# LASER-INDUCED REACTIONS IN ACETYLENE FLOW: SHELL-SHAPED CARBON NANOPARTICLE FORMATION

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Recently it was reported that infrared $CO_2$ CW laser irradiation of acetylene flow can produce continuous layer shell-shaped carbon nanoparticles (SCNP) directly from the gas when the laser power exceeds some critical value [Choi *et al*., 2004]. The transition process is distinguished by the blazing light emission in visible, indicating high electronic excitations in reacting molecules. It is remarkable that acetylene does not absorb the 10.6 μm wavelength laser radiation and a self-sustained reaction should be initiated firstly. After the start-up the process goes though laser-absorbing intermediates leading to SCNP production. It was found in *extra situ* experiments that the SCNPs show the famous ultraviolet (UV) absorption peak at 220 nm, known from interstellar media absorption, as the consequence of the existence of pentagonal topological defects in the continuously closed graphene layers [Pikhitsa *et al*., 2005]. This perfect continuity is the main feature that distinguishes SCNPs from soot.

Yet, the mechanism of the SCNP generation has not been explained. In particular, the question why, instead of chaotic stacks of basic structural units (BSU) characteristic for soot, the perfect continuous carbon layers are formed, remained unanswered. Although it is known that acetylene (after a start-up heating) can be exothermically decomposed into acetylene carbon black and hydrogen, it is unlikely that this thermal reaction alone could self-sustain, considering short residence time of less than 1 msec in the laser beam and temperatures as low as $500^0$ C at 1 mm from the reaction zone so that even the residual hydrocarbons do not burn when contacting air downstream and can be observed in UV and infrared (FTIR). Also acetylene black particles produced in standard way by surface reactions may look similar to SCNPs from [Choi *et al*., 2004] only after a prolonged high temperature post treatment.

Our further experimenting with acetylene flow shielded from air with inert gases revealed the potentials of the process – it occurs that there are conditions when a variety of carbon allotropes can be generated: giant fullerenes of 5 nm (Fig. 1), cubic nanodiamonds (Fig. 2), carbon nanotubes (Fig. 3) and amorphous carbon seen in Fig. 3 and also in Fig. 4 together with giant fullerenes. As fas as nanodiamonds (Fig. 2) are present in our experiment one may conclude that it can not be laser heating that is responsible for the generation of these nanostructures but instead it is *multiphoton infrared laser photochemistry* (MP) that is involved in production of amorphous carbon and nanodiamonds.

