

# WELL-DISPERSED MULTI-WALLED CARBON NANOTUBE/PEEK NANO-COMPOSITES AND THEIR PHOTOLUMINESCENCE PROPERTIES

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## ABSTRACT

Photoluminescence (PL) effects have never been observed on multiwalled carbon nanotubes (MWNTs) due to their complex structures. Here, a nanocomposite film composed of 6.5 wt% multi-walled carbon nanotubes (MWNTs) and PEEK polymer was prepared and the individualization of MWNTs was achieved. PL effects were observed from this nanocomposite film which cannot be ascribed solely to either PEEK or MWNTs, but are likely be an unusual property of the nanocomposite generated from its unique composite structure.

## Introduction

Photoluminescence (PL) is frequently observed in semiconducting single-walled carbon nanotubes due to their Van Hove singularity band structure which originates from their unique one-dimensional crystal structure, wherein electronic transitions induced by external laser excitation lead to emissions of certain wavelengths. This holds promising prospects for single-walled carbon nanotubes in applications such as optoelectronics [1], sensing [2], and other fields. However, interactions between nanotubes, such as bundling, cause severe luminescence quenching. Therefore, individualization of nanotubes is quite critical in PL study of single-walled carbon nanotubes. So far, a few methods have been reported that can enhance the fluorescence phenomenon of single-walled carbon nanotubes, such as surface functionalization of the single-walled carbon nanotubes and dispersion of the single-walled carbon nanotubes in various dispersants [3, 4].

Compared to single-walled carbon nanotubes with only one single wall of graphene, multiwalled carbon nanotubes have much more complex structures since they are composed of many layers of graphene rolled in concentric tubes. The interaction within the walls of the multi-walled carbon nanotubes leads to highly complex band structures and intensifies the luminescence quenching. So far, PL has never been observed in any multi-walled carbon nanotubes beyond double-walled carbon nanotubes [5, 6].

Herein, we report our delicately prepared nanocomposite thin film composed of multi-walled carbon nanotubes (MWNTs) and PEEK polymer for fluorescence studies. In the composite film, carbon nanotubes are separated from each other and embedded in the PEEK polymer matrix. Further

investigation on the anomalous fluorescence phenomenon will be carried out to uncover its underlying mechanisms.

## Experimental

### Synthesis of PEEK and MWNT/PEEK nanocomposite thin films

Multi-walled carbon nanotubes were obtained from Bussan Nanotech Research Institute Inc. (XNRI), which is a subsidiary of Mitsui Corporation (Tokyo, Japan). The obtained MWNTs, synthesized using chemical vapor deposition method, are with a diameter range of (20-100) nm and an average length of a few micrometers. Pure PEEK (151G) were purchased from Victrex, UK. Pure PEEK films and MWNT/PEEK nanocomposite thin films with 6.5 wt% MWNTs loading were prepared using a two-axis extruder.

### Characterization

Scanning electron microscopy (SEM) images were obtained by a Zeiss Auriga 60 on the as-prepared pure PEEK film and MWNT/PEEK nanocomposite film. Transmission electron microscopy (TEM) observation was carried out using a field-emission transmission electron microscope (JEOL JEM-2010F). TEM samples of less than 100 nm in thickness were prepared by focused-ion beam (FIB) method.

To characterize the structures and compositions of the sample films, X-ray diffraction (XRD) was performed on a Bruker D8 diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.5416\text{\AA}$ ); Raman measurements were performed using a Jasco NRS-4500 with 532 nm laser excitations, and multiple locations on the as-prepared MWNT/PEEK nanocomposite thin film were chosen; High resolution thermogravimetric analysis (HR-TGA) was carried out on a TA Q600 HT, one from room temperature to 800 °C at a heating rate of 2 °C min<sup>-1</sup> under nitrogen protection (50 mL min<sup>-1</sup>) and the other from room temperature to 600 °C at a heating rate of 2 °C min<sup>-1</sup> in air (50 mL min<sup>-1</sup>).

