

Investigation of the formation of Carbonaceous Nanoparticles in a Ar-CH₄ RF Plasma through On-Line Particle Separation

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Abstract: We study parameters effecting synthesis of carbonaceous nanoparticles in a 13.56 MHz, capacitively-coupled, nonequilibrium plasma of argon and methane mixtures, while drop outs of the carbon deposits on reactor walls are removed via online particle separation. We investigate the impact of reactor pressure, plasma power, gas stoichiometry and residence time on particle formation and morphology. Through XRD, Raman spectroscopy, TEM, SEM and OES analysis, findings demonstrate residence time plays a key role in particle formation.

1. Introduction

Gas-phase synthesis of particulate nanomaterials has been significantly extended by the use of flow-through RF plasmas within the last two decades [1] however, successful processing of methane, an abundant natural resource, with these reactors has been rather elusive. Multiple studies have reported the difficulty of particle nucleation and rapid film formation on reactor walls. In addition to low yields, the films that form on the reactor walls grow and detach continuously, leading to a contamination in the product that leaves the reactor.

In this work, we employ online size separation methods by centrifugal means and investigate the solid products of a flow-through Ar/CH₄ plasma reactor. We specifically focus on the parameters that affect the formation of crystalline and high-surface-area graphite. The efficiency of size separation and the impact of operation parameters such as pressure, plasma power and residence time on product properties were investigated.

2. Methods

A capacitively-coupled RF plasma was generated in a 12 mm diameter quartz tube to ignite Ar/CH₄ mixture in a pressure range of 10-60 Torr. Optical emission spectroscopy was performed on several points on the reactor to monitor the Swan band peak formation. Generated particles were first subjected to mobility separation and then collected on a steel mesh to be characterized ex-situ via X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

3. Results and Discussion

During operation, a thick film forms and detaches likely due to deposition of polyaromatic hydrocarbons, as evidenced by a smooth and brownish color (Figure 1a). By employing size separation, the desired particulate products are decoupled from film formation, and SEM imaging indicated the selection of a very fine powder, essentially comprised of the particles nucleated in the Ar/CH₄ plasma. A closer look via TEM indicated that particles do not fully form at low residence times, however, spherical primary particles began to appear as residence time was increased (Figures 1b-d). The formation of spherical shapes indicates some sort of sintering is proceeding and the surface energy is getting minimized, but surprisingly XRD indicated that particle formation was not directly accompanied by crystallization (Figure 1e). Crystallite size inferred from the Scherrer equation showed no

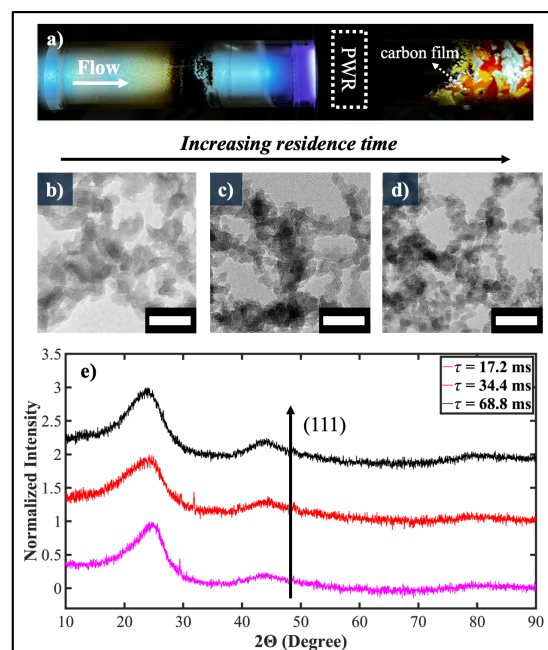


Figure 1. a) Photograph of the plasma reactor, b) $\tau = 17$ ms, c) $\tau = 34$ ms, d) $\tau = 68$ ms, e) XRD patterns at increasing residence times. Ar/CH₄ ratio was 40, and the experiments were conducted at 200 W power and 20 Torr pressure. Scale bars are in 50 nm width.

change and stayed approximately at only 1 nm, about 10 times smaller than particle size in Figure 1d. However, the (111) peak of graphite started becoming more distinct, which we believe to be a sign for the formation of 3-D particle from a few layers of large graphite sheets, in agreement with the sintering hypothesis.

4. Conclusion

In addition to residence time, reactor pressure, plasma power and gas stoichiometry are all expected to be significant. This work will detail the link between material properties and operational parameters through actinometry, XRD, and D/G peak ratio in Raman spectroscopy.

Acknowledgement

This work was supported by TUBITAK-1001, Project No: 122M301.

References

[1] Kortshagen et al., Chem. Rev., **116**, 11061-11127 (2016).