RESEARCH PAPER



Ultrafast Electro-Thermal Responsive Heating Film Fabricated from Graphene Modified Conductive Materials

Yun Zhao,¹ Mingming Niu,¹ Fengxin Yang,¹ Yuqiu Jia² and Yuanhui Cheng^{1*}

Flexible electro-thermal heating film has caught great attentions for their efficient energy conversion and easy to customization in many fields. In this work, an ultrafast electro-thermal responsible heating film was fabricated via silk-screen printing method by using graphene modified carbon black based conductive ink. The graphene modified carbon heating film (CHF) was able to reach an equilibrium-state temperature with rapid heating and cooling rate of 5.6 °C/s and 15.6 °C/s, comparing to the unmodified sample (1.01 °C/s and 1.03 °C/s), for the high electrical and thermal conductivity and huge heat exchanging area. The steady temperature of CHF was controllable by changing the amount of graphene. A dramatic enhancement of steady temperature from 38 to 83 °C was controlled by changing graphene amount from 0 to 35 wt.%. The facile fabrication and superior electro-thermal performance of CHF make it feasible to scale up and customization for various heating conditions.

Keywords: Electro-thermal response; Flexible heating film; Graphene; Silk-screen printing

Received 5 February 2019, Accepted 12 March 2019

DOI: 10.30919/es8d501

1.Introduction

With the growing consumption of energy due to the human activities around the world, energy crisis and environment pollution have become serious problems for human society development. Apart from the development of new clean energy resource, converting the existed power in green way and enhancing the converting efficiency are essential to satisfy the great demand of human society.¹⁻³ Electrothermal materials have caught lots of attention since they can covert electricity into heat energy in a clean, efficient and controllable manner.⁴³ The flexible and two-dimension thermal heater fabricated with electrothermal materials have attracted growing interest in case of a vast potential applications such as outdoor display, vehicle window defrosters, heating retaining windows, physical thermal therapy and other heating systems.912 However, the traditional electrothermal materials, such like silver nanowires,13 Fe-Cr-Al based alloy,10 indium tin oxide (ITO),¹⁴¹⁵ have plenty drawbacks like complicate fabricate process, low transparency, large weight, or limited material source, sensitive to acid and base, brittle substrates and etc. These limitations impede the applications of conventional electrothermal materials but remain lots of opportunities to develop new materials. Nowadays carbon based conductive ink (CCI), which is mainly composed with carbon nanomaterials, has employed for flexible heating film for the low cost, robustness, easy fabrication, long-term stability and safety.¹⁶⁻²⁰ However, most of these carbon based inks are less thermal and electrical conductive comparing to metal based materials, thereby the

²Guangdong Warmtact Electrical Heating Technology Co. Ltd., Foshan, Guangdong, 528139 China ***E-mail:** chengyh@mail.buct.edu.cn electro-thermal conversion efficiency and heating performance are not as good as metal materials. The controllable electrical and thermal conductivity of carbon ink still remains as the crucial challenge for efficient film heater fabrication. Hence improving the electrical and thermal conductivity of CCI by adding highly conductive materials has become the most effective way to regulate its performance.

Carbon nanotubes (CNTs) and graphenes possess excellent thermal, electrical and optical properties as studied by many researchers. Especially the 2D structured graphene exhibits an extraordinary high thermal conductivity of 5300 W·m⁻¹·k⁻¹ (3500 W·m⁻¹·k⁻¹ for CNTs).²¹⁻²² The thermal conductivity of graphene, K, is reported relating to the graphene size and crystallinity.²³ The thermal conduction of graphene is governed by phonon diffusion from lattice vibrations of its covalent sp² bonding network.²³⁻²⁴ Therefore many ways have been tried to synthesize large size graphene nanosheets for better conductivity product.²⁵⁻²⁷ Ballmilling treatment is a solid approach to efficiently exfoliate graphite into graphene or graphene nanoplatelets with high yield and good quality. The feasibility of introducing functional groups on the surface or at the edge of graphene and nanoplatelets are of great interesting in improve the materials' electronic properties.²⁸⁻³⁰ The outstanding thermal conductivity endows graphene very fast response to temperature. As a result, very homogeneous temperature distribution will be achieved on the surface in very short time. It is critical parameter in film heater for many applications. In addition, the 2D conjugated honeycomb lattice structure results in excellent mechanical properties, which leads to robust products for mechanical applications. These merits of graphene make it of great potential as additives to improve the electrothermal materials' conductivity.

