Porphyrin-functionalized Single-walled Nanotubes solution for DMMP detection

Hou Changjun[a]*, Dong Jiale[b], Huo Danqun[b], Ren Guixiang[b], Luo Wei[a], Duan Yujuan[b]

(a. College of Chemistry and Chemical engineering / Key Laboratory of Optoelectronic Technology and Systems of Ministry of Education, Chongqing University, 400030, China; b. Bioengineering College of Chongqing University, 400030, China)

***Abstract*-A novel material of porphyrin functionalized Single-walled Nanotubes was employed on optical property research, aimed to DMMP detection, a simulant to Sarin. The composites were synthesis by condensation Zn-Tetraphenylporphyrin and bonding on SWNTs with non-covalent methods. The results were well characterized with TEM, AFM, as well as UV-visible measurements, demonstrated the diameter of nanotubes we used was estimated to range ~0.9-1.5nm, and the existence of nano-composites. It proved that with using porphyrin- functionalized single-walled carbon nanotubes in DMF solution, the materials were reversible and capable of detecting DMMP (Sigma, 97%) at 9 ppb levels by UV-visible measurements.**

***Keywords*- Single-walled Nanotubes, porphyrin-functionalized, DMMP detection, photophysical application.**

I. INTRODUCTION

Since the first finding in 1991, due to their unique structural and electronic properties, carbon nanotubes have attracted much attention in various fields of nanoscience and nanotechnology. Considerable attention has been focused in the preparation of soluble carbon nanptubes that would find many applications in fundamental and practical research fields. Many previous works used the electronic properties of nanotubes to detect chemical vapor [1-4], including Nitrogen, Amminia, Benzene, even DMMP (dimethylmethylphos- phonate) and DIMP (Diisopropylmethylphosponate). The high surface-to-volume ratio of nanotubes makes chemical phenomena intrinsically surface-related and suggests the value of working with well-characterized samples under controlled conditions [5]. Furthermore, contamination by atmospheric species (e.g., H_2O and O_2) is important to the electronic properties of SWNTs [6]. But the photic properties of nanotubes always be neglected, which won't be influenced by atmospheric molecular contamination. So it is possible for us to model a new, highly sensitive material to detect DMMP (dimethylmethylphosphonate) with a novel method.

Porphyrins, which are functional dyes with a variety of unique chemical, photophysical and biological properties, adsorb strongly on graphite surfaces. The strategies for incorporating light absorbing antennachromophores into SWNTS include both non-covalent [7-9] and covalent [10-12] methods. The fluorescence quenching would be derived from efficient energy transfer from Porphyrins to the nanotubes in both of these methods [7, 10]. However, much of this work has used vibrational spectroscopy (either infrared (IR) or Raman) as the most suitable technique for identifying functional groups and has focused on samples prepared in liquid media and handled in ambient air [5]. The purpose of our present work is to evaluate a method for performing UV-visible studies of adsorption on SWNTs, which is sensitive to DMMP by using the photophysical properties of porphyrins, we provided a novel but simple method, which is highly sensitive on DMMP detection by performing UV-visible studies of the porphyrins adsorption on SWNTs.

In our present work, we can use porphyrin-functionalized single-walled carbon nanotubes in DMF solution to detect DMMP (Sigma, 97%). The DMMP molecules are superimposed on a broad, smoothly varying background of SWNT, improve the concentrations of DMMP around the nanotubes in a micro environment, and these systems are capable of detecting DMMP as low as 1 ppb concertration levels. The results were fully characterized with TEM, AFM,

978-1-4244-1573-1/08/$25.00 ⓒ 2008 IEEE

as well as UV-visible measurements. In our research shows a great potential of a kind material in chemical agent detecting, and also suggests the potential of photophysical application of nanotubes.

II. EXPERIMENTAL DETAILS

The purification procedure of SWNTs (5-15 μ m in length and < 2nm in diameter, Shenzhen Nanotech Port Co., Ltd, China) was described elsewhere [13]. Briefly, SWNTs (0.1 g) were treated with concentrated HNO_3, and kept boiling for 2h, to remove metal catalysts and amorphous carbon. At the same time, the acid treatment cuts SWNTs to yield shortened SWNTs, which has carboxy groups at the open ends and defect sites. The carboxy groups at the terminals and the defect sites are used to attach Zn-porphyrins. Then it was filtered using a membrane filter (0.22 μ m) and washed with ultrapure water (S.A.S 67120 Millipore(Shanghai) Co., China) until the PH equaled to 7.0, then heated at 80℃ to obtain purified SWNTs (refer to as p-SWNTs).

