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THE STATE-OF-THE-ART SCIENCE AND APPLICATIONS OF CARBON NANOTUBES

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Extra-ordinary chemical and physical properties of carbon nanotubes (CNTs) also the success of large-scale production by a catalytic chemical vapor deposition method. It should be noted that lots of CNT-derived products are already in use and their viability strongly depend on their commercialization. We describe the synthesis techniques of various CNTs, and structural characterizations will be discussed, and finally their practical applications of these CNTs will be described from the industrial point of view as well as safety issue of CNTs.

Keywords: Carbon nanotube, Nanostructure, Chemical vapor deposition, Synthesis, Application.

1. Introduction

Carbon nanotubes (CNTs) have attracted lots of attention from scientists in various fields because they exhibit extraordinary physical and chemical properties due to their intrinsic nano-sized and carbon-based natures. Various synthetic methods for producing carbon nanotubes have been reported. The dominant process is to synthesize carbon nanotubes using a catalytic chemical vapor deposition (CCVD) method because this technique is a very effective tool for producing on a large scale and controlling the number of carbon shells, using nanosized iron particles that are dispersed on the substrate or a floating reactant technique [1-4]. Noticeably, highly crystalline and pure CNTs are commercially produced in a semi-continuous system through the right combination of the CCVD method and the subsequent high-temperature thermal treatment.

In this paper, firstly, the current usage of carbon nanotubes in energy storage devices as one of the important components of lithium ion secondary batteries is shown, and supercapacitor and fuel cell applications are demonstrated with a special emphasis on their morphology and texture [4]. The effectiveness of the addition of carbon nanotubes to both the cathode and anode electrode on the performance of lithium ion secondary batteries will be discussed [5]. Second, the application of CNTs as the electrode for supercapacitor will be described in terms of their pore size and distributions [6]. It is thought that the usage of nanotubes in the commercialized energy storage devices will only increase when considering the nature of our energy-oriented society. Third, the industrial usages of CNTs as multi-functional filler in rubber nanocomposites will be described. Finally, for successful developments of CNT's, the safety and toxicity of carbon nanotubes are the most important issue [7-11]. By sharing the all information on risks [7-11] and benefits of the materials with everyone having a stake in their use, we are able to prove CNTs to be green and safe innovative materials, by the responsible productions and uses, as one of the 21st century's leading materials.

2. Synthesis and structures of CNTs by CCVD method

Currently, it is well known that the CCVD method is most commonly used for the synthesis of single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and MWCNTs (Fig. 1) [12,13]. For example, SWCNTs were synthesized by the floating method, and the obtained SWCNTs were directly used to form CNT ropes. In 1988, the industrialization of MWCNTs began experimentally, and the supply of MWCNTs samples began; to this day, the most frequently used catalyst in this synthetic method is iron. Now, many production systems for the industrial-scale synthesis of MWCNTs by various processes using the fluidization CCVD method as a basis have been established; MWCNTs have been industrialized in several countries, such as Germany, France, Japan, the US, Belgium, China, the UK and others. Depending on the intended use, there are several types, including as-deposited MWCNTs and those thermally treated at high temperatures (Fig. 1(b)). Since the 1990's, basic and applied research and the development of single-, double- and multi-walled CNTs, have been accelerated, thus making carbon fibers (CFs) and these materials the leading causes for the worldwide interest in nanotechnology.

