The Journal of Physical Chemistry B

 VOLUME 103, NUMBER 42, OCTOBER 21, 1999

LETTERS

Fabrication of CdS Nanoparticle Chains along DNA Double Strands

Tsukasa Torimoto,*,†,§ Masahiro Yamashita,† Susumu Kuwabata,† Takao Sakata,‡ Hirotaro Mori,‡ and Hiroshi Yoneyama*,†

Department of Materials Chemistry, Graduate School of Engineering, Osaka University, and Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University, Yamada-oka 2-1, Suita, Osaka 565-0871, Japan

Received: June 2, 1999; In Final Form: August 19, 1999

Positively charged CdS nanoparticles having diameter of 3.0 ± 0.2 nm were prepared by the chemical modification of their surfaces with thiocholine. Chains of size-quantized CdS nanoparticles were prepared by using the electrostatic interaction between positively charged nanoparticle surfaces and the phosphate groups of DNA molecules. The observation by transmission electron microscopy revealed that the CdS nanoparticles were arranged in a quasi one dimension with dense packing. The line width of a nanoparticle array was equal to the diameter of CdS nanoparticles that was ca. 3.0 nm. The average distance between the centers of the adjacent nanoparticles was estimated to be 3.5 nm, which was almost equal to the length of 10 base pairs in DNA double strands.

Introduction

Fabrication of size-quantized semiconductor and metal nanoparticles arrays have attracted much attention[1−18] because of their interesting optical and electronic properties, such as photoinduced energy transfers,[2,7] metal−insulator transition,[12,13] and enhanced nonlinear optical effects.[18] A variety of strategies was performed to form nanoparticle arrays: crystallization of nanoparticles,[1−11] Langmuir−Blodgett techniques,[12−17] and chemical cross-linking between nanoparticles.[19−26] Among these methods, the last technique is not principally restricted by both size of nanoparticles and their chemical composition and seems to have advantages in order to arrange nanoparticles into a desired configuration. So far, several approaches have been reported, including the direct cross-linking between surfaces of nanoparticles with use of bifunctional molecules[19−21] and theinteraction of connecting units preattached to the surface of nanoparticles, such as the hydrogen bonding[22] and the hybridization of complementary single-stranded DNA.[23−27]

Recently a double-strand DNA molecule has been a promising construction material for fabrication of nano-structured scaffolds[28,29] because of the physicochemical stability, the linearity of molecular structure, and the mechanical rigidity.[30] For example, Au nanoparticle arrays bridged with DNA double strands have been prepared by hybridization of single-strand DNA, to which surface-modified Au nanoparticles were previously bound.[23−27] The distance between the neighboring Au nanoparticles was controlled by the length of DNA,[24−27] resulting in the exhibition of the absorption spectra characteristic of Au nanoparticles assembly. Furthermore, preparation of nanoparticles wires has been accomplished by the direct deposition of CdS[31] and Ag[32] nanoparticles on DNA double strands. As an alternative approach to prepare a wire-like structure of nanoparticle array, it may be promising to assemble the prepared nanoparticles along DNA double strands with use of an electrostatic interaction between nanoparticles and DNA

* Corresponding authors.
† Department of Materials Chemistry. Graduate School of Engineering.
‡ Research Center for Ultrahigh Voltage Electron Microscopy.
§ E-mail: torimoto@ap.chem.eng.osaka-u.ac.jp.

10.1021/jp991781x CCC: $18.00
Published on Web 09/30/1999

molecules. To our best knowledge, however, such attempts have never been performed.

In this study, we have attempted to prepare CdS nanoparticle chains which have line widths equal to the size of nanoparticles, by using the electrostatic interaction between the cationic surface modifiers on the CdS nanoparticles and the phosphate groups in DNA double strands as a template.

Experimental Section

Thiocholine iodide ((2-mercaptoethyl)trimethylammonium iodide) as a cationic thiol compound was prepared by hydrolysis of *S*-acetylthiocholine iodide under acidic condition.[33,34] Acetylthiocholine iodide was added to 2.0 mol dm^{-3} HCl aqueous solution under N_2 atmosphere and stirred for 12 h, followed by neutralization with addition of 28 wt % NH_3 aqueous solution. The resulting solution which contained 0.86 mol dm^{-3} thiocholine was immediately used for the surface modification of CdS nanoparticles.

