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TUNING THE MATERIAL PROPERTIES OF CARBONACEOUS NANOPARTICLES BY GAS MIXTURE VARIATION

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We present polymerization experiments in low temperature reactive plasmas with variable buffer gases. Such plasmas provide an excellent tool for production and confinement of nanoparticles, enabling the application of different in-situ particle diagnostics. As a result we observe changes in physio-chemical characteristics of the particle bulk material, obtained in a controllable fashion. These results are of key importance for the astrophysical investigations (the sp^2 dependent UV bump) as well as for the dust problem in divertor regions of fusion devices.

1. Introduction

The non-eqilibrium character of low temperature plasmas provides an excellent source for the production of nanoparticles, which find various applications in different fields- from very well known use in technological processes (e.g. catalysis), to the novel idea of metamaterials and to applications in the field of astrophysics (so called astroanalogues) [1-3].

The common request for all these applications is- the production of nanoparticles with variable, tailored characteristics. In the case of hydrocarbon particles the optical properties are of special interest, which means: applications request variable hydrogen amount and the sp^2 concentration within the bulk material.

It is very well known that the gas mixture influences the material properties of the nanoparticles, depending strongly on the chosen precursor gas [4]. In our previous work we showed the influence of the variation of the buffer gases on IR spectra in the case of acetylene as precursor [5]. In this contribution we present in detail effects of the buffer gas variation on the material characteristics of the nanoparticles (for simplicity concentrated on two buffer gasses-argon and helium).

2. Experimental Set-up

The experiments were carried out in the capacitively coupled discharge, with the experimental set-up presented detailed elwhere [3,5,6,11]. The gas mixture was in all measurements 0.5 sccm for acetylene and 8 sccm for the carrier gas (Ar, He). The pressure was kept constant at 0.1 mbar, so that the residence time for the precursor gas was about 60 s. The working frequency was 13.56 MHz and the input power was about 20 W.

The excellent confinement of nanoparticles in such kind of discharges offers one particular advantage: the particles can be analysed during their growth by means of several *in-situ* diagnostics (in this case: Fourier Transform Infrared absorption spectroscopy-FTIR). The controlled collection of particles from the plasma was obtained by means of a special sample probe based on the thermophoretical effect (Figure 1) [6].

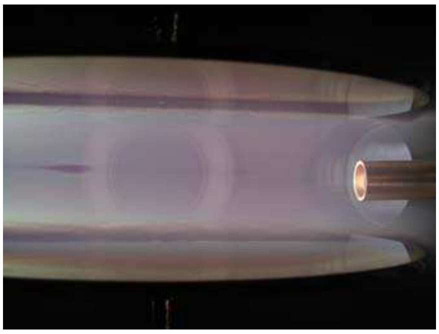

Figure 1: Sampling probe with Peltier element (description in: 6, Godde 2006)

The controlled sampling of nanoparticles from the discharge is an essential requirement for the use of different *ex-situ* diagnostics (e.g. Nuclear Reaction Analysis NRA, Near Edge X-Ray Absorption Fine Structure spectroscopy-NEXAFS).

3. Experimental results

Figure 2 shows two FTIR-spectra: the red line shows a spectrum of particles produced with argon as carrier gas, and the black line a spectrum where helium was used instead of argon.

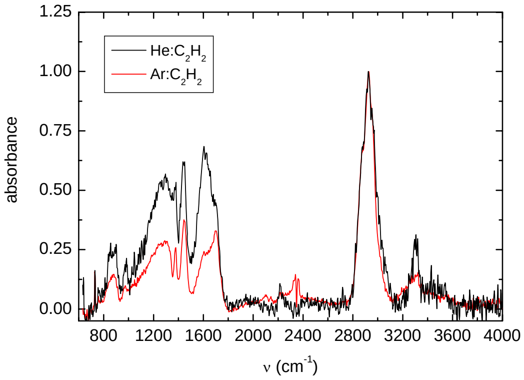

Figure 2: Comparison of FTIR spectra polymerized in a mixture of argon and acetylene (red line) respectively helium and acetylene (black line)

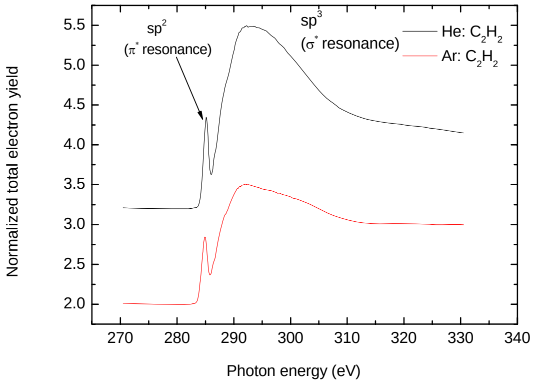

Figure 3 Near Edge X-ray Absorption Fine Structure spectroscopy- spectra for the nanoparticles grown from the acetylene diluted in different carrier gases.

