

# Electrochromatic carbon nanotube/ polydiacetylene nanocomposite fibres

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**Chromatic materials such as polydiacetylene change colour in response to a wide variety of environmental stimuli, including changes in temperature, pH and chemical or mechanical stress, and have been extensively explored as sensing devices<sup>1–4</sup>. Here, we report the facile synthesis of carbon nanotube/polydiacetylene nanocomposite fibres that rapidly and reversibly respond to electrical current, with the resulting colour change being readily observable with the naked eye. These composite fibres also chromatically respond to a broad spectrum of other stimulations. For example, they exhibit rapid and reversible stress-induced chromatism with negligible elongation. These electrochromatic nanocomposite fibres could have various applications in sensing.**

Conjugated polymers have been investigated for a number of applications in optoelectronics and sensing<sup>5–7</sup> because the extended  $\pi$ -electron delocalization along their backbones endows them with useful electronic and optical properties. For instance, polydiacetylene (PDA) typically changes colour from blue to red under various external stimuli (including interactions with ligands or changes in temperature, pH, chemical or mechanical stress), and has been explored as a material for chromatic sensors<sup>7</sup>. This colour change is caused by the conformation change of the PDA as a result of these stimuli. More precisely, the increased motional freedom of the PDA side chains caused by the stimuli leads to a more disordered (and less co-planar) polymer structure with a shorter conjugation length. Significant efforts have already been made to add new sensing functionalities to PDA, but, to the best of our knowledge, no current-induced colour change has ever been reported for this material. Although it is difficult to induce conformation changes of pure PDA under electric fields<sup>8,9</sup>, current-induced chromatic behaviour in PDA could have applications in the non-destructive evaluation and monitoring of structures ranging from aircraft to small electronic facilities<sup>10</sup>.

A convenient approach to solving the above dilemma is the formation of nanocomposites. If an electric current is passed through the nanocomposite, the resultant electric fields might be strong enough to induce conformational changes of the PDA molecules, which would lead to a macroscopic colour change. One of the ideal candidates to meet this requirement is the carbon nanotube (CNT)<sup>11–16</sup>. As already extensively explored, nanotubes show excellent electrical conductivities<sup>16</sup>. For instance, long nanotube arrays have been synthesized through chemical vapour deposition<sup>17</sup>, and conductivity of individual multiwalled nanotubes can be as high as  $10^4 \text{ S cm}^{-1}$  at room temperature<sup>18</sup>. These nanotubes may be spun into macroscopic fibres while maintaining excellent

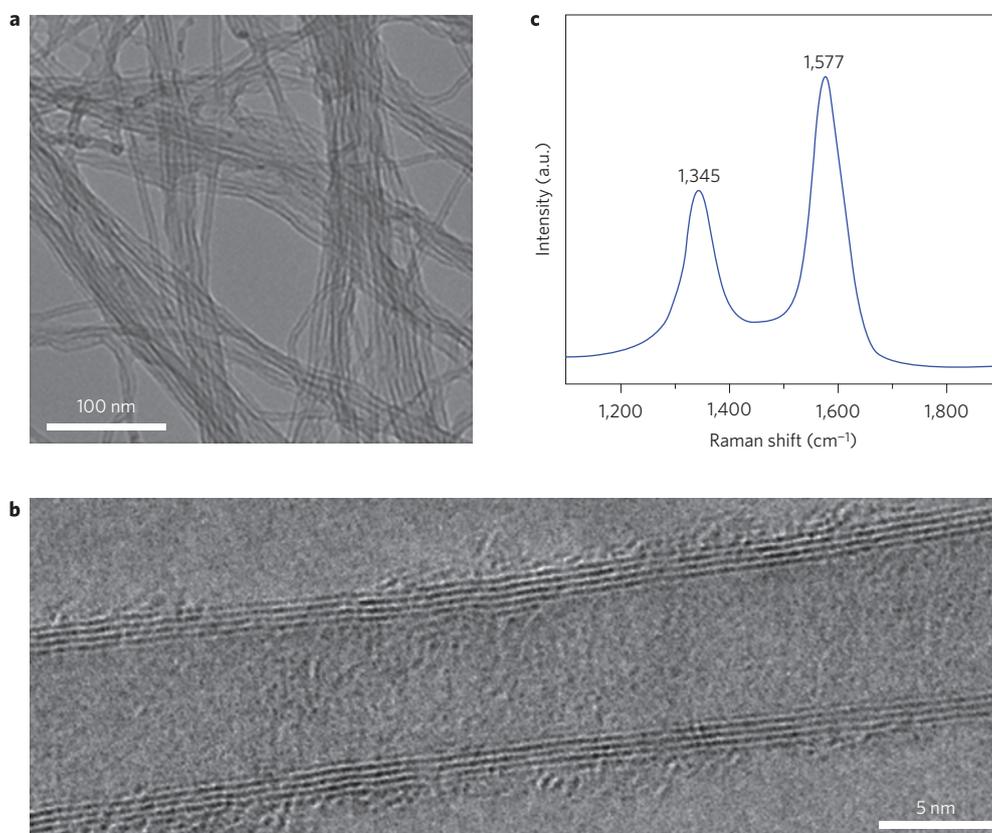
electrical properties<sup>19</sup>. It is therefore the objective of this study to produce a new CNT/PDA composite exhibiting current-induced chromatic changes.