CdS nanoparticles having positive charges on their surfaces were prepared by the inverse micelle techniques under N_2 atmosphere.[35] The inverse micelles were prepared by adding 4.0 cm^3 of water into 200 cm^3 of heptane containing 14.0 g sodium bis(2-ethylhexyl)sulfosuccinate (AOT). Aqueous solutions of 1.0 mol dm^{-3} $Cd(ClO_4)_2$ (0.48 cm^3) and 1.0 mol dm^{-3} Na_2S (0.32 cm^3) were, respectively, added to 120 and 80 cm^3 aliquots of the prepared inverse micelle solution. After being stirred individually for 1 h, they were mixed together and stirred for another 1 h, resulting in the formation of CdS nanoparticles in the inverse micelles. A sample of 0.47 cm^3 of the above-mentioned thiocholine solution was added to the inverse micelle solution containing CdS nanoparticles, followed by stirring for 15 h to modify chemically the surfaces of the CdS nanoparticles with thiocholine molecules. Then, methanol was added to destroy the inverse micelles, resulting in precipitation of thiocholine-modified CdS nanoparticles. The obtained precipitate was filtered and successively washed with heptane and ethanol.

The crude CdS nanoparticles which should contain AOT as an impurity could not be dissolved in pure water, probably due to the electrostatic binding of the sulfonate groups of AOT molecules to the quaternary ammonium groups bound on the CdS surfaces. So the CdS nanoparticles were suspended in 5 cm^3 of an NaCl-saturated aqueous solution, and the solution was stirred for 1 h to exchange AOT bound on nanoparticles with chloride ions, giving a transparent yellow solution with a little amount of undissolved residue. After removing the residue by filtration, the thiocholine-modified CdS nanoparticles were subjected to a size-selective precipitation process[36] using pure water/2-propanol as a pair of solvent/nonsolvent, to narrow the particle-size distribution and to remove impurities. 2-Propanol was added to the CdS nanoparticle colloid solution until the precipitation of CdS nanoparticles appeared. The precipitate was separated by centrifugation and washed by alcohol, and then redissolved in pure water. These procedures were repeated several times. Finally, thiocholine-modified CdS nanoparticle aqueous solution was subjected to ultrafiltration to remove residual impurities by using a 2-nm pore size ultrafilter (Amicon PM-10).

Figure 1 shows schematic illustrations presenting the procedures for preparation of CdS nanoparticle arrays along DNA double strands. A chloroform solution containing both 0.33 mmol dm^{-3} dioleoyl trimethylammonium propane (DOTAP, a cationic amphiphile) (Avanti Polar Lipids) and 0.67 mmol dm^{-3} β-oleoyl-γ-palmitoyl L-α-phosphatidylcholine (OPPC, a zwitterionic amphiphile) (Wako Pure Chemicals) was prepared. This solution was spread over 20 mmol dm^{-3} Tris buffer (pH 7.0) containing 0.5 μmol dm^{-3} (base pair) salmon testes DNA (Sigma) in a Teflon trough at 27 °C to form an amphiphile monolayer having cationic net charges at air−water interface. The surface area was compressed by moving the Teflon-coated barrier until the surface pressure became 10 mN m^{-1}, and the barrier was held for 5 h to deposit DNA double strands with electrostatic interactions between the phosphate groups of DNA molecules and quaternary ammonium groups of DOTAP in the amphiphile monolayer.[37−39]

