Doped and Decorated Carbon Nanomaterials

J. Matos[1*], S.A. Filatov[2*], G.S. Ahremkova[2], D.V. Solovei[2], M.N. Dolgikh[2], G.S. Kuczynski[2], E.V. Batirev[2]

[1]Technological Development Unit, University of Concepción, Av. Coordillera 2634, Coronel, Chile
[2]A.V. Luikov Heat and Mass Transfer Institute, 15, P. Brovka Str., 220072 Minsk, Belarus

Article info

Received:
17 September 2015
Received and revised form:
14 October 2015
Accepted:
5 November 2015

Keywords:
doped carbon,
decorated materials,
plasma discharge,
magnetron sputtering,
chemical vapor deposition

Abstract

This work shows the preliminary results concerning to the synthesis or modification of carbon-based nanomaterials by plasma discharge, magnetron sputtering, and chemical vapor deposition methodologies. As a first approach to show the potential of these techniques, scanning electron microscopy analysis was performed in order to verify morphological changes and to proof that it is possible to design the morphology of doped and decorated carbon nanomaterials. In spite of none further characterization was performed, from the discussion of results in literature, it can be suggest that these methods would permit to design novel carbon-based nanomaterials for the energy production and storage, catalytic and photocatalytic processes related with environment and green chemistry applications.

1. Introduction

Modern energy and ecological problems determine the potential of society progress and currently gain in importance. The creation and commercialization of perfect stationary and mobile power installations [1] depends on the functionality of physicochemical accumulation systems. This includes smart grids with active-adaptive elements [2] of the proton-exchange membrane fuel cell (PEMFC) and direct formic acid fuel cells (DFAFC) [3]. The challenge is to create novel generators [4], consumer electrical installations [5], energy storage devices [6, 7], commutators [8, 9] and controlling grids [10, 11] providing simultaneous transfer of electrical energy and information. For example, simultaneously, dynamic changes in thermal and chemical potentials across the micro/nanostructured materials result in concomitant electrical energy generators [4] induced by charge transfer in the form of a high-output voltage pulse. For the case of electricity transmission and distribution, novel carbon nanomaterials play a vital role in society by connecting electricity producers and consumers with efficiency [5]. In addition, the surface chemistry, type and quantity of heteroatoms and doping elements play not only an important role upon the energy storage capacity in carbon-based devices [6, 7] but also microfluidic analyzer that integrates a complete amperometric detection system based on a highly sensitive carbon nanotube composite electrode [8] and even many small DC motors are used in automotive carbon-based electrical equipment's [9]. Finally, the application of lithium ion batteries in high power applications such as hybrid electric vehicles and electric grid systems [10, 11] critically requires drastic improvement in the electronic conductivity using effective materials design and strategies. Concerning to the production of clean energy, our group have showed [3] that a hybrid TiO_2-C nanostructured material is able to produce up to 3.5 higher maxima power than the commercial catalysts in the direct formic acid fuel cell.

The most perspective materials for creation of energy storage systems are carbon nanostructured materials such as carbon nanofibers (CNF) and nanotubes (CNT) [12], thermally expanded graphite [13], and graphene [14] among others. Activated carbon is not included among this group because although most of the surface area correspond to pores of nanometric size [15] the structure is generally turbostratic and cannot be considered as nanostructured. Carbon materials surfaces are inactive towards acids and bases at room temperature. However, some chemical compounds can be effective in surface doping. High temperatures and high reactive compounds are required for chemical modification. For example, the presence

---

* Corresponding author. E-mail: jmatoslale@gmail.com

of protons in gas discharge plasma is fundamental for the hydrogenated carbon surface formation. In this sense, the main objective of this work is to show the morphological analysis by scanning electron microscopy (SEM) of some specific examples of doped and decorated carbon-based nanomaterials prepared by high energy methodologies and as a first approach, from results in the literature a discussion was presented to show that these methods are very useful to design controlled different types of carbon-based nanomaterials.