Herein, a facile silk-screen printing method is used to fabricate flexible heating film with commercial available carbon based conductive ink. To satisfy the demand of fast heating rate and homogeneous temperature distribution in various application conditions, we used highly conductive graphene particles prepared from ball-milling as

¹State Key Laboratory of Organic-Inorganic Composites. College of Chemical engineering. Beijing University of Chemical Technology, Beijing 100029 China

additive to improve the electrical and thermal conductivity of CHF. The electro-thermal response and steady temperature of CHF were strongly promoted and controlled by adding different amount of graphene. The superior performance along with the facile customization method make the graphene modified CHF of great potential in various heating conditions.

2.Experimental section

2.1 Materials and equipments

Carbon conductive inks were obtained from Nuanfeng Co. Ltd (China). Graphite powders (300 mesh, 99.95 wt.%) were purchased J&K Scientific Co., Ltd. Polyethylene terephthalate (PET) films were purchased from local market.

Edge-carboxylated graphene (ECG) were prepared via ball-milling process according to the reported work with little modification.²⁸ Briefly, 5 g graphite powders were put into a stainless steel tank with zirconia balls (5 mm in diameter). Then the reactor was gently blown with carbon dioxide for 30 min to remove the air. After that the reactor was sealed and pressurized with carbon dioxide at 1.5 Mpa. The graphites was milled at 500 rpm for 48 h to produce ECG. The products were washed with HCl (1 M) and water and dried at 70 °C. ECG was further treated at 1000 °C under argon atmosphere for 3 h to get the final graphene particles. The high temperature treated ECG (HECG) and CCI were thoroughly mixed in vacuum mixer to form the printing carbon composite.

2.2 Fabrication of CHF

The CHF was fabricated by silk-screen printing method as illustrated in Scheme 1. The carbon composites were prepared by adding different amount HECG (0 wt.%, 5 wt.%, 10 wt.% 20 wt.%, 35 wt.%) into the CCI ink and thoroughly mixed. The mixture was then poured on the silk-screen and followed with squeegee printing to transfer the mixture on the surface of PET substrates. The mixture could be printed into different patterns on the PET surface by using patterned silk-screen as mask. In order to seal the CHF for further commercial applications, linear patterns were selected in this work for high heat exchange area and sufficient bonding between two PET films. After curing at 60 °C for 2 h, the film heater were taken out from the oven for further analysis. The different film heater were donated regarding to the HECG amount as 0CHF, 5CHF, 10CHF, 20CHF and 35CHF, respectively.

2.3 Characterizations

Scanning electronic microscope (SEM, HITACHI S-4700, Japan) was used to characterize the microstructures of samples. X-ray diffraction (XRD, 2500VB2, Japan) was used to analyze the crystallinity of different materials. Elemental analysis (EA) were conducted on vairo EL CUBE elementar Analysensysteme, Germany. X-ray photoelectron spectroscopy (XPS, ESCALAB 250, THERMO VG, America) was used to analyze surface elements. Fourier transform infrared spectroscopy (FTIR) were performed on Bruker Vertex-70V, Germany. Raman spectra were performed on a LabRAM ARAMIS Raman confocal microscope (HORIBA Jobin Yvon). The surface morphology of the graphene deposited on silicon wafer was characterized by atomic force microscopy (AFM, AFM5500, Agilent, America). Nitrogen adsorption isotherms were carried out on Micromeritics ASAP2460 instrument at 77 K using liquid nitrogen bath. Specific surface area was calculated using Brunauer–Emmett–Teller (BET) model.

