

Optical absorption spectroscopy for determining carbon nanotube concentration in solution

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Abstract

A simple method of determining concentration of carbon nanotubes in solution was provided by using optical absorption spectroscopy. The extinction coefficient of single-walled carbon nanotubes in Beer's law was determined after subtraction of the plasmon background. We found that the extinction coefficient was strongly dependent on the wavelength in the resonant region, whereas this was independent of wavelength in the non-resonant region after plasmon subtraction. This work demonstrates that the concentration of unknown carbon nanotubes dispersed in aqueous solution can be easily determined by simply measuring absorbance, once the extinction coefficient of the material is determined in advance.

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1. Introduction

In numerous applications of carbon nanotubes (CNTs), dispersion of CNTs in various solvents is an important step to enhance the performance of carbon nanotubes or host materials in composites. This usually involves the sonication and centrifuge step. Information for nominal concentration of nanotubes at early stage is usually lost during centrifuge process, leaving difficulty for obtaining information for CNT concentration in the solution, which is usually necessary for quantitative analysis of the data. For instance, the percolation limit in the electrical conductivity and mechanical strength and some other threshold parameters vary widely [1–3]. Assessing the CNT concentration used in experiment is therefore a necessary step prior to further detailed analysis.

Optical absorption spectroscopy has been widely used for evaluating the purity of the sample [4–6]. The absorption inten-

sity is proportional to the amount of CNTs dissolved in the solution and furthermore, provides information for the resonant peaks originating from van Hove singularities at visible region [7]. Since these resonant peak positions are chirality- and diameter-dependent, this method has been also used to estimate the relative composition of metallic component to semiconducting one by comparing the intensity of metallic peaks with that of semiconducting ones [8]. Another difficulty in measuring the CNT concentration arises from the dispersants that are usually introduced during dispersion process, misleading the assessment of the CNT concentration in solvent.

The issue here is to use absorption spectroscopy to find out the concentration of CNTs in solution. For this purpose, we introduce the Beer's formula and try to extract the extinction coefficient for a given CNT solution. The measured extinction coefficient of the single-walled carbon nanotubes (SWCNTs) generated by arc discharge was $30.3 \pm 0.2 \text{ ml mg}^{-1} \text{ cm}^{-1}$ at wavelength of 1035.3 nm (same as 1.2 eV) in the resonant region. The plasmon effect was also taken account into the calculations. This underestimated the value of extinction coefficient by about 25%.

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2. Experimental

Highly purified SWCNTs synthesized by arc discharge were purchased from Iljin Nanotech Co. Ltd. The transition metal content remaining in the sample was less than 2 wt%. The SWCNT powder was dissolved in 100 ml of D₂O solution with 2 wt% of sodium dodecyl sulfate (SDS), which has been known as a good surfactant for SWCNTs in water [9]. D₂O was introduced to avoid unnecessary contributions from the optical absorption spectroscopy. Several SWCNT concentrations at high concentration limit (1, 5, 10 and 20 mg) were chosen for experiment for practical purpose. We emphasize that these CNT concentrations were relatively higher than those of the previous works [10–12]. The CNT solution was maintained at a pH of 10 in order to avoid the effect of acidic condition in absorption spectra of SDS-suspended nanotubes [9]. The CNT solution was sonicated in a horn type at 350 W for an hour. The CNTs were well macrodispersed in solution. The dispersion stability was ensured by measuring absorbance as described in the text. No centrifuge process was taken in this case in order to know the

nominal CNT concentration precisely. The absorption spectra (Cary-5000 UV–vis–NIR, Varian) were taken from this well-dispersed sample. The CNT solution was filled in 1 cm quartz cuvette. The path length for the light absorption was decremented by filling 0.1 cm of a slide glass in quartz cuvette. The reference was taken with 2 wt% of SDS in D₂O solution and the corresponding slide glass to avoid the effect of surfactants to CNT concentration.

