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Highly visible-light luminescence properties of the carboxyl-functionalized short and ultrashort MWNTs

Yongsong Luo[a,b,*], Xiaohong Xia[a], Ying Liang[a], Yonggang Zhang[a], Qinfeng Ren[a], Jialin Li[a,*], Zhijie Jia[a], Yiwen Tang[a]

[a]*Department of Physics, Central China Normal University, Wuhan 430079, PR China*
[b]*Department of Physics, XinYang Normal University, Xinyang 464000, PR China*

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Abstract

Luminescence of the short multiwalled carbon nanotubes (MWNTs) conjugated with carboxylic acid groups has been studied. The results show that the carboxyl-functionalized short MWNTs could emit luminescence and the emission peak appears at 500 nm with a corresponding optimal excitation wavelength centering at 310 nm. When the short MWNTs are filtered through 0.15 μm polytetrafluoroethylene (PTFE) membrane, the ultrashort MWNTs are obtained from the filtrate. An interesting feature for the ultrashort MWNTs is that the emission intensity is strengthened and the peak is slightly blue shifted to 460 nm. This result indicates that the luminescence properties of MWNTs are strongly affected by the tube length. After chemical oxidization cutting, defects and carboxylic acid groups at the tube end and/or sidewall can be produced; the more shorten of MWNTs, the better dispersion and carboxylic passivation of the nanotubes, and the more intense luminescence emissions. The broad emissions are logically attributed to the trapping of excitation energy by defect sites in the carboxyl-functionalized nanotube structure.

Keywords: Carbon nanotubes; Chemical treatment; Luminescence

1. Introduction

Recently, the optical properties of carbon nanotubes have attracted much attention [1–3], and the study of photoexcited states and emission properties of carbon nanotubes has advanced significance. Several years ago, Riggs et al. [4] reported that carbon nanotubes in solution are luminescent in the visible-light range, which has been confirmed by other research groups subsequently [5–7]. All of these studies were extensively carried out through oxidation routes [8–10] bearing carboxylic acid end and/or sidewall groups that have been further derivatized by reactions with metal nanoparticles, polymeric and oligomeric compounds [11–13], i.e. the functionalization of carbon nanotubes. The process can be achieved either by covalent or non-covalent methodologies [14–17] and has triggered intensive study directed towards numerous applications in many different fields, including gas sensor, catalyst and various biological aspects, etc. [18–22]. Especially in the fields of cancer diagnosis and therapy, this functionalization of carbon nanotubes not only provides a 'cavity' structure for the storage and delivery of drugs, but also can induce luminescence to track and diagnose the effectiveness of the treatment.

Thus far, much work has been reported on the luminescence of carbon nanotubes. However, most of these works focused on the study of single-walled carbon nanotubes (SWNTs) with emission wavelengths appearing at near-IR [4,12,23–26], only limited works have been carried out for multiwalled carbon nanotubes (MWNTs) [27–29] and nearly no reports referred that the carboxylic passivation of short MWNTs can induce visible luminescence. In addition, most of the reported luminescent

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*Corresponding authors. Department of Physics, Central China Normal University, Wuhan 430079, PR China. Fax: +86 276 786 1185.
E-mail addresses: ysluo@mails.ccnu.edu.cn (Y. Luo), lijl@phy.ccnu.edu.cn (J. Li).

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nanotubes were dispersed in organic solutions. In this paper, we successfully obtain dispersed short MWNTs by chemical oxidation in water solution, and then we have further observed that the emission spectrum of short MWNTs appears in the visible spectral region at 500 nm. When the short MWNTs are filtered through 0.15 μm polytetrafluoroethylene (PTFE) membrane, the ultrashort MWNTs are obtained from the filtrate. An interesting feature for the ultrashort MWNTs is that the intensity of emission peak is enhanced and the peak is slightly blue shifted to 460 nm. The luminescence is actually dependent on not only the dispersion and lengths of the MWNTs, but also the concentration of surface carboxylic groups and the passivation of the defect sites of carbon nanotubes. To the best of our knowledge, this is the first report of luminescence from "naked" ultrashort MWNTs (without coating by metal nanoparticles, polymeric and oligomeric compounds).