2. Experimental

Different techniques such as plasma discharge (PD) [16], magnetron sputtering (MS) [17], and chemical vapor deposition (CVD) [18] were used to promote the modification of the surface of carbon materials. A barrier discharge in H_2/Ar or in isobutane atmosphere was used for the plasma discharge method. Further details concerning to PD method has been reported elsewhere [19]. On the other hand, decoration nanoparticles by magnetron sputtering was performed by an alternative method baking the surface of Co and Ni samples in H^2 plasma between 5×10^{-5} bar to 10^{-4} bar. Finally, the chemical vapor deposition (CVD) method on Si substrate with Ni sublayer was used for the carbon nanotubes (CNT) synthesis at 5×10^{-5} bar to 2×10^{-4} bar into the working gas pressure composed by the mixture ferrocene, $Fe(C_5H_5)_2$ and Ar/H_2 (1:20) with initial temperature 800 °C. Once temperature in chamber reaches 450 °C, catalyst vapors [ferrocene, $Fe(C_5H_5)_2$, or a xylene/ferrocene mixture, $C_8H_{10}/Fe(C_5H_5)_2$] with initial temperature 800 °C was added to working gas flow. Catalyst vapors at working zone of the reactor condenses at Ni atoms, where CNT appears at growth velocity 10–20 μm/min warming up to 900 °C the mixture flow (from 20 to 60 sccm).

3. Results and Discussion

3.1. Plasma Discharge (PD) Method

Figure 1 shows SEM images with the modification of the surface of Busofit carbon fiber by PD. The efficiency PD method permits to induce a surface modification from 50 up to 200 times surface area growth [19, 20] of carbon fibers Busofit by barrier discharge in H_2/Ar (Fig. 1a) or in isobutane atmosphere (Fig. 1b), respectively. The remarkable difference in the enhancement of surface area as a function of atmosphere is due to the formation of filamentous structures in the case of H_2/Ar atmosphere where the filament just appear on the surface of the fiber as a consequence of a chemical etching effect of the pristine fiber while for the case of isobutene atmosphere, the remarkable increase in surface area is due to the formation of deposits of nanometric carbon black (CB) as an overlapping domain.

This fact has been recently reported by Sun and co-workers [21]. These authors prepared high surface area carbon black (CB) via arc discharge non-thermal plasma which was enhanced by thermal pyrolysis process, in which propane (in presence of Argon) was cracked into CB with controlled structure and hydrogen. Sun and co-workers [21] reported that the yield of CB could be up to 85.9% under optimal operating conditions; the spherical CB produced by this process possessed a narrow size distribution of nanoparticles and with a BET surface area up to 132 $m^2.g^{-1}$. This value is commonly two times higher that CB obtained by pyrolytic methods. In addition, Sun and co-workers also reported that the resistivity of the CB was decreased with increasing discharge current and pyrolysis temperature suggesting that electrochemical properties can be design it by plasma discharge methodology.

