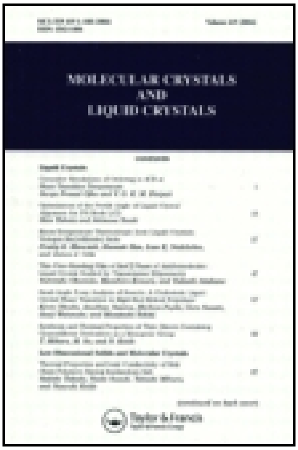

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Tailoring carbon nano structure: Nanocarbons and new devices

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TAILORING CARBON NANO STRUCTURE: NANOCARBONS AND NEW DEVICES

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Nanocarbons, which have been obtained by controlling the structure and bonding nature at the nanometer scale, can provide highly functional performances. Carbon nanotubes and vapor grown carbon fibers of diameter less than 100 nm can have quantum effects, which are very different from those of conventional carbon fibers. In this paper, preparation and properties of nanocarbon, are demonstrated and discussed.

Keywords: nanocarbon; tailoring; energy storage

1. INTRODUCTION

It is not an overstatement that extensive and continuous carbon research of these days can be attributed to the discovery of nano-scale carbon materials. After the identification of fullerenes and carbon nanotubes as new allotropes of carbon element in the end of the 20th century, chemists, physicists, scientists and engineers started to work intensively due to their extraordinary mechanical and electronic properties (see Fig. 1). Basically, carbon is a unique element that has three types of bonding nature: sp^3, sp^2 and sp bonds, which result in diverse allotropes such as diamond, graphite, carbyne and fullerene. So, carbon differs chemically from Si, Ge, and Sn (the other column IV elements, which all have sp^3 bonding). Carbon has plenty of potential since it is the lightest atom in column IV of the periodic table. Now it is becoming the main element instead of silicon for electronic applications in this era, as Professor H. W. Kroto predicted, "21st century is the carbon age". The 19th century can be remembered as an iron age while the 20th century is recognized to be the century founded on silicon technology. Now much attention is paid on carbon "C" as one of the promising candidates and leading element in the 21st century. To date, carbons have contributed to welfares of human being as a "silent force behind the science". This is greatly due to the diverse structural forms and functions

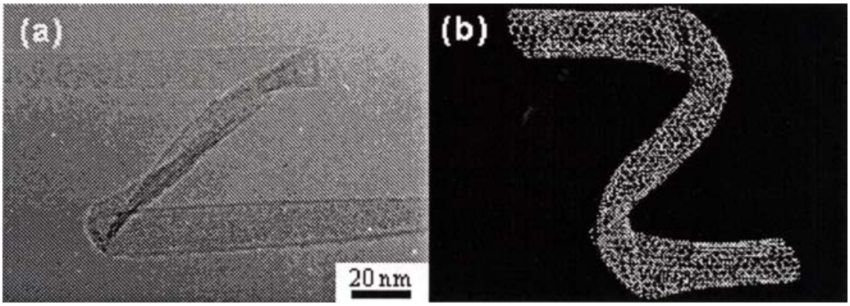

FIGURE 1 (a) HRTEM image of distorted single wall carbon nanotube and (b) computer simulated one.

of carbons. Inherent advantage of carbons materials, originating from the extraordinary ability of the chemical element carbon to combine itself and other chemical elements in different ways, is blooming in the 21st century. Tailoring of carbon structure, that is, controlling the physicochemical properties of carbon materials on the nanomenter scale, will be core technology for obtaining novel carbons with new and extraordinary functions. The function and the added value of novel carbons based on nano-technolgy will provide the industry of my nation with a great business opportunity.

Day by day, the request for revitalizing the global economy is growing. The only way to answer for this request is the technological innovation. According to model of Kondratieff the economist, new science will create a new industry and technology, and as a result, will bring the wave of big economic activity. The generalization of science, technology and products in the 20th century, which led to the recession of world market, is said to be one of the reasons to the present economy slump. Now is the time for new carbons based on carbon science to give rise to the creation of new functional materials, and finally technological innovation.

As literally one of the major newspaper reported, “Carbon is not now”. Many scientists are being “hot” on carbon materials. The author and co-workers have been studying for many years how to control the nano-structure is order to enhance the function and performance, and develop new functions of carbon materials. Our ultimate goal is to be a “carbon tailor” that creates novel carbon structure by making use of sp^3, sp^2 and sp or hexagonal carbon structure to meet our need just like an experienced tailor making a made-to-order outfits. In this paper, new carbons and their physical properties and novel functions from the viewpoint of nano-structure and its control will be presented with an emphasis on author’s studies.

