Carbon Black and Carbon Nano-Tubes Produced from Acetylene Using Non-Thermal Plasmas at Atmospheric Pressure

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DC pulsed corona discharge plasmas have been applied for the co-generation of carbon black and carbon nano-tubes from acetylene and hydrogen under ambient conditions. The carbon nano-tubes thus produced were analyzed by transmission electron microscopy. In the case of pure acetylene feed, only carbon black is produced.

Carbon black is an important carbon material principally used in the rubber industry. Most carbon black has at present been produced by the "furnace process", which employs an incomplete combustion of hydrocarbons. A big drawback of furnace process, however, is that too many pollutants are generated, including CO_2, NO_X, SO_2 and VOC. There is growing interest in using plasmas to produce carbon black.[1,2] Compared to the conventional furnace process, the plasma carbon black production needs electricity and consumes less energy.[3] In addition, no emission of pollutant is observed during the plasma carbon black formation, with which hydrogen is only a by-product. The thermal plasmas, like arc discharge plasma, have been used for plasma carbon black production.[1,3] However, the potential application of non-thermal plasmas for carbon black production has not yet been demonstrated. A major difference between thermal and non-thermal plasmas lies in their gas temperatures. Within non-thermal plasmas, the electron temperature can reach as high as 10^4 eV, while its gas temperature can be as low as room temperature. The thermal plasma is "equilibrium" plasma with which the gas temperature is as high as the electron temperature. Some kinds of non-thermal plasmas, like corona discharges, are easily to be established under ambient conditions. We have previously reported the use of corona discharges for plasma methane conversion.[4–6] During the methane conversion using corona discharge plasmas, we have observed some carbon black formed in the wall of reactor. A heterogeneous catalyst has been used to inhibit the formation of carbon black.[5,6] The carbon black produced has been considered as by-product of the continuous conversion of newly formed ethylene or acetylene from methane. Regarding this, we attempted to apply corona discharges for production of carbon black from ethylene or acetylene. Here, we reported the characteristics of carbon black produced from acetylene using corona discharges.

The corona discharge reactor used here is almost the same as that used for methane conversion.[4] This quartz tube reactor (with an i.d. of 6 mm) consists of two axially centered electrodes, a wire electrode and a lower circular plate electrode. The gap between the two stainless steel electrodes is 8 mm. In this work, a mixture of acetylene and hydrogen was employed as reactants for carbon black production. The initial objective of co-feeding of hydrogen is to reduce the breakdown voltage of reactant. The reactants, acetylene and hydrogen in ca. 2:1 to 4:1 ratio, were fed into the reactor at a total feed rate of 50 mL/min via digital mass flow controllers. A DC pulsed high voltage generator operating at 50 to 200 pps was used to initiate the gas discharge plasmas. The gap between the wire electrode and the grounded cylindrical electrode is 8 mm. The feed and effluent gases were analyzed by an on-line gas chromatograph (HP4890) with a TCD detector. The voltage and current measurements were conducted using a high voltage probe (Tektronix P6015) and a current probe (Tektronix CT-2) with a digital oscilloscope (Tektronix TDS 210). All the experiments were started under ambient conditions. The reactor wall temperature would increase to >100 °C during reactions. It has been observed that plasma acetylene conversion is very fast reaction. Once gas breakdown occurs, a black layer quickly covers the reactor (quartz) wall. After 10-min reaction, the input power was turned off and plasma reactions are terminated. The solid sample was taken out from the quartz tube reactor and collected carefully. Microscopic observations of collected sample were carried out using a transmission electron microscopy (TEM; Jeol, JEM-100CXII).

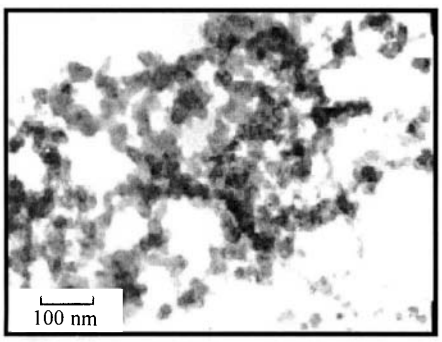
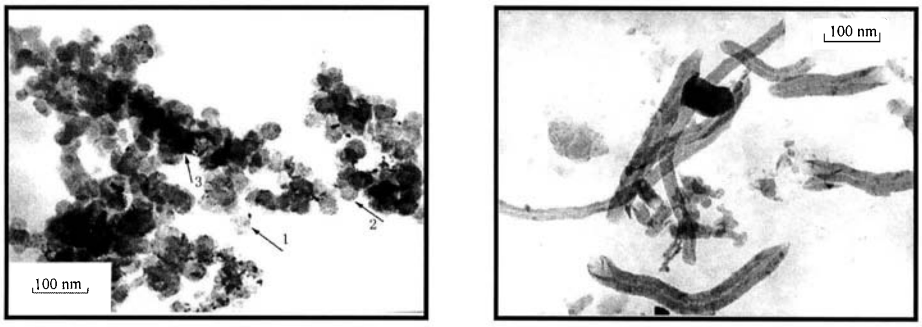


Figure 1. TEM image of acetylene carbon black produced using pure acetylene feed.

Figure 1 presents a TEM image of acetylene carbon black produced using pure acetylene feed. The carbon black produced by this way has a 3 dimension structure similar to the carbon black produced using thermal (arc) plasmas,[1] that were operated at 2600 °C. A more surprising result is that a significant amount of carbon nano-tubes (CNTs) were also produced when hydrogen is a co-feed or co-reactant together with acetylene. When hydrogen presents in discharge plasmas, the initiation of gas discharges was observed at around 5000 V, ca. 1000 V less than that without using hydrogen as co-feed gas. The CNTs produced in this way have diameters from 20 to 40 nm. Compared to arc plasma techniques for CNTs fabrication,[7] the



(a) acetylene carbon black (b) carbon nano-tubes

Figure 2. TEM image of acetylene carbon black and carbon nano-tubes produced in corona discharges (C_2H_2/H_2: 3/1; input voltage: 5000 V).

present corona discharge CNTs production can be performed at atmospheric pressure. Especially, the CNTs are produced in the corona “active” region between electrodes, not in the electrode surface as reported using arc plasmas.[7] It has been observed that the produced CNTs can move around along the reactor tube. A glass-fiber packed bed has been used on the end of reactor in order to keep the CNTs inside the tube. Experiments also suggested that the feed ratio of C_2H_2/H_2, the catalyst applied and some other parameters have an effect on the production of CNTs using atmospheric pressure pulsed DC corona discharges. Further study is under way to understand this unusual chemistry.

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