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Experimental and numerical studies on ballistic phonon transport of cup-stacked carbon nanofiber

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ABSTRACT

A carbon nanofiber material, consisting of a stacked graphene cups, with the potential to conduct heat ballistically has been discovered and tested. Its unexpected high thermal conductivity can be understood by the similarity to a one-dimensional harmonic chain where no phonon is scattered even for an infinite length. A non-equilibrium molecular dynamics simulation for this fiber validated this hypothesis by revealing a uniform temperature distribution between hot and cold reservoirs.

1. Introduction

Pursuing the analogy between heat and electricity, it would be particularly valuable if the phenomenon of electronic superconductivity found in a variety of materials occurs in an analogous fashion in heat transport. The investigation of such ballistic phonon transport has become a key issue in recent researches of micro/nano-scale heat transfer. Carbon nanotubes [1] are a candidate for such a super-thermal conductor and their thermal properties have been explored from both theoretical [2–4] and experimental [5–10] approaches. The measured thermal conductivity of single-walled carbon nanotubes (SWNT) exceeds that of diamond [9]. However, it has been experimentally suggested that the phonon–phonon scattering occurs even in the SWNT [10].

So far, many pioneering research studies have employed nanoscale materials to artificially control the intrinsic material properties [11]. Thermal conductivity is one of the targets of this effort. Phonon-boundary scattering in nanoscale materials decreases the mean free path (MFP) of phonons and lowers the thermal conductivity. This so-called phonon confinement effect is based on the phonon gas theory result, $k = Cvl/3$, where k, C, v and l are the thermal conductivity, specific heat, velocity and MFP of the phonon, respectively. On the other hand, it is known that phonons are never scattered in a one-dimensional (1D) harmonic chain connecting hot and cold reservoirs, resulting in a uniform temperature distribution independent of the number of particles, as shown in Fig. 1(a), corresponding to an ideal ballistic heat conductor [12,13]. Recent theoretical studies have extensively treated this kind of ballistic conduction and predicted that the thermal conductivity of a quasi-1D material is proportional to L^{α}, where L is the length and the exponent α ranges from 0.11 for (10,10)-SWNT [14] to 0.5 for a nonlinear chain [15]. It has to be noted that a value of $\alpha = 1.0$ has only been found for a 1D harmonic chain, which implies that such chain can exceed the SWNT for long-distance heat transport even though it has much lower phonon velocity.

Though the above theoretical discussion is attractive, all the practical fibers ever produced, including the thinnest SWNT, are still three-dimensional. Thus α is much lower than 1.0 and in most cases $\alpha = 0.0$. However, we have discovered a candidate material that well satisfies the conditions for a harmonic chain that has long-term stability, even in the atmospheric environment, at temperatures up to 500 °C. This material consists of a chain of graphene cups, named as cup-stacked carbon nanofiber (CSCNF). This paper reports our experimental and numerical studies on the heat conduction of this nanofiber.

2. Experimental

Structural characteristics of CSCNF have been treated by a previous study [16], which has shown it to be a hollow fibrous material with an outer diameter of 50–150 nm and a length of up to 200 μm. It consists of bottomless graphene cups stacked inside each other in a line, much like a set of soft-drink cups. Both their top and bottom edges are not expected to be covalently bonded to the atoms on the neighboring cups. A remarkable characteristic of this fiber, linked to its thermal properties, is the huge disparity in

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bonding forces between the stiff sp^2 bonds in each graphene cup and the weak cup–cup interlayer interactions. We expect that this gap structure, schematically illustrated in Fig. 1(c), should mimic the 1D harmonic system. Since the theoretical exploration of phonon behavior in this structure is not an easy task, at first we employed experimental techniques [8] to measure its thermal conductivity.

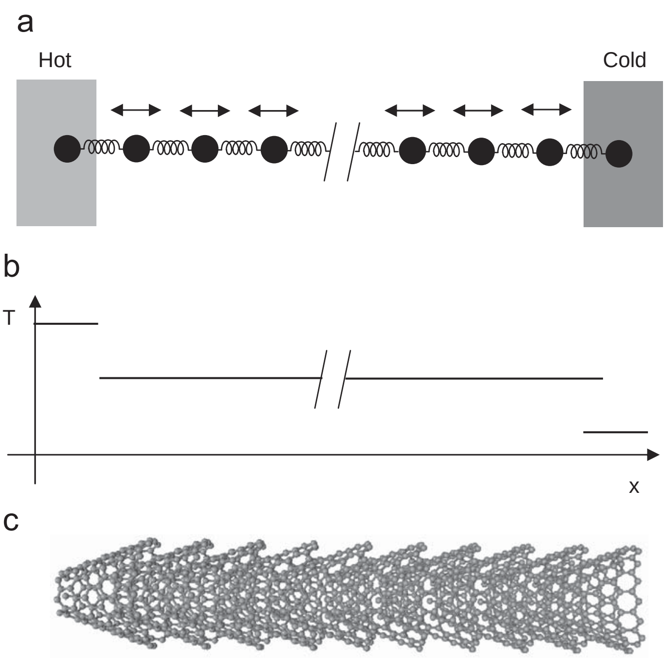

Fig. 1. One-dimensional harmonic chain connected to hot and cold reservoirs (a) its temperature distribution (b) and a schematic of CSCNF (c) for comparison with the harmonic chain.

