

Low-temperature plasmas assisted syntheses of carbon nanomaterials

M. Hori¹, H. Kondo², M. Sekine² and K. Ishikawa²

¹Institute of Innovation for Future Society, Nagoya University, Nagoya, Japan

²Plasma Nanotechnology Center, Nagoya University, Nagoya, Japan

Abstract: The focus of low temperature plasma nanoscience and technology has been shifting from the synthesis of carbon nanomaterials to the programmed assembly of nanostructures and materials. To do this, much more precise control of the processing should be conducted with utilization of quantitative measurements of activated species generated in gaseous and liquid phases and also understanding physicochemical mechanisms on interactions of plasmas using *in situ* plasma diagnosis with spectroscopic methods. The nonequilibrium fields of chemical synthesis for the unique advantage of nanomaterials are attracting potentially much more attentions in future applications.

Keywords: Plasma enhanced chemical vapour deposition (CVD); In-liquid plasma; Graphene nanosheet; Amorphous carbon; Polymer-electrolyte fuel cell (PEFC).

1. Introduction

Low-temperature plasma syntheses of carbon nanomaterials require to understand mechanisms on the basis of quantitative measurements of fluxes of the plasma species in gaseous phase and then *in situ* observation of chemical reactions at real time is necessary. Low-temperature plasma interactions among multiple phases (e.g., ambient air, liquids, and cell-membranes) give rise to various phenomena such as electrical discharge phenomena at the boundaries with microscopically viewable constituents. In this article, we present our recent studies in regard with the carbon nanomaterial syntheses employing low temperature plasmas. Then we will discuss indispensable applications for our future society.

2. Plasma assisted synthesis of carbon nanomaterials

Carbon is unique properties having a variety of compounds because of forming chemical bonds of sp^3 , sp^2 , and sp hybridizations, e.g., diamond, graphite and so on. In the low-temperature plasma enhanced chemical vapour deposition using CH_4/H_2 mixture gas, it is well known to synthesize a variety of carbon nanomaterials such as diamond, hydrogenated amorphous carbon (a-C:H) films, carbon nanotubes (CNT) and carbon nanowalls (CNW), that are vertically standing of wall structures made of a collection of graphene nanosheets (GNs) on substrate [1]. Basically, preparations are carried out by the plasma discharge external parameters. In conjunction with the synthesis conditions like powers, pressures, it should be controlled essentially by internal parameters such as ion and radical densities and ion flux and energy toward the growth surface [1]. To understand these schemes, versatile diagnostics for the plasma parameters should be conducted *in situ* at real time. Furthermore, atmospheric pressure plasma processing on liquids can be utilized for syntheses of GNs, offering easy-use, high-reaction-rate, inexpensive means, etc. Recently the synthesis/growth mechanisms of the carbon nanomaterials; a-C:H film, CNT, CNWs or

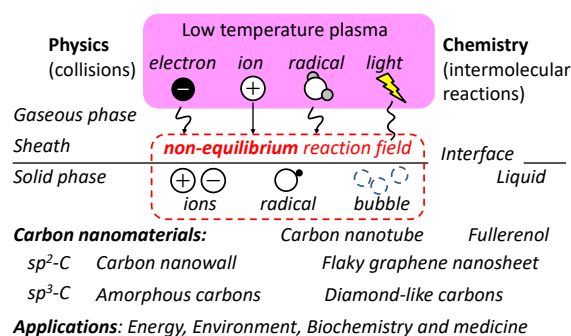


Fig. 1 Nanoscience and technology for low-temperature plasma syntheses of carbon nanomaterials

vertical GNs, and flaky GNs will be discussed in this study (Fig. 1).

2.1 Amorphous carbon (a-C) or diamond-like carbon

The a-C films deposited employing CH_4/H_2 plasma are characterized by contents of hydrogen and sp^2 - and sp^3 -bonding carbons. The structures of bonding properties are determined by compositional ratios of gaseous precursors in the PECVD growth. In the CH_4/H_2 plasma, highly-dissociated C_2 radical dominates the formation of sp^2 -C and CH_3 radicals acted independently on the formation of sp^3 -C [2]. Actually, the CH_3 radical density could be controlled by the gas-flow residence time in the plasma volume [3]. When the total gas flow was only changed, optical emission (OES) intensity ratio of CH (431 nm), C_2 band (516 nm; $\Delta v=0$), H (486 and 656 nm) and Ar (811 nm) can be used as an indicator for the dissociation of CH_4 and H_2 gases. However, the sp^3 fraction in the a-C:H films decreased with increasing the residence time, progressing the respective dissociations of $CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow CH$, C_2 [2]. Using Raman scattering, electron-energy loss spectroscopy (EELS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) techniques, we found that the C_2 densities correlated with a number of sp^2 -clusters in the a-C:H films [4]. Conventionally, the sp^2/sp^3 fractions are described on the basis of the sub-plantation

