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Large-scale production of carbon nanotubes and their applications*

Morinobu Endo[‡], Takuya Hayashi, and Yoong-Ahm Kim

Faculty of Engineering, Shinshu University 4-17-1 Wakasato, Nagano-shi
380 8553, Japan

Abstract: Carbon nanotubes consisting of a rolled graphene layer built from sp^2 units have attracted the imagination of scientists as 1D macromolecules. Here, we will describe the recent progress on selective synthesis of various carbon nanotubes through the judicious control of synthetic conditions and their practical applications of these carbon nanotubes in the fields of electrochemical systems, nanocomposites, and medical devices. It is envisaged that carbon nanotubes will play an important role in the development of nanotechnology in the near future.

Keywords: carbon nanotubes; chemical vapor deposition; purification; electrochemical systems; microcatheters.

INTRODUCTION

One-dimensional carbon nanotubes have attracted a particular interest due to their unique morphology, nano-sized scale, novel physicochemical properties, and, furthermore, their versatile applications [1–7]. Carbon nanotubes could be visualized as rolled sheets of graphene (sp^2 carbon honeycomb lattice) (see Fig. 1a), that are sometimes capped at each end. They could be either single-walled with diameters as small as about 0.4 nm, or multi-walled consisting of nested tubes (e.g., 2–30 concentric tubes positioned one inside the other) with outer diameters ranging from 5 to 100 nm (Figs. 1b–1d). The constituent cylinders within multi-walled carbon nanotubes (MWNTs) may possess different chiral structures. In particular, it has been predicted that the electronic properties of single-walled carbon nanotubes (SWNTs) may vary from semiconductors to metals, depending upon the chiral angle (the way the hexagons are positioned with respect to the tube axis) [3,4]. The bandgap as a function of the nanotube diameter estimated by a tight-binding approach indicates that as the nanotube's diameter becomes larger (the curvature of a graphene cylinder is less pronounced), the value of the bandgap is closer to that of a planar graphene sheet [9]. It is important to emphasize that 3D stacking does not exist in MWNTs [10], even though each individual shell consists of a perfect rolled hexagonal graphene sheet. In MWNTs, the curvature of the graphene sheets is responsible for weaker van der Waals interactions, thus resulting in a larger inter-layer spacing (0.34 nm) when compared to 3D-crystalline graphite (0.335 nm).

In this paper, we will review large-scale synthetic methods for producing carbon nanotubes, their purification technique, and finally we will discuss some applications of these nanomaterials in electrochemical systems and multifunctional fillers in the fabrication of polymer composites.

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[‡]Corresponding author: E-mail: endo@endomoribu.shinshu-u.ac.jp

