Effect of background gas on carbon nucleation in non-thermal plasma

S. Basu[1], X. Xu[2], C. Papson[2], R. Anthony[1,2]
[1]*Chemical Engineering and Materials Science, Michigan State University, Lansing, USA*
[2]*Mechanical Engineering, Michigan State University, Lansing, USA*

Abstract: Low-temperature plasma techniques are widely employed for producing nanomaterials with tunable composition and morphology. However, carbon's structural diversity, including crystalline or amorphous forms and sp² or sp³ hybridization, adds even more complexity. Here we explore carbon nanoparticle synthesis via plasma reactors in two background gases, argon and helium, highlighting the evolving relationships between plasma parameters and material properties.

1. Introduction

The decomposition of methane in nonthermal plasmas presents a promising approach for synthesizing carbon-based materials and valorising greenhouse gases. In this context, the choice of background gas plays a pivotal role in influencing the plasma characteristics and the subsequent chemical pathways for methane breakdown. Nonthermal plasmas in argon provide an efficient medium for dissociating methane due to the lower ionization energy of argon, which facilitates energy transfer to methane molecules via electron collisions and Penning ionization. This promotes the rapid generation of active species such as CH_3, CH_2, and CH radicals, which are essential for carbon nucleation and particle growth. Conversely, helium, with its higher ionization energy and lower inelastic collision cross-section, results in a plasma environment where energy transfer to methane is less efficient. Consequently, the production of reactive intermediates and the onset of nucleation are significantly suppressed in helium plasmas, necessitating higher methane concentrations and input power to achieve comparable dissociation levels. Understanding these distinctions is critical for optimizing plasma processes aimed at controlling the structure and morphology of synthesized carbon materials.

2. Methods

For these experiments, the synthesis of carbon nanoparticles (CNPs) is carried out from plasma decomposition of methane. The radiofrequency-driven reactor consisted of a quartz tube encircled by dual ring electrodes, supplied with 13.56 MHz RF power. Methane (CH_4) and Argon/Helium are flown through the reactor at total flowrates of 50-100 standard cubic centimetres per minute (sccm) and at pressure of 4 Torr. CNPs were collected at the reactor exhaust on stainless steel meshes. We used optical emission spectroscopy (OES) to characterize the reactive species in the plasmas, and Raman spectroscopy, transmission electron microscopy (TEM), and x-ray diffraction to characterize the CNPs.

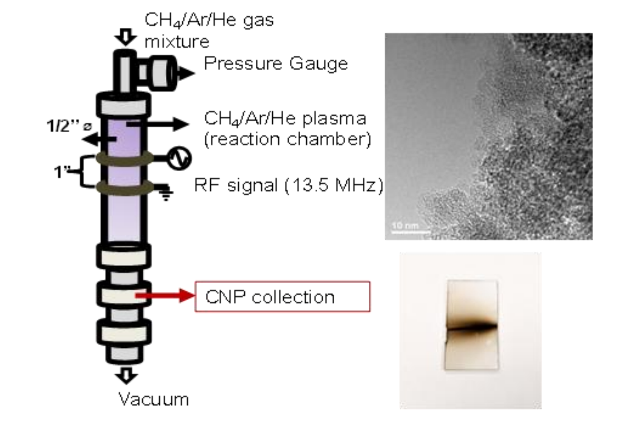

Fig 1. Schematic of non thermal plasma reactor

3. Results and Discussion

The synthesis of carbon nanoparticles in plasma reactors is significantly influenced by the choice of background gas, impacting both the formation kinetics and structural properties of the resulting materials. In this study, we investigated the effects of argon and helium plasmas in a flow-through reactor using methane as the carbon precursor. Our findings reveal that argon plasma facilitates the rapid formation of carbon nanoparticles at relatively low methane concentrations and input power. In contrast, helium plasma exhibits markedly slower nucleation rates, requiring significantly higher methane concentrations and energy input to produce nuclei clusters. Structural analysis using Raman spectroscopy highlights the presence of the D and G bands, corresponding to the disorder band and sp² carbon vibrations, in nanoparticles synthesized in both plasmas. Notably, graphitic carbon structures were obtained using argon plasma, whereas helium plasma consistently yielded amorphous carbon. These results underscore the critical role of background gas in dictating the structural and morphological characteristics of carbon nanoparticles, providing valuable insights for optimizing plasma-based synthesis processes.

4. Conclusion

This study highlights the critical influence of background gas on methane breakdown and carbon nanoparticle synthesis in nonthermal plasmas. Argon plasma enables efficient nucleation and crystalline carbon formation, while helium plasma requires higher energy inputs, yielding primarily amorphous carbon.