Fabrication of Well-Aligned and Highly Dense Cadmium Sulfide Nanowires on DNA Scaffolds Using the Poly(dimethylsiloxane) Transfer Method

Zhenxing Wang,‡ Jinyang Liu,‡ Kun Zhang,‡ Hongbing Cai,§ Guanghui Zhang,‡ Yukun Wu,‡ Tao Kong,‡ Xiaoqiong Wang,∗‡§ Jie Chen,∗‡§ and Jianguo Hou†

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China, Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China, Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada, and National Research Council/National Institute of Nanotechnology, Edmonton, Alberta T6G 2M9, Canada

Received: November 22, 2008; Revised Manuscript Received: February 3, 2009

We have developed a simple, yet highly effective and reliable, poly(dimethylsiloxane) (PDMS) transfer method to fabricate highly dense and well-aligned CdS nanowires on silica substrates, following DNA templates. CdS nanoparticles are selectively deposited and confined on DNA strings aligned on a PDMS sheet to form CdS nanowires. The nanowires are then transferred to the substrate with a low occurrence of parasitic CdS nanoparticles. The mapping of elements in the nanowires by scanning Auger electron spectroscopy reveals the dense distribution of Cd and S elements along DNA scaffolds. The width and length of the nanowires can be controlled by adjusting the incubation time on the PDMS sheet. Atomic force microscopy and field emission scanning electron microscopy show that the height and width of the nanowires reach 45 and 77 nm, respectively, after 72 h of growth. The nanowire can continuously stretch over 10 μm after 96 h of incubation. The method is easily replicable, and controllable, which makes it promising for building nanophotonic devices and nanosensors.

Introduction

A significant challenge in integrating nanoscale building blocks into functional nanodevices or circuits is finding parallel, cost-effective, and simple methods of assembling these components. Because of the unique intramolecular and intermolecular recognition properties, special chemical structure, and mechanical rigidity of DNA,3 DNA was proposed as a template to assemble simple and individual nanocomponents into complex devices or large-scale functional circuits. The “bottom-up” strategy using DNA templates for fabrication of nanopatterns has attracted much research interest and has been extensively investigated recently.2–8 On the basis of the interesting properties of DNA, various geometrical shapes were synthesized such as the “Y” type,9 squares,10,11 and cubes,12 which are particularly useful in the construction of complex large-scale circuits. More complex three-dimensional shapes13 such as the octohedral4 and tetrahedral15 were also hierarchically self assembled. However, DNA is insulating,16–18 except in some particular cases such as short strands (<10 nm) with specific sequences,19–22 which makes it necessary to mineralize DNA. Therefore, various nanowires or nanochains were synthesized on the basis of DNA scaffolds, including metallic copper,23 palladium,24–26 platinum,27 gold,4,5,28 and silver29 nanowires and semiconducting CdSe,30 CuS,31 CdSe/ZnS,32 and CdS nanowires.6,33–37

In general, two methods are usually used in the synthesis of DNA-templated nanowires. One is the solution-suspended DNA method, and the other is the substrate-immobilized DNA method. In the first method, the cations are first attached to the DNA template then reduced (or reacted with the anions) to form nanowires on DNA in solution.36 However, the nanowires are frequently coiled and cross-linked1 in the solution, which make it difficult to align nanowires properly onto the substrates for further fabrication of nanodevices and nanosensors. In the second method, DNA is first aligned on the substrates, and then the substrates are placed into the cation solution to grow nanowires.24 However, many parasitic nanoparticles are frequently formed in adjacent areas around DNA-templated nanowires.2,35 Clearly, further investigation is needed to explore the synthesis of well-aligned nanowires using DNA templates. In this study, we developed a poly(dimethylsiloxane) (PDMS) transfer method to fabricate CdS nanowires. Figure 1 shows the schematic procedures of this method. Combining the alignment of DNA on a PDMS sheet and the formation of CdS nanowires in solution, well-aligned and dense nanowires can be readily transferred to other substrates. Besides the advantage of requiring no additional substrate surface modification, we can easily control the size and morphology of these nanowires by adjusting incubation time. Moreover, because a PDMS sheet is not reactive to the mineralization process of DNA because of its hydrophobic and inert surface,38 most CdS nanoparticles can be selectively deposited only on the DNA scaffolds, and the parasitic nanoparticles on the surface can be dramatically minimized.

