

Optical Spectroscopic Studies of Photochemically Oxidized Single-Walled Carbon Nanotubes

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Abstract

We examined the time-dependent changes in the optical properties of single-walled carbon nanotubes which were consecutively oxidized by irradiation with vacuum ultraviolet light. It is demonstrated that photochemical oxidation is a mild and controllable method for manipulating the surface of nanotubes in order to convert their affinity from hydrophobic to hydrophilic by controlling the density of functional groups on their sidewalls without destroying their tubular morphology.

Keywords: Single-walled carbon nanotubes, Photo-oxidation, Photoluminescence, Vacuum ultraviolet light

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1. Introduction

Single-walled carbon nanotubes (SWNTs), which are essentially one-atom thick graphene sheets rolled in the shape of a tube [1, 2], exhibit fascinating physicochemical properties which make them very promising for application in various fields [3, 4]. As a primary step for their use in fabricating innovative materials, composites, sensors, and electronic devices, SWNTs should be optimally decorated with hydrophilic functional groups in order to resolve the problem of their bundling nature and insolubility in aqueous mediums, as well as to enabling them to be manipulated in a controllable way. Therefore, various oxidative treatments for dispersing tubes in various media without disturbing their intrinsic sharp van Hove singularities have been examined. However, the utilization of strong oxidizing reactants (such as KMnO_4 , H_2SO_4 and HNO_3) severely damages the tubular morphology of the SWNTs [5-8]. In addition, this method entails significant environmental problems, such as the production of acid effluent, and requires many refining processes.

Within this background, a simple, effective, controllable, and environmentally friendly technique is urgently required to modify the outer surface of SWNTs. In this regard, vacuum ultraviolet light has been suggested as a promising alternative to the utilization of strong oxidizing agents [9, 10]. Ultraviolet light has been widely used for the elimination of various organic impurities from inorganic substrates and as a luminous source in the photochemical lithographic technique for the destruction of organic monolayers [11]. Ultraviolet light generates active oxygen species in air and thus leads to an oxidation reaction. However, there have been no systematic investigations of the utilization of ultraviolet light for the oxidation of SWNTs, even though substantial changes in their surface properties and electronic structure are expected to occur as a result of such treatment. Here, we present the results of using photoluminescence (PL) and UV absorption measurements, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) to study the surface and the optical properties of SWNTs subjected to consecutive photochemical oxidation with irradiation times ranging between 1 and 60 minutes.

2. Experimental details

In this study, we used high-purity SWNTs produced with the HiPco method [12] by Carbon Nanotechnologies Inc. (CNI), Houston (U.S.A.) without further purification. The SWNT emulsion was dispersed under strong sonication and was subsequently spin-coated on the glass. A photochemical reaction was then induced by irradiating the prepared SWNT film with ultraviolet light from a xenon excimer lamp (UER172-200, Ushio Inc.) ($\lambda = 172$ nm) in air. The output power of the mercury lamp used in our study is 450 W. The power of the irradiated light was confined to 10 W/cm^2 by fixing the distance between the UV lamp and the sample at 20 mm. The photochemically treated SWNTs were individually dispersed in heavy water (D_2O) with the help of sodium dodecylbenzenesulfonate (SDBS) (0.5 wt%) under strong sonication (UP50H, ca. 600 W/cm^2) for 1 hour at 4°C and subsequent ultracentrifugation (Optima Max-XP, Beckman Coulter, 240,000 g). Finally, their optical features were examined using photoluminescence measured by a NIR-PL system (Shimadzu) with an InGaAs array-type detector cooled with liquid nitrogen, UV-VIS-NIR spectrophotometer using a NIR-PL system (Soildspec-3700, Shimadzu), and Raman spectroscopy (633 laser line, Kaiser HoloLab5000 system). The chemical state of the surface was examined by XPS with a MultiLab2000 spectrometer equipped with a MgK_α X-ray source (1253.6 eV). The pressure during the analysis was maintained in the range of 10^{-9} - 10^{-10} Pa. Finally, we used field-emission scanning electron microscopy (FE-SEM, JSM6335Fs), and transmission electron microscopy (TEM, JEOL2010FEF) for studying the morphology of photochemically oxidized SWNTs.

3. Results and discussion

We carried out detailed SEM and TEM observations in order to study the changes in both the bundled structure and the tubular morphology of SWNTs subjected to photochemical oxidation for up to 60 minutes (see Fig. 1). The absence of any distinctive morphological changes and any loss of mass for tubes irradiated for 10

minutes (see Fig. 1 (c)) suggests that photochemical reactions caused by ultraviolet light occur in mild conditions. However, with further longer treatment, the observation of thick, corrugated carbon tubular structure with deposited amorphous carbons on the sidewall (Fig. 1 (d)) can be explained by the preferential oxidative etching on nanotubes with small diameter, and the densely introduced functional groups on the sidewall. Therefore, in order to analyze the changes observed on the outer surface of SWNTs, we carried out XPS measurements as a function of the irradiation time [13, 14]. Noticeably, we observed the strong but asymmetric C 1s spectra (Fig. 2). The strong peak at 284.3 eV can be assigned to the sp^2 -bonded carbon atoms while the broad peak at 285.2 eV originates from the sp^3 -bonded carbon atoms (i.e., dangling bonds). It is shown that the peak intensity of the sp^2 -bonded carbon decrease linearly with increasing irradiation time. In addition, the linearly increased peak intensities of -COOH, -COO and -C-O- at 290.5, 288.6 and 286.7 eV (Fig. 2) as well as the linearly decreased ratios of sp^2/sp^3 bonds (Table 1) with increasing irradiation time signify the sequential introduction of oxygen-containing functional groups on the outer surface of the tubes.