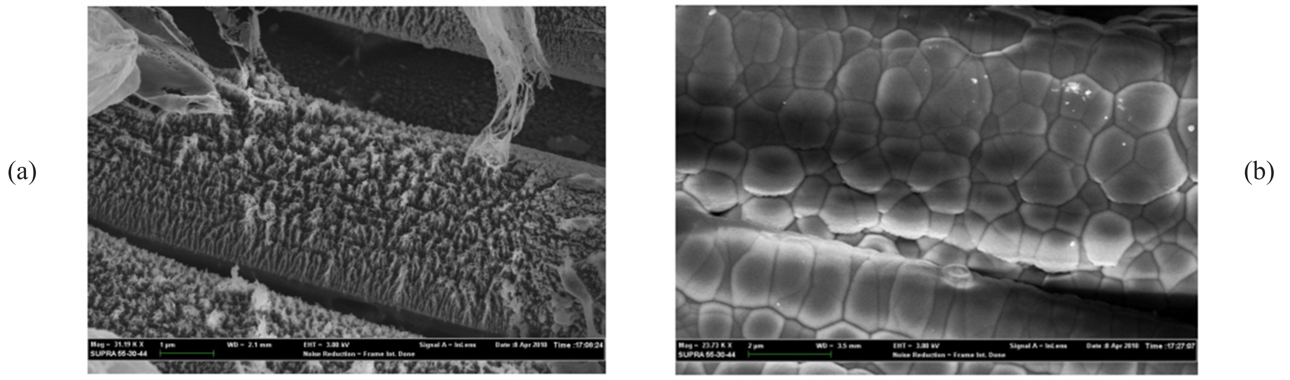

Fig. 1. Modification by PD of Busofit CNF under H_2/Ar (a) and isobutane (b) atmospheres.

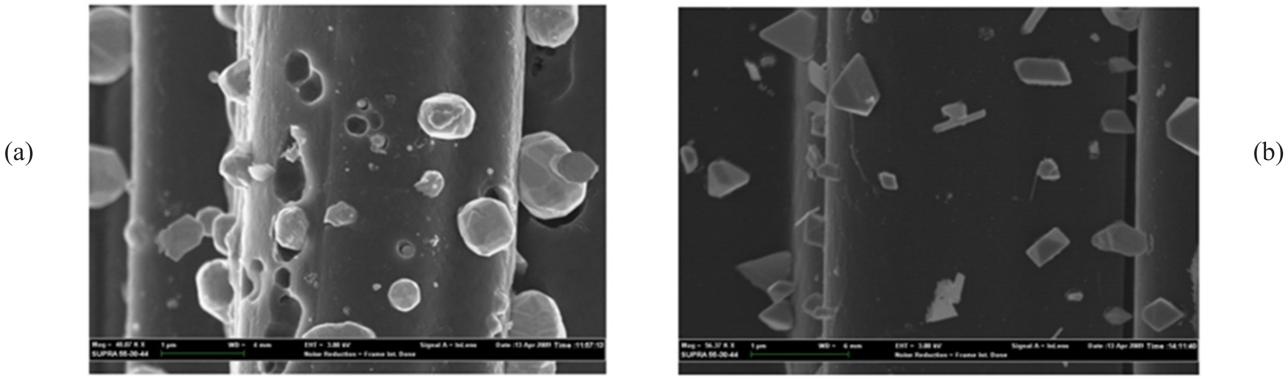

Fig. 2. Decoration of CNF by MS. (a): with Co nanoparticles. (b): with Ni nanoparticles.

This result seems to suggest that the present modified Busofit carbon fiber (Fig. 1) can be used as a candidate for the electricity transmission and distribution (T&D) [5]. For example, Arvesen and co-workers [5] have reported that the impact on the efficiency of electricity T&D is attribute to either power grid losses or to other processes, e.g., type of materials and component manufacturing. Therefore, both power losses and other processes contribute significantly to total impact potentials [5]. Power losses are responsible for 30–43% of the combined electricity T&D impact potentials for climate change, particulate matter, smog-creation and acidification, 21–28% for toxicity and eutrophication, and 14% for metal depletion [5]. In this sense, it is expected that Carbon-based nanomaterials, can help to solve part of these problems because of their high conductivity and low resistance.

3.2. Magnetron Sputtering (MS) Method

Surface decoration of carbon nanofibers (CNF) with metal nanoparticles is also effective by using MS. Decoration nanoparticles with diameter 2–3 nm showed in Fig. 2 were prepared by an alternative method by using Co and Ni films as catalysts. The use of Co films as catalyst leads to the agglomeration of Co nanoparticles in clusters with spherical shape (Fig. 2a) while by using Ni films, a more regular octahedral nanocrystals of smaller size was found (Fig. 2b). The shape of the metals decorating carbon fibers is a key-point for the enhancement of energy storage. For example, Senthilkumar and co-workers [22] have showed that NiO nanoarrays of a few atoms thickness on carbon-supported 3D nickel foams developed an enhanced pseudocapacitive. In addition, carbon-based devices have been also reported for N,S-codoped sponge-like graphene [7] a high reversible capacity as electroactive interlayer for Li-S batteries. An impressive high capacity of 2193.2 mAh g^{-1} can be obtained for the S cathodes with a high energy density of 418.5 Wh g^{-1} which still can be released at the power density of 4.55 kW kg^{-1} based on the total mass of the sulfur cathode and interlayer for the assembled Li-S batteries.

