Fluorescent Carbon Nanowire Made by Pyrolysis of DNA Nanofiber and Plasmon-Assisted Emission Enhancement of Its Fluorescence

Electronic supplementary information (ESI)

Hidenobu Nakao*[a], Shiho Tokonami[b], Yojiro Yamamoto[c], Hiroshi Shiigi[b] and Yoshihiko Takeda[a]

[a]National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

[b]Nanoscience & Nanotechnology Research Center, Osaka Prefecture University,1-2 Gakuen, Naka, Sakai, Osaka 599-8570, Japan

[c]Applied Chemistry, Osaka Prefecture University, 1-2 Gakuen, Naka, Sakai, Osaka 599-8570, Japan

[d]GreenChem. Inc., 930-1 Fukuda, Naka, Sakai, Osaka 599-8241, Japan

Materials and chemicals

All chemicals used were of reagent grade. To prepare the DNAsolution, λ-phage DNA (Wako Nippon Gene, 450 ng μL 1in 10 mM Tris·HCl/1 mM EDTA, pH 8) was diluted in a TE buffer solution (1 mM Tris·HCl/10 mM EDTA/10 mM NaCl, pH 8) to 45 ng μL^{-1} . A PDMS sheet was prepared by funneling liquid prepolymer (a mixture of oligomer (SILPOT 184, Dow Corning) and initiator (CATALYST SILPOT 184, Dow Corning) in a 10 : 1 ratio as recommended by Dow Corning) into a Petri dish. After curing, the PDMS sheet was cut into appropriate sizes (2×8 mm, 0.5 mm thick).

Preparation of AgNPs

The following methods described by Heard et al. (Heard, S. M.; Grieser, F.; Barraclough, C. G. *J. Colloid Interface Sci*., **1983**, *93*, 545) was used in preparing 30 nm diameter silver nanoparticles (AgNPs). A mixture containing 100 mL aqueous solution of *di*-sodium dihydrogen ethylenediaminetetraacetate (EDTA·2Na, 0.16 mM) and 3.68 mL aqueous solution of sodium hydroxide (NaOH, 0.1M) was heated at 100 °C. Subsequently, 1 mL of silver nitrate ($AgNO_3$, 26 mM) was added, and the mixture was vigorously stirred for 15 min at 100 °C, then allowed to cool to room temperature. Characterization using a zeta-potential and particle size analyzer (ELSZ-2Plus, Otsuka Electronics Co., Ltd., Japan) revealed that the AgNPs prepared had a mean diameter of 27.6 ± 5.3 nm and a zeta potential of -33.33 mV. The mean diameter of AgNPs obtained by the particle size analyzer agreed well with that by transmission electron microscopy (TEM). The prepared AgNPs (42.22 ng μL^{-1}) were stored in the dark at 5 °C.

Preparation of DNA nanofibers and metallic nanofibers on a PDMS surface

The experimental set-up for evaporation-induced assembly for generating DNA nanofibers and metallic nanofibers was described in a previous study ((a) H. Nakao, T. Taguchi, H. Shiigi and K. Miki, Chem. Commun., 2009, 1858; (b) H. Nakao, H. Hayashi, H. Shiigi and K. Miki, Anal. Sci., 2009, 25, 1177; (c) H. Nakao, Anal. Sci., 2009, 25, 1387; (d) H. Nakao, S. Tokonami, T. Hamada, H. Shiigi, T. Nagaoka, F. Iwata and Y. Takeda, Y. Nanoscale, 2012, 4, 6814; (e) H. Nakao, Anal. Sci., 2014, 30, 151.). For generating DNA nanofibers, 1 μL of λ-DNA (45 ng μL^{-1}), and 0.5 μ L of 1 M CsCl were totally diluted to 40 μ L solutions by adding TE buffer solution. For generating metallic nanofibers, 1 μL of λ-DNA (45 ng μL^{-1}), 0.5 μ L of 1 M CsCl and 20 μL of AgNPs (42.22 ng μL^{-1}) were totally diluted to 40 μ L solutions by adding TE buffer solution. The mixtures were incubated at 38 C for 1 h. A small amount of CsCl was added to the DNA solution to enhance binding between DNA and AgNPs (decreasing the electrostatic repulsion between negatively charged DNA and AgNPs stabilized by EDTA anions). Without CsCl, metallic nanofibers with well-attached AgNP did not form on the surface. Next, 2 μL of the mixture was added to 8 μL of ethanol

