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Ultrasensitive strain sensors made from metal-coated carbon nanofiller/epoxy composites

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Abstract

A set of resistance-type strain sensors has been fabricated from metal-coated carbon nanofiller (CNF)/epoxy composites. Two nanofillers, i.e., multi-walled carbon nanotubes and vapor growth carbon fibers (VGCFs) with nickel, copper and silver coatings were used. The ultrahigh strain sensitivity was observed in these novel sensors as compared to the sensors made from the CNFs without metal-coating, and conventional strain gauges. In terms of gauge factor, the sensor made of VGCFs with silver coating is estimated to be 155, which is around 80 times higher than that in a metal-foil strain gauge. The possible mechanism responsible for the high sensitivity and its dependence with the networks of the CNFs with and without metal-coating and the geometries of the CNFs were thoroughly investigated.
1. Introduction

Various carbon nanofillers (CNFs) of high aspect ratio, such as carbon nanotubes (CNTs) and vapor growth carbon fibers (VGCFs), possess excellent electrical conductivity. It has been confirmed that the conductivity of a single-walled carbon nanotube (SWCNT) could be changed by introduction of strain using atomic force microscopy (AFM), attributed to the band-gap and structural changes under the mechanical strain [1]. The piezoresistivity of SWCNT and other CNFs make them very suitable for being incorporated into polymers to produce conductive polymer composites. Recently, increasing attention has been paid to development of various strain sensors, in particular in building strain sensors with CNTs or carbon nanofibers [2-24]. Based on working principle, this type of strain sensors can be classified into two categories. The first one is to use the Raman activity observed in CNTs. When blending with a polymer, the strain in the composite can be evaluated via the relationship between the applied strain and the Raman spectrum shift [2,5]. Obviously, implementation of complex equipment in monitoring the Raman shift creates technical difficulties for practical applications. The other is to take the advantage of the piezoresistivity associated with CNT polymer nanocomposites. This kind of sensor can be made in large size (mm or cm), suitable for evaluation of static and low-frequency dynamic strains on the surfaces of a structure. To date, two types of resistance-type strain sensors have been developed, i.e., CNT buckypaper sensors [3,4,6,21] and sensors made from various polymer composites with different fillers, including SWCNTs [3,4,6,10], multi-walled carbon nanotubes (MWCNTs) [6,7-9,11-14,16,18-20] and carbon nanofibers [14,15,17,22]. The advantage of these novel composite sensors, which is of primary importance, is the higher sensitivity compared to conventional strain sensors such as metal-foil strain gauges [6, 9, 11, 16-18, 22]. In general, the higher sensitivity observed in these strain sensors can be mainly attributed to [24]:

1) significant variation of an internal conductive network formed by CNFs under applied strains, such as loss of contact between the conductive CNFs [8,9,16,18];
2) tunneling effect in neighboring CNFs due to distance changes [8,11,13-16,18,22]; and
3) conductivity change or piezoresistivity of CNFs due to mechanical deformation [3,6,7].

The sensing performance of nanocomposite sensors is expected to be dependent on the conductive fillers, polymer matrices, fabrication processes and techniques for strain evaluation as all of these may affect the working mechanisms mentioned above. Consequently, the evaluated gauge factors changed a lot in different studies. Nevertheless, most of the previous work confirmed the high sensitivity in these sensors in comparison to conventional strain gauges (with a gauge factor of 2), except one on SWCNTs based [10] and some MWCNTs based composite sensors [14, 20]. Certainly, due to the possible nonlinear piezoresistivity, for the sensors using MWCNTs and carbon nanofibers, the gauge factor is dependent on the strain level, confirmed in [11,16,18]. Limited investigation has been conducted for the sensor with SWCNTs [6,10,18], and the highest gauge factor is found to be around 5.0~6.0 in [6,18]. For MWCNTs and carbon nanofibers [7-9,11,13-16,19], the best gauge factor reported in tensile is 50, within a nonlinear response region [8].

