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Strong Micro-Dielectric Environment Effect on the Band Gaps of (*n*,*m*)Single-Walled Carbon Nanotubes

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Abstract: The electronic states of carbon nanotubes are one of the most fundamental properties of the nanotubes. We now describe the finding that the band gaps of (*n*,*m*)SWNTs are strongly affected by the change in microdielectric environments around the isolated nanotubes. In situ photoluminescence (PL) spectroelectrochemistry of the films containing 15 isolated (*n*,*m*)single-walled carbon nanotubes (SWNTs) cast on ITO electrodes in organic solvents including DMSO, acetonitirile, DMF, THF, and chloroform was completed and then the oxidation and reduction potentials, and band gaps ($\Delta E_{\mathrm{electr}}$) of the (*n*,*m*)SWNTs in the solvents were determined. We have discovered that the $\Delta E_{\mathrm{electr}}$ of the (*n*,*m*)SWNTs become greater as the solvent dielectric constants decreased, which is in sharp contrast to the optical band gaps (ΔE_{opt}) that show virtually no solvent dependence. Such a strong solvent dependence of the electrochemical band gaps is due to the difference in the solvation energy of the charged SWNTs produced during the electrochemical processes. The $\Delta E_{\mathrm{electr}}$ of both mod types of the SWNTs, mod = 1 and mod = 2, linearly increased versus the reciprocal of the tube diameter, which agrees with the theory. Moreover, the states of the π-electrons in the SWNTs were evaluated from the dependence of the band gaps on the diameter of the SWNTs. Furthermore, the states of the π-electrons on the sidewalls of the SWNTs were evaluated using the γ_0 values, a parameter representing the measure of the stability or the degree of delocalization of π-electrons in the sidewall of the SWNTs, and revealed that the γ_0 values of the mod = 1 and mod = 2 SWNTs increased with a decrease in the dielectric constants of the solvents in the range of 38−79. This study has enabled us to understand the essential electronic properties of the carbon nanotubes.

Introduction

Single-walled carbon nanotubes (SWNTs) consist of graphene sheets rolled into a cylindrical shape and are emerging as materials with significant potentials in several fields, including electronics, biology, and analytical chemistry.[1−5] The structures of the SWNTs are identified by a “chiral index” that specifies a certain diameter and chiral angle. The chiral index (*n*,*m*) is a dominant factor in determining the electronic properties of the SWNTs (i.e., electronic structure, Fermi levels, band gaps, and redox potentials).[6] Photoluminescence (PL) spectroscopy is used to determine the optical band gaps of the semiconducting SWNTs.[7] The chiralities of the SWNTs can be identified using this method. Perturbation of the electronic states of the SWNTs can also be detected by PL.[8−12]

SWNTs are synthesized as bundles containing many different chiralities. Bundles of SWNTs do not exhibit PL due to the presence of metallic SWNTs. The individually isolated states of semiconducting SWNTs are required to detect PL spectra.

Several groups have investigated the environmental effects on the optical properties of SWNTs.[13−18] Dresselhaus et al. evaluated the effects of bundling,[19] contact with substrates,[20]

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and DNA wrapping[21] on the Raman scattering spectra of the SWNTs. Ohno et al. investigated the optical band gaps of the SWNTs in air and organic solvents with dielectric constants ($\varepsilon_{\mathrm{env}}$) ranging from 1.9 to 37 based on the PL spectra.[22] In their report, the optical band gaps decreased by about 0.04 eV when $\varepsilon_{\mathrm{env}}$ was changed from 1 (in air) to about 5 (in chloroform). When $\varepsilon_{\mathrm{env}}$ was greater than 5, the band gap was not sensitive to $\varepsilon_{\mathrm{env}}$, indicating that the optical band gaps of the solvated SWNTs in polar solvents are almost independent of $\varepsilon_{\mathrm{env}}$.