Tetraphenyl porphyrin (TPP) was synthesized and purified as previous published procedures [14, 15]. Zn- porphyrins (ZnTPP) was accomplished in briefly: adding 30 mg TPP in 30 ml N, N- dimethylformamide (DMF), injecting nitrogen gas, heating under reflux for 30 min, extracting with chloroform and ultrapure water for three times, treating chloroform by reduced pressure distillation with natrii sulfas exsiccatus, using chromatographic method to purify the ZnTPP with chloroform and chloroform- ethanol (v/v=10:1) as eluting reagent for the first and second time.

The p-SWNTs (5 mg) was add into 0.1 mM solution of Znic-porphyrin in DMF (50 ml), sonicated with a KQ-50E ultrasonic cleaner (Kunshan Sonicator Instrument Co., Ltd., China) for 1h at room temperature, followed by centrifugation (Anke LXJ-ⅡB centrifuge, Shanghai Tocan Tech. Co. Ltd., China) of the suspension for 20 min to remove insoluble nanotubes, the product refered to as ZnTPP- SWNTs- DMF, as shown in figure 1[16].

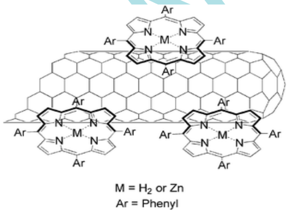

Fig. 1. Representation of SWNT/porphyrin nanohybrids

Touching-mode atomic force microscopy (CSPM5000 AFM, Ben Yuan Ltd., China) and transmission electron microscopy (Tecnai-10 TEM，Philips Co., Ltd., Holland) was used to further characterize the porphyrin-functionalized SWNTs. Dilute solutions of ZnTPP- SWNTs- DMF were dropped on to freshly cleaved mica and directly imaged to reveal a significant amount of ZnTPP functionalized SWNTs. TEM images were obtained at 100 kV, a grid was immersed in the ZnTPP- SWNTs- DMF solution for 10 min, and a minute amount of the solution remaining on grid was soaked with a filter paper, followed drying in a culture dish. UV-visible measurements were carried out with a Unico UV-2100 spectrophotometer (UNICO (Shanghai) Instrument Co., Ltd., China). All regents were of analytical grade and were used as received from the suppliers without further purified.

III. RESULTS AND DISCUSSION

The AFM image of the ZnTPP functionalized SWNTs dropped onto mica from DMF solution was shown in figure 2, proved that the tubes were 0.5 μ m- 2 μ m in length and 0.8-8.4 nm in height. The result means that most of the nanotubes observed were not single SWNT but a bundle of SWNTs. But the height of A, B, C in right figure was 0.83nm, 2.10 nm and 1.46nm, and the thickness of porphyrin ring is about 0.3nm, so the typical porphyrin functionalized nanotube diameter was estimated to range ~1.2-1.8nm, the nanotube diameter was estimated to range ~0.9-1.5nm. At the same time, free porphyrin molecules were found in the scanned area, and they may contribute the absorption of porphyrin functionalized SWNTs in liquid state. And Langmuir adsorption isotherm formula may be useful here.

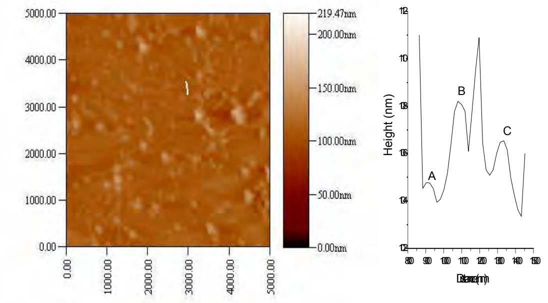

Fig. 2. AFM image of the ZnTPP functionalized SWNTs

With the help of conventional transmission electron microscopy the presence of SWNTs was further corroborated. A representative TEM image (Fig.3) of ZnTPP- SWNTs- DMF is shown, which reveals the existence of porphyrin- nanotube nanocomposites, while the unreacted acid groups and the damages caused due to functionalization may also contribute the existence of this systematic material, it more likely due to the existence of attached porphyrins as observed in other similar reported materials of functionlized SWNTs [9-11].

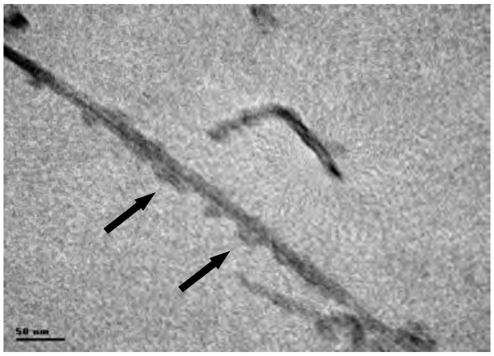

Fig. 3. TEM image of ZnTPP- SWNTs- DMF solution

The chemical formula [4] of the simulants DMMP (dimethylmethylphosphonate) and their corresponding nerve agent sarin (methylphosphonofluoridicacid, 1-methylethyl ester) are shown in figure 4. In our work we have evaluated the detection capabilities of porphyrin functionalized SWNTs toward the nerve agent simulants DMMP.