2. NANO-PARTICLE INDUCED VAPOR GROWN CARBON FIBERS (VGCFs), CARBON NANOFIBER, AND CARBON NANOTUBE [1–3]

Vapor grown carbon fibers (VGCFs) shows very unique morphology such as an annular ring texture, and also contain single walled carbon nanotube or multi-walled carbon nanotube in the core part of the fibers (Fig. 2). Through a precise control of the synthetic conditions such as size of metal particles, it is possible to tailor the diameter, crystallinity and also the orientation of the cone angle with regard to the fiber axis (Fig. 3). As compared with those of arc discharge or laser vaporization, synthesis of carbon nanotube by simple method (catalytic chemical vapor deposition (CVD) method) has shown to be more controllable and profitable for the large-scale production. And also, it is possible to obtain various types of carbon nanotube and nanofiber through an appropriate selection of metal composition and synthetic conditions. As a result, the diversity of microstructure and morphology of one-dimensional carbons are expected to be useful in various fields such as electronic devices, composites, biomaterials, batteries etc. New science and technology based on VGCFs are growing rapidly.

3. DESIGN AND APPLICATION OF CARBON NANO-MATERIALS IN ANODE MATERIAL OF Li ION BATTERY (LIB) [4–6]

After commercialization of Li ion batteries (LIB) by Sony in 1992, they have been used in a wide range of mobile electronic devices, and now become leading product of secondary batteries (five hundred million battery cells per year). It is well known that carbon or graphite materials have been used as a main component of anode electrode in LIB. Actually, the

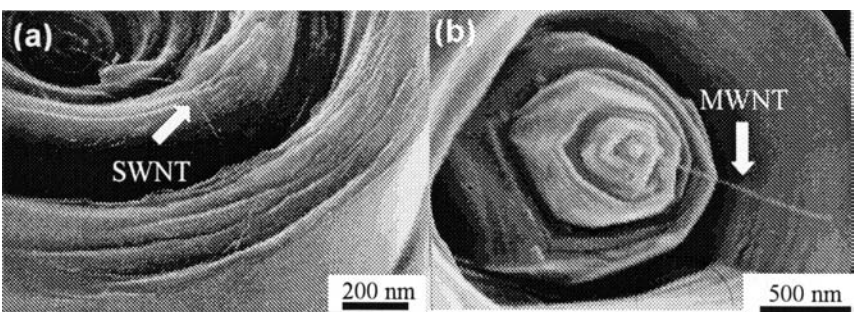

FIGURE 2 SEM images of VGCFs containing (a) SWNT and (b) MWNT.

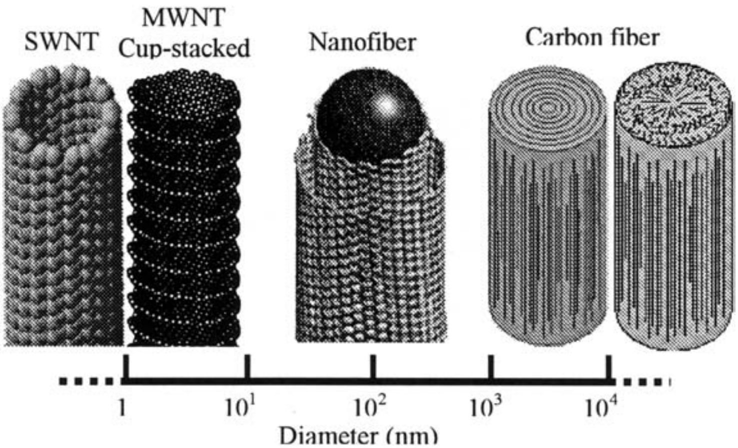

FIGURE 3 Schematic diagram from carbon fiber to carbon nanotube.

advance of carbon science has been supporting the tremendous improvement of capacity of LIB for past 10 years (10% per year). These days, the new generation cellular phones having diverse functions with high data transfer rate requires further enhancement of the battery performance. When considering the diverse and still growing LIB. e.g. from new type of cellular phone, high performance notebook, PC (personal computer), to power supply of 42V-vehicle and hybrid vehicle, it is critical to develop a higher performance LIB with advanced carbon materials as anode.

