

Some Criteria for a Power Producing Thermonuclear Reactor

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Abstract. Calculations of the power balance in thermonuclear reactors operating under various idealized conditions are given. Two classes of reactor are considered: first, self-sustaining systems in which the charged reaction products are trapped and, secondly, pulsed systems in which all the reaction products escape so that energy must be supplied continuously during the pulse. It is found that not only must the temperature be sufficiently high, but also the reaction must be sustained long enough for a definite fraction of the fuel to be burnt.

§ 1. INTRODUCTION

IT has been widely conjectured that some form of controlled thermonuclear reactor, capable of producing a useful amount of power, will some day be constructed. In this paper the power balance in such a reactor is considered, and some criteria which have to be satisfied in a power producing system are derived.

Some of the difficulties of realizing a controlled fusion reaction have been discussed by Thirring (1955) and Thonemann (1956), and a broad survey of fundamentals has been given by Post (1956). The present treatment differs from that of Thirring in the assumptions about the radiation from a hot gas, and it covers in rather more detail some of the points discussed by Thonemann and Post. The analysis is based on simple assumptions; it is designed to illustrate the essential features of the problem, and is neither rigorous nor complete. The assumptions made are in all cases optimistic, so that the criteria established are certainly necessary, though by no means sufficient, for the successful operation of a thermonuclear reactor.

§ 2. BASIC PRINCIPLES

Of the exoergic reactions involving light nuclei those between the hydrogen isotopes (the so-called D-D and T-D reactions) are by far the most probable at low energies. Of these the T-D reaction has the higher cross section, but since tritium does not occur naturally it is necessary to use a system in which it can be bred. This may be done by capturing the neutrons emitted in the T-D reaction in ${}^6\text{Li}$, which then decays into T and ${}^4\text{He}$.

The reactions of interest are shown in table 1.

Table 1

Reaction	Q (mev)	σ_{\max} (barns)	σ_{\max} energy
${}^2\text{H}(\text{d}, \text{n}){}^3\text{He}$	3.3	0.09	2 mev
${}^2\text{H}(\text{d}, \text{p}){}^3\text{H}$	4.0	0.16	2 mev
${}^2\text{H}(\text{t}, \text{n}){}^4\text{He}$	17.6	5.0	150 kev
${}^6\text{Li}(\text{n}, \alpha){}^3\text{H}$	4.8	$1/v$ law	

The energy released per unit time and volume by thermonuclear reactions in a hot gas is given by

$$P_R = n_1 n_2 \bar{v}\sigma(T)E \quad \dots\dots(1)$$

where n_1 and n_2 are the number densities of the nuclei of the first and second kinds, and $\bar{v}\sigma(T)$ is the product of the relative velocities of the nuclei and the reaction cross section averaged over the Maxwellian velocity distribution corresponding to a temperature T , and E is the energy released by one reaction. If the ions are of the same kind (as in the D-D reaction) $n_1 n_2$ is replaced by $2(n/2)^2 = \frac{1}{2}n^2$. Values of $\bar{v}\sigma(T)$ calculated from published values of the cross sections for the D-D and T-D reactions are given in the companion paper by Thompson (1957).

Energy can be lost from the hot gas in two ways, by radiation and by conduction. At temperatures above about 10^6 degrees hydrogen is completely ionized and radiation occurs principally as bremsstrahlung (free-free transitions). The mean free path of such radiation is large (several g cm⁻²) and consequently in a reactor of controllable size virtually all of it would escape. The Stefan-Boltzmann T^4 law does not hold under these circumstances; the variation of intensity with temperature can only be found by a detailed study of the radiation process. The power radiated per unit volume in hydrogen is given by (Spitzer 1956)

$$P_B = 1.4 \times 10^{-34} n^2 T^{1/2} \text{ watts cm}^{-3}. \quad \dots\dots(2)$$

If the hot gas is in a magnetic field the electrons will move in spiral orbits, and additional radiation due to the acceleration towards the axis of the spiral will occur. This radiation is similar to that obtained from electrons in a betatron, and it may be important in very intense fields. It will, however, be neglected in this paper.

Conduction loss is difficult to treat in a general way, since it depends on the geometry of the system, its density and temperature distribution, and also the wall material. In the analysis which follows it is optimistically assumed that the conduction loss is zero.

It is of interest to see at what temperature the nuclear power release is equal to the radiated power. This may be called the 'critical temperature' and is the hypothetical temperature which would be needed for a self-sustaining system if all the radiation escaped but the reaction products were retained. The critical temperature is about 150 million degrees for the D-D reaction (assuming that the tritium is burnt as soon as it is formed, but that the ³He is not burnt), and 30 million degrees for the T-D reaction.

The critical temperature is a somewhat artificial concept; it does not mean that if a thermonuclear fuel is heated to this temperature a reaction will be set off in the way that a chemical explosion is set off, or that the fuel can be ignited as in a gas jet. This would only be true if the energy of the reaction were deposited close to where it was released, i.e. if the range of the reaction products were short compared with the dimensions of the apparatus. In fact, the range of the particles will almost certainly be large compared with the dimensions of the apparatus if the system is to be of controllable size, so that unless the tracks are somehow coiled up it will be the walls of the apparatus which are heated rather than the gas, and energy must be fed in continuously to sustain the reaction.

Various types of system will now be considered in a general way. No suggestions of how to realize them will be given.

§ 3. SYSTEMS IN WHICH THE REACTION PRODUCTS ARE RETAINED

It is not inconceivable that the charged reaction products could be contained in the hot gas by a suitable combination of electric and magnetic fields, though it seems unlikely that the escape of neutrons can be prevented. The temperature at which such a system would be self-sustaining in the absence of conduction loss can be calculated by equating the radiation loss to the energy carried by the charged disintegration products. This temperature is about 3×10^8 degrees for the D-D reaction, and 5×10^7 degrees for the T-D reaction. In the D-D system it is only just possible in principle to sustain the reaction, since above about 10^8 degrees the reaction rate increases with temperature only slightly faster than the radiation loss. At 10^9 degrees for example a conduction loss equal to the radiation loss is sufficient to quench the reaction.

As an example of the orders of magnitude involved, the slowing down range of the charged reaction products in a gas at 10^8 degrees and 10^4 atmospheres pressure ($n = 3 \times 10^{17}$ nuclei/cm³) is of the order of a kilometre. The range of the neutrons is hundreds of kilometres.

