



## OPEN

## Positive temperature coefficient thermistors based on carbon nanotube/polymer composites

You Zeng<sup>1</sup>, Guixia Lu<sup>2,3</sup>, Han Wang<sup>1,3</sup>, Jinhong Du<sup>1</sup>, Zhe Ying<sup>1</sup> & Chang Liu<sup>1</sup>

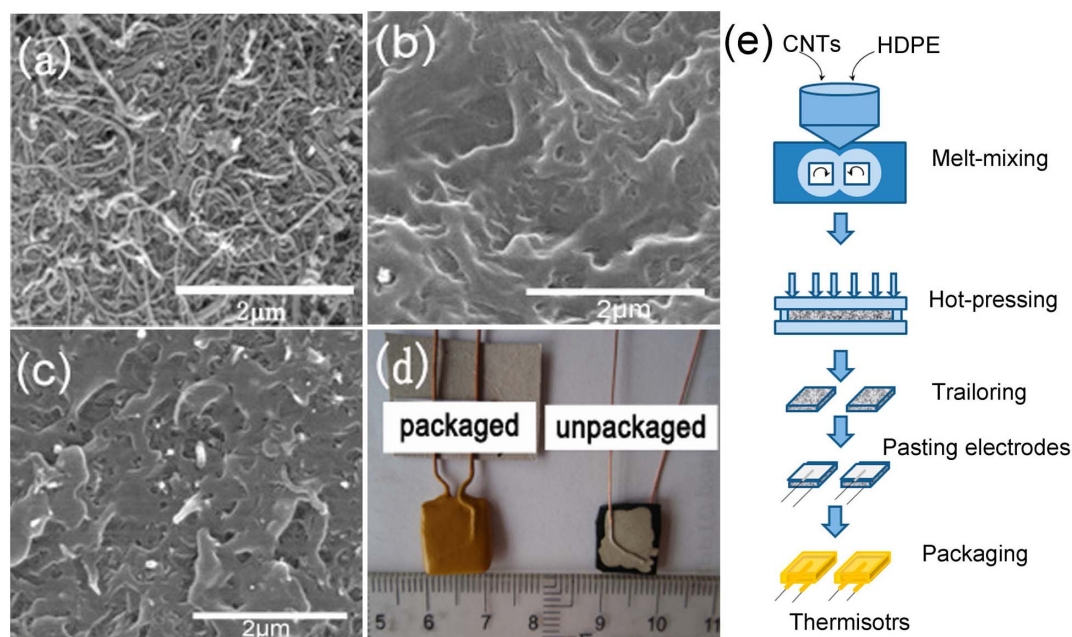
<sup>1</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China, <sup>2</sup>School of Materials Science and Engineering, Shandong University, Jinan, Shandong 250061, People's Republic of China, <sup>3</sup>School of Materials Science and Engineering, Shenyang Jianzhu University, 9 Hunan East Road, Shenyang 110168, People's Republic of China.

Received  
16 June 2014Accepted  
29 September 2014Published  
20 October 2014Correspondence and  
requests for materials  
should be addressed to  
Y.Z. (yzeng@imr.ac.  
cn)

In order to explore availability of carbon nanotube (CNT)-based positive temperature coefficient (PTC) thermistors in practical application, we prepared carbon nanotube (CNT) filled high density polyethylene (HDPE) composites by using conventional melt-mixing methods, and investigated their PTC effects in details. The CNT-based thermistors exhibit much larger hold current and higher hold voltage, increasing by 129% in comparison with the commercial carbon black (CB) filled HDPE thermistors. Such high current-bearing and voltage-bearing capacity for the CNT/HDPE thermistors is mainly attributed to high thermal conductivity and heat dissipation of entangled CNT networks. Moreover, the CNT/HDPE thermistors exhibit rapid electrical response to applied voltages, comparable to commercial CB-based thermistors. In light of their high current-bearing capacity and quick response, the CNT-based thermistors have great potential to be used as high-performance thermistors in practical application, especially in some critical circumstances of high temperature, large applied currents, and high applied voltages.

Positive temperature coefficient (PTC) thermistors are important electronic components as over-current protectors, self-regulating heaters, and resettable fuses in electric circuits. Their electrical resistance can sharply increase with elevation of temperature, showing a typical PTC phenomenon as a result of abrupt breakdown of conductive network at elevated temperatures<sup>1</sup>. Commercial polymeric PTC thermistors, generally consisting of carbon black (CB) filled high density polyethylene (HDPE) composites, have been widely utilized for several decades by virtue of their low cost, quick response and easy operation. However, there exist some intrinsic drawbacks for the CB/HDPE thermistors<sup>2,3</sup>: (1) poor processibility due to high CB-loadings of over 25 wt.% for obtaining acceptable electrical resistance of the order of 10 Ohm; (2) low thermal stability resulting from easy oxidation of amorphous CB particles at elevated temperatures; (3) poor thermal reproducibility due to irreversible motion of small-size CB particles in thermal cycling processes. These drawbacks greatly hinder practical application of the CB/HDPE thermistors, especially in some critical circumstances of high temperature, large applied currents, or high applied voltages.

