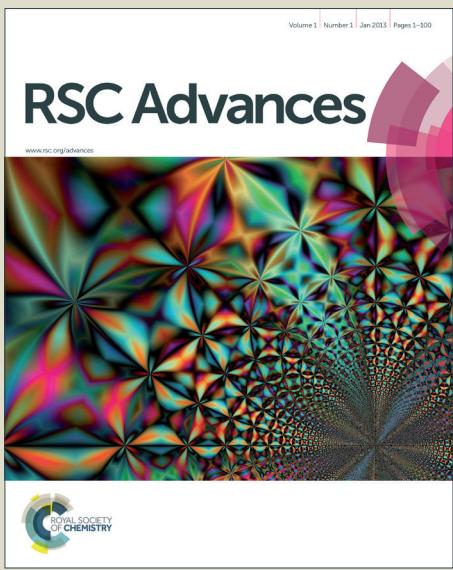
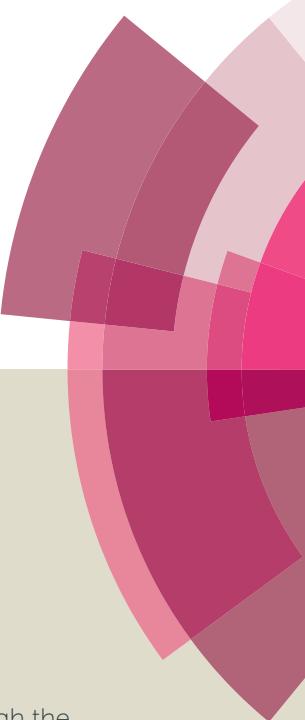


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# Effect of microwave irradiation on carbon nanotube fibers: exfoliation, structural change and strong light emission

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## Abstract

We exposed single- and double-walled carbon nanotube (SWCNT and DWCNT) fibers to microwave radiation. Small carbon clusters of  $C_2$  were detached from the nanotubes, and the process was accompanied with intense heat release. The exfoliation of  $C_2$  made the nanotubes break, while the high temperature made the nanotube bundles transform to large diameter CNTs. Strong visible light emission were observed from the vicinity of the nanotube fibers. The emission spectra excited by the microwave from the as-grown CNT fibers correspond to the Swan band of  $C_2$  clusters. In case of the purified SWCNT fibers, two characteristic peaks at 584 nm and 769 nm emerge in the spectra beyond Swan band of  $C_2$ .

## 1. Introduction

Carbon nanotubes (CNTs) have attracted great attentions because of their unique structure, outstanding properties and attractive potential applications. The interaction between CNTs and electromagnetic waves are of great interest from both fundamental and practical point of view.<sup>1</sup> Attractive potential applications, including nanotube antenna, radio, speaker, microwave absorption, and electromagnetic interference shielding materials have been proposed according to their intriguing behaviors when the CNTs are exposed to electromagnetic waves.<sup>2-10</sup> When the CNTs are irradiated by microwave with frequency of gigahertz, intense heat release, outgassing, and light emission are observed due to their strong microwave absorption ability.<sup>11-13</sup> The temperature of CNTs are promoted to above 1500 °C ultrafast because of intense heat release, leading to reconstruction and higher crystalline of CNTs.<sup>12, 14</sup> Microwave were thus used for CNT purification and chemical functionalization.<sup>14-18</sup> Regarding to light emission, Su *et al.* detected several peaks in the emission spectrum, including narrow-band red, green and blue color.<sup>13</sup> Up to now, the explanations for such light emission in literature are ambiguous. Imholt and Su *et al.* ascribed the light emission to outgas discharge of hydrogen.<sup>12, 13</sup> However, the light spectra do not fit with molecular emission of hydrogen. It needs further work to explore the science of CNTs under microwave irradiations. Here, we demonstrate some novel structural change and strong light emission of CNTs irradiated by 2.45 GHz microwave. We find that the emission spectra correspond to molecular emission of small carbon clusters and sometime to electron transition of single-walled CNTs (SWCNTs).