§ 4. SYSTEMS IN WHICH THE REACTION PRODUCTS ESCAPE

An alternative type of system in which the reaction products are not retained in the gas will now be considered. Since some specific proposals are for pulsed systems we shall consider the following idealized cycle: the gas is heated instantaneously to a temperature T , this temperature is maintained for a time t , after which the gas is allowed to cool. Conduction loss is neglected entirely, and it is assumed that the energy used to heat the gas and supply the radiation loss is regained as useful heat.

An important parameter R will now be introduced; this is the ratio of the energy released in the hot gas to the energy supplied. Now the energy released by the reaction appears as heat generated in the walls of the apparatus, and this has to be converted to electrical, mechanical or chemical energy before it can be fed back into the gas. If η is the efficiency with which this can be done, then the condition for a system with a net power gain is

$$\eta(R+1) > 1. \quad \dots\dots(3)$$

The maximum value of η is about $\frac{1}{3}$, so that R must be greater than 2.

For the pulsed cycle described above we have

$$R = \frac{tP_R}{tP_B + 3nkT} = \frac{P_R/3n^2kT}{P_B/3n^2kT + 1/nt} \quad \dots\dots(4)$$

where P_R and P_B are respectively the reaction power and radiated power per unit volume. The $3nkT$ term represents the energy required to heat the gas to a temperature T . Electron binding energies are neglected, but the contribution from electrons is included (this accounts for the factor 3 rather than $\frac{3}{2}$).

Since P_R and P_B are both proportional to n^2 , R is a function of T and nt . In figure 1 curves of R against T for various values of nt are shown for the D-D reaction assuming that the tritium formed is also burnt. (In practice the tritium would have to be collected and fed back into the system with the deuterium.) The line $R=2$ is shown dotted in the figure, and it is seen that for a useful reactor T must exceed 2×10^8 degrees and nt must exceed about 10^{16} . Thus, for a pulse of 1 microsecond duration, n must be greater than 10^{22} ; this corresponds to

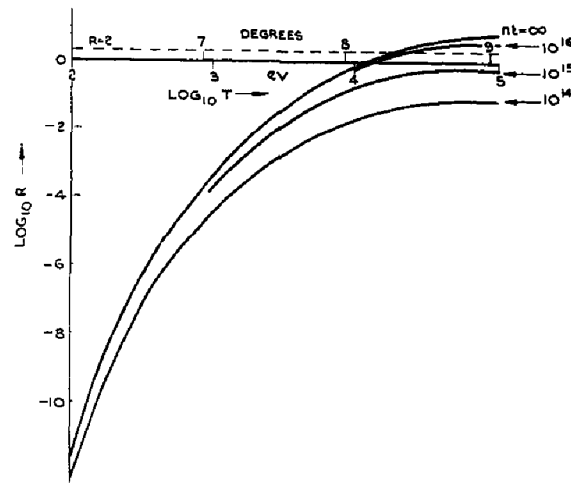


Figure 1. Variation of R with T for various values of nt for D-D reaction.

a pressure of 6×10^8 atmospheres at a temperature of 2×10^8 degrees. Particles move several metres during this time, and the mean free path for momentum transfer is several centimetres even at this high density. These distances are, of course, measured along the track, which may be spiralled or oscillatory.

Figure 2 shows similar curves for the T-D reaction. Conditions are easier, but still severe; nt must exceed 10^{14} , and the minimum temperature is 3×10^7 degrees.

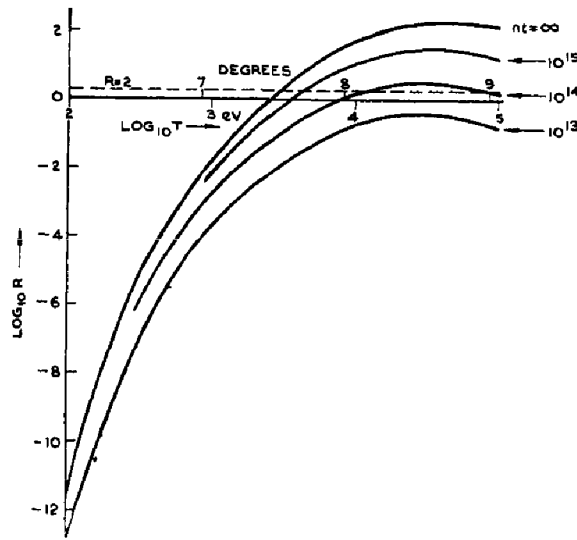


Figure 2. Variation of R with T for various values of nt for T-D reaction.

The curve marked $nt = \infty$ merely shows the ratio of the thermonuclear power release to the radiation loss, and crosses the $\log R = 0$ axis at the critical temperature. The curves are only accurate so long as t is sufficiently short that only a small fraction of the fuel is burnt. The values $nt = 10^{16}$ for a D-D system and 10^{14} for a T-D system both correspond to a burning of about 1% of the fuel.

Although these calculations refer specifically to a system in which the reaction products escape, it may easily be verified that the '1% burn-up' criterion is

almost unaltered in a system in which the reaction products are retained. In any practical system, where conduction loss is present, and where a large circulating power in the system is undesirable, the fraction of fuel burnt would need to be much greater.

§ 5. CONCLUSION

For a successful thermonuclear reactor not only has the temperature to be sufficiently high, but also the reaction has to be sustained for a sufficient time. The reason for this is that the organized energy used to heat the gas is ultimately degraded to the temperature of the walls of the apparatus and, consequently, sufficient thermonuclear energy must be released during each heating cycle to compensate for this degradation.

No claim that the above treatment is complete or applies to all possible types of system is made, but it does give some idea of the order of magnitude of the problems involved.

Systems which depart substantially from the electrically neutral Maxwellian gas assumed here have been carefully considered, but none looks promising. Some reasons for this are discussed by Thonemann (1956).

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Believable statements of uncertainty and believable science

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Abstract Nearly 50 years ago, two landmark papers appeared that should have cured the problem of ambiguous uncertainty statements in published data. Eisenhart's paper in *Science* called for statistically meaningful numbers, and Currie's *Analytical Chemistry* paper revealed the wide range in common definitions of detection limit. Confusion and worse can result when uncertainties are misinterpreted or ignored. The recent stories of cold fusion, variable radioactive decay, and piezonuclear reactions provide cautionary examples in which prior probability has been neglected. We show examples from our laboratory and others to illustrate the fact that uncertainty depends on both statistical and scientific judgment.

