectrodes via hybridization, and then silver ions adsorbed on the DNA via electrostatic interaction, followed by reduction with reducing reagents. A repeat of this cycle produced conductive silver nanowires of ca. 100 nm in width and several micrometers in length.[43] As mentioned above, Berti *et al.*[29] fabricated a silver nanowire through the photo-reduction of adsorbed silver ions catalyzed by DNA. We have studied a selective electroless deposition method, in which small metal were first attached to the intended sites as a catalyst followed by electroless deposition, which mainly proceeded at those sites with the assistance of the preadsorbed small metal particles. We used cisplatin, which is a platinum-based antineoplastic medicine that binds to DNA in preference to consecutive guanines, as a precursor metal. A silver nanowire of 50–100 nm in width and several micrometers in length was successfully prepared through the reduction of cisplatin to platinum metal, followed by extension and immobilization of DNA onto the substrate via the Langmuir–Blodgett method, and electroless plating of silver onto the platinum catalyst (Figure 2).[36,44] A high electric conductivity was observed on this silver nanowire over a length of 6 μm from the edge of a microelectrode using AFM with an electroconductive probe (conductive AFM measurement).[36]

On the other hand, there are many reports on the formation of DNA-templated conductive nanowire through coating with electroconductive polymers.[45,46] We have prepared polyaniline-coated DNA as a conductive nanowire through the $Ru(bpy)_3^{2+}$-catalyzed photoredox reaction of *N*-phenyl-*p*-phenylenediamine (as an aniline dimer); that is, $Ru(bpy)_3^{2+}$-catalyzed photo-polymerization. Further, AuNP–polyaniline hybrid nanowires were prepared through a sequential assembly process consisting of the adsorption of positively charged AuNPs (~1.5 nm in diameter) and $Ru(bpy)_3^{2+}$-catalyzed photo-polymerization of aniline dimers between the AuNPs on the DNA (Figure 3).[47] Point-contact current imaging AFM experiments revealed that the DNA-templated polyaniline nanowire possessed Schottky emission conduction and AuNP–polyaniline hybrid nanowires had a potential room-temperature Coulomb blockade effect as a one-dimensional array of multiple tunnel junctions between the polyaniline and AuNP. As this Coulomb blockade has been the focus of next-generation electronic devices such as single-electron devices, numerous nanostructures within nanogap electrodes have been studied.[48–51] DNA-templated conductive nanowires could bring about great advances in the development of novel charge-transport devices. Recently, metal deposition was performed on DNA origami as well as on extended straight DNA, providing various-shaped metal nanostructures.[6,52–54]

SEQUENCE-SELECTIVE METALLIZATION OF DNA

DNA-templated metallization was mostly applied to long naturally derived DNA such as λ-DNA, which has a random sequence, providing homogenous metal depositions. On the other hand, sequence-selective metallization would expand potential applications by enabling the fabrication of more elaborate metal nanostructures. Braun and co-workers reported sequence-specific patterning of DNA metal coating using RecA protein, which is related to DNA repair or homologous recombination (Figure 4).[55] First, RecA proteins were assembled on single-stranded DNA to form a nucleoprotein filament, the nucleoprotein then bound to an aldehyde-derivatized double-stranded DNA (dsDNA) molecule at a homologous sequence, forming triple-stranded DNA together with RecA proteins. Next, the sample was incubated in an $AgNO_3$ solution, with the Ag ions reduced by the DNA-bound aldehyde on the DNA but not on the RecA-binding position. RecA prevented Ag deposition by serving as a resist. As a