3. Result and discussion

The prepared HECG was firstly characterized as shown in Fig. 1. The Raman spectrum displays a prominent D peak at 1310 cm⁻¹ and G peak at 1583 cm⁻¹. The D peak is from the defectives of graphene created by ball milling. The G band corresponding to the first-order scattering of the E2g mode. The graphitization degree depending on the amount of defects and disorder structures can be simply evaluated through the I_p/I_g ratio (the intensity ratio between the D peak and the G peak). I_p/I_G ratio of the obtained graphene is about 1.2, which suggests significant edge functionalization during the ball-milling process and low graphitization degree of HECG. XRD pattern shows a very broad band in the range from 15-30° in the received HECG (Fig. 1B), suggesting a high degree of edge expansion in solid state grapheme particles.²⁸ The EA result indicates that the HECG composed with about 0.91% O and 93.72% C, which confirms the highly carbonized graphene particles (Fig. 1C). The XPS results demonstrated 81.58 % C and 18.42 % O on the HECG surface, which demonstrated an oxidized surface comparing to total elements distribution. High resolution XPS spectrum of C 1s can be deconvoluted to three components corresponding to C-C, C-O and C=O groups as indicated in Fig. 1D (inset). The C-O and C=O were mainly the unremoved -COOH and the absorbed O2 and H2O. The nitrogen adsorption and desorption thermal plot was the typical physical adsorption behavior of lager pore materials, which resulted in smaller BET surface area (581 $m^2 \cdot g^{-1}$) comparing to the theoretical specific surface area of single layered graphene (~2600 $\text{m}^2 \cdot \text{g}^{-1}$). It might be because the graphene stacked to several layers (~5 nm thick) as analyzed by AFM (Fig. 1F).

After curing at 60 °C for 2 h, the carbon mixture was strongly adhered on the surface of PET. The carbon composite was homogeneously transferred onto PET surface by silk-screen printing method for its applicability for various surfaces including flat or hook surface. The flexibility of the silk-screen make it feasible to closely



Scheme 1 Fabrication of CHF via silk-screen printing method.

attach to PET surface, therefore the patterns were precisely transferred onto PET. Besides it enable to edit the patterns to increase or reduce the size, which is meaningful for scaling up. The surface structure of different CHF were characterized by SEM as shown in Fig. 2. The pure CCI contains lots of particles around hundreds micro-meters embedded inside the ink (Fig. 2A). Fig. 2B~E are the surfaces of carbon composites with 5 wt.%, 10 wt.%, 20 wt.% and 35 wt.% HECG, respectively. It is clear that many holes formed after adding the HECG particles in the CCI ink. The dense structure of carbon ink had become

loose with the HECG amount increasing. After printing and curing, all CHF exhibit very homogeneous patterns on PET surface for the facile control of silk-printing. All the samples have similar printing thickness about 20 μ m. The reason might be that the silk-screen controlled the thickness of carbon composite during squeegeeing. Besides the 35CHF expressed the darkest black color comparing to other samples. It is because the large amount of black HECG changes the surface colour as shown in Fig. 2F.

The specific resistance of different samples were measured by four-



Fig. 1 Characterizations of HECG. Raman spectrum (A), XRD pattern (B), EA analysis (C), XPS spectrum (D), BET plots (E) and AFM image (F).



Fig. 2 SEM images of different heating film with various HECG amount from 0 to 35 wt.%. 0CHF (A), 5CHF (B), 10CHF (C), 20CHF (D) and 35CHF (E), scale bar 500 nm. Optical image of 35CHF (F), scale bar 5 cm.

point probe method to evaluate their conductivity. The results demonstrate that the specific resistance dramatically decreased as the amount of HECG increasing (Fig. 3A), which indicates that the adding HECG strongly enhanced the conductivity of CHF and the higher HECG amount result high conductive heater. The safe working voltage of different CHF were measured with direct-current power as shown in Fig. 3B. All the samples showed very stable properties below 10 V, which indicates a safe running at low power. Base on the equation 1,

$$R = U/I \tag{1}$$

where *R* is resistance, *U* is the applied voltage, and *I* is the current), we can calculate the resistance from Fig. 3B. The resistance decreased while the content of HECG increased in the composite same as specific resistance, and the 35CHF has the lowest resistance about 58 Ω . Further, when the input voltage increased, the current of two samples, 10CHF and 35CHF, display slight inflection at 30 V. The resistance of 10CHF slightly increased while 35CHF gently decreased. The reason of resistance change might be that the heat changes the microstructure of the composite. Especially, when the driving voltage increased up to 50 V, the plenty heat converted from electricity melted the PET substrates with holes in 35CHF. The product stop heating after the patterns were broken, hence the danger of fire breaking out is prevented as well. It makes the CHF very safe for commercial applications. However the

rate working voltage for all of the samples should be set below 50 V for safety.