In the field of electronic properties of carbon nanotubes, many attempts have been made to determine the electronic potentials of SWNTs using redox titrimetry,[23] PL measurements,[24−26] and spectroelectrochemistry;[27−32] however, the level of success in the determination of the redox properties has been low as already reported. We have previously reported a PL spectroelectrochemical method in order to determine the redox potentials of individual (*n*,*m*)SWNTs.[33] In the redox reactions, electrons are withdrawn/donated from/to the SWNTs. Thus, changes in solvation before and after the redox reactions, including the counterions and solubilizer, should be crucial factors affecting the redox processes. Therefore, it is very important to elucidate how individual (*n*,*m*)SWNTs are affected by the surrounding environment. In this study, we determined the redox potentials of the isolated (*n*,*m*)SWNTs on the electrodes in six different solvents including water, dimethylsulfoxide (DMSO), acetonitrile, *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), and chloroform by the PL spectroelectrochemistry and discovered that the obtained band gaps of the isolated (*n*,*m*)SWNTs exhibit a strong dependence on the dielectric constants of the solvents. Moreover, the states of the π-electrons in the SWNTs in the solvents were evaluated from the dependence of the band gaps on the diameter of the SWNTs.

Experimental Section

Materials. The as-produced SWNTs (so-called HiPco), carboxymethylcellulose sodium salt (Na-CMC; for chemical structure, see Supporting Information, Figure S1a), and poly(diallyldimethylammonium chloride) (PDDA, Figure S1b) aqueous solution were purchased from Unidym, Inc., Kishida Chemical, Aldrich, respectively, and were used as received. All other chemicals were of reagent grade and used as received. Sodium perchlorate, acetonitrile, and THF were purchased from Kishida Chemical; tetrabutylammonium perchlorate was from Strem Chemicals; DMSO and DMF were from Wako; and chloroform was from Aldrich. The water was purified using a Milli-Q Plus Ultrapure water system coupled with an Elix-5 kit (Millipore Co.).

Fabrication of a Modified Electrode. The SWNTs were individually solubilized in an aqueous solution of Na-CMC. The SWNTs (0.3 mg) were added to an aqueous solution (8 mL) of Na-CMC (0.1 wt %), and the mixture was sonicated (ultrasonic cleaner, Branson 5510) for 1 h, followed by ultracentrifugation at 150 000 *g* for 5 h.

A 100 μL aliquot of the supernatant was placed on a cleaned indium tin oxide coated transparent quartz glass electrode (ITO) and then heated at ca. 100 °C to obtain an SWNTs/Na-CMC film modified electrode. A 100 μL portion of an aqueous solution of PDDA (20 wt %) was then placed on the film and then rinsed with water to remove the excess PDDA to obtain an SWNTs/Na-CMC/PDDA-modified electrode. In addition, the electrode was dried under vacuum overnight. The durability of the film containing isolated SWNTs on the electrode during spectroelectrochemical experiments was also highly important; this is achieved by the polyion complexation[34] between Na-CMC and PDDA. In situ PL spectroelectrochemistry was carried out using the obtained modified electrode as the working electrode.

In Situ Photoluminescence (PL) Spectroelectrochemistry: Analysis Using Nernst Equation and Determination of Electrochemical Band Gap. In situ PL spectroelectrochemical measurements were carried out in six different solvents including water, DMSO, acetonitrile, DMF, THF, and chloroform, whose $\varepsilon_{\mathrm{env}}$ values are 78.40, 46.68, 37.50, 36.71, 7.58, and 4.81, respectively.[35] The oxidation and reduction potentials of the 15 chiralities of SWNTs were then determined based on the Nernst analysis for the potential dependent PL spectra, and the electrochemical band gaps ($\Delta E_{\mathrm{electr}}$) were also determined.[33] The electrolyte was 0.3 M $NaClO_4$ except for chloroform. For chloroform, 0.3 M tetrabutylammonium perchlorate was used as the electrolyte. All the electrochemical measurements were conducted in a three-electrode system using a Ag/AgCl (saturated KCl) reference electrode in water (a Ag^+/Ag reference electrode in organic solvents), a coiled Pt wire counter electrode, and the modified ITO working electrode under an Ar gas atmosphere. In organic solvents, the potentials of the reference electrode were calibrated after adding a small amount of ferrocene to the electrolyte solutions after the spectroelectrochemical measurements. In situ PL spectroelectrochemistry was carried out using a spectrofluorometer (HORIBA JOBIN YVON, FL3-21) equipped with a potentiostat (TOHO Technical Research Co., PS-06). The SWNTs/Na-CMC/PDDA-modified ITO electrode was vertically inserted in a quartz cell having a light path length of 10 mm. The