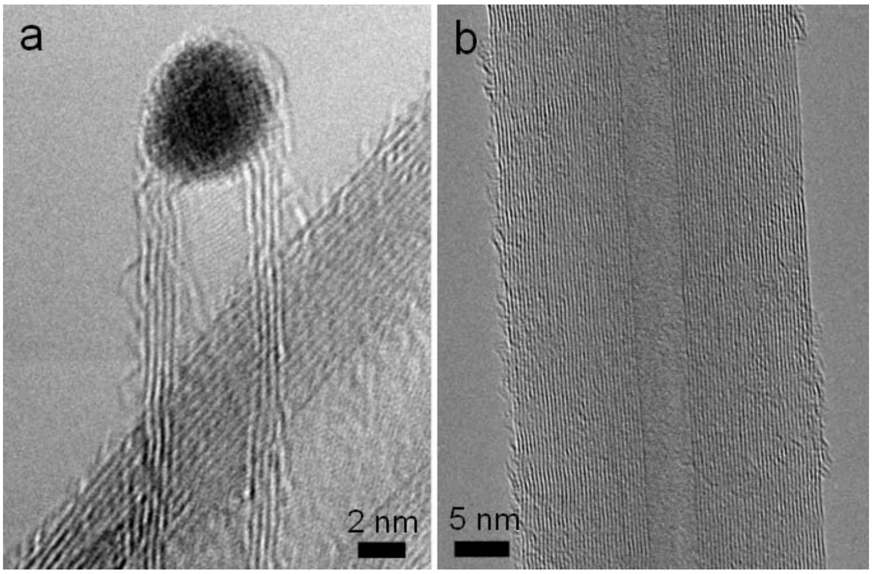

Fig. 1. TEM images of (a) four-walled CNT formed through catalytic effect of iron particles and (b) thermally treated MWCNT

An important factor required for the use of CNTs as a nanotechnology material is the precise control of growth for structures suitable for the required functions. By using the CCVD method, the number of layers, such as single, double, and multiwalled, as described above, can be controlled; we have succeeded in the synthesis of highly-pure DWCNTs with high structural perfection by the seeding method using an iron catalyst, that is, the CCVD method. Other major methods reported for DWCNT synthesis include high-temperature pulsed arc discharge [14] and thermal treatment of peapods, i.e., fullerenes encapsulated in SWCNTs [15]. Iron and cobalt particles, as well as molybdenum alloy particles, are primarily used as catalysts in the CCVD method, and in these methods, the catalyst particle size is precisely controlled on alumina and zeolite supports. We have developed a synthetic method for DWCNTs in which the reaction temperature and the catalyst particle size in particular were optimized using magnesium-oxide and iron catalysts [Fig. 2(a)] [16]. It is worthwhile to note that the high-purity DWCNTs had a small diameter almost equivalent to that of

SWCNTs, with a narrow diameter distribution. Furthermore, we could fabricate paper-like DWCNTs with high flexibility [16]. By thinning the film, the fabrication of a conductive transparent film is possible, 14) and the application of the film as a transparent and conductive film is expected. Additionally, DWCNTs have interesting adsorption characteristics; hydrogen is well adsorbed in nanospaces of DWCNTs [17]. Because the diameter of DWCNTs is approximately 1 nm, which is comparable to that of SWCNTs, it is expected that DWCNTs with properties arising from the double-wall structure will be utilized in electronic and energy device applications. It is even possible to form a hybrid double-wall structure in which only the electronic properties of the outer tube are changed to that of an insulator, by fluorinating the outer tube of the coaxial double wall yet maintaining the intrinsic physical and chemical properties of the inner tube [Fig. 2(b)] [18].

