university of groningen

faculty of mathematics
and natural sciences

Research proposal

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1. **Title of the project**
   Thermopower waves in Carbon nanotube
2. **Applicant**
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3. **FOM research group**
   G-27
4. **Institution**
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5. **Abstract**

The project aims fundamental research and possible applications of thermopower waves in carbon nanowires. Thermopower waves are a new idea for the direct conversion of chemical to electrical energy. Combustion waves — pulse of heat propagating along a wire — have been studied mathematically for more than 100 years and it was shown that such waves could be guided by a nanotube or nanowire and this wave of heat could generate an electrical current along that wire. Due to the fact that carbon nanotubes are efficient guides for phonons and electrons and their thermal conductivity is ten times higher than that for instance of copper, carbon nanotube covered with a material that produces an exothermic reaction can accelerate and conduct a self-propagating reaction wave in one direction. Surprisingly, the reaction wave can create a high-power pulse of high power density (higher than 7 kW/kg) and drives carriers in a thermopower wave. These thermopower waves are very promising for build new types of nanoscale power source, new class of fuel cells, batteries, energy generators etc. The intellectual merits of the proposed work combine research efforts, including fabrications, experimentation, characterization, and understanding of new phenomena in carbon nanotubes.

Duration of the project

4 years, starting from September 2011

6. Personnel

Prof. dr. M.A. (Maria Antonietta) Loi (Professor / Leader of the research group)
I. O. Iezhokin (Applicant/PhD student)
J. Harkema (Technician)
F.van der Horst (Technician)

7. Cost estimates

7.1 Personnel positions

One ‘Onderzoeker in opleiding’ position for four years

7.2 Running budget

10,000 € / year

7.3 Equipment

CVD furnace
High-speed video microscopy (up to 90,000 frames/s)
Micro lens for extreme close-up and general photography
Thermopower measurement:
- Oscilloscope
- Function generator
- 785 nm laser
- Photo detector

Carbon Nanotube Characterization:
- Scanning Electron Microscope
- Transmission Electron Microscope
- Raman system

7.4 Other support

7.5 Budget summary of the funding requested

The expenses are summarized in the table

	2012	**2013**	**2014**	**2015**	**Total**
PhD sudents	**1**	**1**	**1**	**1**	
Postdocs	**-**	**-**	**-**	**-**	
Technicians	**-**	**-**	**-**	**-**	
Guests	**-**	**-**	**-**	**-**	
Personel cost	**37**	**37**	**37**	**37**	**148**
Running Budget	**20**	**20**	**20**	**20**	**80**

Equipment	**100**	**50**	**30**	**20**	**200**
Total	**157**	**107**	**87**	**77**	**428**

8. Research program

8.1 Introduction

During the last decade many nanostructured materials have been studied to advance performance of thermoelectric (TE) devices. Dresselhaus group has proven theoretically that lower dimensional systems like quantum wells, quantum dots and nanowires are very promising for TE device application [1]. Carbon nanotubes (CNTs) are also quasi one-dimensional nanostructures [2] and they have a lot of unique properties such as high mobilities (up to ~ 10 000 $cm^2 V^{-1} s^{-1}$ at room temperature) [3], electrical conductivity (10000 S/cm) [4] and finally high axial thermal conductivity (3000 W/m/K) [5]. According to the calculations which predict that by coupling an exothermic chemical reaction with a nanotube or nanowire it is possible to get high axial thermal conductivity and create a self-propagating reactive wave which can be driven along the nanotube length. Strano et al. showed that multi-walled carbon nanotubes (MWNTs) can provide thermopower waves (self-propagating chemical reaction waves) generated by combustion of cyclotrimethylene trinitramine (TNA) [6]. It was shown that these waves thermally excite electrons and push them along the nanotube so this method is very promising for harvesting electrical energy. It is necessary to mention that nanowires with different thermal diffusivities and electrical properties may change the dynamics of the chemical reaction and change final yield of electrical power as the sequence. Materials with large Seebeck coefficients such as silicon nanowires or bismuth telluride could be alternative thermal conductor but may not be the most suitable due to their low thermal diffusivities and for this fact as based material were chosen carbon nanotubes.

