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S. Yatom and Y. Raitses

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On a probable cause of poor selectivity of carbon nanotubes synthesis by arc discharge

S. Yatom* and Y. Raitses
Princeton Plasma Physics Laboratory, Princeton, NJ 08543, USA

Abstract

We show that synthesis of single wall carbon nanotubes (SWCNT) by carbon arc is not a continuous process, involving switching between two distinctive modes, only one of which ("synthesis on") is capable of producing SWCNTs. The two modes were characterized for a typical arc configuration with a hollow anode filled with powder mix of metal catalysts and graphite powder, using electrical, imaging and spectroscopic diagnostics. The "synthesis-on" mode duration is rare compared to arc run-time, explaining the poor selectivity of the final product, which is the common arc synthesis caveat.

Arc discharges are commonly used for synthesis of nanostructures and particularly high-quality single wall carbon nanotubes (SWCNTs). First nanotubes produced in the arc discharge were reported by Ijima et al. in 1991 [1] and the amount of studies of carbon nanotubes (CNTs) synthesis in arc conditions continues to grow [2, 3]. A typical arc setup is relatively simple in terms of construction and implementation. It includes two electrodes one of which is consumed by ablation during the arc. This electrode is typically a hollow graphite anode filled with powder mix of metal catalysts and graphite to provide carbon and metal catalyst feedstock needed for facilitation of the growth of SWCNTs [2-6]. In spite of this design simplicity, it is commonly accepted that the arc synthesis method of SWCNTs cannot match other synthesis methods (e.g. CVD, laser ablation) in terms of synthesis selectivity, yield and purity of grown CNTs. This is partially because there were almost no studies of fundamental physical and chemical mechanisms responsible for these drawbacks of the arc synthesis. Maximum SWCNT yield reported in arc discharge is 2 g/h [4]. The advantages of arc lies in the superior crystallinity of the synthesized CNTs, especially for MWCNTs.

* Corresponding author, email address : syatom@pppl.gov

The selectivity of the arc synthesis of SWCNTs is generally considered to be poor, as a lot of carbon soot and metal nanoparticles is found in the analyzed samples [5, 6]. The SWCNTs containing samples are usually collected in the chamber in a form of a web-like formation. Journet et al. [7] have found that the collar formed around the cathode is the richest in SWCNTs. In this work, we show that during the arc operation the synthesis occurs in a random fashion for undefined stretches of time and the arc plainly switches between the two modes of operation: the dominant mode, where the discharge essentially happens between two solid graphite electrodes and much rarer mode, which involves the graphite powder and catalyst mixture. The modes are easily distinguishable and characterized by different emission spectrum and different plasma characteristics. To the best of our knowledge no studies ever reported that the synthesis with the carbon arc is random and chaotic.

The carbon arc setup used in these experiments was described in details elsewhere [8]. The electrodes manufactured from a single-piece graphite and have diameters of 1.15 cm and 0.55 cm for cathode and anode respectively. The anode is hollow with the cavity diameter of 0.3 cm. In this work, the anode is filled with tightly pressed graphite powder mixed with a catalyst of Ni and Y. The mixture ratio is 14-4.1-1 of graphite powder, Ni and Y, respectively. The electrodes positioned vertically, with the cathode located on top and the anode location is controlled by a mechanical stepper motor. The chamber was evacuated to a fore-vacuum pressure and subsequently filled with He gas to pressure of 500 Torr. The arc is ignited when the electrodes are in contact and then they are separated to maintain the voltage of 27 V and current of 60 A. Maximal arc run duration was up to 2 minutes, in order not to overheat the chamber. The fast-framing imaging was performed with Phantom V7.3 camera, equipped with an optical filter at central wavelength 470 nm and full-width-at-half-maximum (FWHM) of 10 nm. We have employed a LeCroy WaveSurfer 10 oscilloscope (1 GHz, 10 Gs/s) and recorded the voltage and current waveforms with an active voltage divider and a Pierson current monitor (model 4418), respectively. Optical emission spectrum was recorded with Ocean Optics HR2000+ spectrometer.