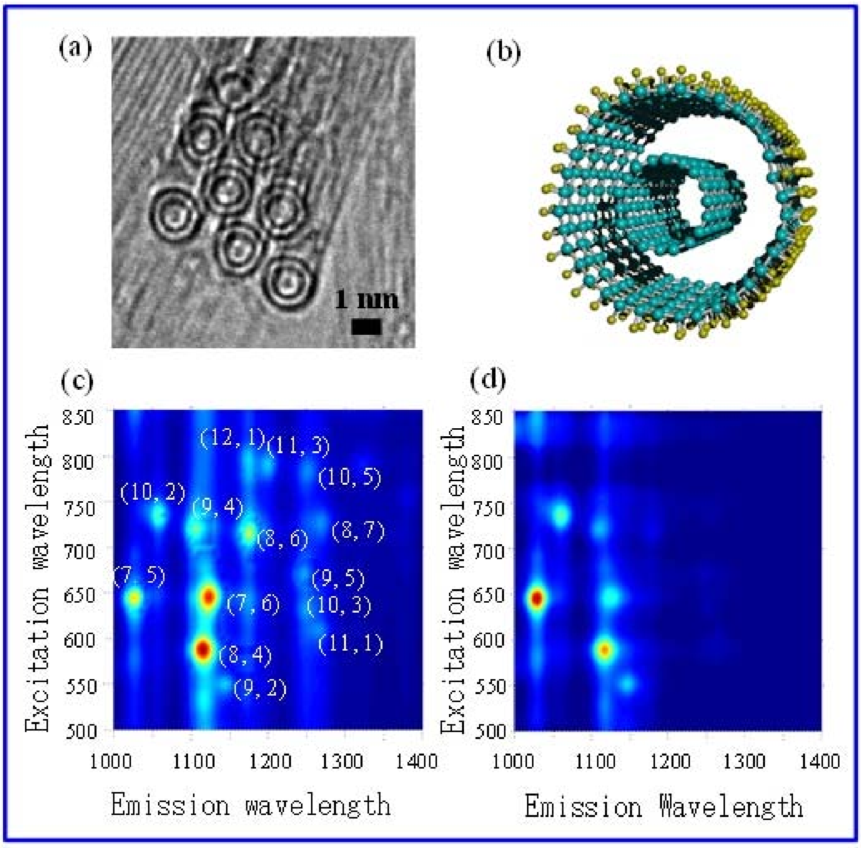

FIG. 2. (a) TEM image of DWCNT and (c) its photoluminescence map; (b) structural model of fluorinated DWCNT and (d) its photoluminescence map[16,18,19]

Figure 3(a) shows a TEM image of a DWCNT with a fluorinated outer tube. As shown in the figure, the shape of the DWCNT was unchanged by fluorination; the shape of the coaxial double-wall structure remains the same. From the Raman spectra acquired with three different laser lines (532, 633, and 785 nm), the Raman radial breathing mode (RBM), which is a vibration mode in the radial direction unique to CNTs, is selectively suppressed in the outer tube ($<$ 200 cm-1) owing to fluorination. Conversely, this vibrational mode is maintained in the inner tube ($>$ 200 cm-1) [Fig. 3(b)]. It is possible to observe the distribution of the chirality (geometrical helical structure) of semiconducting CNTs by photoluminescence (PL) measurement of DWCNTs. SWCNTs are well known to become a metal or a semiconductor depending on the chirality, and Fig. 2(c) shows the PL map for pristine DWCNTs (without fluorination). The map shows the chirality distribution for the inner tube of DWCNTs; three strong PL peaks were ascribed to the inner tubes with chiralities (7, 6), (8, 4), and (7,5). In contrast, Fig. 2(d) shows the photoluminescence map for fluorinated DWCNTs, where the signals corresponding to some chiralities disappeared after fluorination. On the basis of this finding, it was concluded that the electronic states of the inner tube are unaffected by fluorination of the outer tube, indicating that the electronic states of only the outer tube are selectively changed by fluorination. Namely, even when functionalization, such as the modification of a DWCNT with functional groups and the adhesion of metal catalysts, is carried out on the outer tube, the effects of functionalization on the structure and properties of the inner tube are very limited. An ideal property can be maintained in the inner tube because of the double-wall structure with high structural perfection, which is an advantage of DWCNTs when they are applied as a material in electronic devices and sensors, and as a composite material. This could be referred to as "DWCNT chemistry".

