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In situ growth of carbon nanotubes on inorganic fibers with different surface properties

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Abstract

A simple floating catalyst method was used to produce carbon nanotube (CNT) carpets or arrays, tens of micrometers in length on the host inorganic fibers (aluminum silicate or quartz fibers), to form a CNT-inorganic oxide coaxial fiber or brush structure. The insulating inorganic oxide fiber had been changed into an electrical conducting material with a volume resistance of 2–6 Ω cm. The differences in density, length and straightness of the CNTs on different fibers were mainly attributed to the acidic surface properties of the aluminum silicate and quartz fibers.

Keywords: Carbon nanotubes; Chemical vapor deposition; Electrical properties

1. Introduction

Carbon nanotubes (CNTs), having extraordinary mechanical strength, electrical and thermal conductive properties, were widely used to improve the properties of many conventional materials [1–8]. For instance, CNTs were interacted with polymer or alumina ceramic to construct materials with good electrical conductivity and/or high mechanical strength [2–8]. They were integrated with metal nanoparticles or metal oxide nanowires to form the hybrid structures [9–12]. These functional nano-structured materials were considered as one kind of the most potential ones with potential applications in the future. Generally, the methods to construct a functional nano-structured material included the in situ polymerization [3], electro-spinning [4], hot isostatic press (HIP)-sintering [5], melt spinning [6], mixing [7] and so on. However, these methods called for the preparation of CNTs firstly, dispersed CNTs in solution subsequently and mixing CNTs with matrix materials finally [3–7,11]. The above methods involved into the time-consuming CNTs functionalization and the complex dispersion process, which was uneasy to achieve a uniform CNT structure with matrix material [8].

Here, an effective in situ method to improve the electrical conductivity of the inorganic oxide fibers (insulator) was proposed. As using the floating catalyst method and the inorganic oxide fibers as the host for the deposition of CNTs, the CNT carpets or arrays on the aluminum silicate fibers or quartz fibers were fabricated (coated), respectively. The as-prepared CNT-inorganic oxide fibers have excellent electric conductivity. The surface property of the fiber had great effect for the CNT agglomerated structure formation.

2. Experimental

Generally, aluminum silicate or quartz fibers by gel casting methods were purchased from markets. They were with a diameter of about 3–50 μm with a nearly round cross-section. The length of the fibers was with a wide distribution of 100 μm to 10 cm. They were placed in a horizontal quartz tube reactor (25 mm i.d., 1000 mm long). The carried gas was the mixture of Ar and H_2, with flow rate of 600 and 30 ml min^{-1}, respectively. When the reactor was heated to 1073 K, the solution of cyclohexane with a ferrocene concentration of 20 g L^{-1} was injected into the reactor at a rate of 4.8 ml h^{-1}. It was decomposed in situ to produce catalyst (iron nanoparticles) and CNTs quickly. After 60 min, cyclohexane solution was stopped and the system was cooled naturally. The products were characterized by scanning electron microscopy (SEM, JSM 7401F, performed at 3.0 kV), high resolution transmission electron microscope (HRTEM, JEOL 2010, excited at 200 kV) and Raman Microscope (Renishaw, RM2000, excited by 633 nm). The electrical conductivity of the CNT-coated fibers was measured by the multimeter as contacting the two axial ends of the fibers.