Pure nanotube fibres were spun from nanotube arrays synthesized by a chemical vapour deposition process (Supplementary Fig. S1). Diameters of nanotube fibres can be controlled between 4 and 20  $\mu\text{m}$ , depending on initial ribbon widths during the spinning process. A ribbon is defined as a bunch of nanotubes pulled out of the nanotube array at the beginning of the spinning process. Transmission electron microscopy (TEM, Fig. 1a) and high-resolution TEM (HR-TEM, Fig. 1b) demonstrate a multiwalled structure for these nanotubes, with diameter of  $\sim 10 \text{ nm}$ . A representative Raman spectrum (Fig. 1c) shows a weak peak at  $1,345 \text{ cm}^{-1}$  for the D band and a strong peak at  $1,577 \text{ cm}^{-1}$  for the G band, similar to other reported multiwalled nanotubes<sup>20</sup>. Composite CNT/PDA fibres were then synthesized by directly coating diacetylenic precursors such as  $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$  onto nanotubes, followed by topochemical polymerization of diacetylenic moieties under ultraviolet (UV) light (Supplementary Fig. S2). Figure 2 shows scanning electron microscopy (SEM) images of a CNT/PDA fibre with a uniform diameter of 11  $\mu\text{m}$  along the axial direction. As-synthesized CNT/PDA fibres are blue and can be readily observed by the naked eye<sup>21,22</sup>.

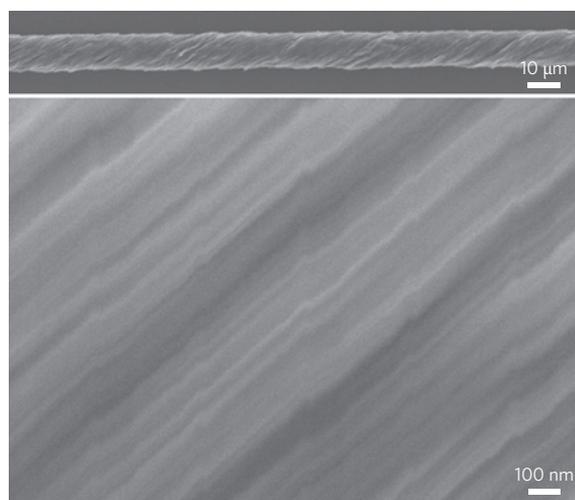
CNT/PDA fibres exhibit high conductivities of between  $1 \times 10^2$  and  $1 \times 10^3 \text{ S cm}^{-1}$  due to the alignment of nanotubes inside them<sup>23</sup>. The temperature dependence of conductivities of CNT/PDA fibres was further investigated by a four-probe approach. As shown in Fig. 3 (also Supplementary Fig. S4), conductivity increases with increasing temperature, which indicates the semiconducting behaviour in CNT/PDA fibres. Two conduction models (the variable range hopping mechanism and the tunnelling conduction mechanism) may be applicable to these composite fibres<sup>23</sup>. According to a previously reported method, electron transport in CNT/PDA fibres is found to be more consistent with the three-dimensional hopping mechanism (Supplementary Fig. S5)<sup>24</sup>. In other words, electrons could not be confined in a one-dimensional channel along the nanotube-aligned direction when a current passes through the fibre. Instead, electrons possibly hop from one localized site to another, or from one nanotube to another. The above behaviour is most likely produced by nanotube defects in composite fibres<sup>25</sup>.