In this experiment, CSCNF samples gifted from GSI Creos Corporation are air oxidized at 500 °C for 1 h to remove amorphous carbon deposited on the as-grown fibers, and also to increase the fraction of open edge sites in the graphene cups. The samples are next dispersed in ethanol and dropped onto a microgrid for HRTEM observation (Fig. 2(a)). After checking for major defects and measuring the outer and inner diameters and the taper angle of the cups, a suitable sample (Fig. 2(b)) is picked up by a manipulator (Fig. 2(c)) and set on a suspended platinum hot-film sensor we have developed for thermal measurements, as seen in Fig. 2(d). Our measurement principle is based on the

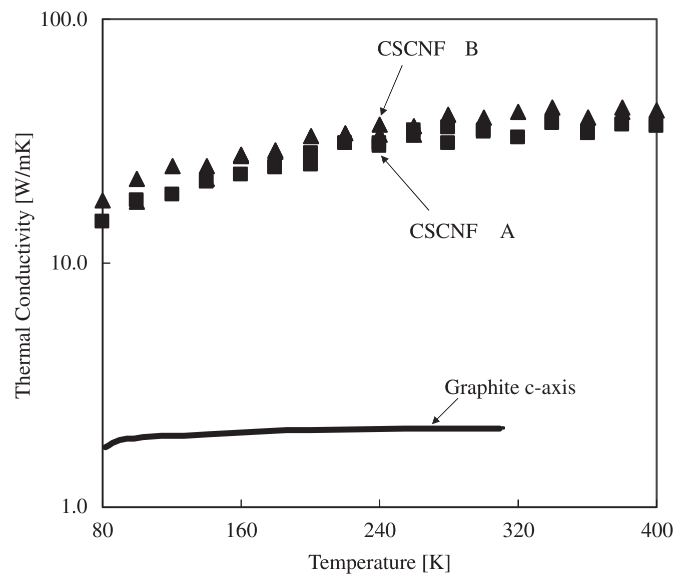

Fig. 3. Measured thermal conductivities of CSCNF samples together with that for bulk graphite along the *c*-axis [18].

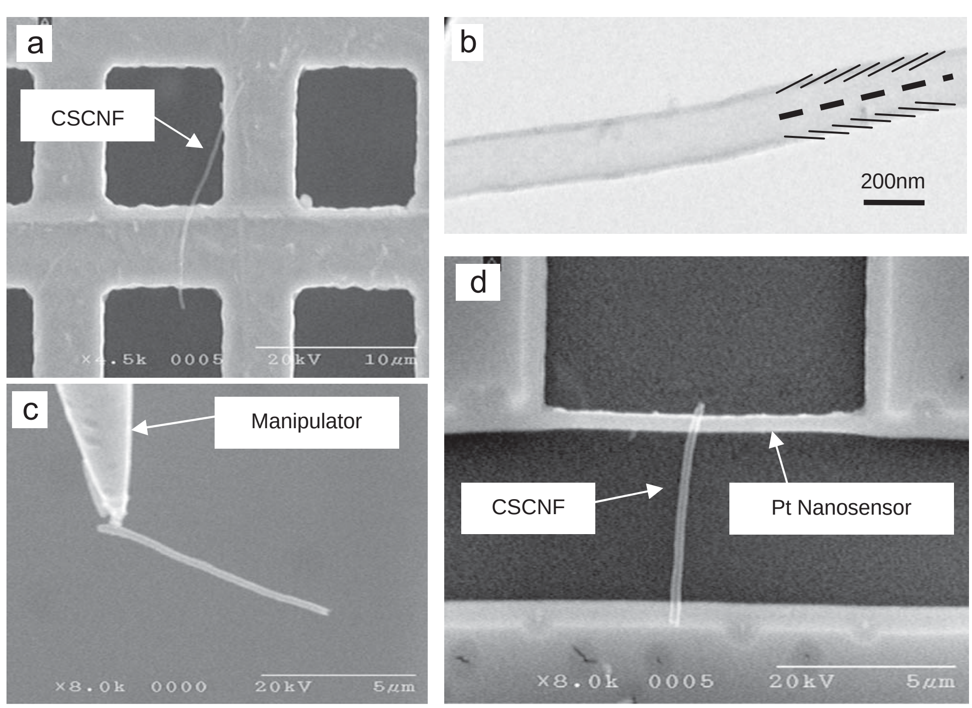

Fig. 2. Experimental procedures: (a) CSCNF sample used for measurements on a microgrid for TEM observation. (b) TEM picture of sample with a schematic of graphene cup, and the fiber axis shown by a broken line. (c) Sample picked up on a manipulation probe after TEM observation. (d) Sample placed on a suspended Pt nanosensor for thermal conductivity measurements.