In order to overcome these intrinsic drawbacks of CB-based thermistors, CNTs have been used as novel conductive fillers in polymeric composites by virtue of their large aspect ratio (length to diameter ratio), integrated graphitic microstructure, high electrical conductivity, and high thermal stability<sup>4,5</sup>. He *et al* first investigated PTC effect of CNT/HDPE composites in 2005 and reported that the presence of CNTs in polymeric matrix could greatly improve thermal stability of CNT/HDPE composites due to entanglement between CNT and HDPE molecular chains<sup>2</sup>. Lee *et al* found that a small amount of CNT loadings could remarkably improve electrical conductivity and thermal cyclic stability of CB/HDPE composites<sup>6</sup>. Kappal and Jeevananda *et al* reported that addition of functionalized CNTs was beneficial for enhancing PTC effects of CB/HDPE composites<sup>7,8</sup>. Furthermore, PTC phenomena of CNT-filled other polymers, such as ultrahigh molecular weight polyethylene (UHMWPE)<sup>9,10</sup>, polyvinylidene fluoride (PVDF)<sup>11</sup>, polyoxymethylene<sup>12,13</sup>, and binary polymer blends<sup>14-17</sup>, have been also investigated recently. It has been widely accepted that the presence of CNTs is beneficial to increase electrical conductivity and thermal stability of composites, but sacrificing PTC intensity (a ratio of the maximum resistivity to initial resistivity at room temperature, standing for electrical sensitivity of thermistors to external stimulus). Such a low PTC intensity for the CNT-based thermistors seems rather adverse to its practical application as high-performance thermistors.



**Figure 1 | Microstructure of CNT/HDPE composites and fabrication schematic of the thermistors.** (a) SEM image of CNTs shows a large aspect ratio of over 100. (b) SEM image of HDPE matrix. (c) SEM image of the CNT/HDPE composites with a 10 wt.% CNT loading reveals a uniform dispersion of CNTs throughout the HDPE matrix. (d) Optical images of the CNT/HDPE thermistors after and before package. (e) Fabrication schematic of the CNT/HDPE thermistors consists of melt-mixing, hot-pressing, and packaging procedures.

In all these studies, the PTC effects of composites were evaluated by measuring change in electrical resistivity ( $R$ ) as a function of temperature ( $T$ ), which is reasonable because  $R$ - $T$  curves can directly reveal intrinsic change in conductive network of composites at different temperatures. However, in practical application, the PTC thermistors are used under applied voltages and subsequently heated up by passing current (not by ambient temperature), showing a sharp increase in electrical resistance (PTC effect). Notably, such a PTC effect induced by applied voltages is somewhat different from that by ambient temperature: the former is a non-equilibrium process which is closely associated with Joule heat generation and energy dissipation<sup>10,18–22</sup>, while the latter reflects change of electrical resistivity at equilibrium temperatures. In that case, the PTC effect of thermistors under applied voltages cannot be evaluated comprehensively by using only conventional resistance-temperature ( $R$ - $T$ ) curves. So far, surface temperature of CB/HDPE composites under applied voltages have been investigated to evaluate their self-heating performance<sup>19,21,23–25</sup>, while electric current response of the CNT/HDPE thermistors under applied voltages has been rarely investigated.

In order to explore availability of the CNT/HDPE thermistors as high-performance thermistors in practical application, we prepared the CNT/HDPE composites by using conventional melt-mixing method, and investigated their electrical and thermal properties,  $V$ - $I$  characteristics, PTC effects under applied voltages, and corresponding response rates. We found that the CNT/HDPE thermistors exhibited much higher hold voltage and larger hold current than commercial CB/HDPE thermistors, implying high voltage-bearing and current-bearing capacity, which is mainly attributed to high thermal conductivity and heat dissipation of entangled CNT-networks. The CNT/HDPE thermistors show great potential to be utilized as high-performance thermistors in commercial applications.