Importantly, CNT/PDA composite fibres rapidly change colour from blue to red in response to an electric current. Figure 4 demonstrates experimental set-ups and chromatic transitions. The minimum current for chromatic transitions of fibres with a diameter

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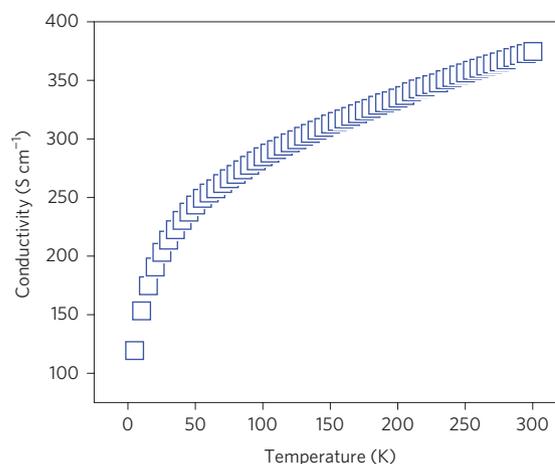


**Figure 1 | Characterization of the nanotubes used to make the CNT/PDA fibres.** **a**, Transmission electron microscopy image. **b**, High-resolution transmission electron microscopy image. **c**, Typical Raman spectrum showing the D band at 1,345 cm<sup>-1</sup> and the G band at 1,577 cm<sup>-1</sup>.



**Figure 2 | Nanotubes are highly aligned in fibres.** Scanning electron microscopy images of a composite CNT/PDA fibre with different magnifications.

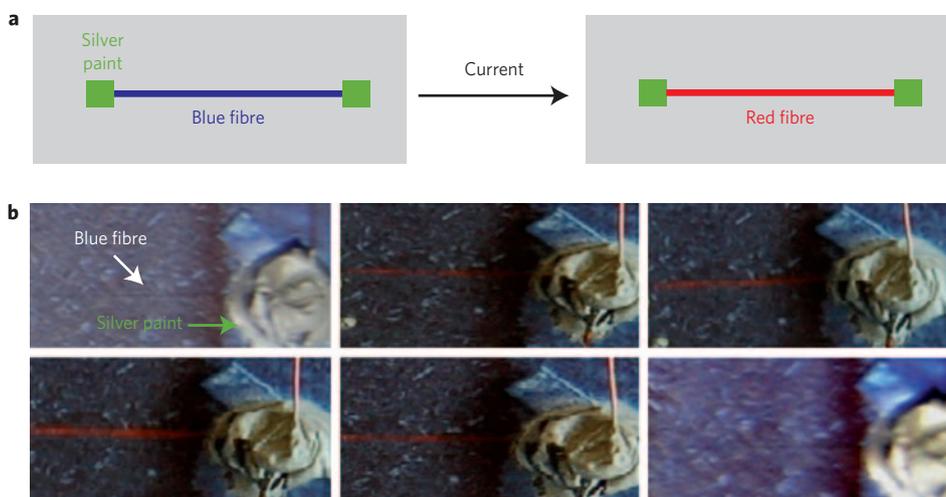
of 11 μm is 10 mA at room temperature. In addition, colorimetric reversibility of CNT/PDA fibres can be controlled by varying the absolute value of the current. For instance, the blue-to-red transition is reversible (Fig. 4b) when current is lower than 30 mA. Such a reversible colour change can continue for cycles (for example, 14 cycles for the fibre in Fig. 4b), which is critical for practical sensing applications. Colorimetric responses, percentages of blue-to-red transitions calculated from UV-vis spectra<sup>21</sup>, are 0–0.3% and 10.9–11.4% for blue and red PDA, respectively. Furthermore, the colour change can respond to current being in ‘ON’ and



**Figure 3 | Electrical properties of a CNT/PDA fibre.** Temperature dependence of conductivity measured by a four-probe method.

‘OFF’ states with a speed of 2 s; that is, blue fibres became red in 2 s when current is passed through and red fibres also switched back to blue in 2 s after the removal of the current. At higher currents, however, the chromatic transition of CNT/PDA fibres is irreversible.

