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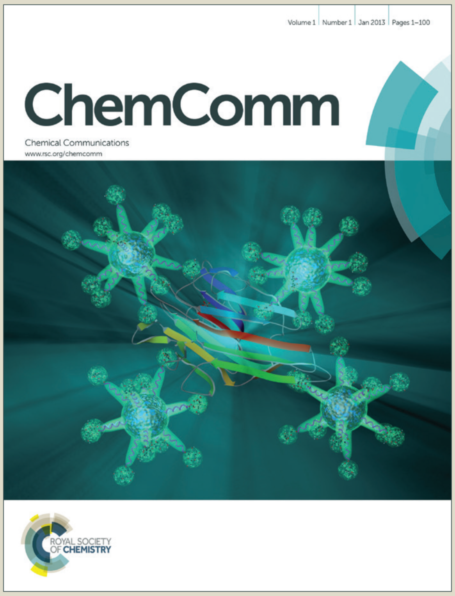

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

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

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We report on a facile method for preparing fluorescent carbon nanowires (CNWs) with pyrolysis of highly aligned DNA nanofibers as carbon source. Silver nanoparticles (AgNPs)-doped CNWs were also produced using pyrolysis of DNA nanofibers with well-attached AgNPs, indicating emission enhancement assisted by localized plasmon resonances.

Recently, fluorescent nanocarbons smaller than 10 nm, known as carbon nanodots (CDs), have attracted a great deal of attention, due to the fact that their size and λ_{ex}-dependent photoluminescence (PL) are similar to those of traditional semiconductor based quantum dots (QDs).[1] Compare with QDs, which usually contain toxic metal elements such as Cd and Se to provide high luminescence, CDs are advantageous due to their green synthesis, low environmental burden and good biocompatibility for applications. Methods for synthesizing CDs can be categorized into two main approaches: top-down[2] and bottom-up.[3] Top-down approaches include arc discharge,[2a] laser ablation,[2b] and electrochemical oxidation,[2c, 2d] where CDs are formed from a larger carbon material such as graphite powder and rods. Bottom-up approaches include combustion soot from candles or natural gas,[3a-3c] thermal decomposition of molecular precursors,[3d-3f] and microwave synthesis.[3g, 3h] However, as-prepared CDs on a substrate also seem to be problematic for use with device fabrications that often require well-aligned and highly ordered architectures. Simple methods of patterning and aligning CDs are highly desirable to achieve low-cost and large-scale fabrication of parallel device arrays.

In this study, we propose a newly-developed method for preparing highly aligned carbon nanowires (CNWs) with λ_{ex}-dependent CD-like photoluminescence (PL). In our previous work,[4a] we demonstrated that continuous bundles of DNA molecules, known as DNA nanofibers, can be driven by solvent evaporation-induced assembly and controlled drying front movement, forming parallel aligned one-dimensional (1D) nanostructures of 40 nm diameter and millimeter scale length on a poly(dimethilsiloxane) (PDMS) sheet. In addition, DNA nanofibers on a PDMS sheet can be transferred onto another surface (e.g., glass or silicon), so they can be restructured and integrated on a surface. Using highly aligned DNA nanofibers on a surface as the carbon source, we directly produced highly aligned fluorescent CNWs on a surface by pyrolysis at 250 °C. Furthermore, fluorescent enhancement from CNWs containing silver nanoparticles (AgNPs) is investigated, while pyrolysis of a single DNA nanofiber during thermal treatments is tracked by surface enhanced Raman scattering (SERS) imaging using a laser Raman microscope.

First, using previous method,[4] aligned DNA nanofibers were pre-pared on a PDMS surface, and then transferred onto a glass surface using transfer printing (TP). DNA nanofibers on a glass surface were heated at 250 °C for 30 min, resulting in pyrolysis of DNA nanofibers into CNWs. Finally, they were steadily cooled to room temperature. Fig. 1A-C exhibit corresponding fluorescent microscope images of prepared CNWs with highly aligned lines in cyan for excitation wave-lengths of 360 to 420 nm, yellow for excitation wavelengths 450 to 490 nm, and red for excitation wavelengths 510 to 560 nm. In addition, the result indicates that arrangements of DNA nanofibers on a surface are maintained after pyrolysis. The PL spectra obtained from single CNWs under different excitation wavelengths are depicted in Fig. 1D. The resulting PL emission spectra were spectrally broad, and the PL peak shifted from 500 to 600 nm with change in excitation wavelength from shorter to longer. In any case, one unifying feature of the PL of CDs is the clear λ_{ex}-dependence of the emission wavelength and intensity. The PL spectra of our CNWs also indicated such characteristics, suggesting that pyrolysis of DNA nanofibers at 250 °C can form 1D nanostructures of fluorescent CDs. Thus, the perfectly straight lines with a longer scale and high contrast formed by our strategy enabled easy utilize large-scale fabrication of parallel device arrays of CDs.