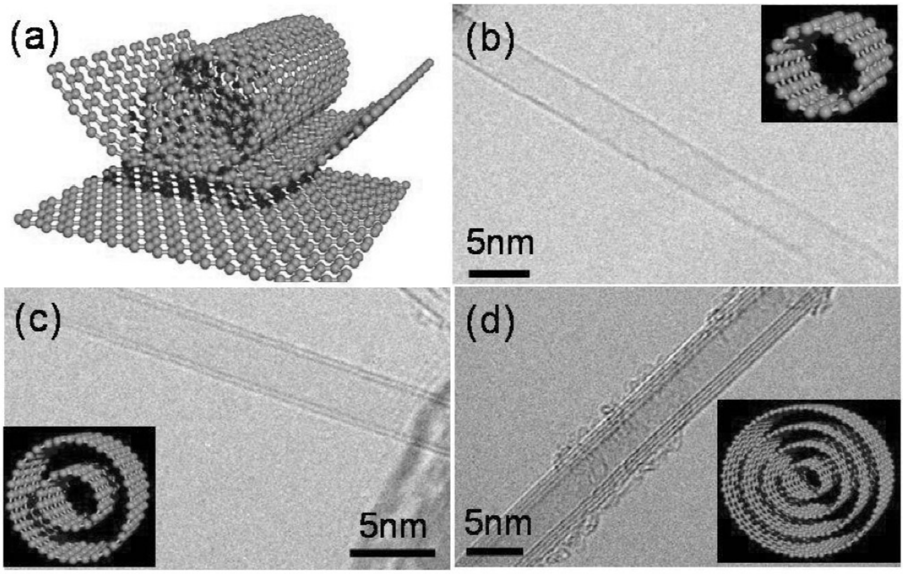

Fig. 1 (a) Schematic diagram of an individual layer of honeycomb-like carbon called graphene, and how this could be rolled in order to form a carbon nanotube; (b)–(d) HR-TEM images of single-, double- and multi-walled carbon nanotubes (insets are their corresponding images).

LARGE-SCALE PRODUCTION OF CARBON NANOTUBES

In order to use carbon nanotubes in novel devices, it is necessary to produce these materials with a high crystallinity in large-scale at economic costs. In this context, the catalytic chemical vapor deposition (CVD) method is considered to be the most optimum to produce bulk amounts of carbon nanotubes, particularly with the use of a floating catalyst method [1,10]. This technique is more controllable and cost-efficient when compared to arc-discharge and laser ablation methods. We reported a possible route for the large-scale synthesis of SWNTs by combining the used of catalytic substrates and floating methods [11,12]. The template (substrate) prevents metal particle aggregation, thus resulting in the formation of high-purity SWNT (see schematic model in Fig. 2). In particular, nano-sized zeolites were impregnated with Fe-containing compounds (seeding method), and placed inside a furnace (ca. 1000 °C) together with benzene vapor, and H_2 as the carrier gas.

Regarding the bulk production of nanotubes (concentric graphene tubules) and nanofibers (irregular carbon nanofilaments) for industrial applications, it is important to mention that in the early 1990s, Hyperion Catalysis International, Inc. (Cambridge, MA) started the large-scale production of MWNTs. This company has a wide range of patents on synthesis and applications of nanotubes and nanofibers of carbon, which expire in 2004. Carbon Nanotech Research Institute (CNRI), a subsidiary of Mitsui & Co., Ltd., plans to engage in developing technologies for the large-scale production of 120 tons of MWNTs annually. Others companies such as Applied Sciences, Inc (API) and Showa Denko (SDK) already have a large-scale production capacity for MWNTs, which exhibits relatively large diameters and wide distribution of diameters ranging from 70 to 200 nm. The most interesting point is that all companies selected a catalytic CVD method, and, furthermore, three companies except Hyperion adopted the floating reactant technique for the large-scale production of MWNTs. The development of the floating reactant/catalyst techniques allows a 3D dispersion of the hydrocarbon together with the catalytic particles derived from the pyrolysis of organometallic compounds [10,13–16]. This results in a semi-continuous production of MWNTs. Therefore, it is clear that a great deal of progress has been achieved related to the bulk synthesis of carbon nanotubes. However, at present, the most important challenge is to tailor the chirality of SWNTs.

