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Au Nanowire Fabrication from Sequenced Histidine-Rich Peptide

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There has been much interest lately in ordered two- and three-dimensional device fabrications by using nanowires as building blocks.[1] Recently, biological recognitions between DNAs or proteins have been incorporated in the nanodevice structures to sense specific chemical species or to align nanocomponents onto desired locations.[2] Although patterning DNA- and protein-assembled nanowires in device conformations is relatively straightforward due to their robust and reproducible recognition functions,[3,4] it is necessary for those nanowires to be conductive to function as electronic devices and sensors.[2b,d] In the past, metallization of nanowires was achieved by electroless coating; however, it was relatively difficult to obtain uniform coating on those biological nanowires due to contamination with precipitates of reduced metal particles. This in turn makes reproducible electronic transport and absorption measurements problematic.[2f,5,6]

Biological systems control mineralizations and nanocrystal synthesis of various metals in organisms.[7] Histidine-containing peptides have been studied extensively because their high affinities to metal ions damage central nervous systems by altering protein conformations into abnormal forms via histidine−metal complexation, and this protein deformation may cause Parkinson's and Alzheimer's diseases.[8] Recently, specific sequences of peptides were used to mineralize specific metals and semiconductors to produce highly crystalline nanocrystals,[9,10] and this mineralization strategy could also be applied in metal nanowire synthesis. An advantage to apply biological recognitions to synthesize metal nanocrystals/nanowires is the efficient and reproducible nanocomponent production in the control of uniformity and the crystallinity without contamination of precipitated metal aggregates. This is important when those nanowires are practically used as the building blocks for electronics and sensor devices because uniform metal coatings with the small and monodisperse domain sizes are crucial to optimize nanowire conductivity and to detect changes in conductivity and absorption induced by analyte adsorption on metal nanotube surfaces.[2b,11]

Here we report a new biological approach to fabricate Au nanowires by using sequenced histidine-rich peptide nanowires as templates. Monodisperse Au nanocrystals were uniformly coated on the histidine peptide nanowires with high-density coverage, and the crystalline phases of the Au nanocrystals were observed as (111) and (220).

Fabrication of the histidine peptide nanowires involved two steps (Figure 1). First, bis(*N*-α-amido-glycylglycine)-1,7-heptane dicarboxylate molecules (10 mM) were self-assembled into nanowires in a pH 5.5 citric acid/NaOH solution.[12] This nanowire incorporates binding sites that have high affinity to biological molecules such as DNAs and proteins.[13,14] Then a histidine-rich peptide with the sequence A-H-H-A-H-H-A-A-D,[15] reported to mineralize Au with

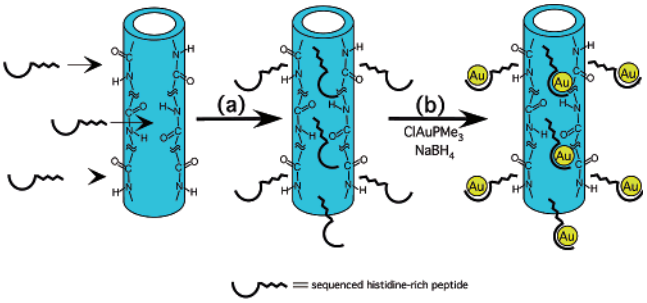

Figure 1. Scheme of Au nanowire fabrication. (a) Immobilization of sequenced histidine-rich peptide at the amide binding sites of the heptane dicarboxylate nanowires. (b) Au coating nucleated at the histidine sites of the nanowires.

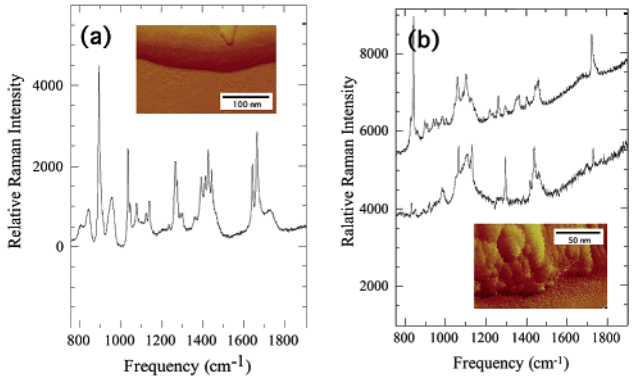

Figure 2. Raman spectra and AFM images (insets) of the nanowires (a) before, and (b) after immobilizing sequenced histidine-rich peptide on the nanowires (top trace). Bottom trace in (b) represents the neat histidine-rich peptide spectrum (also see Supporting Information).