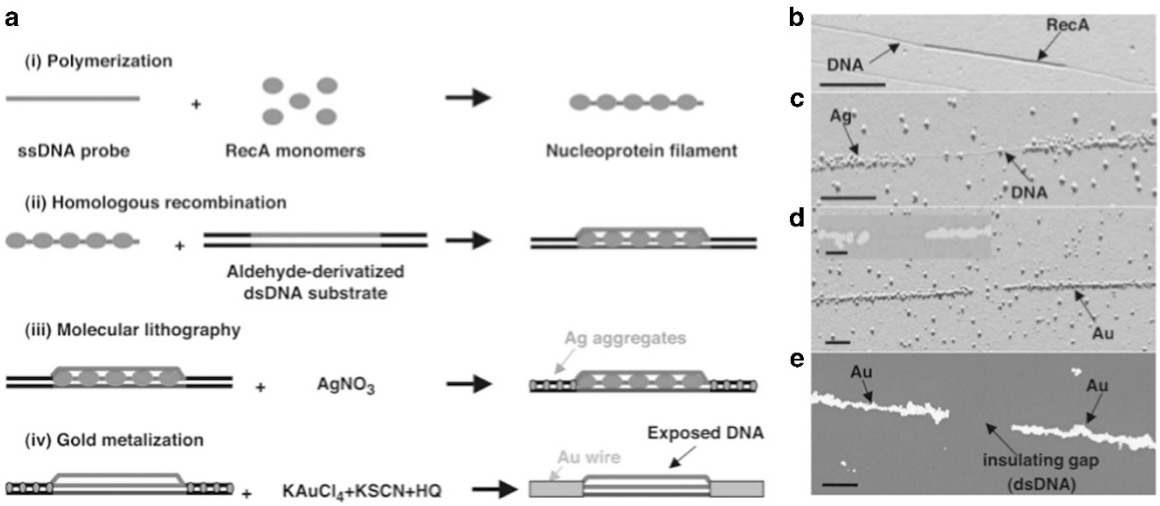

Figure 4 (**a**) Schematic illustrations of the homologous recombination reaction and molecular lithography. (**b**) Atomic force microscopy (AFM) image of a RecA-bound aldehyde-derivatized DNA. (**c**) AFM image of the sample after Ag deposition. (**d**) AFM image of the sample after gold metallization. Inset is a close-up image of the gap. (**e**) Scanning electron microscopy image of the wire after gold metallization. Scale bars in **b** through **e** are 0.5 μm; scale bar in inset **d** is 0.25 μm.[55] These figures were reproduced from Karen *et al.*[55] with permission from the American Association for the Advancement of Science. A full color version of this figure is available at *Polymer Journal* online.