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3. Results and discussion

Firstly, the aluminum silicate fibers were used as the initial substrate for the deposition of CNTs. As shown in Fig. 1a, the fibers were with relatively clean surface. They were round cross-section of 3–50 μm in diameter. After the deposition of CNTs, the products turned into black color macroscopically with rough outer surface (Fig. 1b). The uniform black color of the products indicated the uniform coating by carbon on the host fibers. Notably, the diameter of fiber after CNT growth was about 5–55 μm, significantly larger than that of the host fiber. TEM image in Fig. 1c showed that the tubular CNTs were coated on the host fiber. There were some local regions coated with long CNTs, while the other parts were coated with CNT layer of nearly the same thickness about 1–5 μm (Fig. 1c). Detailed SEM image (Fig. 2b) showed the relative orientation of the CNTs, which were parallel to the fiber axis to some degree, not perpendicular to the fiber axis. There had about 30–40 CNTs on per μm of fiber. The interface of CNT-fiber was uneasy to observe, due to the relatively densely as grown CNT layer or the existence of some amorphous carbon. In some local region, CNTs were tilted to the fiber, in an angle of about 45° (Fig. 2a). Most CNTs coated on the fiber were 10 nm in inner diameter (Fig. 2c), 20–35 nm in outer diameter, and a few tens micrometers in length (Fig. 2a). The tortuosity factors of the as grown CNTs on the surface were about 1.30 ± 0.12 with a calculating scale of 1 μm [13], which was lower than agglomerated CNTs from nanoagglomerate fluidized-bed reactor [14]. The relatively narrow distribution of the relative straight CNTs were obtained on the surface of aluminum silicate fibers.

Secondly, the quartz fibers were adopted the substrate. The morphology of as grown CNTs on the surface was significantly different from that on aluminum silicate fibers. The CNTs grew long and vertically on the quartz fiber to form into CNT arrays. The composites were shown nanobrush structure (Fig. 3a), where the quartz fiber was the brush staff and the aligned CNT arrays were brush hair. Notably, the brush hair was CNT array with 180–200 μm in length and scattered from the quartz fibers in four or five growth directions. Typically, the brush hair formed a quasi-continuous sheet up to 2 mm long (Fig. 3a). Fig. 3b and c showed that the not closely integrated top end and the relatively mess middle section of the brush hair (CNTs), respectively. These growth phenomena were similar to the growth of CNTs on the flat quartz substrate [15–21]. The outer diameter of the individual tube on different fibers was nearly the same and about 30 nm. The CNTs on the quartz fibers in the array form showed more straight morphology, with tortuosity factors of about 1.14 ± 0.09 with a calculating scale of 1 μm [13]. The length of CNTs on the quartz fiber was nearly 180–200 times that on the aluminum silicate fiber, indicating the apparently higher growth efficiency of CNTs on the quartz fiber.

As to the growth of CNTs on the fiber, the seemingly large curvature of the fiber, as compared with the flat substrate, may be unfavorable for the uniform deposition of iron nanoparticles as decomposed from ferrocence and the subsequent uniform growth of CNTs in different region of fibers. However, as peeling off some CNT array or carpets from the inorganic oxide fibers, there were many relatively densely and uniformly distributed iron nanoparticles on the surface of the fibers (Fig. 4a and b). These uniformly distributed catalyst seeds resulted in