the aid of a reducing agent,[16] was immobilized on the heptane dicarboxylate nanowires at the binding sites. After the heptane dicarboxylate nanowires were washed with deionized water several times, a 1-mL solution of the heptane dicarboxylate nanowire was mixed with a 1-mL solution of the histidine peptide (2 μmol) in Tris buffer (0.1M, pH 8.6) for 24 h to immobilize the histidine peptide onto the nanowires. Figure 2 shows the comparison of the nanowire surfaces before and after immobilization of the histidine peptide by atomic force microscopy (AFM, Digital Instruments) and Raman microscopy (JY/Horiba, LabRam). Prior to the histidine peptide immobilization, the nanowire surface was very smooth in the AFM image (Figure 2a, inset), and vibrational frequencies of the nanowire surfaces (Figure 2a) match characteristic vibrational modes of the heptane dicarboxylate.[12] However, after the histidine peptide was immobilized on the nanowire surface, significant changes can be seen in the AFM images and Raman spectra. The Raman spectrum of the histidine peptide-immobilized nanowire surface agrees well with the neat histidine peptide spectrum (Figure

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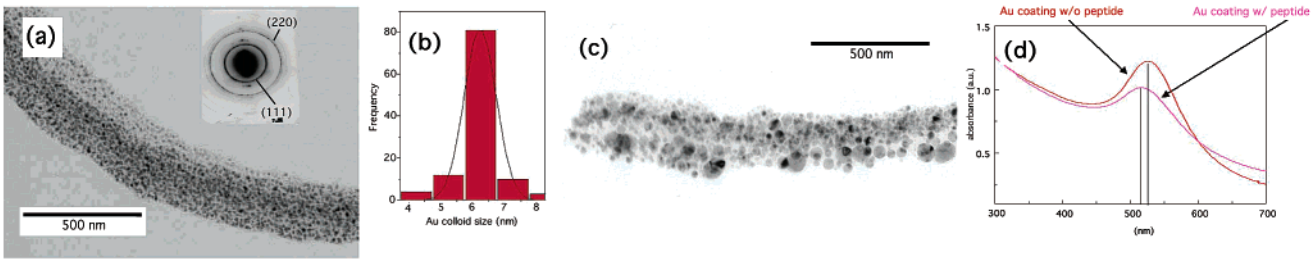

Figure 3. (a) TEM image of Au on the nanowire coated with the sequenced histidine-rich peptide (inset: electron diffraction of Au on the nanowire). (b) Size distribution of Au nanocrystals on the nanowires. (c) TEM image of Au on the nanowire without the sequenced peptide. (d) UV−vis absorption spectra of (a) and (c). TEM was operated at 80 keV of the electron acceleration voltage.

2b), and the nanowire surface structures were altered by the histidine peptide adsorption in the observation of the AFM image (Figure 2b, inset). These results indicate that the histidine peptide was immobilized on the nanowire surface.

To coat the histidine peptide nanowires by Au, 10 mg of $ClAuPMe_3$ was mixed with the histidine peptide nanowire solution (4 mL) (Figure 1). After the mixture was allowed to sit for 5 days to complete immobilization of Au ions with the histidine on the nanowires, 10 μmol of reducing agent, $NaBH_4$, was added to produce Au coatings on the nanowires. The coated Au nanocrystals on the nanowires were observed by transmission electron microscopy (TEM, Philips EM420). The TEM image of the reduced Au−histidine peptide nanowire (Figure 3a) showed uniform Au nanocrystal coating ($3.0 \times 10^4/\mu m^2$ in density) and the nanocrystals on the nanowire were highly monodisperse in diameter (6 nm in average) as shown in Figure 3b. The average nanocrystal diameter matches the distance between the two binding sites in the molecular axis, 6.4 nm,[12] which suggests that the location of the histidine peptides may limit the Au nanocrystal growth and template monodisperse nanocrystals. The electron diffraction pattern of Au on the nanowire (Figure 3a, inset) indicates the presence of crystalline phases in (111) and (220). These observed crystal phases are consistent with the ones of Au nanocrystals synthesized in suspension with the same histidine peptide.[16] An absorbance peak of the Au nanowires at 510 nm (Figure 3d) agrees with the peak observed in the absorption spectrum of nonaggregated Au nanocrystal monolayers.[17,18] A striking difference was observed between the histidine-controlled Au nanocrystals (Figure 3a) and noncontrolled Au nanocrystals (Figure 3c) on the nanowire surfaces. When Au was coated on the heptane dicarboxylate nanowires without the histidine peptide by simply adding $ClAuPMe_3$ to the heptane dicarboxylate nanowire solution and reducing Au ions with $NaBH_4$, the Au coating was not uniform, and the coated Au nanocrystals were polydisperse in the diameter range between 4 and 30 nm. The absorption maximum of the nonhistidine Au nanowires was shifted from 510 to 530 nm (Figure 3d), which seems to be affected by larger Au nanocrystals grown on the nanowires.[11,17]

We have shown that the sequenced histidine-rich peptide molecules were assembled as nanowires and the biological recognition of the sequenced peptide toward specific metal lead to efficient metal coating on the nanowires. The uniformity of the metal coating on the nanowires without contamination of precipitated metal aggregates is advantageous for the fabrication of electronics and sensor devices when the nanowires are used as the building blocks. We believe this simple metal nanowire fabrication method can be applied to various metals and semiconductors with peptides whose sequences are known to mineralize specific ions. Peptide nanowires incorporated with a recognition protein (antibody) have been used to assemble the nanowires onto patterned complimentary protein (antigen) surfaces via the biological recognition process.[2c] Therefore, combinations of sequenced peptides and proteins on nanowires that control biological mineralizations and biological immobilizations may produce various structures of electronics and sensor devices in a simple and economical manner.