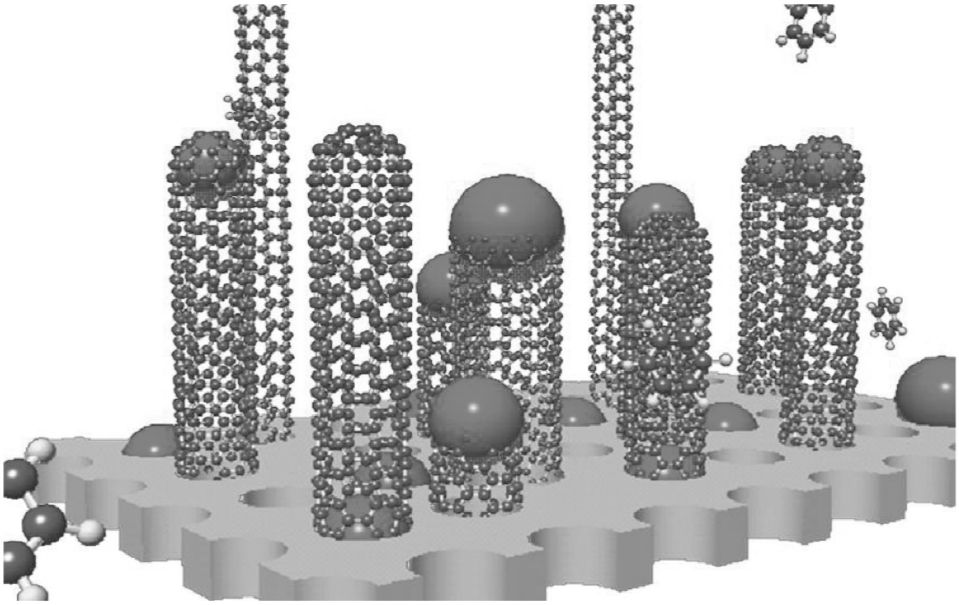

Fig. 2 A graphical descriptions of the tip- and root-growth nanotube models, in which the catalytic particles (red balls) are located at the tip and at the root, respectively. The blue balls are the carbon atoms, and the brown base is the simplified model of the zeolite.

DOUBLE-WALLED CARBON NANOTUBES

In recent years, much attention has been paid to double-walled carbon nanotubes (DWNTs) due to their expected intriguing properties. Very recently we have successfully synthesized a large fraction of DWNTs over SWNT through a catalytic CVD method, specifically, by controlling the solubility of carbon on nano-sized metal particles. Subsequently, we were able to remove chemically active SWNTs, amorphous carbon, incorporated iron particles, and supporting materials through a optimized two-step purification process (e.g., air oxidation and hydrochloric acid treatment) [17]. From a detailed high-resolution transmission electron microscopy (HR-TEM) study, our DWNTs in a bundle structure were clean, and hexagonally packed, and, furthermore, have relatively homogeneous, round, and two small-sized concentric shells (below 2 nm) (see Fig. 3) [17]. Then, we simply fabricated thin, flexible, tough, and black-colored DWNT buckypaper by a filtering a stable suspension of DWNT. It should be note that no surfactant was used for dispersion of DWNT in ethanol [18]. It is envisaged that the high structural integrity and electrical conductivity of the DWNT buckypaper, combined with their relatively high accessible surface area make them applicable in the fabrication of actuators, composites, and sensor and field emissions, etc.