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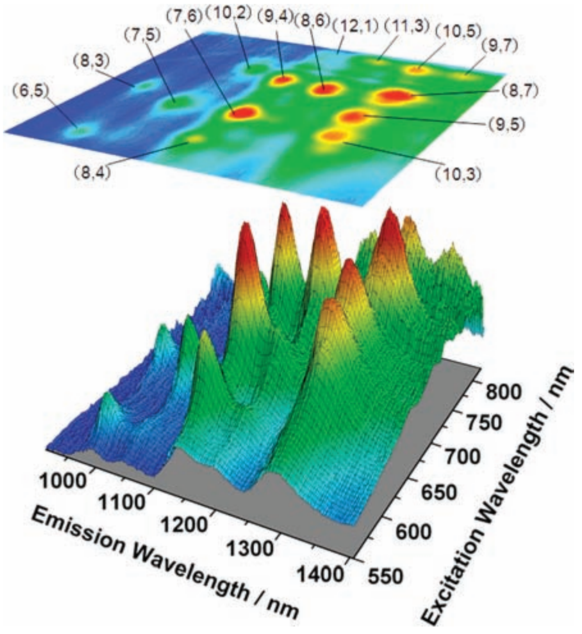

Figure 1. 2D and surface plots of the PL of the film containing isolated (*n*,*m*)SWNTs in DMF containing 0.3 M sodium perchlorate as the electrolyte.

cell was filled with the electrolyte solution, in which the reference and counter electrodes were placed so as not to interfere with the light path.

Results and Discussion

We can detect 15 PL spots from the films containing the SWNTs on the ITO electrodes. As a typical example, the 2D and surface plots of the PL in DMF containing the electrolyte are shown in Figure 1. Similar results were obtained for the other five solvents including water containing sodium perchlorate. We have previously described the PL behavior in water containing 0.3 M NaCl of the modified electrode prepared in a similar way. In both electrolytes, the PL behaviors were virtually identical. In each solvent, the potential was applied to the electrode modified with the isolated (*n*,*m*)SWNT films in arbitrary steps, and after each potential step, the applied potential was returned to the initial potential (for details, see Supporting Information, Figures S2−S25). In all solvents, the modified films on the ITO were stable during the spectroelectrochemistry. For the analysis of the potential-dependent PL responses in the six solvent systems, the ΔPL values of the 15 isolated SWNTs were plotted as a function of the applied potentials and fitted using a nonlinear regression with the Nernst eqs 1 and 2 as we previously described,[33]

$$\Delta\mathrm{PL}_{\mathrm{red}} = \frac{1}{1 + \exp\left[\dfrac{nF}{RT}(E^{0\prime}_{\mathrm{red}} - E)\right]} \tag{1}$$

$$\Delta\mathrm{PL}_{\mathrm{ox}} = \frac{1}{1 + \exp\left[\dfrac{nF}{RT}(E - E^{0\prime}_{\mathrm{ox}})\right]} \tag{2}$$

where SWNTs^{n-} and SWNTs^{n+} denote the reduced SWNTs and oxidized SWNTs in the film and ΔPL_{red} and ΔPL_{ox} represent the fractional content of the neutral SWNTs (denoted as SWNTs^0) in the film on the reduction and oxidation processes; namely, ΔPL_{red} and ΔPL_{ox} represent SWNTs^0/(SWNTs^0 + SWNTs^{n-}) and SWNTs^0/(SWNTs^0 + SWNTs^{n+}), respectively, F is the Faraday constant, R is the gas constant, T is the absolute temperature (298.15 K), $E^{\circ\prime}_{\mathrm{red}}$ and $E^{\circ\prime}_{\mathrm{ox}}$ are the formal potentials, and E is the potential of the working electrode with respect to the reference electrode. From the fitted Nernst analysis curves, we can determine the reduction and oxidation potentials of the SWNTs in the six solvents. We then determined $\Delta E_{\mathrm{electr}}$ as the energy gap between the reduction and oxidation potentials in each solvent. The result obtained in the water (electrolyte: sodium perchlorate) system was virtually identical to the previously obtained result in water (electrolyte: sodium chloride), indicating no electrolyte dependence in these systems (for details, see Supporting Information, Figure S26).