Experimental Section

1. Reagents. A double-stranded 0.3 mg mL−1 λ-DNA solution stored in 10 mM Tris-HCl and a 1 mM ethylenedi-
CdS Nanowires on DNA Using the PDMS Transfer Method


Figure 1. Schematic procedure of fabricating CdS nanowires on fixed DNA scaffolds by using a PDMS transfer method. (I) DNA is aligned and fixed on a PDMS surface. (II) A PDMS sheet is submerged into a solution containing Cd\(^{2+}\) and thioacetamide (TAA) under ultraviolet (UV) irradiation at room temperature. (III) CdS nanowires on PDMS are transferred to other substrates.

Figure 2. (a) Fluorescent microscopic image of combed DNA stained by YOYO-1 transferred from a PDMS sheet onto a quartz surface. (b) AFM image of the stained DNA transferred from a PDMS sheet onto a mica substrate.

Figure 3. (a) FESEM image of CdS nanowires on silica, transferred from PDMS with a 72 h synthesis under UV irradiation. (b) FESEM image to highlight an individual CdS nanowire. (c) AFM image of CdS nanowires on silica, transferred from PDMS with a 72 h synthesis under UV irradiation. (d) Magnified image of the AFM image of CdS nanowires on silica. (e) Profile of line shown in panel d.

Figure 4. AES results from the substrate (curve 1) and nanowire (curve 2). Inset shows the AES spots on the sample. Note that S\(_{LVV}\) and Cd\(_{MNN}\) peaks only occur on the nanowires.

aminetetraacetic (EDTA) buffer (48502 base pairs and a molecular weight of 31.5 \(\times\) 10^6 daltons) was purchased from Fermentas. Poly(dimethylsiloxane) (PDMS, Dow Corning Sylgard 184) was used. YOYO-1 (DNA dye) stored in 1 mM dimethyl sulfoxide (DMSO) was purchased from Molecular Probes. Cadmium perchlorate hydrate [Cd(ClO\(_4\)]_2 \(\times\) H\(_2\)O\] and thioacetamide (TAA) were purchased from Sigma and were used without further purification. Millipore water, with a conductivity of 18 M\(\Omega\) cm, was used in all experiments.

2. Instruments. Fluorescent images were scanned with a confocal laser scanning microscope (Zeiss LSM510 Meta). Atomic force microscope (AFM) images were collected under a dynamic force microscopy (DFM) mode on a SPA 300HV microscope (Seiko Instruments, Inc.). The samples were also observed with a field emission scanning electron microscope (FESEM, Raith e-Line, Germany), and high-resolution transmission microscopy (HRTEM) was performed using a JEM-2010 microscope (JOEL, Japan). All auger data were collected with a field emission auger microprobe JAMP-9500F (JEOL) at the Alberta Centre for Surface Engineering and Science (ACSES, Canada). UV irradiation of 260 nm was provided by a UV lamp, with a power of 18W (ShangHai Anting Scientific Instrument Factory).

3. Preparation and Characterization of Samples. DNA Stain Experiment. \(\lambda\)-DNA and YOYO-1 were used to stain DNA by combing it onto a mica substrate. The mixture gel was prepared by mixing the base with the curing agent at a volume ratio of 10:1, while the base with the curing agent at a volume ratio of 10:1, while

stirring softly. Then the mixture was poured onto a fresh clean silicon substrate in a glass container and stood for 1 h until the air bubbles dispersed. After that, the mixture on the silicon substrate was baked on a hot plate at 150 °C for 15 min. The PDMS was uncovered from the silicon and the side in contact with the silicon was used.

**Combing Stained DNA onto PDMS.** A droplet solution of 7 \(\mu\)L of 4.5ng \(\mu\)L\(^{-1}\) \(\lambda\)-DNA prestained with YOYO-1 was deposited on a PDMS sheet, and then this droplet was driven by a pipet tip at a speed of about 1m ms\(^{-1}\) in one certain direction. The surface tension at the water—air interface stretched DNA molecules onto the PDMS sheet. Repeating the last process on the whole PDMS sheet, we aligned DNA extensively onto the whole PDMS sheet.