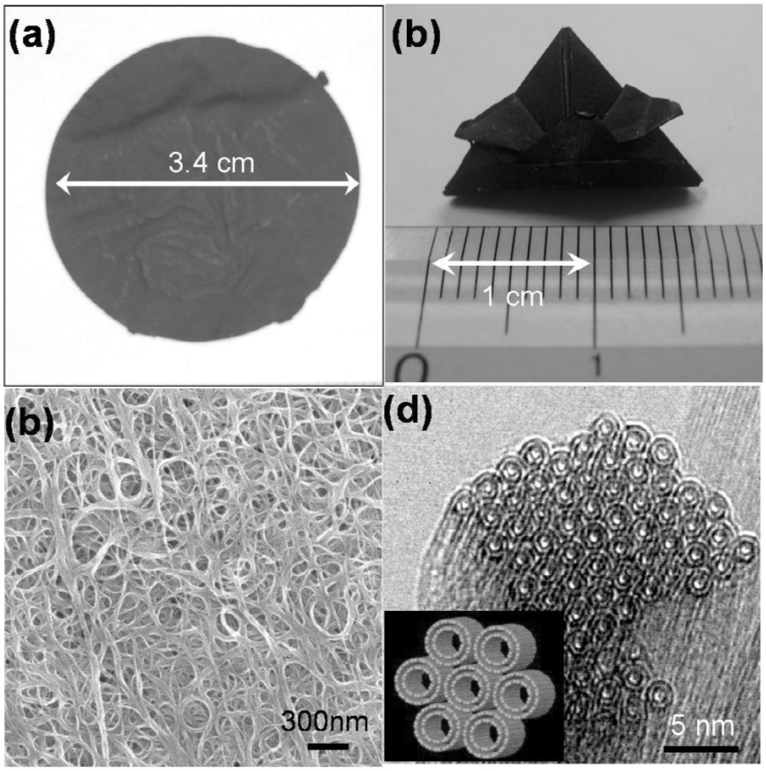

Fig. 3 (a) Photographs of round and thin DWNT-derived buckypaper (thickness = ca. 30 µm); (b) DWNT-derived buckypaper is flexible and mechanically strong enough to fold as origami; (c) low-resolution TEM images indicating a bundled structure; (d) cross-sectional HR-TEM image of a bundle of DWNTs (inset is its schematic model, two concentric shells were regularly packed in a hexagonal array).

PURIFICATION OF CARBON NANOTUBES

Even though synthetic techniques have been improved to obtain high-purity carbon nanotubes, the formation of by-products containing impurities such as metal-encapsulated nanoparticles, metal particles in the tip of carbon nanotube, and amorphous carbon has been an unavoidable phenomenon, because the metal nanoparticles are essential for the nanotube growth. Thus, extensive research has been dedicated to the purification of carbon nanotubes in order to remove foreign nanoparticles that modify the physicochemical properties of carbon nanotubes. Chemical methods have been applied for purifying SWNTs. A generalized method for SWNT purification developed by Smalley and coworkers consists of refluxing as-grown SWNTs in nitric acid solutions [19]. Subsequently, more effective purification techniques have been developed with minor physical damage of the tubes. Martinez et al. [20] reported a combined technique of high-temperature air oxidation in conjunction with microwave acid treatments, thus removing a high portion of metal particles in relatively short periods of time.

For MWNTs, high-temperature treatments in an inert atmosphere (graphitization or annealing) are one of the effective methods to remove structural defects (heptagons, heptagon–pentagon pairs) or impurities such as metallic compounds [21,22]. In this context, Figure 4 shows the structural transformation of a disordered MWNT into a highly ordered MWNT [16,22–24]. This crystallization is a stepwise process: (1) straightening and rearrangement of distorted graphene layers, (2) fusion between graphene layers, (3) growth to larger graphene layers along the tube axis and removal of stacking faults between graphene layers.

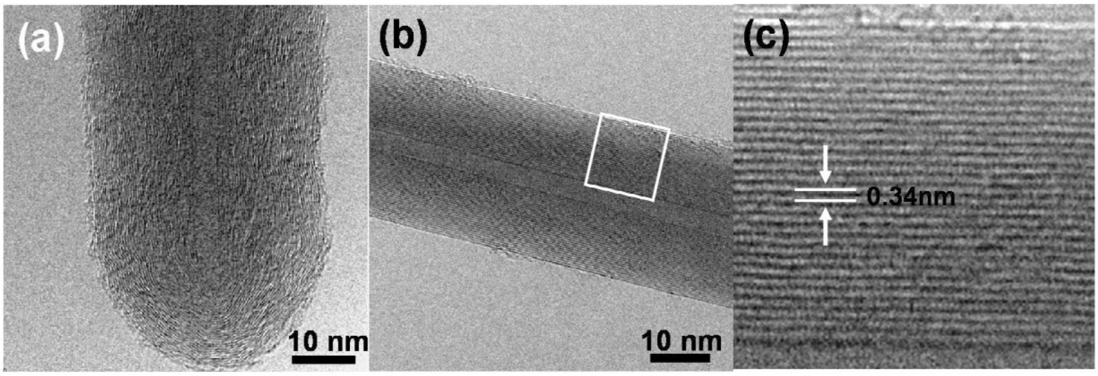

Fig. 4 (a) HR-TEM image of highly disordered carbon nanotubes; (b) HR-TEM image of annealed carbon nanotube at 2800 °C showing linear, stiff graphene layers along the tube axis; (c) enlarged HR-TEM image of (b). Note that 0.34 nm is the distance between adjacent graphene layers.