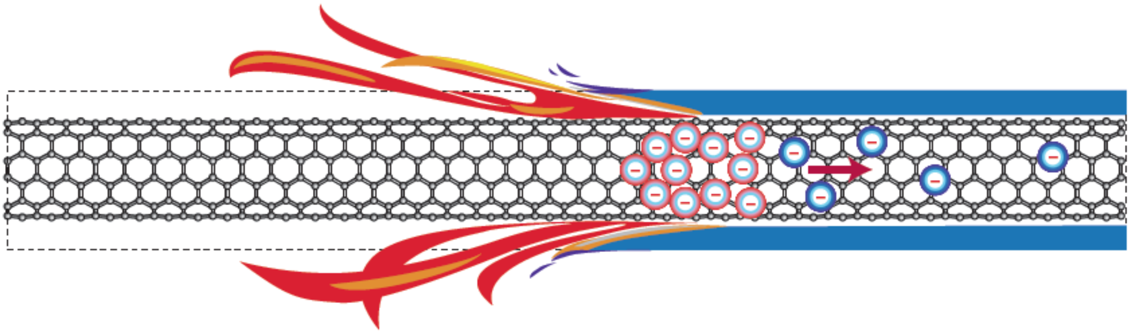
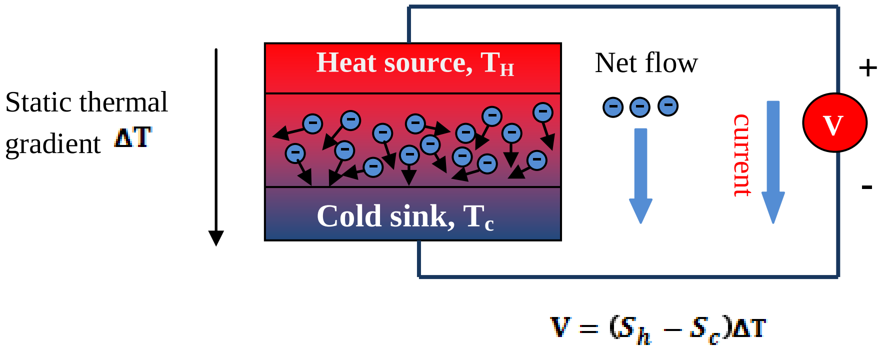


Figure. 1 Schematic illustration of a chemically driven thermal wave (shown in red). Thermally excited electrons flow in the direction of the thermal wave propagation to the cold (blue part) end of the nanotube and can be harvested as electrical energy. Figure captured from [8].

8.2 Research questions

Seedbeck effect was discovered by Johan Seedbeck in 1821 (Fig.2). Nowadays the theory of thermoelectricity is fully understood. The main idea is that the charge carriers (electrons or holes) diffuse from the hot to cold side due to the applied temperature gradient (Fig.2a).
The Seebeck coefficients of nanostructured materials, such as ZnO (-400 μV/K), GaN (-40 μV/K), PbTe thin films (620 μV/K), PbSe (193 μV/K), and InSb (-220 μV/K) have been studied widely. Among one-dimensional conductors, carbon nanotubes have been explored as components of thermoelectric devices, thermal conductivity of crystalline ropes of single-walled carbon nanotubes (SWNT) was measured and it is only 35 W $m^{-1}K^{-1}$ at room temperature [9,10] and it seebeck coefficients are generally small. It was also shown that the thermal conductivity was driven by phonons at all temperatures with a mean free path on the order of 1 μm. The thermal conductivity and Seebeck coefficient in an individual multiwalled carbon nanotube (MWNT) and single-walled carbon nanotubes (SWNT) was measured [10,11]. By contrast, the thermal conductivity of individual nanotubes is much higher, 3,000 W m^{-1} K^{-1} for MWNT and 10,000 W m^{-1} K^{-1} for SWNT. However, the Seebeck coefficient for MWNT 80 μV/K, is higher than that of SWNT 40 μV/K. In fact the Seebeck coefficients of all types of nanotubes are higher than that of graphite.



$$V = (S_h - S_c)\Delta T$$

Figure 2. Schematic set-up for measurement of conventional TE effect.