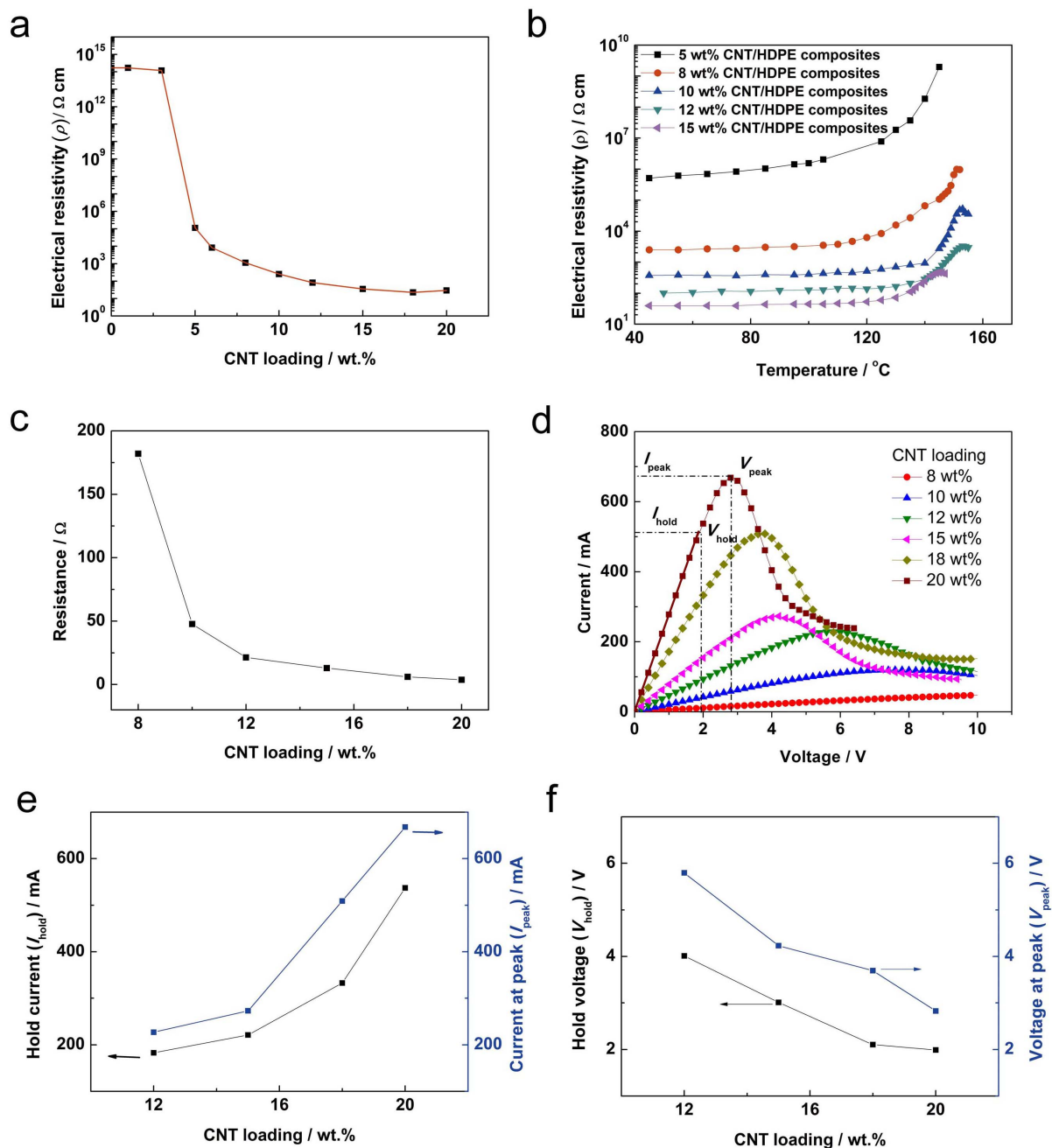
## Results and Discussion

**Microstructure of CNT/HDPE composites.** The CNT/HDPE thermistors were prepared by using conventional melt-mixing, hot-pressing, and packaging methods, and their scanning electron

microscopy (SEM), optical images, and fabrication schematic were illustrated in Fig. 1. Firstly, the CNTs exhibit a large aspect ratio of over 100 in Fig. 1a, which is beneficial to fabricate high-efficiency conductive networks through matrix at a low CNT loading<sup>26</sup>. Secondly, we cannot find obvious aggregation of CNTs on fracture surfaces of the CNT/HDPE composites shown in Fig. 1c, implying a uniform dispersion of CNTs throughout HDPE matrix. It also reveals that the conventional melt-mixing and hot-pressing methods (see the Fig. 1e) are effective to disperse well CNTs into matrix for obtaining high electrical conductivity of composites<sup>27</sup>. In addition, we can see from Fig. 1d that the packaged CNT/HDPE thermistors, combining the CNT/HDPE composites with electrodes together, show a high structural integrity, which is suitable for evaluation and comparison with commercial CB-based thermistors in the same measuring conditions. Notably, in our work, all the manufacturing processes of the CNT/HDPE thermistors shown in Fig. 1e are consistent with that of commercial CB/HDPE thermistors, which is convenient for realizing large-scale production of the CNT/HDPE thermistors.

### Electrical properties of the CNT/HDPE composites and thermistors.

The electrical and thermal properties of the CNT/HDPE composites and thermistors were investigated and shown in Fig. 2. First of all, it can be seen from Fig. 2a that the electrical resistivity ( $\rho$ ) of the CNT/HDPE composites decreases drastically with the increment of CNT loadings, showing a typical percolation phenomenon due to formation of conductive CNT-networks at low CNT loadings (a percolation threshold of 4.0 wt.% CNT loading)<sup>27,28</sup>. Secondly, at elevated temperatures, all the composites exhibit sharp increase in electrical resistivity (a typical PTC phenomenon) as shown in Fig. 2b, which is mainly attributed to breakdown of interconnected CNT-networks resulting from volumetric expansion of HDPE matrix in the melting process<sup>3</sup>. Generally, PTC intensity, a ratio of the maximum resistivity at elevated temperature to initial resistivity at room temperature, is widely used to evaluate electrical sensitivity of composites to external stimuli. It can be seen clearly from Fig. 2b that the PTC intensity of composites is inversely proportional to CNT loadings. Higher the CNT loadings, lower