As for fluorescence study, the data was gathered on a HORIBA Aqualog UV-800 and utilized a 150 W vertically mounted xenon source and a CCD detector. The excitation wavelengths were varied from 200 – 800 nm in 3 nm steps, and emission was gathered from 250 – 800 nm in about 4.64 nm increments.

## Results and Discussion

Figures 1a and 1b show the SEM images of pure PEEK film and the MWNT/PEEK film, showing that MWNTs are incorporated and distributed evenly in the polymer matrix on a microscale. To further show the dispersion of MWNTs in the PEEK polymer on a nanometer scale, the nanocomposite film was cut and polished to a thickness less than 100 nm and characterized using TEM. Figure 1c and 1d show the TEM images gathered from the multi-walled carbon nanotube/PEEK composite. No bundling has been observed, and the multi-walled carbon nanotubes have been well separated from each other, eliminating the inter-nanotube interactions.

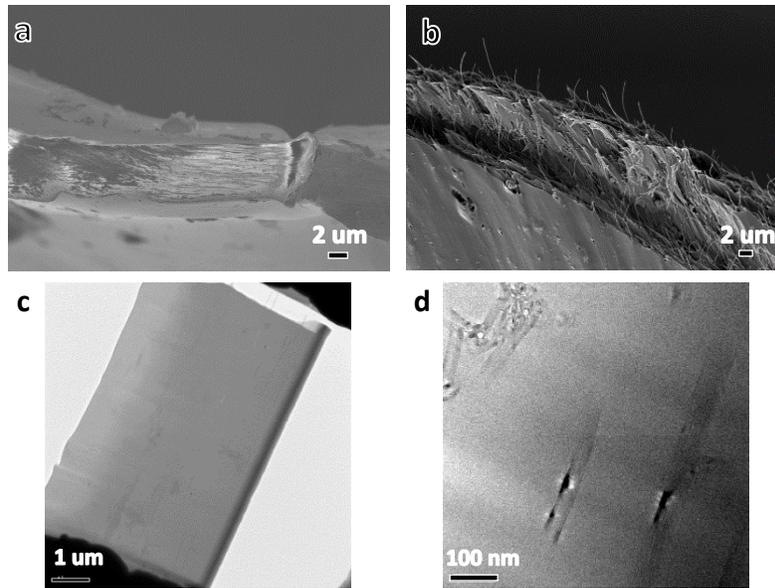


Figure 1. SEM images of pure PEEK (a) and PEEK/MWNT nanocomposite film (b); TEM image (c) and HR-TEM image (d) of MWNT/PEEK nanocomposite, showing well-distributed MWNTs in the PEEK polymer matrix.

To further characterize the pure PEEK film and the MWNT/PEEK film, TGA and XRD were applied.