Keywords Data quality · Uncertainty · Traceability

Introduction

Two papers were published in 1968 that clearly set out the terms of discussion for two fundamental concepts in measurement science. Churchill Eisenhart's four-page paper [1] pointed out the several meanings that the literature might be understood to imply by an uncertainty expressed in the shorthand form $a \pm b$. "If no explanation is given, many persons will take $\pm b$ to signify bounds to the inaccuracy of a . Others may assume that b is the 'standard error,' or the 'probable error,' of a , and hence the uncertainty of a is at least $\pm 3b$, or $\pm 4b$, respectively. Still

others may take b to be an indication merely of the imprecision of the individual measurements, that is, to be the 'standard deviation,' or the 'average deviation,' or the 'probable error' of a single observation." As a consequence, far too great a fraction of the data in the scientific literature "cannot be critically evaluated because the minimum of essential information is not present." Eisenhart recommended unambiguous and statistically valid procedures for expressing uncertainty, which should have cleared the air and set the standards for future publications.

Also in 1968, Lloyd Currie's paper [2] applied eight common definitions of detection limit from the literature to a simple measurement example in radiation counting, and showed that the resulting estimates cover nearly three orders of magnitude. He then re-examined from the statistical point of view of hypothesis testing what *detection* and *measurement* should mean in analytical chemistry, rigorously defining three quantities: critical level, detection limit, and determination limit. Currie's formulation led to an American Chemical Society symposium on the topic [3] and has been incorporated in many rules of practice governing measurement procedures, international standards [4], regulations, and software. The culmination of Currie's early work was seen in the adoption of a harmonized international position (ISO-IUPAC) on the nomenclature, concepts, and formulation of detection, decision, and detection limits [5, 6].

In order to foster consistency of data reporting in all of science, in 1993 the International Organization for Standardization (ISO) issued its Guide to the Expression of Uncertainty in Measurement (GUM) [7] and the International Vocabulary of Basic and General Terms in Metrology (VIM) [8]. Directed toward professional metrologists, these publications incorporated some concepts unfamiliar to practicing laboratory workers. Several organizations,

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e.g., NIST [9], Eurachem/CITAC [10], IAEA [11], and BIPM [12], published supplemental interpretations with examples appropriate to their fields. The intent of these standards is to foster the publication of reliable data, quantitatively and unambiguously traceable to the International System of Units (SI).

Data quality in practice

In practice, of course, not all routine measurements require detailed uncertainty evaluation every time: the effort must be proportional to its importance, following the principle of fitness for use. When numbers are to be published and used by others, however, Eisenhart's admonitions apply despite the effort required. "The concepts of traceability are not always well accepted by the analytical chemistry community. There is a benign kind of neglect towards these ideas or even straight hostility" [13]. Part of the reason is that a full ISO-compliant treatment of uncertainties requires differentiation of the measurement equation, which may be difficult. For example, extracting the derivative of the equation used to reduce counting data to standard conditions

$$A_0 = \frac{C\lambda e^{\lambda t} e^{P\delta/\Delta} (e^{\lambda\Delta} - 1)}{(1 - e^{-\lambda\Delta})(1 - e^{-\lambda\tau})\lambda\Delta}$$

with respect to λ is daunting to most people. However, numerical re-calculations of the measurement equation employing finite differences instead of derivatives [10, 14, 15] can quantitatively show the effect upon the uncertainty of the final result due to uncertainties in the parameters. Applied to neutron activation analysis [16–18], this approach clearly shows the relevant uncertainties.

The two classic 1968 papers [1, 2] and the ISO GUM set the standards for clarity in future publications, yet we still see many papers submitted for review and even published with uncertainties given as simply "±" or omitted completely, or with many more digits than are truly significant. As Eisenhart pointed out, these practices have consequences for the users of these papers. As an example from our own work, a newly published half-life for ^{76}As [19] was accepted by the evaluators because of a plausible (but novel and incomplete) description of the uncertainties in the measurement, even though this value conflicted with previous measurements in the literature (notably a set of seven determinations with six different kinds of detectors [20]). This half-life would have led to an inaccurate INAA value for Arsenic Implant in Silicon (SRM 2134) had we used it in our measurements [21]. A redetermination of the half-life [22, 23] in agreement with the previous consensus is slowly driving out the incorrect value from tabulations of nuclear data.

Data quality and good science

Although science is always open to new ideas, a lack of understanding of the real uncertainties in a measurement, in physics as well as statistics, has led to some conspicuously mistaken conclusions. Scientific judgment (prior probability, in Bayesian terms) needs to be applied, especially to unexpected observations, and the null hypothesis that the observation is in error needs to be explicitly tested. Perhaps the best-known recent example is cold fusion [24] where, in the rush to publish, blank experiments were not adequately done and people knowledgeable in nuclear science were not consulted. Early measurements in our laboratory at NIST [25] *without* the Pd/D electrochemical cell showed neutrons (from cosmic rays) and gammas (mostly from ^{214}Bi) in quantitative agreement with Fleischmann and Pons's paper. Other workers were also unable to duplicate the publicized work electrochemically, so that research in low-energy nuclear reactions (LENR) has nearly, but not entirely, stopped.

Since the discovery of radioactivity, more than eighty attempts have been made to influence the rate of radioactive decay. None has had an effect, with the sole exception of decay modes that involve the orbital electrons, the physics of which is well understood [26]. More recently, an unexplained anomaly in the decay curve of ^{54}Mn was observed to be coincident with a strong solar flare, and statistical anomalies in other decay measurements made at Brookhaven National Laboratory and at the Physikalisch-Technische Bundesanstalt (PTB) were found to have annual periodicity [27, 28]. The cause was hypothesized to be related to solar neutrinos affecting the value of the decay constant.

To test this connection, measurements were done in our laboratory at NIST to compare the decay rates of paired intense sources of ^{198}Au with greatly different surface/volume ratios (sphere vs. foil or wire), and thus greatly different internal antineutrino fluxes [29, 30]. The half-lives of the paired sources were found to be indistinguishable, contrary to the prediction of the neutrino hypothesis. Decay rate measurements at Delft in the presence of neutrinos from the HOR reactor were found to be no different when the reactor was shut down [31], casting further doubt on the hypothesis. Other arguments degrade the solar connection [32]; for example, a ^{137}Cs source decayed at the expected rate as the MESSENGER spacecraft traveled from earth to Mercury's orbit at 0.4 AU [33]. Recent measurements at PTB have caused most of the earlier anomalies to disappear as more sources of experimental bias have been revealed and eliminated [34, 35]. Half-life measurement is subject to many sources of bias, not all of which are readily detected [36]. Although there is

decreasing evidence for non-constant radioactive decay rates, the search continues in some laboratories.