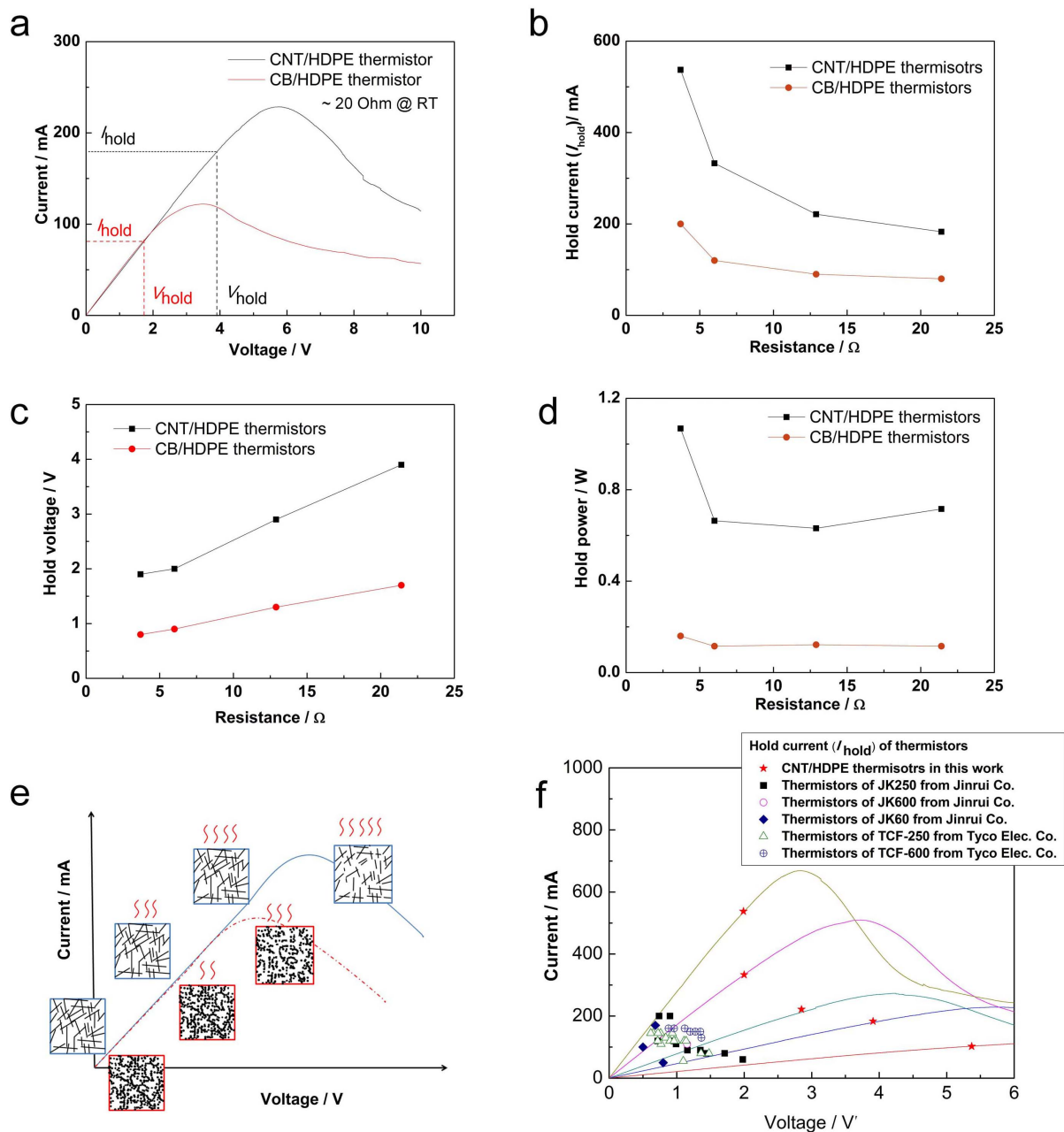


**Figure 2 | Electrical properties of the CNT/HDPE composites and thermistors.** Electrical resistivity ( $\rho$ ) of the CNT/HDPE composites as a function of (a) CNT loadings and (b) temperature; (c) electrical resistance of the CNT/HDPE thermistors at room temperature; (d) voltage-current curves of the CNT/HDPE thermistors, implying a typical PTC effect induced by applied voltages; (e) hold current and (f) hold voltage of the thermistors as functions of CNT loadings.

the PTC intensity, which is closely associated with high structural stability of entangled CNT networks at high CNT loadings<sup>2,6</sup>. It is worth pointing out that the PTC intensity of the CNT/HDPE composites in our work is lower than that of CB-filled HDPE composites reported in literature, which is due to the entanglement between CNTs. Notably, as mentioned above, the  $R$ - $T$  curves and PTC intensity measured in equilibrium temperature conditions cannot evaluate accurately availability of PTC thermistors under applied voltages.

We further investigated PTC effects of the CNT/HDPE thermistors under applied voltages. It can be seen clearly from Fig. 2d that the CNT/HDPE thermistors exhibit non-linear relationship of passing currents with applied voltages, indicating a typical PTC phenomenon of thermistors as a result of temperature elevation induced by

applied voltages, which is closely associated with generation and dissipation of Joule heat. Firstly, at low applied voltages, the generated Joule heat is so little that it can be neglected or quickly dissipated<sup>21</sup>; consequently the thermistors lies in an equilibrium state and exhibits a linear ohmic characteristic (a constant resistance) shown in Fig. 2d, where the maximum current and corresponding voltage at the initial linear region of  $V$ - $I$  curves are denoted as hold current ( $I_{\text{hold}}$ ) and hold voltage ( $V_{\text{hold}}$ ). Secondly, with the increment of applied voltages, the generated Joule heat is too much to be released in time, and consequently the heat accumulation in thermistors results in temperature elevation, volume expansion of HDPE matrix, increment of electrical resistance, and corresponding decrement of current, as shown in Fig. 2d. Therefore, the PTC effect induced by applied voltages is closely associated with generation and dissipation