3. Results and discussion

According to Beer–Lambert's law ($A = \log I_0/I = \epsilon C l$), the absorbance A is expressed in terms of extinction coefficient ϵ , the concentration of nanotubes C and the light path length l . In general, the absorbance is measured from absorption spectroscopy at a given wavelength. The path length l is fixed for a given optical cell in experiment. If the concentration of the CNT in solution is known in advance, the extinction coefficient can be obtained easily experimentally. This is not a simple task in practice because the nominal CNT concentration is usually

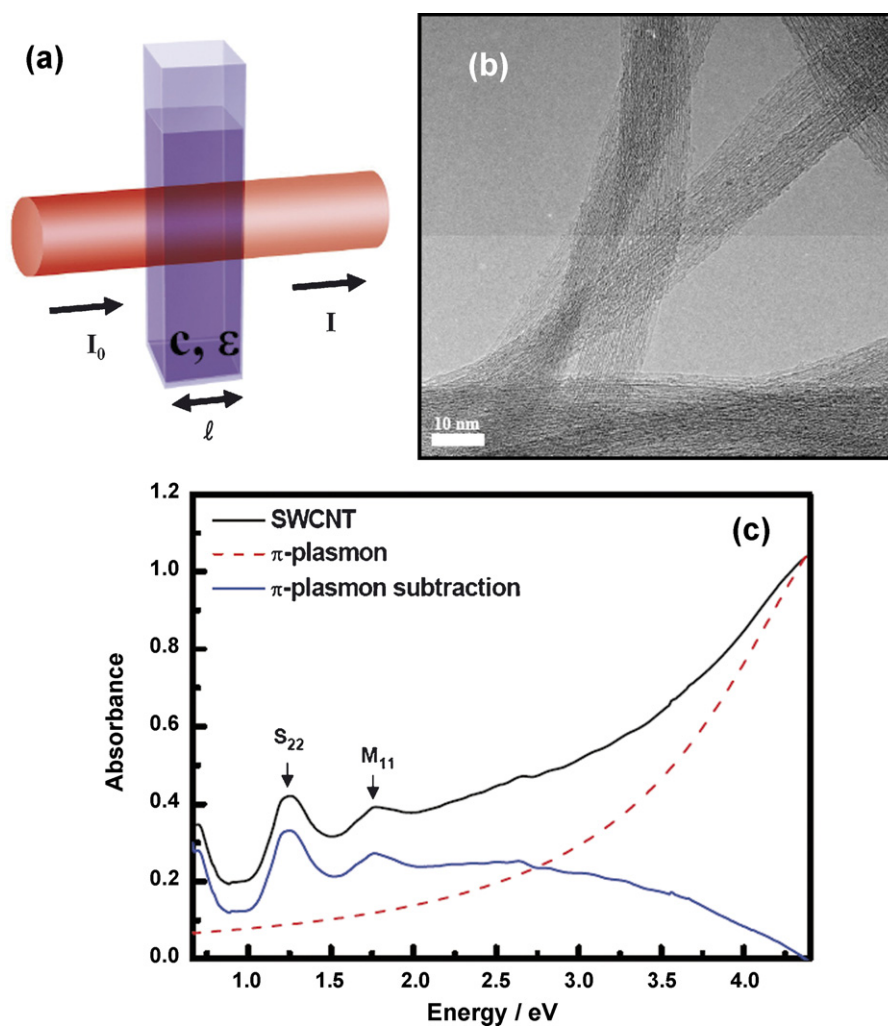


Fig. 1. (a) The schematic experimental setup of optical absorption spectroscopy, (b) the TEM image of pristine SWCNTs (scale bar: 10 nm) and (c) the absorption spectra of the SWCNT sample for 0.01 mg ml⁻¹. The dashed line depicts the contribution for π -plasmon and the bottom line is the absorption curve after subtraction of π -plasmon contribution.

lost during centrifuge. The strategy here is to prepare well-dispersed CNT solution so that no precipitates were observed during measurement time. The nominal value of the CNT concentration was then directly used to measure the extinction coefficient.

