PAPER

Effect of carbon nanotube surface modification on thermal properties of copper–CNT composites

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Carbon nanotubes (CNTs) were functionalized by polymer wrapping (CNT–PSS) and oxidation (CNT–COOH), followed by reduction of copper ions in hydrogen atmosphere, producing copper decorated carbon nanotubes (CNT–f@Cu). Thus synthesized hybrid nanostructures were used as conductive fillers to tailor the heat transport capabilities of a copper matrix. Thermal properties, *i.e.* thermal diffusivity and thermal conductivity, of copper composite were measured and compared with those containing pristine and functionalized carbon nanotubes. Experimental results revealed that thermal diffusivity and conductivity of the composites decrease with increasing content of carbon nanotubes. However, composites enriched with nanohybrids where Cu nanoparticles were covalently bonded to carbon nanotubes had thermal conductivity four times higher than those containing the same content of pristine CNTs. The experimental results were analysed using Nan's model which accounts for contributions from thermal interface resistance at metal–CNT boundary as well as aspect ratio of carbon nanotubes.

Introduction

Owing to their extremely high thermal conductivity,[1,2] carbon nanotubes are potentially the most effective filler for developing high-efficiency heat sinks for thermal enhancement of microelectronics packages. A considerable amount of papers have reported that the incorporation of CNTs into polymers or ceramics can ameliorate the composite thermal conductivity.[3–5] Nevertheless, the obtained increases are still below the values predicted by Nan's or Maxwell's mixing theory.[6,7] In particular, the positive influence of CNTs on effective thermal conductivity of metal composites is so far a challenge,[8,9] mostly due to difficulties in homogeneous distribution of nanotubes in the metal phase as well as possible scattering of heat carrying phonons at the CNT–matrix interface. Few studies to date have discussed the influence of thermal interfacial resistance on heat transfer in composite materials and agreed that thermal contact resistance is the major factor which controls heat transfer in the composites.[7,10,11]

Therefore, in order to realize thermal conductivity enhancement beyond the current level, it is essential to comprehend how to diminish the negative effects of large interfacial resistance present in carbon nanotube composites. It is assumed that a main reason for the high value of interfacial thermal contact resistance is possible weak adhesion between the matrix material and nanotube sidewalls.[12,13] To assuage this problem, one could

consider introducing strong chemical bonds between the nanotubes and the matrix. This, on the other hand, could be done by attaching metal nanoparticles (NPs) on the CNT surface prior to their incorporation into the metal matrix. Such hybrid nanostructures are expected to increase adhesion contact points and therefore to improve interconnectivity between the nanotubes and the metal matrix.

There are numerous studies on the synthesis of hybrid nanomaterials where CNTs act as a support for a variety of metal nanoparticles.[14] Each of these studies offers varying degrees of control on the particle size, distribution along the CNT as well as the nature of bonding between NPs and CNTs. While many studies used nanohybrids as sensors, catalysts and enhancement of the thermal conductivity of polymer composites or nanofluids,[15,16] there are no reports showing the effect of metal coated CNTs on the thermal conductivity of metal composites. What is more, no studies, to our knowledge, investigated the influence of chemical coupling, *i.e.*, covalent and non-covalent, between CNTs and metal NPs on the thermal conductivity of metal composites.

In this paper we study the dependence of CNT chemical functionalization on the interfacial thermal resistance by measuring the thermal diffusivity and conductivity of copper composites. For this purpose, we employed an effective *in situ* synthesis approach to deposit copper nanoparticles on the sidewall of covalently and non-covalently functionalized multiwalled carbon nanotubes. We assume that the nature of bonding between the nanotubes and Cu NPs will influence the heat transport capabilities of such heterostructures in the metal composite.

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Experimental

Raw materials

Multiwalled carbon nanotubes with 5–20 nm outer diameter and 1–10 μm length were kindly provided by Bayer MaterialScience. Poly(sodium 4-styrenesulfonate) (PSS), copper(II) acetate monohydrate ($Cu(CO_2CH_3)_2 \cdot H_2O$), and pure copper powder (3 μm particle size with dendritic shape) were purchased from Sigma-Aldrich and used as obtained.

Preparation of the Cu–CNT composites

The MWCNTs were functionalized by polymer wrapping with PSS. Carbon nanotubes were dispersed in a 1 wt% PSS (M_w = 70 000), sonicated for 2 h and stirred overnight. The excess polymer was removed by filtration and dispersion in water (3 times). Received powder was dried in an oven at 60 °C.