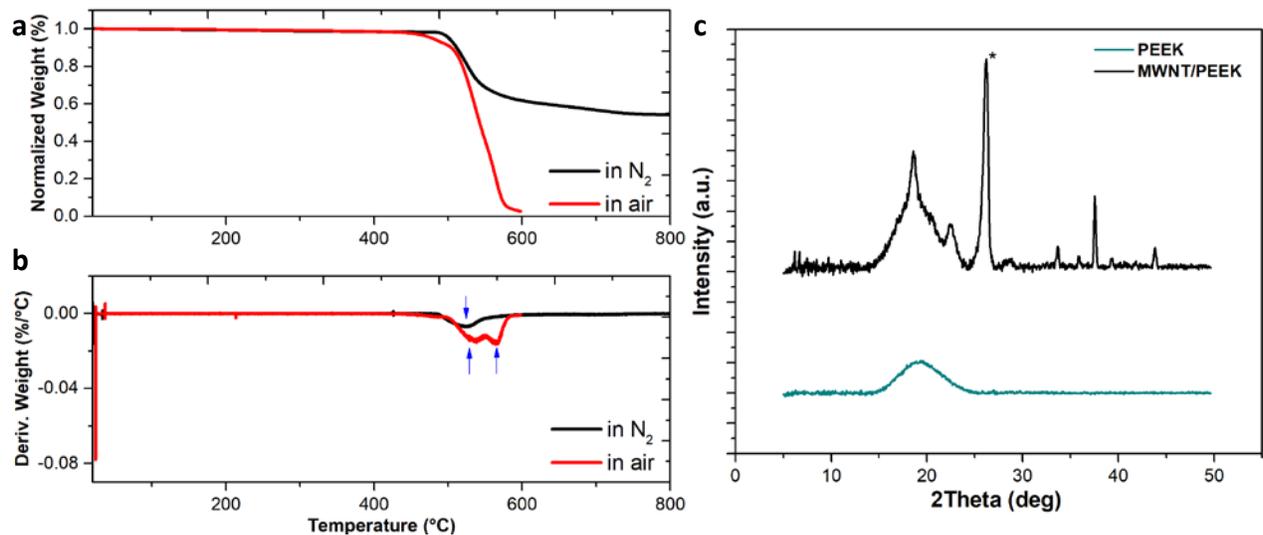


Figure 2. HR-TGA measurements of MWNT/PEEK nanocomposite in nitrogen and in air (a) and its 1<sup>st</sup> order derivative of weight (b). (c) XRD measurements of pure PEEK and MWNT/PEEK nanocomposite.

PEEK is a high-performance thermoplastic polymer. Its glass transition temperature is  $\sim 150$  °C and its melting point is  $\sim 343$  °C. Figure 2 shows a typical TGA curve in nitrogen, where the weight starts to drop at  $\sim 480$  °C and has up to 54% of the initial weight remained at 800 °C since the ether and aromatic structures remain in the residual up to very high temperatures [7-9]; while in air, the weight starts to drop at  $\sim 410$  °C, while the flow temperature of PEEK is  $\sim 390$  °C, and the film is all burned before reaching 600 °C.

To further characterize the TGA curves, 1<sup>st</sup> order derivative of weight is applied (Figure 2b), where the maximum rate of weight loss shows around 526 °C is observed for the in-nitrogen analysis, which is ascribed to the decomposition of PEEK in nitrogen [8, 9]; two peaks of maximum rate of weight loss at 536 °C and 565 °C are observed for the in-air experiment [9].

PEEK is usually considered as a semi-crystalline thermoplastic, and its crystallinity depends on its synthesis process. Usually, its crystallinity ranges from being amorphous to 40%, even though 30-35% is more typical [10]. As seen in Figure 2c, here the pure PEEK film as prepared is amorphous and without long-range order as indicated by the broad band located around  $20^\circ$  ( $2\theta$ ), while MWNT/PEEK film shows noticeable peaks at  $2\theta$  approximately equal to  $18.6^\circ$ ,  $20.3^\circ$ ,  $22.5^\circ$ ,  $28.6^\circ$ ,  $33.6^\circ$ ,  $39.3^\circ$  of PEEK [11, 12] and  $26.2^\circ$  of MWNTs [13].

The different crystallinities of PEEK should result from the existence of MWNTs. MWNTs surface provide nucleation sites for PEEK crystallization during the synthesis process. Similar effects have been studied extensively in carbon fiber reinforced PEEK composites, where carbon fibers tend to nucleate the crystallization of PEEK, generating epitaxially growing rod-like crystals. [14, 15]