A new concept to improve the TE devices was proposed. The main idea is to create a large thermal gradient in the material that conducts both heat and current. One possible way is to create self-sustaining reaction wave. When the material was coupled with exothermically-reactive chemicals, it's possible to create self-propagating waves of heat. However, there are a couple of problems with implementing systems like these. Firstly, the waves generally propagate in all directions, which is not good for high efficiency power-generation. Also, materials that can prevent the wave of the pulse from scattering and can stand up to a large amount of heat are fairly rare and finally such material should be heat-proof up to a few thousand Celsius and have a hard line against heat scattering, preferably concentrating it in a one single direction. It will be perfect if such system will be very small and the created waves would propagate with high velocities and have a mean free path about the same as the length of the material where they propagated. (Fig.3)

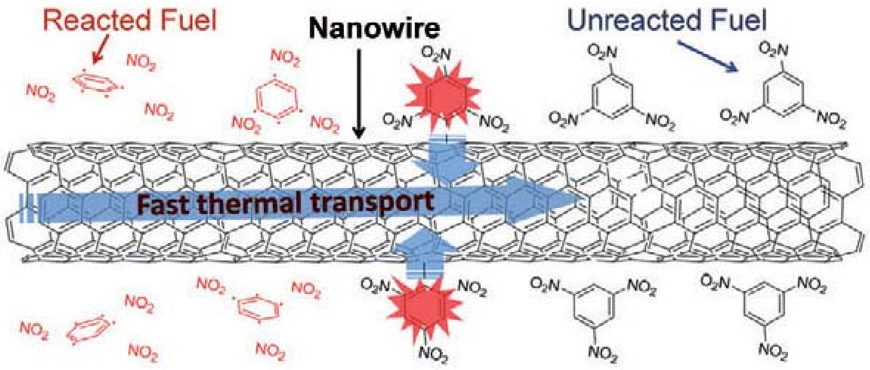


Figure 3. Schematic illustration of exothermic chemical fuel which is wrapped around a thermal conduit, particular a carbon nanotube. Initiation at one end of the tube induces a one dimensional chain reaction with amplified velocity due to fast thermal transport in the conduit. Picture captured from [8].

This idea was firstly realized in March 2010 and it demonstrated the possibility to create thermopower waves (self-propagating chemical reaction waves) guided by a thermally conductive nanotube [6]. Despite the fact that many semiconductor materials can produce an electric potential when heated (Seebeck effect), this effect is very weak in carbon. The combustion-produced thermal wave, that propagate in carbon nanotube, thermally excite electrical charge carriers just as an ocean wave can pick up and carry a collection of debris along the surface. Only phonons that are close to reaction region of the carbon nanotubes contribute to wave propagation and producing a great acceleration when they have mean path comparable to the size of reaction zone. The challenge with conventional TE devices is maintaining a large thermal gradient while allowing a large electrical current to flow through the interface. In devices designed to harvest electrical power from waste heat, the goal of materials scientists has been to select materials that conduct heat primarily as phonons but block their propagation across an interface where electrical conduction is large. An alternative way of creating a large thermal gradient, even in a material that conducts both heat and electrical current well, is to create a self-sustaining reaction wave. So this unique phenomenon allows us to create in future a new type of energy sources and fuel, that’s why further detail experimental and theoretical studies are needed.

8.3 Research methods

Synthesis of TNA-MWNT arrays should be realized at the beginning the project. Vertically aligned MWNT synthesized by CVD technique [9]. Scheme of the MWNT array fabrication is depicted in Fig.4. MWNT with approximately 5 mm in length are used to build the completed arrays.