Carbon nanotubes were oxidized according to the well established procedure,[17] where MWCNTs were dispersed in a mixture of sulfuric and nitric acid (1 : 3 v/v) and heated up to 60 °C with stirring under reflux for 3 h. Subsequently, the nanotubes were washed with the excess of acid by filtration and dispersion in water (3 times). The carboxylic groups on oxidized CNTs were quantitatively measured by Boehm's titration method.[18]

The functionalized nanotubes (CNT–PSS or CNT–COOH) were suspended in water and ultrasonically treated until the homogeneous suspension was obtained. Next, an appropriate amount of copper salt (copper acetate) was added to the suspension and the reaction mixture was stirred overnight at room temperature. After 12 h, the suspension was heated up to 70 °C. During this step, the solvent was evaporated and a blue powder consisting of copper salt and CNTs coated with Cu + 2 phases was obtained. The powder mixture was then calcinated at 200 and 350 °C for 1 h, respectively, in order to decompose copper acetate to copper oxide nanoparticles. The mixture was then reduced under H_2 at 350 °C for 2 h to transform CuO to Cu. Composites with as-received nanotubes were obtained by mixing CNTs with copper powder obtained by decomposition and reduction of copper salt. Different Cu–CNT composites were prepared with 0.2, 1, 3, and 10 wt% of carbon nanotubes in the copper matrix.

The composite powder mixtures were homogenized in a planetary ball-mill machine (Fritsch) at 4500 rpm in rotary speed and 30 min in duration. The homogeneous powder mixtures were consolidated into bulk Cu nanocomposites using cold pressing and plasma sintering techniques. In the cold press approach the composite powder was compacted using a hydraulic lab hand press (PW20, Paul-Otto Weber GmbH) with an applied force of 130 kN. The compressed samples were subsequently sintered in a tube furnace (ROF 7/50, Heraeus) at 600 °C in a vacuum of 10^{-6} Pa for 60 minutes.

Full densification of the composite powder was performed by the spark plasma sintering (SPS) technique (H PD 250, FCT Systeme GmbH). The powder was pre-compacted in a graphite die with 40 mm in diameter under a pressure of 6 kN. Next the samples were sintered at 600 °C for 5 min in a vacuum with an applied pressure of 50 MPa. The heating rate was maintained at 100 °C min^{-1}.

Characterization

The laser flash method was used to measure thermal diffusivity (α) with the XenonFlash XFA 500 instrument (Linseis Messgeräte GmbH). All measurements were performed on cylindrical samples with the size of Ø13 mm × 1 mm, placed in a chamber, where one surface of the sample was heated by an intense energy pulse and the temperature extrusion on the opposite surface was recorded by an infrared detector. The specific heat of the samples was measured by a differential scanning calorimeter (DSC) PT10 (Linseis Messgeräte GmbH) using single-crystal sapphire as a reference material. Thermal conductivity was calculated from the equation $\lambda = \alpha C_p \rho$, where λ, C_p and ρ represent thermal conductivity, specific heat and bulk density of the sample, respectively.

The microstructure characterization was carried out on a scanning electron microscope (SEM) Hitachi S-4800 with a cold FEG and a transmission electron microscope (TEM) Tecnai G^2 20 S-TWIN (accelerating voltage 200 kV).

Results and discussion

Morphology of the CNT–NP heterostructures and Cu–CNT composites

The carbon nanotubes were functionalized by acid treatment and polymer wrapping so as to form carboxylic and amine groups on to CNT sidewalls and thereby enhance reaction efficiency with copper ions in the thermal decomposition process.[19] Fig. 1 highlights the synthesis process scheme associated with CNT functionalization and formation of copper nanoparticles on the nanotube surface.

Fig. 2 presents successful synthesis of CNT–Cu, wherein Cu nanoparticles are bound to nanotubes along the sidewall. Both polymer (Fig. 2, left) and acid-treated CNTs (Fig. 2, central) are uniformly coated with spherical nanoparticles which have an average diameter of 5 nm. It is worth noting that even though carbon nanotubes were modified by different functionalization methods, there is no pronounced difference in the spatial coverage of Cu-NPs on the nanotube surface.

