Synthesis of Carbon Nanofibers and Pt-Nanocluster-Based Electrochemical Microsystems by Combining Low-Pressure Helicon Plasma Techniques

Amaël Caillard, Christine Charles, Rod W. Boswell, and Pascal Brault

***Abstract*—Although carbon-nanofiber (CNFs) or nanotube growth and their applications are well documented, engineering their shape and their integration in a microsystem for successful applications is an important issue. We report on the synthesis of aligned CNFs (ACNFs) covered by metallic catalytic nanoclusters by a combination of different low-pressure deposition techniques based on high-density radio-frequency helicon plasmas. An image of a "bright-dress-shape" helicon plasma and of a synthesized ACNF coated by Pt nanoclusters is presented.**

***Index Terms*—Carbon nanofiber, chemical vapor deposition (CVD), microsystem, nanocluster, plasma.**

ALIGNED and well-separated carbon-nanofiber (CNF) morphology is important for many potential applications that require high electric-field concentration (field emission applications), vertically aligned geometry (nanoelectronic devices: cross-bar addresses transistor network, memories, and logic gates), or large surface area (fuel cell, battery, or chemical sensor applications).

Chemical vapor deposition (CVD) methods enhanced by dc plasma, RF plasma coupled in capacitive or inductive mode, and microwave plasma have been developed to grow CNFs or carbon nanotubes (CNTs). The growth of CNFs involves many processing parameters, such as plasma power, substrate temperature, gas pressure, feed gas composition, and substrate bias. In general, the diameter of CNFs depends on the morphology of the catalyst particles or layer. The shape and the growth direction of the CNTs (or CNFs) can be controlled by the temperature, the nature of the catalyst, the presence of a buffer layer, the plasma composition, and the direction of the electric field applied on the substrate [1]–[3]. Electrochemical microsystems which use CNFs as a support require a combination of various plasma deposition processes: the deposition of a catalyst for the CNF growth, the CNF deposition process, and, finally, the coating of CNFs by catalytic clusters that are active for the microsystem. The growth of CNFs usually requires a mixture of a hydrocarbon gas (methane or acetylene) and an etching gas (hydrogen or ammonia), and a total gas pressure in the 0.1–100-mbar range, whereas the nanoclusters can be grown by sputtering of a target in an argon plasma at few microbars.

Here, we report on the fabrication of aligned-CNF (ACNF) arrays coated by metallic nanoclusters in a low-pressure CVD system enhanced by a helicon plasma source. This previously described [4] reactor (called Southern Cross) consists of a helicon plasma source contiguously attached to a stainless steel diffusion chamber shaped as a cross (55 × 55 cm). The helicon plasma is generated by a 13.56-MHz-radio-frequency-powered double-saddle antenna placed around the 15-cm-diameter glass source tube. The 72-mm-diameter substrate holder is placed between 10 and 18 cm below the plasma source during the deposition. The pressure can be decreased to $5\ \mu\mathrm{bar}$ during the CNF growth, which allows one to simply combine CVD enhanced by plasma processes and plasma sputtering processes by changing the feed gas composition without changing the gas pressure in the reactor. Here, the complete fabrication of the microsystem consists of three consecutive plasma deposition steps at low pressure ($\sim 5\ \mu\mathrm{bar}$).

Initially, a thin nickel film is deposited on the substrate by argon plasma sputtering to act as nuclei for the growth of CNFs. The substrate is then heated to around 400 °C under vacuum. Subsequently, a mixture of methane and hydrogen (flow rate ratio of 1 : 4) is introduced in the reactor, and the 500-W plasma is ignited. A length of $2\ \mu$m aligned perpendicularly (or tilted depending on the shape of the substrate holder) to the dc biased (~ -100 V) substrate surface is obtained after a deposition time of 90 min. The high-density helicon plasma [Fig. 1(a)] induces high ion bombardment and some gas conduction at low pressure, which contributes to the heating of the nickel catalyst layer (probably up to 700 °C as reported by Teo *et al.* [5]). If the substrate temperature is decreased to 300 °C prior to the ignition of the methane/hydrogen plasma, amorphous and curly CNFs are obtained. Finally, metallic nanoclusters (or a metallic thin film) are deposited on the ACNFs by argon plasma sputtering: For fuel-cell electrode applications, a square platinum target is held vertically in the

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A. Caillard, C. Charles and R. W. Boswell are with the Space Plasma, Power and Propulsion, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia (e-mail: ama112@rsphysse.annu.edu.au; christine.charles@anu.edu.au; rod.boswell@anu.edu.au).

P. Brault is with the Groupe de Recherche sur l'Energétique des Milieux Ionisés, UMR6606 Université d'Orléans–CNRS Polytech'Orléans BP6744, F-45067 Orléans Cedex 2, France (e-mail: Pascal.Brault@univ-orleans.fr).