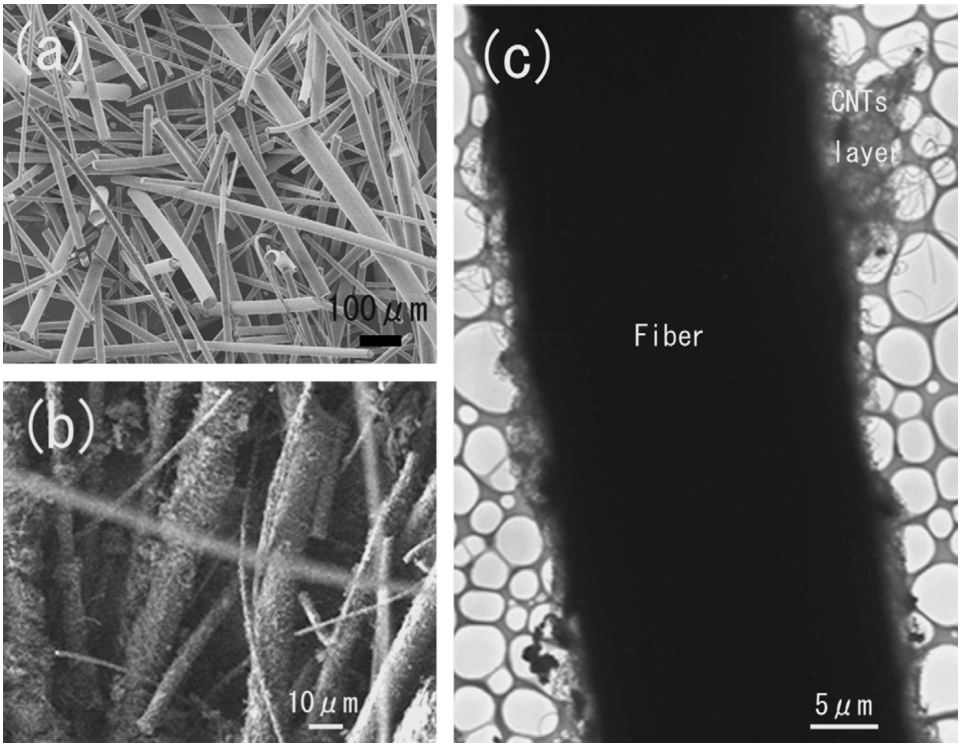

Fig. 1. SEM image of aluminum silicate fiber before (a) and after (b) the deposition of CNTs; (c) TEM image of the CNT-aluminum silicate fiber. The thickness of CNT layer is about 1–5 μm.

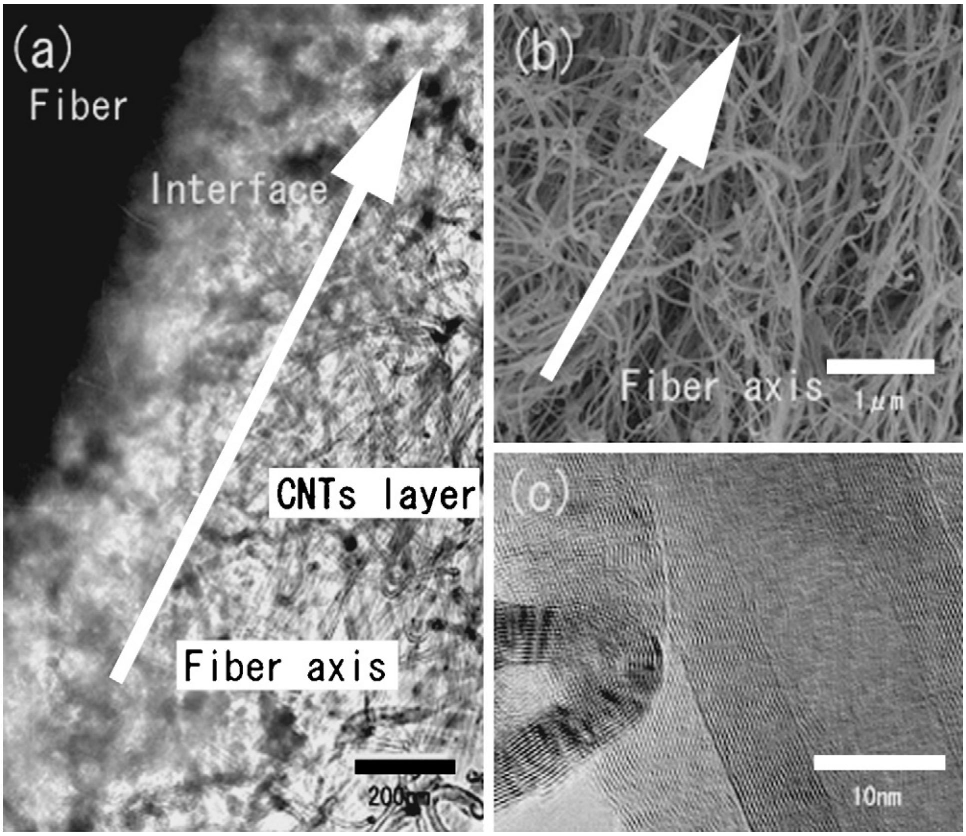

Fig. 2. High magnified SEM image of the CNT-aluminum silicate fiber. (a) CNT network with orientation to some degree parallel to the fiber axis; (b) TEM image of as-grown hollow CNTs with small and uniform diameter and the ambiguous interface between CNTs and fiber; (c) TEM image of an individual CNT tilt to the fiber axis.

