Wrapping single-walled carbon nanotubes with long single-stranded DNA molecules produced by rolling circle amplification†

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Single-walled carbon nanotubes can be readily wrapped in and dispersed by long single-stranded DNA molecules (ssDNAs) synthesized by rolling circle amplification.

DNA has recently been used to disperse, pattern or assemble single-walled carbon nanotubes (SWNTs) for microelectronics,[1] biosensors,[2] and well-defined nanostructures.[3] For instance, Zheng and co-workers used short synthetic DNA oligonucleotides to disperse and sort SWNTs.[4] Braun *et al.* reported the use of DNA-templated carbon nanotubes for fabricating field-effect transistors (FET) in a programmable fashion, exploring the high molecular-recognition specificity of DNA.[1] For some particular applications, such as patterning SWNTs for FET, the ideal DNA length should be comparable to that of the SWNTs (*i.e.* hundreds of nanometers to microns) to ensure the precise localization and interconnection of SWNTs toward larger-scale integrated microelectronics.[1,5] However automated DNA synthesis can typically only produce synthetic DNA oligonucleotides of under 150 nucleotides (nt) (a double-stranded DNA, dsDNA, of this size has a length of ~50 nm). Although longer dsDNAs can be obtained in the form of genomic DNAs, it was found that double-stranded genomic DNAs lacked the capability to wrap and disperse SWNTs, whereas the separation of single-stranded genomic DNAs of a precise sequence is rather difficult.[5] In this communication, we demonstrate that SWNTs can be readily wrapped in and dispersed by long ssDNAs (> 1000 nt) that are easily synthesized by a biochemical technique known as "rolling circle amplification" (RCA). We believe that this simple strategy can offer particular opportunities to investigate the scaffolding and dispersing of SWNTs by long ssDNA, which are potentially important for programmable construction of larger-scale microelectronics.

RCA is a simple biochemical technique used to synthesize long ssDNAs with a repetitive sequence. In a typical RCA process (Fig. 1A), a special DNA polymerase, such as phi29 (ϕ29) DNA polymerase, makes continuous nucleotide additions to a growing DNA chain over a short circular ssDNA as the template under isothermal conditions. As a result, long, linear, ssDNA molecules with a tandemly repeating sequence are produced. Due to their large size and their characteristic repetitive-sequence, RCA products have recently been used as the template for the formation of precisely assembled nanostructures.[6] We have recently communicated that this long ssDNA could direct the assembly of gold nanoparticles in a three-dimensional, periodic manner.[7] Herein, we set out to investigate the capability of the long ssDNAs from an RCA reaction to wrap and disperse SWNTs in order to facilitate the study of using DNA to scaffold SWNTs toward larger-scale integrated microelectronics. Additionally, this long ssDNA wrapped SWNT may also provide a platform for further programmable nanoassemblies due to the repetitive sequence nature of the RCA product.[7]

Our RCA experiment was performed according to a previously reported protocol.[7,8] The length of the ssDNA product was estimated to be significantly larger than 1000 nt.[7] When investigated by atom force microscopy (AFM) (data not shown), the resultant ssDNA appeared to range from hundreds of nanometers to microns in length depending on the experimental factors used (*e.g.* molar ratio of RCA primer and dNTPs).

The capability of the RCA product to disperse SWNTs was then examined. In a typical experiment, the DNA (~20 μg/mL) and SWNTs (0.3 mg, CarboLex AP-grade, Aldrich, 50–70%, 1.2–1.5 nm in diameter and 2–5 μm in length) were mixed in double-distilled H_2O to a final volume of 500 μL. The mixture was kept in an ice–water bath and sonicated (60 W) for 10 min. After sonication, the sample was centrifuged for 30 min at 2000 *g*. The resulting supernatant was then examined using UV-Vis spectroscopy, high-resolution transmission electron microscopy (HRTEM) and AFM.

Before the addition of the ssDNA, SWNTs show poor solubility in aqueous solution because they align parallel to each other and pack into bundles due to strong intertube van der Waals attraction.[9] As expected, in the absence of DNA, SWNTs were

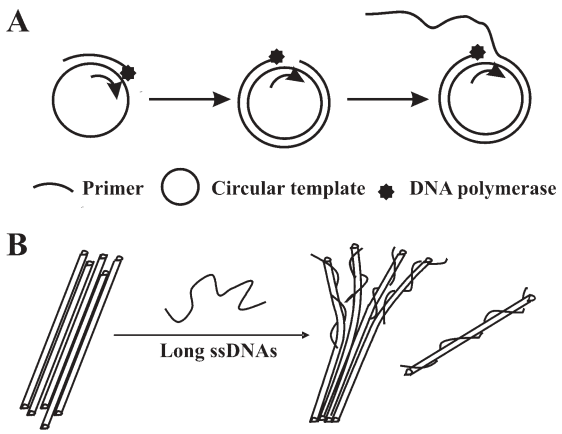

Fig. 1 (A) RCA process. See text for details. (B) De-bundling of SWNTs due to the wrapping of long ssDNA.