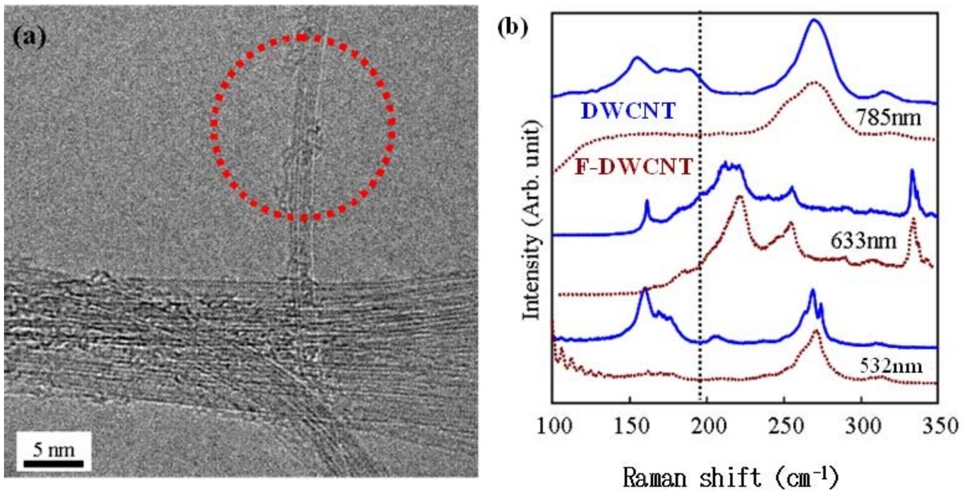

FIG. 3. (a) TEM image of fluorinated DWCNT and (b) Raman spectra of pristine and fluorinated DWCNTs[19]

Due to their unique characteristic of a hollow core, DWCNTs have been considered as templates for metal nanowires, with the encapsulation of lanthanum (La) [19] and gadolinium (Gd) [20] atoms already having been reported. We produced nanowires by a one-dimensional alignment of molybdenum (Mo) and platinum (Pt) atoms inside the DWCNTs [21], aiming at the use of these atoms as new catalysts (Fig. 4). In particular, a unique application of DWCNTs, in which the outer and inner tubes have different functions, is expected; for example, the outer tube may be modified with functional groups to add functions and the inner tube with high structural perfection may be used as a conductive or semiconductive SWCNT. In the future, the exploration of methods of mass-synthesizing high-purity DWCNTs by the floating method and the development of their unique applications are expected. The research achievement on DWCNTs by Shinohara et al. [14] is noteworthy and the research on DWCNTs is one of the scientific fields in which Japan has taken a worldwide leading role.

3. Development of CNTs applications

CNTs were first practically applied because of their mechanical properties. Even when CNTs are subjected to a kneading process within a matrix, the integrity of the tube shape is maintained, which was not the case for conventional carbon fibers (CFs). Therefore, it is possible to add mechanical, electrical, and thermal conductive functions that are derived from a thin laminated graphene cylindrical structure with high structural perfection to various composite materials.

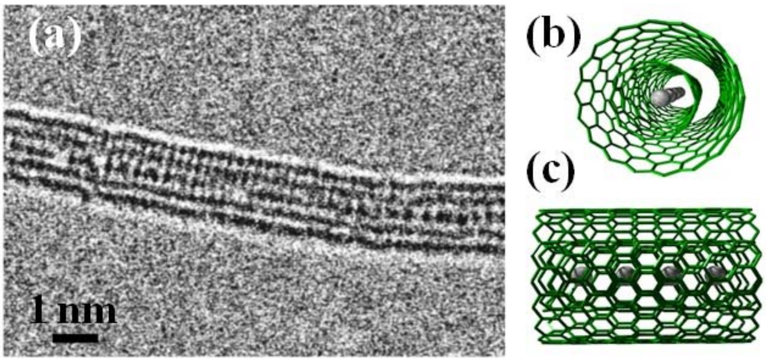

Fig. 4. (a) Encapsulation of Mo atoms inside DWCNT and (b) its structural model[22]