the uniform growth of CNTs around the surface of fibers. The reason was that the diameter (several micrometers) of fiber was relatively large as compared with the relatively small size of iron nanoparticles (10–20 nm), the curved surface of the fiber can be considered as a relative flat substrate in small local region. So the root mechanism for single CNT in the array form was realized in the floating catalyst process [22]. Furthermore, considering CNTs grown on two fibers had nearly the same outer diameters,

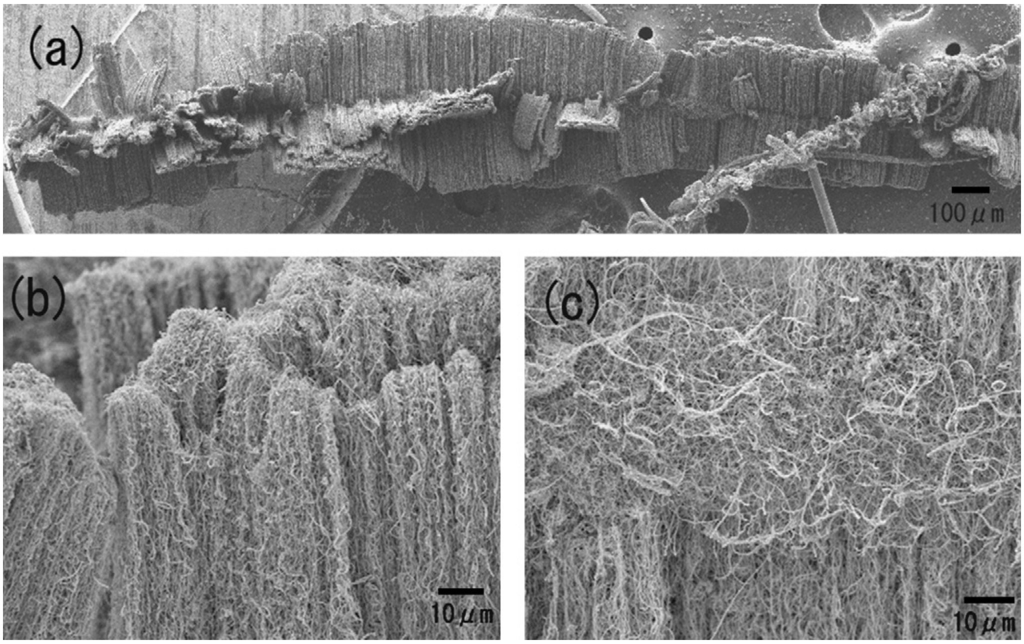

Fig. 3. (a) SEM of the nano-brush structured materials, formed by CNT array on the quartz fiber; (b) SEM image of the magnified top end of the CNT array in (a); (c) SEM image of the relative mess middle part of the CNT array in (a).

it indicated that the formation of iron nanoparticles, from the nucleation of super-cool iron atoms in gas phase, and its deposition on the fibers, were independently of the curved surface of the inorganic oxide fibers. Comparatively, the relatively long aligned CNTs from quartz fiber were much similar to those of CNTs on the flat quartz substrate [15–22], except the scattered direction of long CNTs growing perpendicular to the round surface of the fiber. Thus, it was concluded that the differences in density, length, straightness of CNTs on different fibers were irrelevant to the above effects or processes, but depended on the properties of the host fiber seriously.

