Synthesis of Carbon Nanostructures in an Atmospheric Pressure Arc Discharge

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Abstract: Comprehensive optical and electrical measurements of plasma and combined in-situ and ex-situ measurements of nanoparticles, and results of 2-D fluid simulations of the arc plasma revealed the first insights into the whole chain of synthesis processes starting from generation of the carbon feedstock to the growth of CNTs in plasma.

Keywords: Arc discharge, Synthesis, Nanoparticles, In-Situ diagnostics

1. General

Synthesis of various carbon nanostructures, including fullerenes, single-walled and multi-walled nanotubes and nanoparticles, by moderate (~ 10-100 torr) to atmospheric pressure dc arc discharges relies on ablation of the graphite anode and deposition of synthesized carbonaceous products on the cathode surface and on the reactor chamber walls. Applying a set of the developed diagnostics of plasma, including optical emission spectroscopy, fast filtered imaging, laser-induced fluorescence and electrostatic probes, and also advanced in-situ laser-based diagnostics of nanoparticles, our synthesis experiments revealed that the carbon arc forms a highly inhomogeneous plasma consisting of well distinguishable regions with different dominant species, including ions, atoms, molecules and clusters, and nanoparticles [1-3].

2. Results

A 1 kW atmospheric pressure helium arc was run between a 0.6 cm diameter graphite anode and a 1 cm diameter graphite cathode separated by a gap of about 0.2 cm (Fig. 1). The arc current was varied in the range of 40-70 A. Ex-situ evaluation of the cathode deposit confirmed that it contains multi-walled carbon nanotubes (MWCNTs). For synthesis of single-walled carbon nanotubes (SWCNTs), a powder mixture of metal catalysts (Ni, Yi) and graphite was added to a hollow graphite anode. SWNCTs were produced in volume and collected from the arc chamber walls and electrodes. In some experiments, a small fraction of hydrogen gas (< 5%) was added to a helium atmosphere (500-600 torr) to enable spectroscopic measurements without affecting the plasma and synthesis processes [3].

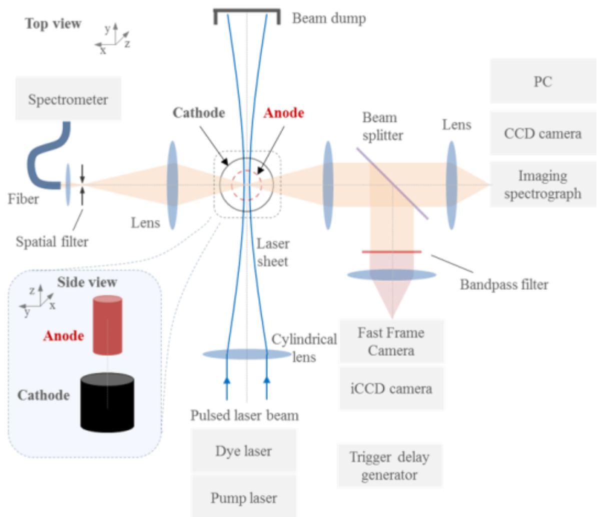

Fig. 1 Schematic of the experimental setup of carbon arc for synthesis of carbon nanotubes with Optical Emission Spectroscopy, Fast Frame Imaging and Laser-Induced Fluorescence diagnostics [3].

We also performed fluid simulations of the arc and atomistic modeling of the synthesis processes [4,5]. Experimental and modeling results demonstrate that different steps of the synthesis process, including generation of a feedstock of atomic and molecular species and ions, formation of larger molecules and clusters, growth of nanotubes, and agglomeration of nanoparticles in large particles and bundles occur in different regions of the arc. These differences are due to a highly non-uniform distribution of the arc current, which is mainly conducted through the arc core which is populated with carbon atoms and ions [6]. This is why the ablation of the graphite anode, which provides the carbon feedstock for nanoparticles synthesis, is governed by the arc core. The dominance of diatomic carbon molecules in the arc periphery (Fig. 2), a probable pre-cursor species for synthesis of carbon nanostructures, and the dominance of C atoms in the arc core are important new findings of these studies. As a result, theories of arc-based synthesis need to be reformulated to account for this finding.

Application of in-situ diagnostics allowed us for the first time to detect nano and macro particles during the arc synthesis. Among the unexpected and interesting findings from these measurements is that in addition to the evaporation of atoms and molecular species from the anode, the carbon feedstock utilized during synthesis is also produced by the evaporation of large macro-particles ejected from the anode [1]. Laser diagnostics also revealed the presence of < 20 nm carbon particles in the far-core periphery [1,2]. Finally, among the most important new results is the discovery that SWCNTs are produced in the near- and fa- core regions containing a high plasma density [7] and therefore, predicted plasma effects (e.g. charging) may play a role in their nucleation and growth [5].

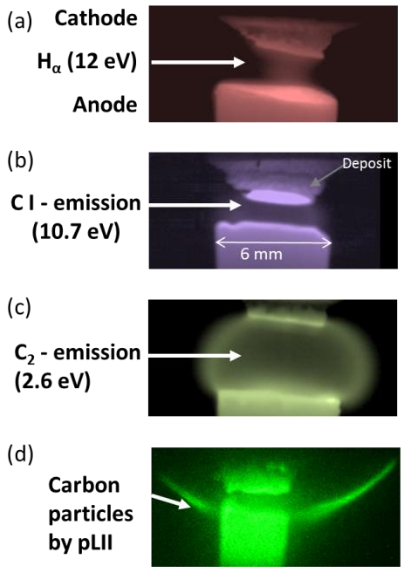

Fig. 2 Spectral images of Hα (a), C I (b), and C2 (c) obtained by filtered fast frame imaging of the carbon arc operated with a 9 mm diameter graphite cathode and 6 mm diameter graphite anode, at the arc current of 50 A, 550 torr of Helium gas [3]. (d) Results of planar laser-induced incandescence diagnostics. Intensity and colors were artificially adjusted to enhance visualization of the emission patterns [1].

3. Acknowledgement

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4. References

[1] S. Yatom, J. Bak, A. Khrabryi, and Y. Raitses, "Detection of nanoparticles in carbon arc discharge with laser-induced incandescence", Carbon **117**, 154 (2017).

[2] A. Gerakis, M. N. Shneider, B. C. Stratton, and Y. Raitses, "An all-optical, in situ diagnostic for large molecule and nanoparticle detection", Proc. SPIE 10093, Synthesis and Photonics of Nanoscale Materials XIV, 100930O (2017).

[3] V. Vekselman, M. Feurer, T. Huang, B. Stratton, Y. Raitses, "Complex structure of the carbon arc discharge for synthesis of nanotubes" accepted for publication in Plasma Sources Sci. Technol. (2017).

[4] V. Nemchinskiy and Y. Raitses, "Anode sheath transition in an anodic arc for synthesis of nanomaterials", Plasma Source Sci. Technol. **25**, 035003 (2016).

[5] L. Han, P. Krstic, I. Kaganovich, and R. Car, "Migration of a carbon adatom on a charged single-walled carbon nanotube", Carbon **116**, 174 (2017).

[6] Y. W. Yeh, Y. Raitses, and N. Yao, "Structural variations of the cathode deposit in the carbon arc", Carbon **105**, 490 (2016).

[7] X. Q. Fang, A. Shashurin, G. Teel, and M. Keidar, " Determining synthesis region of the single wall carbon nanotubes in arc plasma volume", Carbon **107**, 273 (2016).