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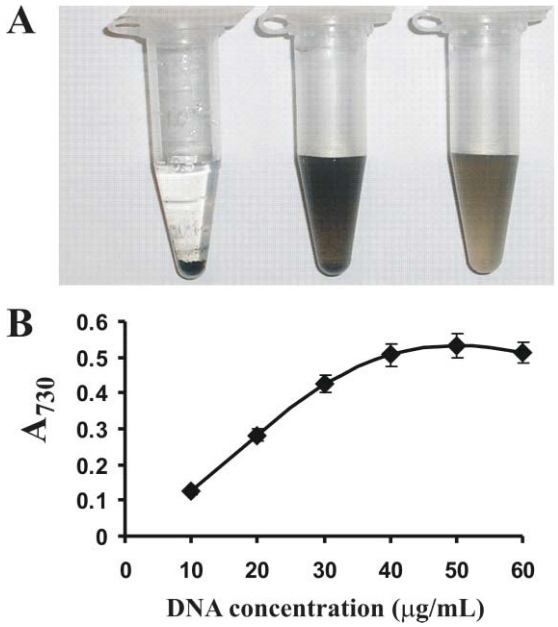

Fig. 2 (A) Photograph of SWNT–water mixture in the absence (*left*) and presence (*middle*) of 20 μg/mL of the RCA product. On the *right* is the supernatant of the *middle* tube after centrifugation at 2000 *g* for 30 min. (B) UV-Vis absorbance of DNA/SWNT solution at 730 nm plotted as a function of DNA concentration. 0.6 mg/mL of SWNT was used in these experiments.

not soluble in water (Fig. 2A, *left*). By contrast, SWNTs were readily dispersed in the presence of the RCA product (Fig. 2A, *middle*) and, after centrifugation at 2000 *g* for 30 min, the supernatant was stable for at least two months (Fig. 2A, *right*). The UV-Vis absorption spectra of the SWNT/DNA solution were then obtained (see Electronic Supplementary Information, ESI) and the absorbance at 730 nm (a wavelength that is relatively invariant with respect to pH changes[4]) as a function of DNA concentration was plotted in Fig. 2B. The data clearly indicate that the solubility of SWNT increased as more RCA product was used until all the SWNTs were dissolved. Specifically, the soluble SWNT concentration can reach ~0.6 mg/mL when 50 μg/mL of DNA is added.

HRTEM analysis was used to investigate the dispersed SWNT structures. A typical experiment was performed by placing 5 μL of the supernatant from the SWNT/DNA mixture onto a perforated carbon-coated copper grid. Some representative HRTEM images in which individual SWNT and small SWNT bundles were clearly observed are shown in Fig. 3. The de-bundling feature (Fig. 3C) suggests that the wrapping of ssDNA led to disruption of the intertube interactions in the big bundles. The SWNT/DNA hybrid was further investigated by AFM. Samples for AFM measurements were prepared by spin-coating the SWNT/DNA suspension (50 μL) onto freshly cleaved mica at 2500 rpm. Representative AFM images (Fig. 4) also contained both individual SWNTs and de-bundled SWNTs as a result of ssDNA wrapping.

The ability of short oligonucleotides to adhere to and facilitate dispersion of SWNTs was previously reported by Zheng and co-workers.[4] It was proposed that the aromatic bases in the DNA backbone could interface with SWNT surfaces *via* π-stacking, and,

