Generation of hydrogen by splitting of water confined in carbon nanotubes with a camera flash

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Several characteristics of carbon nanotubes (CNTs) like their mechanical properties, viz. Young's modulus and tensile strength, field emission, possible storage of hydrogen in CNTs and others will have potential applications[1,2]. There is a controversy on the ability of CNTs to store and release hydrogen under reasonable conditions of temperature and pressure[3]. Since there are several reports on the use of these nanotubes in catalysis[4], it will be of general interest to explore the possibility of producing hydrogen from CNTs. The accidental, but astonishing observation that single-walled carbon nanotubes (SWNTs) can be ignited in air and reconstructed in air by exposure to light from a camera flash (usually emulates sunlight without ultraviolet light) at close range (several cm away from the sample) by Ajayan *et al.*[5] has actually kindled the study of influence of a camera flash on nanostructured materials. This unusual feature has been ascribed to photoacoustic effect with the nonradiative process responsible for producing heat that is confined to within the nanostructure giving rise to temperature of ~1500°C. While confirming Ajayan's observation, a series of simple experiments by Bockrath *et al.*[6] indicates that the photoacoustic effect and ignition are not peculiar to carbon nanotubes. The common features of materials that ignite are the combination of a well-dispersed metal catalyst in intimate contact with a high-surface area carbon. According to Ajayan *et al.*[7] it would also be crucial to test metal-free SWNTs; unfortunately, such samples can only be prepared by purification procedures that effectively densify the samples and, hence, remove the photo-induced effects. Si nanowires also, ignited in air, exhibited a large opto-acoustic effect when exposed to a conventional photographic flash[8]. Because of the enhanced photothermal effect, the microstructure of the Si nanowires was changed. Huang and Kaner[9] have demonstrated that under camera flash irradiation, polyaniline nanofibres 'melt' to form a smooth and continuous film from an originally random network of nanofibres. These authors have also reported that preliminary tests on polyaniline derivatives and other conducting polymers such as polypyrrole and polythiophene indicate that camera flash irradiation is capable of welding them when nanostructures smaller than 100 nm are present.

Ignition experiments carried out quite recently by Guo's group[10] with SWNT in an ultrahigh vacuum (UHV) chamber to confirm Ajayan's results, occasionally generated hydrogen and other gases. This was rather surprising as there was no source of hydrogen in their experiments. This observation and the already available literature on the influence of camera flash on nanostructured materials motivated Guo *et al.*[10] to study the possibility of splitting SWNT-confined water under a visible light flash.

When the sample chamber (V_s) containing water confined in SWNT at a pressure of 10^{-2} to 10^{-1} Pa was exposed to a photographic flash (0.1–0.2 J/cm^2, ~8 ms), the pressure jumped to ~12 Pa implying that some gases have been generated (Figure 1).

The results of the mass spectral analysis of the sample gases generated on irradiation of water confined in SWNTs are shown in Figure 2. While H_2 is the main constituent in the flash-generated gases, other components like He, CH_4, H_2O, CO, C_2H_6 and CO_2 were also present. From the results it is clear that production of H_2 in one flash reaches ~1.5 μmol (about 300 ppm of the mass of SWNTs and to 79.3 mol% of the total flash-generated gases). It has to be noted that the total mass yield of all

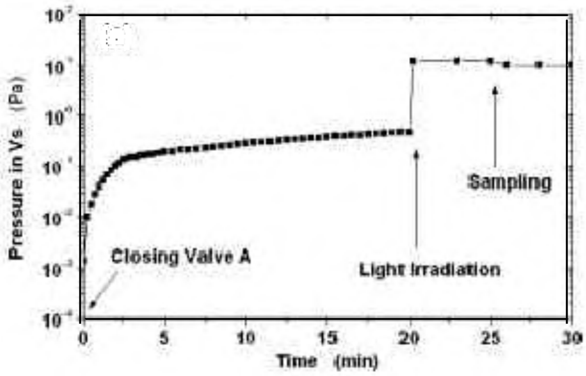

Figure 1. The total pressure in the V_s evolving with time. A step appears when the sample is irradiated with a camera flash (reproduced from ref. 10 with permission from D.-Z. Guo).

