

Electronic Supplementary Information (ESI)

Oxidative corrosion potential vs. pH diagram for single-walled carbon nanotubes

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Experimental Section

Synthesis of SWCNTs on a gold electrode

The single-walled carbon nanotubes (SWCNTs) were synthesized on a gold wire surface using a chemical vapor deposition (CVD) method according to a previous report.^[1-3] A gold wire (99.999%, 0.8 mm diameter) was modified with a catalytic ink containing cobalt (II) acetate tetrahydrate and molybdenum (II) acetate dimer. The SWCNTs were synthesized in a quartz tube (inner diameter: 35 mm, length: 840 mm) equipped with temperature and gas flow control systems. First, to prepare Co-Mo alloy nanoparticles as a catalyst, the modified gold wire was treated under a reducing atmosphere at *ca.* 850 °C for 10 min. Next, ethanol (EtOH, 99.8%) was infused into the chamber at 850 °C for 10 min using H₂ as a carrier gas. The gold wire surface was determined to be completely covered with SWCNTs because the characteristic electrochemical behavior of a gold surface was not observed at any current scale used in this study.

Characterization of SWCNTs by SEM and TEM

The deposition of SWCNT layers on the gold wire was initially confirmed because the gold surface color changed to black, as shown in the photograph in Fig. S1. SWCNT bundles of 5–20 nm in diameter in the layer were observed by FE-SEM, and the thickness of the SWCNT layer was estimated to be *ca.* 20 μm. Fig. S2 shows a TEM image of the SWCNT layer. Individual tube structures with estimated wall thickness of *ca.* 0.35 nm were observed, which indicated that the structures were SWCNTs.^[4-8]

Characterization of SWCNTs via Raman spectroscopy

The prominent feature of the Raman spectra of the SWCNTs is the G-band appearing at ca. 1590 cm^{-1} .^[9,10] The G-band is a doubly-degenerated phonon Raman active mode for sp^2 -structured carbon networks. The other feature is the D-band at ca. 1350 cm^{-1} , which is localized where the lattice structure is not perfect, mostly at the edges and the defects of the sp^2 -hybridized carbon structure.^[9,10] The G/D intensity ratio (I_G/I_D) was used to evaluate the crystallinity of the sp^2 -hybridized carbon structure. The Raman spectra of the SWCNTs are shown in Fig. S3. The I_G/I_D of the SWCNTs was evaluated to be ca. 35 when a 514.5 nm laser was used for excitation. A slight D-band peak was observed. These results indicated that the synthesized SWCNTs were highly crystalline. In other words, the SWCNTs had few defects. The radial breathing mode (RBM) provides information on the diameter distribution of SWCNTs. The diameter distribution of the synthesized SWCNTs was found to be 0.9–1.6 nm using the equation: $d/\text{nm} = 248/(\nu/\text{cm}^{-1})$, where d is the diameter of a SWCNT and ν is the Raman shift.^[11-13]

References

- [1] M. Tominaga, S. Sakamoto and H. Yamaguchi, *J. Phys. Chem. C*, 2012, **116**, 9498.
- [2] M. Tominaga, A. Iwaoka, D. Kawai and S. Sakamoto, *Electrochem. Commun.*, 2013, **31**, 76.
- [3] S. Sakamoto and M. Tominaga, *Chem. Asian J.*, 2013, **8**, 2680.
- [4] Iijima, S. *Nature* 1991, **354**, 56.
- [5] A. K. Geim and K. S. Novoselov, *Nature Mater.* 2007, **6**, 183.
- [6] P. R. Wallace, *Phys. Rev.* 1947, **71**, 622.
- [7] R. Saito, G. Dresselhaus and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998.
- [8] R. L. McCreery, *Chem. Rev.* 2008, **108**, 2646.

- [9] F. Tuinstra and J. L. J. Koenig, *Chem. Phys.* 1970, **53**, 1126.
- [10] F. Tuinstra and J. L. J. Koenig, *Composite. Mater.* 1970, **4**, 492.
- [11] R. Saito, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B* 2000, **61**, 2981.
- [12] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. Lett.* 2001, **86**, 1118.
- [13] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka and Y. Achiba, *Synth. Met.* 1999, **103**, 2555.

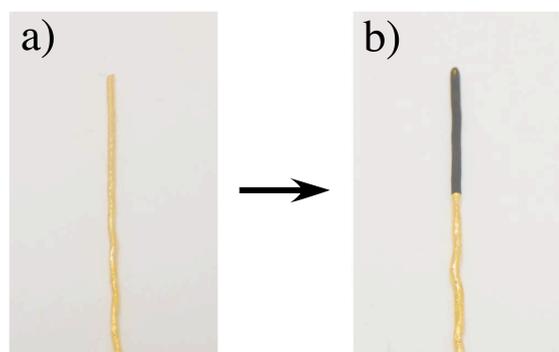


Fig. S1 Photographs of a gold wire (a) before and (b) after the SWCNT synthesis process.