APPLICATION TO ELECTROCHEMICAL SYSTEMS

Li-ion batteries

The outstanding mechanical properties and the high surface-to-volume ratio (due to their small diameter) make carbon nanotubes potentially useful as an anode material [25–28] or as an additive [22] in Li-ion battery systems. A scanning electron microscopy (SEM) image of an electrode containing 10 wt % of carbon nanotubes as the additive shows a homogeneous distribution of nanotubes in synthetic graphite (Fig. 5a). Figure 5b reveals the cyclic efficiency of a synthetic graphite anode as a function of the wt % of MWNTs. With increasing wt % of carbon nanotube, the cyclic efficiency of the synthetic graphite battery anode increases continuously, and in particular, when 10 wt % of the nanofiber/nanotubes was added, the cyclic efficiency was maintained at almost 100 % up to 50 cycles. At higher concentrations, the nanotubes interconnect graphite powder particles together to form a continuous conductive network. The characteristics of carbon nanotubes when used as the functional filler in the electrodes of Li-ion batteries can be summarized as follows [22].

- The small diameter of the nanofiber makes it possible to distribute the fibers homogeneously in the thin electrode material and to introduce a larger surface area to react with the electrolyte.
- The improved electrical conductivity of the electrode is related to the high electrical conductivity of the tubes.
- The relatively high intercalation ability of nanotubes did not lower the capacity of anode materials upon cycling.
- A high flexibility of the electrode is also achieved due to the network formation of the nanotube in a tube-mat structure.
- The high endurance of the electrode because nanotubes absorb the stress caused by intercalation of Li-ions.
- Improved penetration of the electrolyte due to the homogeneous distribution of the tubes surrounding the anode material.
- The cyclic efficiency of the Li-ion battery was improved for a relatively long cycle when compared to that of carbon black.

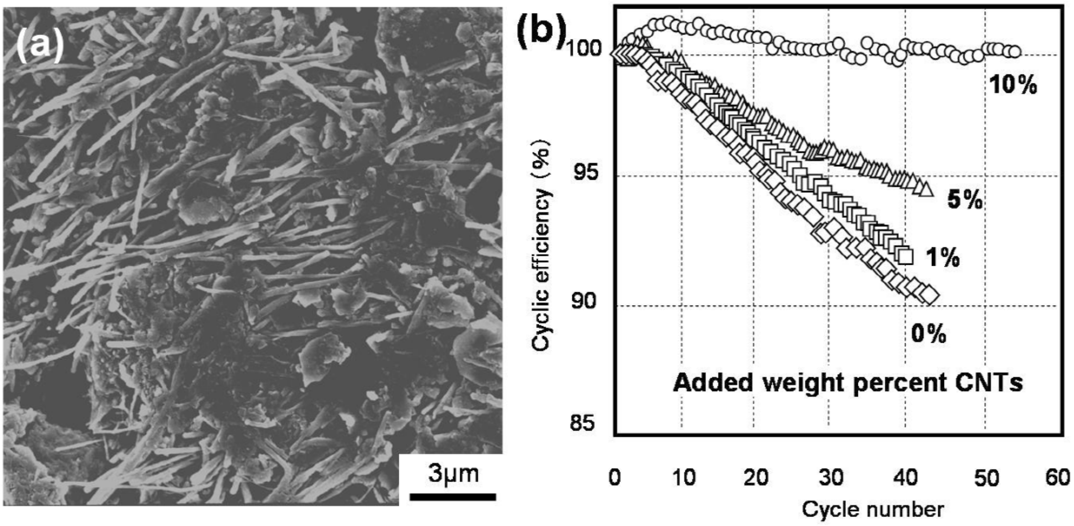

Fig. 5 (a) SEM micrographs of the anode sheet containing carbon nanofibers/nanotubes in a commercial Li-ion battery; and (b) the cyclic efficiency of synthetic graphite, heat treated at 2800 °C, as a function of wt %, in the range 0 to 1.5 V, with a current density of 0.2mA/cm^2.