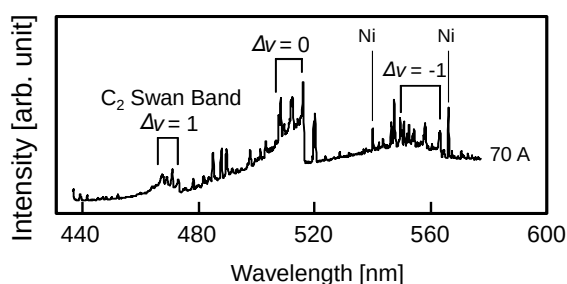


Fig. 2 Emission spectrum of the dc arc plasma evaporation after 30 s of start of discharge.

model dealing with ion bombardment control [5]. Accordingly, in this study, gaseous radical compositions play a key role for the determination of structural composition of the a-C:H films. The experimental data show that the electrical conductivity and optical bandgap of a-C:H films can be controlled through the mechanism of the precursor dissociation by changing the residence time and the other plasma parameters such as substrate bias powers and pressure [2-4].

2.1 Carbon nanotube

Single-walled (SW) CNT is synthesized by the dc arc plasma evaporation of graphite electrodes using Ni-Y catalysts in the mass production. At present, the Ni-Y is achieved with the best synthesis rates and high crystallinity as indicated the Raman I_G/I_D ratio of more than 15 [6, 7]. To control the crystallinity, OES of Ni (566 nm), Y (554 nm) and C₂ (563 nm; $\Delta v = -1$) are good indicators (Fig. 2). Experimentally, conditions such as helium pressures and arc currents enabled to optimize the synthesis of high-crystallinity SW CNT by the monitoring of the C₂, Ni, and Y lines [6, 7].

2.2 Carbon nanowall

The CNW is unique material that was originally discovered by our group [8]. In the CH₄/H₂ plasma, the ion bombarded surface turned graphitic compositions which promoted the vertically grown graphene nanosheets and

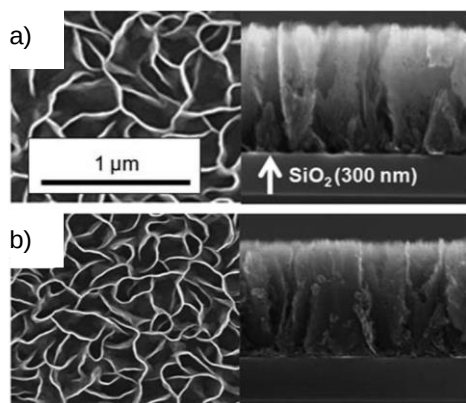


Fig. 3 Plan and cross-sectional images of CNWs grown at different conditions at pressure of 1 Pa and plasma excitation power 200 W (a) and 400 W [10].

details are described elsewhere [1]. The growth mechanism is explained as follows. the precursor of CH₃ or CF₃ adsorb on the edge of graphitic sp² carbons, and terminating atoms of H or F atoms are abstracted by gaseous H atoms to form H₂ or HF [9, 10]. Actually, the C₂F₆ precursor and the oxygen addition increased the crystallinity of CNW [8]. Defective portions of graphene are chemically removed by small addition of O₂. In electrical conductivity of CNW, nitrogen doping and wall density control were successfully realized [11]. The doping of N on graphene sheets has the four types of pyridinic, pyrrolic, graphitic and the others [12]. (Fig. 3) The wall density is determined by a number of nuclei on the substrate at the initial stage, which can be controlled in the growth pressure and the ion bombardment conditions [12]. Recently, the growth has been modelled on adsorption and diffusion of radicals [13,14]. Therefore, monitor and controls of ions and radicals such as C_xH_y or C_xF_y and H in plasmas are crucial in the view point of material syntheses.

Moreover, the other control methods are reactive ion etching of the grown CNW after the CNW deposition [15]. The asperities structure and the regrowth of hierarchical small wall structure on the large CNW were studied [16-18]. At present, we can grow them with utilization of the multiple top-down and bottom-up approaches with parameterized wall-density and electrical conductivity of each wall.