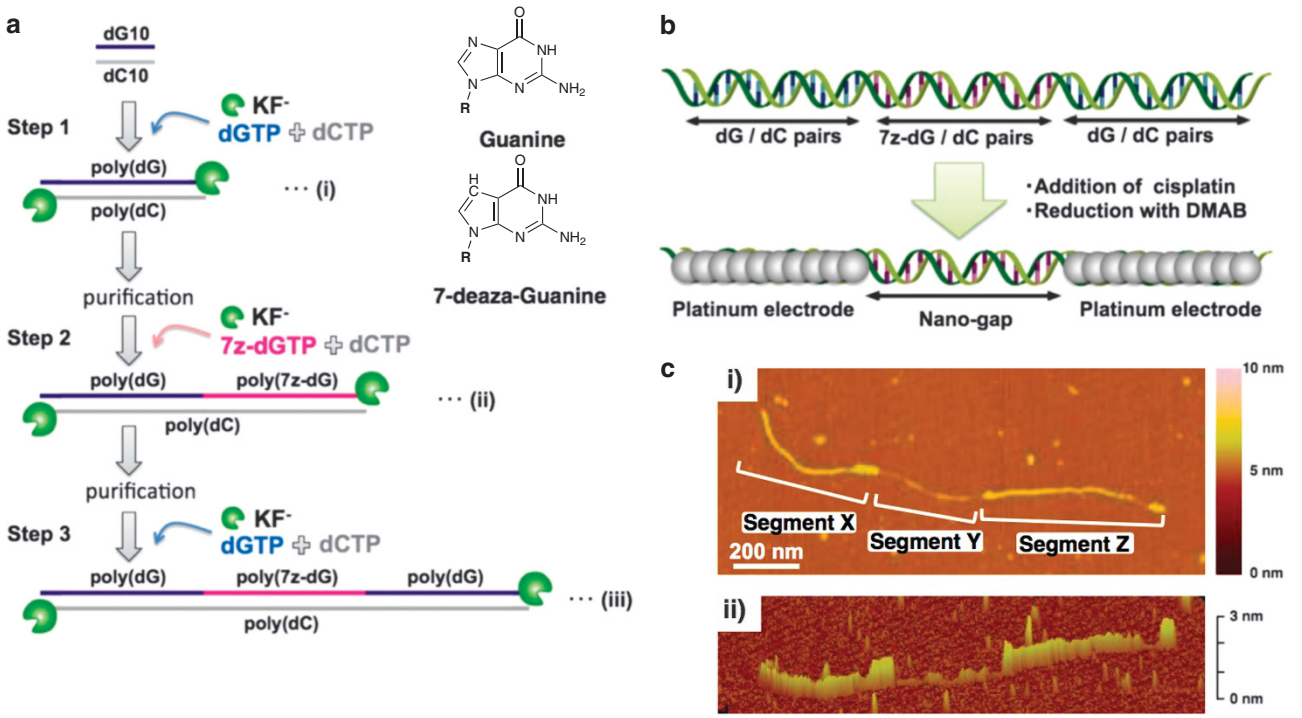

Figure 5 (**a**) Schematic illustration of the preparation of tri-block copolymer DNA using Klenow fragment exonuclease minus (exo-) and (**b**) sequence-selective metallization on this tri-block DNA. (**c**) Atomic force microscopy image (i) and bird's-eye view (ii) of the metal-deposited tri-block DNA copolymer.[69] These figures were adapted from Mitomo *et al.*[69] with permission from WILEY-VCH Verlag GmbH & Co. KGaA.

result, a gap was created between the Ag-loaded DNA segments. Finally, subsequent electroless gold deposition was performed on the Ag aggregates, which work as a catalyst, producing two continuous gold wires separated by the predetermined gap. This procedure has been further developed by Braun's and other research groups.[37,56] The use of RecA is a clever method of utilizing protein-binding ability and DNA molecular recognition. The production of various kinds of precise DNA-templated nanowire, however, requires a multitude of DNAs with adjusted lengths and sequences. Conventional synthetic DNA can only provide ca. 120 mer, in general, which is too short for application to nanowire production. Therefore, enzymatic polymerization provides another promising approach to prepare long DNAs with controlled lengths and sequences as a template. PCR is a widely used tool for amplifying specific dsDNA. Combining PCR and sequence-specific patterning using RecA enables various types of nanoscale programmable metallization.[57]

As an alternative approach to sequence-specific metallization, we have focused on the guanine-selective binding of cisplatin. To utilize guanine-selective cisplatin binding for designed metal depositions, the local control of DNA guanine content is required. For the preparation of this DNA, we studied the unique polymerase reaction mediated by Klenow fragment exonuclease minus (KF^-) of *Escherichia coli* DNA polymerase I. KF^- can provide high-molecular-weight dsDNA molecules with a narrow molecular-weight distribution from a pair of complementary oligonucleotides, which has homo-sequence or doublet or triplet repeats, as the template primer through the slippage extension reaction explained by the strand-slippage model.[58–61] First, we synthesized poly(dG)/poly(dC)-poly[d(AT)] as a diblock copolymer composed of continuous G (guanine) and repetitive AT sequences by the slippage extension reaction of the repetitive sequences from three template-primers, dG_{20}, dC_{10} and $dC_{10}d(AT)_{10}$.[62] Sequence-selective metallization was successfully performed on this diblock copolymer with cisplatin. Although the length of the domains can be changed by adjusting reaction conditions, it has a critical limit in terms of the flexibility of domain control; for example, it is impossible to make more than three domains. Fortunately, nucleotide analogs with unnatural bases offer may allow us to overcome these drawbacks. Because of their utility, various kinds of nucleotide analogs have been developed and are now on the market. Catalogs now offer unnatural nucleotides with 7-deaza-purin bases (7z-dG and 7z-dA), which have been applied to the analysis of the interactions between DNA and proteins,[63] or as a marker with a lower redox potential than natural bases.[64,65] As the cisplatin-binding site is the nitrogen atom at the 7-position of the guanine base, 7-deaza-guanine is a good candidate for a non-cisplatin-binding nucleotide, while the chemical structure is similar to the guanine of the nucleotide that cisplatin preferentially binds.[66–68] This similarity in chemical structure also allows it to be used in the enzymatic polymerization by KF^- as well as the sequential polymerization of poly(dG)/poly(dC) and poly(7z-dG)/poly(dC) from one simple pair of template-primer DNAs (oligo(dG) and oligo(dC)) as a living polymerization, as the complimentary base, cytosine, is the same (Figure 5).[69] In that report, we demonstrated the preparation of a tri-block copolymer composed of poly(dG)/poly(dC) parts and a poly(7z-dG)/poly(dC) part with sequence-selective platinum metal deposition on the GC part of the DNA block copolymers, providing sophisticated nanowires with a nanogap structure. This extended method allows the length and number of segments of the DNA block polymer to be easily controlled by adjusting the reaction time or conditions, such as solution temperature or substrate concentration, as well as the number of reaction cycles. This research indicated that the effective arrangement of molecular recognition, in this case the critical recognition of the 7-position of guanine by cisplatin and a relatively blunt recognition of the nucleotide bases by the polymerase, could expand the possible applications of DNA to nanofabrications.

