JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

DNA-Templated Fabrication of Two-Dimensional Metallic Nanostructures by Thermal Evaporation Coating

Yu He, Tao Ye, Alexander E. Ribbe, and Chengde Mao*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

Supporting Information

ABSTRACT: A biotemplating strategy for fabrication of metallic nanoparticle arrays has been developed. The templates are self-assembled DNA nanostructures, which dictate nanoparticle synthesis in the gas−solid phase (during thermal evaporation).

This communication reports an approach for the preparation of two-dimensional (2D) arrays of gold nanoparticles (AuNPs) through dry coating (thermal evaporation) of self-assembled 2D DNA nanoarrays (templates). The DNA templates dictate the AuNP patterns, and the amount of thermally evaporated gold controls the AuNP size. We have demonstrated this strategy by the preparation of tetragonal and hexagonal AuNP superlattices, which were characterized by transmission electron microscopy (TEM) imaging.

Metal and semiconductor nanoparticles have been extensively investigated for their unique physical properties in electronics, plasmonics, etc.[1] AuNPs are one of the most important materials among them. Considerable efforts have been devoted to organize AuNPs into well-defined assemblies in searching for novel functions.[2] To prevent AuNPs from randomly aggregating, DNA is often used as a protecting and organizing ligand.[2c,2d] In a typical process, thiolated DNA molecules are conjugated with AuNPs through Au−S interactions. After conjugation, DNA strands retain their hybridization capability and can associate with their complementary DNA strands. Hence, DNA can guide the self-assembly of AuNPs. This strategy has been widely used to control reversible AuNP aggregation and forms the basis for many bioanalytical methods.[3] An alternative method to control the geometry of AuNP assemblies is based on structural DNA nanotechnology.[4] DNA forms well-defined nanostructures independent of AuNPs and provides structural scaffolds for AuNPs. In both strategies mentioned above, AuNPs are prepared in advance. Here we report a complementary approach for preparing 2D AuNP arrays via a simple spray-painting (thermal evaporation coating) process. During this process, Au atoms/clusters (the ink material) are thermally evaporated onto self-assembled DNA nanostructures (the templates) and assemble into nanoscale particles (AuNPs). The AuNP superstructure is determined by the geometry of the DNA template. In this method, DNA molecules are not conjugated to AuNPs that have been prepared in advance; instead, they serve as inert physical substrates for in situ AuNP synthesis.

DNA is an ideal building block for molecular self-assembly and provides great potential in material sciences and nanotechnology. DNA can readily assemble into complex 2D patterns[5] with feature sizes as small as 5 nm,[6] which is far smaller than those obtained by traditional photolithography. Recently, a family of symmetric, star-shaped DNA motifs were developed for the self-assembly of large periodic 2D DNA lattices with all allowed 2D symmetries.[7] In this work, we used the tetragonal[7c] and hexagonal DNA lattices[7a] for synthesizing 2D AuNP arrays to demonstrate the so-called spray-painting approach. The fabrication process involves the following steps (Figure 1): (1) DNA 2D lattices are assembled in an aqueous buffer and ligated with T4 DNA ligase to improve their mechanic strength.[8] (2) The DNA arrays are then deposited onto a copper-grid-supported lacey carbon film and stained with uranyl acetate. The pore size of the lacey film ranges from several hundred nanometers to several micrometers. The DNA arrays that span across pores have no support. (3) Finally, gold metal is thermally deposited onto the DNA lattices. Because the DNA arrays are porous (their cavity sizes are slightly larger than 15 nm), the evaporated gold accumulates only along the DNA molecules and forms patterned AuNP arrays. The AuNP size is dependent on the amount of gold deposited.

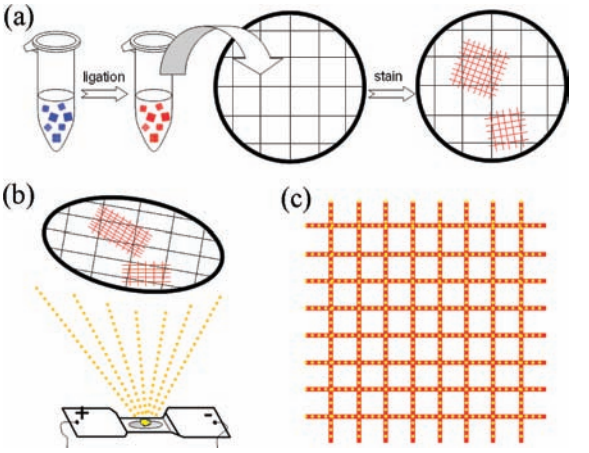

Figure 1. Schematic drawing of the formation of 2D AuNP lattices: (a) 2D DNA arrays are assembled in solution and then ligated to enforce stability; the ligated 2D DNA arrays are transferred onto a nonbacking lacey carbon film-covered copper grid and then stained with 4% uranyl acetate solution. (b) The sample-loaded copper grid is then coated with a thin layer of gold by thermal evaporation. Since both the lacey carbon film and DNA lattices are porous, the evaporated gold atoms and clusters accumulate only along the DNA backbones and lacey carbon films. (c) An expected metallic structure consisting of gold nanoclusters, which can be visualized by TEM.