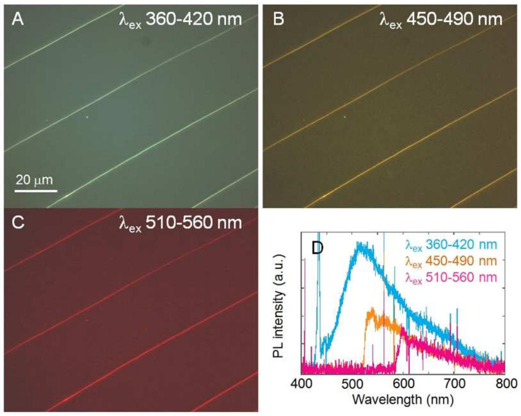

Fig. 1 (A-C) Fluorescent images of CNWs under different excitation wavelengths. (D) PL spectra of a single CNW obtained from microscopic areas in images (A-C) at different excitation wavelengths.

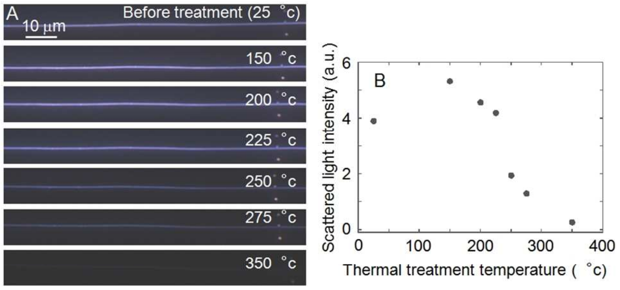

Fig. 2 (A)Dark-field scattering images of CNWs prepared by pyrolysis of DNA nanofibers at different temperatures. (B) Dark-field scattering intensity changes of a single CNW as function of thermal treatment temperature.

Since glucose,[3e, 3f, 3h] citric acid,[3g] and ascorbic acid[3d] used as carbon sources contain carboxyl groups to facilitate dehydration and carbonization, some aromatic compounds and oligosaccharides are formed under hydrothermal conditions. CDs are generally synthesized at high concentrations of molecules, resulting in a short single burst of nucleation.[3e] However, DNA molecules used as carbon sources in the present study consist of many base pairs that contain many reaction sites for dehydration and carbonization. Additionally, base pairs in bundled DNA are very densely concentrated, so the reaction can be promoted in limited spaces. Some studies have investigated the thermal stability of DNA molecules using differential scanning calorimetry (DSC) analysis.[5] Such analysis indicated an exothermic peak at 200 °C by pyrolysis, then the sample blackens after heating above 200 °C.[5b] Fig. 2 presents dark-field light scattering images depicting morphological changes of identical single DNA nanofibers during thermal treatment. In thermal treatment from 25 °C (before treatment) to 225 °C, contrasts of observed images were almost identical. However, the scattering intensity of a single DNA nanofiber after thermal treatment at 250 °C dramatically decreased to 50 % of that before treatment. Furthermore, intensity continued to decrease at temperatures above 250 °C to 350 °C, then reduced to 5 % of that before treatment. The scattering intensity of a single DNA nanofiber during thermal treatment indicated volume reduction or shrinkage of the DNA nanofiber. In addition, AFM observations indicated that the volume of an identical single DNA nanofibers reduced to 26 % after thermal treatment at 250 °C (Fig. S1, ESI†). Pyrolysis is accompanied by significant volume reduction, resulting in the shrinkage of micro-sized photoresist structures into nanoscale carbon structures.[6] These results seemed to indicate that drastic pyrolysis process of DNA nanofibers occured around 250 °C, resulting in the conversion of DNA nanofibers into CNWs.

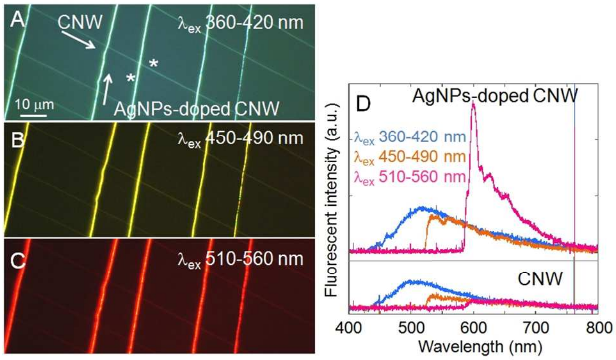

Fig. 3 Comparison of PL emissions between CNWs and AgNPs-doped CNWs. (A-C) Fluorescent images of 2D arrays consisting of CNWs and AgNPs-doped CNWs at different excitation wavelengths. (D) PL spectra of a single CNW and AgNPs-doped CNW obtained at microscopic areas "*"in images. White arrows denote alignment directions for CNWs and AgNPs-doped CNWs. The sample was heat-treated at 250 °C for 30 min.