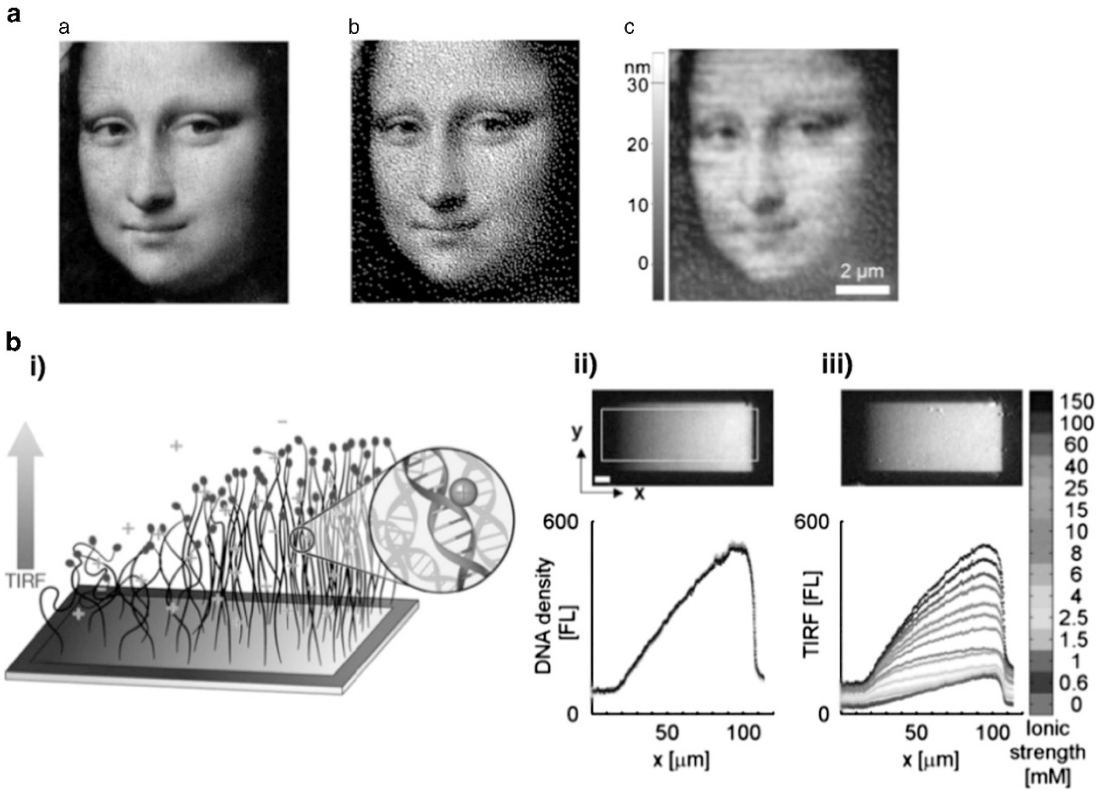

Figure 6 (**a**) (a) Gray-scale and (b) bitmap images of the Monalisa. (c) Atomic force microscopy topographic image of the Monalisa obtained from PMETAC brushes.[81] (**b**) Measurement of 1 kb DNA brush density and height. (i) Scheme of DNA brush along a density gradient. DNA ends labeled with a fluorophore (blue) excited by total internal reflection fluorescence (TIRF) and by standard epiFL. (ii, upper) The epiFL image of a DNA density gradient. (Lower) DNA density profile in arbitrary fluorescence units along the *x* axis averaged along the symmetric *y* axis at various NaCl concentrations (color code bar in ionic strength). Scale bar represents 10 μm. (iii, upper) TIRF image of a DNA density gradient. (Lower) TIRF profiles along the gradient taken as a function of salt (NaCl) concentration. The TIRF profiles support the salt-reflecting compression of height.[84] **a** was adapted from Zhou *et al.*[81] with permission from WILEY-VCH Verlag GmbH & Co. KGaA. A full color version of this figure is available at *Polymer Journal* online.