2D DNA arrays were assembled according to the reported method (see the Supporting Information for details).[7,8] Briefly, phosphorylated peripheral DNA strands and circular central DNA strands were mixed in TAE/Mg^{2+} buffer at the desired

Received: July 7, 2010
Published: January 19, 2011

dx.doi.org/10.1021/ja1060092 | J. Am. Chem. Soc. 2011, 133, 1742–1744

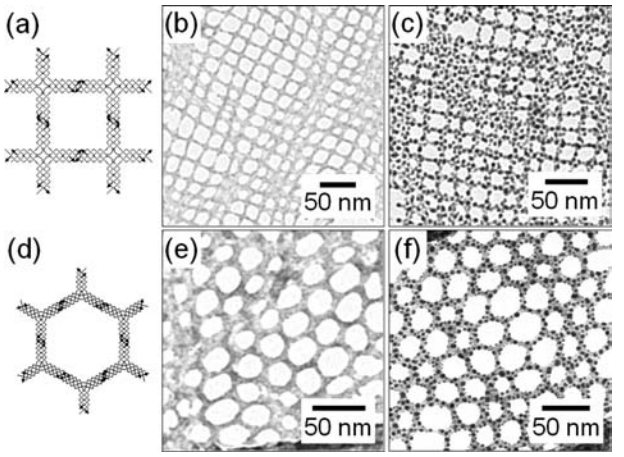

Figure 2. (a, d) Schematic representations of tetragonal and hexagonal DNA arrays composed from a symmetric four-pointed- and three-pointed-star motifs, respectively. (b, e) Uranyl acetate-stained DNA arrays visualized by TEM. (c, f) 2D DNA arrays deposited with 8 Å of gold, irradiated under an electron beam, and imaged by TEM.

ratio. The self-assembly was then performed by slowly cooling the mixture solutions from 90 to 25 °C over 48 h. T4 DNA ligase and ATP were then added into the DNA solutions to partially seal the nicks in the sugar−phosphate backbones of the DNA lattices. After ligation, the DNA 2D arrays were stable and resistant to heat treatment at 65 °C. The as-prepared DNA 2D arrays were mechanically strong enough to span across several micrometers and were readily visualized by TEM after being stained with uranyl acetate. Two different DNA arrays were tested. One was a tetragonal array assembled from a symmetric four-pointed-star motif (Figure 2a). The observed average edge length of each square was close to 20 nm (Figure 2b), which is consistent with the reported value.[7c] The other array was a honeycomb-like hexagonal array with a repeat distance of ~30 nm (Figure 2e) that was assembled from a symmetric three-pointed-star motif (Figure 2d). Gold evaporation was performed in a vacuum chamber, and the amount of the evaporated gold was monitored by a quartz crystal thickness monitor. After 8 Å of gold was deposited onto the DNA arrays, the deposited samples were characterized by TEM (Figure 2c,f). Since the contrast of the gold was much higher than that of the uranyl acetate-stained DNA, it was clearly evident that discrete AuNPs with a size of 4 ± 2 nm were formed along the patterned DNA lattices. Inheriting the well-defined order of the template DNA arrays, the AuNPs exhibited clear tetragonal and hexagonal patterns in the present experiments.

Interestingly, the gold on the DNA arrays formed discrete nanoparticles instead of continuous nanowires. Furthermore, the observed particle size was much larger than the evaporated gold thickness. We speculate that the initially deposited gold atoms/clusters are not stable and that they migrate along the DNA backbone and fuse into large, stable clusters either during the thermal evaporation process or under electron-beam irradiation during TEM imaging. It is well-documented that evaporated metal atoms and clusters are fairly active and motile on substrates.[9] Thermal or electron-beam treatment should facilitate the diffusion of Au clusters, leading to the formation of larger-sized discrete AuNPs. On the basis of this speculation, we expected to observe larger AuNPs when more gold was deposited. In our following experiment (Figure 3), a 3 nm thick layer of gold was deposited; the products were still discrete AuNPs, but the AuNP size increased to 9 ± 3 nm. This experiment not only supports our reasoning but also suggests an easy way to control the AuNP size on the 2D arrays.

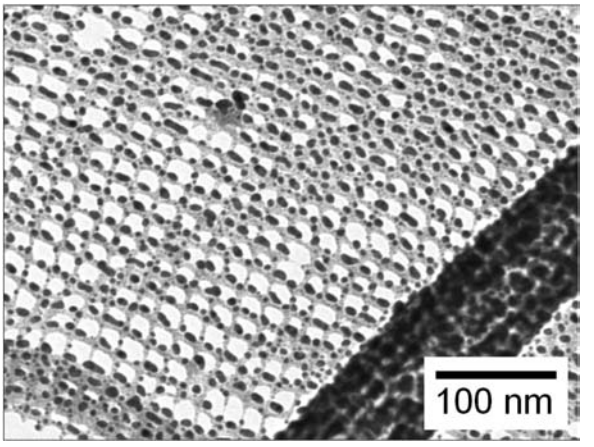

Figure 3. TEM image of tetragonal 2D DNA arrays coated with 3 nm gold.