MWCNTs have been practically used as an electrode additive in lithium-ion batteries (LIBs) from relatively early in their development, and have accumulated market achievements.[5] A MWCNT electrode additive has contributed to the improvement of LIB performance and great expectations are placed on plug-in hybrid cars and electric vehicles equipped with LIBs. Figure 4 shows a SEM image of LIB graphite anode to which MWCNTs have been added and are uniformly distributed among graphite particles. Depending on the proportion of MWCNTs added to the LIB anode graphite, the cycle life, namely the cyclability, of the battery is significantly improved; the cycle life increases with an increasing proportion of MWCNTs [5]. This improvement is considered to be due to the formation of a flexible conductive network between particles owing to the highest resiliency of MWCNTs resulting from their carbon nanostructure among various materials. Also, it is expected that the addition of CNTs will enhance the electrochemical performance of the LIB, such as rate capability. MWCNTs can also be used as an additive to the cathode of LIBs; the practical application of MWCNTs in this field is already under way. The contribution and application ranges of MWCNTs in power sources other than LIBs for portable electronic devices have been increasing. The use of MWCNTs in lead-acid batteries and electric double-layer capacitors is also strongly expected.

The advantage of the electric double-layer capacitor (EDLC) is considered to be its high discharge rate [18], thus making it applicable as a hybrid energy source for electric vehicles and portable electric devices [19]. EDLC containing carbon nanotubes in the electrode exhibited relatively high capacitances resulting from the high surface area accessible to the electrolyte [17,20,21]. On the other hand, the most important factor in commercial EDLC is considered to be the overall resistance on the cell system. In this context, carbon nanotubes and nanofibers with enhanced electrical and mechanical properties can be applied as an electrically conductive additive in the electrode of the EDLC. The addition of carbon nanotubes has been shown to result in an enhanced capacity at higher current densities, when compared with electrodes containing carbon black [22].

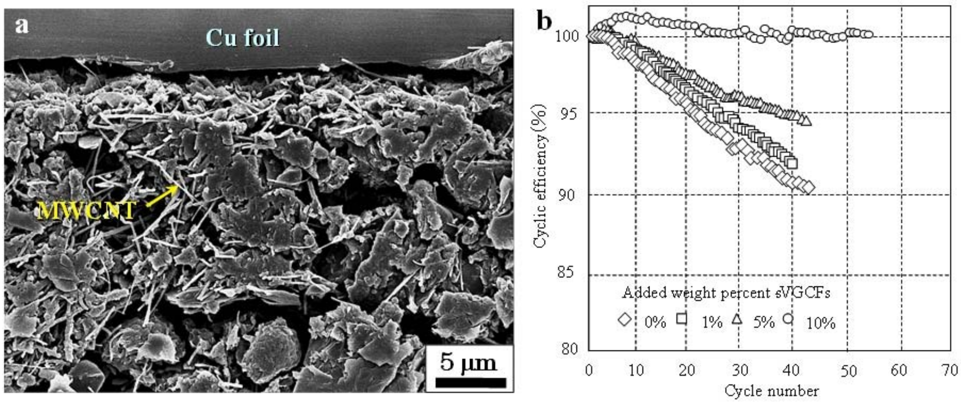

Fig. 5. (a) SEM image of anode sheet containing MWCNTs in commercial LIB, and (b) cyclic efficiency of synthetic graphite, heat-treated at 2900 $^\circ$C, as a function of weight percent, from 0 to 1.5V, with a current density of 0.2mA/cm^2[5]

The applications of composite materials of various matrix resins, rubber, and metals using MWCNTs as a filler are being developed. Research on the practical use of MWCNTs, such as for containers used in semiconductor fabrication, automobile parts, and windmills for wind power generation, has been active. MWCNTs are expected to add new functions, e.g. as the third additive for the PAN-based CF composite material, in order to strengthen such as compressive strength. In addition, the composite of MWCNTs with aluminum is applied to a plate with high thermal conductivity. SWCNTs and MWCNTs are expected to have a high thermal conductivity of 3,000–6,000 W/mK at room temperature, which may open up new applications in the fields of metal composite materials used for electronic devices and the cooling of laser elements. Because of this, an advanced composite metal with a light density, comparable to that of plastics, can be expected.