Since Raman spectroscopy has been regarded as a sensitive tool for characterizing the structural changes of SWNTs [15], we measured the Raman spectra at 633 nm excitation. There are strong Raman peaks around 1590 cm^{-1} (tangential mode) in the high frequency region (Fig. 3 (b)) and multiple peaks (radial breathing mode (RBM)) in the low frequency region (Fig. 3 (a)), which were inversely proportional to the tube diameter. We noted that the G^+ band near 1592 cm^{-1} was continuously suppressed and the D band (defect-induced mode) [16] became linearly intensified in proportion to the irradiation time. This result suggests that a certain amount of structural disorder was generated by the continuous decoration of functional groups on the sidewall of the tubes. The covalent functional groups which were introduced to the sidewall of the tubes are assumed to cause difficulties with maintaining their perfect cylindrical shape and, in addition, the breakdown of van Hove singularities, resulting in the suppression of the RBM. In particular, the diameter-dependent depression of RBM (Fig. 3 (a)) indicates that smaller tubes are more chemically reactive due to their high curvature-derived strain, and are thus preferentially decorated with functional groups on their sidewall [17].

In order to study the photochemically induced optical changes in SWNTs in detail, we measured the optical absorption spectra for the homogeneous SWNT solutions dispersed with the help of SDBS (Fig. 4 (a)). Well-resolved and sharp absorption peaks corresponding to excitonic transitions between van Hove singularities indicate that individual SWNTs were isolated [18]; the absorption peaks in the 920-1300 nm, 620-920 nm, and 400-620 nm regions can be assigned to the semiconducting E_{11} and E_{22} transitions and the metallic E_{11} transition, respectively. We observed a minor blue shift of the absorption peaks of tubes irradiated for 1 and 5 minutes, as compared with those of the pristine SWNTs. This result can be explained by considering a modified energy band gap resulting from the covalently attached functional groups on the sidewalls of the SWNTs. Further increases of the irradiation time to 10 minute yielded depressed, broad, and red-shifted absorption peaks, indicating the presence of thicker optically active tubes resulting from the preferential decoration of functional groups on the sidewall of thinner SWNTs. In addition, the disappearance of absorption peaks for SWNTs irradiated for 30 and 60 minutes [9] suggests that the sidewall of the tubes is densely covered with functional groups, which subsequently leads to the breakdown of van Hove singularities.

In order to obtain evidence for the altered optical properties of SWNTs, we prepared PL maps of photochemically treated SWNTs by using slit widths of 10 nm and scan steps of 1 nm (Fig. 4 (b-e)). Each peak in the PL map corresponds to an excitation involving the second excitonic transition E_{22} of semiconducting SWNTs, and the emission from the corresponding first excitonic transition E_{11} of semiconducting SWNTs [1, 18]. The pristine SWNTs exhibited three strong PL peaks, which were assigned to (9,4), (8,6) and (7,6). However, the substantial changes in the dominant PL peaks for the tubes irradiated for 1 and 5 minutes, and the highly depressed PL for the oxidized tubes irradiated for 10 minutes are consistent with the results of optical absorption spectroscopy. From these PL maps, we observed a blue shift in both E_{11} and E_{22} of the photochemically oxidized SWNTs irradiated for 1 and 5 minutes as compared to the pristine SWNTs. It is noteworthy that the average differences ΔE_{11} and ΔE_{22} for the oxidized SWNTs irradiated for 1 and 5 minutes increased from 1.08 to 1.78 meV and

from 1.18 to 2.82 meV, respectively. This result can be explained by the sequentially decreased exciton excursion range below 90 nm [19], which is related to the fact that covalently functionalized sites act as energy drains which quench the PL signal of the SWNTs.

4. Conclusions

We employed optical spectroscopy to perform systematic studies on the altered optical properties of single-walled carbon nanotubes which were consecutively oxidized by using vacuum ultraviolet light. SWNTs treated for 1 and 5 minutes exhibited strong sustained optical activities due to the partial decoration of functional groups on the sidewall. With further longer treatment, the depressed radial breathing mode, the quenched luminescence, and weak, broad absorption peaks were observed as a result of the substantial decoration of functional groups on the sidewall of the SWNTs, which led to the breakdown of van Hove singularities. It is expected that this simple, cost-effective, and environmentally-friendly surface modification technique can be used as a powerful tool for decorating functional groups on the sidewalls of SWNTs in a controllable way without the destruction of their tubular morphology.

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Figure Captions

Figure 1 (a) FE-SEM image of the pristine, (b) TEM images of the pristine (b) and (c, d) the photochemically oxidized SWNTs irradiated for 10 and 60 minutes, respectively. Note that there are no distinctive changes in the bundled structure and the tubular morphology after the photochemical reaction.

Figure 2 The C 1s XPS spectra of the pristine and the photochemically oxidized SWNTs for irradiation times ranging from 1 to 60 minutes.

Figure 3 (a) Low frequency and (b) high frequency Raman spectra of the pristine and the photochemically oxidized SWNTs for irradiation times ranging from 1 to 60 minutes.

Figure 4 UV absorption spectra (a) and photoluminescence maps of the pristine (b) and the photochemically oxidized SWNTs irradiated for (c) 1, (d) 5 and (e) 10 minutes.







