Separation of semiconducting carbon nanotubes using isomaltodextrin and thin-film transistor applications

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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. 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. 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,[1] gel chromatography,[2] electric layer formation,[3] selective dispersion,[4] and aqueous two-phase (ATP) extraction,[5] have been reported.

Recently, we developed a rapid and single-step ATP extraction of high-purity s-SWCNTs using isomaltodextrin (IMD), which a highly branched α-glucan containing 66.3% α-1,6-glucosidic linkages (Fig 1a).[6] IMD is produced from starch via the α-glucosyltransferase and α-amylase activities of Paenibacillus alginolyticus. IMD is commercially available at a low cost because it was originally developed as a water-soluble dietary fiber. The extraction of s-SWCNTs was achieved at >98% purity, as determined via optical absorption spectra and Raman spectroscopy measurements. It was revealed that the ATP separation of SWCNTs occurred due to both the hydrophobic/hydrophilic difference and the interaction with helical structures possessing continuous α-1,6-glucosidic linkages.

We also developed the cross-linking gelation of IMD, enabling the high-purity separation of s-SWCNTs (Fig 1b).[7] The cross-linking reaction with epichlorohydrin under precisely controlled basic conditions gave the sub-micrometer porous IMD gels, which was important for achieving gel chromatographic SWCNT separation. Column chromatography performed using the IMD gel, which possessed submicrometer porous structures, provided s-SWCNTs with an excellent 98.7% purity.

Furthermore, an efficient method for the fabrication of SWCNT thin films using cross-linked methoxycarbonyl polyallylamine (Moc-PAA) was established (Fig 1c).[8] The cross-linked Moc-PAA layer provided a smooth surface terminated with amino groups to form the s-SWCNT networks. We successfully manufactured SWCNT-TFTs on both rigid and flexible substrates. The devices exhibited good on/off ratio, carrier mobility, and on-current density with small variations. The suppression of characteristic variability of SWCNT-TFTs led to the operational stability of practical devices.

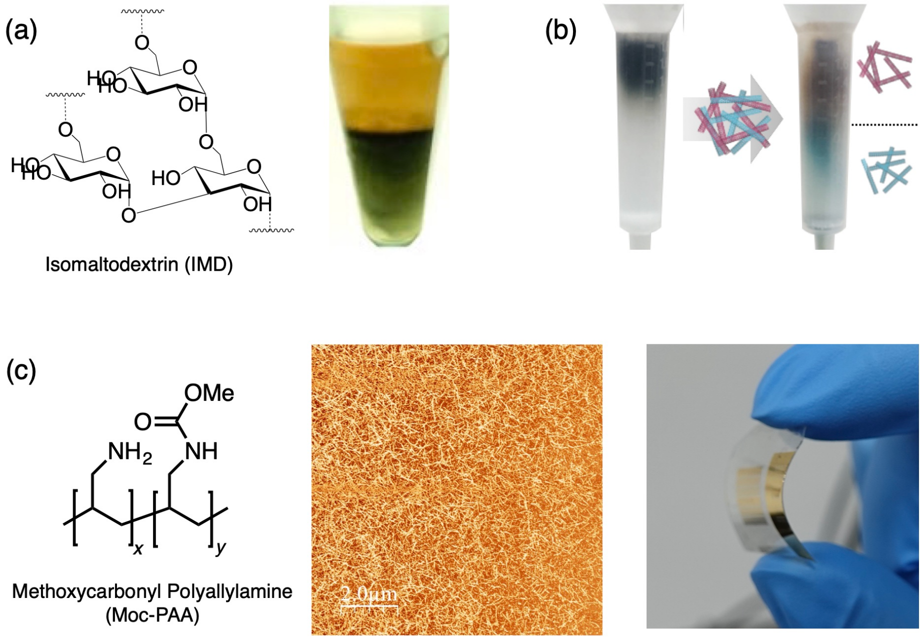

Fig 1. (a) Chemical structure of IMD and photograph of ATP extraction of SWCNTs using IMD. (b) Photographic image of column chromatography separation of SWCNTs using the IMD gel. (c) Chemical structure of Moc-PAA, atomic force microscopy (AFM) image of the fabricated s-SWCNT film, and photograph of SWCNT-TFT on the flexible PEN substrate.

1) M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, M. C. Hersam, *Nat. Nanotechnol.* **2006**, *1*, 60.

2) T. Tanaka, Y. Urabe, D. Nishide, H. Kataura, *Appl. Phys. Express* **2009**, *2*, 125002.

3) K. Ihara, H. Endoh, T. Saito, F. Nihey, *J. Phys. Chem. C* **2011**, *115*, 22827.

4) K. S. Mistry, B. A. Larsen, J. L. Blackburn, *ACS Nano* **2013**, *7*, 2231.

5) C. Y. Khripin, J. A. Fagan, M. Zheng, *J. Am. Chem. Soc.* **2013**, *135*, 6822.

6) H. Omachi, T. Komuro, K. Matsumoto, M. Nakajima, H. Watanabe, J. Hirotani, Y. Ohno, H. Shinohara. *Appl. Phys. Express*, **2019**, *12*, 097003.

7) Y. Matsunaga, J. Hirotani, Y. Ohno, H. Omachi, H. *Appl. Phys. Express*, **2021**, *14*, 017001.

8) K. Matsumoto, K. Ueno, J. Hirotani, Y. Ohno, H. Omachi, *Chem. Eur. J.*, **2020**, *26*, 6118.