To evaluate the electro conversion of different samples, same direct current power of 10 watts was applied to the device, and their response were recorded by infrared camera (FLIR T660). After switching on the power, the response time, which is defined as the time required to reaching 90 % of the steady-state temperature, is less than 100 s for all the products, indicating a fast thermal response characteristic (Fig. 4A).⁵ Once the power was cut off, the temperature of CHF fell back to room temperature again at an equally high speed as ramping. At the same driving power of 10 W, the 0CHF, 5CHF, 10CHF, 20CHF and 35CHF can reach a steady-state temperatures of 38, 73, 74, 75 and 83 °C, respectively, according to the time dependence temperature plot (Fig. 4A). The steady-temperature of CHF is an equilibrium-state between electrical heating and environmental heat exchange. Because all of the CHF samples had same surface area for heat exchange and the electrothermal performance was measured at the same environment, the reason for different steady-temperature should be the different electro and thermal conductivity of CHF. The 35CHF showed the highest temperature for its highest conductivity among these samples. In Joule heating, the electrical power follows equation 2,

$$P = U^2 / R \tag{2}$$



Fig. 3 The specific resistance (A) and resistance evolution (B) of different samples.



Fig. 4 The electrothermal performance of flexible heater.

where P is the input power, U is the driving voltage and R is the resistance of CHF. When the input power is kept as constant, the decline of resistance will result in the reduction of driving voltage. The low driving voltage is more safe in application as well as reduces the cost of power equipment.

The pure CCI (0CHF) showed very slow heating and cooling rate of 1.01 °C/s and 1.03 °C/s (Fig. 4B). On the contrary, the heating and cooling rate of HECG modified composites dramatically increased, especially the 35CHF sample showed 5.6 °C/s for heating and 15.6 °C/s for cooling (Fig. 4B). The result indicates that the HECG strongly enhanced the electro-thermal response. The reason for the fast electrical and thermal response relies on the super electrical and thermal conductivity of HECG, which strongly promotes the performance of CCI.

In addition, we used IR camera to record the heat distribution of CHF. Fig. 5 are the IR images of different samples with steady temperature at 10 W. As can be seen, the heat distribution is quite homogeneous for all CHF. It indicates the silk-screen printing is a facile way to produce very homogeneous patterns on PET. As a result, the CHF has homogeneous temperature distribution. Besides the 35CHF shows the brightest colour, which represents the highest temperature and consists with the resistance measurement. By simply designing the patterns of heating materials and shapes of film heater, the HCF is feasible to machine into different products for various heating application such as house warmer.



Fig. 5 The IR images of different samples with steady temperature under 10 W power.

Conclusions

In this paper, we have proposed a facile way to fabricate ultrafast electro-thermal responsive heating film with carbon based materials via silk-screen printing method. The facile fabrication paves the way to massively prepare various patterned flexible heater for diverse applications. The conductivity and electro-thermal conversion performance of CCI is dramatically promoted by HECG for its superior electrical and thermal properties. The modified 35CHF sample exhibits the fastest heating and cooling rate of 5.6 °C/s and 15.6 °C/s and a quite high steady-temperature of 83 °C respect to its lowest resistance and huge heat exchange surface area. The ultrafast electro-thermal responsive behavior of CHF make it promising in house warming, wearable heating cloth, portable device and so on.

Acknowledgements

The authors are grateful for the support and funding from the National Key Research and Development Program of China [2017YFA0206500]; NSF of China [21606015, 51502012; 21676020; 21620102007]; Beijing Natural Science Foundation [17L20060, 2162032]; Young Elite Scientists Sponsorship Program by CAST [2017QNRC001]; The Startup fund for talent introduction of Beijing University of Chemical Technology [buctrc201420; buctrc201714]; Talent cultivation of State Key Laboratory of Organic-Inorganic Composites; Distinguished scientist program at BUCT [buctylkxj02] and the "111" project of China [B14004].