Fig. 1(a) presents the experimental schematic for optical absorption spectroscopy. The TEM image of the pristine CNT sample was shown in Fig. 1(b). The SWCNTs were usually bundled with an average bundle diameter of about 10–20 nm. After sonication with SDS in a horn-type sonicator, this bundle size became smaller with an average bundle size of less than 10 nm and the abundant individual SWCNTs were observed. These remained well dispersed in water. We presume here that the absorbance is determined by the total CNT concentration, not by the degree of macrodispersion, i.e., the bundle size, as long as they float around in the solution. Fig. 1(c) present the absorption spectroscopy of SWCNTs solution at a CNT concentration of 0.01 mg/ml. Clear two peaks near 1.8 and 1.2 eV were visible, which were known as van Hove singularity transitions for metallic M_{11} and semiconducting S_{22} SWCNTs, respectively [13]. High absorption with the peak positions near 4.53 and 4.93 eV at high-energy side originates from the π -plasmon absorption [14–16]. The dual peaks resulted from the randomly oriented CNTs in solution so as to observe two plasmon peaks parallel and perpendicular to the CNT axis [17]. The Lorentzian curve has been known as a solution of plasmon mode by using damped harmonic oscillator [10]. The dotted line indicates the contribution for the π -plasmon that is fitted by Lorentzian curve, $L(x) = a/[1 + \{(x - b)/c\}^2]$. In this equation, a is the peak amplitude, b the peak energy and c is a measure of the peak width. The Lorentzian curve was fitted by taking average of these two positions and simultaneously fitting the shoulder at low energy side. The bottom blue line in Fig. 1(c) is the absorption spectra after subtraction of π -plasmon contribution. Another possibility of using a simple linear subtraction was excluded due to the uncertainty of the specified linear region [10]. The path length was controlled by filling 0.1 cm of a slide glass in quartz cuvette. The initial absorbance was taken for D_2O with SDS 2 wt% and slide glass in quartz cuvette as a reference.

The dispersion stability was ensured by measuring absorption spectra in Fig. 2 [18]. The SWCNTs were dropped in the SDS dispersed in D_2O initially. All the SWCNTs were precipitated. With increasing the sonication time, the amount of precipitated SWCNTs was reduced, while the absorbance kept increasing. At about 20 min, the absorbance was gradually saturated but some of the precipitated SWCNTs were still visible with bare eyes. The absorbance was completely saturated at around 60 min with no appreciable precipitation for at least several hours. We therefore chose a minimum sonication time of 1 h to ensure no precipitation was observed during the rest of the measurements.

Fig. 3(a) presents the absorption spectra in terms of the path length without π -plasmon subtraction. The absorbance decreased linearly with increasing number of slide glasses (path length), following Beer's law. The absorbance was drawn as a function of path length at a resonant energy of 1.2 eV in Fig. 3(b). The attenuation coefficient α ($= \epsilon C$) was 0.41 ± 0.003

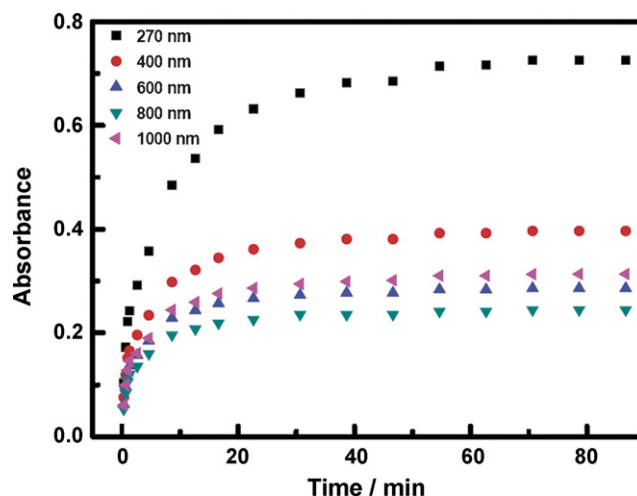


Fig. 2. Absorption spectra to check the dispersion stability as a function of sonication time at different wavelengths.