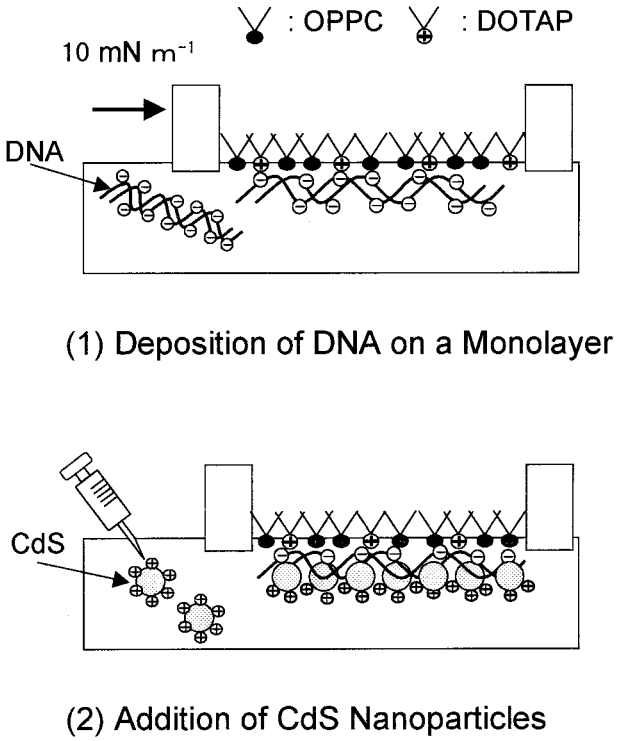

Figure 1. Schematic illustration of the deposition of a CdS nanoparticle chain along a DNA molecule on a DOTAP−OPPC mixture monolayer at air−water interface by using electrostatic interactions.

The thiocholine-modified CdS nanoparticle colloid was gently added in the water subphase so as to give 1.2×10^{17} particle dm^{-3} CdS nanoparticles at the constant surface pressure of 10 mN m^{-1}. This situation gave four CdS nanoparticles per 10 base pairs of DNA. This amount of CdS nanoparticles was four times greater than the experimentally obtained amount for densely packed CdS nanoparticle arrays along DNA double strands, as described below. The trough was left to stand for 2 h to induce electrostatic deposition of CdS nanoparticles along DNA double strands. Specimens observed by a transmission electron microscope (TEM) were prepared by transferring the DOTAP−OPPC mixture monolayer onto a copper TEM grid with an amorphous carbon overlayer. For this purpose, the TEM grid was vertically dipped through the monolayer at the air−water interface and then lifted up at 5.0 mm min^{-1}. During the deposition procedures, the surface pressure of the monolayer was kept at 23 mN m^{-1} in order to obtain the densely packed amphiphile monolayer on the TEM grid.

Results and Discussion

Thiocholine-modified CdS nanoparticles had an absorption peak due to the first exciton transition at 420 nm and an absorption onset at 470 nm as shown in Figure 2a. It is noteworthy that the obtained CdS nanoparticles exhibited the

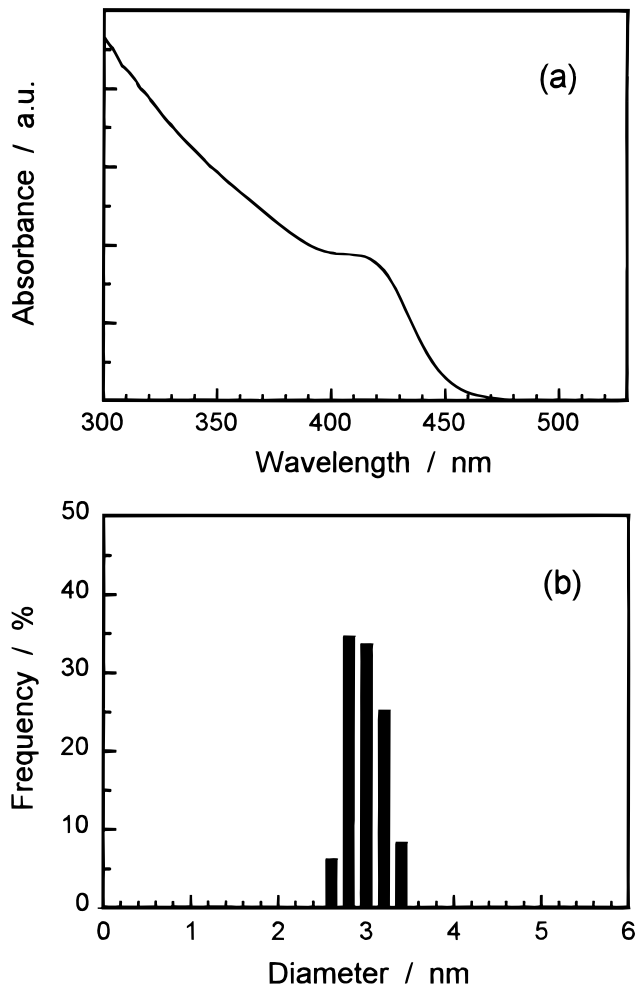

Figure 2. Absorption spectrum of thiocholine-modified CdS nanoparticles in aqueous solution (a), and their size distribution determined by TEM observations (b).