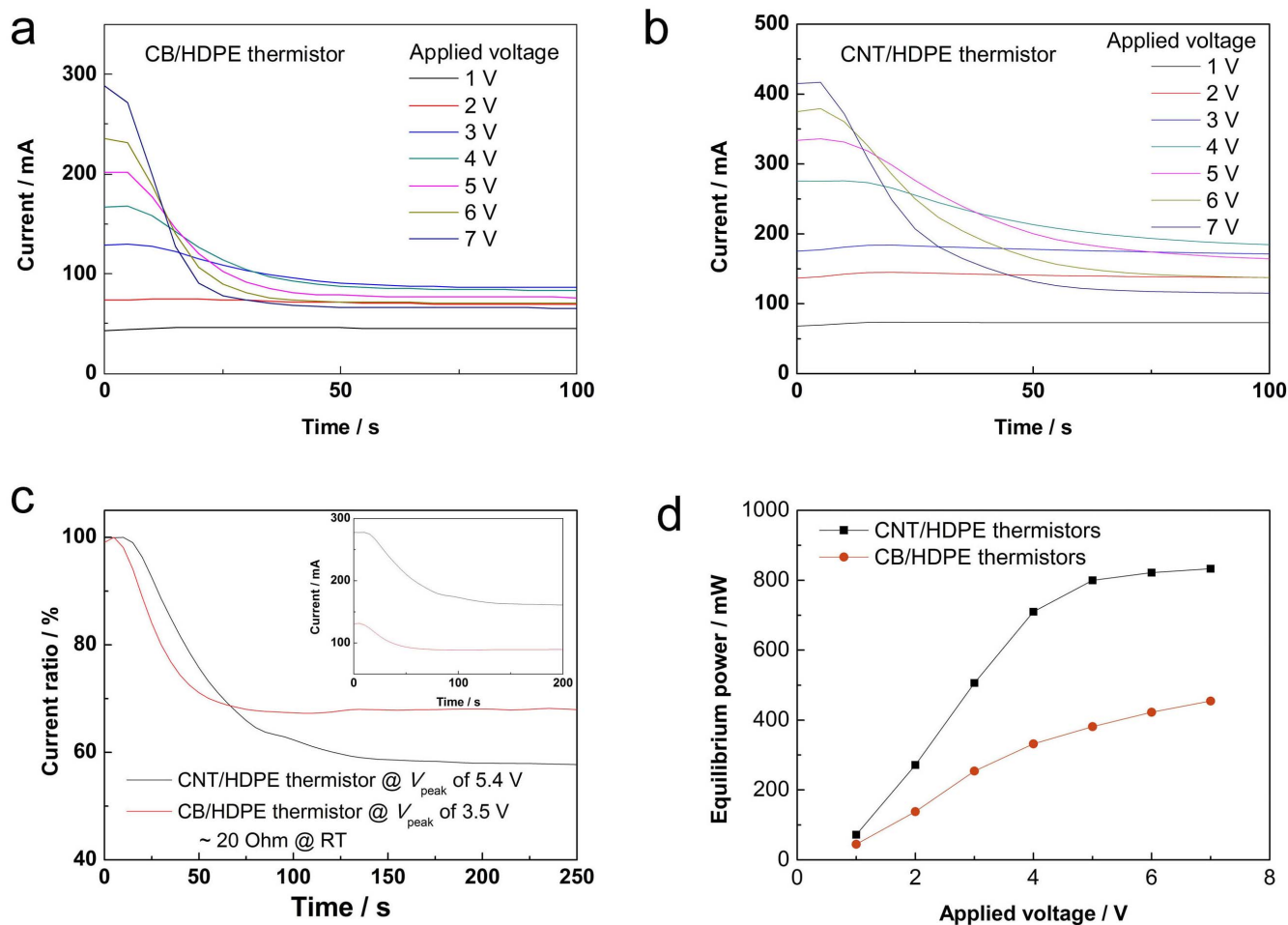
**Figure 3 | Voltage-current responses of thermistors.** Comparison of (a) voltage-current curves, (b) hold current, (c) hold voltage, and (d) hold power between the CNT/HDPE and CB/HDPE thermistors; (e) PTC effect mechanism revealing high heat dissipation of the CNT/HDPE thermistors, and (f) comparison of hold current and hold voltage between various thermistors (some data from technical specification of commercial thermistors).

of Joule heat, obviously different from that PTC effect induced by ambient temperature.

The PTC effect induced by applied voltages for the CNT/HDPE thermistors strongly depends on CNT loadings. It can be seen clearly from Fig. 2d that the PTC phenomena of those thermistors with high CNT loadings are easier to occur at low applied voltages than that with low CNT loadings. For convenience of comparison, some related parameters, such as current at peak ( $I_{peak}$ ), corresponding voltage at peak ( $V_{peak}$ ), hold current ( $I_{hold}$ , the maximum current at initial linear region of  $V$ - $I$  curves, standing for the maximum passing current which thermistors can bear without any PTC phenomena), and corresponding hold voltage ( $V_{hold}$ ), were also plotted as functions of CNT loadings in Figs. 2e-f. It can be seen clearly that, with the increment of CNT loadings, the PTC phenomena of thermistors are prone to occur at low applied voltages or large applied currents. That is because, for the CNT/HDPE thermistors with high

CNT loadings and low electrical resistance, only high applied currents and low applied voltages are necessary to generate enough Joule heat for melting HDPE matrix and causing PTC effects. Such a relationship between PTC characteristics and electrical resistance for the CNT/HDPE thermistors is consistent with that for CB/HDPE thermistors<sup>2</sup>.

**Comparison of PTC effect between CNT/HDPE and CB/HDPE thermistors.** We compared  $V$ - $I$  characteristics of the CNT/HDPE thermistors with that of the commercial CB/HDPE thermistors (see Fig. 3). It can be seen clearly from Fig. 3a that the CNT/HDPE thermistors exhibit much larger hold current ( $I_{hold}$ ) and higher hold voltage ( $V_{hold}$ ) than the CB/HDPE thermistors with same electrical resistance of about 20 Ohm at room temperature (the same slope in the initial linear region for these two  $V$ - $I$  curves). The values of  $I_{hold}$  and  $V_{hold}$  for the CNT/HDPE thermistors are



**Figure 4 | Response rate of thermistors under applied voltages.** Current-time curves of (a) CB/HDPE and (b) CNT/HDPE thermistors under different initial voltages. (c) Comparison of current decay between the CNT/HDPE and CB/HDPE thermistors with the same resistances under applied voltages at peak ( $V_{peak}$ ) reveals a quick response of current delay of the CNT/HDPE thermistors. (d) Equilibrium power of the CNT/HDPE and CB/HDPE thermistors.

182.9 mA and 3.9 V, respectively, increasing by 129% in comparison with the  $I_{hold}$  of 80 mA and  $V_{hold}$  of 1.7 V for the commercial CB/HDPE thermistors, indicating that the CNT/HDPE thermistors can bear much larger passing currents and higher applied voltages without any PTC phenomena than the CB/HDPE thermistors. Moreover, we further compared  $V$ - $I$  characteristics of all thermistors and found that all the CNT/HDPE thermistors exhibited much larger  $I_{hold}$ , higher  $V_{hold}$ , and higher corresponding hold power (the product of  $I_{hold}$  and  $V_{hold}$ ) than the CB/HDPE thermistors with same electrical resistances at room temperature, as shown in Figs. 3b-d. Such high current-bearing or voltage-bearing capacity for these CNT/HDPE thermistors is extremely important in practical applications, especially in some critical circumstances.