## 2. Experiments

Macroscopic CNT fibers used in the experiments were prepared by floating chemical vapor deposition method (FCVD).<sup>19, 20</sup> The samples were purified by immersing the fibers into hydrogen peroxide and then in hydrochloric acid to remove amorphous carbon and iron catalyst particles. The purified samples were 0.05~0.5 mm in diameter, and 5~10 cm in length. In order to eliminate oxidation in air during the irradiation experiments, CNT fibers were sealed into quartz tubes at a vacuum of  $\sim 10^{-6}$  Torr. The CNT samples were then placed at the center of a household microwave oven (700 W) operating at 2.45 GHz with wavelength of 12.2 cm. The emission spectra were recorded by a spectrometer (USB2000+, Ocean Optics) through a quartz window opened in the front door of microwave oven. The CNTs were characterized by scanning electron microscope (SEM, Leo 1500), transmission electron microscope (JEOL 2100), Raman spectroscope (Renishaw 2000), photoluminescence spectrometer (FP-6600) with excitation of 405 nm laser before and after microwave irradiation.

## 3. Results and discussion

Fig. 1a demonstrates an optical image of the purified CNT fibers sealed inside of the quartz tubes before and after microwave irradiation. After microwave irradiation, some carbon evaporate and deposit on the wall of the quartz tube. The long fibers were broken or cut into several pieces with length of  $\sim 1$  cm for long time irradiation. Fig. 1b is a SEM image of a purified CNT fiber before microwave irradiation, showing clean and ultra-long CNT bundles in the fibers. After several minutes'

irradiation, the CNT fibers were covered by a layer of carbon flakes (see Fig. 1c). Fig. 1d gives a higher magnification SEM image of the carbon flakes, showing that the carbon flakes stand separately to each other on the CNT bundles. It might be due to the electric repulsion generated by electromagnetic wave.<sup>4,5</sup> The carbon flakes derive from the re-arrangement of carbon clusters and then deposit on the surface of CNT bundles. The carbon flake layers are hundreds of nanometers to several microns in thickness depending on the irradiation time. Fig. 1e shows an interface between the CNT bundles and carbon flakes. The morphology of nanotubes under the carbon flakes are similar to those of the purified samples before microwave irradiation (Fig. 1b).

The carbon flakes distribute not only on the surface of the CNT fibers, but also on the inner wall of the quartz tube, resulting in dark materials on the quartz tube (see Fig. 1a). Fig. 1f shows a SEM image of these carbon flakes on the quartz tube. The morphology of such carbon flakes are similar but smaller than those depositing on the CNT bundles (see Fig. 1c and 1d), which resulted from longer diffusion distance and lower concentration of carbon clusters.

TEM images clearly reveal the structural change of CNTs exposed to microwaves. For comparison, we provide two TEM images of the CNTs before microwave irradiation in Fig. 2a and 2b. The CNTs consist of numerous ultra-long SWCNT and DWCNT bundles with diameter of 10-50 nm. It is hard to observe the tips of CNTs during TEM examination. Amorphous carbon deposited on the CNT bundles and some catalyst particles are observed in the as-grown samples (Fig. 2a). Most of

amorphous carbon and catalyst particles are removed from the samples by purified procedure. Fig. 2b shows a TEM image of the purification CNTs, revealing clean and clear wall of SWCNTs and DWCNTs.

Figs. 2c-2e clearly reveal various structural changes of CNTs after microwave irradiation, including reconstruction, breakdown, purification, and increased crystalline. Some individual single-, double-, and even multi-walled CNTs and small bundles with several CNTs with diameters varied from 3 nm to 10 nm are frequently observed in the samples (Fig. 2c-2e). This kind of larger diameter tubes were not observed in the samples before the microwave irradiation. These large diameter CNTs are derived from merging or reconstructing of CNT bundles due to significant temperature increase.<sup>12</sup> The MWCNTs are well crystallized because of forming at high temperature (see Fig. S1a). Some CNTs are partially broken or cut into short nanotubes due to exfoliation of carbon (see Fig. 2c and 2d). As shown by arrow in Fig. 2d, the exfoliation of carbon generally starts from the outer most walls of nanotubes. The tips of the broken CNTs close spontaneously (see Fig. 2d). Most of the amorphous carbon are detached and removed from CNT bundles due to carbon exfoliation in comparison with the as-grown CNT samples. The iron catalyst particles encapsulated by amorphous carbon evaporated due to high temperature during the microwave irradiation, which leave some nano-cages with diameter of ~20 nm in the samples (see Fig. 2e).