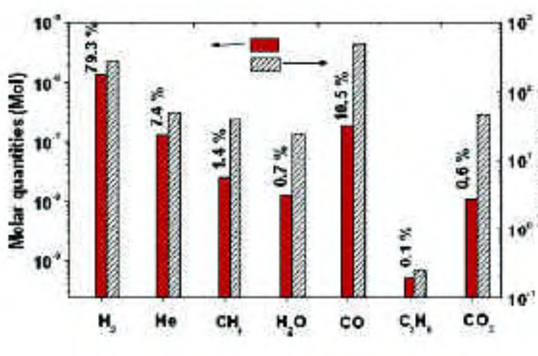

Figure 2. Quantitative estimation of the gas components generated from the water-containing SWNT in one flash irradiation (reproduced from ref. 10 with permission from D.-Z. Guo).

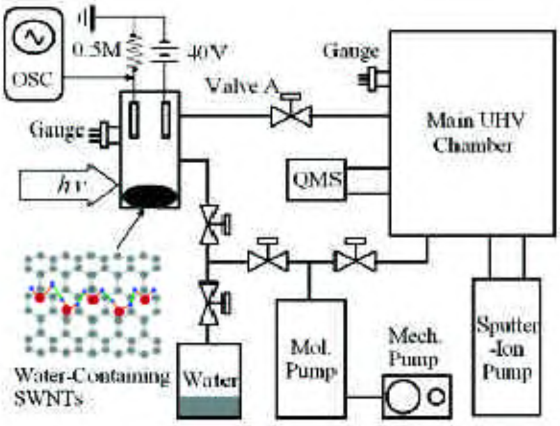

Figure 3. The experimental setup for the gas release and charge release from water-containing SWNTs under a visible light flash. The inset shows water-containing SWNT (reproduced from ref. 10 with permission from D.-Z. Guo).

of the gases in one flash reached about 900 ppm (0.09%) of the mass of the SWNT sample. When one takes into account that the time for the gas release is very short (<1 s), the yield is fairly high.

Guo *et al.*[10] also report that during a period of 1000 s, 20 irradiation flashes were carried out and the H_2 generated during this time comes to about 54 μmol. This quantity is comparable to the amount reported for the photoelectrochemical splitting of water[11].

A mechanism has also been suggested for the release of gases from water confined in SWNTs during a photographic flash. Due to the ultra-photothermal effect, the water molecule dissociates to hydrogen and oxygen atoms. 'The local pressure in nanotubes would dramatically increase, so a local explosion would occur in nanotubes, liberating some carbon atoms. As a result, H_2 and some C–H and C–O compounds as well as H_2O could be detected'[10]. It is not clear how He is formed, although it is involved in the synthesis of SWNT and needs further study.

That the generation of H_2 is manifested only by SWNT and not by any other forms of carbon has been demonstrated by extending the study to graphite. During camera flash on graphite powder mixed with Ni-Y catalysts in a similar experimental setup, the total gas yield is very low (<0.01%).

In their experimental setup, ~10 mg SWNT prepared by arc-discharge method with Ni-Y as the catalyst in He atmosphere was placed in a glass tube (sample container, V_s) and connected through valves to an UHV system and to a bottle containing distilled water (Figure 3). V_s could be evacuated using four-stage pumps and the sputter-ion pump through different valves and the pressure could be measured. For detecting charge emission, suitable gadgets like electrodes and digital oscilloscope have been attached to V_s. After heating at 180°C for about 24 h and evacuating, UHV ($P < 5 \times 10^{-7}$ Pa) was realized both in the V_s and in the main chamber which was attached to a qudrupole mass spectrometer (QMS). Water vapour (~3500 Pa) was introduced into V_s from the water bottle by closing the valve A. After 1 h, V_s was heated and evacuated. The sputter-ion pump was also stopped and the two chambers reached a quasi-stable state. Then the water confined SWNT sample was exposed to a photographic flash. The rapid rise of pressure in the V_s chamber was recorded with concomitant monitoring of the response of the oscilloscope. By slightly opening the valve A, the gas components were analysed by QMS.

Charge emission has also been occasionally observed during the camera flash and this possibly suggests that generation of plasma could accompany the gas release when water containing SWNTs was irradiated. The cause of this is yet to be understood. The work of Guo *et al.* has certainly ushered in a new source of hydrogen.

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