In this study, to further increase the sensor sensitivity, a set of resistance-type strain sensors were fabricated using epoxy and metal-coated CNFs fillers. Ultrahigh sensitivity of the sensors was successfully achieved in these sensors obtained, which is much higher than all of the previously reported data, based on the best of our knowledge. At 0.6% tensile strain, the highest gauge factor in the sensor with for 3 wt.% silver coated VGCFs was estimated identified to be 155. We also conducted detailed investigation into the underlying mechanisms responsible for the ultrahigh sensitivity, with a focus on the geometrical features and network structure of the CNFs and the effects of metal coatings.

2. Microstructures of Metal-coated CNFs

Two types of nanofillers were used, i.e., MWCNT (Nano Carbon Technologies, Japan) and VGCF (Showa Denko, Japan). The general properties of these fillers are shown in Table 1. The CNFs was coated with a metal layer using non-electrolytic plating at Tsukada Riken,
Japan [25]. For MWCNT, nickel and copper were chosen as coating metals, referred to as M-Ni and M-Cu. For VGCF, nickel, copper and silver were chosen, referred to as V-Ni, V-Cu and V-Ag, respectively. The mass ratios between C and various metals are also shown in Table 1. First, the microstructures of the various metal-coated CNFs were observed using scanning electron microscopy (SEM, Hitachi SU-70) equipped with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-2100F). The typical images are shown in Figure 1a, Figure 2, and Figure 4d. For M-Ni, as shown in the low magnification insert in Figure 1a, there are massive fine adherent Ni particles on the surface of MWCNTs, which cause severe agglomeration. The high magnification image (insert of Figure 1a) shows that the MWCNTs have an diameter of about 100 nm, and the average thickness of the coated Ni particles ranges from 50 to 100 nm. Figure 2a shows both the SEM images and the EDS element maps (Ni-Kα and C-Kα) for the V-Ni sample. A lot of Ni particles of a thickness ranging from 50~100nm on the surface of VGCFs of a diameter from 80~200nm can be identified. In the EDS element mapping, C and Ni maps are believed to correspond to the VGCFs and the Ni particles, respectively. The TEM images in Figure 2b further uncover the detailed shapes of the Ni particles. From the low magnification insert of Figure 2b, the length of the VGCFs is estimated to be 1~10μm, shorter than that of the MWCNTs (Table 1). Moreover, in the high magnification insert of Figure 2b, there are massive Ni particles of a thickness from 50~100 nm on the surfaces of the VGCFs in monolithic or clumping forms. Compared to the similar case of M-Ni in Figure 1a, there seems to be a trend of more clumping or agglomeration of Ni on the VGCFs. A similar trend was observed in other as-received metal-coated CNFs, e.g., V-Ag (Figure 4d). The severe agglomeration of the as-received metal-coated CNFs makes the dispersion very difficult in a polymer matrix, resulting in a very high percolation threshold. Therefore, any improvement in dispersion can reduce the loading of the expensive metal-coated CNFs and increase the
stability or repeatability of a sensor. In this work, we introduced acid pre-processing for the as-received CNFs.

