

## Synthesis of Methane in Nanotube Channels by a Flash

Deng-Zhu Guo,<sup>\*,†</sup> Zeng-Quan Xue,<sup>†</sup> Qi Chen,<sup>†</sup> Geng-Min Zhang,<sup>†</sup> Zhao-Xiang Zhang,<sup>†</sup> and Zhen-Nan Gu<sup>‡</sup>

Key Laboratory for Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, China, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received September 25, 2006; E-mail: guodz@pku.edu.cn

Recent discoveries of ignition and reconstruction of nanostructured materials such as catalyst-containing single-walled carbon nanotubes (raw SWNTs),<sup>1–3</sup> silicon nanowires,<sup>4</sup> and polyaniline nanofibers<sup>5</sup> by exposing to a camera flashlight have suggested that nanomaterials could enormously absorb visible-light photons and instantly release huge energy in local spots. More recently, Manaa et al. reported that raw SWNTs could be used as optical ignition and initiation materials of explosives,<sup>6</sup> and we also demonstrated that water confined in the channels of SWNTs could be photolyzed to form hydrogen-rich gases.<sup>7</sup> Here we will give a further investigation of the methane synthesis in the channels of SWNTs under a visible-light exposure, demonstrating a new possible origin of methane, which is one of the most important starting materials for the primordial life.

In general, natural methane is largely formed by the thermal decomposition of organic matter or by microbial processes,<sup>8</sup> both of which could be named as biogenic methane origin. It is also well-known that methane can be synthesized from inorganic carbon sources such as CO and CO<sub>2</sub> gases by hydrogen reduction on catalyst surfaces under high pressure (tens of MPa) and high temperature (hundreds of celsius degree) conditions, famed as Fischer–Tropsch (FT) synthesis.<sup>9</sup> In recent years, some geophysical discoveries also provided evidence of the occurrence of an abiogenic (inorganic) source of methane synthesized from mineral water interaction in the ocean bed.<sup>10–12</sup> Moreover, methane has been discovered in the atmosphere of the planet Mars<sup>13</sup> and Saturn's largest moon, Titan,<sup>14</sup> leading to a much more complicated understanding of the methane origin.<sup>15</sup> Our results presented here will show that methane can be inorganically synthesized at room temperature even in an ultrahigh vacuum (UHV) environment, providing an alternative explanation of abiogenic methane origin and, moreover, implying a novel possibility of prebiotic hydrocarbons photosynthesized from inorganic materials.

The experiments were carried out in a conventional metallic UHV system, mainly pumped with a sputter-ion pump (Figure 1). The total and partial pressure of the UHV chamber was measured with a B-A gauge and a quadrupole mass spectrometer (QMS, Inficon Transpector 2-H200M), respectively. A glass chamber containing ~17 mg of SWNT raw materials (homemade) was connected to the UHV chamber through a valve. The SWNT sample was synthesized by using a DC arc discharge method with Ni–Y particles as the catalyst,<sup>16</sup> without any post-treatment. After sufficient heating and evacuating, an ultrahigh vacuum ( $P < 5 \times 10^{-7}$  Pa) was achieved in both chambers. Then, under room temperature, the SWNT sample was exposed to a conventional photographic flash (0.1–0.2 J/cm<sup>2</sup>, ~8 ms) from the outside of the glass chamber when the valve was closed. The released gases were then sampled through the valve and analyzed by using the

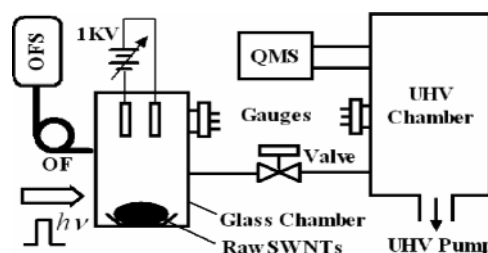


Figure 1. Schematic of the experimental setup.