When exposed to microwave, small carbon clusters, such as C<sub>2</sub>, are exfoliated from CNTs. Actually, small carbon clusters of C<sub>2</sub> are usually detected during the synthesis

of CNTs by the laser ablation method.<sup>21, 22</sup> It was believed that CNTs grow by the mean of adding clusters of C<sub>2</sub>. It seems to be a reverse process of CNT growth for carbon cluster exfoliation. At the same time, it releases intense heat from CNTs due to their strong microwave absorption ability, which makes a significant temperature increase. The quartz tube under the CNT fibers melts after long time irradiation.

Fig. 2f shows a high resolution TEM image of the carbon flakes taken from the inner wall of the quartz tube. The carbon flakes consist of multiple stacked graphite layers, which derive from re-arrangement of C<sub>2</sub> clusters. The structure of carbon flakes depositing on the CNT bundles are similar to those on the inner wall of the quartz tube (see Fig. S1b and S1c).

Fig. 3 shows the Raman spectra of the purified CNT fibers before and after microwave irradiation. A high ratio of intensity of G-band (1590 cm<sup>-1</sup>) to D-band (1327 cm<sup>-1</sup>) of ~13 shows low defect density in the CNTs. Two characteristic radial breath mode (RBM) peak at 196 cm<sup>-1</sup> and 215 cm<sup>-1</sup> are identified in the Raman spectrum (inset of Fig. 3), corresponding to SWCNTs with diameter of ~1.2 nm and ~1.1 nm, respectively.<sup>23</sup> After microwave irradiation, the  $I_G/I_D$  ratio drops significantly from 13 to ~3, resulting from defective carbon flake deposition on the CNT fiber. The RBM peaks are also suppressed seriously but can still be identified; this suppression might be derived from damage of CNT bundles and deposition of the carbon flakes on bundles' surface. The  $I_G/I_D$  ratio of the carbon flakes on the wall of quartz tube is only ~0.6. The decrease of  $I_G/I_D$  ratio reflects the structure change of the CNTs under microwave irradiation, which is consistent with the SEM and TEM results.

Besides structural change, strong visible light are observed from the CNT fibers several seconds after microwaves irradiation. Fig. 4a shows an optical image of light emission during the microwave irradiation. The strong white light are observed not only from the CNT fibers but also from volume of the quartz tube vicinity of the fibers, which indicates that the light emission derives from small carbon clusters diffusing around the fibers.

Fig. 4b shows three emission spectra of an as-grown CNT fiber taken with time interval of 5 seconds during the microwave irradiation. There are several sharp peaks located at 383, 408, 434, 445, 477, 513, 554, 584, 601, and 653 nm. These emission peaks correspond well to the Swan band of small carbon cluster of  $C_2$  excited by laser,<sup>24,25</sup> which indicates that the light emission derives from molecular spectra of  $C_2$  plasma rather than from outgassing of hydrogen.<sup>12, 13</sup> The intensity of the light emission increases quickly at the beginning of the process and then remains stable at a high level. The variation of light intensity reflects the  $C_2$  concentration during irradiation. The concentration of  $C_2$  increases quickly at the beginning of microwave irradiation due to exfoliation, and then stabilizes due to the balance of exfoliation of  $C_2$  and formation of carbon flakes. A broad peak deriving from black body emission is also observed in the emission spectra, indicating heating effect of CNTs irradiated by microwave. The temperature of CNTs can reach above 1500 °C,<sup>12</sup> which leads to structural change of the CNTs.

Fig. 4c shows emission spectra of a purified CNT fiber taken with time interval of ~3 seconds during microwave irradiation. At the beginning of irradiation, the