There are several possible causes of current-induced chromatism of composite fibres. It is possible that temperature increases and induces colour changes when current passes through CNT/PDA fibres. However, the following facts may exclude the possibility of thermally induced colour changes. First, PDA colour changes from blue to red start at ~56 °C, and the thermochromatism is irreversible; (Supplementary Fig. S6). In contrast, current-induced chromatism is



**Figure 4 | Chromatic transitions of a composite CNT/PDA fibre in response to an electric current.** **a**, Schematic showing that the colour of the CNT/PDA fibre changes from blue to red when a current is passed through it in a two-probe experiment. **b**, Passing a d.c. current of 10 mA through a CNT/PDA fibre (diameter, 11  $\mu\text{m}$ ) causes a blue fibre (top left) to become red after 1 s (top middle). The current is turned off after 3 s (bottom left), and the fibre becomes blue again after a further 2 s (bottom right). Silver paint was used to hold the CNT/PDA fibres in place and to connect to the external current sources. All experiments were performed at room temperature.

reversible. Second, no temperature increase has been detected in CNT/PDA fibres when passed with a current of 30 mA using an infrared thermometer. Third, to further investigate the electrochromatism, CNT/benzophenone (benzophenone was found to melt at 44  $^{\circ}\text{C}$ ) fibres were fabricated by coating ultrafine benzophenone powder on the outer surface of nanotube fibres. Nanotube/benzophenone fibres before and after having a current of 30 mA passed through them were compared under optical microscopy. No melting was observed for benzophenone that touched the fibres, indicating that the composite fibres must be at a temperature lower than 44  $^{\circ}\text{C}$  (Supplementary Fig. S7); significantly, thermochromatism occurs at  $\sim 56^{\circ}\text{C}$  or higher.

The current-induced colour change in CNT/PDA fibres is more likely to be derived from interactions between nanotubes and polymers and the unique electrical properties enabled by nanotubes. CNT/PDA fibres exhibit high conductivities with three-dimensional hopping conduction; that is, electrons hop from one nanotube to another inside a fibre<sup>24,25</sup>. Therefore, electric fields exist among neighbouring nanotubes, which might result in polarization of COOH groups in side chains and conjugated PDA backbones in neighbouring nanotubes<sup>26</sup>. The above polarizations decrease  $\pi$ -electron delocalization of the PDA backbone, which reflects colour changes of fibres similar to other reported stimuli (Supplementary Fig. S2). In the case of low currents, PDA conformation can return to the original state after removal of current, so the colour change is reversible. However, higher currents may destroy the recovery capability of PDA, leading to irreversible chromatism.

Although a chromatic response to mechanical stress has previously been demonstrated in poly(urethane-diacetylene)<sup>3</sup>, this was achieved with a large level of elongation, which may limit its sensing applications. Nanotubes are the strongest material ever discovered<sup>17</sup>, and nanotube fibres exhibit high mechanical strength<sup>23</sup>. High strengths may provide PDA with mechanochromatism at negligible elongation. This hypothesis was confirmed by experiments. Colour changes in CNT/PDA fibres at high tensile stress were observed using a UV-vis spectrometer. Absorption maxima of blue and red PDAs are located at 600–700 nm and 500–600 nm, respectively. A CNT/PDA fibre with a tensile strength of 0.55 GPa remained blue at tensile stresses lower than 0.48 GPa and suddenly became red beyond this point (Supplementary Fig. S8). If the stress was immediately released on reaching the range 0.48–0.51 GPa, the

red colour reverted to blue. As the tensile strength of this composite fibre is 0.55 GPa, we can readily decide the application range of a composite fibre making use of a colour change achieved under tensile stress.

CNT/PDA fibres also respond chromatically to a wide variety of other environmental stimuli such as mechanical abrasion, and chemical and organic vapour. Composite fibres change colours from blue to red under mechanical abrasion in seconds (Supplementary Fig. S10). Similarly, when heated to a temperature equal to or higher than 56  $^{\circ}\text{C}$ , fibres switch from blue to red in less than a minute. Composite fibres show different degrees of response to chemicals (Supplementary Fig. S11). For instance, on exposure to tetrahydrofuran, *N,N*-dimethyl formamide, *N,N*-dimethyl acetamide and 1-methyl-2-pyrrolidinone the fibres completely change colour. When exposed to styrene, methyl sulphoxide, benzene, toluene and methylacrylate, the fibres partially change colour from blue to red. With water, methanol, ethanol and ethylene glycol, no colour changes have been found. CNT/PDA fibres also change colour in response to organic vapours, such as tetrahydrofuran and *N,N*-dimethyl formamide (Supplementary Fig. S12). In an atmosphere of tetrahydrofuran at 1 atm and room temperature, fibres immediately start to switch from blue to red, but the total transition is completed in  $\sim 30$  min as vapour diffusion into the fibre takes time. Compared with tetrahydrofuran vapour, the response to *N,N*-dimethyl formamide vapour is much slower (for example, two days). It should be noted that abrasion-, chemical- and vapour-induced chromatism are not reversible.

