Aqueous two-phase extraction of semiconducting single-wall carbon nanotubes with isomaltodextrin and thin-film transistor applications

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Semiconducting single-wall carbon nanotubes (s-SWCNTs) are promising materials with potential applications in thin-film transistors (TFTs). However, separation techniques are required to obtain highly enriched s-SWCNTs since conventional as-grown SWCNTs are a mixture of 70% semiconducting and 30% metallic SWCNTs. Here, we developed a rapid single-step aqueous two-phase extraction of high-purity s-SWCNTs using isomaltodextrin, which is a cost-effective polysaccharide that contains a large amount of α-1,6-glucosidic linkages. We also succeeded in fabricating high-density uniform films directly from the high-purity s-SWCNT extract. Fabricated TFTs exhibited an excellent on/off ratio, carrier mobility, and on-current density.© 2019 The Japan Society of Applied Physics

Aqueous two-phase extraction of semiconducting single-wall carbon nanotubes with isomaltodextrin and thin-film transistor applications

Single-wall carbon nanotubes (SWCNTs) possess a range of potential applications for high-performance electronic devices, such as thin-film transistors (TFTs), due to their excellent electronic properties, chemical/mechanical strength, flexibility, and solution processability.1–3 However, the electrical properties of SWCNTs can be modified by changing the SWCNT chirality from a semiconducting to a metallic character. As-synthesized SWCNTs typically contain one-third metallic (m-) and two-thirds semiconducting (s-) SWCNTs.4–9 Therefore, high-purity s-SWCNT separation techniques are required prior to their application in electronic devices. A variety of s-SWCNT separation techniques, such as density gradient ultracentrifugation,10 gel chromatography,11–15 ion exchange chromatography,16 electric layer formation,17,18 selective dispersion,19–22 and aqueous two-phase (ATP) extraction,23–26 have been reported.

ATP extraction is one of the most powerful purification methods for obtaining high-purity s-SWCNTs using simple operations and upscaling. Zheng and co-workers developed an SWCNT separation technique that employs ATP extraction,23 which is primarily utilized for the purification of proteins and related biopolymers.24 A highly concentrated aqueous mixture of polyethylene glycol (PEG) and dextran (DX) was spontaneously separated into two phases by tuning the surfactant concentrations, such as sodium cholate (SC) and sodium dodecyl sulfate (SDS), where s-SWCNTs and m-SWCNTs were partitioned into the hydrophobic PEG phase and hydrophilic DX phase, respectively. By removing undesired m-SWCNTs to the DX phase, the high-purity separation of s-SWCNTs in PEG phase is accomplished. Although there are many examples that identify the DX polymer as a necessary component in ATP-based SWCNT separation, this necessity is unclear. However, it is worth noting that DX and its corresponding polymers are unsuitable for large-scale separation due to their high cost compared to synthetic macromolecules.

The chemical structure of DX and the α-1,6-linkages of D-glucose units [Fig. 1(a)] inspired us to adopt isomaltodextrin (IMD),28 a highly branched α-glucan containing 66.3% α-1,6-glucosidic linkages [Fig. 1 and Table I] in our ATP extraction technique. IMD is produced from starch via the α-glucosyltransferase and α-amylase activities of Paeunibacillus alginolyticus. IMD is commercially available at a low cost because it was originally developed as a water-soluble dietary fiber.29–32 Here we describe a successful s-SWCNT purification technique via single-step ATP extraction with IMD. The direct fabrication of s-SWCNT films and TFT applications were also investigated using these separated high-purity s-SWCNTs.

Three different IMD materials were prepared via enzyme treatment and chromatographic separation of the original IMD to reveal the effect of α-1,6-glucosidic linkages (Table I). Both the weight average ($M_w$) and number average ($M_n$) molecular weights were determined via gel permeation chromatography analysis. The percentages of the α-glucosidic linkage contents were investigated via methylation analysis.28 Enzyme-digested IMD (E-IMD) was provided via the treatment with Glucoamylase, which selectively hydrolyzes the continuous α-1,6-glucosidic linkages of IMD from the non-reducing end to the branching point. E-IMD therefore possesses a smaller $M_w$ and lower ratio of total α-1,6-glucosidic linkages than those of the original IMD. Size separation via size exclusion chromatography yielded corresponding high (L-IMD) and low (S-IMD) molecular weight polysaccharides. Both L-IMD and S-IMD possess similar α-1,6-glucosidic linkages and superior $M_w/M_n$ ratios to those of the original IMD. Pullulan (PUL),33 a polyglucose linked via repeating α-1,4-, α-1,4-, and α-1,6-bonds, as shown in Fig. 1(c), was also employed for further comparison.