Additives to the electrodes of lead-acid batteries

In order to increase the conductivity of electrodes in lead-acid batteries, different wt % of carbon nanotubes are added to the active anode material (average diameter = 2~5 μm) of the positive electrode. The resistivity of the electrode is lowered for the case of 1.5 % nanotube addition. When this sample (0.5~1 wt %) is incorporated into the negative electrode, the cycle characteristics are greatly improved as compared to that of an electrode without additive [22]. This is probably due to the ability of carbon nanotubes to act as a physical binder, resulting in electrodes that undergo less mechanical disintegration and shedding of their active material than electrodes without carbon nanotube.

Electric double-layer capacitor

The merit of the electric double-layer capacitor (EDLC) is considered to be a high discharge rate, thus making them applicable as a hybrid energy source for electric vehicles and portable electric devices [29]. EDLC-containing carbon nanotubes in the electrode exhibited relatively high capacitances resulting from the high surface area accessible to the electrolyte [30,31]. 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 high electrical and mechanical properties can be applied as an electrical conductive additive in the electrode of EDLC. It has been demonstrated that the addition of carbon nanotubes results in an enhanced capacity at higher current densities, when compared with electrodes containing carbon blacks [32].

Fuel cell

Fuel cells have been considered as next-generation energy devices because these types of systems transform the chemical reaction energy from hydrogen and oxygen into electric energy. Carbon nanotubes decorated with metal nanoparticles as electrodes have doubled the fuel performance due to increased catalytic activity of nanotube-based electrodes [33]. In this context, we have reported the efficient impregnation of Pt nanoparticles (OD < 3 nm) on the cup-stacked type carbon nanotubes [34]. The method involves the dispersion of the fibers in H_2PtCl_6, followed by low-temperature annealing. The Pt particle deposition is always homogenous and can be controlled selectively on the outer or inner core using the hydrophobic nature of the material (Fig. 6). Astonishingly, the cell performance of PtRu/cup-stacked nanotube is approximately 2 times larger than that of the PtRu/Vulcan XC-72 sample [35]. The high power of PtRu/CSCNT electrodes proposes practical interest and importance for applications for various devices.

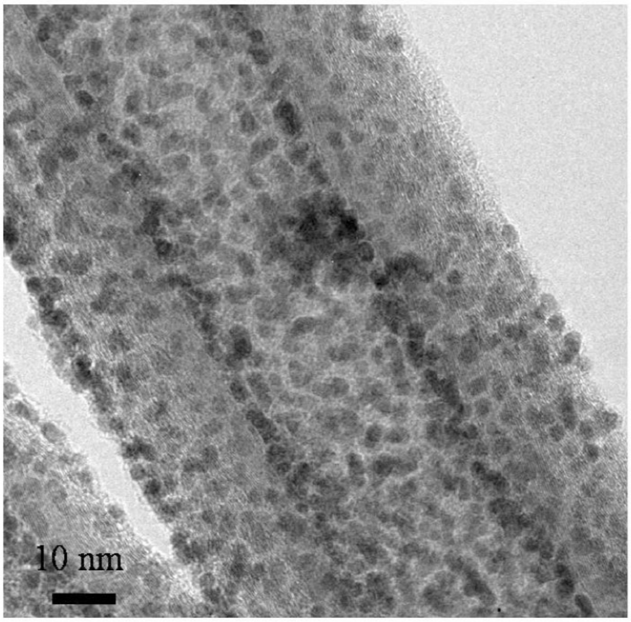

Fig. 6 HR-TEM image of highly dispersed Pt nanoparticles deposited on both outer and inner surfaces of shortened stacked-cone nanotubes/nanotubes.