2. Experimental

The preparation of short and ultrashort MWNTs samples is shown as follows. Initially, raw MWNTs were synthesized by the catalytic decomposition of acetylene at 700 °C using Al and Fe catalysts. The obtained MWNTs were further purified with concentrated mixed acid (65% HNO_3, 37% HCl, and 40% HF) to remove nanoscale impurities (carbon nanofibers, amorphous carbon, remnant catalysts and others). Then, the above-purified MWNTs were prolongedly sonicated in a mixture of concentrated sulfuric and nitric acids (the volume ratio is 3:1, 98% H_2SO_4, and 70% HNO_3) as Liu et al. [30] reported to form primary shortened nanotubes and produce many carboxylic groups at the open end and/or sidewall. Later the primary shortened nanotubes were diluted with water to neutral pH and filtered through a 0.025 μm PTFE membrane under vacuum to remove few small carbon molecules or smaller carbon clusters (which were produced by the chemical oxidation under ultrasonication); the residual samples on the membrane were referred to as short MWNTs. Finally, the short MWNTs were further filtrated through 0.15 μm PTFE membrane under vacuum, the ultrashort MWNTs were obtained from the filtrate.

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopy were employed to characterize all CVD-grown samples and cutting samples. TEM was performed on a Hitachi H810 microscope at 200 kV. SEM was conducted at 5 kV using a JEOL-6700F field emission instrument (Japan). FTIR spectra were measured on a Nicolet AVATAR-360 FT-IR spectrophotometer with a liquid-N_2-cooled MCT detector. PHI5300 X-ray photoelectronic spectroscopy was used to make XPS analysis. The PL spectra of short MWNTs were measured at room temperature using a RF-5301PC spectra fluoro photometer (Japan).

3. Results and discussion

Some electron microscopy images of the MWNTs are shown in Fig. 1. The electron microscopy images (Figs. 1a and b) of the short MWNTs show that the lengths of most of carbon nanotubes are in the nanoscale range. However, there are still parts of the lengths of short MWNTs in the microscale.

The luminescence emission spectra have been widely used to investigate the efficiency of charge carrier trapping, immigration and transfer. Fig. 2 illustrates the luminescence spectra of different MWNTs (raw MWNTs and short MWNTs) in aqueous solution. The results show that short MWNTs could emit luminescence, the broad emission peak appears at 500 nm (curve b in Fig. 2) and the optimal excitation wavelength centers at 310 nm (curve a in Fig. 2). However, this visible luminescence vanishes completely for raw MWNTs (curve c in Fig. 2).

When the above short MWNTs were filtrated using 0.15 μm PTFE membrane, the ultrashort MWNTs were obtained from the filtrate. The lengths of the ultrashort MWNTs are about 50 nm and there are no MWNTs in the microscale range, moreover, most of the ultrashort MWNTs have uniform size in length and width, as shown

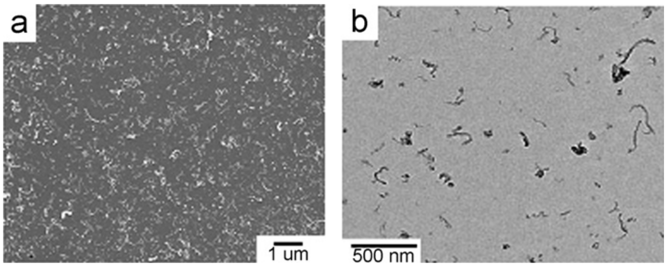

Fig. 1. (a) SEM images and (b) TEM images of short MWNTs.