3. Pre-processing of Metal-coated CNFs

The pre-processing procedures were designed based on the mass ratios between C and the metal elements (Table 1). For M-Ni and V-Ni, CNFs were firstly refluxed in 2mol/ℓ dilute nitric acid for 6 h with mixing by a magnetic stirrer, and then put into 1mol/ℓ dilute nitric acid for 1 h with mixing. After filtration, the taken-out CNFs were washed thoroughly with distilled water to be acid-free and then finally dried in a vacuum oven at 80°C for 24h. For M-Cu, V-Cu and V-Ag, they were refluxed in 1mol/ℓ dilute nitric acid for 1 h with mixing. After filtration and washing by distilled water, they were finally put into the vacuum oven at 100°C for 24h. After weighing the CNFs before and after the above acid treatment, based on the assumption of that the mass loss of the CNFs is only caused by the dissolved metals, the mass ratios between C and the various metals after the acid treatment can be approximately estimated and shown in Table 1. From it, we can see that Ni was removed in the highest amount ratio due to its highest reaction rate with nitric acid and Ag was dissolved in the lowest amount ratio due to its slowest reaction rate with nitric acid. The microstructures of the various acid-treated CNFs are shown in Figure 1b, Figure 3 and Figures 4a-4c, respectively. Comparing Figure 1b with Figure 1a, it can be identified that Ni has been removed massively without severe clumping, and spacing among Ni particles increases. The diameter of the Ni particles ranges from 10~50 nm (high magnification insert of Figure 1b). After the acid treatment, the cylindrical shape of MWCNTs becomes more clearly and there is no obvious change of their diameter. Therefore, it can be estimated that excessive Ni has been dissolved without causing obvious damaging to the MWCNTs. From Figure 3a containing SEM images and EDS maps (Ni-Kα and C-Kα), compared with Figure 2a, it can be found that the amount of Ni for V-Ni has been reduced significantly. Similar to the case of M-Ni,
there is no obvious change of the diameter of VGCFs. We could then estimate that the acid treatment mainly removed excessive Ni particles from the surface of the VGCFs. In Figure 3b, i.e., TEM images of V-Ni after the acid treatment, there are still some Ni particles in monolithic or clumping forms. The size of the Ni particles ranges from 50 nm to 100 nm, without obvious change compared with that before the acid treatment. However, compared with Figure 2b, there is no severe clumping or agglomeration of Ni, Figure 3b. Therefore, the acid treatment mainly washed away those Ni particles in the form of severe clumping or agglomeration. Figure 4a demonstrates the SEM image and EDS maps (Ag-\(\alpha\) and C-\(\alpha\)) for V-Ag after the acid treatment. It shows that, compared with Ni particles, the Ag particles tend to be more uniformly distributed on the surface of VGCFs. Compared with the EDS map of Ni-\(\alpha\) in Figure 3a, the EDS map in Figure 4a also confirms this point. Usually, ionization of Ag is much weaker than that of Ni, which leads to its difficult dissolution in acid compared with Ni. Therefore, the acid treatment for V-Ag only removed a smaller amount of Ag particles on the surface of the VGCFs compared with that of Ni in V-Ni. In Figure 4b, it can be seen that, compared with Ni particles, comparatively smaller Ag particles of the size from 30 nm to 100 nm are uniformly attached on the VGCFs. Being different from that in Figure 3b, there is no obvious clumping or agglomeration in the Ag particles, which are almost in a monolithic form. Furthermore, from the high resolution TEM image in Figure 4c, on the surface of the Ag particles, lattice fringes of 0.24 nm spacing corresponding to (111) Ag can be identified. It implies that oxidation did not happen on the surface of the Ag particles. Furthermore, there is no evidence to show the oxidation at the interface between Ag and VGCF, which means that the Ag particles are physically attached on the surface of the VGCFs. Since there is no evidence to show the existence of oxidation on the Ag surface and at the interface between Ag and VGCF, the electrical conductive capability from one VGCF to another through contacting should not be decreased by the acid treatment, which is very attractive for making composite strain sensors. Moreover, by comparing Figure 4b with
Figure 4d (before the acid treatment), it can be found that the acid treatment effectively removed excessive Ag particles.

4. Results and Discussion

4.1. Electrical conductivity of composites

First, we experimentally investigated the electrical conductivity of metal-coated CNFs based composites. The CNF/polymer composite was fabricated by in situ polymerization. An insulating bisphenol-F epoxy resin (JER806, Japan Epoxy Resins Co., Ltd.) and an amine hardener (Tomaido 245-LP, Fuji Kasei Kogyo Co., Ltd.; Japan) were used. The composite was prepared by mixing the epoxy resin and the hardener with the ratio of (5:3) using a planetary mixer (AR-100, THINKY Co., Ltd.; Japan) at 2000 rpm for 30 seconds. Then, various CNFs were added into the mixture according to the different loadings in Table 2 and mixed again at 2000 rpm for 10 minutes. The final mixture was poured into a silicon mold, and cured in a vacuum oven at 80°C for 2 h. The specimens with a length of 70 mm, a width of 20 mm, and a thickness of 2 mm were prepared from the cured CNF/epoxy mixture. Silver paste was placed on the two sides of the specimens to maintain good contact between the sample surfaces and electrodes. The electrical conductivity of the composites was evaluated using a four-probe resistance method in dry air at ambient temperature. A LCR meter (HIOKI 3522-50, HIOKI Co., Ltd.; Japan) with Cu electrodes was used. Five specimens were measured to obtain the average values of electrical conductivity of the current composites.