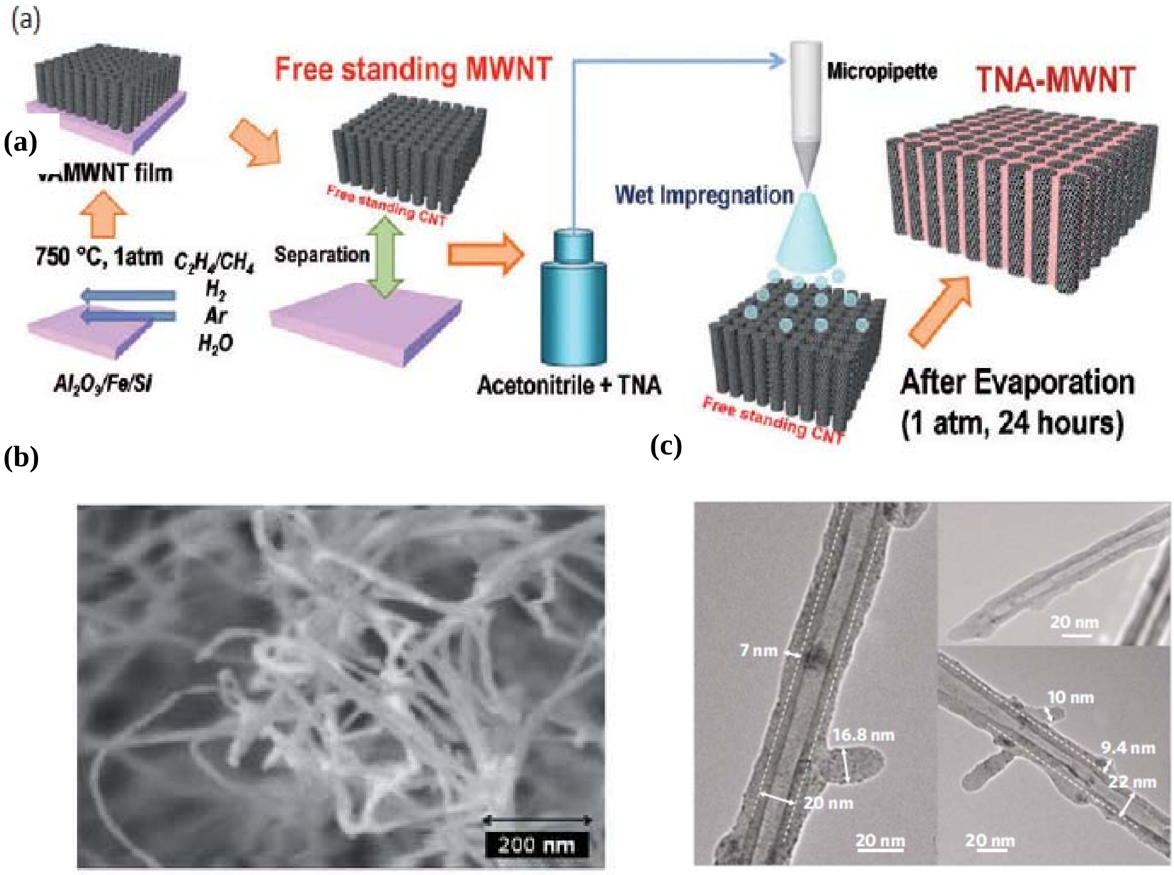


Figure 4. (a) Synthesis process for TNA-MWNT arrays by wet impregnation. **(b)** Forcibly disordered TNA-MWNT array. **(c)** Image of TNA-MWNT array done by Transmission electron microscopy diameter is 22 nm, and thickness of TNA layer is in the range of 9 nm. (reprinted from [10] © 2010 Nature Publishing group.)

In (Fig.4a) wet impregnating procedure, basic method to coat fuel on CNTs, is shown. The first fuel that was taken is cyclotrimethylene-trinitramine (TNA) in acetonitrile solution. After fuel was dropped into the pores of a MWNT array and after liquid evaporated from the sparse MWNT array. Due to the strong van der Waals interactions between CNTs the TNA solution was trapped between CNTs. Transmission electron microscopy (Fig. 4c) indicate the complete wrapping TNA on MWNTs.

