DNA-Templated Assembly of Au Nanoparticles via Step-by-Step Binding Reaction

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We demonstrated DNA-template assembly of gold-nanoparticles AuNP via step-by-step binding reaction. The control of hydrophilicity for mica surface makes it possible to preserve the structure of AuNP-binded DNA network with resistance to Au-thiolate reaction in ethanol solvent. This method realizes the formation of a continuous AuNP array with uniform height and small width. [DOI: 10.1380/ejssnt.2004.222]

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Molecular electronics, first suggested by Amirav and Ratner, has attracted much attention in the last quarter-century. This idea includes the concept that individual organic molecules can satisfy the requirements of electronic devices with their stable nanoscale structure and have energy levels that can be tailored by chemical synthesis. Notwithstanding the great anticipation of the potential of molecular-scale electronics, it is very difficult to fabricate molecular-devices, owing to the lack of effective technologies for assembling and wiring molecules.

DNA is a key material in the fabrication of nanostructures by the 'bottom-up' process, which incorporates highly selective chemical recognition and self-assembly [1–6]. In particular, DNA-templated assembly of nanoparticles has been studied intensively in the hope of building nanoscale circuits where nanoparticles might play roles such as conductive nanowires [7–10], quantum dots [11], anchor sites for molecules [12, 13], and so on.

Recently, we have found that gold nanoparticles (AuNP) can be combined with a DNA network [14] on the substrate by a convenient one-pot procedure [15]. Based on this finding, we propose a new strategy to assemble AuNPs by using a step-by-step Au-thiolate reaction. This method realizes formation of a continuous AuNP array with uniform height and small width.

Figure 1 shows a schematic illustration of DNA-templated, step-by-step growth of AuNP nanowires. Initially, an AuNP-combined DNA network is prepared on the substrate. Second, alkanedithiol molecules are attached to the network of AuNP combined with DNA. Third, AuNPs are attached to the opposite end of alkanedithiol molecules. After repeating the cycle of steps two and three above, the AuNPs, which were initially separated, are bridged along the DNA by the array of AuNPs and alkanedithiol. As a result, quasi-one-dimensional nanowires of AuNPs are formed along the DNA strands.

In this study, we chose butanedithiol for linker molecule. This is because that the length of butanedithiol is approximately 0.5 nm, which is short enough to prevent formation of undesired structures like hairpin loops and to permit electron tunneling for hopping conduction. Furthermore, butanedithiol satisfy the well-known condition that the formation of self-assembled monolayer with standing molecules on Au surface requires molecular length to be longer than that of alkane chain with three or four carbons.

All chemicals used to form AuNP nanowire were commercial products of reagent grade. The DNA used for network formation was a synthetic double-stranded complex of the polydeoxyriboadenylic acid and polydeoxyribo-
FIG. 2: (a) AFM image of gold-nanoparticle (AuNP)-combined DNA network. (b) AFM image following the ethanol treatment for AuNP-combined DNA network formed on hydrophilic mica surface. The DNA structure is completely destroyed and no AuNPs remain on the substrate. (c) AFM image following the ethanol treatment for AuNP-combined DNA network formed on hydrophobic mica surface. The AuNP-combined DNA network is preserved with resistance to ethanol treatment.

FIG. 3: AFM images and height analysis of gold-nanoparticle nanowires: (a) wide scan image (3 µm × 2 µm), (b) magnified image, (c) height profile for the line in Fig. 3(b), (d) histogram of height distribution for the whole surface of Fig. 3(b), (e) image of an extremity of gold-nanoparticle wire.

Bothymidylic acid (Poly(dA)-Poly(dT)) (Amersham Bioscience). The DNA was dissolved in distilled water to produce a concentration of 25 U (1 U = 50 ng/l). The AuNPs (BBInternational, EM.GC5) used had an average diameter of 5 nm and were supplied as an aqueous solution at a concentration of $5 \times 10^{14}$ particles/ml. The solution was centrifuged at 15,300 G at 4°C for 1 hour. After centrifugation, we removed the clear supernatant and separated the useful portion, which contained an AuNP concentration of $3 \times 10^{14}$ particles/ml. In the case of cyclic reactions for growing the AuNP nanowire, ethanol was added to avoid the denaturing of AuNP-combined DNA networks. Butanedithiol (Sigma-Aldrich) used for linking molecules was diluted in ethanol to a concentration of 1 mM. Atomic force microscopy (AFM) observation was conducted by a scanning probe microscope (JEOL, JSPM4200) using tapping-mode operation in air at room temperature.