It was found that the PL responses of the modified electrodes in both the reduction and oxidation processes can be well fitted by the Nernst equation similar to the film in water using NaCl as the electrolyte as we previously reported in ref 33. As an example, the change in the PL spectra at the 650-nm excitation in acetonitrile is shown in Figure 2. The responses of the (7,5), (7,6), (10,3)SWNTs were detected. The plots of ΔPL showed inflection points from which we can easily determine the formal potentials of the (7,5), (7,6), (10,3)SWNTs for the reduction process ($E^{\circ\prime}_{\mathrm{red}}$), −0.86, −0.78, −0.69 V versus Fc$^+$/Fc, and for the oxidation process ($E^{\circ\prime}_{\mathrm{ox}}$), 0.24, 0.19, 0.13 V versus Fc$^+$/Fc, respectively. The $\Delta E_{\mathrm{electr}}$ values were then determined as the energy gap between the reduction and oxidation potentials; $\Delta E_{\mathrm{electr}}$ of the (7,5), (7,6), (10,3)SWNTs in acetonitrile are 1.10, 0.97, 0.82 eV, respectively (for all the Nernst analysis results and the electrochemical data, see Supporting Information, Figures S2−S25 and Tables S1−S6).

Figure 3 shows the plots of the optical band gaps (ΔE_{opt}) of the 15 isolated (*n*,*m*)SWNTs in the six solvent systems that were calculated from the wavelengths of the PL peak maxima of the SWNTs, in which we observed almost no solvent dependence of ΔE_{opt}; namely, the ΔE_{opt} values were <0.01 eV. This result agrees well with that reported by Ohno et al.[12] In Figure 4a and b, we show the solvent dependence of the electrochemical band gaps, $\Delta E_{\mathrm{electr}}$, together with the averaged ΔE_{opt} (in the six solvents) as a function of the tube diameters for the modified films on the ITO electrodes in the six different solvents, in which $\Delta E_{\mathrm{electr}}$ is defined as the difference between the oxidation and reduction potentials of the SWNTs (see ref 33 for details). From the figure, we see a strong solvent dependence of $\Delta E_{\mathrm{electr}}$, which is in sharp contrast to that of the ΔE_{opt} that exhibits almost no solvent dependence as shown in Figure 3. From Figure 4a and b, the intensity of the band gaps of the 15 (*n*,*m*)SWNTs are in the following order: the averaged ΔE_{opt} (open squares) > $\Delta E_{\mathrm{electr}}$ in chloroform > $\Delta E_{\mathrm{electr}}$ in THF ≈ $\Delta E_{\mathrm{electr}}$ in DMF > $\Delta E_{\mathrm{electr}}$ in acetonitrile > $\Delta E_{\mathrm{electr}}$ in DMSO > $\Delta E_{\mathrm{electr}}$ in water. The results strongly suggest that the solvation energies for the reduced and oxidized (*n*,*m*)SWNTs are in the following order: water > DMSO > acetonitrile > DMF > THF > chloroform. Interestingly, this tendency strictly reflects the dielectric constants of the solvents.

The difference between the $\Delta E_{\mathrm{electr}}$ and ΔE_{opt} in water was ∼0.20 eV and almost independent of the chiralities of the (*n*,*m*)SWNTs, indicating that all of the chiralities of the (*n*,*m*)SWNTs are similarly solvated in water during the redox reactions. In contrast, in organic solvents, the $\Delta E_{\mathrm{electr}}$ values of the SWNTs became greater as the $\varepsilon_{\mathrm{env}}$ decreased (Figure 4a and b). The intensities of the $\Delta E_{\mathrm{electr}}$ of the SWNTs with smaller diameters are greater than those of the SWNTs with larger