Such large  $I_{hold}$  and high  $V_{hold}$  of the CNT/HDPE thermistors is closely associated with high heat dissipation of entangled CNT networks. Fig. 3e illustrates different mechanisms of PTC effect between the CNT/HDPE and CB/HDPE thermistors. In our work, the CNT/HDPE and CB/HDPE thermistors with same electrical resistances can generate equal Joule heat under the same applied voltages. The generated Joule heat ( $Q_{oule}$ ) can be classified into two parts, one is the heat for temperature elevation of thermistors ( $Q_{heating}$ ) and the other is the heat released as energy dissipation ( $Q_{dissipation}$ ). It is worth mentioning that the CNT network possesses much higher thermal conductivity and thermal diffusion coefficient than the CB-based network due to integrated graphitic structure and large

aspect ratio of CNTs<sup>29,30</sup>. In that case, the CNT/HDPE thermistors can dissipate much more Joule heat than the CB/HDPE thermistors (see the Fig. 3e), and only less Joule heat is for heating up thermistors. As a result, the CB/HDPE thermistors exhibit a rapid elevation of temperature, resulting in a PTC phenomenon even at a low applied voltages; while, at that voltage, the CNT/HDPE thermistors still remain its equilibrium state and show ohmic characteristic due to its rapid heat dissipation. Only at high applied voltages (much more generated Joule heat), the CNT/HDPE thermistors can be heated up to the melting point of HDPE and produce PTC phenomena, consequently showing high values of  $V_{hold}$  and  $I_{hold}$ . On the other hand, the entanglement of CNTs also plays a key role in hindering volumetric expansion of thermistors<sup>2,6</sup>, so that the PTC phenomenon of CNT/HDPE thermistors occurs only at high applied voltages.

We further compared the CNT/HDPE thermistors with other commercial thermistors, and their  $I_{hold}$  and electrical resistances at room temperature (same data from technical specification of commercial thermistors) were plotted in Fig. 3f. It can be seen clearly that these CNT/HDPE thermistors exhibit much larger  $I_{hold}$  and higher  $V_{hold}$  than all the corresponding commercial thermistors with same electrical resistances (the same slope of initial linear regions), exhibiting high current-bearing and voltage-bearing capacity of the CNT-based thermistors. It is worth pointing out that the high values of  $I_{hold}$  and  $V_{hold}$  for PTC thermistors are unprecedented, and they cannot be obtained for the commercial CB/HDPE thermistors by simply increasing or decreasing CB contents without any variation of elec-



trical resistance of thermistors. The unique characteristics of large  $I_{\text{hold}}$  and high  $V_{\text{hold}}$  for the CNT/HDPE thermistors are mainly attributed to high thermal conductivity and energy dissipation of entangled CNT networks. By virtue of their high current-bearing and voltage-bearing capacity, the CNT/HDPE thermistors have great potential to be applied as high-performance thermistors in practical application.

**Responsive behavior of the CNT/HDPE thermistors.** In order to evaluate response rate of the CNT/HDPE thermistors, we compared current-time curves of the CB/HDPE thermistors under applied voltages with that of the CNT/HDPE thermistors. We can clearly see from Figs. 4a-b that both thermistors exhibit strong dependence of current decay on initial applied voltages, which is closely associated with the generated Joule heat at different applied voltages. At low initial applied voltages, the generated Joule heat is so little that it can be released quickly, the thermistors exhibit typical ohmic characteristics (constant currents at certain voltages). With the increment of applied voltages, the generated Joule heat is too much to be released quickly, and the resultant elevation of temperature causes a typical PTC phenomenon, showing a sharp decay of current as a function of time. As shown in Figs. 4a-b, higher the initial applied voltages, more quickly the current decay, and more pronounced the PTC effect induced by applied voltages.

Considering the dependence of current decay on initial applied voltages, we chose the voltage at peak ( $V_{\text{peak}}$ ) of the  $V$ - $I$  curve as the initial applied voltage for each measurement, and corresponding current-time curves of the CNT/HDPE and CB/HDPE thermistors with the same resistance of about 20 Ohm were shown in Fig. 4c. We can see clearly that the CNT/HDPE thermistors exhibit a quick current decay, and its current ratio decreases by over 40% within 150 s, even larger than 22% for the CB/HDPE thermistors, indicating high electrical sensitivity of the CNT/HDPE thermistors to external over-voltages. Furthermore, we compared output power of thermistors at equilibrium states under different applied voltages to evaluate heat dissipation capacity of thermistors<sup>21</sup>. It can be seen clearly in Fig. 4d that the CNT/HDPE thermistors exhibit much higher equilibrium power than the CB/HDPE thermistors, implying much higher heat dissipation and higher surface temperature at equilibrium states, which is mainly associated with high thermal conductivity and energy dissipation of the entangled CNT networks<sup>19,21</sup>. Therefore, the CNT/HDPE thermistors under applied voltages exhibit quick response of current decay, comparable to the commercial CB/HDPE thermistors, implying great potential for the CNT-based thermistors to be used as high-performance thermistors in practical application. Notably, the responsive behavior of thermistors also strongly depends on many influencing factors, such as ambient temperature, cooling rate of thermistors, geometrical shape, cyclic repeatability, measurement procedures, and so on. Many research should be further carried out for pushing forward practical application of these CNT/HDPE thermistors.

In this work, we prepared the CNT/HDPE thermistors by using melt-mixing, hot-pressing, and packaging technique, and investigated related electrical and thermal properties in order to explore availability of these CNT-based thermistors as high-performance over-current protectors. We found that the CNT/HDPE thermistors exhibit much larger hold current and higher hold voltage than the commercial CB/HDPE thermistors; such high voltage-bearing or current-bearing capacity for the CNT/HDPE thermistors is mainly attributed to the high thermal conductivity and heat dissipation of entangled CNT networks. Moreover, the CNT/HDPE thermistors also exhibit quick response of current decay to applied voltages, comparable to the commercial CB/HDPE thermistors. By virtue of their high voltage-bearing capacity and quick current-decay response, the CNT/HDPE thermistors have great potential to be applied as high-performance thermistors in practical application, especially

in some critical circumstances of high temperature, large applied currents, and high applied voltages.