deposited on a PDMS sheet under ambient conditions. The PDMS sheet was tilted at 15 ° during solvent evaporation to move the drying front downwards. Solvent evaporation decreased the volume of the solution, leaving behind line patterns. Line patterns with or without AgNPs were thus formed when DNA molecules were continuously deposited at highly concentrated finger positions.

Transfer printing onto a glass surface

To transfer the prepared DNA nanofibers or metallic nanofibers onto a coverslip, the PDMS sheet with nanofibers was brought into contact with the surface for 30 min without external pressure and then peeled away. Coverslips (24×36 mm, Matsunami Glass) were sonicated for 60 min in ethanol (99.5%), rinsed in distilled water, and then dried with N_2 flow. The coverslip was moisturized with ethanol to enhance transfer efficiency. In our condition, the success rate for transfer printing was over 80%. To make 2D patterns, a second contact printing was performed on the same printed nanofibers.

Pyrolysis of DNA nanofibers or metallic nanofibers on a glass surface

DNA nanofibers or metallic nanofibers on a glass surface were pyrolyzed in air using a glass tube oven (SHIBATA , GTO-350). During pyrolysis, the coverslip with nanofibers were maintained at 250 °C for 30 min and converted into fluorescent carbon nanowires. Finally, the coverslip was steadily cooled to room temperature.

Fluorescent microscope imaging and microscopic spectroscopy

Fluorescent micrographs of prepared CNWs or metallic CNWs were taken by a fluorescent microscope (ECLIPSE 80i, NIKON) equipped with a digital camera (DS-Ri1 digital camera, NIKON). The sample was excited using a conventional mercury lamp with a violet excitation filter (EX: 380-420 nm, DM: 430 nm, BA: 450 nm, NIKON),a blue excitation filter (EX: 450-490 nm, DM: 505 nm, BA: 520nm, NIKON), and a green excitation filter (EX: 510-560 nm, DM: 575 nm, BA: 590 nm, NIKON), and imaged with a ×100 oil-immersion objective (NIKON, NA=1.30). PL spectra from a single CNW or metallic CNW were collected by a miniature grating spectrometer (Ocean Optics, USB4000, spectral resolution 1.55 nm), which was connected to the microscope using an optical fiber (core diameter 400 μm). Typical acquisition times was around 5 s.

AFM measurements

AFM measurements were performed using a Nanowizard II (JPK Instruments). The set-point voltage was adjusted to the lowest value so as not to damage the samples. We used a tapping mode and a standard silicon nitride probe with a 42 N m^{-1} spring constant (Model OMCL-AC160TS, Olympus Optical). The scanning rate was usually 0.5 Hz.

Raman imaging

The Raman images and SERS spectra were recorded on a laser Raman microscope (RAMANplus, Nanophoton, Osaka), using a laser operating at a wavelength of 532 nm with a power of 0.02 mW. The laser beam was expanded into a line when beamed onto the sample, which was illuminated through a 100× objective. Raman scattering with 350 nm spatial resolution was detected simultaneously from 400 points on the sample illuminated by the line beam.