The electrical conductivity of various composites is shown in Table 2. It is clear that the electrical conductivity of the M-Ni and M-Cu composites is about 2~3 orders lower than those of the MWCNT composites. For these composites, the conductivity increases with the CNF loading. For the M-Ni and M-Cu composites, the electrical conductivity tends to converge to around 0.1 S/m at 5.0 wt% CNF loading. By using the following percolation power law: \[ \sigma_{\text{com}} = \sigma_0 \left( \phi - \phi_c \right)^t \] when \( \phi > \phi_c \), where \( t \) is the critical exponent, \( \phi \) the volume
fraction of CNFs, $\phi$, the percolation threshold, and $\sigma_0$ is the conductivity of CNFs, to match the experimental data, the percolation thresholds for the MWCNT, M-Ni and M-Cu composites were estimated (Table 2). Note that the percolation threshold is of the unit of volume percentage which can be converted into a weight percentage using the specific gravity of the CNFs and the formulation [26]. For VGCF, V-Ni, V-Cu and V-Ag composites, from, it can be seen in Table 2 that the electrical conductivities of the V-Ni and V-Cu composites are around 1~2 orders lower than those of the VGCF composites. For the V-Ni and V-Cu composites, their electrical conductivity converges to around 0.1 S/m at 7.0 wt.% CNF loading, implying the formation of a stable conductive network. The lowest electrical conductivity identified for the V-Ag composites is around 3~4 orders lower than those of the VGCF composites. The electrical conductivity of the V-Ag composites converges to around 0.001 S/m at 7 wt.% CNF loading. The percolation thresholds for the VGCF, V-Ni, V-Cu and V-Ag composites are shown in Table 2.

It can be concluded from Table 2 that the metal-coating on CNFs leads to the lower electrical conductivity and higher percolation threshold in the composites. Compared with the MWCNT, M-Ni and M-Cu composites, the VGCF, V-Ni, V-Cu and V-Ag composites have a lower electrical conductivity but a higher percolation threshold.

4.2. Piezoresistivity of composite strain sensors

The procedure mentioned in section 4.1 was applied to making thin film type composite sensors. These sensors have a thickness of 200 $\mu$m with a width of 5mm and a length of 13 mm. Silver paste was placed on the two sides of the sheet [16, 18]. To evaluate the sensing performance, similar to the previous work [16, 18], the thin film sensor was attached to the top surface of an insulating cantilevered beam (thickness of 2.0 mm and the width of 40 mm), and a traditional metal-foil strain gauge for calibration was glued to the bottom surface of the beam, in a symmetrical position to the composite sensor. With this arrangement, the strain
gauge was able to measure the strain close to the bottom surface of the beam under bending. The position of the two sensors was close to the clamped end of the beam. Under static loading, the piezoresistivity of the CNF/epoxy sensors in tensile was obtained by using the LCR meter directly. The static response of the strain gauge was measured by using a bridge box (NR-500 Bridge box: NR-ST04, KEYENCE Co., Ltd.; Japan). For each type of composite sensor, 5 specimens were measured to obtain the average gauge factor. The gauge factors were obtained as: 

\[ K = \frac{\Delta R}{R_0}/\varepsilon, \]

with the initial resistance \( R_0 \), the resistance change \( \Delta R \), and the applied strain \( \varepsilon \) [18].