## Methods

**Materials.** Multi-walled CNTs produced by chemical vapor deposition (CVD) methods were supplied from Chengdu Organic Chemicals Co., Ltd. of Chinese Academy of Sciences. Average diameter of the received CNTs is about 20–40 nm, and their electrical conductivity is about 330 S/cm measured by using a Nanofactory piezo-driven STM-TEM work station. HDPE pellets (GF7750) were supplied from Liaoyang Chemical Fiber United Factory of China, and their melting point and melt index are 135°C and 0.42 g/10 min, respectively.

**Fabrication of CNT/HDPE composites and thermistors.** The weighted CNTs and HDPE pellets were first mixed well in an internal two-roller mixer at 160°C and 64 rpm for 10 min. Next, the obtained CNT/HDPE blends were transferred into a hot pressing machine and were molded into CNT/HDPE composite sheets of 1 mm in thickness under a pressure of 10 MPa at 160°C. After cooling down to room temperature, the CNT/HDPE composites with various CNT loadings from 2 to 20 wt.% were obtained. Thereafter, the CNT/HDPE composite sheets were tailored into many square specimens of 10 mm × 10 mm, and both the upper and lower surfaces of specimens were coated with conductive silver paint and pasted with copper wire electrodes for measurement of electrical properties and preparation of thermistors. Next, epoxy molding compounds as packaging materials, supplied from Shenzhen Jinrui Electric Materials Co. Ltd., were used to package the composites and electrodes together, and consequently the CNT/HDPE thermistors were obtained by following the same procedure with manufacture of commercial CB/HDPE thermistors.

**Electrical and thermal properties of CNT/HDPE composites.** Electrical resistance ( $R$ ) of the CNT/HDPE composites was measured using a digital multi-meter for  $R < 10^7 \Omega$  or a high-resistance meter for  $R > 10^7 \Omega$  alternatively, and volume resistivity ( $\rho$ ) of composites was calculated according to the following formula:

$$\rho = R \times A / t$$

where  $A$  is the effective area of measuring electrodes, and  $t$  is the thickness of specimens. Thereafter, the CNT/HDPE composites were put into a programmable electrical thermostat and heated up at a constant heating rate of 2°C/min, and  $R$  at different temperatures was recorded automatically to evaluate PTC effects of composites in the heating process.

**Voltage-current characteristics of the PTC thermistors.** Voltage-current ( $V$ - $I$ ) characteristics of the CNT/HDPE thermistors were measured by using an electrochemical station (LK3200A, Lanlike Chemical Electronic High-Tech Co., Ltd, Tianjin, China) at a scan rate of 50 mV/s, and the applied voltages and corresponding currents were recorded automatically to describe PTC effects induced by external electrical fields. Moreover, electric current of the CNT/HDPE thermistors under applied voltages from 1 V to 7 V was also measured as a function of time to evaluate current response rates of thermistors. For convenience of comparison, commercial CB/HDPE thermistors of JK250 series with various electrical resistances at room temperature were supplied from Shenzhen Jinrui Electric Materials Co. Ltd., and these commercial thermistors have nearly the same geometrical shape and size with the CNT/HDPE thermistors for ensuring the comparability between experimental data of thermistors. In this work, the  $V$ - $I$  characteristics of the commercial CB/HDPE thermistors were measured following the same procedures for comparison with that of the CNT-based thermistors.

- Nan, C. W., Shen, Y. & Ma, J. Physical properties of composites near percolation. *Annu. Rev. Mater. Sci.* **40**, 131–151 (2010).
- He, X. J., Du, J. H., Ying, Z., Cheng, H. M. & He, X. J. Positive temperature coefficient effect in multiwalled carbon nanotube/high-density polyethylene composites. *Appl. Phys. Lett.* **86**, 062112 (2005).
- Park, E. S. Resistivity and thermal reproducibility of high-density polyethylene heaters filled with carbon black. *Macromol. Mater. Eng.* **291**, 690–696 (2006).
- Ajayan, P. M. & Tour, J. M. Nanotube composites. *Nature* **447**, 1066–1068 (2007).
- Endo, M., Strano, M. S. & Ajayan, P. M. in *Carbon Nanotubes* Vol. 111, (eds Jorio, A. Dresselhaus, G. & Dresselhaus M. S.) 13–61 (Springer, 2008).
- Lee, J. H., Kim, S. K. & Kim, N. H. Effects of the addition of multi-walled carbon nanotubes on the positive temperature coefficient characteristics of carbon-black-filled high-density polyethylene nanocomposites. *Scripta Mater.* **55**, 1119–1122 (2006).
- Kalappa, P. *et al.* Effect of polyaniline functionalized carbon nanotubes addition on the positive temperature coefficient behavior of carbon black/high-density polyethylene nanocomposites. *IEEE T. Nanotechnol.* **7**, 223–228 (2008).
- Jeevananda, T. *et al.* Investigation of multi-walled carbon nanotube-reinforced high-density polyethylene/carbon black nanocomposites using electrical, DSC and positron lifetime spectroscopy techniques. *Polym. Int.* **58**, 775–780 (2009).
- Lisunova, M. O., Mamunya, Y. P., Lebovka, N. I. & Melezhyk, A. V. Percolation behaviour of ultrahigh molecular weight polyethylene/multi-walled carbon nanotubes composites. *Eur. Polym. J.* **43**, 949–958 (2007).