A more detailed analysis of spectra shows most remarkable difference in the wavenumber region between 1500 and 1750 cm^{-1}. The peak between 1660 and 1730 cm^{-1} has to be attributed to carbonyl (C=O) stretching vibrations. It is clearly visible in both spectra due to the high intrinsic strength of the absorption band associated with the C=O stretching mode, (making even small traces of carbonyl detectable). The difference between both spectra concerns the peak at 1600 cm^{-1}. This peak must be ascribed to C=C double bond stretching vibrations [6, 8]. In the "Ar case" it is arising only as a shoulder on the low wavenumber tail of the carbonyl feature. In the "He case", this peak is dominant, broad, well defined and overblending the C=O vibrations, and the strength of this feature is comparable with that of the sp^3 CH_3 doublet (1450 cm^{-1} and 1375 cm^{-1}). From the width of this feature it is possible to conclude that the C=C bonds are found here in many different configurations, both alkene and aromatic, and that these configurations are probably distorted [4, 6, 8].

This spectroscopic results suggest that the sp^2 fraction in the helium case is higher than in the argon case, an idea that was confirmed by NEXAFS measurements performed at BESSY (Berliner Elektronen Speicherring für Synchrotonstrahlung). This measurements gave us the information on carbon K-edge spectra, revealing multiple C (*1s*) electron transitions in the fine structure of C NEXAFS region (284–290 eV) [9]. Figure 3 shows comparison of two NEXAFS spectra, one obtained from particles polymerized in helium/acetylene (black line) and one obtained from particles polymerized in argon/acetylene (red line). The presented preliminary results reveal even without the quantitative analysis changes in the shape of the NEXAFS resonant lines. The most important feature in this spectrum with respect to the sp^2 fraction is the peak at 285 eV, which can be attributed to transitions to the π^* state. This peak is stronger in the helium case (also relative to the plateau towards higher energies) which confirms the spectroscopic results.

Furthermore, NRA measurements showed decrease in the amount of hydrogen in the "He case"(40% H vs 50% in the "Ar case"[11]).

Discussion

Although the experimental results are quite clear it is difficult to give one unique and stringent explanation for these observations. Fact is that the sp^2 fraction is increasing with the ionisation potential of the carrier gas: Ar:15.8 eV; He:24.6 eV (and with the energy of the metastable states). The inverse "correlation" holds for the masses of the atoms of the carrier gas: the smaller the atomic mass the higher the sp^2 fraction. Both dependencies can in principle explain the observations: The collisions of ions (respectively metastables) with particles lead to an efficient energy transfer form the gas phase to the particle. The energy release in collisions of positive ions with negatively charged particles - which is responsible for the heating of the particle - equals the ionisation potential of the carrier gas plus the impact energy of the ions.

The energy that the particles gain per collision with one ion is thus higher for helium than for argon. Since the heating of the particle favours in principle the release of hydrogen atoms and thus the formation of sp^2 bonds this different energy transfer could possibly explain the experimental observations. One of the crucial problems in this interpretation concerns the ion densities. Only if the He^+ density is comparable to the Ar^+ density – which is highly questionable - the real (total) energy transfer to the particles is in fact higher in the He-case than in the argon case. Moreover it is difficult to say whether the increase of the particle temperature is sufficiently high to release enough hydrogen atoms (see for example the article from Daugherty and Graves concerning the particle temperature [10]). The same problem holds for the second possible explanation. The smaller mass ratio He/H - compared to Ar/H – favours the replacement of hydrogen atoms from the carbon network due to the impact of helium ions which could also explain the observations concerning the sp^2 content. Without detailed quantitative information about the ion densities both interpretations remain rather speculative. Moreover it is also possible that the differences in the plasma parameters (higher electron temperature and lower electron density in the helium case [11]), are finally responsible for the differences in the composition of the particles.

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