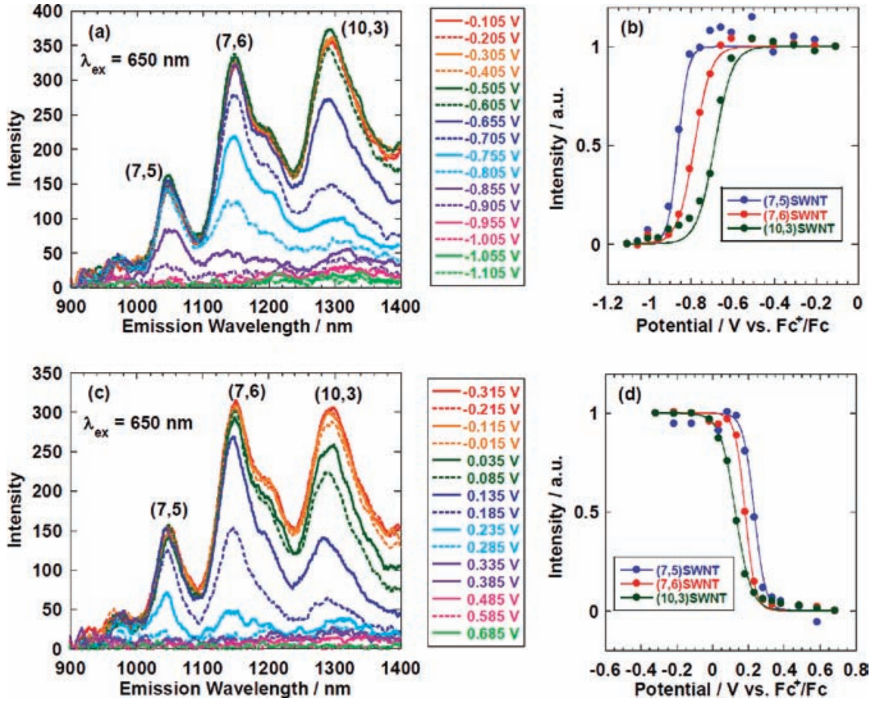

Figure 2. Applied potential dependence of the PL spectra of the film containing isolated SWNTs on an ITO electrode in acetonitrile (a, c) and normalized PL intensities of the (7,5), (7,6), (10,3)SWNTs (b, d). The potential was applied to the electrode by an arbitrary step from −0.105 to −1.105 V vs Fc^+/Fc (a) and from −0.315 to 0.685 V vs Fc^+/Fc (c). The excitation wavelength is 650 nm. The normalized PL intensities of the (7,5), (7,6), (10,3)SWNTs in the reduction process (b) and oxidation process (d) are plotted as a function of the applied potential. The potentials of the reference electrode were calibrated after adding a small amount of ferrocene to the electrolyte solution at the end of each spectroelectrochemical measurement.

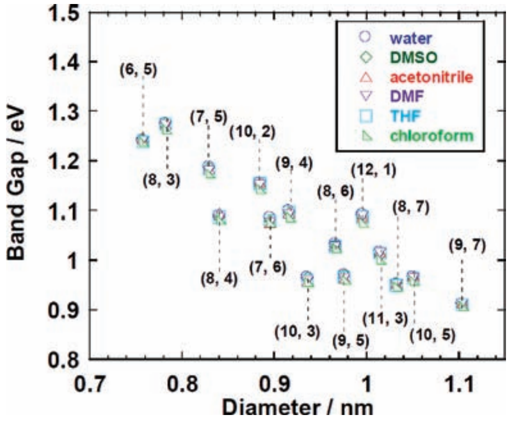

Figure 3. Optical band gaps (ΔE_{opt}) of the 15 isolated (*n*,*m*)SWNTs in the six solvent systems calculated from the wavelengths of the PL peak maxima of the SWNTs.

diameters, indicating that the solvation energy shows nanotube chirality dependence.

In order to clarify the dependence of the band gap energy on the ε_{env}, each band gap was normalized between the ΔE_{electr} in water and the averaged ΔE_{opt} (Figure 4c). Because the solvation of the SWNTs in water is independent of the chirality of the SWNTs, this plot indicates the degree of the solvation of each chirality of the SWNTs in different organic solvents. In chloroform and THF, the tube diameter dependence of the normalized band gaps was smaller than that in acetonitrile (red squares). This tendency is shown by a solid red line as well as dotted pink and light blue lines in Figure 4c. The results indicate that, in acetonitrile, the solvation energy of the charged SWNTs with large diameters is larger than those of the SWNTs with smaller diameters. Based on this dependence, a large normalized band gap difference observed for the larger-diameter SWNTs is decreased as the tube diameter decreases, and for the (6,5)SWNTs, their band gaps are virtually identical.