In summary, we have developed a simple spray-painting strategy for the preparation of 2D AuNP arrays. The rapidly developing DNA nanotechnology provides ample candidates as structural templates, which could expand the scope of application of this technique. In addition, it is conceivable that this strategy could also be applied to nanofabrications using other metallic or semiconducting materials. With further elaboration, not only nanoparticle arrays but also metallic nanomeshes are expected, which could meet the increasing interest in studying the electronic properties of hyperbranched conductive networks.[10] We believe that the strategy reported here could facilitate the development of state-of-the-art nanoelectronics and nanodevices.

■ ASSOCIATED CONTENT

Supporting Information. Experimental methods and additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
mao@purdue.edu

■ ACKNOWLEDGMENT

This work was supported by the Office of Naval Research (N000140910181 and N000140911118). The AFM study was carried out in the Purdue Laboratory for Chemical Nanotechnology (PLCN).

■ REFERENCES

(1) (a) Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346. (b) Alivisatos, A. P. *Science* **1996**, *271*, 933–937. (c) He, L.; Musick, M. D.; Nicewarner, S. R.; Salinas, F. G.; Benkovic, S. J.; Natan, M. J.; Keating, C. D. *J. Am. Chem. Soc.* **2000**, *122*, 9071–9077.

(2) (a) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell, T. P.; Rotello, V. M. *Nature* **2000**, *404*, 746–748. (b) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690–1693. (c) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607–609. (d) Alivisatos, A. P.; Johnsson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P.; Schultz, P. G. *Nature* **1996**, *382*, 609–611. (e) Park, S. Y.;

Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2008**, *451*, 553–556. (f) Nykypanchuk, D.; Maye, M. M.; van der Lelie, D.; Gang, O. *Nature* **2008**, *451*, 549–552.

(3) Rosi, N. L.; Mirkin, C. A. *Chem. Rev.* **2005**, *105*, 1547–1562.

(4) (a) Sharma, J.; Chhabra, R.; Cheng, A.; Brownell, J.; Liu, Y.; Yan, H. *Science* **2009**, *323*, 112–116. (b) Deng, Z.; Tian, Y.; Lee, S. H.; Ribbe, A. E.; Mao, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 3582–3585. (c) Pinto, Y. Y.; Le, J. D.; Seeman, N. C.; Musier-Forsyth, K.; Taton, T. A.; Kiehl, R. A. *Nano Lett.* **2005**, *5*, 2399–2402. (d) Zheng, J.; Constantinou, P. E.; Micheel, C.; Alivisatos, A. P.; Kiehl, R. A.; Seeman, N. C. *Nano Lett.* **2006**, *6*, 1502–1504.

(5) For recent reviews, see: (a) Seeman, N. C. *Nature* **2003**, *421*, 427–431. (b) Feldkamp, U.; Niemeyer, C. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1856–1876. (c) Lin, C.; Liu, Y.; Rinker, S.; Yan, H. *ChemPhysChem* **2006**, *7*, 1641–1647. (d) He, Y.; Liu, H.; Chen, Y.; Tian, Y.; Deng, Z.; Ko, S. H.; Ye, T.; Mao, C. *Microsc. Res. Tech.* **2007**, *70*, 522–529. (e) LaBean, T. H.; Li, H. *Nano Today* **2007**, *2*, 26–35. (f) Seeman, N. C. *Mol. Biotechnol.* **2007**, *37*, 246–257. (g) Aldaye, F. A.; Palmer, A. L.; Sleiman, H. F. *Science* **2008**, *321*, 1795–1799.

(6) Zhang, C.; He, Y.; Chen, Y.; Ribbe, A. E.; Mao, C. *J. Am. Chem. Soc.* **2007**, *129*, 14134–14135.

(7) (a) He, Y.; Chen, Y.; Liu, H.; Ribbe, A. E.; Mao, C. *J. Am. Chem. Soc.* **2005**, *127*, 12202–12203. (b) He, Y.; Mao, C. *Chem. Commun.* **2006**, 968–969. (c) He, Y.; Tian, Y.; Chen, Y.; Deng, Z.; Ribbe, A. E.; Mao, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 6694–6696. (d) He, Y.; Tian, Y.; Ribbe, A. E.; Mao, C. *J. Am. Chem. Soc.* **2006**, *128*, 15978–15979.

(8) O'Neill, P.; Rothemund, P. W. K.; Kumar, A.; Fygenson, D. K. *Nano Lett.* **2006**, *6*, 1379–1383.

(9) Bechtolsheim, C. v.; Zaporojtchenko, V.; Faupel, F. *Appl. Surf. Sci.* **1999**, *151*, 119–128.

(10) Zhu, J.; Peng, H.; Chan, C. K.; Jarausch, K.; Zhang, X. F.; Cui, Y. *Nano Lett.* **2007**, *7*, 1095–1099.