large size quantization effects since the bulk CdS particles show absorption onset at 520 nm. Figure 2b shows the size distribution of thiocholine-modified CdS nanoparticles obtained by TEM measurements. The observed CdS nanoparticles were almost spherical in shape. The average diameter was estimated to be 3.0 nm with a standard deviation of 0.20 nm. The obtained size distribution, which was 6.7% of the average diameter, was narrow enough to call the prepared CdS nanoparticles as nearly monodisperse particles. The electron diffraction patterns simultaneously obtained in the TEM measurements showed clearly only four diffraction rings corresponding to the interplanar spacings of 3.33, 2.06, 1.77, and 1.19 Å, which were assignable to diffractions from (111), (220), (311), and (422) planes of a cubic crystal structure of CdS, respectively.

Figure 3 shows surface pressure (π) − surface area (A) isotherms of amphiphiles spread on water subphase. As shown by a curve (a), the surface pressure of a DOTAP−OPPC mixture monolayer on the Tris buffer increased gradually with decrease in the area, and the monolayer collapsed at the surface pressure of 40 mN m^{-1} where the area per molecules of about 0.4 nm^2 was given. This minimum area obtained is in good agreement with the molecular cross sectional area of the dialkyl chains. The amphiphiles gave essentially the same isotherms even if the water subphase contained either DNA molecules or CdS nanoparticles as indicated by curves (b) and (c) in Figure 3, suggesting that polyion complex formation between DNA molecules and DOTAP did not influence the properties of the

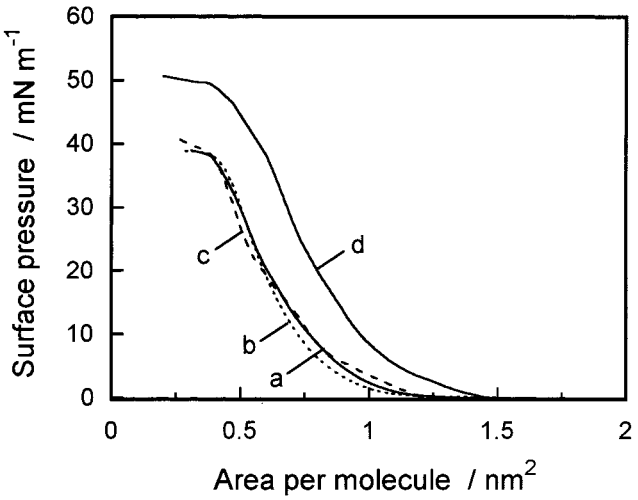

Figure 3. Surface pressure−surface area isotherms of DOTAP−OPPC (1:2) mixture monolayer on the tris buffer (pH 7) (a), and those taken on the tris buffer (pH 7) containing 0.5 μmol dm^{-3} (base pair) DNA (b), 1.2×10^{17} particle dm^{-3} CdS nanoparticles (c), and 0.5 μmol dm^{-3} (base pair) DNA and 1.2×10^{17} particle dm^{-3} CdS nanoparticles (d).

monolayer at the air−water interface, as already reported.[38] However, different behavior of $\pi-A$ isotherms was observed in the presence of DNA double strands and CdS nanoparticles together in water subphase (curve (d)). The surface area was greater at a given surface pressure, and the larger collapse pressure of 50 mN m^{-1} was obtained. These results indicated that the rigidity of DNA double strands attached on the amphiphiles monolayer would increase by the deposition of CdS nanoparticles on DNA double strands, resulting in higher stabilization of the amphiphiles monolayer.

