

PRODUCTION OF TEMPLATED CARBON NANO MATERIALS, CARBON NANOFIBERS AND SUPER CAPACITORS

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Introduction

i. Porous carbons are usually obtained via carbonization of precursors of natural or synthetic origin, followed by activation. To meet the requirements, a novel approach, the template carbonization method, has been proposed. Replication, the process of filling the external and / or internal pores of a solid with a different material, physically or chemically separating the resulting material from the template, is a technique that is widely used in microporosity and printing. This method has been used to prepare replica polymers [1,2] metals [3] and semiconductors [4] and other materials [5,6]. Zeolites represent an interesting case for replication processes, because the dimensions of their cages and channels are quite similar to those organic molecules that constitute the replica. If such as nanospace in a zeolite is packed with carbon and then the carbon are extracted from the zeolite framework, one can expect the formation of a porous carbon whose structure reflects the porosity of the original zeolite template. Owing to the disordered and inhomogeneous nature of the starting materials, the resulting carbon has a wide and poorly controlled distribution of pore sizes. Zeolites with three-dimensional pore structures were found to be suitable as templates [7,8], whereas zeolites with one-dimensional structures were not effective [9]. These carbons obtained using zeolite templates with three-dimensional pore structures retained the shapes of zeolite particles, but did not retain their internal periodic structure.

ii. Many methods have been proposed for carbon nanofiber (CNF) production, among them, we have chosen chemical vapor deposition (CVD) method for CNF synthesis because of its potential for scaling up the production and low cost[10]. Recent developments showed that alignment, positional control on nanometer scale, control over the diameter, as well as the growth rate of the carbon nanotubes (CNT) and CNFs can be achieved by using CVD[11-13]. Many catalyst supports and metal catalysts were proposed for CNF production through CVD technique. Silica (SiO_2) [14], alumina (Al_2O_3) [15], quartz [16], titania (TiO_2) or calcium oxide (CaO) [17] were used as the catalyst support because of their chemical inertness and high-temperature resistance. However, all of these support materials require harsh chemical treatment i.e. concentrated bases (NaOH) or strong acids (HF) to remove them, and these reagents may also damage the carbon nanostructure. Additionally, strong acids and bases are less desirable for large-scale production due to environmental concerns. Our goal in synthesizing CNFs is to achieve a control in tailoring the diameter, and morphology at the same time. We believe that understanding the chemistry involved in the catalyst and nanofiber growth process is the critical point to be able to produce defectless, property controlled CNFs. Thus, knowing the effect of the catalyst on CVD production of carbon nanofibers is very important for producing the desired CNFs. A very unique material, NaCl in the field of catalytic CVD process for carbon materials production, was selected as the support material which provides easy production and easy removal properties to the catalyst system. Together with the support material, the metal catalyst preparation step was differentiated from the conventional wet catalyst methods in which a liquid solution containing the catalyst in salt form is applied to the substrate via spray coating [16,18,19], spin coating [20-22], or

microcontact printing [23] as well. The most active metals that were used previously in the catalytic CVD process for carbon materials production were Fe, Co [24], and Ni. The reason for choosing these metals as catalyst for CVD growth of nanotubes was the thermodynamic behavior of the metals at high temperatures, in which carbon is soluble in these metals and this solubility leads to the formation of metal-carbon solutions and therefore the desired carbon nanomaterial formation nucleates. In this study, transition metal based organometallic complex catalysts of Fe, Co, Ni and Cu were synthesized by a new approach of simultaneous synthesis of the support material and the catalyst. Therefore an easy production method for catalyst to use in CVD was developed by using only wet chemistry.

iii. Electrochemically conducting polymers (ECPs) are of interest in late years and they are promising materials for realization of high performance supercapacitors, as they are characterized by high specific capacitances, by high conductivities in the charged states and by fast charge-discharge processes. The charge processes pertain to the whole polymer mass and not only to the surface. These features suggest the possibility to develop devices with low ESR and high specific energy and power. However, the long-term stability during cycling is a major demand for an industrial application of ECPs. Swelling and shrinkage of ECPs, caused by the insertion/deinsertion of counter ions required for doping the polymer, is well known and may lead to degradation of the electrode during cycling. This obstacle has been overcome to some level by using composite materials made of carbon materials such as CNTs or activated carbons with CPs. Carbon material in the bulk both ensures a good electrical conductivity even the CP is in its insulating state and improves the mechanical properties of the electrodes. As mentioned in the earlier chapters, using carbon nanotubes, CPs, or both as composites for the active material of the supercapacitor applications comes with some disadvantages as well as the advantages. CPs although being a promising energy source for the job, lack the flexibility for insertion/deinsertion of the dopant ions resulting in shorter recycling life times than desired. CNTs are employed to gain more flexibility however whether they are used as active materials solo, or engaged in a composite with a CP, they could not supply enough energy for the job. Therefore, the objective of this study is, to obtain a new material for supercapacitor active material; by depositing a conducting polymer, polypyrrole, on to carbon nanotubes via electropolymerization. By this method, the problem of bulk charging in conducting polymers is aimed to be overcome. Since the coating is in magnitudes of nanometers, only surface charging will exist, which is desirable for supercapacitor applications.