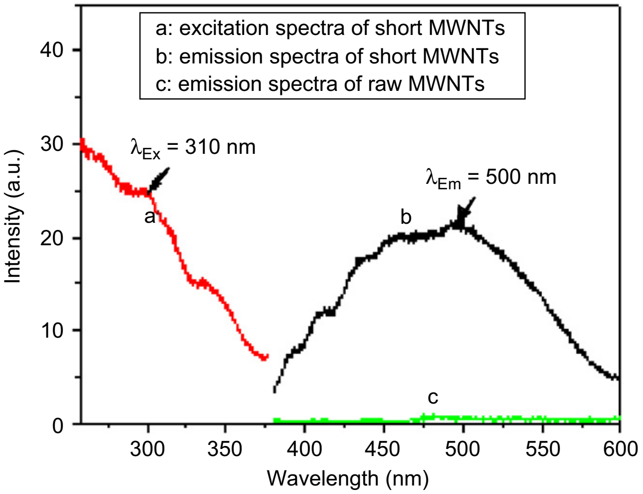

Fig. 2. Luminescence emission spectra of short MWNTs (curve b), raw MWNTs (curve c) dispersed in the distilled water solution.

in Fig. 3a. Fig. 3b shows the bright field TEM image of the ultrashort nanotubes with hollow structure, the results of HRTEM analysis clearly reveal that the lattice spacing of the ultrashort nanotube is 0.341 nm, a value similar to the layer spacing in graphite, which would further confirm that this nanotube is the ultrashort MWNT. An interesting feature for these ultrashort MWNTs is that the intensity of emission peak is enhanced and the peak is slightly blue shifted to 460 nm compared with the short MWNTs (Fig. 4). It should be pointed out that all samples were excited at 310 nm and were investigated in the same concentration (0.027 g/L).

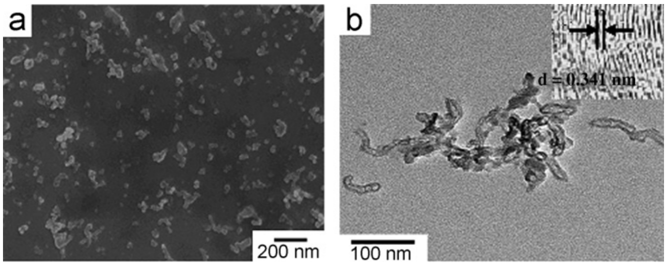

Fig. 3. (a) SEM images of ultrashort MWNTs. (b) TEM images of ultrashort MWNTs. The inserted picture is the corresponding HRTEM.

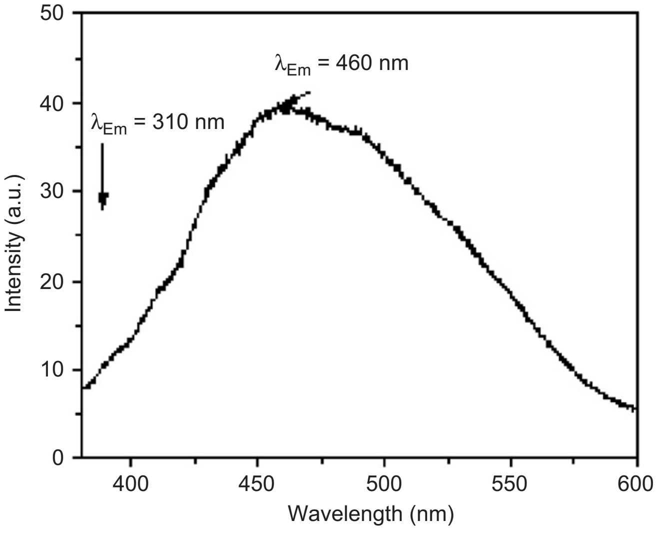

Fig. 4. Luminescence emission spectra of ultrashort MWNTs dispersed in the distilled water solution.