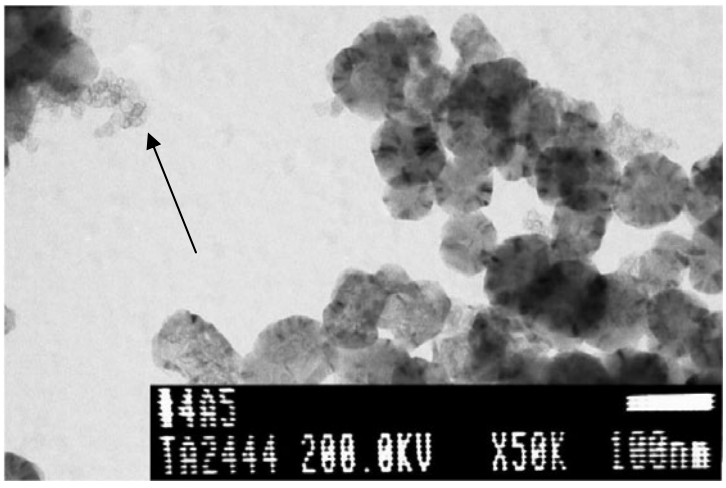


**Figure 1**. Along with SCNPs a cluster of giant fullerenes of 5 nm is shown by the arrow in the left upper corner.

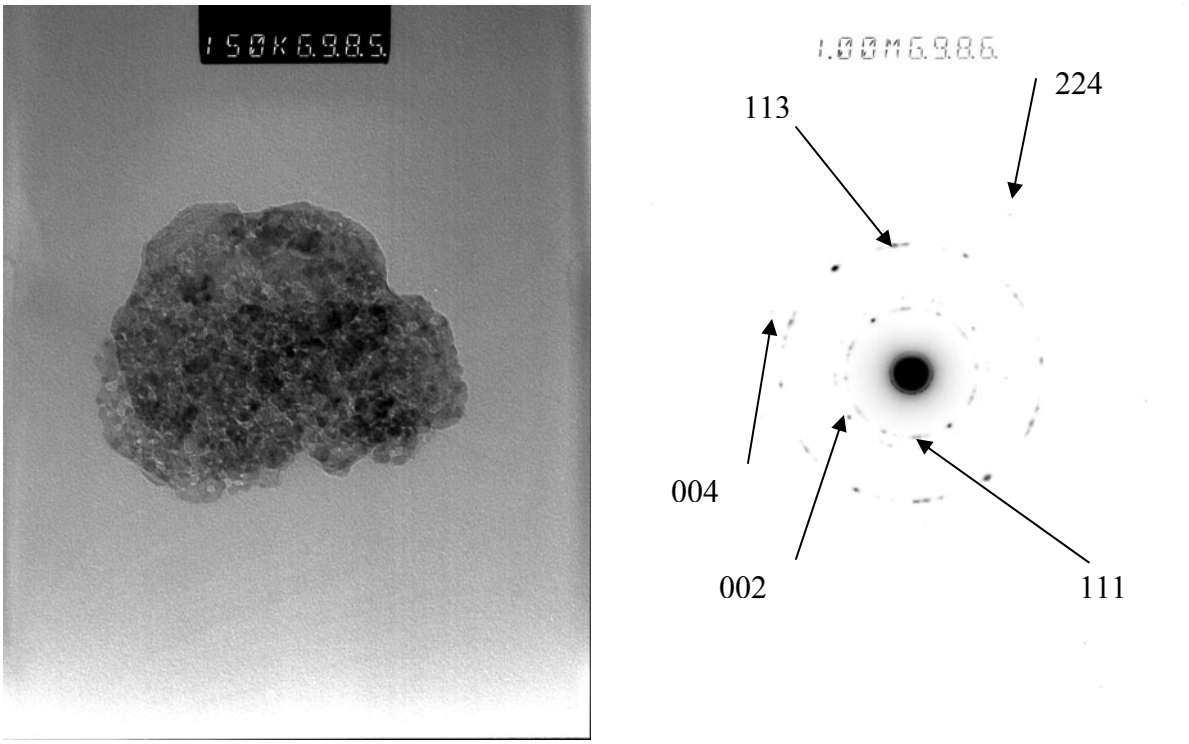


**Figure 2**. Cubic nanodiamonds. Diffraction pattern shows monocrystal spots (right).

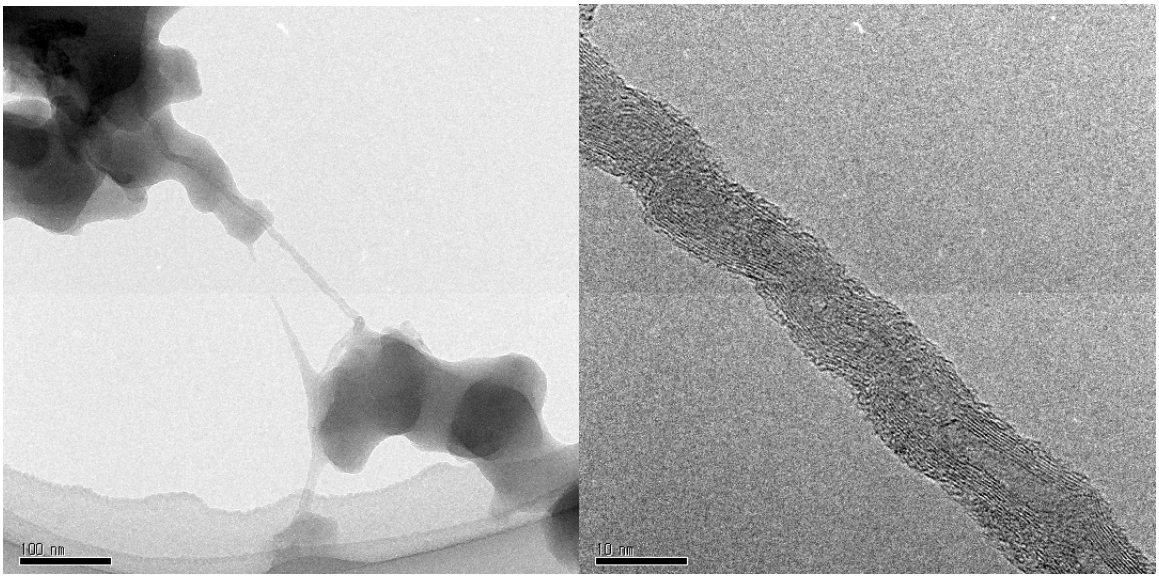


**Figure 3**. Carbon nanotubes are seen on the background of amorphous carbon. One of the nanotubes is multiwalled (HRTEM image on the right), the other - amorphous.