Figure 4 shows high-resolution TEM images of amphiphiles monolayers which were transferred to the TEM grids from the water subphase. In the case of the Figure 4a, the water subphase used for the preparation of the monolayer contained only CdS nanoparticles. As recognized, there were a very small number of CdS nanoparticles and they were randomly dispersed, indicating that deposition of CdS nanoparticles on the amphiphile monolayer hardly occurred in the absence of DNA in the water subphase. On the contrary, as clearly shown in the Figure 4b, some separate chains of CdS nanoparticles were found in the amphiphiles monolayer prepared on the water subphase which contained both CdS nanoparticles and DNA double strands. Individual chains had a width of ca. 3.0 nm which accorded well with the diameter of CdS nanoparticles, suggesting that CdS nanoparticles made a single line along a DNA molecule. This was confirmed by a high magnification TEM image shown in Figure 4c. Individual CdS nanoparticles were clearly recognized, and they had the lattice fringes with the interplanar spacing of 0.33 nm assigned to the (111) plane of the cubic CdS structure. It was clearly shown that densely packed particles made a quasi-one-dimensional array without coalescence of the particles. Unlike the case of the crystallized Ag nanoparticles,[9,10] there was no correlation in the crystallographic directions between adjacent nanoparticles.

The separate CdS nanoparticle chains with dense packing were found with high reproducibility in the different amphiphile monolayers even if the concentration of DNA in the water subphase used for the preparation of the monolayer was decreased to 0.25 μmol dm^{-3} (base pair). As in the case of the preparation of the cationic liposome-bound DNA,[40] the ratio of the cationic amphiphile and the zwitterionic amphiphile in the monolayer influenced the density of the CdS nanoparticle chains