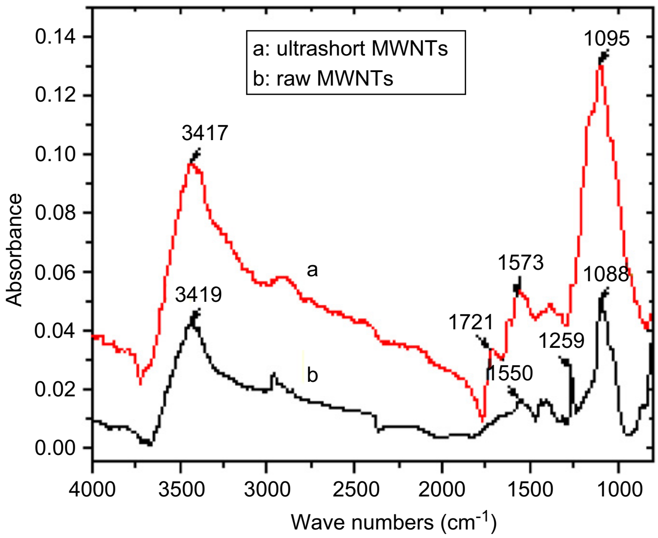

Fig. 5. Typical FTIR spectrum of raw MWNTs (curve a) and ultrashort MWNTs (curve b).

In principle, the electronic properties of MWNTs, although less well known, have been shown to exhibit either metallic [31] or semiconducting [32] characteristics depending on their outermost shell. Acid-oxidized carbon nanotubes may have significantly different properties from those of pristine materials. Most importantly, this would introduce abundance of carboxylic acid groups. A typical FTIR spectrum of the ultrashort MWNTs treated with the mixed acid is shown in Fig. 5, in which a new peak around 1721 cm^{-1} appears (curve a in Fig. 5) compared to raw MWNTs (curve b). It is normally assigned to the C=O-strength vibration in the COOH group [33], which means that the mixed acid-treatment introduced some carboxylic acid groups to the end or the side of the ultrashort MWNTs. The abundance of—COOH groups increased the dispersion and solubility of ultrashort MWNTs. The degree of dispersion and solubility for ultrashort MWNTs in solution can, in some cases, affect significantly the observed properties of the nanotubes, such as their Raman and luminescence properties. This has been confirmed in previous work [34]. On the other hand, the shortening of MWNTs caused by chemical oxidation treatment could increase energy bandgap between the lowest unoccupied molecular orbital and the highest occupied molecular orbital [25]. Venema et al. [35] were able to cut nanotubes into segments of a few tens of nanometers in length using tunneling spectroscopy, which obtained evidence of increased bandgaps in these short tubes. Rochefort et al. [36] also indicated that the electronic structure of finite-length armchair carbon nanotubes and, using several ab-initio and semiempirical quantum computational techniques, the additional confinement of the electrons along the tube axis leads to the opening of a band-gap in short armchair tube. The value of the band-gap decreases with increasing tube length. (Moreover, carbon nanotubes have shown two distinct types of behavior: 1/3 of the tubules is metallic and 2/3 is semiconducting [37–39].) It is well known that, when the dimensions of nanocrystalline particles approach the exciton Bohr radius, the quantum confinement effects will induce a blue shift in energy, this confinement effect can be clearly explained using the particle energy relation of three-dimensional single-particle box [40]: $E = A(n_x^2/X^2 + n_y^2/Y^2 + n_z^2/\underline{Z}^2)$, where A is a constant; n_x, n_y, n_z, are the quanta number; X, Y, Z are the scales in each dimension. Here for the raw MWNTs, taking the direction perpendicular to the cross section as the z-axis direction, accordingly, the cross section as the x–y plane, and considering the energy ground state (i.e. $n_x = n_y = n_z = 1$), then Z can be approximately infinite and the above energy relation can be simplified as $E = A(1/X^2 + 1/Y^2)$. Comparatively, for short MWNTs, a decreased Z value (the length of MWNTs) leads to an increased energy E. The reduction of lengths of MWNTs produces a blueshift of the bandedge. This is a good demonstration of the quantum confinement effect in the ultrashort MWNTs.

The intensity of emission peak increased and was blue shifted for ultrashort MWNTs, this should be related to both of the content of carboxylic acid groups and length of MWNTs. Based on the discussion above, we propose the ultrashort MWNTs would have more carboxylic acid groups compared with the short MWNTs in the same concentration, i.e. better carboxyl-functionalized surface. At the same time, the role of carboxylic acid groups on the nanotube surface may keep the nanotubes well dispersed. The carboxylic acid groups may also provide passivation of the defect sites to make the trapping of excitation energy more efficient and/or the energy traps more emissive [23,41]. In the nanotube samples with more carboxylic acid groups and shorter lengths, there are more individually dispersed nanotubes and thus less intertube quenching and more effective passivation of the defects for higher luminescence emission yields. As regards the visible luminescence vanishes completely for raw MWNTs, because they are highly tangled and weakly solubilized in the water solution. Photoinduced charge transfer process may be involved in the luminescence quenching, so raw MWNTs exhibit a very broad and featureless spectrum.