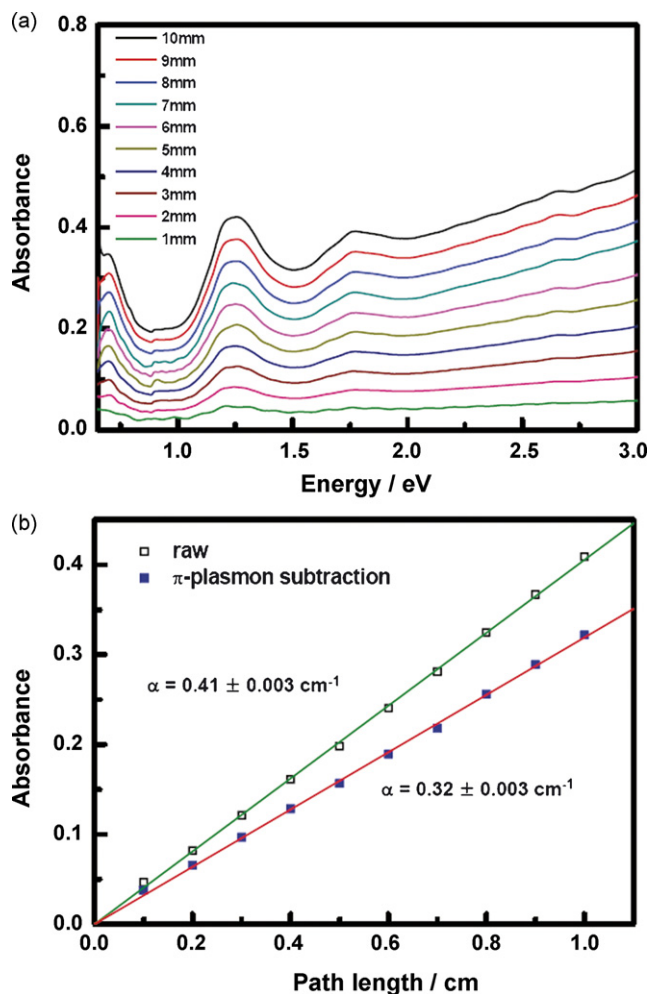


Fig. 3. (a) The absorption spectra in terms of the path length without π -plasmon subtraction. (b) Absorbance as a function of path length for the pristine sample and that after subtraction of π -plasmon contribution at a resonant energy of 1.2 eV. The straight lines are attenuation coefficient α ($= \epsilon C$) before (empty square) and after (filled square) π -plasmon subtraction.

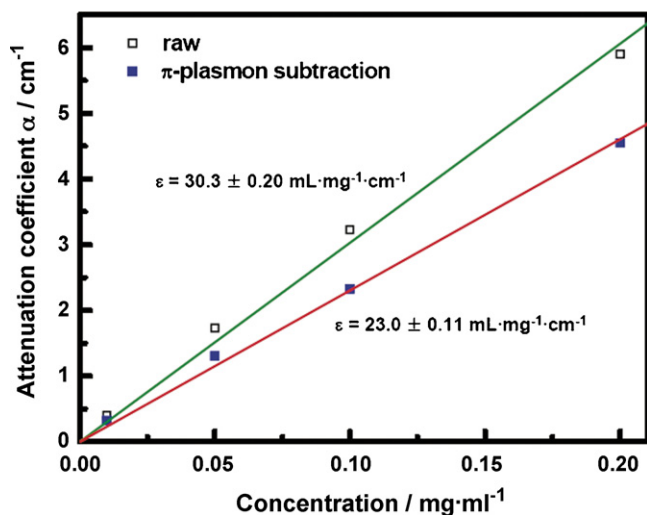


Fig. 4. Attenuation coefficient as a function of SWCNT concentration. The slope is the extinction coefficient ϵ before (empty square) and after (filled square) π -plasmon subtraction at 1.2 eV.