2.3 In liquid synthesis of graphene nanosheet

Conventional syntheses of graphene are used as methods such as epitaxial growth and chemical vapour deposition (CVD). Also, exfoliation and reduced graphite oxide (GO) are used to prepare sheets of graphene. In 2004, Sano reported that a method of graphene synthesis possible employed the submerged plasma with the graphite electrodes in the liquid phase [19]. The methods are roughly categorized into three types (Fig. 4), (i) submerged [20]. (2) discharge above liquid surface, and (3) discharges on and in liquid [21]. Recently, nanographenes were successfully synthesized using pure ethanol by the in liquid plasma which had two electrodes sandwiched the boundary between gas and liquid phases [21]. The proposed synthesis mechanism is hydrogenation and hydration of ethanol and intermediates, conjugate dienes induced for aromatic ring formations via Diels-Alders reactions [21-24]. As iron-phthalocyanine (FePc) dissolved in solvent dimethyl formamide (DMF) to ethanol can be synthesized micron-sized flakes made of GNs (Fig. 5) [24]. A detailed

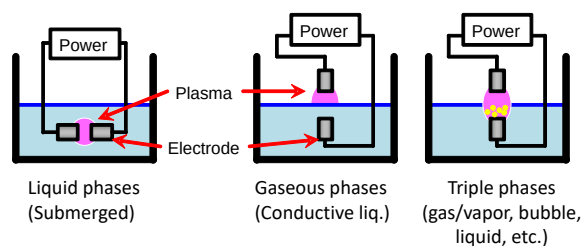


Fig. 4 Category of the in-liquid plasma synthesis.

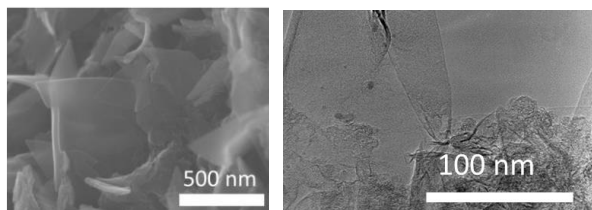


Fig. 5 The in-liquid plasma synthesized flaky graphene nanosheet observed by SEM (left) and TEM (right) [24].

synthesis mechanism has not been solved. However we believe that iron may be a key function to regulate the ordering of GNs with its catalytic reactions involving the aggregation or removal of a-C [23].

In the OES analysis, the gaseous discharges were estimated to be Wien black-body radiation temperature of approximately 4,800K [22] and rovibrational temperature (T_r) of approximately 2,000K of C_2 radical, inducing the high T_r of C_2 to a-C formations or structural imperfections in graphene [23]. The reaction field around 5,000K enhanced dehydration, dangling bonds that trigger the fragmentation of long-carbon chains via β -scission and yields numerous radicals and small carbon chained molecules [22]. The radical-mediated reaction fields of the in-liquid plasma offer to provide the unique synthesis fields and thus further investigations are strongly needed for comprehensive understanding of mechanisms.

3. Applications of the carbon nanomaterials

Carbon nanomaterials involving graphene are candidate materials for wide applications in capacitors, fuel cells, sensors, transparent films, membranes, etc., because of its excellent electrical conductivity, as well as in-printed electronic devices. Here we demonstrate the states of the art of our low-temperature plasma technologies.

3.1 Energy material - Fuel cells

In the fuel cells, Pt catalysts are supported by carbon black and the catalysts act on catalysing the electrochemical reactions of hydrogen oxidation: $H_2 \rightarrow H^+ + e^-$ at anode; and oxygen reduction $O_2 + 2e^- \rightarrow H_2O$ at cathode. The supported materials are acted as the electrical conduction of generated electrons.

For polymer electrolyte fuel cell (PEFC) applications, CNW were synthesized by radical-injection plasma-enhanced chemical vapour deposition (RI-PECVD), and a high density of Pt nanoparticles ($>10^{12} \text{ cm}^{-2}$) was supported on the CNWs using a metalorganic supercritical fluid deposition (MOSCFD) system [25]. In the high potential cycle tests, the electrochemical surface area of the Pt nanoparticle-supported CNWs maintained without degradation even after 20,000 cycles for the CH_4/H_2 deposition [25] and 60,000 cycles for C_2F_6/H_2 deposition [26]. It is clear that the structure of high-surface area and high graphene crystallinity CNW has a high durability for fuel cell applications.

Alternatives of Pt catalysts are provided by the in-liquid plasma syntheses of nonprecious metal catalysts made of

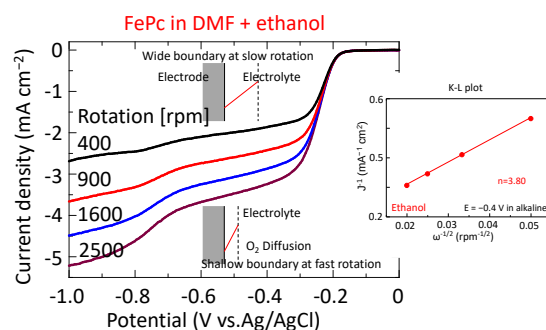


Fig. 6 Oxygen reduction reaction properties of nitrogen incorporated graphene nanosheets synthesized by the in-liquid plasma of ethanol, FePc, and DMF. Linear sweep voltammogram (LSV) curves in O_2 -saturated 0.1M HClO₄ at a scan rate of 10 mV/s. (c) Koutecky–Levich plots [27].

nitrogen-doped carbon and iron metal oxides using phthalocyanine [24]. Indeed, high catalytic activities of the flakes of the highly crystalline GNs are experimentally almost close to the ideal number of 4, even in alkaline media (Fig. 6) [27]. Notably, these GNs contained relatively large amounts of Fe–N bonding states. The Fe–N–C structure on graphene nanosheets achieved highly disperse active sites to facilitate the smooth movement of electrons during electron transfer [27].