Previously we have investigated the operation of the carbon arc with two solid electrodes under same conditions, but without catalysts [8,9]. In these works, the low [9] and high [8] frequency regimes of arc oscillations were observed and characterized. In the current setup with powder and catalyst anode, we have observed a correlation of the transition between the modes

and changes in the sound produced by the arc. With the powder and catalyst filled anode the arc sounds regularly transitions to a uniform, low-frequency sound, prompting us to investigate the matter. Visual inspection showed that the hissing arc features oscillations but when the sound transitions to uniform the arc stabilizes. As soon as the arc is stable the CNT-rich web starts to form and fly around the chamber. Consequentially, we have designated the hissing mode – "synthesis off" and the stable mode as "synthesis on".

The following study was the fast-framing imaging of the discharge and of the transition between the two modes. Several frame rates were tested to record the movies. Very quickly it was clear that the sound transition distinguishes between very different behaviors of the arc. In "synthesis on" mode, the arc oscillates as in the case of solid anode [8, 9]. In "synthesis on" mode, the oscillations disappear and instead a strong jet appears from the anode. Brief jumping between the modes usually occurs for tens to hundreds milliseconds, before the continuous "synthesis on" mode settles, which can go on for tens of seconds. Exemplary results can be seen at Figure 1, where a set of frames depicts the alteration between the two modes. The images are taken through a 470 nm filter and as such they emphasize the emission of Swan band of molecular C_2. In that frame sequence first 5 images show the low-frequency (~100 Hz) arc oscillations, in the hissing mode. After 8 milliseconds a stable emission in a form of diffuse jets originates from the anode cavity, signifying the transition to "synthesis on" mode.

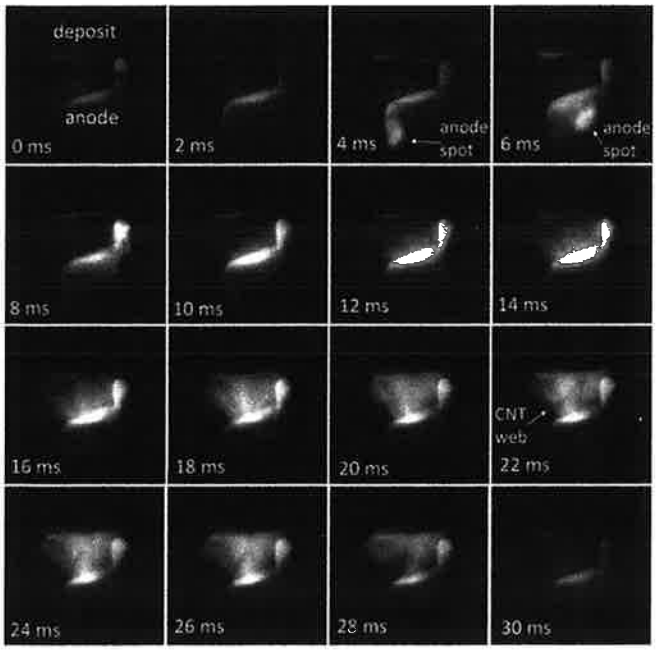

Figure 1. Transitions between "Synthesis-on" and "Synthesis-off". At the images the synthesis starts at 10 ms image and goes back to "synthesis off" at 30 ms.

At several frames, the jet emission is partially abstracted by a prolonged black structure (t=22-28 ms), which is a piece of a CNT rich web, flying towards the camera. After a period of ~ 18 ms the strong jet disappears and the arc goes back to the oscillating regime. Multiple arc runs and views of the recorderd movies have allowed us to come up with a phenomenological explanation of the two modes (Figure 2).

- Arc oscillations occur when the anode is partially empty, at the least to the depth of several millimeters. This case is identical to the case of the solid graphite anode without catalyst and hence displaying the characteristic behaviour and oscillations of the arc.
- Arc oscillations slowly ablate the walls of that hollow anode, untill the powder mixture is exposed to the arc.
- Now the oscillating arc engages the powder mixture resulting in short spurts visible as intense, light emissionin a form of the jet protruding from the anode cavity towards the cathode deposit.
- After a series of spurts, a quasi steady "synthesis on" mode settles. This mode may continue from seconds to tens of seconds.
- The mode transfers back to "synthesis off" as soon as the powder mixture at the top of the anode is depleted and so the arc moves back to the graphite wall of the anode. After this transition arc oscillations resume.
- These oscillations slowly ablate the anode walls, until the powder inside the hollow anode is again exposed to the arc.
- Cycling of the arc between two regimes continues until the powder is fully utilized or the arc stops.