emission spectra of purified CNT fiber are similar to those of as-grown fiber, although there are some peak shifts, such as 383 nm to 385 nm, 445 nm to 449 nm, 476.6 nm to 477.7 nm, and 652.7 nm to 651.3 nm. The shifts are derived from the different pressure inside the quartz tubes.<sup>25-27</sup> It is surprising that two evident emission peaks centered at 584 nm and 769 nm emerge in the emission spectra several seconds after light emission, which are never observed in MWCNTs and as-grown SWCNT fibers.<sup>12, 13</sup> The intensity of the peak at 584 nm increases quickly as microwave irradiation and becomes the strongest peak in the spectra within 20 seconds. The photon energy of peaks at 584 nm and 769 nm are 2.1 eV and 1.6 eV, which correspond to  $E_{11}$  transition of metallic SWCNTs with diameter of ~1.2 nm (corresponding to the RBM peak at  $196\text{ cm}^{-1}$ ), and  $E_{22}$  transition of the semiconducting SWCNTs with diameter of ~1.0 nm (corresponding to the resonance RBM peak at  $215\text{ cm}^{-1}$ ).<sup>23</sup> We believe that these two new peaks are derived from SWCNTs excited by carbon cluster plasma. Generally, the temperature of  $\text{C}_2$  plasma might reach to 4000-6000 °C, which is much higher than that of the CNTs. The electrons in CNTs are excited to high energy level, and then  $E_{11}$  and  $E_{22}$  transition occurs. It is hard to observe these two peaks for the as-grown samples because of the impurity on the CNTs. For the purified CNTs, most of the amorphous carbon are removed from samples, resulting in direct exposure of SWCNTs under  $\text{C}_2$  plasma.

As illustrated in Fig. 4d, a mechanism of light emission from CNT fibers is proposed here based on the above experimental results. When the CNTs are exposed to microwave irradiation, carbon clusters of  $\text{C}_2$  are exfoliated from nanotubes and

from amorphous carbon. The  $C_2$  clusters diffuse in the space around the nanotubes quickly. The temperature of CNTs increase quickly because of intense heat release. At the same time, the microwave induce charge re-distribution along the CNTs due to antenna effect,<sup>3, 5</sup> resulting in high electric field among nanotubes and electron emission. Plasma of carbon clusters were induced by the electron emission and high temperature. And the SWCNTs with clean and clear walls are further excited by plasma, resulting in  $E_{11}$  and  $E_{22}$  transition and light emission at 584 nm and 769 nm.

#### 4. Conclusions

When CNTs were exposed to microwave, significant structural change occur due to high microwave absorption and intense heat release. The change include carbon exfoliation, reconstruction, breakdown, purification, higher crystalline, and formation of carbon flakes. Small carbon clusters of  $C_2$  are exfoliated from the outer layer of CNTs. The  $C_2$  clusters diffuse around the fibers and reorganize into carbon flakes. Strong visible light are observed from the CNT fibers a few seconds after microwave irradiation. The light derives mainly from Swan band of molecular emission of  $C_2$  plasma, as well as from  $E_{11}$  and  $E_{22}$  transition of SWCNTs excited by  $C_2$  plasma.