Nonoxidation cutting strategies have also been explored to further investigate the luminescence property of ultrashort MWNTs. When the above short MWNTs further shortened through physical method without filtration using 0.15 μm PTFE membrane, i.e. ball milling (500 r/min, from 0 to 24 h)(many reported that the short CNTs were produced by this method [42–45]), different results were discovered. The luminescence spectra are shown in Fig. 6a. We can see that there is a gradual decrease in the luminescence intensity, which is unlike the behavior induced by chemical oxidation cutting. This maybe, no—COOH groups appear in the new defect sites, and new ultrashort MWNTs will form aggregation easily. In addition, these aggregates are weakly soluble in the water solution. Thus, the reduction in luminescence is caused by quenching from the aggregation of new ultrashort MWNTs present. In comparison, one part of the new ultrashort MWNTs samples (milling 24 h) were treated with HNO_3 solution to fully recover the carboxylic acid groups, another were treated through annealing in the high vacuum oven (1200 °C, 10^{-5} pa). An interesting feature for the new ultrashort MWNTs with acidification treatment is that a strong luminescence is obtained (curve d in Fig. 6b); the intensity is about seven times of that of the former ultrashort MWNTs (curve c in Fig. 6b). Comparatively,

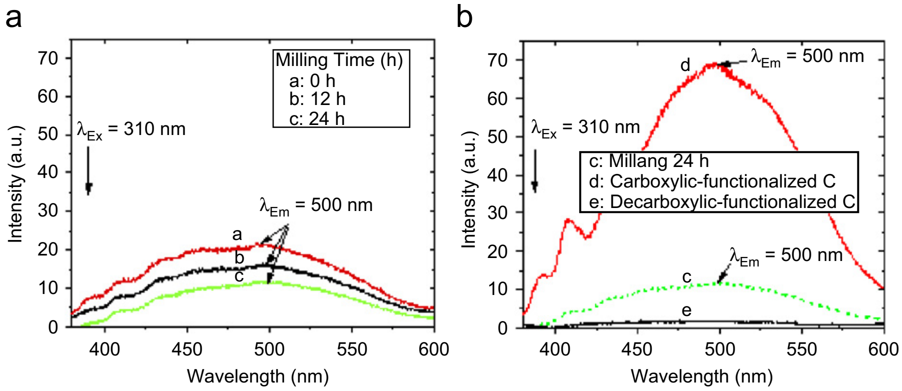

Fig. 6. (a) Luminescence spectra of short MWNTs after milling for different times. (b) Luminescence spectra of short MWNTs obtained after post-treatment. All samples were investigated in the same concentration (0.027 g/L).

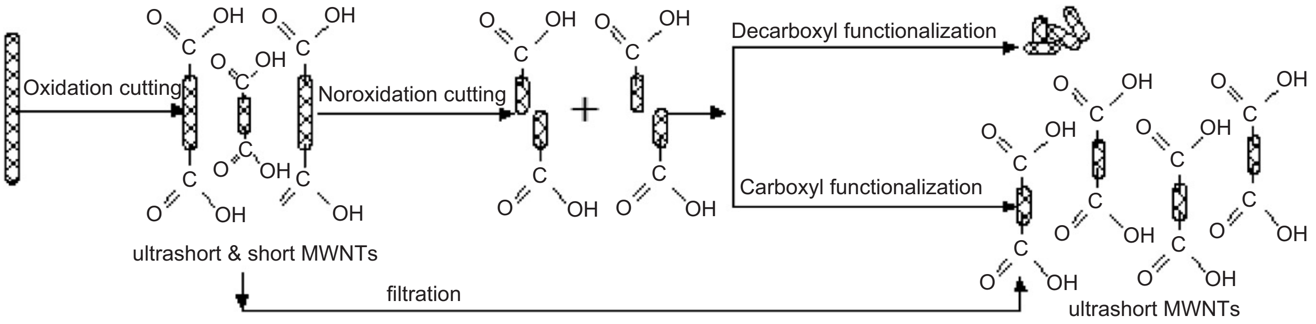

Fig. 7. Schematic depiction of oxidation cutting and nonoxidation cutting of MWNTs (For the briefness, the carboxyl acid groups on the tube sidewall are not drawn).