In summary, we have synthesized CNT/PDA composite fibres that reversibly change colour in response to electrical current and mechanical stress with negligible elongation. CNT/PDA fibres can potentially be used as sensing components that can collectively and chromatically respond to the widest environmental stimuli so far. These CNT/PDA composite fibres are very promising for applications in many fields such as sensors, actuators and other electronic devices.

## Methods

Preparation of nanotube fibres has been reported elsewhere<sup>15</sup>. For the fabrication of CNT/PDA composite fibres, diacetylenic precursors were first dissolved in tetrahydrofuran with a concentration of 10  $\text{mg ml}^{-1}$ . Pure nanotube fibres were dipped into the precursor solution, followed by evaporation of solvent at room

temperature. Before polymerization, treated fibres were exposed to the open air in a hood for 24 h. Dry fibres were black, the colour originating from the nanotubes. Diacetylenic moieties were polymerized at room temperature under UV light with a wavelength of 254 nm. Polymerization time varied from minutes to hours, depending on fibre diameters. After polymerization, CNT/PDA fibres became blue.

Nanotubes were characterized by SEM (JEOL 6300FXV operated at 5 kV and Hitachi FE-SEM S-4800 operated at 1 kV) and TEM (JEOL JEM-2100F and Philips CM30 operated at 200 kV). SEM samples were coated with a thin layer of gold/platinum (5 nm) before observation. TEM samples were prepared by dropcasting nanotube/ethanol solutions onto copper grids in the open air. Mechanical tests were performed by a Shimadzu Table-Top Universal Testing Instrument. Nanotube fibres were mounted on paper tabs with a gauge length of 5 mm. Fibre diameter was measured using a laser-diffraction method and further confirmed by SEM. Raman measurements were performed on a Renishaw inVia Reflex with an excitation wavelength of 514.5 nm and laser power of 20 mW at room temperature. UV-vis measurements were recorded on a Shimadzu UV-3150 spectrometer.

Received 22 June 2009; accepted 12 August 2009;  
published online 13 September 2009; corrected online 27  
September 2009