Thus, the inorganic oxide fiber had no negative effect on the activity of the iron nanoparticles. High density dispersion of catalysts and the subsequent growth of CNTs with high density and long length on the fiber were realized (Fig. 3). However, the aluminum silicate is of acidic properties, which has similar negative or poisonous effect to that of liquid acids on the iron species [9,20,23–26], resulting in the low activity of the catalyst seeds (Fig. 4b) and consequently the growth of CNTs with low density and short length (Fig. 1). Apparently, CNTs with low density were uneasy to keep a relatively straight state, but tend to tilt and to form a network (Fig. 1a and b). Moreover, it was noted that aluminum silicate with acidic properties was able to decompose carbon source directly to produce amorphous carbon [25,26]. If this process occurred before the deposition of iron nanoparticles on the aluminum silicate fiber, the fiber first was coated by a layer of amorphous carbon. Thus, it may be unfavorable for the subsequent deposition of iron nanoparticles on the fiber and the oriented growth of CNTs. Our deduction had been proved by the Raman characterization of the CNTs on different inorganic oxide fibers. As shown in Fig. 4d, the G band (~1580 cm^{-1}) in Raman spectra for CNTs on the quartz fiber was more intensive than that for CNTs on the aluminum silicate fiber. And the intensity of G band was stronger than that of the D band (~1340 cm^{-1}) for the CNTs on the quartz fiber, not for the CNTs on the aluminum silicate fiber. The intensity ratio of G band to D band was 1.12 and 0.92 for the CNTs on the quartz and aluminum silicate fiber, respectively. Since the low intensity ratio of G band to D band of CNTs indicated the relatively poor graphitization [27], many defects, much amorphous carbon in the product, the above results confirmed the negative effect of the acidity of aluminum silicate on the CNT growth. Due to the negative effect of acidity of aluminum silicate, the iron catalyst density was lower than that on the quartz fiber (Fig. 4a and b). Then the CNTs were easy to grown randomly on aluminum silicate fiber to form CNT carpet (Fig. 1a). While on the quartz fiber surface, for the large diameter of the host fiber and the small diameter of CNT, the catalyst were kept in high density, which was beneficial for the woven structure formation (Figs. 3b,c, and 4c) and synchronous growth of CNT arrays [28]. By modulation of the surface, different CNT agglomerate structures were obtained.

The two initial fiber hosts were insulating. However, as coated by the relatively dense CNT film or array, its resistance was significantly decreased to 22 and 10 Ω for CNT-aluminum silicate fibers and CNT-quartz fibers column with a diameter of 1 cm and a length of 3.5 cm, respectively. The volume resistances of them were just 4.9 and 2.2 Ω cm for the composites of fibers coated with CNTs, respectively. These data indicated CNTs formed an electrical conducting network on the surface of fibers. Thus, the