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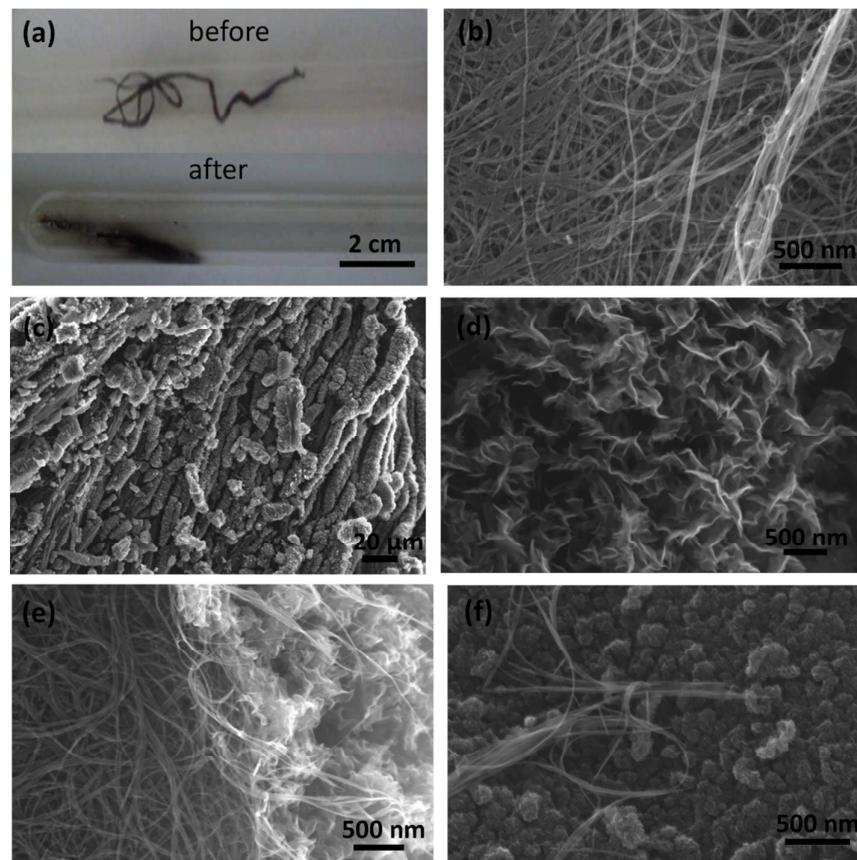
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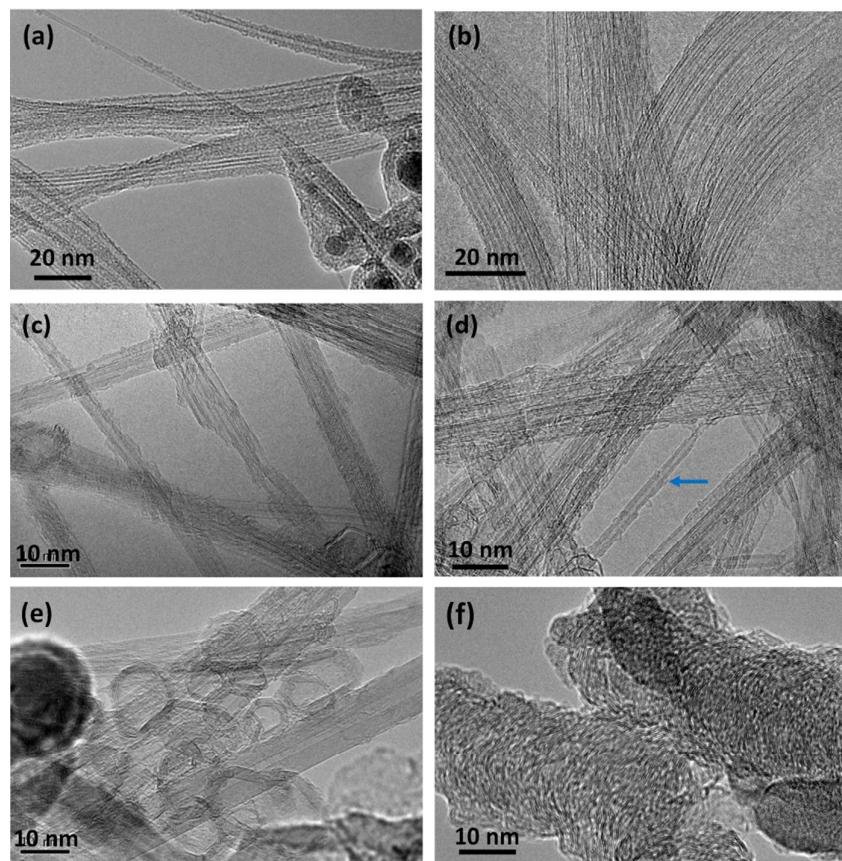
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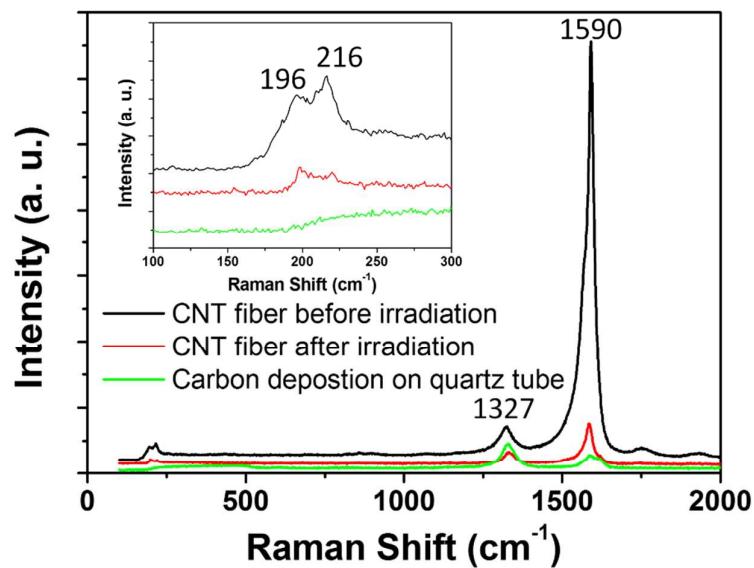
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**Figures**