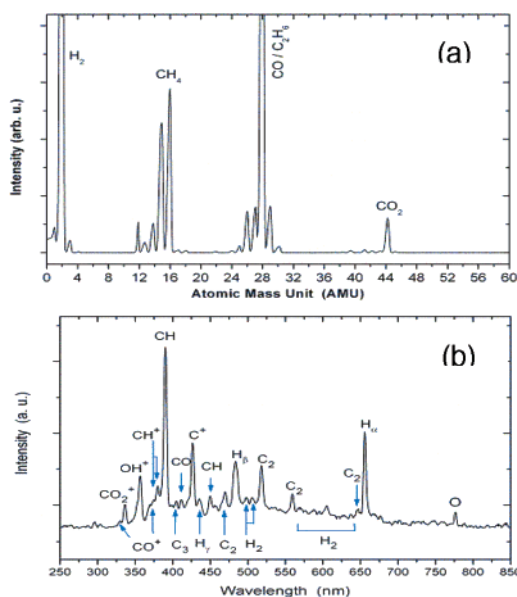


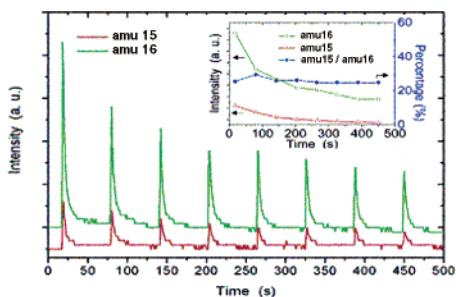
Figure 2. Analysis of the gases released from the flash-irradiated raw SWNTs: (a) a typical mass spectrum (the base data obtained before sampling have been subtracted); (b) an optical emission spectrum under DC discharge. Note the amu 15 and 16 peaks in (a) and CH peaks in (b).

QMS. For verification, an optical fiber spectrometer (OFS, Ocean Optics, HR-4000) was also used to detect the emission light from the glass chamber when the accumulated gases were discharged between two electrodes (5 mm spacing) under 0.8–1 kV DC voltage. For a comparison purpose, we also used ~25 mg of graphite powder (~20 μm in diameter) containing the same catalyst (Ni–Y particles) and the catalyst-removed SWNTs, respectively, as the sample to do the same experiments described above.

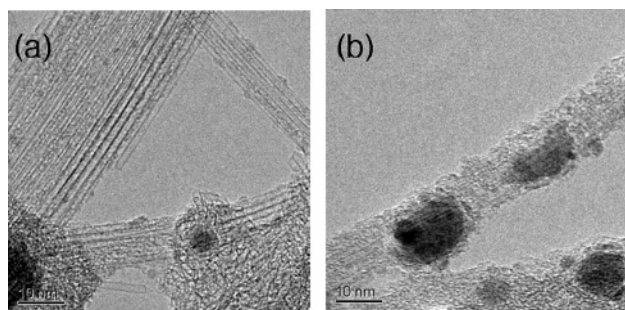
After the pulsed-light exposure, a sharp increase of the total pressure (within 1 s, up to tens of Pa) in the glass chamber was observed. A typical mass spectrum obtained with the QMS was shown in Figure 2a; here the base data collected before sampling have been subtracted. The peaks at atomic mass unit (amu) 15 and 16 could generally be seen as the existing evidence of methane, corresponding to CH<sub>3</sub><sup>+</sup> and CH<sub>4</sub><sup>+</sup>, respectively. We noted that the

<sup>†</sup> Department of Electronics.

<sup>‡</sup> College of Chemistry and Molecular Engineering.



**Figure 3.** Signals of amu 15 and 16 versus time when the raw SWNTs were flashed in consequence. Inset: signal intensities and their ratios.



**Figure 4.** TEM images of the raw SWNT sample before (a) and after (b) the fast light exposure experiment.

peak-height ratio ( $PH_{amu15}/PH_{amu16} \sim 80\%$ ) is in good agreement with the standard QMS data of methane.<sup>17</sup> In order to exclude the other possibilities ( $NH^+$ ,  $NH_2^+$ , etc.) of the peaks at amu 15 and 16, an optical emission spectrum (OES) was also shown in Figure 2b, in which a distinct peak at 390 nm of CH radicals can be seen, with other CH and  $CH^+$  peaks as labeled.<sup>18</sup> However, no peaks about  $NH^+$  and  $NH_2^+$  were observed. These results definitely indicate that methane has been released from the raw SWNT sample after a fast light exposure.

In order to investigate the reproducibility of the methane production, we irradiated the sample in sequence with the same light when the valve was slightly opened and recorded the ion-current data with the QMS, which worked in the “two-ions” mode; that is, only the amu 15 or 16 signal was recorded quickly (Figure 3). With flash irradiation, ion-current peaks immediately appear and then attenuate to the base value due to the pump. The inset in Figure 3 shows the intensities of amu 15 and 16 peaks and their ratios versus time. We found that the production of methane is decreasingly reproducible in several 10-folds, owing to the approximately constant peak-height ratios (here the ratios are 25–30%, lower than the reference data<sup>17</sup> due to the special working mode of QMS we adopted).

The transmission electron microscope (TEM) images of the sample before and after the experiments are shown in Figure 4a and b, respectively. We found that the original sample mainly consists of SWNT bundles and some nanoparticles. The surface of the bundles is clearly formed with SWNTs. However, after the experiments, the bundle surface seems amorphous. Moreover, some exfoliated carbon patches are also observed.

The comparison experiments showed that nearly no methane signals could be detected with the micro-graphite-catalyst sample and the catalyst-removed SWNT sample. We also did the experiment with water-containing raw SWNTs by inputting saturated water vapor before pumping UHV and found that the methane signal (and the other gas signals) enhanced considerably.