Another important example of how the chemical nature of the element used as catalyst influence the shape of the nanoparticle decorating the CNF is showed in Fig. 3. Figure 3 shows the thermally expanded graphite under H_2 atmosphere at 400 °C which surface has been decorated with Mg nanoparticles by MS method. In this case, it is clear that Mg nanoparticles are characterized by randomly network overlapping layers with distorted polygonal sizes. These type of random network materials are very important for the energy storage and magnetic sensors. For example, in an early work, our group have found that introducing changes in the Euler's polygonal distribution of randomly carbon-based polygonal 2D and 3D cell-network prepared from the controlled pyrolysis of saccharose [23] a remarkable hydrogen storage capacity was found. Then, in follow-up works our group firstly found that the use of KOH as catalysts to obtain K-doped carbon-based networks not only affect remarkably the textural properties such as BET surface area and pore volume and pore size distribution [24] but also is responsible of the appearance of a double-component in the magnetic behavior of carbon nanostructured materials [25].

In addition, Takaoka and co-workers have reported [9] that the wear of metal-graphite and carbon brushes is much larger in gasoline than in air, and severe wear was sometimes observed [9]. In other words, a DC motor for a fuel pump has a distinctive feature that its brush and commutator work in gasoline is required. In this sense, these authors reported a carbon-fiber brush tested in wear and sliding performance in gasoline and compared with a carbon brush alone, and they showed that the carbon-fiber brush is better than the carbon brush alone for the commutation ability and wear in gasoline. Thus, MS methodology would be an interesting methodology to prepare novel Metal-expanded graphite composites for the commutator applications.

Fig. 3. Thermally expanded graphite surface decorated with Mg nanoparticles by MS.

3.3. Chemical Vapor Deposition (CVD) Method

For CNT synthesis, the CVD method on Si substrate with Ni sublayer was used. Carbon nanofibers decorated with single-walled and multi-walled carbon nanotubes (SWCNT and MWCNT, respectively) by CVD synthesis is showed in Fig. 4a and 4b, respectively.

In previous works our group have found [19, 20] SWCNTs at working gas pressure of 5×10^{-5} to 2×10^{-4} bar. To control this, it is necessary to use catalyst nanoparticles with diameter of about 1 to 5 nm, or catalyst layer of 0.5 to 2 nm thickness deposited on the wafer. In the present work, we showed the results obtained with a process containing Si wafers together with Ni sublayer with thickness of 0.3 nm coats where its surface was polished by magnetron deposition. The wafers were placed in CVD reactor chamber, and when the working gas ($Fe(C_5H_5)_2$ and Ar/H_2 (1:20)) flow through chamber, temperature is slowly increased. In order to synthesize CNT perpendicularly oriented to the substrate surface, a negative potential from -40 V down to -1000 V was applied to the surface allowing a more arranged oriented structure of carbon nanotubes comparing with purely thermal schemes of CVD synthesis. The results are shown in the Fig. 4a where SWCNT where prepared perpendicularly oriented to the surface of the fiber.

On the other side, to obtain mainly a preferential growth of MWCNTs on CNF surface, catalytic nanoparticles with diameter of 10–100 nm or catalytic layers of 4–10 nm thickness are required. In addition, the possibility to control the morphology of MWCNT by changing of thickness of catalytic metallic layer from 0.1 up to 2 nm was confirmed. The results obtained on catalytic layers of about 7 nm thichness are showed in Fig. 4b. It can be seen that in the fiber decorated with MWCNT prepared by controlled CVD-synthesis showed preferential diameter and a remarkably homogeneity and orientation. Further experiments are being conducted to a better understanding of the influence of hydrocarbons CH_4, C_2H_2, C_2H_4, C_2H_6 as carbon source together with Ar or Ar/H_2 mixtures.