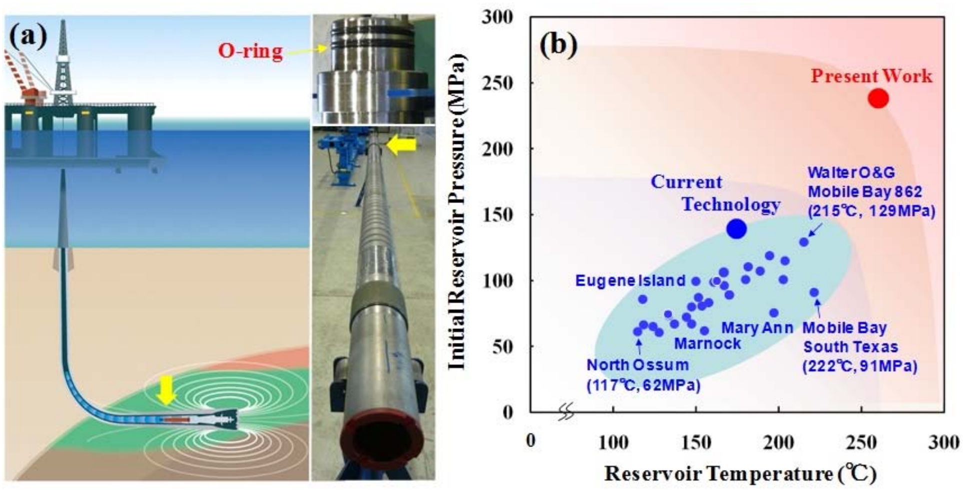

Fig. 6. (a) Downhaul devices in underground resources probing using rubber seals as a key component and (b) the distribution of temperature and pressure of the current oil wells, for example (Schlumberger Oilfield Review, 50-67, 1998)[23]

The technologies for oil development and exploration are used under harsh conditions; the temperature and pressure of oil wells are as high as 175 $^\circ$C and 140 MPa, respectively. That pressure corresponds to the hydraulic pressure in the sea at a depth of 14,000 m. An innovative improvement of rubber functions was achieved through the use of a CNT composite rubber, as realized by the cellulated structure in which CNTs are dispersed in rubber matrices as if they are cell membranes [23]. An environmentally resistant rubber seal (CNT/fluoroelastomer (FKM) composite) with a sealing ability of 260 $^\circ$C and 239 MPa, which far exceeds the current sealing ability (175 $^\circ$C and 140 MPa, standard specification), has already been developed (Fig. 6) [23]. Thanks to this development, the drilling rate of raw oil is expected to significantly improve, contributing to the stable supply of oil resources.

The 21st century is called the century of water. Humans face water shortages and conflicts over the water supply because of rapid industrialization and population expansion. However, considerable amounts of water are being lost due to leaks; the leakage rate is the lowest at about 3 % in Germany, but it is very high even in developed countries, for example, in the UK with over 20 %, France with 30 %, and the US with 20 %. The predominant reason for such leaks is known to be the premature failure of rubber sealants (e.g., O-ring packing and gaskets) in valves by the presence of chlorine in tap water. There is a strong demand for developing a chemically and environmentally sustainable nanocomposite-rubber sealant to prevent such water leakage. The incorporation of the optimum surface-modified and high-crystalline carbon nanotubes allows rubber sealants to maintain their sealing properties without any distinctive degradation over a wide range of temperatures and environmental conditions for the expected lifetime. The addition of carbon black is generally known to improve strength, but deteriorate chlorine-resistance of the rubber composite. We have demonstrated that the surface-modified MWCNT-incorporated rubber composite exhibits outstanding resistance to chlorine (Fig. 7) [24], as well as excellent mechanical and thermal properties. Our developed MWCNTs-incorporated rubber nanocomposites are very promising as high-performance sealants to transport tap water and hot water (or steam) without water-leakage and chlorine-contamination, which can also contribute as a green technology to saving electric power in the water century.