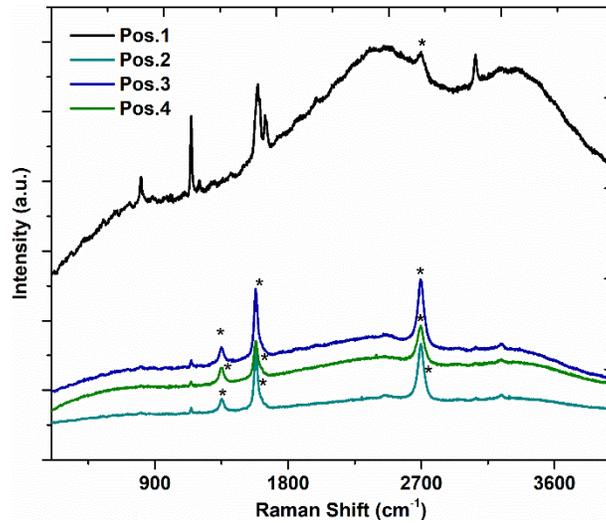


Figure 3. Raman spectra collected on four different locations on the MWNT/PEEK nanocomposite.

Position	D band/ $\text{cm}^{-1}$	G band/ $\text{cm}^{-1}$	$I_D/I_G$
#2	1350.9	1582.9	0.215
#3	1350.0	1581.0	0.237
#4	1347.2	1581.2	0.445

Table 1: Parameters analysis from Raman results.

Figure 3 presents the original Raman results of the as-prepared MWNT/PEEK film. With 532 nm excitation, four different positions were chosen. Pos.1 is mainly focused on the PEEK polymer; Pos.2 and Pos.3 are focused on both MWNTs and PEEK; and Pos.4 is mainly focused on the MWNT. As shown in Figure 3, Pos.1, admits peaks at  $806\text{ cm}^{-1}$ ,  $1145\text{ cm}^{-1}$ ,  $1200\text{ cm}^{-1}$ ,  $1594\text{ cm}^{-1}$ ,  $1644\text{ cm}^{-1}$ , and  $3067\text{ cm}^{-1}$ , all typical Raman peaks from PEEK [16]; Pos.2, 3 and 4 all give distinct peaks of carbon nanotubes such as the D band ( $\sim 1350\text{ cm}^{-1}$ ), the G band ( $\sim 1581\text{ cm}^{-1}$ ) and the 2D band ( $\sim 2697\text{ cm}^{-1}$ ) [17]. In Pos.1, peaks of MWNTs cannot be distinguished except the 2D band (asterisked), and the G band might exist but its position partially overlaps with the band shoulder of PEEK's  $1594\text{ cm}^{-1}$  peak. With no other peaks detected, the Raman results further demonstrate the chemical composition of the as-prepared nanocomposite film.

One thing worth noticing is that from Figure 3, it is obvious that different positions will produce different Raman spectra depending on the relative intensities of PEEK peak signals and MWNT peak signals.

Firstly, Pos.1 shows completely different peaks, indicating substantially high content of PEEK compared to the other three; Then, Pos.2, Pos. 3 and Pos. 4 all give similar Raman spectra, however, as shown in Table 1, the  $I_D/I_G$  ratio calculated based on their D band and G band are different for each position. Pos.4, which focused on the MWNTs, gives the highest  $I_D/I_G$  ratio, suggesting that the higher MWNTs content, the higher the  $I_D/I_G$  ratio.

This relation between MWNTs content and  $I_D/I_G$  ratio can be applied to qualitatively analyze the relative content of MWNTs in PEEK or other polymers.

Profound emission has been detected induced by 532 nm excitation on the MWNT/PEEK nanocomposite (Pos.1), which is absent from the other three positions, suggesting interesting photoluminescence properties of our MWNT/PEEK nanocomposite. The details are discussed below.