The assessment of the data accumulated in numerous studies on carbon nanotube composites revealed that effective reinforcement of these materials strongly depends on homogeneous dispersion of the CNTs in a matrix.[20,21] In contrast to polymer composites, a good dispersion of nanotubes in a metal matrix is particularly challenging due to the extreme difference in the density of CNTs (1.6 g cm^{-3}) and metal particles (e.g., copper 8.96 g cm^{-3}). The high-energy ball milling process, also called mechanical alloying is a favourable technique for homogenization of CNTs with metal powders.[22] A representative SEM image of the 1 wt% Cu–CNT composite microstructure after ball milling is shown in Fig. 2 (right). There is no obvious boundary between the CNTs and copper matrix. Moreover it can be seen that carbon nanotubes are homogeneously dispersed in a copper matrix and embedded in the metal powder rather than aggregated on the surface, which should ensure the good coupling of mutual thermal properties.

Thermal properties of the composites

It is expected that various functionalization of carbon nanotubes and decoration with Cu nanoparticles will influence the interfacial interactions between the composite elements.
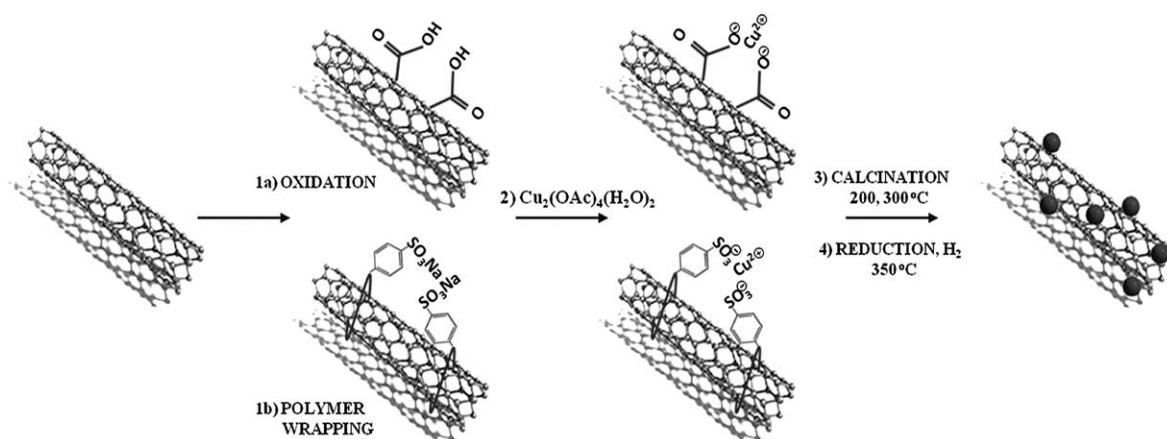
Fig. 1 Schematic presentation of surface functionalization of carbon nanotubes and synthesis of copper nanoparticles on the CNT sidewall.

Thermal diffusivity (α) was measured and used to calculate thermal conductivity (λ) of composites following the relationship $\lambda = \alpha C_p \rho$. Fig. 3 shows thermal diffusivity as a dependence of the MWCNT content. The experimental results show that the thermal diffusivity of Cu–MWCNT composites decreases upon addition of nanotubes and show an inversely proportional relationship to the adding content of carbon nanotubes, even though the thermal conductivity of an individual nanotube (3000 W m^{-1} K^{-1}) is one order of magnitude higher than that of the copper matrix (400 W m^{-1} K^{-1}). This observation is consistent with previous reports on thermal properties of metal–CNT composites.[8,9,23] Composites containing carbon nanotubes with varying functionalities differ in their thermal behavior as we show now. It is natural to think that site defects produced by acid treatment decrease the thermal transport abilities of carbon nanotubes, since defects will act as scattering centers for the heat-carrying wave packages. Nevertheless, acid-treated CNTs show higher thermal diffusivity as compared to the untreated ones. The difference is in particular visible for 1 and 3 wt% composites in Fig. 3. Decoration of oxidized nanotubes with Cu nanoparticles further improves the heat transport within the composite. For a CNT content of 1 wt% thermal diffusivity increases from 0.35 to 0.54 cm^2 s^{-1}, showing the advantage of CNT–COOH@Cu as effective conducting filler. Overall, the thermal diffusivity of CNT–copper composites increased upon NP functionalization

by a factor of two for 1–10 wt% nanotube contents. The composites containing non-covalently functionalized nanotubes (PSS wrapped) exhibit less pronounced enhancement in thermal diffusivity, in particular, for higher CNT content. Apart from 1 wt% composites, there is no considerable difference in thermal diffusivity between the composites. Surprisingly, α is practically unaffected by the presence of copper nanoparticles on CNT–PSS sidewalls.