**General Route for the Synthesis of DNA-Templated CdS Nanowire on a Substrate.** A 10 ng \(\mu\)L\(^{-1}\) \(\lambda\)-DNA solution was prepared by diluting the 0.3 mg mL\(^{-1}\) \(\lambda\)-DNA stock solution. Cadmium perchlorate (30 mM) and 30 mM thioacetamide (TAA) were also prepared by dissolving appropriate amounts of chemical agents in 18.2 M\(\Omega\) cm Milli-Q water and stirring strongly using a vortex mixer. As shown in Figure 1, first the 10 ng \(\mu\)L\(^{-1}\) \(\lambda\)-DNA was used to comb the DNA onto the PDMS sheet. Second, the PDMS sheet was submerged into the reaction solution containing 400 \(\mu\)L of a 30 mM Cd\(^{2+}\) solution, 2 \(\mu\)L of...
ethanol, and 800 µL of Milli-Q water in a small cuvette covered by a piece of clean quartz. After 24 h standing at 4 °C, 800 µL of 30 mM TAA was added to the reaction solution. Meanwhile, the cuvette was directly placed under 260 nm UV radiation for different irradiation times at room temperature and under ambient pressure. The distance between the sample and lamp is about 1 cm. Third, the CdS nanowires on the PDMS sheet were transferred onto other substrates for FESEM, AFM, and other surface analysis.

**Preparation of Samples for HRTEM Studies and Energy Dispersive X-ray Analysis.** In the first step, 400 µL of 100 ng µL⁻¹ λ-DNA was incubated with 400 µL of 30 mM Cd²⁺, 400 µL of Milli-Q water and 2000 µL of ethanol for 24 h in a glass cuvette. In the second step, 800 µL of 30 mM TAA was added to the mixture, and the cuvette was placed under 260 nm UV radiation for 6 h. In the final step, enough reaction product was added onto copper grids with thin carbon films to complete HRTEM studies.

**Results and Discussion**

To confirm unidirectional alignment of DNA on PDMS sheets, we first stained DNA with YOYO-1 and aligned the DNA on a PDMS sheet using combing technology; then, the DNA was transferred onto a quartz wafer by the transfer method. The detailed description of the process can be found in the Experimental Section. Figure 2a shows a typical fluorescent image of DNA transferred from a PDMS sheet to a clean quartz wafer. As shown, most DNA strings can be well-aligned unidirectionally on a PDMS substrate. These stained DNAs were also transferred onto a freshly cleaved mica surface, and the corresponding topology of very straight and highly aligned DNA was observed by AFM (Figure 2b). The results demonstrated that the DNA can be readily aligned on the surface of a PDMS sheet along one certain direction without adjusting the Mg²⁺ concentration, pH and Mg⁷⁺ concentration. Furthermore, we found that the DNA could stick firmly onto the PDMS substrate, resulting in a low incidence of detachment and distortion of DNA when the PDMS sheet was immersed into a salt solution. This characteristic can ensure the success of the following mineralization procedure of formation of CdS nanowires along the combed DNA on a PDMS surface in a Cd²⁺ solution.