The importance of the present SWCNT and MWCNT obtained by controlled CVD can be figure out by examining some works from literature. For example, it has been reported by Hwang and co-workers [4] that thermal CVD and the wet impregnation process are respectively employed for the synthesis of a multi-walled carbon nanotube array and a hybrid composite of picric acid/sodium azide/multi-walled carbon nanotubes. The prepared hybrid composites have been efficiently used to fabricate a thermopower wave generator with connecting electrodes [4]. In addition, Hsieh and co-workers have recently reported [6] that hierarchical carbon nanotubes (CNTs) and graphene nanosheets (GNs)

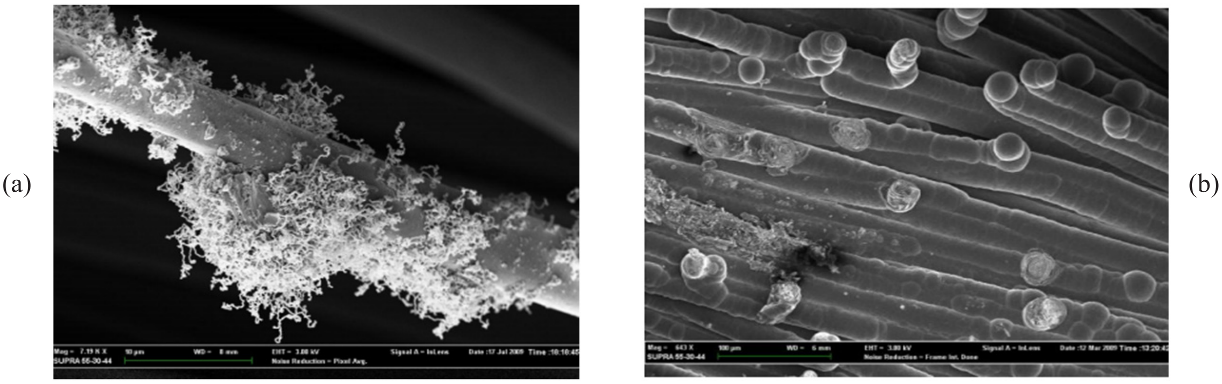

Fig. 4. Carbon fibers decorated with CNT. (a): SWCNT. (b): MWCNT.

supported MnO_2 nanoneedles can be efficiently used as an electrochemical capacitive device. These authors reported a synergistic effect between MnO_2 crystals and the nanocarbon supports, which permit the raising of more active sites for formation of charge transfer and electric double-layer in the hybrid architecture [6].

In short, we do believe that the preliminary results obtained in the present work opens a door to design SWCNT and MWCNT upon different types of substrates by using controlled CVD in presence of different carbon sources and just only by changing the chemical nature of the wafer or nanoparticle catalysts, these materials would be important applications as electrodes, supercapacitor, and other energy production and storage devices.

4. Conclusions

It can be concluded that plasma discharge, magnetron sputtering, and chemical vapor deposition methodologies can be useful technologies for the synthesis or modification of carbon-based nanomaterials. Morphology of doped and decorated carbon nanomaterials was verified by scanning electron microscopy analysis. Results reported in the recent literature was used to discuss and emphasizes the potential applications of carbon nanomaterials prepared by the different methodologies. In spite of none further characterization was performed it can be suggested that these methods would show a clear potential to design novel nanomaterials for the energy production and storage, catalytic and photocatalytic processes related with environment and green chemistry applications.

Acknowledgements

J. Matos thanks to the Chilean Basal Program PFB-27 for the funds. S.A. Filatov thanks to the Belarus-Venezuelan Program for the funds granted to the project.