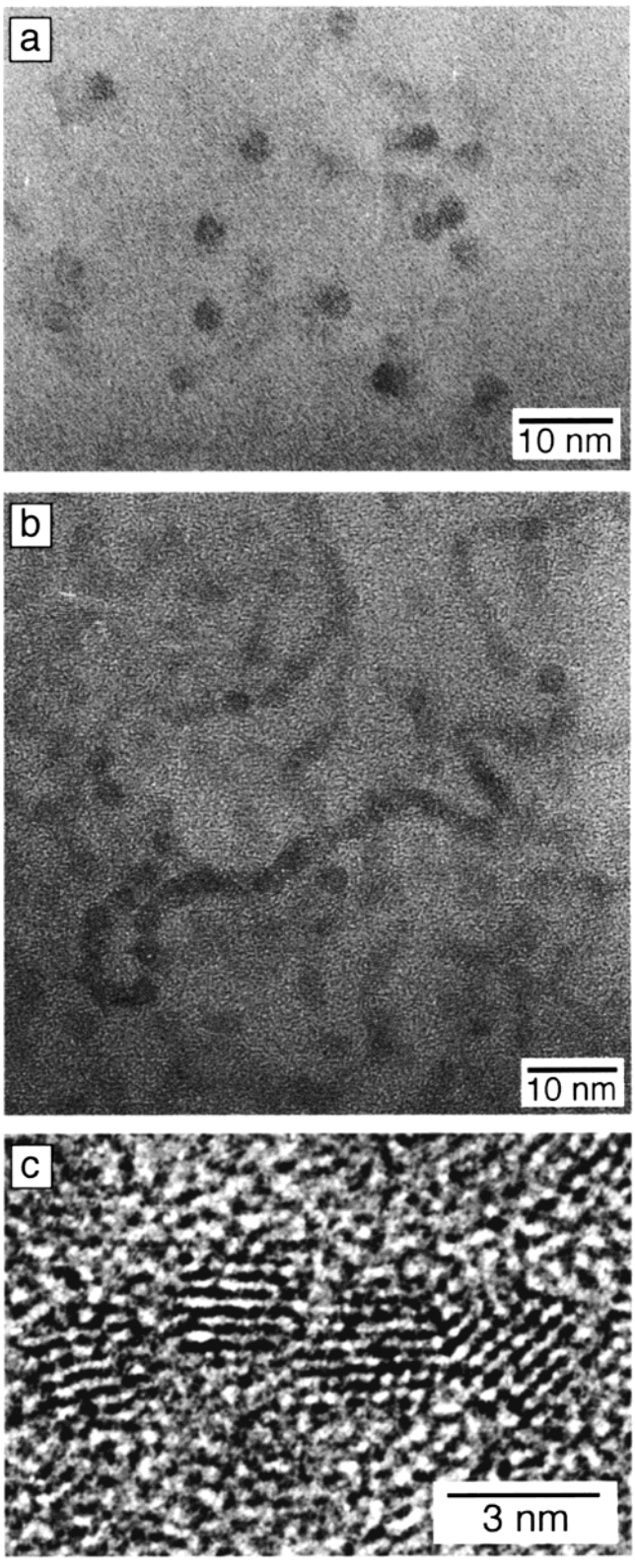

Figure 4. TEM images of the mixed monolayer of DOTAP and OPPC transferred from the air−water interface. The water subphase used contained only CdS nanoparticles (a) and both DNA double strands and CdS nanoparticles (b and c). A picture (c) is a high magnification image of CdS nanoparticles in the array shown in the picture (b).

fixed in the monolayer. If the monolayer composed of only DOTAP was used, a TEM image of the resulting monolayer showed numerous CdS nanoparticles which did not allow us to distinguish individual chains. It was concluded from the obtained results that the CdS nanoparticle chains were generated by the electrostatic attraction between negatively charged DNA molecules and positively charged nanoparticles. This was also supported by the fact that no wire-like assembly of CdS nanoparticles in the DOTAP−OPPC mixture monolayer were observed by the TEM measurements if the CdS nanoparticles surface-modified with 2-mercaptoethane sulfonate having negative charge were used.

The TEM pictures allowed us to determine the distance (d_{c-c}) between the centers of the adjacent CdS nanoparticles in the chain. The value of d_{c-c} was varied from 3 to 4.5 nm, giving the average of 3.5 nm with the standard deviation of 0.52 nm. Since the base-pair separation in DNA double strands is 0.34 nm,[30] the results suggested that a CdS nanoparticle per 10 base pairs was bound to DNA double strands. Considering that the average diameter of CdS core was 3.0 nm and the thiocholine layer modified on CdS surface was about 0.5 nm thickness, d_{c-c} was expected to be 4.0 nm in dense packing of nanoparticles. The observed difference may result from the size distribution of CdS nanoparticles and/or the interdigitation of the modified layer[41] between the nanoparticles.

Conclusion

The present study showed one successful approach to preparation of CdS nanoparticle chains by electrostatically immobilizing CdS nanoparticles along DNA double strands as a template. This methodology principally permits the fabrication of nanoparticle chains which are composed of the various nanoparticle sizes and/or the different chemical compositions. Furthermore, by combining with the techniques that have been reported to allow DNA molecules to be immobilized and assembled on solid substrates,[29,32,38,42,43] CdS nanoparticle chains can be produced on a desired position having an appropriate structure. This will be useful to fabricate the optoelectronic devices with use of nanoparticles which are prepared by wet chemical processes and have a narrow size distribution, because these devices must contain the connection between the nanoparticles and electrodes.

Acknowledgment. This research was supported by Grant in Aid for Scientific Research of Priority Area of "Electrochemistry of Ordered Interface" (No. 09237104) and by Grant in Aid for Encouragement of Young Scientists (No.10750595) from the Ministry of Education, Science, Culture and Sports.

References and Notes

(1) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.

(2) Kagan, C. R.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. B* **1996**, *54*, 8633.

(3) Vossmeyer, T.; Reck, G.; Schulz, B.; Katsikas, L.; Weller, H. *J. Am. Chem. Soc.* **1995**, *117*, 12881.

(4) Motte, L.; Billoudet, F.; Lacaze, E.; Douin, J.; Pileni, M. P. *J. Phys. Chem. B* **1997**, *101*, 138.

(5) Taleb, A.; Petit, C.; Pileni, M. P. *J. Phys. Chem. B* **1998**, *102*, 2214.

(6) Moritz, T.; Reiss, J.; Diesner, K.; Su, D.; Chemseddine, A. *J. Phys. Chem. B* **1997**, *101*, 8052.