Recently, we tried to fabricate various 1D nanostructures with DNA nanofibers as a template, resulting in the formation of metallic nanofibers consisting of 1D assembly of metal nanoparticles (MNPs) such as Au or Ag.[4] Most recently, we also reported on strong plasmon coupling of AgNPs in metallic nanofibers, indicating that metallic nanofibers served as highly localized light fields for enhancing SERS.[4d, 4e] In addition to SERS, surface enhanced fluorescence has also been reported for molecules in localized light fields.[7] Thus, pyrolysis of our metallic nanofibers would be expected to produce AgNPs-doped CNWs with fluorescence enhancements via highly localized light fields along the nanowire axis. To compare PL characteristics of CNWs and AgNPs-doped CNWs, crossed 2D arrays of aligned CNWs and AgNPs-doped CNWs were prepared on the same glass surface using TP. Fluorescent images of crossed 2D arrays presented in Fig. 3 indicate that PL intensities of all AgNPs-doped CNWs were stronger than those of CNWs. Compared to the fluorescence of CNWs without AgNPs, that of AgNPs-doped CNWs at excitation wavelengths of 510 to 560 nm is the strongest (Fig. 3). Many studies have demonstrated that for maximum excitation-emission efficiency, the LPR wavelength lies between the peak excitation wavelength and the peak emission wavelength of emitters.[7] Our previous study confirmed that metallic nanofibers with well-attached AgNPs have double LPR wavelength (transversal LPR mode at ~550 nm and longitudinal LPR mode at ~800 nm) because of strong 1D coupling of AgNPs plasmon,[4d] which is similar to LPRs observed for long nanorods or nanowires.[8] AgNPs-doped CNWs produced by pyrolysis of metallic nanofibers also maintained such LPR properties. Among the excitation wavelengths used in this study, wavelengths of 510 to 560 nm are approximately overlapped for transversal LPR of AgNPs-doped CNWs; thus the PL intensity from metallic CNWs is strongly enhanced. Compared with the emission from CNWs and AgNPs-doped CNWs at different excitation wavelengths, the peak intensities at excitation wavelengths of 360 to 420 nm were enhanced 1.2 times; those at excitation wavelengths of 450 to 490 nm were enhanced 2 times; and those excitation wavelengths of at 510 to 560 nm were 10 times.

Utilizing the LPR of AgNPs-doped CNWs, the generation of PL and carbonization involved in pyrolysis of DNA molecules could be monitored with high sensitivity via enhancement of fluorescence and SERS. Fluorescent microscopy images of metallic nanofibers treated as a function of thermal treatment temperature are presented (Fig. S2, ESI†). No PL emission was observed up to 150 °C, but significant PL emission was observed above 200 °C, which then reached a maximum at 250 °C. This result conforms well with the drastic volume reduction of DNA nanofibers at 250 °C (Fig. 2). Raman images of metallic nanofibers treated as a function of thermal treatment temperature are presented in Fig. 4. A previous study indicated that strong Raman signals are obtained only from metallic nanofibers with

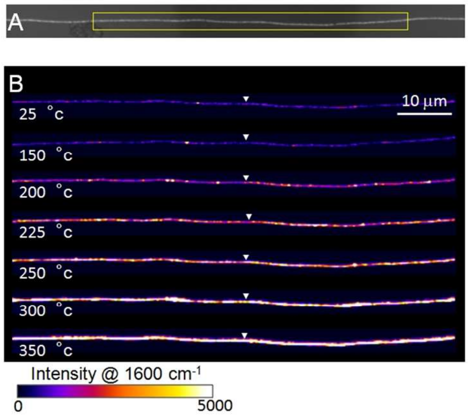

Fig. 4 Generation of the carbonization involved in pyrolysis of metallic nanofiber. (A) Optical image of a single metallic nanofiber. (B) Raman images of identical single metallic CNWs prepared by pyrolysis of metallic nanofibers at different temperatures. Raman images were obtained from segments marked by the yellow rectangle in optical image (A). Raman scattering intensity at 1600 cm^{-1} was mapped as Raman images.