SWCNTs that were synthesized via the arc-discharge method (Meijo Nano Carbon, Meijo Arc SO type) (15 mg) were dispersed into 1 wt% SC (TCI chemical, 98%) aqueous
solution (aq.) (15 ml) using a bath-sonicator (BM EQUIPMENT, Nanoruptor NR-350) for 16 h. The dispersion was then centrifuged at 27,600 g for 1 h using an ultracentrifuge (Hitachi Koki S52ST). The upper 80% of the resultant dispersion was collected as a dispersion sample. The typical ATP extraction process is shown below [Fig. 1(d)]. The dispersion sample (100 μl) was added to a mixture containing 50% IMD aq. (300 μl), 50 wt% PEG 6,000 (Wako chemical) aq. (80 μl), 5 wt% SDS (Aldrich, 99%) aq. (60 μl), 2 wt% SC aq. (54 μl), and deionized (DI) water (106 μl). The amount of SC aq. and DI water was optimized based on the target SWCNT dispersion. The resultant mixture was allowed to settle for 15 min, and then centrifuged at 4,000 g for 5 min using a microcentrifuge (Eppendorf MiniSpin®) to promote the phase separation. The upper PEG phase containing desire s-SWCNTs was collected and then diluted with 1% SC aq. four times. The extract was evaluated using the absorption spectra measured with an ultraviolet–visible–near infrared spectrophotometer (JASCO V-570). Raman spectroscopy measurements were also acquired using a Renishaw inVia Raman Microscope with 532 and 785 nm excitation. The as-separated s-SWCNT dispersion (60 μl) was then dropped onto an amine-functionalized Si/SiO2 substrate with 3-aminopropyltriethoxysilane to promote SWCNT deposition. The sample was allowed to settle for 1 h, and then blown dry with pressurized N2 gas to remove any remaining solution. The substrate was subsequently washed via repeated dipping in hot DI water and 2-propanol to remove any surfactants and impurities. Atomic force microscopy (AFM) measurements were acquired using a Dimension Fastscan AFM with a Nanoscope V stage controller (Bruker). A metal electrode was deposited onto the substrate via the vapor deposition method. Photolithography was used to deposit the metal electrode in a predetermined shape. A 10-nm thickness of titanium (Ti) metal was deposited onto the substrate to provide good contact with the SWCNTs. A 100-nm thickness of gold metal was subsequently deposited on top of the Ti layer to obtain an electrode with high electrical conductance. A photoresist was spin-coated onto the device and patterned via lithography to remove excess SWCNTs from the device channel, exposing the area out of the channel. Oxygen plasma was subsequently applied to the protected device to burn out any excess SWCNTs. The photoresist was then carefully removed via chemical etching. The resultant device was measured using a probe station connected to a
semiconducting device analyzer (Agilent Technologies B1500A) at room temperature in open air.

Figure 2(a) shows the optical absorption spectra of pristine SWCNT dispersion and the extracted SWCNTs in PEG phase. The diameters of the analyzed SWCNTs, which were formed in arc discharge, are ∼1.4–1.6 nm, with the peaks at ∼900–1100 nm assigned to the optical transition of s-SWCNTs (S22)34) and the peaks at ∼600–800 nm indicating the presence of m-SWCNTs (M11). The efficiency of s-SWCNT enrichment was evaluated based on the peak reduction of the M11 region, with most of the M11 peaks removed after the ATP extraction using IMD. Unlike some reported ATP procedures,35) which require a 3–5 step extraction procedure to obtain highly enriched s-SWCNTs, our optimized conditions enable effective s-SWCNT extraction in a single-step. The efficiency was slightly improved with L-IMD, yielding a high molecular weight. The purities of the s-SWCNT extracts provided by IMD and L-IMD were estimated to be around 98% and 99%, respectively, via a comparison with the reported absorption spectra.36) Raman spectroscopy measurements were then acquired to evaluate the purity of the s-SWCNTs in the IMD-extract [Fig. 2(b)].37) The Kataura plot34) indicates the excitation of the ∼160–180 cm−1 radial breathing mode (RBM) peaks at 532 and 785 nm were representative of around 1.5-nm diameter m-SWCNTs and s-SWCNTs, respectively. The m-SWCNT peak was largely suppressed after ATP extraction with IMD, and the intensity ratio of m-SWCNT to s-SWCNT (Iα/Is) changed from 5:1 to 1:6. A 98.4% purity of the s-SWCNTs in the IMD-extract was estimated by assuming that the m-SWCNTs and s-SWCNTs were synthesized in the pristine sample at a 2:1 ratio, which was consistent with that from the absorption spectra.