It is well known that boron atoms can be substituted in the hexagonal carbon plane of graphite up to 3 atomic %. Up to now, boron atom is considered as graphitization promoter, but this effect is only for c axis direction of graphite materials. When carbon materials are graphitized with boron containing compounds, the increase of crystallite thickness, and the decrease of interlayer spacing even lower than a single crystal of graphite, are observed. Hexagonal carbon plane containing substituted boron atoms in a-b plane is considered to be distorted due to different bond length of B-C, even resulting in decrease of interlayer spacing. STM image of boron doped HOPG reveals some mottled bright area (–1 nm) (Fig. 4). An unequal brightness, reflecting the localized electron density, is found in the boron-substituted areas. Substitution of boron, which is electron deficient compared to the carbon host, produces vacancies at the top of the valence band, resulting in an increase in the density of state near Fermi level. The effect is not restricted only to the boron sites themselves, but extends to the surrounding carbon sites due to the delocalized nature of the boron-induced defeat. It is reported that the electronic structure is modified

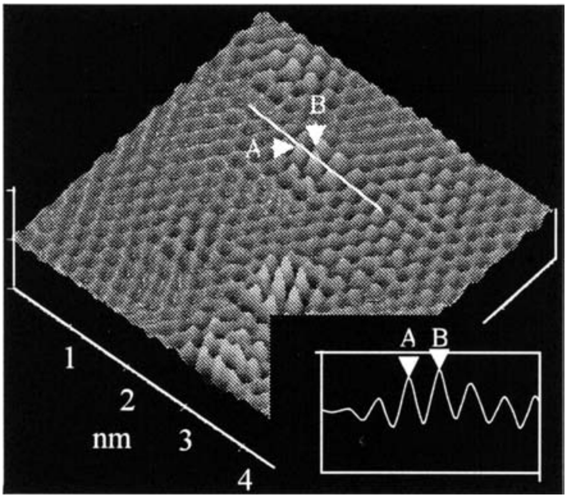

FIGURE 4 STM image of a three-dimensional surface plot and sectional atomic analysis corresponding to the line indicated (see the inset) B-doped graphene surface.

largely by boron doping. Graphite plane can be tailor-made both atomically and electronically, and the boron doping can contribute to controlling the properties of the hexagonal carbon network and also to practical application, because boron doped graphite reveals improved anode capacity around 15% as compared with that of undoped graphite. Based on this study, other atoms can be used in order to tailor the hexagonal carbon plane for specific application. By applying this technique on disordered carbons heat treated at low temperature, we are expecting for a super performance LIB in the near future.

4. CORRELATION BETWEEN THE PORE SIZE WITH NANO-SIZE AND THE CAPACITANCE OF EDLC [7–9]

Electric double layer capacitor (EDLC) has been expected as the electric energy storage device of the next generation, such as hybrid electric vehicle (HEV), fuel-cell vehicle, and power back-up system. Since the new interpretation of the pore structure is required in order to understand the mechanism of EDLC, we have developed an effective method for analyzing the nanopore with the help of TEM observations and image processing. For capacitance of EDLC, the theory for the conventional parallel plate condenser has been applied. The structure of the pore has been assumed to be

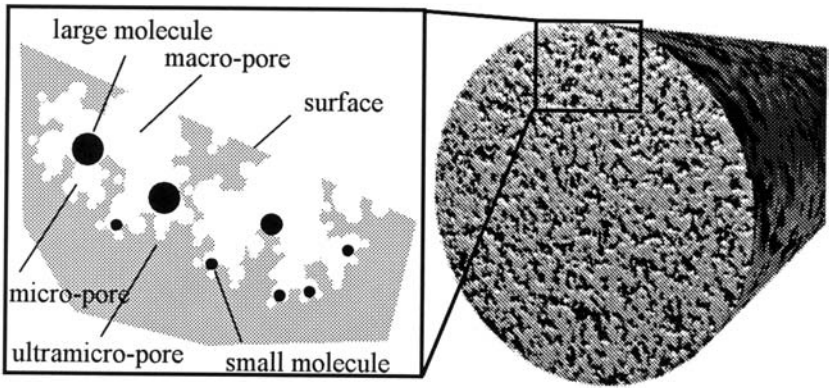

FIGURE 5 Schematic pore model of ACF consisting of fractal structure of pores.

the ideal structure such as slit and tube etc. However, actual pores that are quite different from these ideal models should be determined according to the TEM observations and image analysis process. The result of novel method we have developed is consistent with that of conventional gas adsorption method. Furthermore, it is very helpful to understand the pore structure because the novel method analyzes the pore structure from different viewpoint (Fig. 5). The novel method will be used as a powerful tool to develop a new carbon electrode for EDLC with high specific capacitance. Consequently, novel method shows some clues to control the nanostructure of carbon, and to get a final product with high performance. This enables us to effectively form an activated-carbon electrode with ideal pore size, which has the right room for the solvated ions in an aqueous and aprotic solvent system. All parameter in the process of preparing the capacitor (i.e. the choice of precursor, pyrolysis, activation etc.) should be considered for the end use. The creation of the new industry in relation with carbon based EDLC will be realized by the cooperation of carbon-related science and technology.