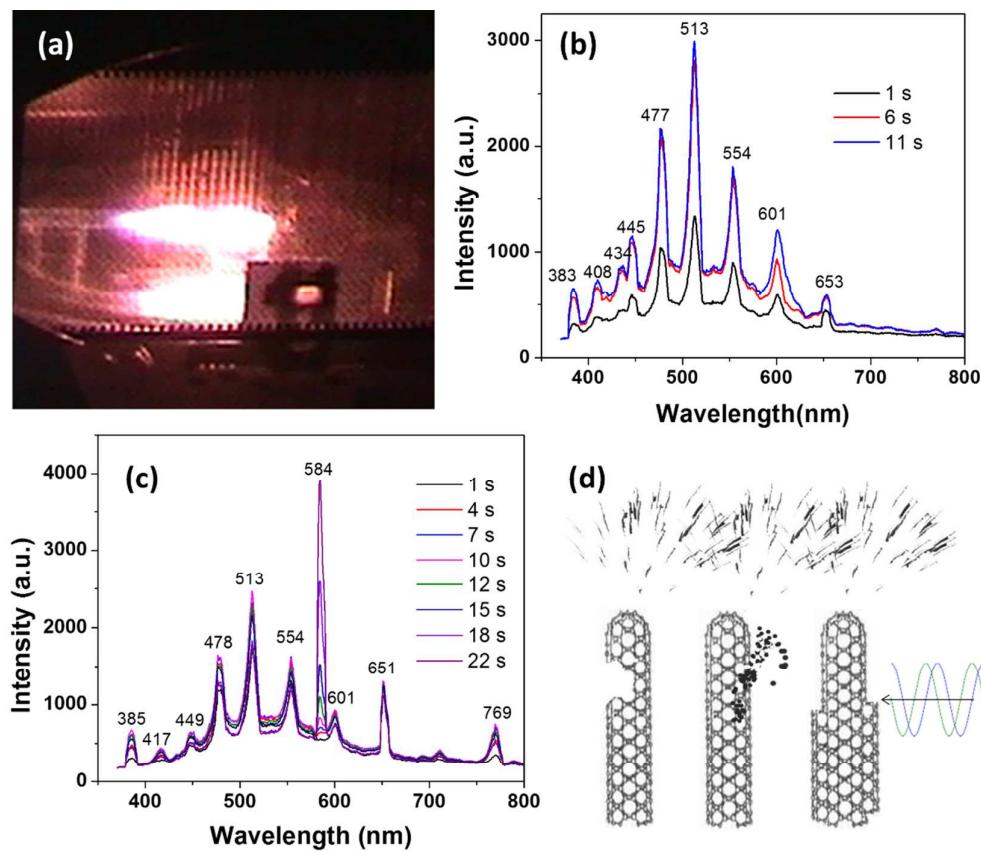
**Figure 1.** Morphology of the carbon nanotube fibers. (a) Optical image of CNT fibers sealed in a quartz tube before (up) and after (down) microwave irradiation. SEM images of a purified CNT fiber (b) before and (c) after microwave irradiation. High magnification SEM images of (d) carbon flakes on the CNT bundle and (e) of the interface between the CNT bundles and the carbon flakes. (f) SEM image of the carbon flakes collected from the inner wall of a quartz tube.



**Figure 2.** TEM images of (a) as-grown and (b) purified SWCNTs and DWCNTs before microwave irradiation. (c) CNTs after microwave excitation, showing that some bundles merged into large diameter CNTs. (d) SWCNTs and DWCNTs with diameter varied from 3-10 nm which are derived from melting and reconstruction of bundles. The arrow shows an exfoliating CNT from the outer most walls. (e) MWCNTs and nano-cages. (f) Carbon flakes.



**Figure 3.** Raman spectra of CNT fiber before and after microwave irradiation, and carbon flakes depositing on the inner wall of quartz tube. Inset shows the corresponding RBM peaks.



**Figure 4.** (a) Optical image of light emission from a purified CNT fiber under microwave irradiation. (b) Emission spectra of an as-grown CNT fiber. (c) Emission spectra of a purified CNT fiber. (d) Schematic image of carbon exfoliation and light emission from CNTs under microwave irradiation.