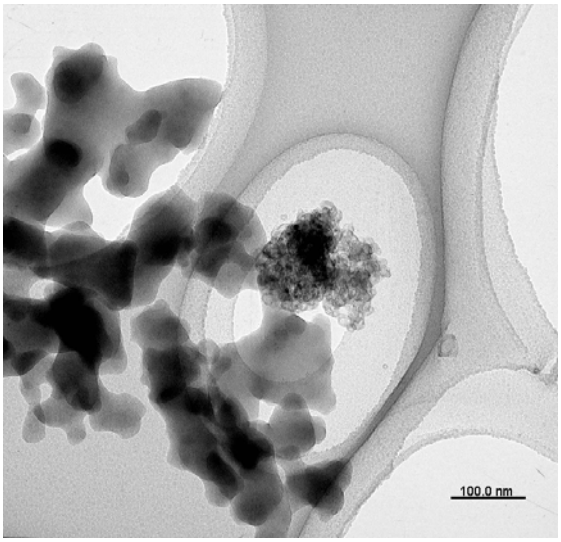


**Figure 4**. Amorphous carbon along with giant fullerenes.

Close inspection of the reaction zone (where the laser beam crosses the vertical acetylene flow) reveals a curious structure (Fig. 5): above some critical flow velocity the needle-like reaction zone interrupts in the central region where the laser power has maximum.

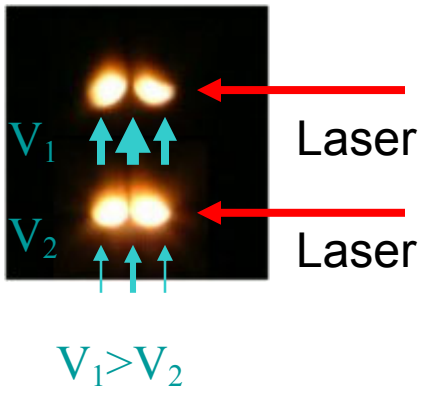


**Figure 5**. Photographic images of the reaction zones for two flow velocities. Blue arrows indicate flow direction and parabolic profile; red arrows indicated the laser beam size and direction for the two cases.

This interruption allows one to study the critical reaction diagram of the reaction for three relevant parameters: laser power, acetylene concentration and flow velocity.

The HRTEM image given in Fig. 4 closely resembles the image from [Iijima *et al.*, 1996] where a graphite target was laser-ablated in an inert atmosphere and the $C_2$ dimers quickly condensed. We suggest the following mechanism that governs the generation of the amorphous carbon and nanodiamonds.

1. A chain MP reaction with excited molecules and CO2 laser-absorbing intermediates - atomic hydrogen, $C_2H_3^*$ and vinylidene - takes place.
2. Atomic hydrogen goes downstream and reacts with fresh acetylene to produce laser-absorbing intermediates as described in [Payne *et al.*, 1976, Smith *et al.*, 2001].
3. Laser-absorbing intermediates dissociate under the laser beam to reproduce atomic hydrogen and $C_2$ dimers [Herlin *et al.*, 1998]. Therefore the whole reaction is self-sustained.
4. $C_2$ dimers quickly condense into amorphous carbon and nanodiamonds.

We claim that these low-temperature metastable amorphous carbon structures are the precursor for SCNPs. Indeed, recently it was shown that several millisecond heating is enough to reconstruct an

amorphous nanotube into a multiwalled nanotube [Huang *et al.,* 2006]. That means that returning into the laser beam can turn amorphous carbon nanoparticles into SCNPs. Fast coalescence of giant fullerenes under infrared multiphoton absorption may happen as well [Ferretti *et al.*, 1996].

Note that preheating of acetylene destroys the chain reaction described above. Acetylene pyrolysis may lead to intensive soot formation as is observed. In fact, experiments with adding ethylene (which absorbs the laser through MP and effectively heats up the system) to acetylene led mostly to soot formation [Morjan *et al.,* 2003, Galvez *et al.*, 2002]. Oxygen (as contamination) can also react with acetylene and the PAH to stimulate production of soot particles.

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