5. CONCLUSIONS

It is estimated that the world market of nano materials is a twenty seven thousand billion yen market. This sum doubles when we include surrounding correlative industrials and as a result, exceeds present automobile industry of this country. Novel carbons with new function and technology, constructed by tailor-made technology in nanoscale, will function as a starting point of industrial innovation. The technical development until the 20th century was mainly raised from the market needs. In the 21st century when there is no clear market needs, needs provoking-type technical innovation based on material technology is awaited. Applications fields of new carbons such as fuel cell, new type battery, composite with novel function, gas storage, and purification of water/air is considered to be the fundamental technology of the century. Conversion from conventional gasoline based vehicle to hybrid vehicle and fuel cell based vehicle, supported by new carbon technology, will cut the gas consumption to less than a half than usual. It has been expected that HEV and FEV will occupy around 10 to 20% of the domestic car sales in 2002–2003 years, and at the same time, nano carbon industry is also expected to bloom. Widespread impact of nanocarbon related technology on automobile industry and to the housing field as well enable to further promote the structural reform of the industry and economy, which our nation is aiming. Japanese consumers are renown to be “green consumers” in the world, and this fact has much to do

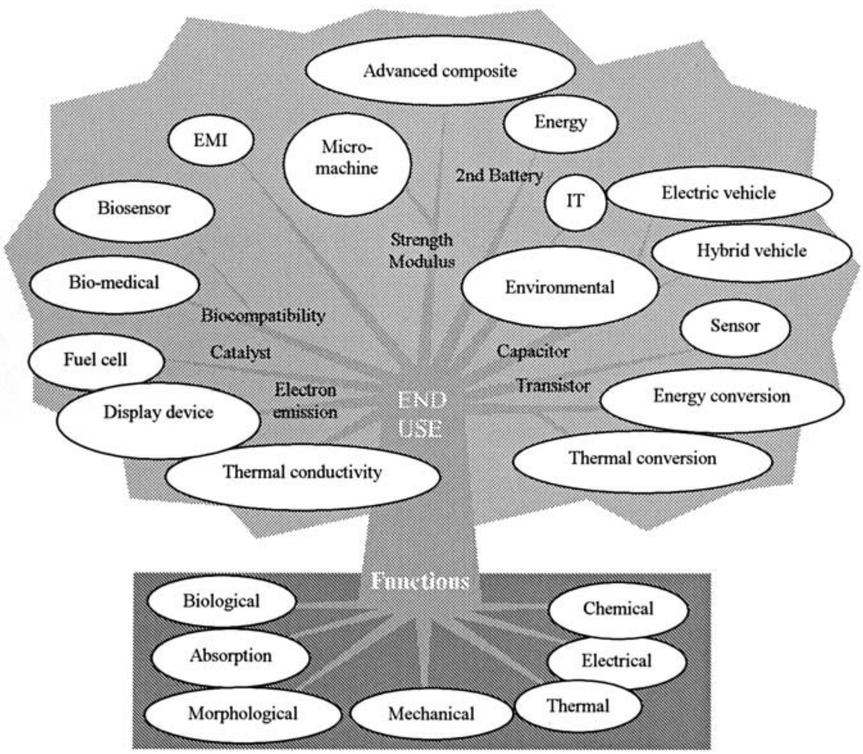

FIGURE 6 Tree of nanocarbons with basic properties and applications.

with the expansion of low environmental impact advanced vehicle market. Also, NEMS (nano electron mechanical system) will be developed by the contribution of nanocarbons as a sensor and actuator. New carbon as a key material of the twenty first century will grow to a great industry and contribute to environmental, energy and IT both directly and indirectly.

Intellectual production of nano carbon, that is, scientific results has been accumulated to a considerable amount, and it is time to the creation of the value (Fig. 6). When considering the recent research trend of carbons, we believe that this is not anymore a dream, and we are on the starting line.

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