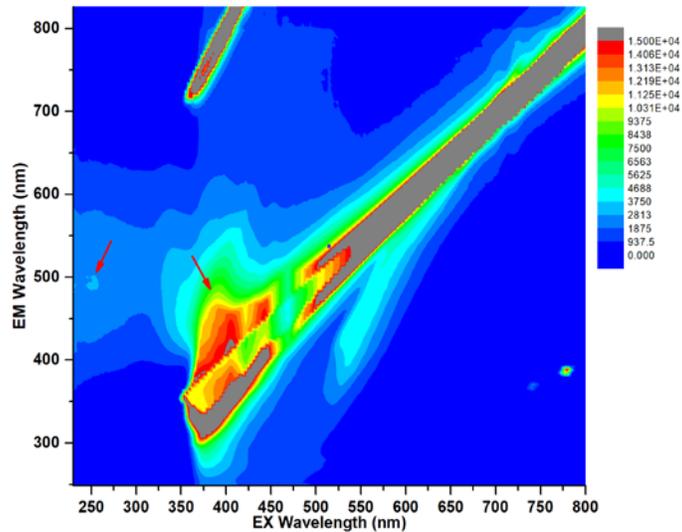


Figure 4. PL map collected on the as-prepared MWNT/PEEK nanocomposite.

The PL map for the MWNT/PEEK nanocomposite film is plotted in Figure 4. The two labelled emission peak areas with red arrows present the fluorescence signals. The peak area at longer excitation wavelength could be assigned to PEEK [18] but there are few report on PEEK PL study, and moreover, much stronger signals are observed here on the Pos. 1 of the MWNT/PEEK film compared to the other positions (Figure 3).

What is more interesting is the labelled peak area at shorter wavelength. The underlying mechanism for the formation of this peak area is unclear. No such peak has been detected for pure PEEK so far, while MWNTs, due to their complex multilayer structure, have never been shown to produce PL peaks. Therefore, further investigation needs to be carried out to study the underlying mechanism of this phenomenon.

Here, to explain the significant PL effects, a hypothesis is proposed. The MWNT/PEEK nanocomposite thin film holds unique composite structure - that individualized MWNTs are embedded within the PEEK polymer of low crystallinity. Due to the fine dispersion, even at nanoscale, MWNTs are separated from each and fail to form a conducting network for electron channelling, and PEEK is intrinsically electrically insulating. Therefore, the excited electrons and holes cannot be conducted away or filled out but localized possibly within one MWNT, that leaves energy to be relaxed only in the way of emitting light, despite the possible quenching from internanotube interaction. The electrical conductivity of the nanocomposite film ( $\sim 100,000 \Omega \cdot \text{cm}$  at 10kHz) falls within the semiconductor range, which further supports this hypothesis.

## Conclusions

Conclusively, dispersion of MWNTs in PEEK polymer matrix is obtained such that the MWNTs are individualized and separated from each other. Due to the individualized MWNTs in PEEK, electron channelling is blocked, leading to the semi-conducting feature of the as-prepared MWNT/PEEK nanocomposite film. Hypothesis of the localization of electrons/holes has been proposed to explain the unusual PL effects of the MWNTs/PEEK.

## References

- [1] Jia Chen, Vasili Perebeinos, Marcus Freitag, James Tsang, Qiang Fu, Jie Liu, and Phaedon Avouris, Bright Infrared Emission from Electrically Induced Excitons in Carbon Nanotubes, *Science*, **18**, 2005, pp. 1171-1174
- [2] Paul W. Barone, Seunghyun Baik, Daniel A. Heller and Michael S. Strano, Near-infrared optical sensors based on single-walled carbon nanotubes, *Nature Materials*, **4**, 2005, pp. 86-92.
- [3] Sang-Yong Ju, William P. Kopcha and Fotios Papadimitrakopoulos, Brightly fluorescent single-walled carbon nanotubes via an oxygen-excluding surfactant organization, *Science*, **323**, 2009, pp. 1319-1323.
- [4] Konstantin Iakoubovskii, Nobutsugu Minami, Yeji Kim, Kanae Miyashita, Said Kazaoui, and Balakrishnan Nalini, Midgap luminescence centers in single-wall carbon nanotubes created by ultraviolet illumination, *Appl. Phys. Lett.*, **89**, 2006, pp. 173108