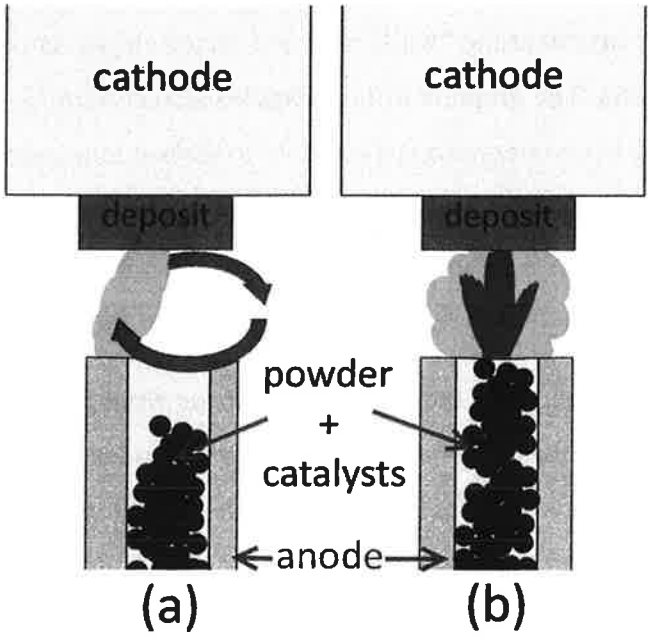

Figure 2. Transitions between "Synthesis-on" and "Synthesis-off" modes. (a) Arc oscillates around the surface of the hollow anode and is unable to interact with the powder mixture of the graphite and metal catalysts that were depleted from the top part of the anode (b) When the arc engages the graphite and catalyst powder it proceeds in a stable mode, which no longer oscillates and in characterised by much more intensive C_2 emission.

The transition between the synthesis modes is also evident on the voltage and current waveforms,(figure 3). Brief mode changes (so called spurs) are manifested on the voltage and current waveforms as a rapid increase of the voltage from 27 V to 40 V and decrease back to 27 V. In the continuous "synthesis on" case, the voltage also increases to 40 V and than slowly lowers to a 32-34 V level. Figure 3 shows that just before the continuous "synthesis on" mode is over the voltage again jumps from 33 to ~48 V. The current oscillates in a correlation with the voltage, however the amplitude of these oscillations is very low, which is quite reasonable when operating with a constant current power source. Why does the voltage demonstrate such dramatic increase ? Voltage rise during constant current means a surge in resistance, according to Ohm's law. Resistance apparently increases due to a combination of two factors: plasma losses to micron sized graphite particles and resistance due to increased electron-neutral collisions. The graphite particles are the majority composites of the anode filling, ranging in sizes between 5-10 μm. The plasma losses associated with the graphite particles are akin to the wall losses, where electron diffuse and get lost in the chamber walls. Injection of many large particles into the

dischrage gap effectively increases the "wall" area and therefore preventing a significant part of electrons to reach the anode. The graphite micro-particles also sublime in hot region of the plasma channel, resulting in disintegration of graphite to carbon molecules and atoms. The surge in neutral density boosts the electron-neutral collision rate accordingly, i.e. raising the plasma resistance. Each one of thes mechansims can be responsible for the observed increment in voltage, however in the arc conditions it is likely that it is the combination of two.

It is reasonabale to expect that the emission spectrum from the arc should change significantly between the "synthesis on" and "synthesis off" modes, because as is apparent from imaging and the electrical characteristics the plasma in these modes is drastically different. Indeed a survey of the broadband optical emission shows that in "synthesis off" mode the only prominent features are the Swan bands emission of C_2 and the blackbody emission of the hot electrodes and plasma.

