Journal of Materials Chemistry A
Journal of Materials Chemistry A
Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Communication

# Flexible, Sandwiched High-Performance Super-Insulation Fabric†

**Fan Bai, Juntao Wu*, Guangming Gong, and Lin Guo***

**Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX**

**DOI: 10.1039/b000000x**

**The rapid development of modern technology has put forward higher requirements on thermal insulation materials in many fields. Due to the inevitable defects of common insulation materials, a novel super-insulation material with high performance should be explored. In this article, a flexible, sandwiched super-insulation polyimide (PI) fabric has been designed and fabricated by using an electrohydrodynamics jet technology simply. This unique sandwiched fabric possessed a ultra-low thermal conductivity (16.7 mW·m$^{-1}$·K$^{-1}$), excellent mechanical property and wide operating temperature range. Furthermore, it still has some other multifunction, such as great cryogenic resistance, self-extinction and thermal stability. Such sandwiched PI fabric with remarkable integrated performance will have a potential engineering application in harsh conditions, such as the aerospace field.**

With the development of modern technology, the demand of high-performance thermal insulation materials is becoming more urgent in many fields, such as the extravehicular activity (EVA) suits or flexible thermal protection systems (TPS) in the aerospace applications.[1-3] However, in most cases, the common thermal insulation materials can not meet the harsh requirement, so that a kind of super-insulation materials with remarkable integrated performance will be the next generation of exploration.[4,5] Due to the ultra-low thermal conductivity and extra light weight, the super-insulation material has gained widespread attention around the world.[6-8] This unique material can be divided into two categories, inorganic and organic. As a representative of inorganic insulation material, silica aerogels possess a high porosity of more than 90% and a ultra-low thermal conductivity. Nevertheless, because of the weak binding force between silica particles, the silica aerogel monoliths are quite fragile, which inevitably hinders its applications.[9-11] On the other hand, for most organic aerogels and foams, the poor thermal stability in high temperature and brittleness in low temperature are hard to overcome simultaneously.[12,13] Thus, exploring a kind of flexible or even folding super-insulation materials with wide operating temperature has become an attractive topic of the next generation of thermal insulation industry.

With a rigid molecular chain structure, polyimide (PI) is a kind of high-performance polymer with excellent thermal, mechanical and electrical properties,[14,15] so that it can be an attractive candidate for thermal insulation materials. To this end, several PI aerogels with low thermal conductivity and density have been fabricated by using supercritical drying technology, vacuum freeze drying method and so on.[16-21] However, it should be noted that the complexity and time-consuming of preparation process hamper its applications, so that a more simple preparation technology should be developed. Electrohydrodynamics jet technology is an efficient and low-cost method to prepare superfine fibers and micro/nanometer spheres with different hierarchical structures.[22,23] It has been reported that electrospun fibers also could be used as insulation materials with high porosity and low thermal conductivity at room temperature.[24-27] But, owing to the subsize of the electrospun fibers, good mechanical property has become a big challenge to overcome. Thus, a type of unique optimized structure ought to be designed and fabricated to improve the integrated performance of the insulation materials.

To this end, we have designed a fibers/spheres/fibers (FSF) sandwich structure, which includes a layer of porous spheres and two layers of nanogrooved fibers, expecting to obtain a kind of high-performance super-insulation material. Researches have revealed that the small size pore structure (<70nm, the average free path of air molecules) could limit the collision of air molecules and reduce the convection heat transfer sequentially,[28,29] so that the porous PI spheres can be prepared by using electrospray technology. In order to maintain the

* Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education School of Chemistry and Environment,
Beihang University,
Beijing 100191 (P. R. China)
E-mail : wjt@buaa.edu.cn; guolin@buaa.edu.cn
†Electronic supplementary information (ESI) available: Experimental details, Scheme S1, Fig. S1-S2, Movie 1-2
See DOI: 10.1039/xxxx

freestanding property of the prepared porous spheres, electrospun PI fibers can be utilized to form a FSF sandwich structure. What is more, the introduction of nanogroove structure will increase the interfacial interaction between the PI fibers, resulting in the increase of mechanical property.[30] Here, by using electrohydrodynamics jet technology and a simple sacrificial template method, we have fabricated a flexible sandwiched super-insulation PI fabric. This unique super-insulation material possessed excellent integrated performance, such as ultra-low thermal conductivity, good mechanical property and cryogenic resistance. So this sandwiched PI fabric had a promising application in some harsh conditions.