The surprising observation that light is emitted from collapsing bubbles produced by ultrasonic agitation of water has led to the hypothesis that the energy of the collapse might be sufficient to cause nuclear fusion, a process called sonofusion. Indeed, both tritium and neutrons were claimed to be detected in deuterated acetone under cavitation [37]. Other laboratories failed to duplicate these measurements, and the pursuit quickly collapsed as a combination of self-deception and fraud was revealed. Inspired by this, another group searched for nuclear transformations in sonicated water, and found increased amounts of uranium and even transuranic nuclides [38].

Subsequently [39] it was claimed that neutrons generated in the ultrasonic probe caused measurable changes in element concentrations. That work was accepted for publication with the editor's comment "This paper has been evaluated by six peers and has been considered to contain questionable results. However, as it reports on results difficult to prove but indisputably important if correct, the editor takes full responsibility for making it public." Other observations led the same group to believe that cavitation increases the rate of alpha decay of ^{228}Th [40]. The physical evidence has been sharply criticized [41], and more reasonable explanations of the observations have been proposed [42].

More recently, piezonuclear transmutations of ^{63}Cu to ^{65}Zn via multiple neutron capture were claimed [43], even though gamma spectrometry showed that the ultrasonic probe itself was no more radioactive after operation than before. The publication of this report resulted in strong criticism [44, 45] from the neutron activation analysis community, with the admonition, echoing others [41, 42], that the reviewers and editors of journals have an important responsibility to see that only verifiable facts and theories appear in the published literature.

Error and bias have many ways to creep into laboratory measurements. Currie (pers. comm., 1990) has pointed out that in a real measurement process " $d.f. < 0$ always; since the number of variables exceeds the number of observations, scientific insight is essential." Anomalous observations may indeed point to new phenomena, but simple explanations are usually most probable. "The first principle is that you must not fool yourself—and you are the easiest person to fool" (R. P. Feynman, 1974 Caltech commencement address).

Summary and conclusions

Science is a communal activity whose practitioners build upon each others' work. To exploit the literature we must understand its limitations, which is possible only if the authors of publications understand the uncertainties in their

measurements and conclusions, and make us, the readers, understand them in the same way.

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A check in the amount of \$750.00 is submitted herewith.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)
)
Christopher H. Cooper et. al.) Group Art Unit: 3646
)
Application No.: 13/089,986) Examiner: Davis, Sharon M.
)
Filed: April 19, 2011) Confirmation No.: 1497
)
For: METHOD OF GENERATING)
ENERGY AND ⁴He USING THREE)
DIMENSIONAL NANOSTRUCTURED)
CARBON MATERIALS)

Attention: Mail Stop Appeal Brief-Patents

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TRANSMITTAL OF APPENDICES FOR APPEAL BRIEF UNDER 37 C.F.R. § 41.37

The Appeal Brief filed for this application included Appendices A-C. The Brief, a Petition for Extension of Time and a check for the appropriate fee was mailed but failed to include Appendices A-C. They are attached hereto.

Respectfully submitted,

Dated: January 8, 2019

By: Stephen L. Peterson
Stephen L. Peterson
Reg. No. 26,325
202 251 9367

Attached: Appendices A-C

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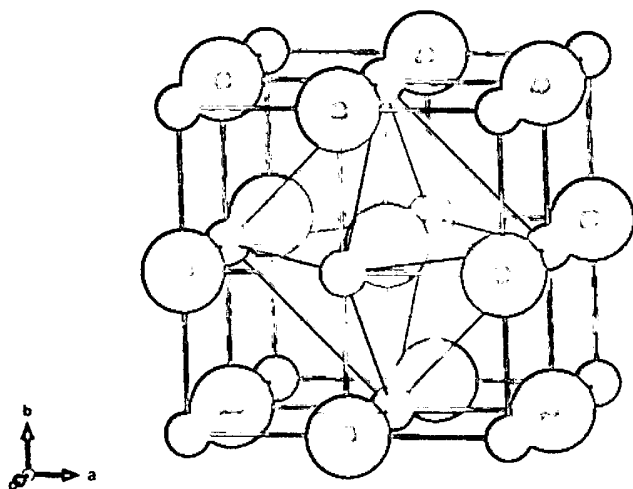
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Appendix A – NaCl Crystalline Structure

Application No.:13/089,986

Attorney Docket No. DE-1

A unit cell representation of sodium chloride is shown in the following figure.



The salient features of its structure are:

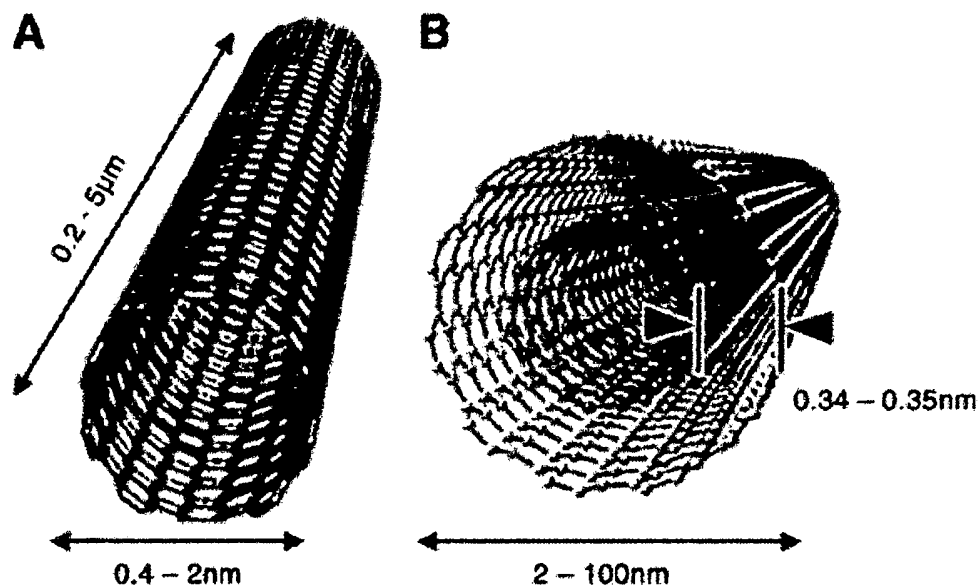
- Chloride ions are *ccp* type of arrangement, *i.e.*, it contains chloride ions at the corners and at the center of each face of the cube.
- Sodium ions are so located that there are six chloride ions around it. This equivalent to saying that sodium ions occupy all the octahedral sites.
- As there is only one octahedral site for every chloride ion, the stoichiometry is 1 : 1.
- For sodium ions to occupy octahedral holes and the arrangement of chloride ions to be close packed the radius ratio, r_{Na^+}/r_{Cl^-} , should be equal to 0.414. The actual radius ratio 0.525 exceeds this limit. To accommodate large sodium ions, the arrangement of chloride ions has to slightly open up.
- It is obvious from the diagram that each chloride ion is surrounded by **six** sodium ions which are disposed towards the corners of a regular octahedron. We may say that cations and anions are present in equivalent positions and the structure has 6 : 6 coordination.
- The structure of sodium chloride consists of eight ions a unit cell, four are Na^+ ions and the other four are Cl^- ions.