Drastic decrease in diffusivity for 3 and 10 wt% composites (CNT concentration well above the percolation threshold) is not surprising, taking into account that heat flow in these composites is limited not only by interfacial thermal resistance between carbon nanotubes and the surrounding matrix but also by large tube–tube contact resistance.[24] As shown by Aliev et al.,[25] coupling between nanotubes can suppress the phonon modes and consequently decrease the room thermal conductivity of CNT bundles by a factor of four relative to that of a single nanotube. Thermal diffusivity results indicate that the highest interfacial thermal barrier exists between polymer-wetted carbon nanotubes, when compared to acid-treated CNTs. According to the results obtained from classical molecular dynamics simulations,[26] 1 nm thick soft matrix material (e.g. polymer) around the carbon nanotubes introduces, from the thermal point of view, a 10–20 nm gap due to interfacial resistance. Simply speaking, the polymer network inhibits the phonon transportation along
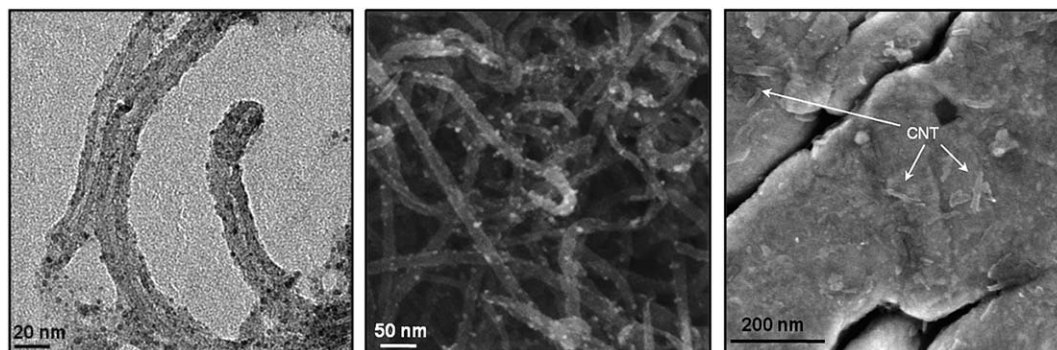

Fig. 2 TEM (left) and SEM (central) images of MWCNT decorated with Cu nanoparticles and embedded in the copper matrix (right) via the ball milling process.
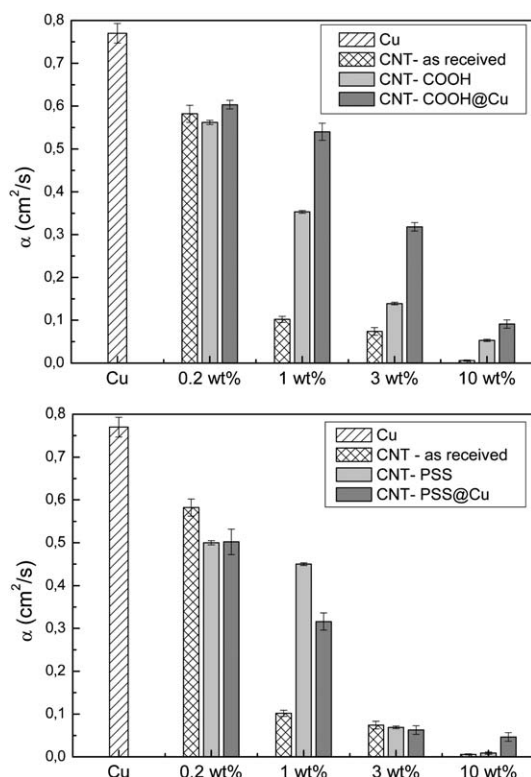
Fig. 3 Effect of nanotube chemical functionalization on composite thermal diffusivity with varied content of CNTs.

CNTs and increases the interfacial thermal resistance by affecting the damping behavior of the phonons' vibration. This provides the explanation for the lowest thermal diffusivity of copper–CNT–PSS composites.