10. Gao, J. F., Li, Z. M., Peng, S. & Yan, D. X. Temperature-resistivity behaviour of CNTs/UHMWPE composites with a two-dimensional conductive network. *Polym.-Plast. Technol. Eng.* **48**, 478-481 (2009).
11. Jiang, S. L. *et al.* Positive temperature coefficient properties of multiwall carbon nanotubes/poly(vinylidene fluoride) nanocomposites. *J. Appl. Polym. Sci.* **116**, 838-842 (2010).
12. Zeng, Y., Ying, Z., Wu, F. Y. & Cheng, H. M. in *Carbon2006, the International Carbon Conference* (Scotland, 2006).
13. Zeng, Y. *et al.* Increasing the electrical conductivity of carbon nanotube/polymer composites by using weak nanotube-polymer interactions. *Carbon* **48**, 3551-3558 (2010).
14. Li, Q., Basavarajiah, S., Kim, N. H., Heo, S. B. & Lee, J. H. Synergy effect of hybrid fillers on the positive temperature coefficient behavior of polypropylene/ultra-high molecular weight polyethylene composites. *J. Appl. Polym. Sci.* **116**, 116-124 (2010).
15. Lu, C. *et al.* Influence of morphology on PTC effect for poly (ethylene-co-butyl acrylate)/nylon6 blends with multiwall carbon nanotubes dispersed at interface and in matrix. *Polym. Bull.* **71**, 545-561 (2014).
16. Pang, H. *et al.* Temperature resistivity behaviour in carbon nanotube/ultra-high molecular weight polyethylene composites with segregated and double percolated structure. *Plast. Rubber Compos.* **42**, 59-65 (2013).
17. Zha, J.-W., Li, W.-K., Liao, R.-J., Bai, J. & Dang, Z.-M. High performance hybrid carbon fillers/binary-polymer nanocomposites with remarkably enhanced positive temperature coefficient effect of resistance. *J. Mater. Chem. A* **1**, 843-851 (2013).
18. He, L. X. & Tjong, S. C. Direct current conductivity of carbon nanofiber-based conductive polymer composites: effects of temperature and electric field. *J. Nanosci. Nanotechnol.* **11**, 3916-3921 (2011).
19. Isaji, S., Bin, Y. Z. & Matsuo, M. Electrical and self-heating properties of UHMWPE-EMMA-NiCF composite films. *J. Polym. Sci., Part B: Polym. Phys.* **47**, 1253-1266 (2009).
20. Isaji, S., Bin, Y. & Matsuo, M. Electrical conductivity and self-temperature-control heating properties of carbon nanotubes filled polyethylene films. *Polymer* **50**, 1046-1053 (2009).
21. Song, Y. H. & Zheng, Q. Electric self-heating behavior of acetylene carbon black filled high-density polyethylene composites. *Polym. Int.* **53**, 1517-1522 (2004).
22. Song, Y. H., Yi, X. S. & Pan, Y. The electric self-heating behavior of carbon black loaded high density polyethylene composites. *J. Mater. Sci. Lett.* **19**, 299-301 (2000).
23. Lu, W., Lin, H. F. & Chen, G. H. Voltage-induced resistivity relaxation in a high-density polyethylene/graphite nanosheet composite. *J. Polym. Sci., Part B: Polym. Phys.* **45**, 860-863 (2007).
24. Song, Y. H. & Zheng, Q. Influence of irradiation crosslinking on the self-heating and conduction of an acetylene carbon black filled high-density polyethylene composite in the electric-thermal equilibrium state. *J. Appl. Polym. Sci.* **110**, 3009-3013 (2008).
25. Song, Y. H. & Zheng, Q. Nonlinear conduction of irradiation-crosslinked high-density polyethylene/acetylene carbon black composites at the electric-thermal equilibrium state. *J. Polym. Sci., Part B: Polym. Phys.* **44**, 1979-1984 (2006).
26. Sandler, J. K. W., Kirk, J. E., Kinloch, I. A., Shaffer, M. S. P. & Windle, A. H. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. *Polymer* **44**, 5893-5899 (2003).
27. Du, J. *et al.* Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/high density polyethylene composites with a segregated network structure. *Carbon* **49**, 1094-1100 (2011).
28. Stauffer, D. & Aharony, A. *Introduction to Percolation Theory*. 2nd edn, 34-40 (Taylor and Francis, 2003).
29. Wu, F., He, X., Zeng, Y. & Cheng, H. M. Thermal transport enhancement of multi-walled carbon nanotubes/high-density polyethylene composites. *Appl. Phys. A* **85**, 25-28 (2006).
30. Zeng, Y., Ci, L. J., Carey, B. J., Vajtai, R. & Ajayan, P. M. Design and reinforcement: vertically aligned carbon nanotube-based sandwich composites. *ACS Nano* **4**, 6798-6804 (2010).

## Acknowledgments

The authors acknowledge financial supports from Ministry of Science and Technology of China (No. 2012AA030303), the Scientific Research Foundation for the Returned Overseas Chinese Scholars of State Education Ministry, the Hundred Talents Program of Chinese Academy of Sciences, and the Fund for Creative Research Groups (No. 51221264). The authors also thank Xinye Liu, Wendong Wu, Long Zhao for their helpful discussion.

## Author contributions

Y.Z. proposed and supervised the project, Y.Z. and J.D. designed the experiments, Y.Z., G.L., J.D. and Z. Y. carried out experiments, Y.Z., H.W., G. Lu, J.D. and C. Liu analyzed data and wrote the manuscript. All the authors participated in discussions of the research.

## Additional information

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Zeng, Y. *et al.* Positive temperature coefficient thermistors based on carbon nanotube/polymer composites. *Sci. Rep.* **4**, 6684; DOI:10.1038/srep06684 (2014).



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-sa/4.0/>