(7) Micic, O. I.; Jones, K. M.; Cahill, A.; Nozik, A. J. *J. Phys. Chem. B* **1998**, *102*, 9791.

(8) (a) Zhu, Z.; Tsung, L. Y.; Tomkiewicz, M. *J. Phys. Chem.* **1995**, *99*, 15945. (b) Zhu, Z.; Lin, M.; Dagan, G.; Tomkiewicz, M. *J. Phys. Chem.* **1995**, *99*, 15950.

(9) Harfenist, S. A.; Wang, Z. L.; Alvarez, M. M.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem.* **1996**, *100*, 13904.

(10) Wang, Z. L.; Harfenist, S. A.; Whetten, R. L.; Bentley, J.; Evans, N. D. *J. Phys. Chem. B* **1998**, *102*, 3068.

(11) Korgel, B. A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. *J. Phys. Chem. B* **1998**, *102*, 8379.

(12) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978.
(13) Remacle, F.; Collier, C. P.; Markovich, G.; Heath, J. R.; Banin, U.; Levine, R. D. *J. Phys. Chem. B* **1998**, *102*, 7727.
(14) Kotov. N. A.; Meldrum, F. C.; Fendler, J. H. *J. Phys. Chem.* **1994**, *98*, 8827.
(15) Tian, Y.; Fendler, J. H. *Chem. Mater.* **1996**, *8*, 969.
(16) Dabbousi, B. O.; Murray, C. B.; Rubner, M. F.; Bawendi, M. G. *Chem. Mater.* **1994**, *6*, 216.
(17) Doherty, S.; Fitzmaurice, D. *J. Phys. Chem.* **1996**, *100*, 10732.
(18) Takagahara, T. *Surf. Sci.* **1992**, *267*, 310, (b) Takagahara, T. *Optoelect. Dev. Technol.* **1993**, *8*, 545.
(19) Brust, M.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *Adv. Mater.* **1995**, *7*, 796.
(20) 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
(21) Peng, X.; Wilson, T. E.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 145.
(22) Cusack, L.; Rizza, R.; Gorelov, A.; Fitzmaurice, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 848.
(23) Alivisatos, A. P.; Johnsson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P., Jr.; Schultz, P. G. *Nature* **1996**, *382*, 609.
(24) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.
(25) Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078.
(26) Storhoff, J. J.; Elghanian, R.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 1959.
(27) Mucic, R. C.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 12674.
(28) Seeman, N. C. *Acc. Chem. Res.* **1997**, *30*, 357.
(29) Niemeyer, C. M. *Appl. Phys. A: Mater. Sci. Process.* **1999**, *68*, 119.
(30) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: Berlin, 1987.
(31) Coffer, J. L.; Bigham, S. R.; Li, X.; Pinizzotto, R. F.; Rho, Y. G.; Pirtle, R. M.; Pirtle, I. L. *Appl. Phys. Lett.* **1996**, *69*, 3851.
(32) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature* **1998**, *391*, 775.
(33) Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science* **1991**, *252*, 688.
(34) Tien, J.; Terfort, A.; Whitesides, G. M. *Langmuir* **1997**, *13*, 5349.
(35) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046.
(36) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
(37) Tanaka, K.; Okahata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 10679.
(38) Okahata, Y.; Kobayashi, T.; Tanaka, K. *Langmuir* **1996**, *12*, 1326.
(39) Spink, C. H.; Chaires, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 10920.
(40) Rädler, J. O.; Koltover, I.; Salditt, T.; Safinya, C. R. *Science* **1997**, *275*, 810.
(41) Terrill, R. H.; Postlethwaite, T. A.; Chen, C.; Poon, C.; Terzis, A.; Chen, A.; Hutchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Falvo, M.; Johnson, C. S., Jr.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 12537.
(42) Kabata, H.; Kurosawa, O.; Arai, I.; Washizu, M.; Margarson, S. A.; Glass, R. E.; Shimamoto, N. *Science* **1993**, *262*, 1561.
(43) Kelley, S. O.; Barton, J. K.; Jackson, N. M.; McPherson, L. D.; Potter, A. B.; Spain, E. M.; Allen, M. J.; Hill, M. G. *Langmuir* **1998**, *14*, 6781.