In Situ Photoluminescence Spectroelectrochemistry of Single-walled Carbon Nanotubes with Nine Different Chiral Indices

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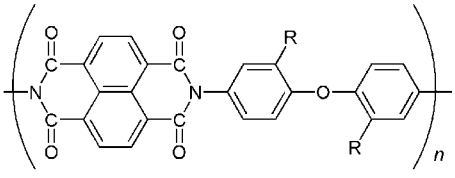
In situ photoluminescence spectroelectrochemistry was carried out for single-walled carbon nanotubes (SWNTs) having nine different chiral indices and their oxidation potentials have been determined based on the analysis using the Nernst equation.

Electronic structures of carbon nanotubes (CNTs), one of the most fundamental features of nanotubes, strongly depend on the chirality of the nanotubes.[1] Spectroelectrochemistry of CNTs is a powerful technique for investigating the potential-controlled electronic structures of the nanotubes and many spectroelectrochemical studies have been carried out using bundled CNTs as materials.[2] However, no report has been published describing a strategy for the direct determination of the redox potentials of isolated SWNTs. In this study, we report a simple method for determining the redox potential of many different SWNTs having varying chiral indices (here denoted (n, m)).

We previously reported that a totally aromatic polyimide (PI, Scheme 1) bearing disulfonic acid moieties individually dissolves SWNTs.[3] In this study, we have conducted in situ near-IR photoluminescence (PL) spectroelectrochemistry for a film of the SWNTs/PI on a tin oxide-coated transparent glass electrode (SnO_2) (for detailed experimental procedures, see Supporting Information; SI)[4] and have discovered that we can readily determine the redox potentials of the isolated SWNTs with chiral indices.

Applied potentials were changed in the range of 0.0–1.2 V vs. Ag|AgCl (sat'd KCl) because in this potential range, PI is electroinactive. The open-circuit potential (OCP) of the modified electrode was around 0.0 V, which is almost identical with the OCP value[2c] reported earlier; although in this work the SWNTs are neutral (denoted $SWNT^0$). The potential was applied to the electrode from 0.0 to 1.2 V to obtain oxidized SWNTs (denoted $SWNTs^+$).

Individually dissolved SWNTs in a surfactant solution exhibit PL in the near-IR region,[5] and the chiralities of the SWNTs can be determined by two-dimensional (2D) PL mapping. From the 2D-PL mapping,[4] we recognize the existence of individual SWNTs having chiral indices of (6,5), (7,5), (8,4), (7,6), (9,4), (8,6), (9,5), (8,7), and (9,7)-SWNT in the film on the electrode



Scheme 1. Chemical structure of PI.

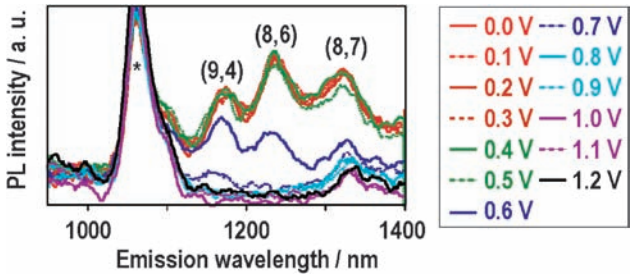


Figure 1. Applied potential dependence of the PL spectra (excitation: 740 nm) of the film containing isolated SWNTs on an SnO_2 electrode. The PL spectra shown by asterisk (*) are originated from the used SnO_2 substrate.

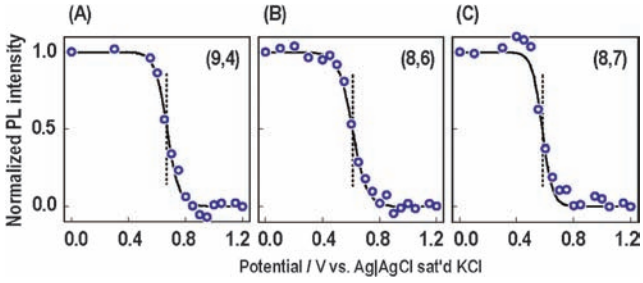


Figure 2. Normalized PL intensity (excitation: 740 nm) of the isolated SWNTs film on an SnO_2 electrode as a function of applied potential and curve fitting using nonlinear regression with the Nernst equation (solid lines) for the PL change. Figures A, B, and C represent the PL responses from (9,4), (9,6), and (8,7)-SWNTs, respectively; their emission wavelengths appear at 1170, 1335, and 1320 nm, respectively.

(see SI, Figure S1).[4] Figure 1 shows the PL spectra excited at 740 nm having chiral indices of (9,4), (8,6), and (8,7)-SWNT at given applied potentials (for the other (n, m)-SWNTs, see Figure S2).[4] It is evident that the PL shows a strong applied potential dependence. The peaks shown by the asterisk mark (*) are derived from the PL of the electrode substrate.