Figures 5a and 5b show the resistance change ratio \( (\Delta R/R_0) \) of pristine MWCNT and VGCF based composite sensors. For comparison, the result of the metal-foil strain gauge (obtained from \( K=2 \)) is also plotted. From these figures, it can be found that the piezoresistivity changes nonlinearly for the MWCNT or VGCF based composite sensors, which is much higher than that of the strain gauge. The piezoresistivity of the VGCF sensors are much higher than those of the MWCNT sensors. Moreover, with the decrease of CNF loading, the piezoresistivity increases monotonically. For metal-coated CNFs based composite sensors, the results of three typical cases, i.e., M-Ni, V-Cu and V-Ag are shown in Figures 5c, 5d and 5e. Compared with the pristine CNFs based composite sensors, it can be found that the piezoresistivity of the M-Ni, V-Cu and V-Ag sensors are much higher. Especially, the V-Ag composite sensor yields the highest piezoresistivity among all metal-coated CNFs based composite sensors. It is worthwhile to note that there are the nonlinear piezoresistive behaviors in all of the above composite sensors, it can be explained from the exponential relationship between the tunneling resistance and the distance among neighboring CNFs [8, 11, 13, 16-18, 22, 24], i.e., 

\[ R_{\text{tunnel}} \propto h d \exp(\lambda d) \]

with the \( R_{\text{tunnel}} \) as the tunneling resistance, \( d \) as the distance between CNFs and \( h \) and \( \lambda \) as constants. These nonlinear experimental results can be calibrated into a linear form using a log-log (natural logarithm) plot as shown in Figures 5f.
The gauge factors $K$ of all the composite sensors are summarized in Figures 6a and 6b, and Table 2. Note that the gauge factors were estimated at a strain level of $+6000 \mu e$ from Figures 5a–5e. In Figure 6a, it can be found that the gauge factors of the M-Ni and M-Cu sensors are much higher than those of the MWCNT sensor. At low metal-coated CNF loadings, the data of gauge factor are very scattered. However, the gauge factor of the metal-coated CNF sensors becomes almost a constant at high CNF loadings, e.g., 5 wt.%, which corresponds to the threshold value at which the stable electrical conductivity is achieved (section 4.1). These stable gauge factors (highlighted in blue in Table 2) are much required for practical applications. Figure 6b also shows the much higher gauge factors of the metal-coated VGCF composite sensors. Similarly, the gauge factor tends to be stable corresponding to a high CNF loading, e.g., around 7 wt.%. The gauge factors of the V-Ag sensors are higher than those of the V-Ni and V-Cu sensors as shown in Figure 6b. As shown in Table 2, the highest gauge factor is associated with the V-Ag sensor (3wt.% loading), i.e., 155, which is about 80 times higher than that of the metal-foil strain gauge. The stable gauge factor obtained at 7wt.% V-Ag loading is still very high (97.35). The gauge factors of the V-Ag sensors are believed to be the highest among the reported results to date.

To explain the possible reason for the higher gauge factors observed in the metal-coated CNF sensors, the fractured surfaces of some typical samples of 3wt.% CNF loading were examined using SEM, as shown Figure 7a. It can be seen that compared with the pristine CNFs, the dispersion of the metal-coated CNFs even after the acid pre-processing is still not uniform, leading to lower electrical conductivities and higher percolation thresholds (Table 2). Therefore, it can be estimated that there is a sparse electrical conductive network in the metal-coated CNF composites compared with those in the pristine CNF composites. Another reason for this sparse network of metal-coated CNFs may be that, at the same weight fraction (loading), the metal-coated CNFs should be fewer than the pristine ones due to the higher density of metals. A sparse conductive network, which leads to the higher resistance of
composites, can result in the higher sensitivity in the composite sensors, attributed to the easy change of the conductive network, i.e., loss of contact among CNFs or breakup of conductive path. For instance, as shown in Figure 7b, for an intensive conductive network with a high CNT loading, if one conductive path is broken down, the total nanocomposite resistance shows a minor variation. However, for a sparse conductive network with a very low CNT loading, for a special case of only two conductive paths in Figure 7b, $\Delta R/R_0$ is at least around 50%, which, therefore, leads to a higher sensitivity as identified in many previous studies, e.g., [16, 24]. Another factor from the aspect of mechanism of tunneling effects may also play a role in the high gauge factor of the metal-coated CNF composite sensors. As numerically investigated in [27], a high electrical conductivity of CNFs can effectively increase the gauge factor of composite sensors. In fact, the overall resistance of a composite with internal CNF networks is mainly contributed by the resistance of CNFs and the tunneling resistance. The resistance of CNFs decreases with increase of their conductivity, which leads to a higher ratio of the tunneling resistance to the overall resistance of the composite. Therefore, the tunneling effects are amplified, leading to a higher sensor gauge factor. The electrical conductivities of the metal-coated CNFs should be higher than those of the pristine CNFs due to the partially coated metal particles, which may also contribute to the higher sensor gauge factor as explained above.

