Plasma-assisted Synthesis of Carbon Nanomaterial Studied by Spatially-resolved Laser-induced Fluorescence and Optical Emission Spectroscopy

Tanvi Nikhar[1], Sankhadeep Basu[2], Shurik Yatom[3], Yevgeny Raitses[3], Rebecca Anthony[2], Sergey Baryshev[1]

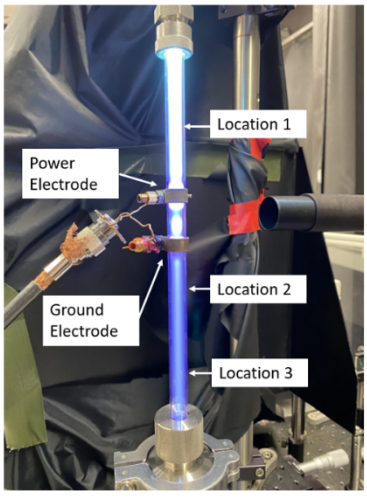
[1] *Electrical Engineering, Michigan State University, 428 S. Shaw Lane, East Lansing, MI 48824,USA*
[2] *Mechanical Engineering, Michigan State University, 428 S. Shaw Lane, East Lansing, MI 48824,USA*
[3] *Plasma Sciences and Technology, Princeton Plasma Physics Laboratory, 100 Stellarator Road, Princeton, NJ 08544, USA*
nikharta@msu.edu

Crystalline nanographite and carbon nanodots in particular have been of great interest for their applicability in energy conversion, optoelectronics, and sensing including biosensing due to their low toxicity. In this work, we report a scalable synthesis of sp^2 carbon nanomaterial consisting of crystalline carbon nanodots and nanographite. This chemical vapor deposition (CVD) approach takes a nonthermal argon-methane capacitively coupled plasma actuated by a radiofrequency source in a flow-through tubular reactor. Plasma enhanced CVD synthesis from gaseous phase offers several advantages over traditional routes used previously (like laser ablation, electrochemical or hydrothermal synthesis.) In particular, this route is a simple (inexpensive, solvent-free, one step) process that allows to deposit the target material on the substrate at room temperature. In the described process radiofrequency power of 200 W was supplied at 13.56 MHz and argon-methane gas mixture was kept at ~4 Torr. Raman spectroscopy confirmed sp^2 hybridization. TEM image analysis indicated that the average particle size was around 6 nm.

With inputs and outputs being known, this work takes a step further to study the pathways connecting the molecular precursors/reactor parameters and the final products. To gain insights into kinetics of such growth process, it is critical to conduct spatially resolved measurements of 1) atomic/molecular species and their densities and 2) molecular species-to-nanoparticle conversion. With this in mind, we used 1) laser-induced fluorescence (LIF) to capture C_2 species distribution in the discharge/reaction zone and 2) high resolution optical emission spectroscopy (OES) to evaluate vibrational, rotational and gas temperatures. Together with the detailed performance of the reactor, these diagnostics could allow for understanding how C_x species evolve from the center of discharge to form ~10 nm particles thereby allowing for a comprehensive description of spatiotemporal evolution of graphite nanoparticle growth.

The operating reactor is shown in **Fig.1 (left)**. The gases flow in from the top of the quartz tube with the pump attached at the bottom end where a stainless-steel mesh is placed to capture the nanoparticles formed in the plasma. The LIF measurements for C_2 are taken at three different locations along the length of the tube for plasmas from two gas compositions: Ar(100 sccm)/CH_4(2, 10 sccm). A rotational temperature of ~1200K was estimated from the OES measurements and then used to calulate the C_2 number density from LIF data. C_2 density was found to be decreasing down the length of the tube in both 2 and 10 sccm cases, see **Fig.1 (right).** The yield of the sample collected was observed to be higher for the 10 sccm case while the corresponding C_2 density was ~10 times lower as compared to the 2 sccm case. Since C_2 is considered a proxy for the sp^2 phase growth, the higher production yield for 10 sccm CH_4 can be attributed to a higher conversion rate of C_2 to nanographite and hence a lower available amount of C_2 to be measured in the plasma. The higher CH_4 flow in the 10 sccm case could also be a contributing factor towards the observed higher sample yield.

The work at the Princeton Collaborative Research Facility (PCRF) was supported by the U.S. Department of Energy (DOE) under Contract No. AC02-09CH11466. Plasma diagnostic resources used in this work were provided by PCRF. The work at MSU was supported by DOE under contract DE-SC0023211.



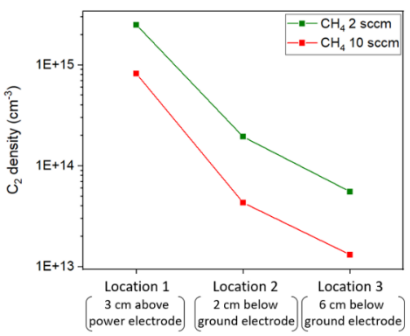


Fig. 1 (left) Setup of the CCP reactor with the plasma; **(right)** C2 density at various locations in the plasma.