MULTIFUNCTIONAL FILLER IN POLYMER COMPOSITE

It has been shown that carbon nanotubes could behave as the ultimate 1D material with remarkable mechanical properties [36]. The density-based modulus and strength of highly crystalline SWNTs are 19 and 56 times that of steel. Based on a continuum shell model, the armchair tube exhibits larger stress-strain response than the zigzag tube under tensile loading. Also, highly expected mechanical properties due to strong carbon–carbon covalent bond are strongly dependent upon the atomic structure of nanotubes and the number of shells. Moreover, carbon nanotubes exhibit high electrical and thermal conducting properties, better than copper. Therefore, carbon nanotubes (single- and multi-walled) have been studied intensively as fillers in various matrices, especially polymers [37,38]. The best utilization of the intrinsic properties of these fibrous nanocarbons in polymers could be achieved by optimizing the interface interaction of the nanotube surface and the polymer. Therefore, surface treatments via oxidation in conjunction with the polymer or epoxy could be used in order to improve adhesion properties between the filler and the matrix. This results in a good stress transfer from the polymer to the nanotube. There are various surface oxidative processes, such as electrochemical, chemical, and plasma techniques. From the industrial point of view, the ozone treatment is a very attractive technique. In addition, the dispersion of the nanotubes/nanofibers in the polymer should be uniform within the matrix.

The smallest working composite gear has been prepared by mixing nanotubes into molten nylon and then injecting into the tiny mold. As shown in Fig. 7, this gear is as small as the diameter of human hair. This piece exhibits a high mechanical strength, high abrasion resistance, and also good electrical and thermal conductivity.

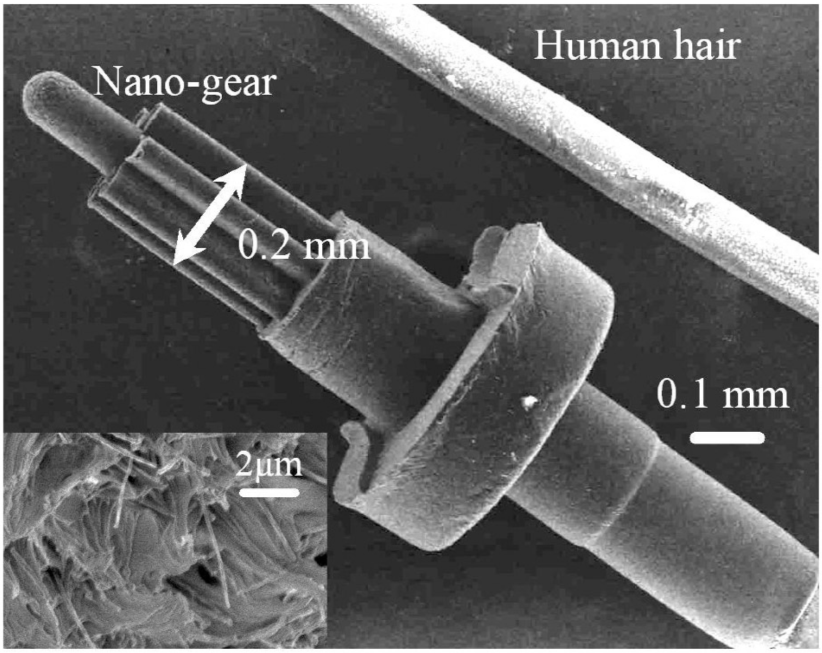

Fig. 7 SEM image of the smallest working gear (carbon nanotube/nylon composite); inset exhibits the fractured surface.

When cup-stacked-type carbon nanotubes are incorporated in polypropylene, an improvement of the tensile strength with increasing nanotubes is really remarkable (up to 40 %). This remarkable result can be explained by the particular morphology of cup-stacked-type carbon nanotubes. In other words, a large portion of edge sites on the outer surface of nanotubes might act as nucleation sites and then higher crystallization of polypropylene, resulting in good adhesion between nanotubes and polymers (good stress transfer).