In this structure, each corner ion is shared between eight unit cells, each ion on a face of the cell by two cells, each ion on a[n] edge by four cells and the ion inside the cell belongs entirely to that unit cell.

Source - <https://minerva.mlib.cnr.it/mod/book/view.php?id=269&chapterid=101>

Appendix B – Carbon Nanotube Crystalline Structures

Application No.:13/089,986
Attorney Docket No. DE-1



A is a single walled CNT

B is a multi-walled CNT (MWCNT)

Source - https://www.researchgate.net/figure/Conceptual-diagram-of-A-single-walled-carbon-nanotube-and-B-multi-walled-carbon_fig1_42588327

Appendix C – The Guo Article

Application No.:13/089,986
Attorney Docket No. DE-1

Visible-Light-Induced Water-Splitting in Channels of Carbon Nanotubes

Deng-Zhu Guo,^{*,†} Geng-Min Zhang,[†] Zhao-Xiang Zhang,[†] Zeng-Quan Xue,[†] and Zhen-Nan Gu[‡]*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: October 17, 2005; In Final Form: December 4, 2005*

The visible-light-induced split of water confined in channels of single-walled carbon nanotubes (SWNTs) was experimentally studied. Arc-discharging synthesized SWNTs were used to adsorb water vapor and then were irradiated in a vacuum by using light from a camera flash. It was found that a great amount of hydrogen-rich gases could be repeatedly produced under several rapid flashes of light, occasionally accompanying evident charge emission phenomena. A quantitative method was developed to estimate the relative amount of gas components on the basis of the data acquired with an ion gauge and a quadrupole mass spectrometer. The results indicated that hydrogen occupied about 80 mol % of the photogenerated gases, with other components such as carbon oxides, helium, methane and trace of ethane, and the total gas yield in one flash (0.1–0.2 J/cm², 8 ms) reached 400–900 ppm of the mass of the SWNTs. Such a yield could be repeatedly obtained in serial flashings until the adsorbed water was depleted, and then, by sufficiently adsorbing water vapor again, the same phenomena could be reproduced.

Introduction

Nanomaterials generally exhibit diverse and unique properties. Recently it has been reported that by exposure to light from a camera flash, single-walled carbon nanotubes (SWNTs)^{1–3} and silicon nanowires⁴ can be ignited and reconstructed in air and polyaniline nanofibers can be welded together to form a smooth and continuous film.⁵ These surprising phenomena have been ascribed to an unprecedented photothermal effect in nanomaterials, in which the absorbed photons generate heat through nonradiative dissipation and/or photochemical reactions. The heat would be confined within individual nanostructures and difficult to be transferred to the neighboring materials and the environment, so that local hot spots of above 1500 °C in nanostructures under flashing irradiation is expected, although the input energy is only a short-pulsed white light.^{1–5} These interesting facts inspired us to think about the possibility of splitting SWNT-confined water under a visible light flash.

Water-containing SWNTs were originally suggested theoretically as a wetting phenomenon by Dujardin and co-workers.⁶ Since then, many theoretical studies on the structure and dynamics of water confined in SWNTs by molecular dynamics (MD) simulations have been reported,^{7–14} and a few experimental observations have also been carried out to investigate its unique properties.¹⁵ Up to now, although some disagreements about the structure of SWNT–water exist among these papers, it is in high agreement that the existing status of nanotube water is very different from that of the bulk one due to the SWNT confinement. Very recently, Kolesnikov and co-workers¹⁵ studied nanotube water by both neutron scattering and MD simulation and revealed anomalously soft dynamics in it. Either

the intramolecular covalent bonds or the intermolecular hydrogen bonds have been verified as considerably different from that of bulk water/ice; especially, the hydrogen bonds among the water chains inside SWNTs are highly softened, so the water molecules have a high mobility in SWNTs. However, the interactions between the entrapped water and the SWNT wall are very strong. The SWNT–water system has been expected to have potential applications in nanofluidic and proton storage devices. In this paper, we will show a new application possibility for such a system.

Now that the nanotube water has a special structure and dynamics different from that of the bulk one and SWNTs have a highly efficient photothermal effect under a flash, one can naturally wonder what would happen when the water-filled SWNTs were irradiated. This question has never been answered until now to our knowledge. Three years ago, for reproduction Ajayan's SWNT ignition experiments,¹ our group occasionally found that by serially exposing SWNT samples in an ultrahigh vacuum (UHV) chamber with the light from a camera flash several times, remarkable hydrogen and other gases could be continually generated. This result has puzzled us for a long time, because there was not any hydrogen source involved in our SWNT sample elaboration, and the adsorption of hydrogen from the ambient air would be very little since hydrogen content in the atmosphere is very low (~0.5 ppm in volume), and moreover, our UHV chamber containing the SWNT sample had been sufficiently heated under a high temperature. To find a reasonable solution, recently we designed a special experimental procedure, carefully analyzed the flash-released gases by using a quadrupole mass spectrometer (QMS), and managed to obtain some quantitative results. We found that the flash-released gases evidently arose from the split of water encapsulated inside SWNT channels and the chemical reactions between them. Moreover, occasional charge emission phenomena accompanying the gas release have also been observed. We suppose that

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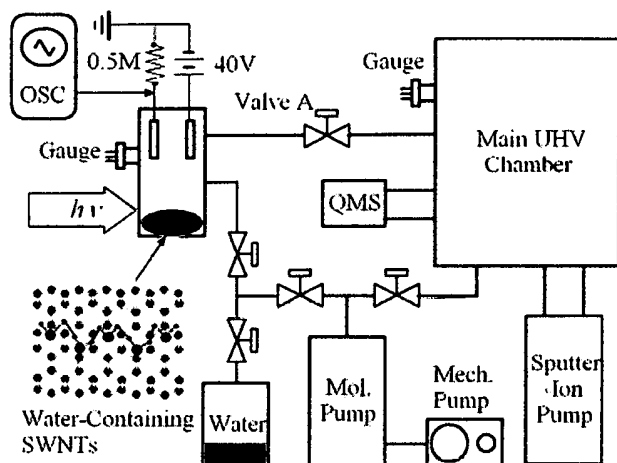


Figure 1. Schematic showing the experimental setup. The gas and charge release from water-containing SWNTs under a visible light flash can be detected by using an ionization gauge and a special circuit, respectively. Then the gases can be sampled and analyzed by using a QMS. The insert is a schematic showing a water-containing SWNT.

our research is of significance both in exploration of new hydrogen energy sources and in fundamental research regarding SWNT–water systems.