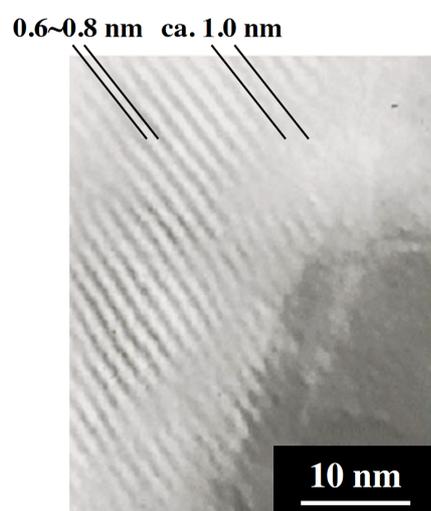


Fig. S2 TEM image of the SWCNTs.

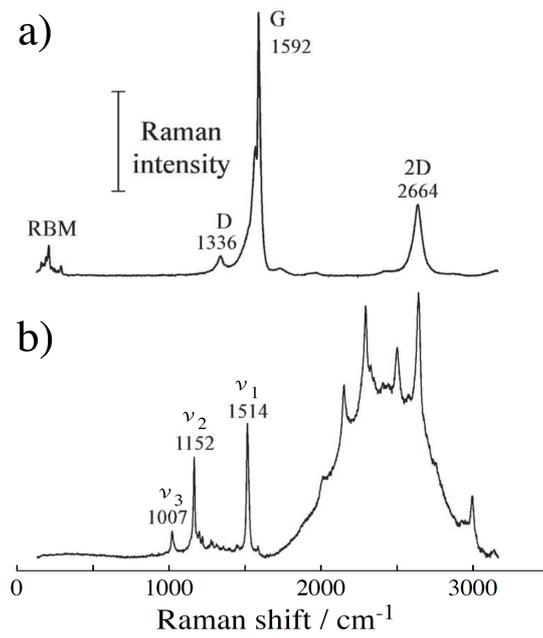


Fig. S3 Raman spectra of (a) SWCNTs and (b) β -carotene. Excitation laser wavelength: 514.5 nm (2.41 eV)

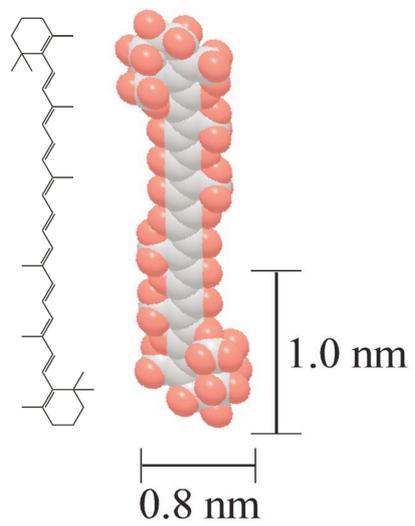
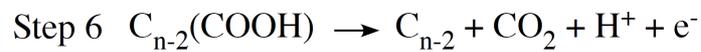
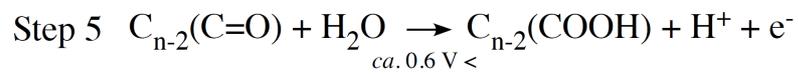
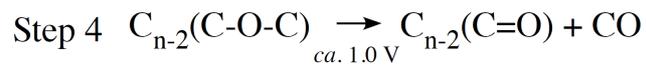
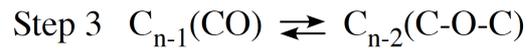
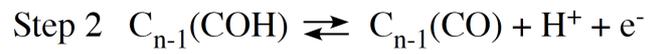
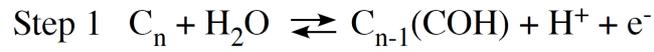


Fig. S4 Chemical structure and CPK model for β -carotene.



Scheme S1 Expected steps of the oxidative corrosion of SWCNTs.

Table S1 XPS results for the C(1s) region of the SWCNTs

SWCNTs	C=C, C-C / % (284.4, 285.2 eV)	C-O / % (286.6 eV)	C=O / % (288.0 eV)	O-C=O / % (289.2 eV)	$\pi - \pi^*$ shakeup / % (290.5 eV)
Pristine SWCNTs	77	11	1.5	5.3	5.2
CPE-SWCNTs ^a	76	12	2.0	5.5	4.5

^a Controlled potential electrolysis was carried out at 1.0 V in pH 7 solution for 30 min.