For the pristine CNF sensors, compared with the MWCNT sensors, the much higher sensitivity of the VGCF sensors can be explained from Figure 6c based on the lengths of the two CNFs (Table 1). It can be seen that in a complete conductive path formed by a shorter CNF (i.e., VGCF), there should be much more junctions or contact points compared with that constructed by a longer CNF (i.e., MWCNT). Therefore, the probability of breakup or triggering tunneling effect in the path with shorter CNFs should be higher than that with longer CNFs. Another reason may be due to the fact that the volume of VGCF with a larger diameter is much higher than that of a MWCNT (see Table 1). At the same filler loading, the
number of the VGCFs is much smaller than that of the MWCNTs, which leads to a coarser conductive network formed by the VGCFs in the polymer matrix.

The highest sensitivity of the V-Ag sensors can be attributed to the larger amount of Ag particles with much higher density on the surface of VGCFs after the acid treatment (see Table 1). For the same weight loading of V-Ni, V-Cu and V-Ag, the volume and the number of the V-Ag should be smaller than those of the V-Ni and V-Cu. Therefore, a coarser V-Ag conductive network may exist compared with those formed by the V-Ni and V-Cu. Figure 6d shows the fractured surfaces of the V-Ni, V-Cu and V-Ag composites at 5wt.% CNF loading, confirmed that the number of the V-Ag is relatively lower than those of the V-Ni or V-Cu. This is consistent with the lowest electrical conductivity observed in the V-Ag (Table 2). Another reason may be attributed to the much higher electrical conductivity of Ag as compared to Ni and Cu. Moreover, as shown in Figure 4c, there is no oxidation layer on Ag particles and at the interface between Ag particle and VGCF due to its weaker ionization. Therefore, it can be estimated the electrical conductivity of the V-Ag and that between contacting V-Ag nanofillers may be higher than those of the V-Ni and V-Cu. As explained previously, this higher electrical conductivity of V-Ag and that among contacting V-Ag nanofillers can lead to the higher gauge factor of the V-Ag composite sensors.

In general, it should be noted that the effect of piezoresistivity of CNFs themselves might to be very small from the following reasons:

a) Very limited deformation is expected in CNFs due to the poor stress transfer from the epoxy matrix to them, caused not only by the large mismatch of Young’s modulus between the CNFs and the epoxy but also by the weak interface strength as identified experimentally [11]. Even for a perfect bonding interface between the CNFs and the epoxy, for instance, for a cylindrical unit cell of the epoxy (Young’s modulus: 2.73 GPa) containing a CNT (Young’s modulus: 1.0 TPa) under 0.6% tensile strain, we numerically identified that the strain of the CNT only ranged from 0.04% for 5wt.% CNT loading to 0.17% for 1wt.% CNT loading.
b) The linear resistance change of a zigzag SWCNT and some other SWCNTs of a special chirality is not so obvious, e.g., the piezoresistivity $P_{CNT} = 3.84\%$ [28] and $P_{CNT} = 4.2\%$ for SWCNT(8,1) [29], and $P_{CNT} = -4.2\%$ for SWCNT(8,0) [29] at 0.6\% axial strain. For armchair SWCNTs, there is no piezoresistivity. For MWCNTs practically used in experiments, the amount of the above piezoresistive SWCNTs as the outmost wall of the MWCNTs is unknown. By considering this point, based on the assumption of that CNTs of different types are contained in equal quantities and all behave ideally, an average equivalent behavior of SWCNTs was provided in [29], which indicated that at 0.6\% axial strain on a CNT, its piezoresistivity is only around 1.25\%.