Experimental Section

Our experimental setup is schematically shown in Figure 1. A glass tube containing ~ 10 mg of SWNT raw materials, synthesized by using a direct current (DC) arc-discharge method¹⁶ with Ni–Y particles as the catalyst under a helium pressure of about 500 Pa, was connected through valves to an ultrahigh vacuum (UHV) system and to a vacuum bottle containing distilled water. The sample container (V_s) could be evacuated by using the forestage pumps and the sputter-ion pump through different valves, and its pressure can be measured by using a high-pressure ionization gauge. Two electrodes for charge emission measurement are suspended in the V_s and connected to the ground through 40 V DC batteries and a 0.5 M Ω resistor, respectively. One digital oscilloscope (Tektronix TDS3052) was used to monitor the electrical current passing through the resistor. After sufficient heating (at 180 °C for longer than 24 h) and evacuating, a UHV ($P < 5 \times 10^{-7}$ Pa) was achieved both in the V_s and in the main chamber, to which a homemade quadrupole mass spectrometer (QMS) is attached. Then valve A was closed, and the saturated water vapor (~ 3500 Pa) from the water bottle was introduced into the V_s and kept for 1 h. Next, the V_s was heated and evacuated again. Subsequently, by stopping the sputter-ion pump and closing valve A, the two rooms were in a pressure-increasing state separately. When the pressures in the two rooms became quasi-stable, the water-containing SWNT sample was exposed to a photographic flash (0.1–0.2 J/cm², ~ 8 ms). The rapid rise of the total pressure in the V_s was recorded. At the same time, the response of the oscilloscope was also monitored. At last, by slightly opening valve A for gas sampling, the gas components were analyzed by using the QMS. When the gas-releasing properties of the sample were obviously degraded, saturated water vapor was introduced into the V_s again, and the same experiments were repeatedly conducted.

For comparison purposes, we also used ~ 25 mg of graphite powder (~ 20 μ m in diameter) containing the same catalyst (Ni–Y particles) as the sample to do the experiments described above.

Quantitative Analysis Methods

After flash irradiation, the total pressure increment in the V_s indicated by the high-pressure ionization gauge, $\Delta P_t(\text{gauge})$, comes from the combination of all of the real partial pressure increments, ΔP_i , as following

$$\Delta P_t(\text{gauge}) = \sum_i \alpha_i \Delta P_i \quad (1)$$

where α_i is the relative ionization coefficient of the i th gas in the gas mixture ($\alpha_{N_2} = 1$).¹⁷ However, when the gas mixture was sampled for QMS analysis, all components will be reflected in the mass spectra as peaks of ion current increments, ΔI_j . Each peak can be factorized into several gas sources

$$\Delta I_j = SGK \sum_k \alpha_k \beta_k^j \Delta P_k \quad (2)$$

where S and G are the ionization sensitivity of N_2 and the multiplier gain of the instrument, respectively. K is the sampling factor, k is the index of the gases that contribute ions to the peak at the atomic mass unit (AMU) j , α_k is the relative ionization coefficient of the k th gas, which is assumed to be the same as that in the ionization gauge, and β_k^j is the relative intensity coefficient at AMU j in the cracking patterns of the k th gas.¹⁷ To eliminate the unknown proportionality constants S , G , and K , we divide the concrete formulas as shown in eq 2 for different AMU peaks by that of AMU 2, because the intensity of the flash-released H_2 is stable relative to other gases with increase in the flash times

$$\frac{\Delta I_j}{\Delta I_2} = \frac{\sum_k \alpha_k \beta_k^j \Delta P_k}{\sum_n \alpha_n \beta_n^2 \Delta P_n} \quad (j \neq 2) \quad (3)$$

where n is the index of the gases that produce ions at AMU 2. Combining eq 3 with eq 1, one can get a set of linear equations regarding the unknown quantities ΔP_i . The number of the ion current peaks in the mass spectrum is usually more than the number of the gas components, so the equation system is generally overdetermined. (The number of unknown quantities is less than the number of equations.) So, a mean-square method was used to obtain the best-fit solution. After the values of ΔP_i are obtained, the molar amount of each flash-released gas, Δv_i , can be calculated as

$$\Delta v_i = \frac{\Delta P_i V_s}{RT} \quad (4)$$

where $R = 8.314$ J mol⁻¹ K⁻¹ is the gas constant, T is the temperature in Kelvin (taking $T = 300$ K for room temperature), and V_s is the volume (~ 200 mL) of the sample container. The molar percentage of the i th gas was defined as

$$\eta_i = \frac{\Delta v_i}{\sum_j \Delta v_j} \quad (5)$$

The mass yield of gases, defined as the ratio of gas masses to

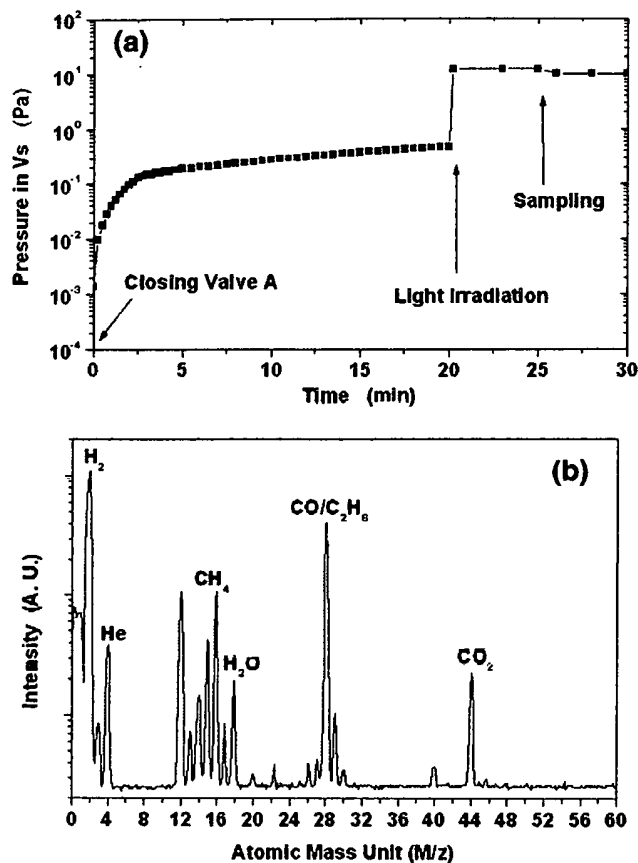


Figure 2. Typical experimental result of gas release. (a) The total pressure in the V_s evolving with time. A step appears when the sample is irradiated. (b) One mass spectrum of the sampled gases. The base spectrum obtained before sampling has been subtracted from the original data. The main components have been labeled above the corresponding peaks.

the mass of SWNTs, m , can be expressed in ppm

$$\epsilon_i(\text{ppm}) = \frac{\Delta \nu M_i}{m} \times 10^6 \quad (6)$$

where M_i is the molar mass of i th gas.