On the basis of the above experimental results, the mechanism involved in this discovery could be tentatively discussed. First, the

C and H sources should be clarified. In the raw SWNT sample, there are many carbon nanoparticles accompanying the SWNTs, both of which could possibly provide active C atoms once they are irradiated. As for hydrogen, it might come either from the adsorbed hydrogen existing in the residual atmosphere of the UHV system or from the photolyzed hydrogen from the adsorbed water confined within the channels of the SWNTs (the water adsorbed on the outside surfaces has been mostly removed during the heating–pumping process). Second, taking into account the unprecedented photothermal effect of nanomaterials and observing locally in one nanotube a catalyst particle residing on its end, one can imagine that, under a flash irradiation, the local instant temperature of the nanotube and the catalyst would be dramatically increased, releasing some free C and H atoms in the nanotube, so that a local instant high-pressure environment could also be formed. Such a scenario means that all the necessary conditions in the FT synthesis,<sup>9</sup> namely, free C and H atoms, magnetic catalyst, high temperature, and high pressure, all are possibly ready for the generation of methane. However, for the two comparison experiments, one has difficulty forming a local high-pressure environment and the other lacks catalyst, so there is nearly no methane signal detected.

We conclude that methane can be synthesized in the channels of raw SWNTs even under the UHV and room temperature conditions. The keys of such a process are the ultra-photothermal effect of nanomaterials, the existence of the catalyst nanoparticles, and the confinement of hydrogen-containing adsorbates in the SWNT channels, supposing the FT mechanism holds true. Our results provide a special example of the transformation of inorganic materials into simple organic molecules just with visible light as the input energy.

**Acknowledgment.** D.Z.G. thanks Dr. M. S. Wang and Prof. S. M. Hou for technical help. This work was supported by the NSFC (Grant Nos. 60231010, 60471008, and 60571003).

**Supporting Information Available:** Comparison of experimental results, more TEM images, and complete ref 14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Ajayan, P. M.; Terrones, M.; de la Guardia, A.; Huc, V.; Grobert, N.; Wei, B. Q.; Lezec, H.; Ramanath, G.; Ebbesen, T. W. *Science* **2002**, *296*, 705.
- (2) Smits, J.; Wincheski, B.; Namkung, M.; Crooks, R.; Louie, R. *Mater. Sci. Eng. A* **2003**, *358*, 384.
- (3) Braidy, N.; Botton, G. A.; Adronov, A. *Nano Lett.* **2002**, *2*, 1277.
- (4) Wang, N.; Yao, B. D.; Chan, Y. F.; Zhang, X. Y. *Nano Lett.* **2003**, *3*, 475.
- (5) Huang, J.; Kaner, R. B. *Nat. Mater.* **2004**, *3*, 783.
- (6) Manaa, M. R.; Alexander, R.; Mitchell, A. R.; Garza, R. G.; Pagoria, P. F.; Bruce, E.; Watkins, B. E. *J. Am. Chem. Soc.* **2005**, *127*, 13786.
- (7) Guo, D. Z.; Zhang, G. M.; Zhang, Z. X.; Xue, Z. Q.; Gu, Z. N. *J. Phys. Chem. B* **2006**, *110*, 1571.
- (8) Lollar, B. S.; Westgate, T. D.; Ward, J. A.; Slater, G. F.; Lacrampe-Couloume, G. *Nature* **2002**, *416*, 522.
- (9) Gur, T. M.; Huggins, R. A. *Science* **1983**, *219*, 967.
- (10) Horita, J.; Berndt, M. E. *Science* **1999**, *285*, 1055.
- (11) Foustoukos, D. I.; Seyfried, W. E. *Science* **2004**, *304*, 1002.
- (12) Boetius, A. *Science* **2005**, *307*, 1420.
- (13) Formisano, V.; Atreya, S.; Encenaz, T.; Ignatiev, N.; Giuranna, M. *Science* **2004**, *306*, 1758.
- (14) Niemann, H. B.; et al. *Nature* **2005**, *438*, 779.
- (15) Krasnopolsky, V. A. *ICARUS* **2006**, *180*, 359.
- (16) Shi, Z. J.; Lian, Y. F.; Zhou, X. H.; Gu, Z. N.; Zhang, Y. G.; Iijima, S.; Zhou, L. X.; Yue, K. T.; Zhang, S. L. *Carbon* **1999**, *37*, 1449.
- (17) Kuentzel, L. E. *Index of Mass Spectral Data: Listed by Molecular Weight and the Four Strongest Peaks*, 1st ed.; ASTM Special Technical Publication No. 356: Philadelphia, PA, 1963, p 1.
- (18) Pearse, R. W. B.; Gaydon, A. G. *The Identification of Molecular Spectra*, 4th ed.; John Wiley & Sons Inc.: New York, 1976; pp 90–92.

JA066909K