c) Moreover, for a randomly orientated CNT in a matrix, its effective piezoresistivity is further weakened as $P_{CNT} \cos^2 \phi$ due to the strain transformation, where $\phi$ is the angle between the axial direction of the CNT and the strain direction, which can be set to be 45° with the highest probability. If we further consider the previous argument in a), for instance, 0.6\% strain on composites corresponds to 0.17\% strain on the CNT (1wt.% CNT loading) in the unit cell, which consequently leads to a very small CNT piezoresistivity, e.g., lower than 0.18\% (evaluated from $(0.17\%/0.6\%) \times 1.25\% \times \cos^2 45°$).

5. Conclusions

We reported a new type of piezoresistive strain sensors with ultrahigh sensitivity, which were fabricated from metal-coated CNFs and epoxy composites. Two nanofillers, i.e., MWCNTs and VGCFs with three coating metals were used. To improve the dispersion of the metal-coated CNFs, acid treatment for the as-received metal-coated CNFs was carried out to remove the excessive coated metals. The electrical conductivity of the composites and the piezoresistivity of the composites sensors were evaluated. Compared to the composites with pristine CNFs, the electrical conductivity of the metal-coated CNFs based composites is much lower. On contrary, their percolation thresholds are much higher. This implies that coarser
conductive networks forms in the metal-coated CNFs based composites, as confirmed by SEM observations. This leads to a much higher sensor sensitivity. Moreover, compared with the MWCNTs, the shorter VGCFs of a larger diameter can increase the sensitivity. This phenomenon can be attributed to the change of conductive networks under strain. The VGCFs coated by Ag, possesses the highest sensitivity, i.e., 155 at 3.0wt.% V-Ag loading. This ultrahigh sensitivity is associated with the coarser conductive network formed by V-Ag and its higher electrical conductivity compared with other CNFs. The contribution of the CNF piezoresistivity to the sensor piezoresistivity seems to be small. To obtain a desirable network and stable sensor sensitivity in metal-coated CNFs composites, it is critical to optimize the acid processing window, in particular the acid concentration and processing time.

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References


Captions of Figures and Tables

Figure 1. SEM images of M-Ni. a) Before acid-treatment. b) After acid-treatment

Figure 2. SEM and TEM images of V-Ni before acid-treatment. a) SEM image and elemental map. b) TEM images.

Figure 3. SEM and TEM images of V-Ni after acid-treatment. a) SEM image and elemental map. b) TEM images.

Figure 4. SEM and TEM images of V-Ag. a) SEM image and elemental map (after acid-treatment). b) TEM images (after acid-treatment). c) high magnification TEM image (after acid-treatment). d) TEM and SEM images (before acid-treatment).

Figure 5. Piezoresistivity of various strain sensors. a) Resistance change ratio versus applied strain (MWCNT). b) Resistance change ratio versus applied strain (VGCF). c) Resistance change ratio versus applied strain (M-Ni). d) Resistance change ratio versus applied strain (V-Cu). e) Log-Log plot of c) for M-Ni.

Figure 6. Gauge factor of various strain sensors. a) Comparison of gauge factors of various MWCNT based strain sensor. b) Comparison of gauge factors of various VGCF based strain sensor.

Figure 7. Dispersion states of nanofillers, and influences of internal conductive network on strain sensor behaviors. a) Comparison of dispersion states between pristine and metal-coated nanofillers. b) Working mechanisms of conductive network. c) Influence of nanofiller length
on sensor behaviors. d) Comparison of fractured surfaces of V-Ni, V-Cu and V-Ag specimens (5wt.% loading)

Table 1. Property of MWCNT and VGCF, and mass ratio of carbon and metals

Table 2. Gauge factor and conductivity of composite strain sensors