NANOTUBE-BASED MICROCATHETERS

Here, we describe one of the recent advances in the application of carbon nanotubes toward medical devices: microcatheters [39]. Homogeneously dispersed carbon nanotubes in nylon polymer make them possible in the fabrication of small-sized, mechanically strong, and black-colored microcatheters that exhibit highly reduced thrombogenicity and blood coagulability (see Fig. 8). In addition, highly stable biological responses of carbon nanotubes themselves [40] and nanotube-filled microcatheter were confirmed by measuring the systematic T-cells as well as a histopathological study. Thus, it is clear that the carbon nanotube-filled, nanocomposite-derived catheter exhibited outstanding properties when compared with neat polymer-derived catheters, and it is envisaged that these system will be widely utilized in various medical devices.

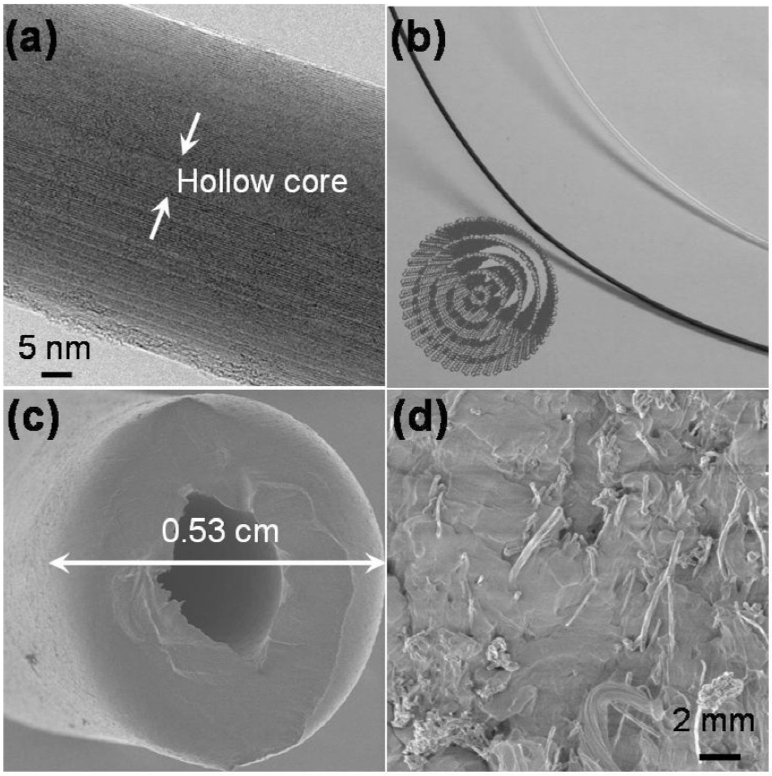

Fig. 8 (a) HR-TEM image of carbon nanotubes (note that linear graphene layers are highly developed along the tube length); (b) photographs of transparent nylon-derived and opaque black-colored nanotube-filled nanocomposite-derived microcatheters; SEM images of cross-section at low resolution (c) and (d) high resolution. It is noteworthy that carbon nanotubes were dispersed homogeneously in nylon polymer.

CONCLUDING REMARKS

This account has mainly described the possible routes to large-scale synthesis of carbon nanotubes, with emphasis on their applications in electrochemical systems and polymer nanocomposites. The unique electronic properties of nanotubes make them also good candidates in the electronic industry so that silicon-based technologies could be replaced by nanocarbons. At present, researchers are working on the following areas in order to apply carbon nanotubes in emerging technologies: (i) Production of defect-free and high-purity carbon nanotubes; (ii) establishment of useful techniques for quantifying the number of defects (types, location, and amount, etc.) in the nanotube structure; (iii) development of effective purification techniques (below ppm level) for the metal particles within carbon nanotubes, especially for biological and electronic applications; and (iv) achieving homogeneous carbon nanotube dispersions in polymer composites. The possibilities of applications using carbon nanotubes range from electronics, field emission display to energy storage devices and functional fillers in composites. These have attracted both industrial and academic interest. Therefore, it is important that some of the basic knowledge is transferred to industry very shortly so that real technologies appear commercially.

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