Further step is initiation of thermopower waves. In principal there are two methods for initiation of reactive waves in the sample: high voltage electrical discharge and laser ignition. A laser pulse (785 nm, 400 mW) applied to one end of an array can induce exothermic chemical reaction. The other way is high voltage electrical discharge. During the reaction propagation it is possible to measure velocity of the reaction. There are three possible ways for doing that. Firstly, optical fiber array can be used for detecting emitted light from a series of spots in the reaction region. The optical fiber array is situated parallel to the reaction region and measures the time differences between successive fibers as the reaction wave propagates across the sample. A second possible method is high-speed photography and for this we should use high-speed video microscopy (up to 90000 frames per second). A high-speed CCD camera with a microscopic lens is used to record the reaction wave propagation in real time. Third method to measure velocity is connecting to measurement of thermopower energy generation. Set-up for this purpose is very similar to the common setup for conventional TE measurement except for the presence of the reaction initiation system and absence of temperature controllers on either side of the sample. TNA-MWNT array is fixed between two electrodes, which are connected to an oscilloscope (Fig. 5a). The reaction is initiated at one end, and the wave propagates across the sample. Fig. 5b shows real time high-speed microscopic images of the thermopower waves launched and their propagation process.

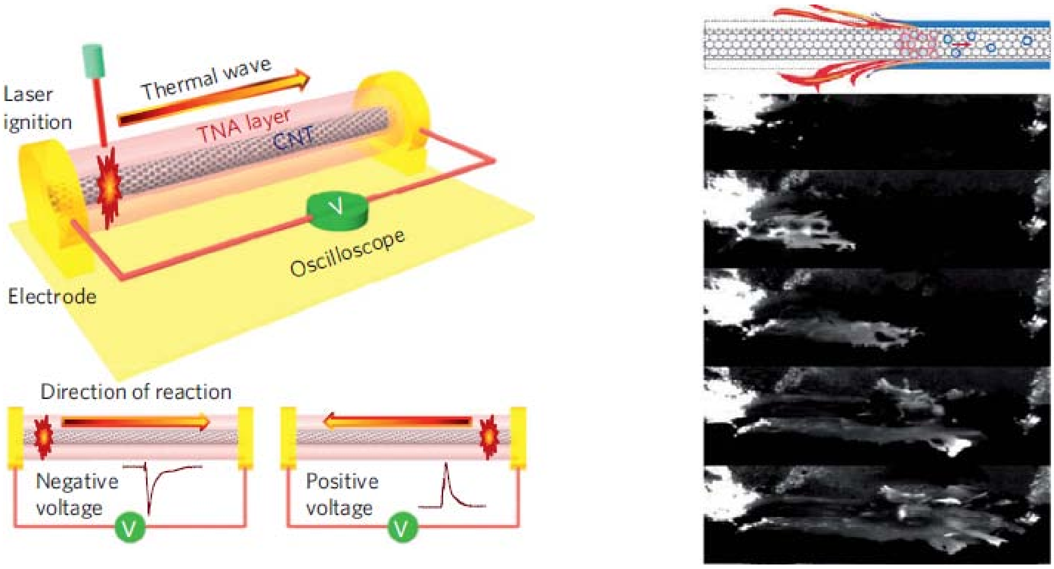


Figure 5. (a) Scheme of thermopower wave measurement set-up with TNA-MWNT array. When ignited at one end, the reaction propagates in one direction through the sample. **(b)** Real time high-speed microscopic images of thermopower wave propagation along TNA-MWNT array**.**
(reprinted from [7,8])

During the processes of reaction propagation and further cooling stages, when a temperature gradient exists, the obtained voltage signal reflects the electrical energy that the thermopower wave generates. This signal contains a lot of information about the thermopower wave. For instance it can be classified into two regions (Fig. 6). First region is strongly oscillating part and the second smooth region defines conventional thermoelectric effect. It is possible explain this behavior in the way that velocity oscillations of reaction wave can lead to creation of significant oscillations in the voltage signal synchronously with the reaction propagation along the length of the tube. As the sequence, the reaction time corresponds to the duration of the oscillating voltage signal, and velocity can be calculated easily. The smooth region can be explained due to the conventional TE voltage generation from the temperature gradient remaining after the fast propagation of thermopower wave has finished. The voltage will return to zero after temperature back to equilibrium.