One of the more interesting features that we have obtained is the electronic behavior in chloroform whose dielectric constant is the lowest among the solvents used in this study, namely, as can be seen in Figure 4a, b, and c; the ΔE_{electr} in this solvent is the highest among the solvents, and the values are close or virtually identical to the ΔE_{opt}, which is due to the low solvation of the charged (*n*,*m*)SWNTs in the solvent.

The changes in the band gaps would be related to the states of the π-electrons in the SWNTs depending on the environmental conditions. According to the $\mathbf{k}\cdot\mathbf{p}$ theory[36] and the tight-binding method,[37,38] the band gap E_g of the semiconducting SWNTs is predicted to be inversely proportional to the tube diameter d based on the equation $E_g = 2a_{c\text{-}c}\gamma_0/d$, where $a_{c\text{-}c}$ and γ_0 are the nearest-neighbor carbon−carbon distance and the π-orbital transfer integral between the adjacent carbon sites, respectively. The 1/*d* dependence of the electrochemical band gaps was then investigated. Figure 5 shows the band gap energies (ΔE_{electr}) in the six solvents plotted as a function of 1/*d*. In all the solvents, the plots were fitted by two lines depending on the mod types, mod ($n-m$, 3) = 1 or 2.[39−41] Interestingly, the fitting results using the two lines are quite consistent with the theoretical model.[37,38] Thus, it is clear that

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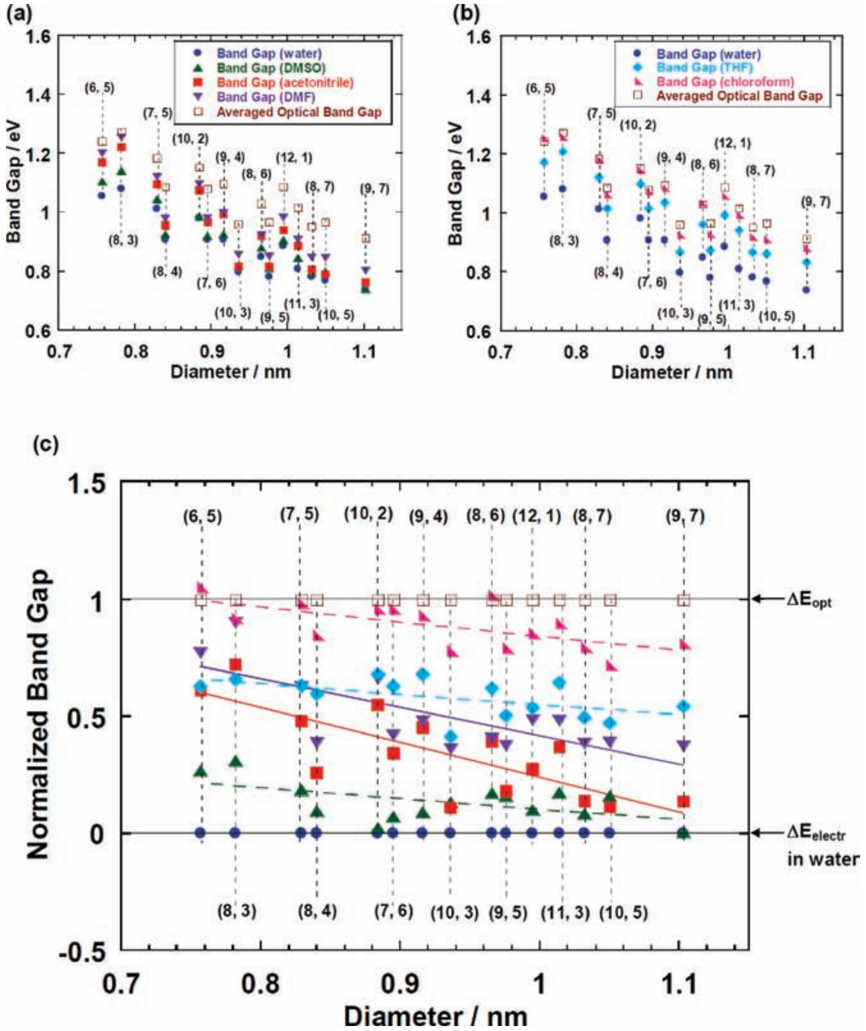