Recently, Kotlyar and co-workers reported a novel sequence-selective approach to silver deposition.[70] The incubation of oligonucleotide-coated AgNPs of 15 nm in a diameter with poly (dG)/poly(dC) yielded a uniform DNA nanowire of a few nanometer thickness, which is slightly thicker than the original DNA, while neither poly(dA)/poly(dT) nor the random sequence plasmid (pUC19) DNA underwent transition during incubation with the AgNPs. Although the detailed mechanism remains to be clarified, it is thought that the higher affinity of silver to G and C rather than to A and T leads to specific binding and the low ionization potential of guanine provides for the preferential oxidation of silver atoms in the NPs.

DNA BRUSHES AS NEW TEMPLATES FOR METAL NANOARCHITECTURES

Although there are a large number of reports on DNA-templated nanostructures, which have enormous potential, the integration of these nanostructures on a macroscopic scale with precise control of positioning is required for their practical application. This is one of the critical issues regarding the bottom-up approach, including that for DNA nanotechnology. One possible solution to this issue is fabrication on a substrate. One example of this is nanoparticle assembly to form superlattices via DNA hybridization. Mirkin *et al.*[71] set weak interactions between the AuNPs and the substrate, as well as between the AuNPs covered with DNAs, and then prepared crystals as extensive orientation- and thickness-controlled AuNP superlattices on the DNA-tethered substrate. DNA-tethered substrates, particularly short DNAs such as synthetic oligonucleotides, have been well developed and widely used for biosensing or for biomedical use on DNA microarrays.[72,73] On the other hand, polymer-tethered surfaces, particularly dense surfaces known as polymer brushes, have recently been attracting a good deal of attention in the fields of polymer science and surface chemistry.[74–77] Polymer brushes exhibit many novel and unique properties, such as wettability, adsorption and lubrication, due to the limited polymer chain structure under densely grafted conditions.[78–80] Moreover, polymer brushes can be three-dimensional-patterned (Figure 6a).[81,82] These reports suggest that a DNA brush could provide a good platform as a template for metal nanoarchitectures.

The characteristics of the dsDNA brush were reported by Bar-ziv *et al.*,[83,84] who reported that DNA brushes composed of long dsDNA (0.3–2.5 kb) over 500 chains per μm^2 in density-exhibited polymers in an extended state under low-salt conditions. This density is much lower than that of polymer brushes composed of synthetic polymers (Figure 6b).[84] This is speculated to result from the rigidity of the double-stranded helical coiled structure and the strongly charged property of the DNA. At a DNA density of 1200 chains per μm^2, the interchain distance is estimated to be ca. 30 nm, which could allow the insertion of nanoparticles. Thus, we applied DNA brushes as a template for the immobilization of rod-shaped AuNGs (gold nanorods: AuNRs).[85] To provide an appropriate electrostatic attraction, the AuNRs were modified with a mixture of cationic and nonionic surface