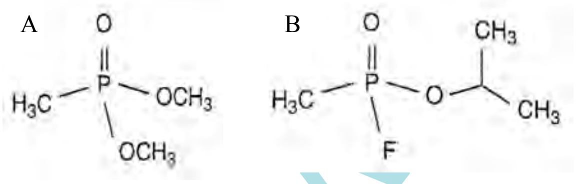

Fig. 4. Chemical structures of the nerve agents (A) DMMP (dimethylmethylphosphonate) and (B) sarin (methylphosphonofluoridicacid, 1-methylethyl ester).

The figure 5 shows the spectral change of ZnTPP- SWNTs- DMF membrane with adding 9 ppm DMMP (room temperature). We droped certain solution on glass,and dry, then adding a certain concentration DMMP. Before and after adding DMMP, the absorbance reduced 0.117, about 47.9% lose. The result proved that ZnTPP- SWNTs- DMF solution was sensitive to DMMP at a low concentration. The peak position was 433nm, a red shift happened without adding any acid, showed that protonation of the porphyrin molecule exist in the solution. In our opinions, The DMMP molecules are superimposed on the broad, smoothly varying background of SWNT improved the concentrations around the nanotubes in a micro environment.

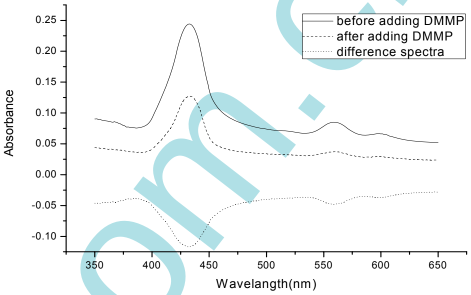

Fig. 5. Spectral change of ZnTPP- SWNTs- DMF film with adding 9 ppm DMMP

Figure 6 displays the absorbance changes with adding different concentration DMMP at room temperature, the absorbance decreased following with the concentration of DMMP reducing, the detection limit as low as 9 ppt. Inset represents a part of spectrum from 415nm-435nm (A), and the change of peak value(B). The absorbance reduced 0.051 at least, and it was an evident change compare with conventional materials at low concentration. The red shift was remained in this figure (the peak value is 425nm), but the position was different from figure 5. The protonation of ZnTPP- SWNTs- DMF solution may be due to something unknown at present stage. But previous work of Silvia Giordani group studied the similar questions [17], they reported the spectroscopic changes of porphyrin (tetraphenylporphyrin) functionalized SWNTs in a different chlorinated solvents such as chloroform, dichloroethane and dichlorobenzene upon sonication, they thought an enormous amount of acid was generated by sonication, the rate of porphyrin protonation was increased by the presence of carbon nanotube.

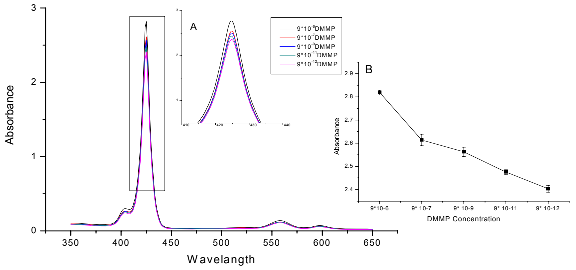

Fig. 6. Absorbance changes with adding different concentration DMMP. Inset (A) represents a part of spectrum from 415nm-435nm. Inset (B) represents the change of peak value.

In general SWNTs are excellent electron acceptors for its huge π-electron system and high electron affinity, and different linkages have shown strong impact to the porphyrin energy transfer mechanism. And porphyrin is well known for its excellent optical properties in natural photosynthesis systems as well as in artifical photovoltaic devices [10]. Efficient energy transfer from Porphyrins to the nanotubes had derived from the fluorescence quenching in previous works, though the detail of the interaction of the porphyrin and nanotubes at molecule level is unknown at present stage, the π - π bond and van der Waals interaction seem to be key features for physical adsorption of porphyrins onto the side wall of nanotubes.

IV. CONCLUSION

The unique properties of the porphyrin functionalized SWNTs lead to excellent optical and electrical characteristics in the solution. These results of key influence factors include sensitivity, detection limits and others provide a potential material for low concentration levels DMMP detection that would be different or impossible to achieve with conventional materials. After all, this project is expected not only to develop the study of nanotubes new application, integration of new methods and mechanisms in DMMP detection, but also promote the research, the development of new sensing materials and new mechanisms. Meanwhile, this work particularly has wide application potential on chemical agent detection, foodsafety, public health, etc., and it is valuable in theoretical approach and engineering technology at the same time.