However, the absorption spectra of the SWCNT extracts using E-IMD, which shows a lower ratio of α-1,6-glucosidic linkages than that of original IMD, contained obvious M11 peaks [Fig. 2(a)]. Furthermore, PUL, which does not possess a repeating saccharide structure via α-1,6-bonds, was completely ineffective in the ATP extraction of s-SWCNTs. These two results indicate that continuous α-1,6-glucosidic linkages play a crucial role in the purification of s-SWCNTs. Buijs and co-workers recently proposed that the helical geometry of the α-D-glucose oligomer in an aqueous environment through intermolecular hydrogen bonding networks.38) The pitch of the helical structure is around 1.5 nm, which provides a suitable cavity for interactions with the SWCNTs. This hypothesis is consistent with the gel filtration purification of s-SWCNTs using agarose,11,12) which also forms a helical structure in the gel state.39,40)

Although low-Mα S-IMD possess similar α-1,6-glucosidic linkages to original IMD and high-Mα L-IMD [Table I], s-SWCNT purity in the S-IMD extract was decreased [Fig. 2(a)]. The molecular weights of IMD and corresponding derivatives also affect the efficiency of the extraction. To archive the high purity extraction of s-SWCNTs, both continuous α-1,6-glucosidic linkages and the long-chain structures of polysaccharides are required.

Solution-based thin-film fabrication and TFT device performance were also investigated using the high-purity s-SWCNTs. A typical AFM image of the fabricated film directly from the s-SWCNT extract is shown in Fig. 3(a), which confirms the formation of high-density, uniform SWCNT networks. In the previous report by Gui and co-workers, a precipitation-resuspension process of s-SWCNT was demonstrated to remove PEG polymer before fabricating the thin-film networks.35) However it was intrinsically unnecessary for film fabrication. The height profile of the fabricated film in Fig. 3(b) revealed that there were two distinct heights (∼1.5 and ∼3.0 nm). Given the 1.4–1.6-nm diameters of the SWCNT extracts, the profile indicates that individual SWCNTs were interconnected with each other.

The transfer characteristics of the fabricated CNT-TFTs with a channel length (L) of 50 μm at a drain voltage (VDS) of −5 V are shown in Fig. 4(a). The TFTs exhibited a p-type behavior due to the absorption of oxygen molecules or remaining dispersants to the SWCNTs.41,42) The average on/off ratio and on-current density of nine devices were $2.75 \times 10^6$ and 111 μA·mm−1, respectively. This on-current

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**Fig. 2.** (Color online) (a) Absorption spectra of the pristine dispersion and ATP-extracts in PEG phase. (b) Raman spectra of pristine SWCNT (top panel) and s-SWCNT extracted with IMD (bottom panel). The ratios of the s-SWCNT RBM peak intensities under 532 nm excitation (blue) to the m-SWCNT RBM peak intensities under 785 nm excitation (red) are listed. The Raman measurement parameters were maintained for the same excitation wavelength.
density is the top-level value, comparable to the previous examples.\textsuperscript{43–46} The carrier mobilities and on/off ratios of TFTs with various channel lengths at $V_{DS} = -0.5 \text{ V}$ are summarized in Fig. 4(b). The carrier mobilities were calculated via the parallel plate model and the average mobility of nine devices was 4.21 cm$^2$·V$^{-1}$·s$^{-1}$ ($L = 50 \mu$m). Small characteristic variations were observed in all of the cases due to the uniformity of the fabricated SWCNT film. In particular, the TFTs with a channel length of only 10 \mu m exhibited a high on/off ratio of $\sim 10^6$, which validates the successful extraction of high-purity s-SWCNTs.\textsuperscript{35,47,48}

In conclusion, we successfully demonstrated the single-step ATP extraction of s-SWCNTs using IMD. The extraction of s-SWCNTs achieved at >98% purity, as determined via optical absorption spectra and Raman spectroscopy measurements. We also revealed the ATP separation of SWCNTs occurred due to both the hydrophobic/hydrophilic difference and the interaction with helical structures possessing continuous $\alpha$-1,6-glucosidic linkages. Furthermore, we demonstrated the direct film fabrication and TFT measurements using the as-extracted s-SWCNT dispersion. Our CNT-TFTs exhibited an excellent on/off ratio, carrier mobility, and on-current density, proving the successful extraction of high-purity s-SWCNTs.

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