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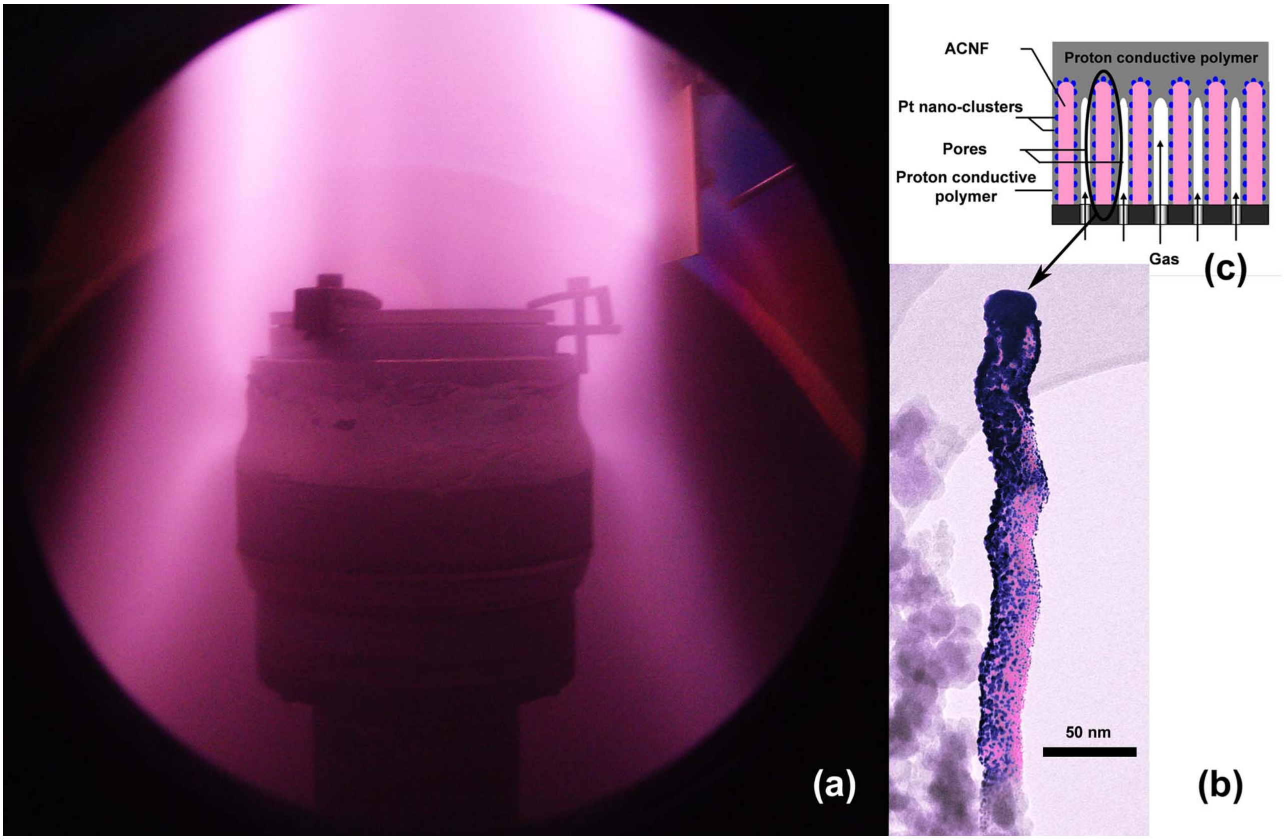

Fig. 1. (a) Methane/hydrogen “bright-dress-shape” helicon plasma. (b) ACNF covered by platinum nanoclusters. (c) Schematic of an ACNF embedded microsystem for fuel-cell electrode applications.

diffusion chamber above the substrate holder, as shown on the right side of “bright-dress-shape” helicon plasma [Fig. 1(a)].

In Fig. 1(b), a transmission electron microscopy (TEM) micrograph displays the top of a single 35-nm-diameter ACNF (pink) covered by well-dispersed Pt nanoclusters (blue and black) with a mean diameter of 5 nm. Previous TEM images performed on an uncoated CNF suggested a “tip” CNF growth model, a stacked CNF, and a Ni particle at the upper end of the CNF in a facetted shape [4].

ACNFs can be grown on various substrates (flat- or open-pore metal, carbon, and inorganic material) without any buffer layer. For a fuel-cell electrode, the substrate must be porous and electron conductive. Stainless grid, carbon cloth, or nickel foam can be used. Subsequently, ACNFs can be embedded in an organic or inorganic material to create a composite microsystem for fuel cells or for gas separation devices involving gas transport and electrochemical reactions.

In summary, ACNFs covered by catalytic nanoclusters that are synthesized by a combination of low-pressure helicon plasma processes have been presented. The ACNF growth in a low-pressure and low-temperature apparatus is important for their integration in microsystems such as micro-fuel cells.

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