Table 1

The extinction coefficients for comparison

SWCNTs	Resonant region		Non-resonant region
	1.2 eV	1.8 eV	
This work	30.3 (23.0)	32.3 (21.4)	30–45 (18.9)
Landi et al. ^a	35.0	30.0	–

The values in parentheses are after π -plasmon subtraction.

^a Ref. [10].

and $0.32 \pm 0.003 \text{ cm}^{-1}$ before and after π -plasmon subtraction, respectively. This value is CNT concentration-dependent.

We repeated the measurement with different concentrations. Since we were interested in dispersing high CNT concentration for application purpose, the attenuation coefficient was obtained for high concentration, as shown in Fig. 4. The atten-

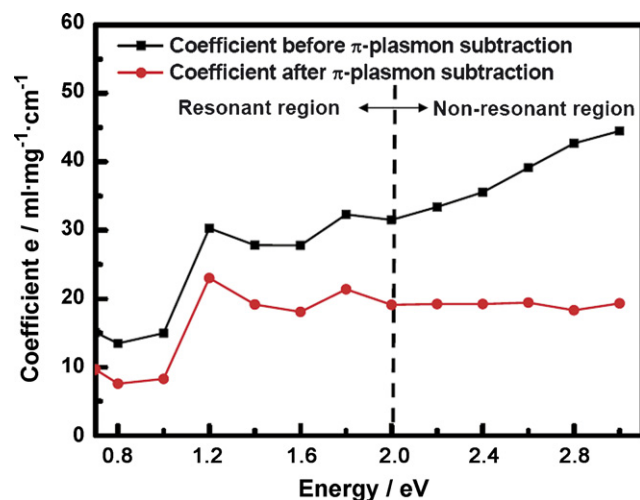


Fig. 5. The extinction coefficient ϵ as a function of light energy before and after π -plasmon subtraction.

uation coefficient revealed linear relationship with the CNT concentration. The extinction coefficient ϵ was obtained from the slope before (empty square) and after (filled square) π -plasmon subtraction. The extinction coefficient before π -plasmon subtraction was $30.3 \text{ ml mg}^{-1} \text{ cm}^{-1}$ at a resonant region (S_{22}) of 1.2 eV and $32.3 \text{ ml mg}^{-1} \text{ cm}^{-1}$ at a resonant region (M_{11}) of 1.8 eV. These values were comparable to the previously reported ones, as listed in Table 1 [10]. The values after π -plasmon subtraction were consistently smaller than those before subtraction. The extinction coefficient was decreased after π -plasmon subtraction.

The extinction coefficient can be wavelength-dependent. We therefore present the data for extinction coefficient as a function of energy in Fig. 5. The extinction coefficient revealed significant changes in the resonant region similar to the absorption strength, independent of the π -plasmon subtraction. On the other hand, the extinction coefficient was almost constant after π -plasmon subtraction.

4. Conclusions

We proposed a method of determining the CNT concentration dispersed in solution by optical spectroscopy with control of light path lengths. The extinction coefficient of CNTs in solution was obtained by measuring the absorbance in our test case. Hence the CNT concentration could be determined by simply measuring absorbance in practice. This method can be used to determine the CNT concentration in various solvents. The extinction coefficient before π -plasmon subtraction was $30.3 \text{ ml mg}^{-1} \text{ cm}^{-1}$ at 1.2 eV and $32.3 \text{ ml mg}^{-1} \text{ cm}^{-1}$ at 1.8 eV. One can use this value and predict the SWCNT concentration of unknown samples by simply measuring absorbance in optical absorption spectroscopy.

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