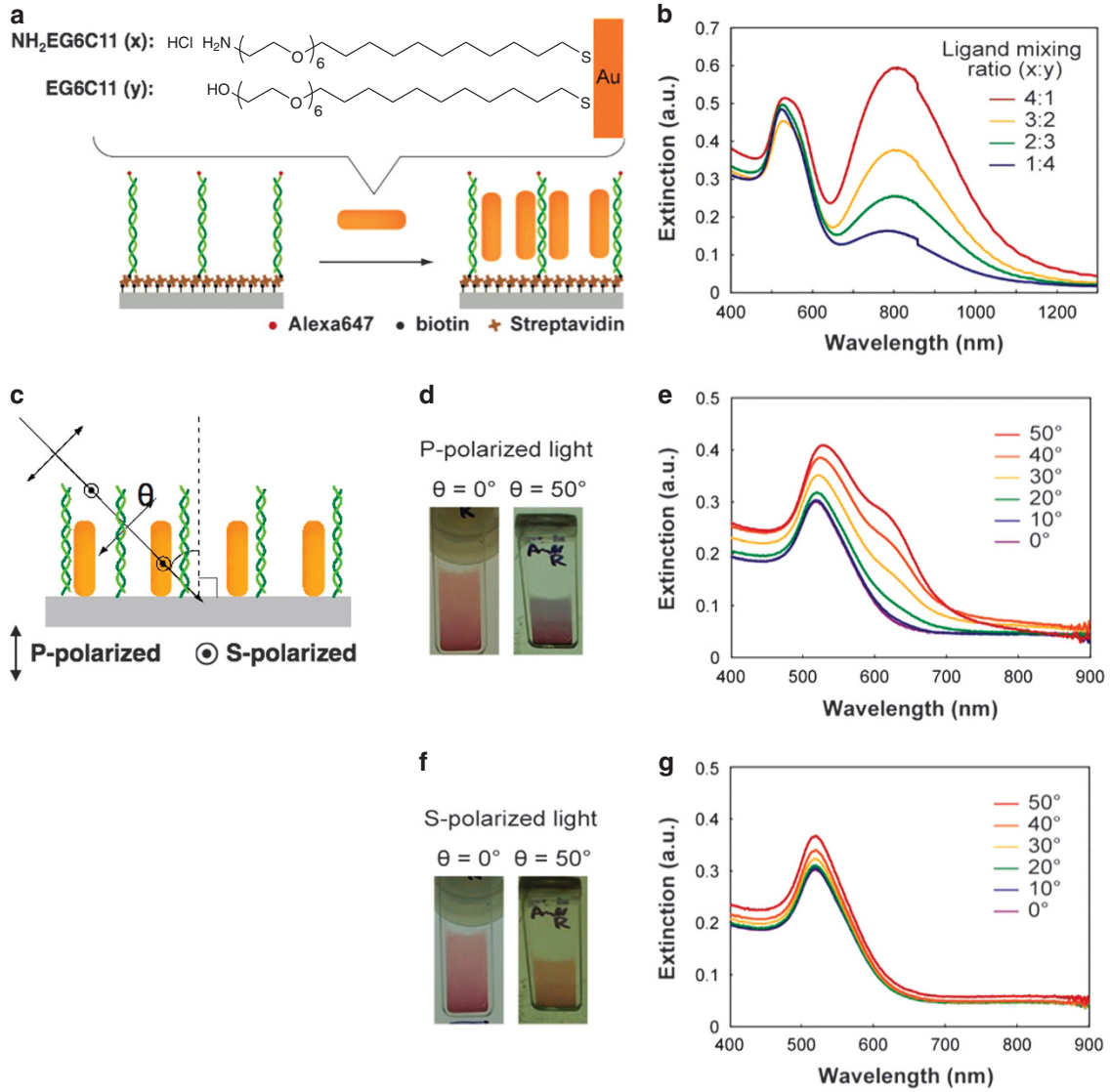

Figure 7 (**a**) Schematic illustration of the vertical assembly of gold nanorods (AuNRs) with the assistance of a double-stranded DNA brush. (**b**) Extinction spectra of AuNRs adsorbed on a DNA brush in a buffer (pH = 7.7). Various mixing ratios of surface ligands were used as shown. (**c**) Scheme showing the extinction of AuNRs under *p*- and *s*-polarized light with tilt angles. (**d**, **f**) Photos of the cuvette containing the adsorbed AuNRs through a polarizer (*p*-polarized for **d** and *s*-polarrized for **f**). (**e**, **g**) Extinction spectra of AuNRs (cationic:nonionic ligands = 1:4) adsorbed on a DNA brush (1200 chains per μm^2) under *p*-polarized (**e**) and *s*-polarized (**g**) light.[85]