The conductivities of composites with varying nanotube contents as deduced from the diffusivity are shown in Fig. 4. The λ exhibits an analogous trend as for thermal diffusivity. The high conductivity obtained for composites with oxidized nanotubes (stars in Fig. 4) arises from covalent attachment of copper nanoparticles to the nanotubes, which provides the strongest possible coupling between the CNTs and the matrix. The enhancement in thermal conductivity indicates that strong
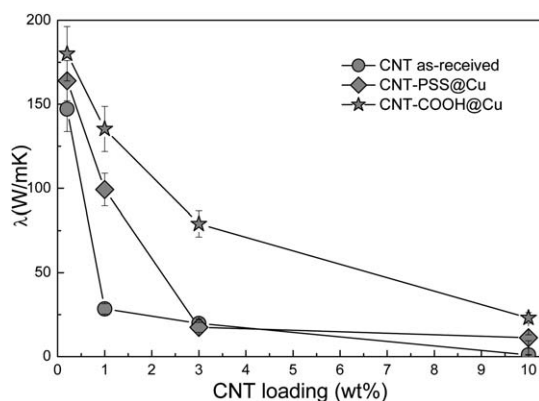

Fig. 4 Effect of chemical functionalization on composite thermal conductivity enhancement with varied content of CNTs.

chemical bonds between the phases can improve the interfacial thermal conductance in spite of the degradation of the tube intrinsic conductivity. According to the results obtained from Boehm titration, we can quantitatively estimate that for the amount of carboxylic groups on CNT–COOH equals 3.41 mmol g^{-1}, the maximum loading of Cu-NPs is 1.70 mmol g^{-1}. Perhaps by increasing the amount of COOH groups one could further improve the nanotube interface with the metal matrix and thereby enhance thermal conductivity of such a composite.[27] In the case of coupling between the polymer-wetted nanotubes and copper particles/matrix, it is limited due to weak van der Waals interaction forces. Even though the non-covalent functionalization of CNTs with polymer preserves the structure of CNTs, as opposite to the destructive acid treatment, the associated presence of polyelectrolyte shields the intrinsic thermal properties of the nanotubes.

These results confirm that the thermal conductivity of a composite depends critically on the thermal interface between the components. The heat transfer in a composite material is hence limited by the interface thermal resistance, Kapitza resistance, R_K, defined as

$$Q = \frac{\Delta T}{R_K} \quad (1)$$

with the heat flux Q and the temperature drop across the interface ΔT.[28]

One way to estimate the influence of thermal interface resistance on a composite's thermal conductivity enhancement is based on the effective medium approach proposed by Nan et al.[28] According to this method, the effective thermal conductivity (λ_e) of composites with small loading of randomly dispersed, non-interacting CNTs in a matrix can be derived as

$$\frac{\lambda_e}{\lambda_m} = \frac{3 + f(\beta_x + \beta_z)}{3 - f\beta_x} \quad (2)$$

with

$$\beta_x = \frac{2(\lambda_{11}^{CNT} + \lambda_M)}{\lambda_{11}^{CNT} + \lambda_M}, \quad \beta_z = \frac{\lambda_{33}^{CNT}}{\lambda_M} - 1 \quad (3)$$

where f is the volume fraction of the nanotubes in the composite. λ_{11}^{CNT} and λ_{33}^{CNT} are equivalent thermal conductivities along transverse and longitudinal axes of a composite unit cell and can be expressed as

$$\lambda_{11}^{CNT} = \frac{\lambda_{CNT}}{1 + (2a_K/d)(\lambda_{CNT}/\lambda_M)}, \quad \lambda_{33}^{CNT} = \frac{\lambda_{CNT}}{1 + (2a_K/L)(\lambda_{CNT}/\lambda_M)} \quad (4)$$

where d and L ($p = L/d$) are the diameter and length of the nanotubes, respectively. The so-called Kapitza radius a_K is defined as

$$a_K = R_K \lambda_m. \quad (5)$$

In the calculations, the thermal conductivity of copper is 230 and 331 W m^{-1} K^{-1} as measured for cold-pressed and spark plasma sintered Cu, respectively. The λ value of CNTs is taken to be 3000 W m^{-1} K^{-1}. Fig. 5 shows thermal conductivities with simulated curves obtained from eqn (2) when varying the Kapitza resistance. It can be seen that the experimental values are
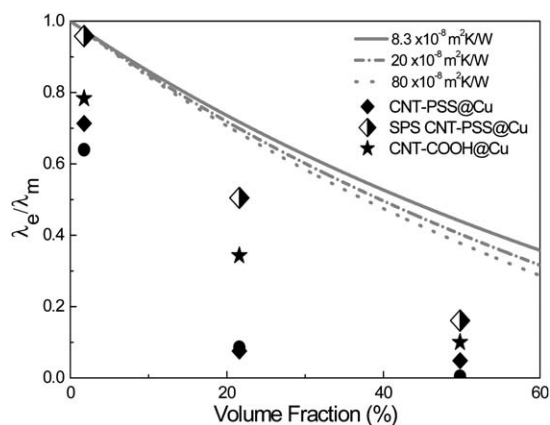
Fig. 5 Comparison of measured and theoretical thermal conductivities of copper composites enriched with CNT–*f*@Cu nanohybrids. Calculations obtained for various R_K.