The AuNP-combined DNA network was formed by a simple procedure in which the mixed solution of AuNP and DNA, wherein the DNA concentration is adjusted to 10 U, is dropped on the substrate and the droplet was blown off a minute after the dropping it. Figure 2(a) shows an AuNP-combined DNA network. When the sam-
ple was soaked in ethanol, which is the solvent of the Au-thiolate reaction, for 15 minutes, the DNA network is completely destroyed and no AuNPs remain on the surface as shown in Figure 2(b). To form an AuNP nanowire based on the AuNP-DNA network, it is necessary that the network does not degrade by the cyclical process represented in Fig. 1. To improve the adherability of the mica substrate surface to the DNA molecules, we examined the extent of the mica surfaces hydrophilicity and attempted to control it. The inset of Fig. 2(b) shows the contact angle for freshly cleaved mica, indicating its hydrophilic property. The mica surface can be changed to become hydrophobic by rinsing it with distilled water as shown in the inset of Fig. 2(c). After this treatment, AuNP-combined DNA network are not destroyed by ethanol exposure. The mechanism of this change is presumed to be a stoichiometry variation of surface cation of mica surface and the effect is often utilized for the fixation of biological materials in AFM imaging.

After the two cycle of the bonding reaction, the wire-like structures along DNA strands can be clearly observed, as shown in Fig. 3(a). The AuNP nanowire has an unbroken length of more than 1 mm. Figure 3(b) shows a magnified image of AuNPs nanowires in which individual AuNPs are resolved. The sectional profiles (Fig. 3(c)) show that the AuNP wire has a uniform height of 7 nm. Since the height is greater than the 5 nm diameter of the used AuNPs, we can conclude that the AuNPs are adsorbed onto the DNA molecules. On the other hand, height difference between the first and second AuNP layer is smaller than the diameter of the AuNPs. This is because the second layer of AuNPs are adsorbed on not on-top of, but hollow sites of first layer of AuNPs.

This height analysis is true of the whole surface, as shown in the histogram of height distribution (Fig. 3(d)). The histogram indicates four peaks: the first to fourth peaks correspond to the height of substrate surface, DNA network, first AuNP layer, and second AuNP layer, respectively. The peak intensity of the second layer is smaller than 2% of that of the first, which indicates that the binding reaction between the AuNPs prevent three-dimensional growth, instead forcing growth to occur only along DNA strands. Actually, Fig. 3(e) shows that the extremities of AuNP wires are necessarily located on DNA strands and that AuNP wire has many kinks, reflecting the structure of the DNA network.

Previous works have shown that it is difficult to produce fine, continuous AuNP wires of uniform height. For example, the electrolysis method provides continuous AuNP wires, but their shape is rugged and not well controlled. In contrast, the assembly of AuNP wires using the DNA-templated bonding reaction can satisfy these factors concurrently. Moreover, we could not find any gaps between the AuNPs in the AFM images. Since the AuNPs are connected by butanedithiol molecules, the gap width is expected to be less than 0.5 nm, so electrons might penetrate any gap by tunneling.

The binding reaction using the Au-thiolate reaction can be extended to various organic molecules possessing electronic, magnetic and photonic functions. Step-by-step assembly using DNA templates shows promise for becoming a basis for realizing nanoscale molecular devices.

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[1] Y. Maeda, T. Nakamura, K. Uchimura, T. Matsumoto, H. Tabata and T. Kawai, J. Vac. Sci. Technol. B 17, 494 (1999).
[2] K. Keren, Y. Soen, G. B. Yoseph, R. Gilad, E. Braun, U. Sivan and Y. Talmon, Phys. Rev. Lett. 89, 088103 (2002).
[3] K. Jiang, A. Eitan, L. S. Schadler, P. M. Ajayan and R. W. Siegel, Nano Letters 3, 275 (2003).
[4] R. P. Fahlman, M. Hsing, C. S. Sporer-Tuhten and D. Sen, Nano Letters 3, 1073 (2003).
[5] M. Mertig, L. C. Ciaccchi, R. Seidel and W. Pompe, Nano Letters 2, 841 (2002).
[6] R. Jin, G. Wu, Z. Li, C. A. Mirkin and G. C. Schatz, J. Am. Chem. Soc. 125, 1643 (2003).
[7] K. Keren, M. Krueger, R. Gilad, G. Ben-Yoseph, U. Sivan and E. Braun, Nature 297, 72 (2002).
[8] E. Braun, Y. Eichen, U. Sivan and G. Ben-Yoseph, Nature 391, 775 (1998).
[9] O. Harnack, W. E. Ford, A. Yasuda and J. M. Wessels, Nano Letters 2, 919 (2002).
[10] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor and H. v. Löhneysen, Phys. Rev. Lett. 88, 176804 (2002).
[11] D. Wang, A. L. Rogach and F. Caruso, Nano Letters 2, 857 (2002).
[12] S.-J. Park, T. A. Taton and C. A. Mirkin, Science 295, 1503 (2002).
[13] F. P. Zamborini, M. C. Leopold, J. F. Hicks, P. J. Kulesza, M. A. Malik and R. W. Murray, J. Am. Chem. Soc. 124, 8958 (2002).
[14] T. Kanno, H. Tanaka, N. Miyoshi and T. Kawai, Jpn. J. Appl. Phys. 39, L269 (2000).
[15] Y. Sacho, H. Tabata and T. Kawai, Jpn. J. Appl. Phys., submitted.