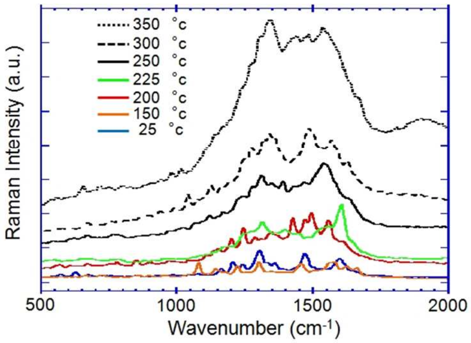

Fig. 5 Changes in Raman scattering spectra involved in pyrolysis of metallic nanofibers at different thermal treatment temperatures. Raman spectra were obtained at white triangles in Raman images in Fig. 4B.

well-attached AgNPs because of SERS enhancement. Before thermal treatment (25 °C), many peaks attributed to DNA bases were observed from 1300 to 1600 cm^{-1} (Fig. 5).[4d] At 150 °C, they change positions because of some structural changes by the denaturation (or melting) of DNA, but they are essentially the same as at 25 °C. However, broad peaks began to appear at 1000 to 1700 cm^{-1} at the temperatures above 200 °C, overlapping peaks from DNA bases. The broad peaks involved mainly two peaks (at 1300 cm^{-1} and at 1600 cm^{-1}), and their intensities increased with further increased temperature. The peak at 1300 cm^{-1} has been assigned to the ‘‘disorder’’ (D) band of graphite, and that at 1600 cm^{-1} have been assigned to the ‘‘graphite’’ (G) band of graphitic carbon, suggesting the production of amorphous carbon (carbonization). Raman studies of CDs produced by the oxidation of candle soot[3b] and by electrochemical means[2c] also indicated both D and G bands. Additionally, the Raman spectrum is also found to be superimposed onto a strong PL background of fluorescent CNWs. While carbonization continued at 200 to 350 °C, PL emission reached maximum intensity at 250 °C, and decreased above 250 °C (Fig. S2, ESI†). These results indicated that treatment at 225 to 250 °C was sufficient to complete carbonization for the best optical performance of CNWs, whereas treatment at above 250 °C over-heated CNWs, led to significant structural destruction, and hence decreased the PL emission.

Since the thermal treatment in this study was carried out in the air, oxidations of AgNPs might occur during pyrolysis. Dark-field scattering images and spectra of identical single AgNPs-doped CNWs prepared by pyrolysis of metallic nanofibers at different temperatures are presented (Fig. S3, ESI†). The scattering intensity of DNA nanofibers is less than 5% of that of metallic nanofibers, then spectra changes of DNA nanofibers during pyrolysis are negligible. In thermal treatment from 25 °C (before treatment) to 275 °C, the LPR intensity gradually increased, and the peak maximum shifted toward shorter wavelength. This might be due to rearrangements of AgNPs attributed to morphological change of DNA nanofibers. AFM observations indicated that drastic height reductions of an identical single metallic nanofibers were not found after thermal treatment at 250 °C (Fig. S4, ESI†). The total volume of resultant Ag-doped CNWs were occupied almost exclusively by 30 nm AgNPs because heights (Fig. S1. (E), ESI†) of resultant CNW was much lower than that of Ag-doped CNWs. On the other hand, local morphological changes with raised height (Fig. S4. (F), ESI†) along nanowire were observed after pyloysis. This result strongly supports rearrangements of AgNPs attributed to morphological change of DNA nanofibers involved in pyrolysis. Although LPRs of AgNPs-doped CNWs are rather different from that of metallic nanofiber, they still overlap for excitation wavelengths (400-600 nm) of fluorescent CNWs. On the other hand, the intensity of LPR of AgNPs-doped CNWs after thermal treatment at 350 °C dramatically decreased. Though significant oxidation of AgNPs involving the LPR decrease occur over 275 °C, it does not at least occur at 225-250 °C for the best optical performance of CNWs.

In summary, we have developed a facile pyrolysis method to synthesize fluorescent CNWs from DNA nanofibers; the prepared CNWs exhibit excitation wavelength-dependent PL. Furthermore, pyrolysis of metallic nanofibers with well-attached AgNPs converts them to AgNPs-doped CNWs with enhanced fluorescence. Maximum fluorescence enhancement from AgNPs-doped CNWs is observed when the transversal LPR wavelength of AgNPs-doped CNWs is well-matched with the excitation wavelength. Also, we observed the generation of carbonization involved in pyrolysis of DNA molecules by SERS imaging using a laser Raman microscope. Highly aligned CNW or AgNPs-doped CNW arrays on a surface enable easy microscopic observation of various photochemical phenomena on a nanoscale. Recently, the capacity for photo-induced energy or charge-transfer in CDs has been reported,[9] thus providing new opportunities for potential uses of our CNWs for long-range transport of excitation energy. Another advantage of our method is that CNWs or AgNPs-doped CNWs can be restructured by TP, and integrated into a desired position on various substrates, such as glass or silicon. Our developed method will be helpful for device fabrications to harvest and transport solar energy in devices for sustainable energy production.

We gratefully acknowledge the financial support provided by the Japan Society for the Promotion of Science (JSPS) through a Grant-in-Aid for Exploratory Research (26620161).

Notes and references

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† Electronic supplementary information (ESI) available: Experimental procedures and supporting figures. See DOI: 10.1039/b000000x/

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