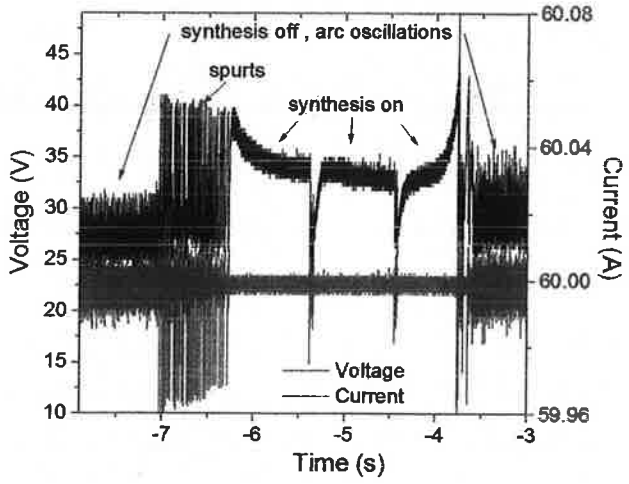

Figure 3. Voltage and current waveforms bearing evidence to the transitions. The voltage increases rapidly when the synthesis starts, even if it happens in short pulses (spurts). When the continuous "synthesis on" mode is established, the voltage slowly decreases but still remains significantly higher, when in the "synthesis off" case.

When "synthesis on" starts the Swan bands emission intensifies, but also the emission of the metals emerge. Most of the time this emission consists of Y and Ni neutrals, however for a brief periods of time the emission is augmented by multiple Y ion lines and a single N ion line.

Because these lines only appear for a short duration we tend to attribute them to the fast pulsations of jet when the brief transitions between the modes happen. The described emission patterns showed at figure 4. This is a crucial evidence that the synthesis of SWCNTs is only happening during the stage what we call "synthesis on" mode, because the metals are essential for formation of SWCNTs [3,5,6].

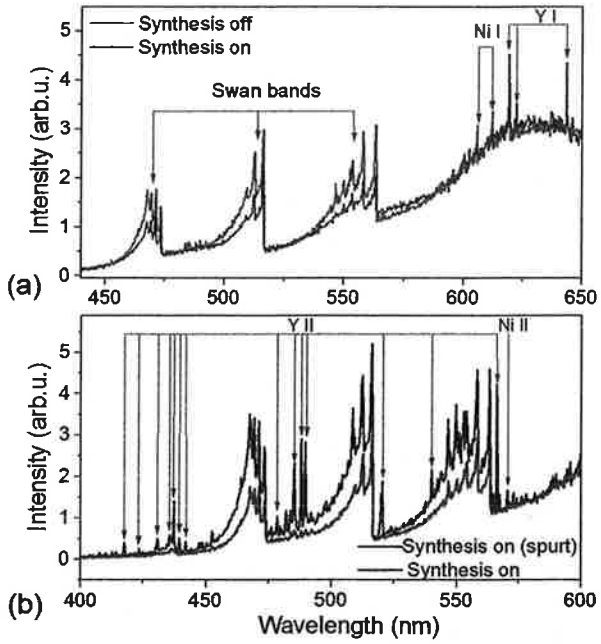

Figure 4. (a) Emission in "synthesis off" and "synthesis on" modes (b) Occurrence of metal ions lines when a spurt happens.

The results described above show that the nano-synthesis in the case of carbon arc occurs in a sporadic fashion, due to the uneven consumption of the graphite walls of the anode and the filling of the anode, which includes the catalyst of the synthesis. If we consider a single anode filled with powder and catalyst- during its lifetime, most of the discharge happens in the "synthesis off" mode, accounting for approximately 95% of the anode lifetime. The main implications are that whenever one conducts the analysis of the nanostructure synthesis with the carbon arc a full distinction is necessary between the two modes. Specifically, so far the carbon arc method for the synthesis was described as having poor selectivity. This is because the products of the discharge are usually collected on in an integrated fashion, usually in after and not during the arc operation. The samples are usually the web formations collected in the chamber or the stationary witness plates situated in the chamber, without differentiating between

the modes and the durations of the modes. Along with the high-quality SWNTs a collection of soot particles, metal nanoparticles, nano-horns etc. is routinely plagues these samples. Therefore a true measure of the selectivity of arc synthesis method can only provide with consideration of the findings of this paper: e.g. deploying a retractable collecting probe [10] only during the "synthesis on" mode.

Acknowledgement

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