significantly lower than that of the theoretical calculations. This deviation might be explained by the porosity of the cold-pressed samples, which by itself decreases the conductivity of the composites. In order to exclude the influence of sample porosity, the composite powders were fully consolidated *via* the spark plasma sintering process (see the Experimental section). As shown in Fig. 5, it is clear that the sintering process improves the conductivity of the composites by shifting λ_e/λ_m to the higher values. When Kapitza resistance R_K is 8.3×10^{-8} m^2 K W^{-1}, which is a value measured by picosecond transient absorption of CNTs suspended in surfactant micelles in water,[11] the calculated thermal conductivity enhancement (0.971) is in agreement with the experimental data (0.958) for 1.75 vol% Cu–CNT composite. However, the effective thermal conductivity of the composites with a higher content of nanotubes is remarkably lower than predicted λ_e. The experimentally measured conductivity for 10 wt% composites is about a factor of 2 smaller than that obtained from deduced data. One possible reason for this discrepancy is the fact that Nan's model is based on the assumption of perfect dispersion of individual CNTs that are in direct contact with matrix material. In the experiment, however, it is likely that at high volume fraction, carbon nanotubes are entangled.
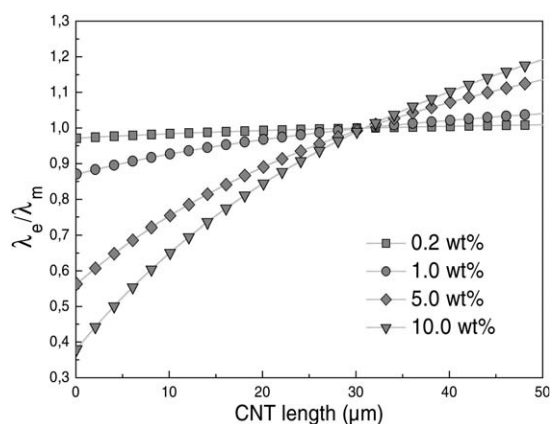
The aggregates of MWCNTs are expected to have high thermal resistance, which has a negative contribution to the effective thermal conductivity of the composite.

Existing studies on thermal properties of carbon nanotube composites showed that at a given volume fraction measured thermal conductivity is much higher than for composites with spherical, *i.e.* lower aspect ratio, particles.[29–31] The significance of aspect ratio can be understood from the fact that increasing the nanotube length causes shifts in the phonon dispersion towards lower frequencies.[32] Since the large acoustic mismatch between the metal–CNT interfaces causes inelastic phonon scattering,[33] by tuning the length of the nanotube one could reduce the influence of thermal interface resistance. In view of these correlations, another route toward conductivity enhancement is to increase the nanotube length or aspect ratio for constant diameter. Accordingly, the Nan's model results show that effective thermal conductivity is sensitive to the nanotube length (see Fig. 6). Despite the high Kapitza resistance between the nanotube–metal interface, the λ value of the composite might be improved by incorporating nanotubes with the length over 30 μm.

Conclusions

The interfacial thermal contact resistance, which inevitably exists between carbon nanotubes and the metal matrix, decreases a composite's thermal conductivity even for a very low volume fraction of nanotubes. Although no improvement in metal composite thermal conductivity could be observed, our results show that covalently functionalized carbon nanotubes are a better choice for phonon propagation in heat management composites than polymer functionalized nanotubes. We have experimentally demonstrated that decoration of CNT–COOH with Cu NPs increases the composite λ by a factor of four when compared to pristine nanotubes. Copper nanoparticles covalently attached to the nanotubes provide strong coupling between the nanotube–matrix interface, which in turn improves the interfacial thermal conductance in spite of the degradation of the tube's intrinsic conductivity. The obtained experimental results along with theoretical calculations suggest an optimal way of carbon nanotube surface modification and effective CNT length for enhancing thermal conductivity of nanotube metal composites. Accordingly, the future work on providing higher thermal conductivity of copper composites should focus on incorporation of long nanotubes and preserving a high aspect ratio of the CNTs during composite processing.

Fig. 6 Predictions of the Nan's model for thermal conductivity enhancement as a function of the CNT length.

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