ligands (chemical structures are shown in Figure 7a). Interestingly, the extinction spectra of the AuNRs adsorbed on the DNA brushes varied with the mixing ratio of the surface ligand; in other words, the extinction spectra were dependent on the electrostatic attraction (Figure 7b). In reverse proportion to the ratio of cationic ligands, the extinction peak for longitudinal surface plasmon resonance, which is located at around 800 nm, became weaker, while that for transverse surface plasmon resonance located at 530 nm did not show any significant change. This result indicates that weak electrostatic attraction leads to the vertical alignment of AuNRs on the substrates. Angle-dependent spectral changes and scanning electron microscopic images supported this notion (Figure 7c–g). Although there have already been several reports on the procedure for the vertical alignment of anisotropic nanoparticles, such as drop casting,[86,87] lithographic nanotemplate-assisted techniques[88,89] and interfacial assembly,[90] the extensive self-assembly of rod-shaped nanoparticles with a controlled density remains challenging due to thermal fluctuations and diffusion. Our DNA brush-templated assembly could afford a breakthrough from this perspective. Further, as DNA brush conformation was rather flexible and can change depending on the external condition, such as salt concentration,[84] much focus has been placed on a dynamic tuning of AuNR alignments on DNA brushes now.

Further, to expand the potential applications of DNA brushes, the fabrication of thicker three-dimensional-nanostructured DNA brushes is needed. In general, when longer polymer chains are applied to a substrate for the preparation of a polymer brush, known as the grafting-to method, the polymer density is lower due to the steric hindrance from the globule structure, leading to a poorly extended state. Therefore, in the field of polymer science, surface-initiated polymerization via the atomic transfer radical polymerization method, or the grafting-from method, has received a good deal of attention for the fabrication of dense polymer brushes composed of long polymers.