Figure 4. (a and b) Electrochemical band gaps for the 15 chiralities of the SWNTs in water (blue circles), DMSO (green triangles), acetonitrile (red squares), and DMF (purple inverted triangles) as well as the averaged optical band gaps in the six solvents (open squares) (a) and the electrochemical band gaps of the SWNTs in water (blue circles), THF (light blue diamonds), and chloroform (pink triangles) as well as the averaged optical band gaps in the six solvents (open squares) (b). (c) Normalized electrochemical band gaps for the data shown in plots a and b, assuming the energy gap between the optical band gaps and electrochemical band gaps in water is 1.

the electrochemical band gap is an inherent property of the conjugated π-electrons of the SWNTs.

In the above analysis, $a_{\text{c-c}}$ can be assumed to be constant ($a_{\text{c-c}} = 0.144$ nm) since the Raman scattering spectroscopy indicated that the radial breathing mode (RBM) of the SWNTs was independent in the solvents used in this study (see Supporting Information, Figure S27). The RBMs are the vibration modes in the radial direction of the SWNTs. The C−C bonds forming the skeleton of an SWNT are rigid and insensitive to the solvents. Therefore, the slopes of the fitting lines allow the magnitudes of γ_0 for every SWNT to be simply elucidated. The parameter γ_0 is a measure of the stability or the degree of delocalization of π-electrons in the sidewall of the SWNTs. As shown in Figure 5, γ_0 showed a solvent dependence. This means that the states of the π-electrons are sensitive to the properties of the solvents. In Figure 6, γ_0 in each solvent is plotted versus the dielectric constants of the solvents, and it was found that the highest γ_0 value was obtained in acetonitrile, while the values of γ_0 in THF and chloroform are similar to that in DMSO. It was revealed that in the solvents with $\varepsilon_{\text{env}} = 35-80$, the γ_0 values became greater as the ε_{env} values decreased. However, in THF and chloroform, no such dependence was observed. This would be due to their lower solvation energies for the charged nanotubes; namely the relationship between the γ_0 values and dielectric constants of the solvents somewhat differs in polar and the nonpolar solvents.

Conclusions

In this study, we have investigated the solvent dependence of the electronic states of the isolated (n,m)SWNTs using the PL spectroelectrochemistry as well as the Nernst analysis for the results and discovered that the ΔE_{electr} of the (n,m)SWNTs exhibited a strong effect by the dielectric constants of the solvents, which is in sharp contrast to that of the ΔE_{opt} that shows no solvent dependence. Interesting features obtained are as follows: (i) for all the (n,m)SWNTs, the ΔE_{electr} values were the lowest in the aqueous system, in which we see virtually no SWNT chirality (tube diameter) dependence; in contrast, a high SWNT chirality dependence was observed in the organic solvents, and (ii) the ΔE_{electr} became greater as the dielectric constants of the solvents become smaller due to the smaller solvation for the tubes. Furthermore, the states of the π-electrons on the sidewalls of the SWNTs were evaluated using the values of γ_0, and the relation between the γ_0 and the band gaps of the (n,m)SWNTs was discussed. The present study provides useful information for a deep understanding of the fundamental