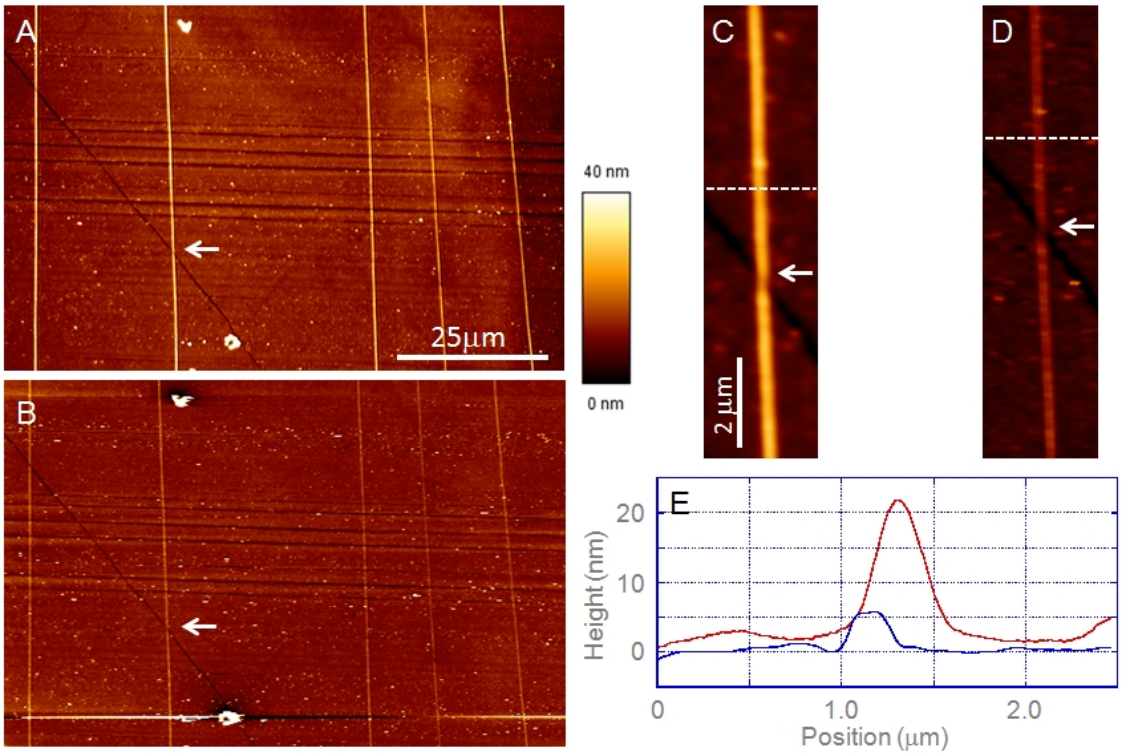

Fig. S1. AFM images of DNA nanofibers before and after thermal treatment at 250 °C for 30 min. (A) Image in a large scan range before thermal treatment. (B) Image in a large scan range after thermal treatment at 250 °C for 30 min. (C) Image in the smaller area indicated by the white arrow in image A. (D) Image in the smaller area indicated by the white arrow in image B. (E) Comparison of scan profiles before (red) and after (blue) thermal treatment along the white lines of images C and D.