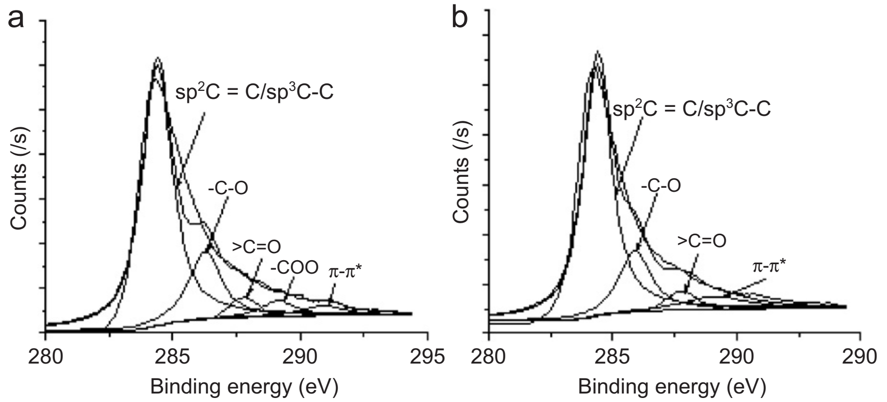

Fig. 8. XPS C1s peak of the ultrashort MWNTs (milling for 24 h). (a) The carboxyl-functionalized ultrashort MWNTs was obtained with HNO_3 acidification. (b) The decarboxyl-functionalized ultrashort MWNTs were obtained in high vacuum oven annealing.

even a partial removal of carboxylic acid groups from the carboxyl-functionalized nanotubes can result in a substantial reduction in the observed emission intensity which annealed in high vacuum oven (curve e in Fig. 6b). These phenomena can confirm that the luminescence ascribe the carboxyl functionalization of the ultrashort MWNTs. To shed light on the formation mechanism of these carboxyl-functionalized ultrashort MWNTs, the process of the shape transition from raw MWNTs to ultrashort MWNTs is summarized in Fig. 7.

In fact, the decarboxyl functionalization (often making the nanotubes insoluble again) has been effective in the elimination of the overwhelming luminescence. XPS analyses of different ultrashort MWNTs (fully recover and fully remove of the carboxylic acid groups) also support this conclusion, as shown in Fig. 8. The carboxylic acid groups of ultrashort MWNTs highly increased through the acidification (Fig. 8a), the ratio of O/C is 1.049, the carboxylic acid groups appear at 289.16 eV position and the content is 3.35%, respectively. However, the decarboxyl-functionalized ultrashort MWNTs presented the content of carboxyl far from the acidification (the ratio of O/C is 0.718; the content of carboxylic acid groups is nearly zero) (Fig. 8b).

4. Conclusion

Luminescence of the short MWNTs-conjugated with carboxylic acid groups has been carried out. It is found that the luminescence properties are strongly related to carboxylic acid groups at the tube end and/or sidewall. The luminescence of short MWNTs in the visible-light range is very sensitive to surface concentration of carboxylic groups, and the ultrashort MWNTs possessing the most carboxylic acid groups display strongest luminescence with a slight blue shift. The emissions are logically attributed to the trapping of excitation energy by defect sites in the carboxyl-functionalized nanotube structure, the blue shift may be related to the quantum confinement effect in the ultrashort MWNTs. The efficiently luminescent ultrashort MWNTs not only provide a 'cavity' structure for the storage and delivery of drugs, but also can be a useful probe to track and diagnose in physical and biological fields.

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