3.2 Biochemistry and medicine

Hydrogen peroxide (H_2O_2) exists as reactive oxygen species in human body and has oxidative effect in human body and the H_2O_2 induced damage causes several diseases. One of important indicators H_2O_2 for those diseases has to be readily measured accurately. Therefore, the electrochemical H_2O_2 sensor was developed by CNW deposition on the carbon fibre papers [28]. The very large surface areas of Pt decorated CNW based devices suffer to high sensitive detection of H_2O_2 as low as 10nM [28]. The CNW is one of promising candidates as a novel catalytic electrode with a very large specific surface area [28].

CNW Scaffolds were developed for cell culture [29]. Recently, the electrical conductivity of CNW was utilized for electrical stimulation (ES) to osteoblast-like cells, Saos-2, in culture with the CNW scaffold [30]. At the ES with a frequency of 10 Hz, the Saos-2 cells promoted the proliferation and suppression of bone formation [30]. These results potentially show the utility of osteogenic cell culture in the regenerative medicine.

In cancer therapy, there are many reports of usages of nanoparticles. For instance, fullereneol has hydroxyl groups bonded to the skeletal structure of fullerene C_{60} , rendering fullereneol highly water soluble [31]. Interestingly, when the plasma-irradiated fullereneol (PF) that was altered by introducing carbonyl groups, ether bonds, and intercalated nitrate anions was added to the cell culture medium. It was found that the PF induced the apoptotic cell death [31]. Namely, by the plasma irradiation, the remarkable

functionalization of endocytic fullereneol that is cytotoxic is useful for a trigger of the antitumor effect.

3.3 Environmental science and technology

The large surface area property is applicable for environmental pollutant decomposition. Using the MOCFD of TiO₂ nanoparticles for CNW, photocatalytic decomposition was enhanced in the TiO₂-supported CNW under ultraviolet irradiations [32].

For analysis of biomolecules and small organic compounds, surface assisted laser desorption/ionization mass spectrometry (SALDI-MS) represents a powerful tool especially for samples containing alkali-metal ions, as ionization inhibitors [33]. Herein, CNW edge structures are functionalized by OH group which enhanced actually the SALDI signals to detect a trace amount of low-weight organic compounds [33, 34]. The carbon nanomaterials are useful for the SALDI-matrices substrate.

The carbon nanomaterials are unique in electrical, optical, and mechanical properties [35]. For gas sensing, these properties show changes in the response to chemical environments such as gas or vapour [36]. The sensitivity and selectivity of gases in sensing have not been yet unsolved. Therefore, further studies are needed on the utilization of CNWs in gas sensors.

4. Discussion

The low-temperature plasma syntheses of carbon nanomaterials are versatile in non-equilibrium reaction fields under electrical discharge phenomena at the boundaries. Understanding of the physicochemical reaction fields shows not only their kinetic control processes, but also their thermodynamic equilibriums. In the other word, the particles such as electrons, ions and photons would activate physical collisions to the precursor molecules to excite or to dissociate and so on. This process creates chemical reactive species as called as radicals. Accordingly, radicals mediated chemical reactions. Therefore, in such overall reactions, the observed phenomenon occurs under the kinetic control and the target fields would be temporally evolved. In this situation, the reactive species should be monitored *in situ* at real time. For examples, in alcohol reactions activated by the plasma,

it has been shown that C–C bonds breaking are induced in the thermodynamic control while nominal photochemical reactions induce to break C–H bonds in the kinetic control. Notably, in low temperature plasma's reaction fields, [•]OH radicals are substantially generated from alcohol and subsequently the [•]OH mediated H abstraction to form relatively stable organic radicals (Fig. 7) [37]. The characteristic schemes are essential to present in the carbon nanomaterial syntheses.

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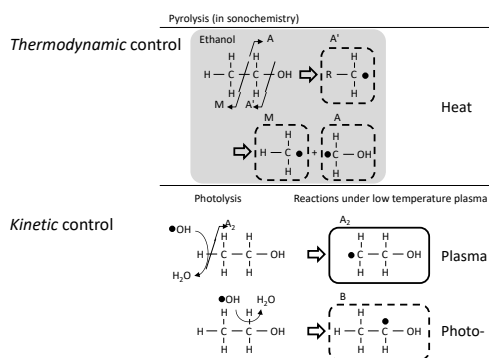


Fig. 7 Differences in radical generation schemes in ethanol reactions under heat, photo, and plasma [37].