Figure 3 illustrates FESEM and AFM images of typical homogeneous well-aligned nanowire patterns from transferring the DNA-templated nanowires on a PDMS sheet to the silica substrate. The nanowires were fabricated by incubating DNA templates in the cadmium perchlorate solution for 24 h and then with thioacetamide (TAA) for 72 h under UV irradiation at room temperature and ambient pressure. As compared to the previous report, our PDMS transfer method used to fabricate CdS nanowires with DNA templates has apparent advantages. First, the formation of nanowires is well-aligned, thick, and quite uniform. The width and height of these nanowires approaches 77 and 45 nm, respectively (Figure 3b,e, respectively). Additionally, the size of the nanowires can also be easily controlled through incubation time (this point will be discussed in more details later in the paper). Second, most of the CdS are selectively deposited and confined only to DNA backbones, and there are very few parasitic CdS nanoparticles in a large area on the substrate (Figure 3a). We used the quantitative approach described by Becerril et al. to estimate the number of the parasitic nanoparticles (Figure S1 of the Supporting Information). In the cases of the 72 and 96 h incubation times, the number of parasitic nanoparticles is only 0.2 and 0.5 per µm², respectively. This can be attributed to the hydrophobic and inactive surface of the PDMS sheet. Third, our method also has very high reproducibility and yield. For example, multiple synthesis experiments under identical conditions have been performed and almost the same sizes and morphologies of the nanowires were obtained. These well-aligned CdS nanowires could also be fabricated in a very large area on the substrates. For instance, the uniform CdS nanowires could be observed in approximately a 75 µm × 55 µm area by FESEM (Figure S2 of the Supporting Information). Moreover, the nanowires synthesized on the PDMS sheet could also be readily transferred.
to other substrates such as silicon and silicon dioxide. The process of the PDMS transfer method has some important features: (1) It is crucial to keep the PDMS surface and substrate dry enough to reduce the chance that parasitic nanoparticles stick onto the substrate. (2) Different substrates have different adhesive forces for nanowires, which can affect the directional alignment of these nanowires. On the basis of our experimental results, the CdS nanowire has stronger adhesion to a silicon substrate than to a silicon dioxide substrate. (3) The strain, originated from the press force of PDMS during the transfer process, may result in the fragmentation of nanowires. These features can be further optimized to obtain well-aligned and continuous nanowires.

The chemical composition and element mapping of the nanowires were determined by auger electron spectroscopy (AES) and scanning auger electron spectroscopy (SAES), respectively. In Figure 4, curve 1 and curve 2 are AES results obtained from the substrate and the nanowires, respectively. Obviously, there are only peaks of Si, O, and C in curve 1, which come from the silica substrate. However, two new auger electron peaks, SiLVV around 146.5 eV and CdMNN around 371.2 eV, occur in curve 2, indicating that the nanowires are really composed of Cd and S elements. Mappings of S and Cd elements in nanowires are shown in panels b and c in Figure 5, and the corresponding FESEM image is shown in Figure 5a. The images show that most of S and Cd are densely distributed along DNA strings and not elsewhere on the substrates, which further confirm that CdS clusters were deposited only on the DNA scaffolds. To our knowledge, this is the first time that the chemical composition of nanowires has been analyzed directly using SAES method, which can give credible results.

From Figure 3a, one can see that a thick CdS nanowire was formed from the assembly of many nanoparticles. TEM was used to investigate the structure of these nanowires and nanoparticles. In order to prepare the sample suitable for TEM observation, we exploited the solution-suspended DNA method to synthesize the CdS nanowires. Using this method, we found that the morphology of the nanowire was greatly influenced by the molar ratio of Cd²⁺ to DNA. Generally, the nanowires were coiled and cross-linked (Figure 6a), and the higher the ratio, the more the nanoparticles agglomerated (Figure S3 of the Supporting Information). This behavior may be attributed to the coiled DNA string in the solution and the electrostatic interactions between the CdS nanoparticles without electrostatic balance. Comparing Figure 6a with Figure 3a, we believe that our PDMS transfer method can overcome the aggregation of the nanowires and obtain highly aligned nanowires. Figure 6b shows a magnified TEM image of CdS nanowires. It shows that the nanowires are composed of a large quantity of CdS nanocrystals. From the SAED image (Figure 6c), a series of d-spacing parameters, 3.57, 2.12, and 1.86 Å indexed in the (100), (110), and (103) planes of CdS, can be observed in the nanocrystals, indicating its hexagonal primitive-type structure (JCPDS 80-0006). The plane with the d-spacing of 3.56 Å was also observed in the HRTEM image shown in Figure 6d. At the same time, the P element signal, which originates from the phosphate groups of DNA, can be found from the nanowires by energy dispersive X-ray (EDX) spectroscopy (Figure S4 of the Supporting Information). This result further confirmed that CdS nanowires grew along a DNA backbone.

The size and the morphology of synthesized nanowires can be readily controlled by varying the incubation time in our PDMS transfer method. We prepared the nanowires under various incubation times ranging from 6 to 96 h (not including the 24 h required to mix the DNA with Cd²⁺ to form the DNA–Cd²⁺ complex). The changes in size and morphology of CdS nanowires after 6, 12, 24, 48, 72, and 96 h incubation have been extensively characterized by FESEM, and the results are shown in Figure 7. As shown, when the incubation time was less than 12 h, the nanowires were not formed, and they demonstrated only chain-like structures (Figure 7a,b). As the incubation time increased, the morphologies of the nanowires gradually changed from coarse and discontinuous to a continuous shape (Figure 7a–f). It should be noted that the longer incubation time did not increase the amount of parasitic CdS clusters on the surface. The result shows that the hydrophobic PDMS surface reliably excludes CdS deposition irrespective to incubation time.