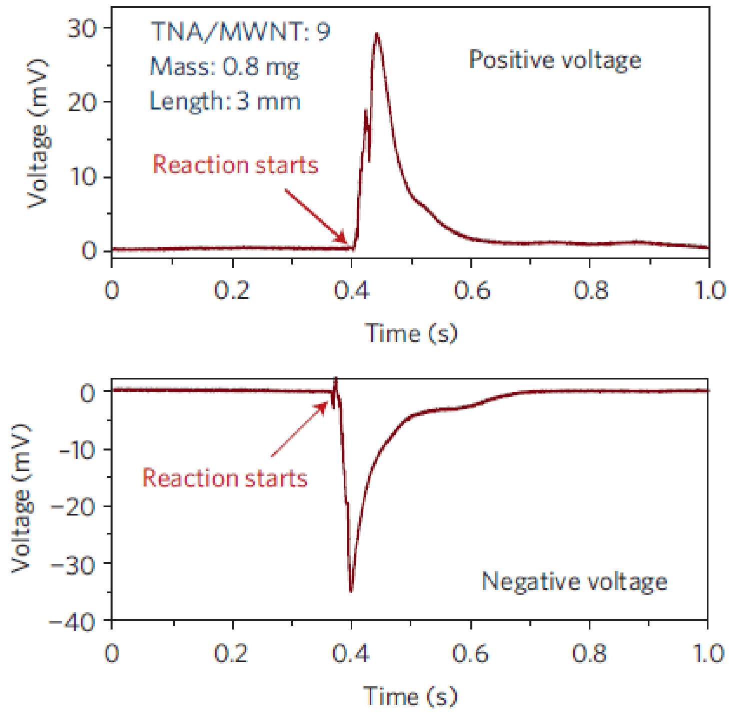


Figure 6. Illustration of measurement reactivity velocity and thermopower energy generation. From these graphs is possible to make comparision of voltage traces and high speed photographs and to see that oscilating region corresponds to the time of reaction wave propagation. Also these graphs demonstrate that electrical pulse can be either positive or negative depending of the direction of reaction propagation.

In principal the reaction velocity of the thermopower wave depends on many factors, such as thickness of fuel, diameter of thermal conductor, and the dimensions of the sample and the thermal diffusivity of the conduit. Higher degree of alignment of CNTs, lower quantity of amorphous carbon, and small cross-sectional area of the sample increases the average reaction velocity. As we show above the thermal reaction wave leads to generation of a high specific power electrical pulse with constant polarity (Fig.6). The electrical charge carriers tend to move from the hottest area, reaction zone, to the unreacted zone in the CNT, (the coldest area) as shown in Fig.3. One should note about the difference between samples which have different length. TNA-MWNT arrays in the first study were around 5 mm long in their alignment direction. Also, variations in mass correspond to variations in the cross-sectional area and the number of nanotubes in one array should be taken into account. The simulated results of the thermopower wave model show that a small-mass sample with fast reaction velocity generates a sharp electrical pulse of constant polarity. On the contrary, a large-mass sample with slow reaction velocity will cool strongly behind the reaction front and create opposite thermal gradients and thus almost zero voltage. This case can be explained as asymmetrical thermal pulses moving across the sample to meet each other also like in the case if the initiation of the reaction was applied in the middle of the sample and create two opposite temperature gradients, and the voltage signal will have peaks of both polarities during the chemical reaction. Obviously this cancellation of voltage leads to the loss of electrical energy. Although MWNTs have a relatively low Seebeck coefficient (80 μV/K, the temperature gradient is preserved for the duration of reaction propagation, which indicates that materials with low TE figures of merit could still generate electrical energy with higher efficiency compared to conventional TE devices. It should also be mentioned that Raman spectroscopy allows us to study and to compare the characteristics of carbon nanotube array before and after reaction showing that the materials are re-usable.(Fig.7).