Reference

- Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, 44, 2060-2086.
- R. Amirante, E. Cassone, E. Distaso and P. Tamburrano, *Energy Convers.* Manage., 2017, 132, 372-387.
- 3. D. Champier, Energy Convers. Manage., 2017, 140, 167-181.
- S. P. Alpay, J. Mantese, S. Trolier-McKinstry, Q. Zhang and R. W. Whatmore, MRS Bull., 2014, 39, 1099-1111.
- 5. D. Janas and K. K. Koziol, Nanoscale, 2014, 6, 3037-3045.
- Y. Zhou, X. Wang, X. Liu, D. Sheng, F. Ji, L. Dong, S. Xu, H. Wu and Y. Yang, *Carbon*, 2019, **142**, 558-566.
- W. Wu, X. Huang, K. Li, R. Yao, R. Chen and R. Zou, *Appl. Energ.*, 2017, 190, 474-480.
- 8. R. Chen, R. Yao, W. Xia and R. Zou, Appl. Energ., 2015, 152, 183-188.
- J. H. Kim, B. Du Ahn, C. H. Kim, K. A. Jeon, H. S. Kang and S. Y. Lee, *Thin Solid Films*, 2008, 516, 1330-1333.
- Z. P. Wu and J. N. Wang, *Physica E Low Dimens. Syst. Nanostruct.*, 2009, 42, 77-81.
- T. J. Kang, T. Kim, S. M. Seo, Y. J. Park and Y. H. Kim, *Carbon*, 2011, 49, 1087-1093.
- 12. R. Zhou, P. Li, Z. Fan, D. Du and J. Ouyang, J. Mater. Chem. C, 2017, 5, 1544-1551.
- 13. S. Yao, J. Cui, Z. Cui and Y. Zhu, Nanoscale, 2017, 9, 3797-3805.
- J. Ederth, P. Johnsson, G. Niklasson, A. Hoel, A. Hultåker, P. Heszler, C. Granqvist, A. Van Doorn, M. Jongerius and D. Burgard, *Phys. Rev. B*, 2003, 68, 155410.
- 15. K. Im, K. Cho, J. Kim and S. Kim, Thin Solid Films, 2010, 518, 3960-3963.
- 16. J. Ning, L. Hao, M. Jin, X. Qiu, Y. Shen, J. Liang, X. Zhang, B. Wang, X. Li and L. Zhi, *Adv. Mater.*, 2017, **29**, 1605028.
- C. Phillips, A. Al-Ahmadi, S. J. Potts, T. Claypole and D. Deganello, J. Mater. Sci., 2017, 52, 9520-9530.
- L. R. Pahalagedara, Induni W. Siriwardane, N. D. Tissera, R. N. Wijesena and K. M. N. de Silva, RSC Adv., 2017, 7, 19174-19180.
- M. Hatala, P. Gemeiner, M. Hvojnik and M. Mikula, J. Mater. Sci. Mater. Electron., 2018.
- 20. J. T. Han, B. K. Kim, J. S. Woo, J. I. Jang, J. Y. Cho, H. J. Jeong, S. Y. Jeong, S. H. Seo and G. W. Lee, ACS Appl. Mater. Interfaces, 2017, 9, 7780-

7786.

- A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, *Nano Lett.*, 2008, 8, 902-907.
- 22. E. Pop, D. Mann, Q. Wang, K. Goodson and H. Dai, *Nano Lett.*, 2006, 6, 96-100.
- 23. L. Peng, Z. Xu, Z. Liu, Y. Guo, P. Li and C. Gao, *Adv. Mater.*, 2017, 29,1700589.
- 24. A. C. Ferrari and D. M. Basko, Nat. Nanotechnol., 2013, 8, 235-246.
- S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558-1565.
- 26. S. Pei and H. M. Cheng, Carbon, 2012, 50, 3210-3228.

- 27. S. Tian, P. He, L. Chen, H. Wang, G. Ding and X. Xie, *Chem. Mater.*, 2017, 15, 6214-6219.
- 28. I. Y. Jeon, Y. R. Shin, G. J. Sohn, H. J. Choi, S. Y. Bae, J. Mahmood, S. M. Jung, J. M. Seo, M. J. Kim, D. Wook Chang, L. Dai and J. B. Baek, *Proc. Natl. Acad. Sci. USA.*, 2012, **109**, 5588-5593.
- 29. J. Xu, I. Y. Jeon, J. M. Seo, S. Dou, L. Dai and J. B. Baek, *Adv. Mater.*, 2014, **26**, 7317-7323.
- I. Y. Jeon, H. J. Choi, M. Choi, J. M. Seo, S. M. Jung, M. J. Kim, S. Zhang, L. Zhang, Z. Xia, L. Dai, N. Park and J. B. Baek, *Sci Rep.*, 2013, 3, 1810.

Publisher's Note Engineered Science Publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.