As for the measurements of charge emissions, we directly monitor the electrical potential difference between the two ends of the 0.5 M Ω resistor by using an oscilloscope and then apply Ohm's law to obtain the current passing through it

$$I (\text{nA}) = U/R = 2U \quad (U \text{ in mV}) \quad (7)$$

At last, the charge quantities can be obtained by using a digital integral method.

Results and Discussion

Figure 2 shows a typical experimental result of gas release. As shown in Figure 2a, the total pressure in the V_s approximately stabilized between 10^{-2} to 10^{-1} Pa several minutes after valve A was closed. Then, when the sample was exposed to a flash, it immediately rose to ~ 12 Pa, suggesting that a great amount of gases were generated. The mass spectrum of the sampled gases is shown in Figure 2b, noting that the base spectrum obtained before sampling has been subtracted from the original data. One can see that hydrogen is the main component of the flash-generated gases. Besides H_2 , other components such as He, CH_4 , H_2O , CO, C_2H_6 , and CO_2 can also be found, as

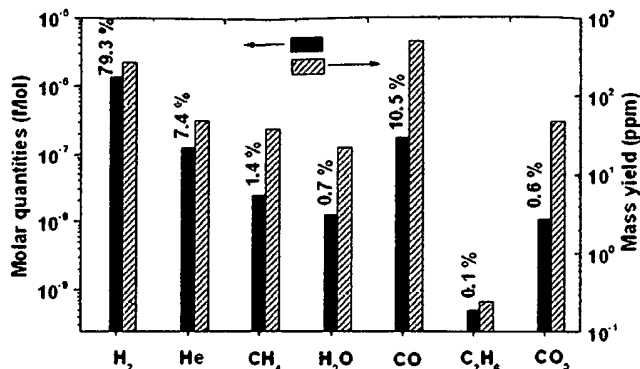


Figure 3. Quantitative estimation of the gas components generated from the water-containing SWNTs in one flash irradiation.

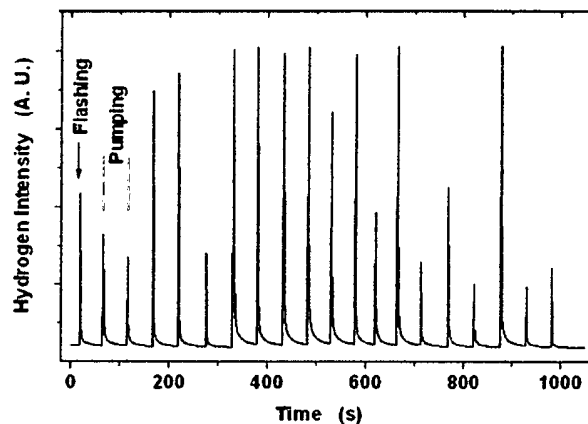


Figure 4. Hydrogen intensity changes with sequent times of flash irradiation, obtained with QMS while the V_s was pumped.

indicated in Figure 2b. The nonlabeled peaks are either attributable to the fragments of these gases or rather insignificant. It should be argued that the presence of N_2 (mainly at AMU 28) in the flash-released gases is nearly impossible. To confirm this, we additionally did a comparison experiment in which dry SWNTs were exposed to dry N_2 instead of H_2O vapor and found that no obvious gas was released under a light flash. We believe that the N_2 adsorbed by the SWNTs in air had been completely desorbed during the heating–pumping process even before the light flash.

The above experimental results were quantitatively calculated, and the result is shown in Figure 3, in which one can see that the production of H_2 in one flash reaches $\sim 1.5 \mu\text{mol}$, equaling to ~ 300 ppm of the mass of SWNTs and to 79.3 mol % of the total flash-generated gases. CO is the second one, occupying about 10.5% (~ 500 ppm of the mass of SWNTs). All of the other components, He, CH_4 , H_2O , CO_2 , and C_2H_6 , occupy the residual percentage. The total mass yield of all of the gases in one flash reaches about 900 ppm ($\sim 0.09\%$) of the mass of the SWNT sample. Such a yield is considerably high, noting that the time for the gas release is very short (< 1 s).

We also found that when the flash times are increased, the total mass yield was in a range of 400–900 ppm, and the relative quantity of each flash-generated gas could change. However, a similar hydrogen yield could last for more than 10 exposures of the sample to the rapid light flash. The spectrum shown in Figure 4 was obtained with the QMS in “single-ion” mode, namely, only H_2^+ ions were detected versus time, by serially irradiating the sample while valve A was open and the sputter-ion pump was working. Each peak corresponds to one hydrogen release in one flash irradiation, and the period between two

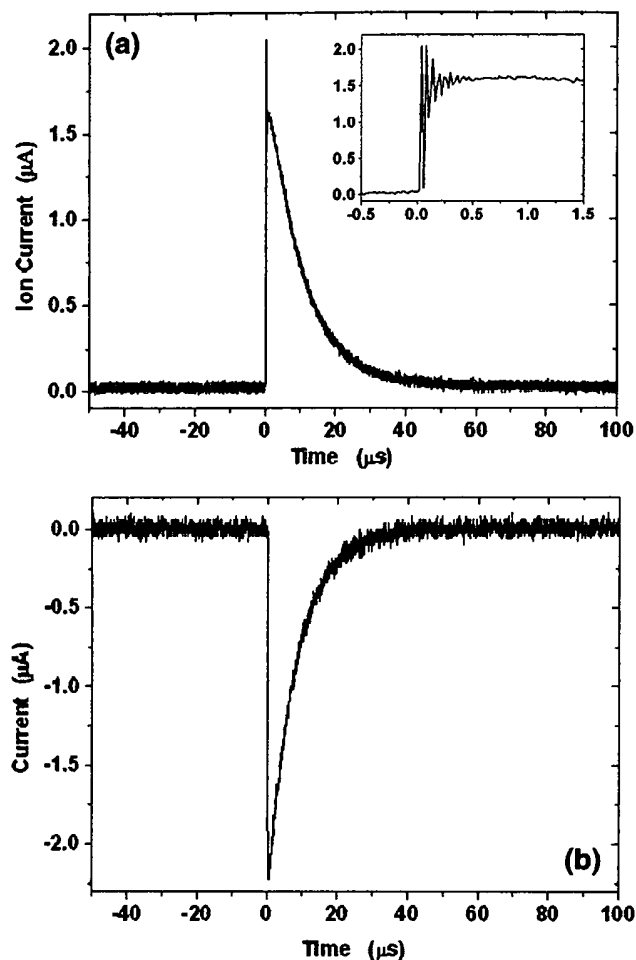


Figure 5. Measurements of charge emission accompanying gas release. (a) A typical result of flash-induced positive current. The insert is an *x*-axial magnification of the measured signal near $t = 0$; the damping oscillation phenomenon is apparent. (b) A typical result of flash-induced negative current.