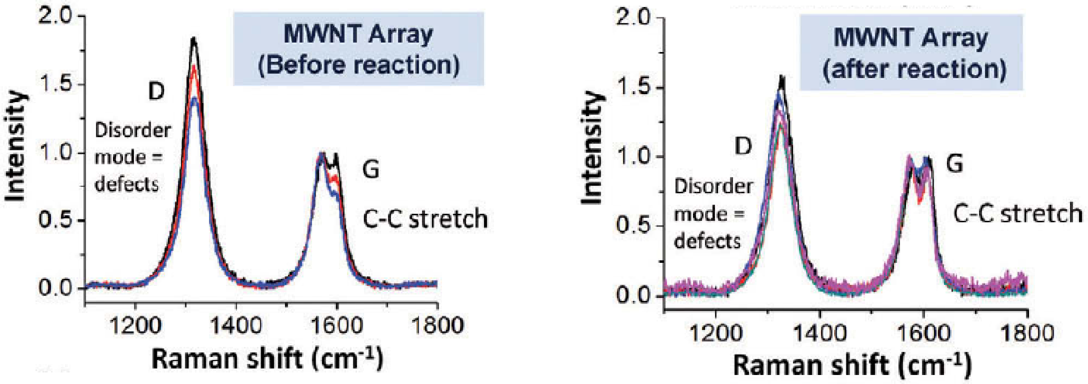


Figure 7. Raman spectra of MWNT array before and after reaction. Original structure and properties of carbon nanotuebes remain the same direction of reaction propagation. (reprinted from [8])

9. Project Aim

This project aims to investigate a new phenomenon in carbon nanotubes – thermopower waves. The project combines research efforts, including sample fabrications, optical and electrical characterization, and theoretical analysis of thermopower waves. Main purpose is to optimize the existing set-up and to improve power generation efficiency. For example, solution processable method can be used for device preparation instead of CVD technique. As first step, we will try to optimize the existing MWNT-TNA system. The influence of sample structure on the reaction velocity and energy generation process will be studied such as the length of MWNTs and thickness of array, alignment of CNT. Furthermore we want to investigate the possibility to use another kind of carbon nanotubes to improve efficiency of power generation, for instance double-walled or single-walled carbon nanotubes. Second part of the project involves the investigation of repeatable process for energy generation. One possible way is to build efficient generator with solution processable method. We propose to use carbon nanotube suspension incorporated in micro (nano)-channel chip by dielectrophoresis technique [12,13]. It gives the opportunity to obtain percolation channel formed by dispersed nanotubes and to greatly reduce the cost of sample preparation. The third step of project is to use conventional fuels like gasoline, ethanol, methane ethanol or formic acid in order to broaden the application of this energy generator. In fact this replacement will lead to changes of reaction velocity and efficiency of electrical power generation. Micro (nano)-channel devices can be laser transparent which helps on the real time monitoring of the process. The device can be easily refilled with using liquid delivery system and can be incorporated into conventional engine system. Finally the project is also of great interest for the understanding of TE effects and thermopower wave phenomena in nanostructured materials. Nanowires with different thermal diffusivities and electrical properties may alter the dynamics of the chemical reaction wave as well as the electricity generation. Materials with large Seebeck coefficients such as bismuth telluride or silicon nanowires could be alternative thermal conductors even though the low thermal diffusivities are inferior to carbon nanotubes. This project could help in understanding the fundamental difference between thermopower waves and static thermopower.

9.1 Research plan

September 2011 - August 2012	To build experimental set-ups for the measurement of thermopower waves. Using TEM technique to estimate structure of MWNT – TNA arrays. Using high-speed video microscopy to measure reaction velocity of thermopower waves. To estimate efficiency of thermopower wave generator.
September 2012 - August 2013	Test of two methods of ignition of reactivity waves (laser ignition and high-voltage electrical discharge) will be used. Study the propagation characteristics and generated electrical power versus alignment of CNT in arrays, length of samples and thickness of fuel. Using several reactive fuels for making layers of coating instead of TNA.
September 2013 - August 2014	Reproducible energy generation and conduct the reaction monitoring in real-time. Fabrication of micro (nano)–channel device and exploration of novel solution processable method. To replace MWNT nanotubes to another types, for instance to DWNT and SWNT nanotubes.
September 2014 - August 2015	Investigation of possible applications of other materials such as gasoline, ethanol, methane, or formic acid to enable wider applications of thermopower wave generator. The final step will be to realize catalysts with thermopower waves to lower activation energy barriers and to increase the reaction rates. Writing a Ph.D thesis.

References

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