Experimental

i. The novel approach of template carbonization method has been used in this study for the production of mesoporous carbons. The effects of different templating mixtures and different carbonization temperatures on the structure of carbons were studied using furfuryl alcohol as the carbon source. Furfuryl alcohol was polymerized and carbonized at various temperatures in the channels of natural zeolite. The porous carbon samples obtained contained 91-99% carbon with a surface area of 400-800 m²/g. Template method seemed to increase the surface area of the porous carbons produced. The XRD results put forward in the present work might be considered as indications to the presence of turbostratic structures in the carbons obtained in the temperature range of 700°C-1000°C.

ii. Carbon nanofibers were synthesized by thermal chemical vapor deposition (CVD) method over transition metal based catalyst by using acetylene as the synthesis gas. In one approach, iron, cobalt, nickel, copper and zinc were used as catalyst metals in metal tartrate form with sodium chloride as the support material. This soluble support material and metal tartrates is a novel catalyst system for this CVD application and works with a high efficiency. In another approach MCM-41 supported catalysts containing different amounts of iron,

cobalt, nickel and copper synthesized via microwave radiation were used for carbon nanofibers production. Due to the more uniform heating throughout the reaction vessel, the microwave-induced heating results in more homogeneous nucleation and shorter crystallization times significantly compared to the hydrothermal method by which microwave-induced heating reduce the synthesis time from days to hours. The catalysts were characterized by using X-Ray diffraction (XRD), scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS), BET surface analyzer and thermal gravimetric methods in order to relate the structural effects of the catalyst on CVD process. In addition, the effects of the type of the metal, temperature and concentration of the synthesis as on CVD for production of carbon nanofiber using the same conditions were investigated.

iii. CNT synthesized were used as supporting material that pyrrole monomer can be deposited on electrochemically. The electro-deposition took place in an UV cuvette, using an ITO glass coated with copper plate with one side is stuck to ITO and the other side coated with carbon nanotubes as the working electrode, a Ag wire as the reference electrode and a Pt wire as the counter electrode. The electrolyte used was 0,1 M NaClO₄ prepared in acetonitrile. Although conducting polymers are coated on carbon nanofibers by using one-step vapor deposition polymerization technique, in this study the coating has been achieved electrochemically which is a more accurate way to have the specific amount of coating thickness. So far, polypyrrole coated CNT's are still being optimized to have maximum deposition with the highest possible capacitance while possessing the highest possible surface area. It sure will be a promising active material for the use of supercapacitors.

Results and Discussion

i. With increasing pyrolyzing temperature, crystalline structures of natural zeolite were changed. BET area of TEOS-FA carbon was 804 m²/g. BET surface areas of natural zeolite templated carbons were 397.2, 349.9, 404.7 and 367.1 m²/g at 700, 800, 900 and 1000°C, respectively. The d_{002} values of the carbon synthesized by carbonization of FA in the channels of zeolite were 0.358, 0.347, 0.349 and 0.346 nm at 700, 800, 900 and 1000°C, respectively. L_c values and average number of graphene sheets per stack were increasing with carbonization temperature. The size of the microcrystallites increases quickly with increasing pyrolytic temperature L_c values were increased from 2.79 nm to 6.64 nm, and average number of graphene sheets increased from 8 to 19 when temperature was increased from 700°C to 1000°C. The crystallite boundary area decreased from turbostratic crystallite growth and number of graphene sheets increased. EDS showed that 91-99 % C was obtained with the carbonization of PFA in the zeolite at 700-1000°C. The success of the demineralization step was indicated by both the high carbon content and the small quantities of silicon and aluminum. The sp^3 C, sp^2 C and sp hybridized carbon was detected.

ii. Carbon nanofibers with different morphologies were prepared by catalytic decomposition of acetylene between 500° and 700°C using NaCl supported metal (Fe, Co, Ni and Cu) tartrate catalyst systems. At moderate temperatures between 500°C and 600°C the CNF growth was controlled by the nature and activity of the catalyst which had been affected by calcination and reduction steps. Furthermore it was observed that as the temperature increased the catalyst particles experienced a shape transformation from a particle with different active surfaces to a spherical particle during the CNF growth process which led to linear CNF formation. We also found that the presence of sulfurous structures could affect the activity of surfaces at moderate temperatures and at temperatures near 700°C and above all the catalyst systems formed only linear CNFs.