consecutive peaks corresponds to the pumping time. One can see, during a period of 1000 s, 20 irradiation flashes were carried out, and obvious hydrogen peaks were detected for each time, with a peak intensity difference of a factor of 3–4. If we make an assumption that $\sim 0.75 \mu\text{mol}$ of H_2 has been generated on average during each flash irradiation, then during the total period of 1000 s, $15 \mu\text{mol}$ of H_2 had been released, meaning that the H_2 production rate was $54 \mu\text{mol/h}$, which is at least comparable with the data obtained from the photoelectrochemistry (PEC)-based water-splitting method reported by Zou et al.¹⁸ It should be noted that the PEC method requires sophisticated functional (high conversion efficiency and working stability, long lifespan, and low cost, etc.) materials as the photoelectrode, which is the main technical challenge now.¹⁹

In addition to the gas emission, we also occasionally observed charge emission phenomena. We used the photovoltaic signal of the light of the camera flash as the external trigger of the oscilloscope and monitored the voltage across the $0.5 \text{ M}\Omega$ resistor. A typical result is shown in Figure 5a. At the very beginning of the flash irradiation, a positive current pulse, $2.2 \mu\text{A}$ in peak value and $50 \mu\text{s}$ in bottom width, was generated. The total charge in the pulse can be estimated to be $\sim 2.6 \times 10^{-11} \text{ C}$, corresponding to $\sim 1.6 \times 10^8$ singly charged ions. A damping oscillation with a frequency of about 20 MHz appears within the first $0.5 \mu\text{s}$, and then the positive current could keep nearly constant for several microseconds before exponentially

decreasing, as shown in the insert of Figure 5a. Also, when the polarity of the DC batteries in the measurement was reversed, the polarity of the current pulse could be accordingly reversed, i.e., negative pulses could be obtained. One such example is given in Figure 5b. The above results suggest that generation of plasma could accompany the gas release when the water-containing SWNTs were illuminated by a visible light flash. Here, we have to emphasize that such current pulses could not be always detected in every flash irradiation. They emerged only occasionally, although gases could be definitely generated once the sample was irradiated by a flash. The reason is not clear to us at the present stage.

More importantly, we also found that when the flash-released gases obviously decreased due to the depletion of nanotube water, i.e., no obvious pressure increase in the sample container could be detected after a flash irradiation and no charge emission could be observed for a long time, the gas generation and charge emission ability could be recovered by inputting water vapor into the sample container again. We repeatedly conducted the above experiments for more than 20 times with the same SWNT sample and found no obvious degradation in gas release and charge emission in the end.

The comparative experiments on a micro-graphite-catalyst sample, in contrast, showed a poor outgassing abilities under the same conditions. For such a sample, we found that the gas-release phenomena appeared only for the first few times of rapid light exposure, and the total gas yield is far lower ($<0.01\%$) than that of the SWNTs, and moreover, no charge emission phenomena have been observed during 20 flash exposures. The components of the released gases mainly included H_2 , CO , and CO_2 but no He , H_2O , CH_4 , and C_2H_6 have been detected. It means that most water adsorbed on the powder surfaces has been removed during the heating–pumping process, and the few residual water molecules could also be decomposed to form H_2 and carbon oxides through chemical reactions. But some important reactions in the SWNT cases did not occur in this situation.

At last we will give a tentative discussion on the mechanism of the gas release from water-containing SWNTs under a flash. Here, the SWNTs were used both as the carrier of nanowater and as the photocatalyst. Taking the ultra-photothermal effect of nanomaterials^{1–5} into account, one could imagine that under an optical flash SWNTs and the confined water absorbed photons, disassociating the water molecules and generating O and H atoms. The local pressure in nanotubes would dramatically increase, so a local explosion would occur in the nanotubes, liberating some C atoms. As a result, H_2 and some C–H and C–O compounds as well as H_2O could be detected. We noted that the molar quantity of oxygen in all of the generated gases was very low compared with that of hydrogen. We think that because atomic O is very active, it could preferentially react with the catalyst particles in the SWNT sample (we indeed found some lumps such as ore in the sufficiently flash-irradiated SWNT sample) and react with the hot filaments of tungsten in our QMS and ionization gauge under high temperature. As for He, although it could be attributed to the synthesis process of SWNTs, it really seems strange to us at the present stage and deserves further investigation. The occasionally observed charge emission phenomena mean that some ionization process, such as thermal ionization and photon ionization, could occur accompanying the gas release under special conditions. Since the first ionization energies for the involved atoms and molecules are between 6.217 eV (for Y) and 24.587 eV (for He),²⁰ if thermal ionization has occurred, one can infer that the instant

local temperature within the channels of the SWNTs should be at least 10^4 K. However, photon ionization seems impossible because visible light does not have high energy. Although the concrete ionization process is not clear at the present stage, this observation makes us believe that some local high-energy spots in the water-containing SWNTs would be generated by exposure to a visible light irradiation. That supports the opinion of thermo-splitting of water confined within the channels of the SWNTs.

Conclusion

In conclusion, on the basis of the unusual photothermal effects of nanomaterials and the special status of the nanotube-confined water, we proposed a simple way to generate hydrogen-rich gases from water-containing SWNTs by only an optical flash. The flash-released gases were quantitatively analyzed by using an ion gauge and a QMS, which shows that H_2 and CO are the main components in the gas mixture. Totally, the mass of the flash-released gases reaches 900 ppm of the mass of the SWNTs. Meanwhile, sometimes we detected charge emissions accompanying the gas release, which deserves further research.

Acknowledgment. D.-Z. Guo thanks Professors X. Wang and Z.-G. Shi for experimental support. This project was supported by the National Natural Science Foundation of China (Grant Nos. 60231010, 60471008, and 60571003).

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