## References

- Motiei, L., Lahav, M., Freeman, D. & van der Boom, M. E. Electrochromic behavior of a self-propagating molecular-based assembly. *J. Am. Chem. Soc.* **131**, 3468–3469 (2009).
- Ahn, D. J. & Kim, J.-M. Fluorogenic polydiacetylene supramolecules: immobilization, micropatterning and application to label-free chemosensors. *Acc. Chem. Res.* **41**, 805–816 (2008).
- Nallicheri, R. A. & Rubner, M. F. Investigations of the mechanochromic behavior of poly(urethane-diacetylene) segmented copolymers. *Macromolecules* **24**, 517–525 (1991).
- Ryu, S., Yoo, I., Song, S., Yoon, B. & Kim J.-M. A thermoresponsive fluorogenic conjugated polymer for a temperature sensor in microfluidic devices. *J. Am. Chem. Soc.* **131**, 3800–3801 (2009).
- Huynh, W. U., Dittmer, J. J. & Alivisatos, A. P. Hybrid nanorod-polymer solar cells. *Science* **295**, 2425–2427 (2002).
- Kim, J. Y. *et al.* New architecture for high-efficiency polymer photovoltaic cells using solution-based titanium oxide as an optical spacer. *Adv. Mater.* **18**, 572–576 (2006).
- Lu, Y. *et al.* Self-assembly of mesoscopically ordered chromatic polydiacetylene/silica nanocomposites. *Nature* **410**, 913–917 (2001).
- Jin, H., Heller, D. A., Kim, J.-H. & Strano, M. S. Stochastic analysis of stepwise fluorescence quenching reactions on single-walled carbon nanotubes: single molecule sensors. *Nano Lett.* **8**, 4299–4304 (2008).
- Dai, H., Wong, E. W. & Lieber, C. M. Probing electrical transport in nanomaterials: conductivity of individual carbon nanotubes. *Science* **272**, 523–526 (1996).
- Lampert, C. M. Chromogenic smart materials. *Mater. Today* **7**, 28–35 (March 2004).
- Yao, Y. *et al.* Temperature-mediated growth of single-walled carbon-nanotube intramolecular junctions. *Nature Mater.* **6**, 283–286 (2007).
- Dalton, A. B. *et al.* Super-tough carbon-nanotube fibres. *Nature* **423**, 703 (2003).
- Li, S., He, P., Dong, J., Guo, Z & Dai, L. DNA-directed self-assembling of carbon nanotubes. *J. Am. Chem. Soc.* **127**, 14–15 (2005).
- Zhou, X. J., Moran-Mirabal, J. M., Craighead, H. G. & McEuen, P. L. Supported lipid bilayer/carbon nanotube hybrids. *Nature Nanotech.* **2**, 185–190 (2007).
- Li, Q. *et al.* Sustained growth of ultralong carbon nanotube arrays for fiber spinning. *Adv. Mater.* **18**, 3160–3163 (2006).
- Bachtold, A. *et al.* Contacting carbon nanotubes selectively with low-ohmic contacts for four-probe electric measurements. *Appl. Phys. Lett.* **73**, 274–276 (1998).
- Zhang, M., Atkinson, K. R. & Baughman, R. H. Multifunctional carbon nanotube yarns by downsizing an ancient technology. *Science* **306**, 1358–1361 (2004).
- Hiura, H., Ebbesen, T. W., Tanigaki, K. & Takahashi, H. Raman studies of carbon nanotubes. *Chem. Phys. Lett.* **202**, 509–512 (1993).
- Sakamoto, M. *et al.* Enhanced electrical conductivity of polydiacetylene crystals by chemical doping and ion implantation. *J. Appl. Phys.* **60**, 2788–2796 (1986).
- Liu, Y., Yu, Z., Zhang, Y., Guo, D. & Liu, Y. Supramolecular architectures of  $\beta$ -cyclodextrin-modified chitosan and pyrene derivatives mediated by carbon nanotubes and their DNA condensation. *J. Am. Chem. Soc.* **130**, 10431–10439 (2008).
- Peng, H. *et al.* Responsive periodic mesoporous polydiacetylene/silica nanocomposites. *J. Am. Chem. Soc.* **128**, 5304–5305 (2006).
- Peng, H. *et al.* Polydiacetylene/silica nanocomposites with tunable mesostructure and thermochromatism from diacetylenic assembling molecules. *J. Am. Chem. Soc.* **127**, 12782–12783 (2005).
- Peng, H., Jain, M., Peterson, D. E., Zhu, Y. T. & Jia, Q. X. Composite carbon nanotube/silica fibers with improved mechanical strengths and electrical conductivities. *Small* **4**, 1964–1967 (2008).
- Peng, H. Aligned carbon nanotube/polymer composite films with robust flexibility, high transparency and excellent conductivity. *J. Am. Chem. Soc.* **130**, 42–43 (2008).
- Li, Q. W. *et al.* Structure-dependent electrical properties of carbon nanotube fibers. *Adv. Mater.* **19**, 3358–3363 (2007).
- Cheng, Q. & Stevens, R. C. Charge-induced chromatic transition of amino acid-derivatized polydiacetylene liposomes. *Langmuir* **14**, 1974–1976 (1998).

## Acknowledgements

This work was supported by the Shanghai Pujiang Program (09PJ1401100) and start-up fund at Fudan University, and partly supported by the US Department of Energy (Los Alamos National Laboratory Directed Research and Development Project). The authors thank M. Jain, J.O. Willis and D.E. Peterson for help with the conductivity measurements and for their critical reading of the manuscript.

## Author contributions

Q.L. contributed materials. X.S., F.C., Y.Z., G.L. and H.P. carried out experiments. X.C., D.C., Y.L., Y.Z. and Q.J. contributed to preparation of the manuscript. H.P. directed the research, analysed the data and wrote the manuscript.

## Additional information

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