The mean width and maximum length of nanowires growing under the various incubation times are plotted in Figure 8 (Figure S5 of the Supporting Information). The data are estimated on the basis of the FESEM images for all samples collected. The results actually reflect the morphological quality of the nanowires. (Note that the maximum length is unavailable in the cases of 6 and 12 h incubation because of their discontinuous structures.) As shown in Figure 8, the width of nanowires

![Figure 7. FESEM images of CdS nanowires synthesized from various incubation times: (a) 6 h, (b) 12 h, (c) 24 h, (d) 48 h, (e) 72 h, and (f) 96 h.](image-url)
increased rapidly before 24 h and then began to slow down. Specifically, the width increased about three times from 6 to 24 h, but grew only about 8% from 48 to 96 h. The maximum length, however, increased from the beginning. When the time approached 96 h, the maximum length of the nanowire still increased significantly, while the width varied very slowly. This trend may be ascribed to the interconnection of discontinuous segments of nanowires along the same DNA template as incubation time increased.

The underlying mechanism of forming thick and highly dense CdS nanowires can be explained with a three-step growing process. Similar to the metallization of DNA,64 the first step is usually called the activation step, where Cd$^{2+}$ binds to DNA strands and forms Cd$^{2+}$–DNA complexes. In our experiment, it took about 24 h for Cd$^{2+}$ to form CdS nanowires on a PDMS sheet submerged in a Cd$^{2+}$ solution to form Cd$^{2+}$–DNA complexes and ensure the completely dynamic diffusion balance between Cd$^{2+}$ and Cd$^{2+}$–DNA complexes. The second step is the addition of TAA to the reaction solution under UV irradiation. S$^{2-}$ can be slowly released from TAA under UV irradiation17 and react with Cd$^{2+}$ to form CdS nuclei on the DNA backbone. The third step is the controlled and continuous growth of CdS nuclei along the DNA during incubation and, eventually, the formation of thick and highly dense CdS nanowires. Note that because PDMS is inactive to polar CdS nanoparticles due to its insert and hydrophobic surface, the dispersed CdS nanoparticles in solution can be consequently confined and deposited only on DNA or Cd$^{2+}$–DNA to form the dense CdS nanowires, while the formation of parasitic nanoparticles on the surface can be avoided.

**Conclusion**

In summary, a simple, reliable, and effective PDMS transfer method has been proposed to fabricate highly dense and well-aligned CdS nanowires on silica substrates using DNA templates and a PDMS sheet. We have demonstrated that size and morphology can be easily controlled by adjusting the incubation time. The maximum length and average width of the nanowires can reach over 10 µm and 73.8 nm, respectively. The method can also minimize the parasitic nanoparticles on the substrate dramatically. The thick and well-aligned CdS nanowires fabricated by this proposed method is promising for wide applications in nanophotoelectronics and nanodevices, while the optical and electrical characteristics of the nanowires will be investigated in further work.

**Acknowledgment.** The authors acknowledge Dr. Shihong Xu at ACSES (Alberta Centre for Surface Engineering and Science, University of Alberta, Canada) for his support in performing scanning auger electron spectroscopy. X. P. Wang acknowledges financial support from the National Key Basic Research Program (Grant 2006CB922002) and the Natural Science Foundation of China (Grants 50721091, 90406009, 10874165, and 50532040). J. Chen acknowledges support from the National Research Council/National Institute of Nanotechnology and the grant from the Natural Sciences and Engineering Research Council of Canada.

**Supporting Information Available:** Number of parasitic nanoparticles, CdS nanowires observed by FESEM, agglomerated nanoparticles, P element signal found by energy dispersive X-ray (EDX) spectroscopy, and mean lengths of the nanowires. This material is available free of charge via the Internet at http://pubs.acs.org.
CdS Nanowires on DNA Using the PDMS Transfer Method


JP810274K