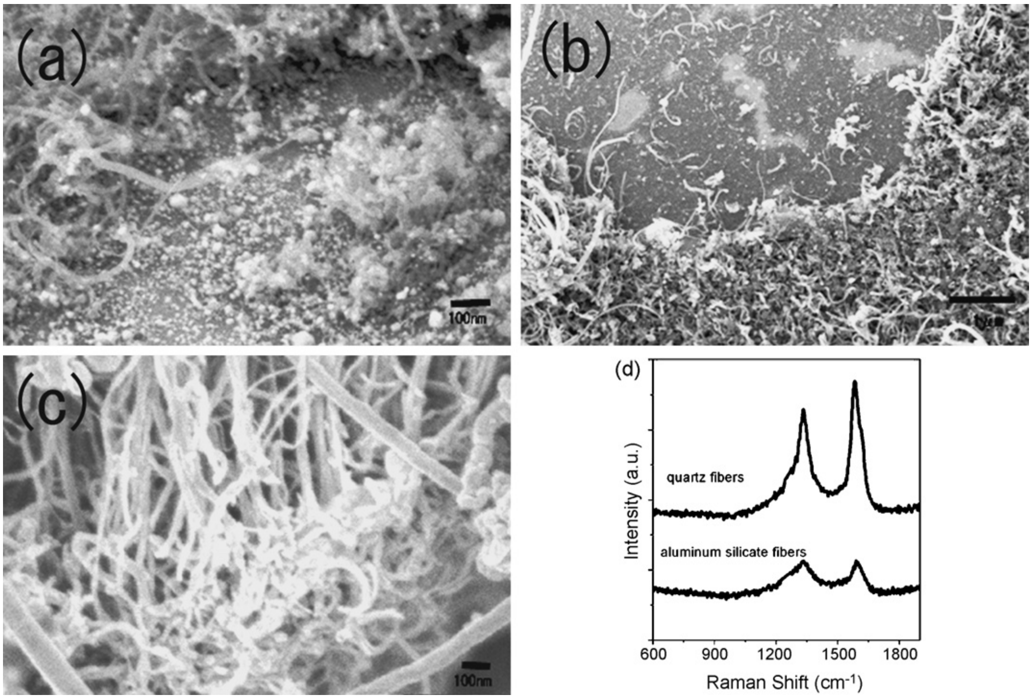

Fig. 4. (a) The densely distributed iron nanoparticles on the surface of the quartz fiber; (b) The relative sparsely distributed iron nanoparticles on the surface of the aluminum silicate fiber; (c) SEM image of the top end of the CNT array on the quartz fiber; (d) Raman spectra of the CNT-inorganic oxide fiber. The upper, lower line is that for CNTs on the quartz fiber and aluminum silicate fiber, respectively.

method in the present work was an effective coating method to prepare the electrical conducting CNT-inorganic oxide fibers. Comparatively, the vertical CNT array on the quartz fiber had better conductivity than those entangled CNTs on the alumina silicate. Since the contact between the absolutely vertical and paralleled CNT bundle was relatively poor, its better conductivity implied that some curved CNTs enhanced the contact between different vertical CNT bundles to form a network on the quartz fiber. SEM images (Figs. 3b,c and 4c) indicated that the integration of the vertical CNT bundle, to form an electrical conducting network, occurred both at the top and in the middle section of CNT array. Comparatively, though CNTs on the aluminum silicate fiber form a much tightly connected network (Fig. 1a), its relatively low electrical conductivity was attributed to the existence of amorphous carbon layer between CNTs and fibers (Fig. 1b). However, regardless of these slight differences, they were good electrical conducting materials. The result indicated our method was effective to change the electrical properties of the host fiber. Also, if amorphous carbon were coated on the fiber, the electrical connected networks were contributed from the connections among fibers. While for the CNTs on fiber, the connections among CNTs were also beneficial for the formation electrical connected networks among fibers. The nanobrush-like CNT-quartz fiber may be used to clean nanoparticles on certain surfaces [10]. Furthermore, it was noted that the inorganic oxide fiber and CNTs were both effective reinforced materials for the polymer [2]. Due to small entangle degree and lower tortuosity factors of CNT grown on the fiber, the CNT more easily dispersed than the agglomerate CNTs grown on powder catalysts [14], then homogenous dispersion in polymer matrix were obtained, which provided a new selection to increase the mechanical strength and electrical conductivity of the polymer matrix easily. Finally, this coating method was easy repeatable and the CNT-inorganic oxide fiber, with yield of several to several tens grams per hour, can be easily prepared. It was favorable for the production of the CNT-inorganic oxide fibers at low cost and was useful for its further application studies.

4. Conclusions

As adopting the floating catalyst method and the inorganic oxide fiber host, it was effective to coat inorganic oxide fiber (aluminum silicate and quartz fiber) with CNT carpet or array, following a growth mechanism of CNTs similar to those on the flat substrate. Characterized by TEM, Raman spectra, differences in density, length, orientation and straightness of CNTs on different fibers depended on the surface properties of host fiber seriously. The aluminum silicate fiber with acidic surface was unfavorable for the highly efficient and oriented growth of CNTs, as compared with the quartz fiber. These CNT-inorganic oxide fibers with excellent electrical conductivities can be produced by this method in large scale and at low cost.

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