- [5] Konstantin Iakoubovskii, Nobutsugu Minami, Said Kazaoui, Taro Ueno, Yasumitsu Miyata, Kazuhiro Yanagi, Hiromichi Kataura, Satoshi Ohshima, and Takeshi Saito, IR-Extended Photoluminescence Mapping of Single-Wall and Double-Wall Carbon Nanotubes, *Journal of Physical Chemistry B*, **110**, 2006, pp. 17420-17424.
- [6] Konstantin Iakoubovskii, Nobutsugu Minami, Taro Ueno, Said Kazaoui, and Hiromichi Kataura, Optical Characterization of Double-wall Carbon Nanotubes: Evidence for Inner Tube Shielding, *Journal of Physical Chemistry C*, **112**, 2008, pp. 11194-11198.
- [7] Hongsong Wang, Guibin Wang, Wenlei Li, Qitong Wang, Wei Wei, Zhenhua Jiang and Shuling Zhang, A material with high electromagnetic radiation shielding effectiveness fabricated using multi-walled carbon nanotubes wrapped with poly(ether sulfone) in a poly(ether ether ketone) matrix, *Journal of Materials Chemistry*, **22**, 2012, pp. 21232-21237.
- [8] Ana M. Díez-Pascual, Mohammed Naffakh, Marián A. Gómez, Carlos Marco, Gary Ellis, Teresa M. Martínez, Alejandro Ansón, José M. González-Domínguez, Yadienka Martínez-Rubi, Benoit Simard, Development and characterization of PEEK/carbon nanotube composites, *Carbon*, **47**, 2009, pp. 3079-3090.
- [9] Mohammed Naffakh, Ana M. Díez-Pascual and Marián A. Gómez-Fatou, New hybrid nanocomposites containing carbon nanotubes, inorganic fullerene-like WS<sub>2</sub> nanoparticles and poly(ether ether ketone) (PEEK). *Journal of Materials Chemistry*, **21**, 2011, pp. 7425-7433.
- [10] J.R. Atkinson, J.N. Hay, M.J. Jenkins, Enthalpic relaxation in semi-crystalline PEEK, *Polymer*, **43**, 2002, pp. 731-735.
- [11] Maureen Reitman, David Jaekel, Ryan Siskey, Steven M. Kurtz, *Morphology and Crystalline Architecture of Polyaryletherketones*, PEEK Biomaterials Handbook, William Andrew Applied Science Publisher, Chapter 4, 2012.
- [12] J.N. Hay, J.I. Langford, J.R. Lloyd, Variation in unit cell parameters of aromatic polymers with crystallization temperature, *Polymer*, **30**, 1989, pp. 489-493.
- [13] Bao-Ku Zhu, Shu-Hui Xie, Zhi-Kang Xu, You-Yi Xu, Preparation and properties of the polyimide/multi-walled carbon nanotubes (MWNTs) nanocomposites, *Composites Science and Technology*, **66**, 2006, pp. 548-554.
- [14] J.C. Seferis, Polyetheretherketone (PEEK) processing structure and properties studies for a matrix in high performance composites, *Polymer Composites*, **7**, 1986, pp. 158-169.
- [15] Chris N. Velisaris, James C. Seferis, Crystallization kinetics of polyetheretherketone (PEEK) matrices, *Polymer Engineering and Science*, **26**, 1986, pp. 1574-1581.
- [16] B.H. Stuart, A Fourier transform Raman spectroscopy study of the crystallisation behaviour of a poly(ether ether ketone)/poly(ether sulphone) blend, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **53**, 1997, pp. 107-110.
- [17] PingHeng Tan, Long An, LuQi Liu, ZhiXin Guo, Richard Czerw, David L. Carroll, Pulickel M. Ajayan, Nai Zhang, and HongLi Guo, Probing the phonon dispersion relations of graphite from the double-resonance process of Stokes and anti-Stokes Raman scatterings in multiwalled carbon nanotubes, *Physical Review B*, **66**, 2002, pp. 245410.

[18] Jasmin Althaus, Celestino Padeste, Joachim Köser, Uwe Piele, Kirsten Peters, Bert Müller, Nanostructuring polyetheretherketone for medical implants, *European Journal of Nanomedicine*, **4**, 2012, pp. 7-15.