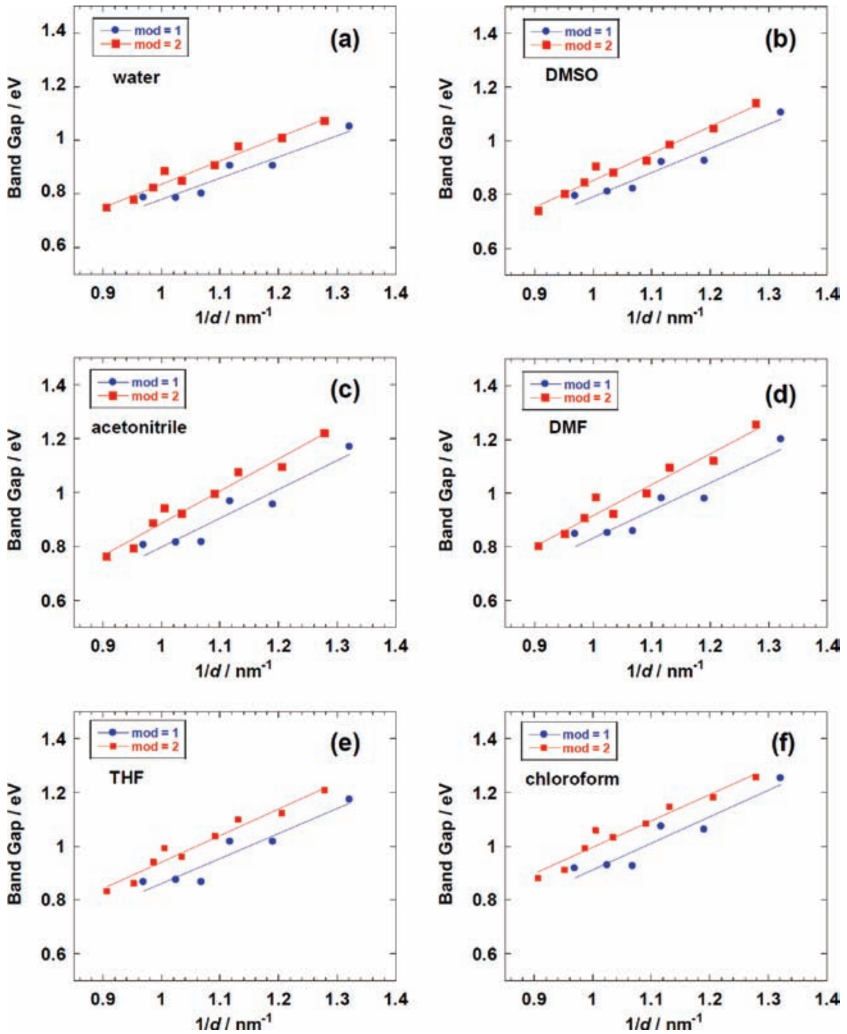

Figure 5. Dependence of the electrochemical band gaps of the (*n*,*m*)SWNTs (mod = 1 and mod = 2) as a function of 1/*d* in water (a), DMSO (b), acetonitrile (c), DMF (d), THF (e), and chloroform (f).

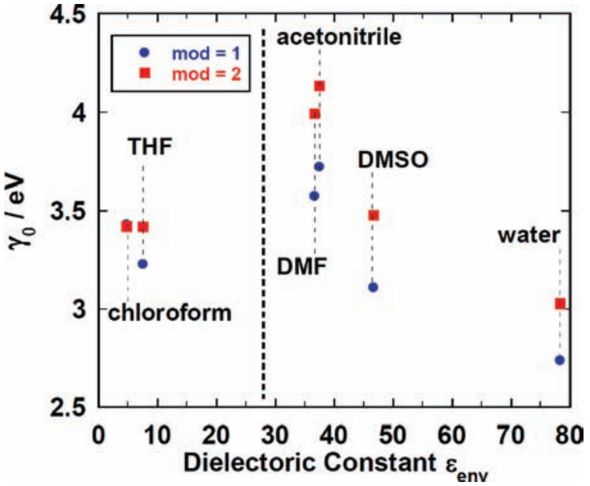

Figure 6. Dependence of the π-orbital transfer integral between adjacent carbon sites (γ_0) for the (*n*,*m*)SWNTs with mod = 1 and mod = 2 as a function of the dielectric constant of the solvent.

electronic properties of isolated (*n*,*m*)SWNTs in solvents. Future work includes a similar study using individually dissolved SWNTs in solution as well as a study of how the functional groups in solvent molecules and physically adsorbed molecules on the tubes affect the electrochemical band gaps of the (*n*,*m*)SWNTs.

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Supporting Information Available: Complete ref 21; numerical data of the reduction/oxidation potentials and electrochemical band gaps of the 15 (n,m)SWNTs in water (electrolyte: sodium perchlorate), DMSO, acetonitrile, DMF, THF, and chloroform; chemical structures of CMC and PDDA; applied potential dependence of the PL of the isolated (*n*,*m*)SWNTs on ITO electrodes in the six solvents as well as the normalized PL intensities of the SWNT films on ITO as a function of applied potential in the six solvents; plots of the redox states and Fermi levels of the (*n*,*m*)SWNTs in these solvents; Raman spectra (RMB region) of the SWNT films. This material is available free of charge via the Internet at http://pubs.acs.org.

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