DNA-mediated electrostatic assembly of gold nanoparticles into linear arrays by a simple drop-coating procedure

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The assembly of nanoparticles in topologically predefined superstructures is an important problem in the area of nanoscale architecture. In this letter, we demonstrate the electrostatic assembly of lysine-capped colloidal gold particles on drop-coated DNA films. Electrostatic interaction between the positive charges on the gold nanoparticles and the negative charges on the phosphate groups of the DNA template molecules leads to the assembly of the gold nanoparticles in linear superstructures. The use of DNA as templates for the assembly of nanoparticles shows promise for extension to more complex geometries through rational design of the DNA base sequences as well as in the realization of nanowires by stringing together metal nanoparticles. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1370993]

Bottom-up approaches for realizing ordered nanoscale structures are currently gaining in popularity. One aspect of nanoscale self-assembly that remains relatively unexplored is the organization of nanoparticles into predefined, topologically intricate structures. An attractive alternative to the more popular lithographic[1] and masking[2] procedures to achieve nanoparticle patterning is the use of biological templates for assembling nanoparticles. Different biological templates such as the tobacco mosaic virus[3] and bacterial S layers[4] have been used to grow and entrap the technologically important semiconductor quantum dots. DNA molecules, in particular, are being investigated as exciting templates for the generation of quantum wires.[5–9] The cylindrical double-helical structure of DNA molecules together with capability of the negatively charged phosphate groups in DNA to bind metal cations make them ideal templates for growing nanowires by stringing together metal nanoparticles.[5–9]

In this letter, we demonstrate the DNA-mediated electrostatic assembly of gold colloidal particles in thin film form into linear superstructures. More specifically, drop-dried films of synthetic DNA double-helical molecules were deposited on suitable substrates and thereafter, addition of lysine-capped gold colloidal particles to the film lead to spontaneous ordering of the gold particles into linear structures via attractive electrostatic interaction between the positively charged gold particles and the negatively charged phosphate groups of the DNA template molecules. This relatively simple (and DNA-friendly) process for the realization of linear superclusters of gold nanoparticles shows promise for application to nanowire synthesis by stringing together metal nanoparticles as well as extension to topologically more intricate structures. Our approach is different from other methods reported in the literature wherein ion exchange followed by reaction was used to assemble both semiconductor quantum dots (CdS)[5–7] and metal nanoparticles such as Ag[8]and Pd[9] on the surface of DNA molecules.

A 10^{-6} M concentrated solution of synthetic double-helical 30-mer DNA molecules of the primary sequence CCT TAA GCT TTT GTA GAA TCT ATC TAC ATA[10] was prepared and films of the DNA molecules cast on quartz and highly conducting Si wafers by placing drops of the DNA solution on the different substrates and evaporation of the aqueous component. This process was repeated three times to get a fairly thick DNA film. Gold colloidal particles were prepared by borohydride reduction of $HAuCl_4$ solution as described elsewhere.[11] This resulted in a clear ruby-red gold solution at *p*H = 9 with particles of size 3.5 ± 0.7 nm.[11] The *p*H of the colloidal gold solution was adjusted to 7 using dilute HCl following which the gold particles were capped with molecules of the amino acid, lysine (Sigma chemicals) to yield an overall amino acid concentration in the colloidal solution of 10^{-5} M. Lysine molecules were used to cap the gold particles since the isoelectric point of lysine (termed ''pI'' and defined as the *p*H at which the net charge on the amino acid is zero) is relatively high (pI = 8.5, by virtue of two amine functional groups in the amino acid). The lysine molecules, and consequently the colloidal gold particles, would be positively charged at physiological *p*H which is an important requirement in the electrostatic assembly protocol described herein. A small redshift in the gold surface plasmon resonance from 530 to 538 nm was observed in the UV-*VIS* spectra of the gold colloidal solution indicating surface co-ordination of the lysine molecules. All UV–*VIS* spectroscopy measurements in this study were carried out on

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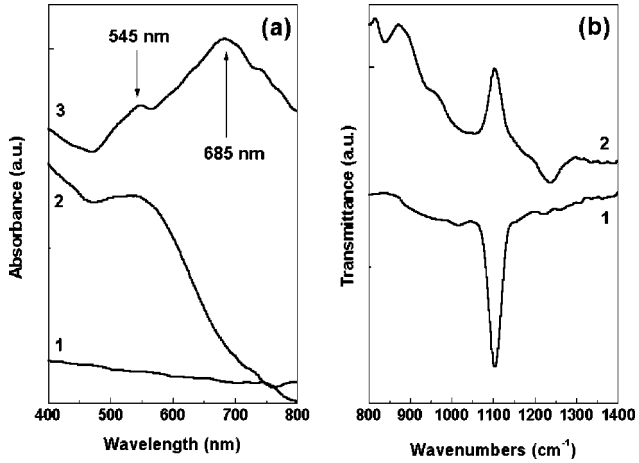

FIG. 1. (a) UV-*VIS* spectra recorded from a drop-dried DNA film deposited on quartz (curve 1); a lysine-capped gold nanoparticle film deposited by solution casting onto quartz (curve 2), and a drop-dried DNA film to which lysine-capped gold nanoparticles were added (curve 3). The transverse and longitudinal surface plasmon resonances are indicated in the figure. (b) FTIR spectra recorded from a DNA film deposited on a Si (111) substrate by solution casting (curve 1) and from a drop-dried DNA film on Si (111) substrate after addition of lysine-capped gold nanoparticles (curve 2).