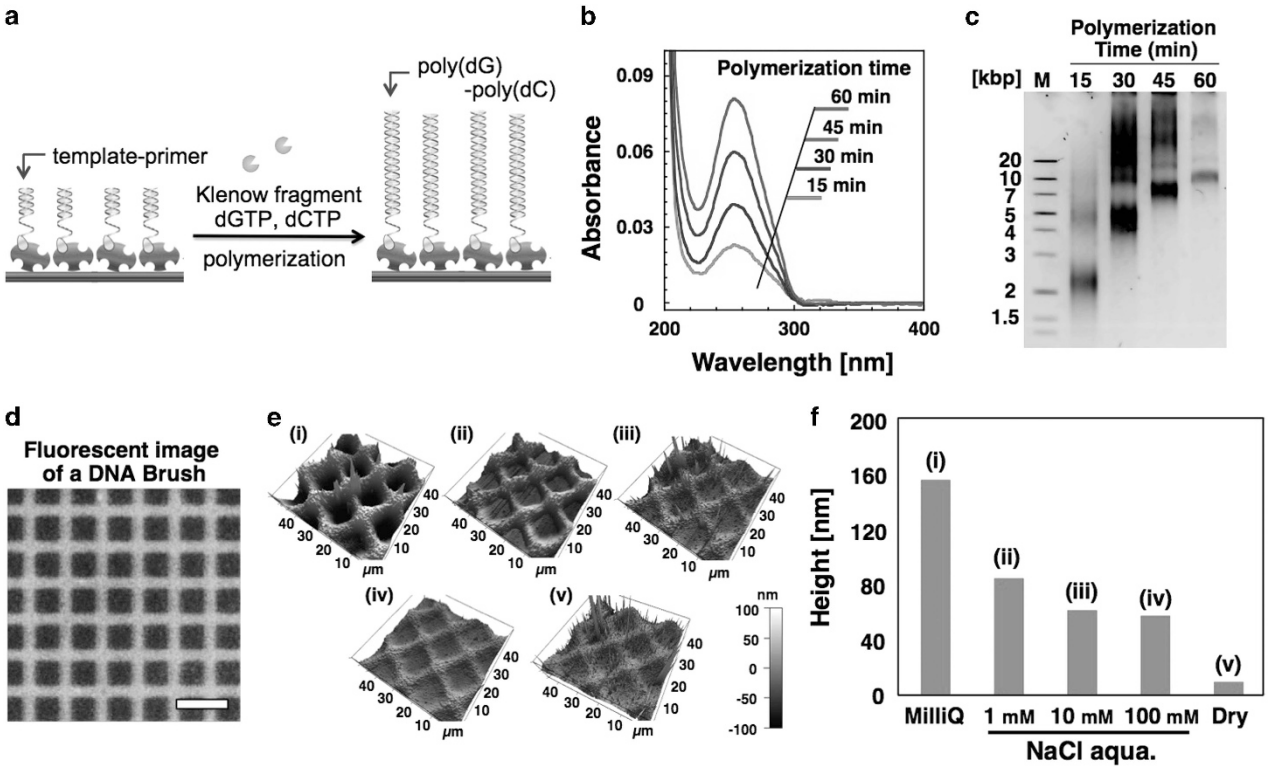

Figure 8 (**a**) Schematic illustration of double-stranded DNA (dsDNA) brush preparation on streptavidin substrates by surface-initiated enzymatic polymerization. (**b**) Absorption spectra of dsDNA brushes after 15, 30, 45 and 60 min polymerization on the substrate. (**c**) Agarose gel electrophoresis of the polymerized DNA after removal from the substrate. (**d**) Fluorescent image of a two-dimensional (2D)-patterned DNA brush stained with SYBR Green I. Scale bars represent 20 μm. (**e**) Atomic force microscope images (bird's-eye view) of a 2D-patterned DNA brush and (**f**) its height in MilliQ water (Merck Millipore, Tokyo, Japan) (i), 1 mM NaCl aq. (ii), 10 mM NaCl aq. (iii), 100 mM NaCl aq. (iv) and under dried conditions (v).[95] A full color version of this figure is available at *Polymer Journal* online.

For DNAs, there have been several reports on the preparation of single-stranded DNA brushes via surface-initiated enzymatic polymerization with a terminal deoxynucleotidyl transferase, or rolling-circle amplification method, as a grafting-from method.[91–93] However, there are only a few reports on the preparation of dsDNA brushes via the grafting-from method, despite the marked interest.[94] As mentioned above, we have studied slippage extension reaction by the Klenow fragment, providing long homo-sequence DNA.[62,69] A good living property at the terminus in the slippage extension reaction, such as the atomic transfer radical polymerization, allows the surface-initiated enzymatic polymerization of dsDNA on substrates. Double-stranded oligo(dG)/oligo(dC) was immobilized on the substrate via streptavidin–biotin interaction at one end, and then polymerized by KF^- (Figure 8a).[95] The length of the polymerized DNA showed good linearity to the reaction time, at least up to 10 kb (Figure 8b and c). The DNA density was constantly over 1500 chains per μm^2 independent of the chain length. Photo-patterning by ultraviolet irradiation through a photomask provided two-dimensional-patterned DNA brushes (Figure 8d) and these DNA brushes showed environment-responsive morphologic changes on AFM measurement similar to those in previous reports[84] (Figure 8e and f). Step-wise polymerization with various substances provides block copolymer-type DNA brushes. It is expected that successful combination with sequence-selective metallization will afford a three-dimensional-metal nanopatterning technique. Furthermore, although it is not related to metal nanofabrication, due to the specific biodegradability of DNA by nucleases, DNA brushes prepared by this procedure showed great potential as cell culture substrates, enabling the collecting of cells from the substrate by nuclease reaction without any damage.[96]

SUMMARY AND OUTLOOK

DNA has valuable characteristics of not only easy preparation, sequence controllability and sequence-specific binding in hybridization but also a long rigid structure with easily controllable length, recognition of various molecules, catalytic activity, chirality and so on. Thus, DNA has been attracting a good deal of attention as a template for the nanoarchitecture fabrication, particularly metal nanostructures. In this review, we have described DNA-templated metal nanoarchitecture fabrications with particular focus on DNA-mediated metal nanoparticle formation, DNA-templated conductive nanowire fabrication by metal deposition, sequence-selective metal deposition onto DNA for elaborate nanowire fabrication and DNA brushes as novel templates on solid substrates. Various techniques in relation to DNA have been developed based on a huge amount of research work. Now DNA nanotechnology has opened up a new world through its combination with metal nanostructures, which is expected to lead to practical applications in not only nanoelectronics but also nanophotonics and nanomedicine. Again, DNA is an extremely convenient and useful material. Therefore, it is expected that the use of DNAs as templates for metal nanoarchitectures can help us to identify valuable new products such as metamaterials, which are materials engineered to have properties not found in nature, based on their plasmonic properties.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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