iii. In this study, pyrrole monomer is polymerized on carbon nanofibers via electropolymerization. Its optimization has done by means of deposition amount and

deposition speed. A new technique has been developed to have chemically bonded CNF-PPy active material unlike the composites used for supercapacitor technology nowadays. This new technique can have many derivations with different types of CNFs and CPs, to obtain a better active material with higher surface area and higher specific capacitance. Optimization has proven that the high deposition amounts result in blocks of polymers, which can be overcome by optimizing the amount of polymerization. The optimum deposition amount is found out to be 6 times cycling at 25 mV/s which is a relatively slow scan rate.

References

- [1] R.V. Parthasarathy, C. Martin, *Nature* 369 (1994) 298.
- [2] S.A. Johnson, P. J. Ollivier, T.E. Mallouk, *Science* 282 (1999) 963.
- [3] C. R. Martin, *Advanced Materials* 3 (1991) 457.
- [4] J.D. Klein, R.D.I. Herrick, D. Palmer, M.J. Sailor, C.J. Brumlik, C.R. Martin, *Chem.Mater.* 5 (1993) 902.
- [5] C.R. Martin, *Chem. Mater.* 8 (1996) 1739.
- [6] A.J.G. Zarbin, M.A. Paoli, O.L. Alves, *Synthetic Metals* 99 (1999) 227.
- [7] T. Kyotani, T. Nagai, S. Inoue, A. Tomita, *Chem. Mater.* 9 (1997) 609.
- [8] J. Rodriguez-Mirasol, T. Cordero, L.R. Radovic, J.J. Rodriguez, *Chem. Mater.* 10 (1998) 550.
- [9] S.A. Johnson, E.S. Brigham, P.J. Ollivier, T.E. Mallouk, *Chem. Mater* 9 (1997) 2448.
- [10] M.S. Dresselhaus, M. Endo, *Relation of Carbon Nanotubes to Other Carbon Materials*. In *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*, Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P., Eds. 2002.
- [11] S.H. Jeong, O.J. Lee, K.H. Lee, S.H. Oh, C.G. Park, *Chem. Mater.* 14 (2002) 1859.
- [12] C.L. Cheung, A. Kurtz, H. Park, C.M. Lieber, *J. Phys. Chem. B* 106 (2002) 2429.
- [13] V.I. Merkulov, D.K. Hensley, A.V. Melechko, M.A. Guillorn, D.H. Lowndes, M.L. Simpson, *J. Phys. Chem. B* 106 (2002) 10570.
- [14] K. Kakehi, S. Noda, S.S.M. Chiashi, *Chemical Physics Letters* 428 (2006) 381.
- [15] Z. Yu, D. Chen, B. Totdal, A. Holmen, *Journal Physical Chemistry, B*. 109 (2005) 6096.
- [16] E. Terrado, M. Redrado, E. Muñoz, W.K. Maser, A.M. Benito, M.T. Martínez, *Diamond and Related Materials* 15 (2006) 1059.
- [17] R.L. Vander Wal, T.M. Ticich, V.E. Curtis, *Carbon* 39 (2001) 2277.
- [18] J. Geng, H.W. Li, V.B. Golovko, D.S. Shephard, D.A. Jefferson, B.F.G. Johnson, S. Hofmann, B. Kleinsorge, J. Robertson, C. Ducati, *J. Phys. Chem. B*. 108 (2004) 18446.
- [19] E. Terrado, M. Redrado, E. Munoz, W.K. Maser, A.M. Benito, M.T. Martinez, *Mat. Sci. Eng. C* 26 (2006) 1185.
- [20] L. Jodin, A.C. Dupuis, E. Rouviere, P. Reiss, *J. Phys. Chem. B* 110 (2006) 7328.
- [21] M.J. Pender, L.A. Sowards, B. Maruyama, R.A. Vaia, M.O. Stone, *Chemistry of Materials* 2004, 2544-2550.
- [22] Y. Kobayashi, H. Nakashima, D. Takagi, Y. Homma, *Thin Solid Films* 464 (2004) 286.
- [23] J.M. Bonard, P. Chauvin, C. Klinke, *Nano Letters* 2 (2002) 665.
- [24] S.M. Bachilo, L. Balzano, J.E. Herrera, F. Pompeo, D.E. Resasco, R.B. Weisman, *J. Am. Chem. Soc.* 125 (2003) 11186.