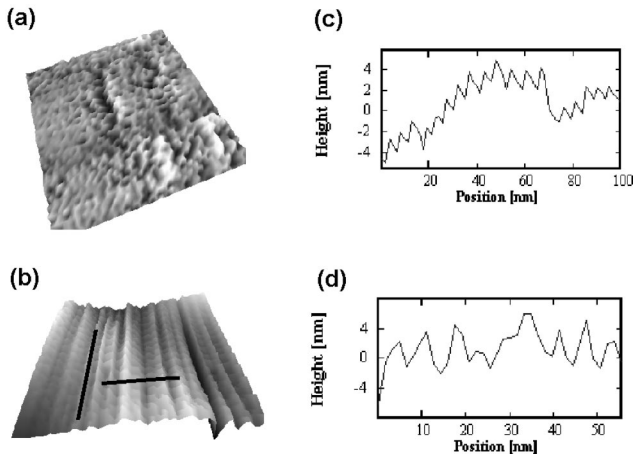

FIG. 2. (a) STM image recorded from a drop-dried DNA film deposited on a conducting Si substrate. The extent of this image is 100 nm×100 nm. (b) STM image recorded from a drop-dried DNA film deposited on a conducting Si substrate after addition of lysine-capped gold nanoparticles. The extent of this image is 100 nm×100 nm. (c) Surface height variation with distance along the vertical line shown in the STM image of the DNA-gold nanoparticle film (b). (d) Surface height variation with distance along the horizontal line shown in the STM image of the gold nanoparticle-DNA film (b).

a Hewlett-Packard HP8542A diode array spectrophotometer operated at a resolution of 2 nm.

After stabilization of the lysine-capped gold nanoparticle solution, drops of the gold solution were added to the DNA films on quartz and Si wafers and the films allowed to dry. For comparison, a film of lysine-capped gold nanoparticles was also cast on a bare quartz substrate. Figure 1(a) shows the UV-*VIS* spectra recorded from the plain DNA film (curve 1); a film of lysine-capped gold nanoparticles (curve 2), and the DNA film after complexation with lysine-capped gold nanoparticles by simple drop-coating (curve 3). A number of interesting features are seen which may be interpreted as follows. A strong resonance is observed at 545 nm [indicated by an arrow in Fig. 1(a)] in both the lysine-capped gold nanoparticle film (curve 2) as well as the DNA film complexed with lysine-capped gold nanoparticles (curve 3). This resonance is due to excitation of surface plasmon vibrations in the gold nanoparticles and is responsible for the ruby-red color of the nanoparticle films and solutions.[11,12] This resonance is clearly absent in the bare DNA film (curve 1). In addition to the resonance at 545 nm, the DNA film complexed with lysine-capped gold nanoparticles shows an additional resonance at 685 nm [indicated by an arrow in Fig. 1(a)]. It is well known that aggregation of noble metal colloidal particles such as silver and gold into quasilinear superstructures leads to the appearance of a longitudinal surface plasmon resonance, redshifted with respect to the transverse component (in this case, the 545 nm resonance).[13,14] The presence of the longitudinal plasmon resonance at 685 nm in the DNA–Au nanoparticle conjugate film (curve 3) is therefore strongly indicative of assembly of the gold nanoparticles in extended, open structures mediated by the underlying DNA template. Attractive electrostatic interaction between the positive charges in the lysine molecules bound to the gold nanoparticles and the negative charges on the phosphate groups of the DNA molecules drives the assembly of the gold nanoparticles into close-packed, open structures inferred from the UV-*VIS* measurements. The DNA molecules thus act like counterions and screen the repulsive interactions between the positively charged gold nanoparticles thus enabling their assembly into close-packed superstructures.