The expected application areas of CNTs range widely. The commercialization of the PAN-based CFs started from fishing rods and golf clubs; then in approximately 10 years, it expanded to aerospace-related fields. Since then, the demand for carbon fibers in common industries has also been increasing. CNTs appear to be heading in a similar direction of development, and scientific support for the development of CNTs from fundamental to application fields is hoped for in the future.

4. Safety, responsible production and uses of CNTs

The development of CNT-related material technology should be based on the concept of “safety for success” and abide by the correct risk control, from the initial to the final processes of products, following the principle of “responsible production and application” [25-28]. It is important to establish and share international evaluation criteria developed for the complete safety and toxicity evaluation of CNTs; moreover, it is hoped that the development of the CNTs applications will be promoted further on the basis of such criteria. As Takagi et al. [7] reported, malignant mesothelioma was induced in mice in which CNTs had been intraperitoneally administered. Without question, we must pay special attention to all processes related to CNTs until a socially acceptable risk control system can be established. The practice of responsible production, application, distribution, and disposal should be carried out under a life-cycle assessment for the commercialization of CNTs. I hope that a leading

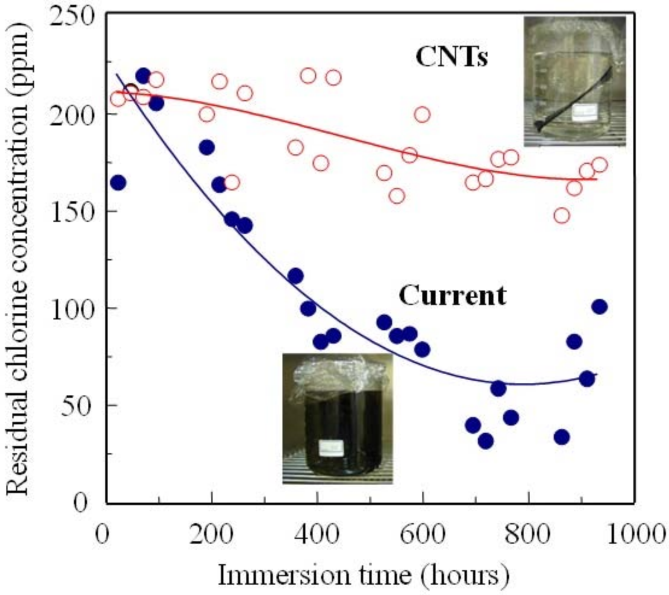

FIG. 7. Variations of the chlorine concentrations of chlorine solutions containing the carbon black (Current) - and multi-walled carbon nanotubes - incorporated rubber composites as a function of immersion time. The chlorine solution containing the current sample become opaque whereas there is no changes in the solution[24]

model to promote scientific and technological research and industrial promotion of CNTs will be established on the basis of the precautionary approach or control banding, which all of academia should pay attention and expend effort to this end. To achieve this, the risks and benefits of CNTs should be correctly understood. At the same time, it is necessary for all stakeholders to participate in open discussion, and for the use of CNTs to be widely accepted by society through the disclosure of information, promoting to a safe and green innovation of using CNTs under social agreement beyond the scheme of science and technology. Steady progress in the safety evaluation of CNTs will lead to great success for CNTs (safety for success) [25,29]. It is hoped that CNT science and technology, expected to greatly contribute to green technology, can serve as a 21st-century model of material development.

5. Conclusion

In this paper, we have shown the synthesis of CNTs by the CCVD method, and their practical applications in energy storage devices such as lithium-ion secondary batteries, supercapacitors, and as multi-functional filler in rubber nanocomposites. Finally, the safety studies of carbon nanomaterials were shown. By using the CCVD method, we are expecting improvements such as the precise control of chirality, the suitable and designed length control and synthesis efficiency of CNT. The advancement of the applied and basic science used to create innovative applications, performing biological safety evaluation that will encourage the social acceptance of CNTs, and the development of safe-controlled CNT structures are highly anticipated in the near future. Through these activities, CNTs will surely contribute to green innovations in the 21st century.

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