Figure 2 shows the plots of the normalized PL intensity of (9,4), (8,6), and (8,7)-SWNT as a function of the stepped applied potentials (for the other (n, m)-SWNTs, see Figure S3).[4] For the data shown in Figure 2, the normalized PL intensity values were fitted by using nonlinear regression with the following Nernst equation,

$$x = \frac{1}{1 + \frac{nF}{RT}[(E - E^{0\prime}_{ox})]} \quad (1)$$

Table 1. Electrochemical parameters for nine different isolated SWNTs

(n,m)	Diameter/nm	Band gap[a] /eV	$E_{ox}^{0'}$/V	$E_{red}^{0'}$ [b]/V	E_F[c]/V
(6,5)	0.757	1.272	1.06	−0.21	0.42
(7,5)	0.829	1.212	1.01	−0.20	0.40
(8,4)	0.840	1.114	0.90	−0.21	0.34
(7,6)	0.895	1.105	0.90	−0.21	0.35
(9,4)	0.916	1.126	0.87	−0.26	0.31
(8,6)	0.966	1.058	0.81	−0.25	0.28
(9,5)	0.976	0.997	0.77	−0.23	0.27
(8,7)	1.032	0.979	0.78	−0.20	0.29
(9,7)	1.103	0.937	0.76	−0.18	0.29

[a]Ref. 6. [b]$E_{red}^{0'} = E_{ox}^{0'} -$ band gap. [c]$E_F = (E_{ox}^{0'} + E_{red}^{0'})/2$. The potentials are presented referring to SHE (V vs. SHE).

where x is the ratio of $SWNT^0$ ($x = SWNT^0/(SWNT^0 + SWNT^+)$), F is the Faraday constant, n is the number of electrons transferred during the reaction, R is the gas constant, T is the absolute temperature (298.15 K), $E_{ox}^{0'}$ is the formal potential of $SWNT^+/SWNT^0$, and E is the applied electrode potential. By analysis using eq 1, the obtained correlation coefficients (R^2-values) were 0.951–0.996, indicating that the experimental data are in good agreement with the analysis using the Nernst equation. The plots of x show inflection points from which we can easily determine the formal potential ($E_{ox}^{0'}$) to be: 0.86, 0.81, 0.70, 0.70, 0.61, 0.58, 0.67, 057, and 0.56 V vs. Ag|AgCl (sat'd KCl) for the SWNTs with chiral indices of (6,5), (7,5), (7,6), (8,4), (8,6), (8,7), (9,4), (9,5), and (9,7)-SWNT, respectively. Note that the analysis with Nernst equation is applicable to the direct determination of the oxidation potentials of isolated SWNTs.

We used the band gap values provided by Weisman and Bachilo[6] to estimate semiquantitative reduction potentials ($E_{red}^{0'}$) of the isolated SWNTs because the excitonic energies of (n,m)-SWNTs is still complex[7–9] and are unable to incorporate in this study. In Table 1 and Figure 3, we show the electrochemical parameters including Fermi levels (E_F) of nine different isolated SWNTs.

The obtained slope of chirality-dependence of the $E_{red}^{0'}$, $E_{ox}^{0'}$, and E_F on the diameter of SWNTs is much less steep compared to those reported in the previous works. Both Murakoshi et al.[2d] and O'Connell et al.[10] evaluated the Fermi levels using the SWNTs whose diameters are larger than 1.07 nm. On the contrary, the diameters of the SWNTs in this study are smaller than 1.1 nm. It is therefore strongly suggested that the difference in diameter dependence of the electronic states of SWNTs between our results and theirs is due to the difference in the diameter range of the SWNTs.

In conclusion, we have described a method of determining the redox potentials of nine different isolated SWNTs having their own chiral indices by regression analysis using the Nernst equation of the in situ PL spectroelectrochemical data of the isolated nanotubes in a film. The present method is very simple and the determination of redox potentials of many isolated SWNTs is easy when the PL detection of their nanotubes is possible. It is known that surface microenvironments around SWNTs affects the PL of isolated SWNTs.[11] Detailed such microenvironment effects are under investigation and results will be reported in a subsequent paper.

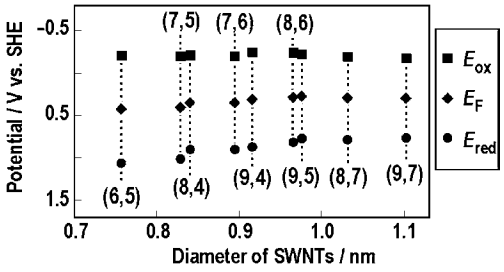


Figure 3. Oxidation (circles), reduction (squares), and Fermi (diamonds) potentials of nine isolated SWNTs are plotted as a function of SWNT diameters.

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