Figure 1(b) shows the Fourier-transform infrared (FTIR) spectra recorded from the DNA film on a Si (111) wafer (curve 1) and the DNA film after complexation with lysine-capped gold nanoparticles (curve 2). These measurements of the DNA and DNA–Au nanoparticle films were carried out in the diffuse reflectance mode on a Shimadzu FTIR-8201 PC instrument operated in the diffuse reflectance mode at a resolution of 4 cm^{-1}. A strong absorption band centered at 1105 cm^{-1} is clearly observed in the as-prepared DNA film (curve 1). This resonance is assigned to the deoxyribose band, the presence of which is known to be a strong indicator of the hybridization of the DNA molecules in a double-helical structure.[15] On complexation of the DNA film with lysine-capped gold nanoparticles, this resonance is broadened and shifted to smaller wavenumbers. This indicates some destabilization of the double-helical structure consequent to electrostatic assembly of the gold nanoparticles. However, as will be seen from the microscopy studies later, this factor does not affect the linear gold nanoparticle superstructure formation, which is the goal of this protocol.

Direct evidence of the formation of linear assemblies of gold nanoparticles mediated by the DNA template and indirectly inferred from the UV-*VIS* results [Fig. 1(a)] is obtained from scanning tunneling microscopy (STM) measurements. STM measurements of the as-prepared DNA film as well as the DNA film after complexation with lysine-capped gold nanoparticles deposited on highly conducting Si wafers were carried out in a low-current, home-built instrument operated at a current of 17 pA and a bias voltage of 1 V.[16] The STM image obtained from the as-deposited DNA film is shown in Fig. 2(a). While the individual structural units such as the bases in the DNA molecules are not resolved in this image, it is observed that the molecules have organized themselves into aggregates with some indication of long-

range order. Earlier STM studies of DNA films on highly oriented pyrolytic graphite[17] and Au (111) substrates[18] have revealed similar aggregated structures of DNA. The films were extremely stable in time and repeated scans did not result in the movement of the DNA molecules over the surface. This indicates fairly strong binding of the DNA molecules with the underlying Si substrate, possibly through interaction of the phosphate groups in the DNA with Si atoms on the surface of the substrate. Another possibility is the strong interaction of the adenine bases in the DNA molecules with Si, an aspect which has been observed in other STM related studies.[19] An estimate of the thickness of the DNA film deposited by drop-coating on a highly conducting Si wafer was made using ellipsometry.[20] The film was fairly uniform over the surface of the substrate with an average thickness of 5 nm. This thickness corresponds to roughly 2.5 DNA double-helical molecules stacked one on top of the other.

The STM image recorded from this DNA film after addition of lysine-capped gold nanoparticles and thorough drying of the film is shown in Fig. 2(b). This image clearly shows highly organized, parallel linear assemblies of the gold nanoparticles. In order to ascertain whether the dimensions of the features seen in Fig. 2(b) agree with expected sizes of the gold nanoparticles and the DNA molecular length, the surface height variation with distance along two nearly perpendicular directions [indicated in Fig. 2(b)] was plotted and are shown in Figs. 2(c) and 2(d). The surface height variation with distance along the length of one of the linear nanoparticle assemblies is plotted in Fig. 2(c) and clearly shows the presence of a high degree of order in the supercluster. The average size of the structures along the length of the Au ''nanowire'' was estimated to be ~4 nm in excellent agreement with the size of the nanoparticles (3.5 nm). A plot of the surface height variation along a direction perpendicular to that of Fig. 2(c) is shown in Fig. 2(d). In this case as well, a highly regular and periodic assembly of structures is seen. The average size of these structures is ~10 nm. The length of a 30-mer DNA molecule is ~11 nm and indicates that the DNA molecules are organized parallel to the direction of measurement of Fig. 2(d). We would like to add that STM images of films of lysine-capped gold nanoparticles deposited by drop coating on bare Si substrates did not show any ordering into superstructures. The STM results thus provide unequivocal evidence for the templating action of the DNA molecules by a simple drop-coating method described earlier. We believe that the DNA molecules which are locked into a fairly rigid structure prior to addition of lysine-capped gold nanoparticles [Fig. 2(a)] are rendered sufficiently mobile due to solvation by water during addition of drops of the lysine-capped gold nanoparticle solution on the DNA film surface. This process facilitates reorganization into highly regular linear nanoparticle superstructures during electrostatic complexation. The reorganization of the DNA molecules by electrostatic interaction with the gold nanoparticles may be viewed as the in-plane analogue of the well-known electrostatically driven layer-by-layer assembly of nanoscale systems along a direction normal to the substrate surface.[21] A sandwich structure consisting of alternate layers of positively charged gold nanoparticles and negatively charged DNA molecules constrained to grow along a plane parallel to the surface of the substrate would lead to an energetically stable situation as seen in the STM images [Fig. 2(b)].

In conclusion, a simple procedure based on drop-casting films of DNA followed by lysine-capped gold nanoparticles on solid supports has been described which leads to the spontaneous ordering of the nanoparticles into linear superstructures. This ordering is mediated by electrostatic interaction between the positively charged gold particles and the negatively charged DNA template molecules. This approach shows promise for extension to topologically more intricate structures based on rational DNA design as well as in the generation of nanowires.

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