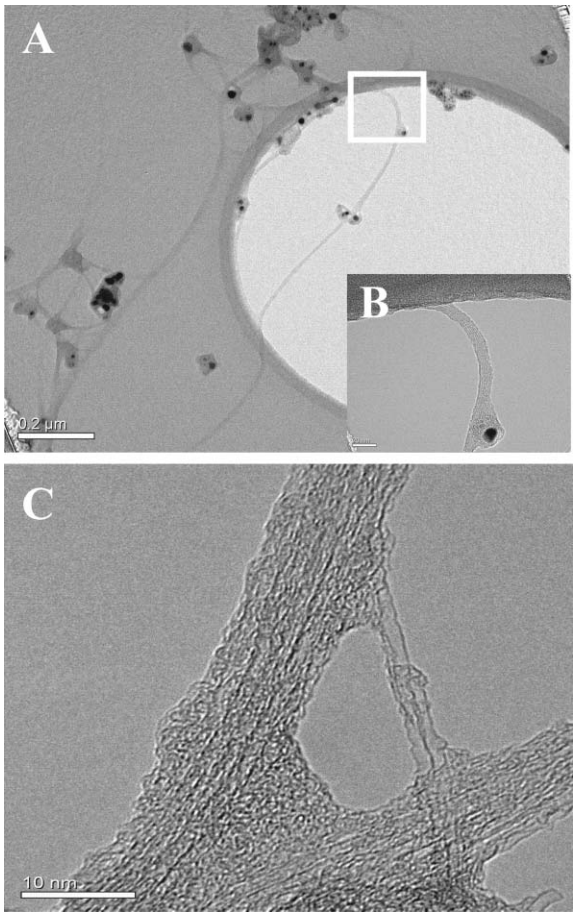

Fig. 3 HRTEM images for long ssDNA-wrapped SWNTs. (A) Individual and small bundles of SWNTs were clearly observed. Inset (B) is a magnified version of the boxed area in (A). (C) SWNTs were de-bundled by ssDNA wrapping. Scale bar: (A) 200 nm, (B) 10 nm, and (C) 10 nm.

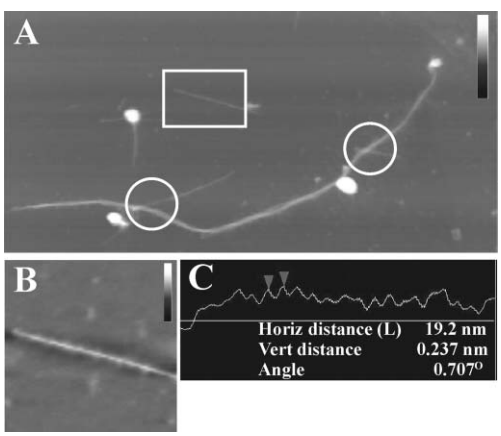

Fig. 4 AFM analysis (height profile) of long ssDNA-wrapped SWNTs. (A) ssDNA-dispersed SWNTs. Two white circles indicate the de-bundling of SWNTs due to DNA wrapping. (B) A magnified version of the boxed area in (A). (C) Section analysis of the ssDNA-wrapped SWNT structure in (B). Scale: (A) 2.5 × 1.25 μm^2, (B) 400 × 400 nm^2. Height bar: (A) 60 nm, (B) 10 nm.

therefore, these negatively charged SWNT/DNA hybrids could be dispersed effectively due to electrostatic repulsion. In our study, this wrapping mechanism was supported by the AFM images (an individual SWNT/DNA hybrid is depicted in Fig. 4B). The DNA wrapped SWNT showed distinct periodic pitches of ~19 nm (Fig. 4C), which is consistent with the previous observations reported by Zheng *et al.*[4]

In conclusion, we demonstrate that SWNTs can be easily dispersed by long ssDNA molecules synthesized by the RCA technique. In comparison to genomic DNAs, the sequence of an RCA product can be easily controlled simply because a defined circular DNA is used as the template to generate the required ssDNA. We believe that this long ssDNA, with length comparable with that of SWNTs, will be potentially useful for scaffolding SWNTs to fabricate precisely assembled larger-scale microelectronics. Additionally, the repetitive-sequence nature of RCA products can provide a unique opportunity for further programmable nanoassemblies.[7] Furthermore, the length of the RCA product could be relatively easily adjusted by altering the concentrations of dNTPs, polymerase, the circular template and the DNA primer. The controllable DNA sequence and length should facilitate the fundamental study of how the sequence and length of ssDNA might affect the solubility and other properties of SWNTs.

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8 All DNA samples used were purchased from the Central Facility, McMaster University; circular template sequence: 5′-TGTCTTCGCCTTCTTGTTTCCTTTCCTTGAAACTTCTTCCT-TTCTTTCTTTCGACTAAGCACC; primer sequence: 5′-GGCGAAGACAGGTGCTTAGTC; for the synthesis of radioactive RCA product in the gel electrophoresis study, [a-^{32}P]-dGTP (Amersham Biosciences; 2 mL, specific activity: 3000 Ci/mmol) was incorporated.

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