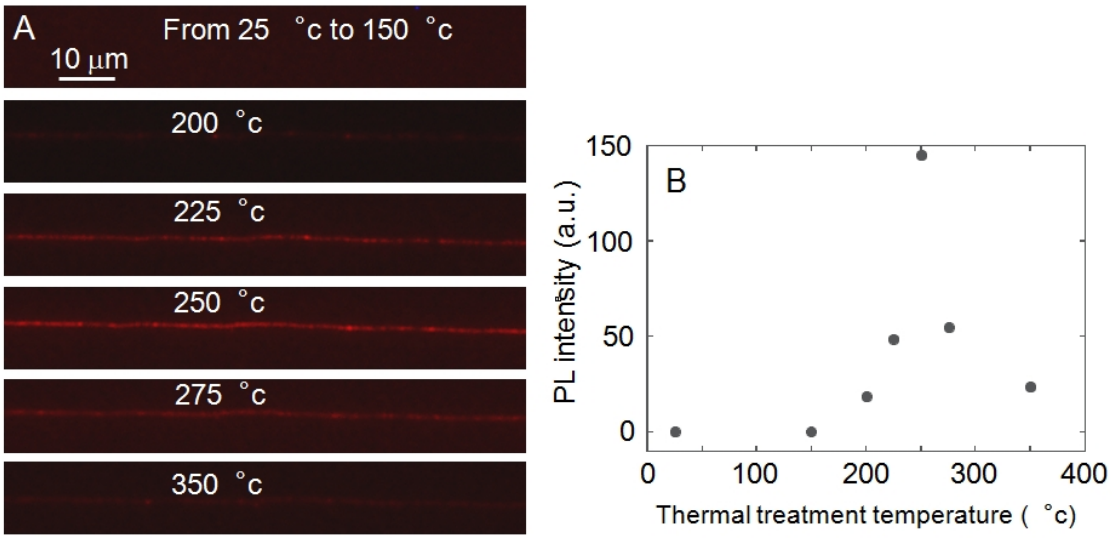

Fig. S2. Generation of PL of a single Ag-doped CNW involved in pyrolysis of metallic nanofiber. (A) Fluorescent microscope images of a single Ag-doped CNW prepared by pyrolysis at different temperatures. (B) PL intensity changes of a single Ag-doped CNW as function of thermal treatment temperature.

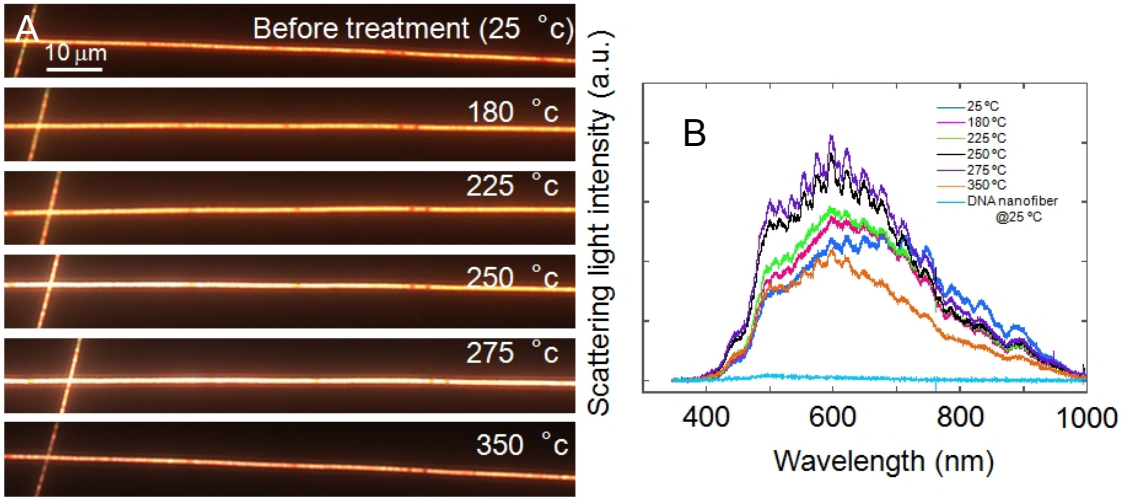

Fig. S3. (A)Dark-field scattering images of a single Ag-doped CNWs prepared by pyrolysis of metallic nanofibers at different temperatures. (B) Dark-filed scattering spectra changes of a single Ag-doped CNWs as function of thermal treatment temperature.

.