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Supporting Information Available: Raman spectra in Figure 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Cui, Y.; Wei, Q. Q.; Park, H. K.; Lieber, C. M. *Science* **2001**, *293*, 1289. (b) Huang, Y.; Duan, X.; Cui, Y.; Lauhon, L. J.; Kim, K. H.; Lieber, C. M. *Science* **2001**, *294*, 1313. (c) Diehl, M. R.; Yaliraki, S. N.; Beckman, R. A.; Barahona, M.; Heath, J. R. *Angew. Chem., Int. Ed.* **2001**, *41*, 353. (d) Collins, P. G.; Arnold, M. S.; Avouris, P. *Science* **2001**, *292*, 706. (e) Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. *Science* **2001**, *294*, 1317. (f) Lvov, Y. M.; Price, R. R.; Selinger, J. V.; Singh, A.; Spector, M. S.; Schnur, J. M. *Langmuir* **2000**, *16*, 5932.

(2) (a) Shim, M.; Kam, N. W. S.; Chen, R. J.; Li, Y. M.; Dai, H. J. *Nano Lett.* **2002**, *2*, 285. (b) Park, S.-J.; Taton, T. A.; Mirkin, C. A. *Science* **2002**, *295*, 1503. (c) Matsui, H.; Porrata, P.; Douberly, G. E. J. *Nano Lett.* **2001**, *1*, 461. (d) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature* **1998**, *391*, 775. (e) Mbindyo, J. K. N.; Reiss, B. D.; Martin, E. R.; Keating, C. D.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **2001**, *13*, 249. (f) Harnack, O.; Ford, W. E.; Yasuda, A.; Wessels, J. M. *Nano Lett.* **2002**, *2*, 919. (g) Wang, S.; Mamedova, N.; Kotov, N. A.; Chen, W.; Studer, J. *Nano Lett.* **2002**, *2*, 817. (h) Liu, M.; Amro, N. A.; Chow, C. S.; Liu, G.-Y. *Nano Lett.* **2002**, *2*, 863. (i) Loweth, C. J.; Caldwell, W. B.; Peng, X.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1808. (j) Hamad-Schifferli, K.; Schwartz, J. J.; Santos, A. T.; Zhang, S.; Jacobson, J. M. *Nature* **2002**, *415*, 152.

(3) Mann, S.; Shenton, W.; Li, M.; Connolly, S.; Fitzmaurice, D. *Adv. Mater.* **2000**, *12*, 147.

(4) Seeman, N. C.; Belcher, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 6451.

(5) Matsui, H.; Pan, S.; Gologan, B.; Jonas, S. *J. Phys. Chem. B* **2000**, *104*, 9576.

(6) Matsui, H.; Gologan, B.; Pan, S.; Douberly, G. J. *Eur. Phys. J. D.* **2001**, *16*, 403.

(7) Brown, S.; Sarikaya, M.; Johnson, E. *J. Mol. Biol.* **2000**, *299*, 725.

(8) Pappalardo, G.; Impellizzeri, G.; Bonomo, R. P.; Campagna, T.; Grasso, G.; Saita, M. G. *New J. Chem.* **2002**, *26*, 593.

(9) Whaley, S. R.; English, D. S.; Hu, E. L.; Barbara, P. F.; Belcher, A. M. *Nature* **2000**, *405*, 665.

(10) Ziegler, J.; Chang, R. T.; Wright, D. W. *J. Am. Chem. Soc.* **1999**, *121*, 2395.

(11) Sample, J. L.; Beverly, K. C.; Chaudhari, P. R.; Remacle, F.; Heath, J. R.; Levine, R. D. *Adv. Mater.* **2002**, *14*, 124.

(12) Matsui, H.; Gologan, B. *J. Phys. Chem. B* **2000**, *104*, 3383.

(13) Douberly, G. J.; Pan, S.; Walters, D.; Matsui, H. *J. Phys. Chem. B* **2001**, *105*, 7612.

(14) Matsui, H.; MacCuspie, R. *Nano Lett.* **2001**, *1*, 671.

(15) This peptide was sequenced by Applied Biosystems Peptide Synthesizer 432A and purified with Beckman 110 HPLC with the C-18 reverse phase column at the CUNY Gene Center.

(16) Slocik, J. M.; Moore, J. T.; Wright, D. W. *Nano Lett.* **2002**, *2*, 169.

(17) Schmitt, J.; Machtle, P.; Eck, D.; Mohwald, H.; Helm, C. A. *Langmuir* **1999**, *15*, 3256.

(18) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098.

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