ACKNOWLEDGMENT

We gratefully acknowledge financial support from Tech Research and Development Program of China (“863” Program, # 2006AA04z349), National Natural Science Foundation (# 30770568), and Chongqing Natural Science Foundation (# 2006BB7005) of China.

REFERENCES

[1] E.S. Snow, F.K. Perkins, E.J. Houser, et al, “Chemical Detection with a Single-Walled Carbon Nanotube Capacitor”. *Science*, 2005, vol. 307, pp. 1942-1945.

[2] Ashish Modi, Nikhil Koratkar, Eric Lass, et al, “Miniaturized gas ionization sensors using carbon nanotubes”. *Nature*, 2003, vol. 424, pp. 171-174.

[3] Kyle Cattanach, Rashmi D Kulkarni,Mikhail Kozlov, et al, “Flexible carbon nanotube sensors for nerve agent simulants”. *Nanotechnology*, 2006, vol. 17, pp. 4123-4128.

[4] A.R. Hopkins and N.S. Lewis, “Detection and Classification Characteristics of Arrays of Carbon Black/Organic Polymer Composite Chemiresistive Vapor Detectors for the Nerve Agent Simulants Dimethylmethylphosphonate and Diisopropylmethyl-phosponate”. *Anal. Chem*., 2001, vol. 73, pp. 884-892.

[5] V.M. Bermudez, “Adsorption on Carbon Nanotubes Studied Using Polarization-Modulated Infrared Reflection-Absorption Spectroscopy”. *J. Phys. Chem. B,* 2005, vol. 109, pp. 9970-9979.

[6] A. Goldoni, R. Larciprete, L. Petaccia, et al, “Single-wall carbon nanotube. interaction with gases: Sample contaminants and environmental monitoring”. *J. Am. Chem. Soc.*, 2003, vol. 125, pp. 11329-11333.

[7] Hiroto Murakami, Takuro Nomura, and Naotoshi Nakashima, “Noncovalent porphyrin- functionalized single-walled carbon nanotubes in solution and the formation of porphyrin- nanotube nanocomposites”. *Chemical Physics Letters*, 2003, vol. 378, pp. 481-485.

[8] L. Valentini, M. Trentini, F. Mengoni, et al, “Synthesis and photoelectrical properties of carbon nanotube–dendritic porphyrin light harvesting molecule systems”. *Diamond & Related Materials*, 2007, vol. 16, pp. 658-663.

[9] Akiharu Satake, Yoshiyuki Miyajima, and Yoshiaki Kobuke, “Porphyrin-Carbon Nanotube Composites Formed by Noncovalent

Polymer Wrapping". *Chem. Mater.,* 2005, vol. 17, pp. 716-724.

[10] Dongmei Ren, Zhen Guo, Feng Du, et al, "A Nanohybrid Material of SWNTs Covalently Functionalized with Porphyrin for Light Harvesting Antenna: Synthesis and Photophysical Properties". *Journal of Nanoscience and Nanotechnology,* 2007, vol. 7, pp. 1-7.

[11] Fuyong Cheng and Alex Adronov, "Suzuki Coupling Reactions for the Surface Functionalization of Single-Walled Carbon Nanotubes". *Chem. Mater.*, 2006, vol. 18, pp. 5389-5391.

[12] Tomokazu Umeyama, Mitsuru Fujita, Hiroshi Imahori, et al. "Electrophoretic Deposition of Single-Walled Carbon Nanotubes Covalently Modified with Bulky Porphyrins on Nanostructured SnO2 Electrodes for Photoelectrochemical Devices". *J. Phys. Chem. C,* 2007, vol. 111, pp. 11484- 11493.

[13] Jie Liu, A.G. Rinzler, Hongjie Dai, et al, "Fullerene Pipes". *Science*, 1998, vol. 280, pp.1253-1256.

[14] A.D. Adler, F.R. Longo and W.J. Shergalis. "Preliminary Studies on meso-Tetraphenylporphin". *J. Am. Chem. Soc.*, 1964, vol. 86, pp. 3145-3149.

[15] A.D. Adler, F.R. Longo, J.D. Finarelli, et al, "A Simplified Synthesis for meso- tetraphenylporphyrin". *J. Org. Chem.*, 1967, vol. 32, pp.476.

[16] G.M. Aminur Rahman, Dirk M. Guldi, Stéphane Campidelli, et al, "Electronically interacting single wall carbon nanotube–porphyrin nanohybrids". *J. Mater. Chem.*, 2006, vol. 16, pp. 62-65.

[17] E'imhin M. Ni Mhuircheartaigh, Werner J. Blau, Silvia Giordani, et al, "Spectroscopic changes induced by sonication of porphyrin–carbon nanotube composites in chlorinated solvents". *Carbon*, 2007, vol. 45, pp. 2665-2671.