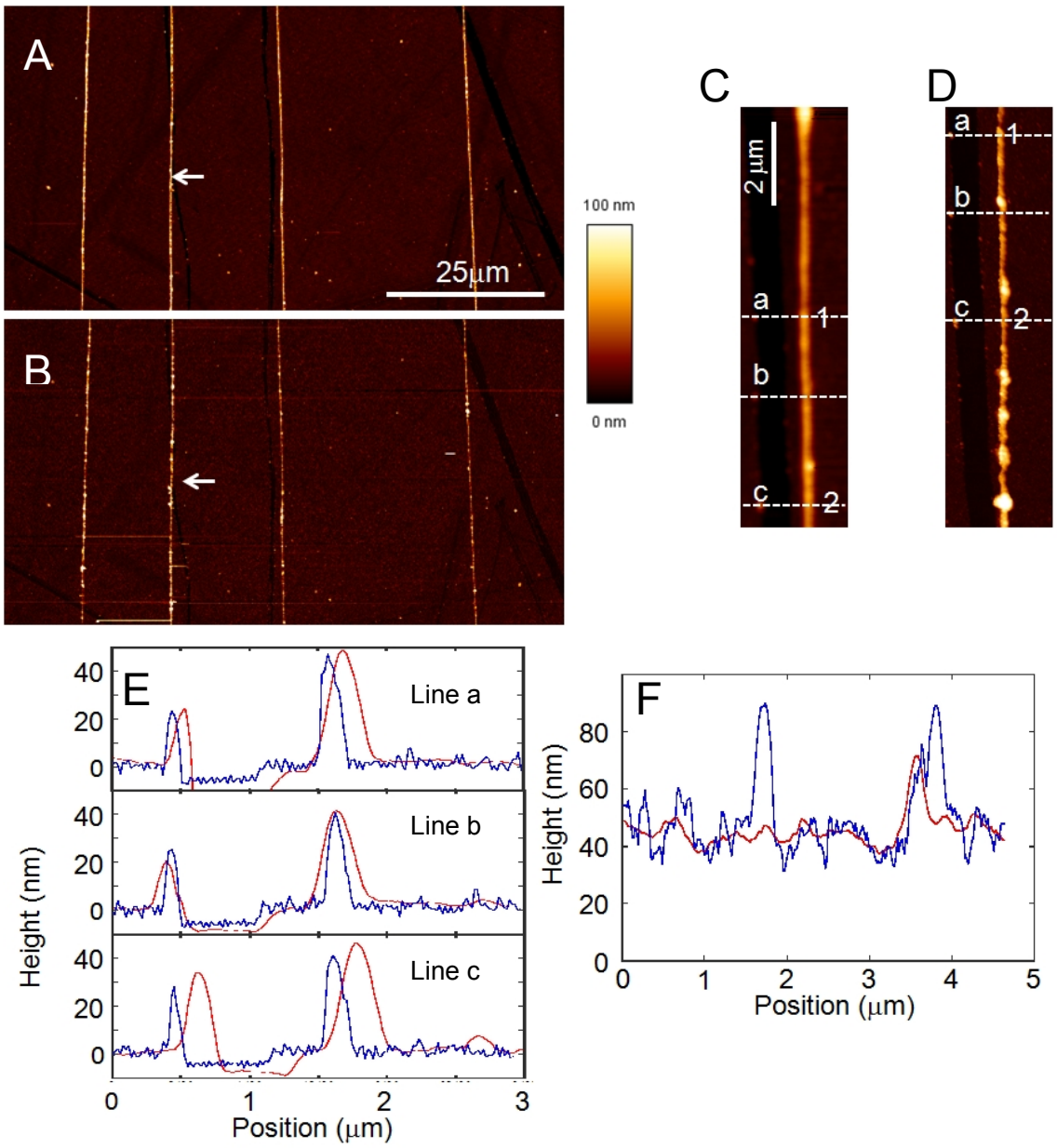

Fig. S4. AFM images of metallic nanofibers before and after thermal treatment at 250 °C for 30 min. (A) Image in a large scan range before thermal treatment. (B) Image in a large scan range after thermal treatment at 250 °C for 30 min. (C) Image in the smaller area indicated by the white arrow in image A. (D) Image in the smaller area indicated by the white arrow in image B. (E) Comparison of scan profiles before (red) and after (blue) thermal treatment along the white lines (a-c) of images C and D. (F) Comparison of scan profiles before (red) and after (blue) thermal treatment along nanowire lines from 1 to 2 in images C and D.