References

[1]. A.J. Appleby. J. Power Sources 58 (1996) 153–176.
[2]. S. Gamburzev, A.J. Appleby. J. Power Sources 107 (2002) 5–12.
[3]. J. Matos, A. Borodzinski, A. Mikolajczuk Zychora, P. Kedzierzawski, B. Mierzwa, K. Juchniewicz, M. Mazurkiewicz, J.C. Hernández-Garrido. Appl. Catal. B: Environ. 163 (2015) 167–178.
[4]. H. Hwang, T. Yeo, Y. Cho, D. Shin, W. Choi. J. Vis. Exp. (98), e52818, doi:10.3791/52818 (2015).
[5]. A. Arvesen, I.B. Hauan, B.M. Bolsøy, E.G. Hertwich. Appl. Energy 157 (2015) 144–151.
[6]. C.-T. Hsieh, D.-Y. Tzou, W.-Y. Lee, J.-P. Hsu. J. Alloys & Compounds 660 (2016) 99–107.
[7]. L.-B. Xing, K. Xi, Q. Li, Z. Su, C. Lai, X. Zhao, R.V. Kumar. J. Power Sources 303 (2016) 22–28.
[8]. R. Olivé-Monllau, C.S. Martínez-Cisneros, J. Bartrolí, M. Baeza, F. Céspedes. Sens. Actuat. B: Chem. 151 (2011) 416–422.
[9]. M. Takaoka, T. Aso, K. Sawa. A commutation performance and wear of carbon-fiber brush in gasoline. Electrical Contacts. Proc. Annual Holm Conf. Electrical Contacts (2001) 44–49.
[10]. F. Hao, P.B. Dong, Q. Luo, J. Li, J. Lou, H. Lin. Energy&Environ. Science 7 (2013) 2003–2019.
[11]. C.H. Lim, A.G. Kannan, H. –W. Lee, D.K. Kim. J. Mater. Chem. A. 1 (2013) 6183–6190.
[12]. J. Smithyman, Q.H. Do, C. Zeng, Z. Liang. J. Power Sources 277 (2015) 59–63.
[13]. R.J. Warzoha, R.M. Weigand, A.S. Fleischer. Appl. Energy 137 (2015) 716–725.
[14]. C.C. Li, H. Yu, Q. Yan, H.H. Hng. J. Power Sources 274 (2015) 310–317.
[15]. V. Fierro, V. Torné-Fernández, A. Celzard. Microp. Mesop. Mater. 92 (2006) 243–250.
[16]. L. Yang, Z. Shi, W. Yang. Electrochim. Acta 153 (2015) 76–82.
[17]. N. Bouts, A.A. El Mel, B. Angleraud, P.Y. Tessier. Carbon 83 (2015) 250–261.
[18]. X. Xu, G. Wang, H. Wang. Chem. Eng. J. 266 (2015) 222–232.
[19]. S.A. Zhdanok, I.S. Krylov, M.A. Silenkov, S.A. Filatov, S.V. Shushkov. J. Enginee. Phys. Thermophysics 84 (2011) 540–545.
[20]. S.A Filatov, J. Matos Lale, G.S. Ahremkova, D.V. Solovei. M.N. Dolgikh, G.S. Kuczynski, E.V. Batirev. Doped and decorated carbon nanomaterials for accumulation of energy. Proc. VII Intern. Conf. “Fullerenes and Nanostructures in Condensed Matter”, 2013, Minsk, Belarus.
[21]. D.L. Sun, F. Wang, R.Y. Hong, C.R. Xie. Diamond and Related Materials 61 (2016) 21–31.
[22]. V. Senthilkumar, F.B. Kadumudi, N.T. Ho, J.-W. Kim, S. Park, J-S. Bae, W.M. Choi, S. Cho, Y.S. Kim. J. Power Sources 303 (2016) 363–371.
[23]. J. Matos, J. Laine. J. Mater. Sci. Letters 17 (1998) 649–651.
[24]. J. Matos, M. Labady, A. Albornoz, J. Laine, J.L. Brito. J. Molec. Catal. A: Chemical 228 (2005) 189–194.
[25]. J. Matos, T. Dudo, C.P. Landee, P. Silva, M.M. Turnbull. The Open Mater. Sci. Journal 3 (2009) 28–32.