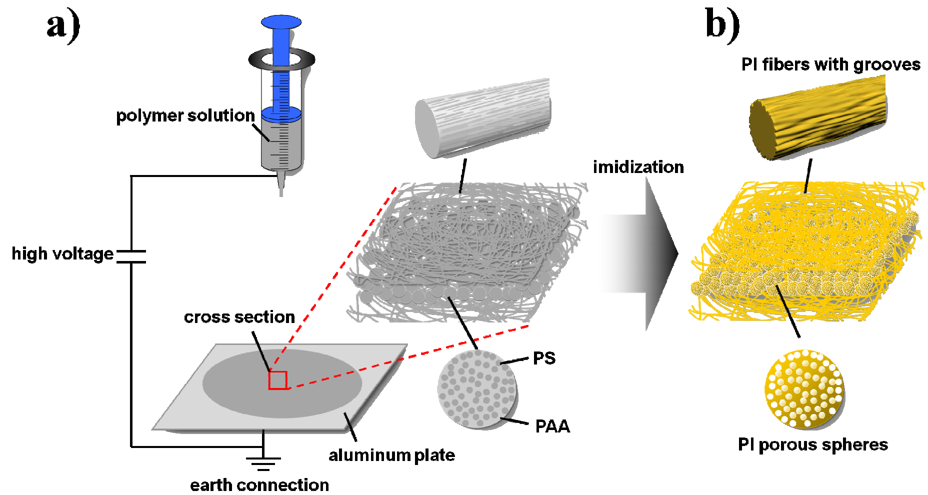


**Figure 1.** Fabrication procedure of the FSF sandwiched PI fabric. (a) Two different concentrations of PAA-PS mixed solutions (15 wt% and 2 wt%) were alternately electrospun and electrosprayed to form a kind of sandwich structure. (b) A high-temperature treatment was taken to remove the sacrificial PS for the formation of porous spheres and nanogrooved fibers.

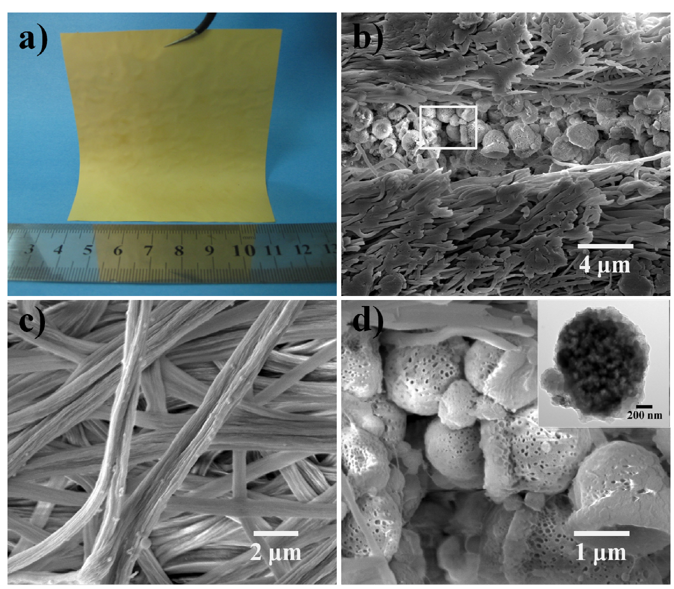


**Figure 2.** Morphologies of the prepared FSF sandwiched PI fabric. (a) Optical image of the fabric. (b) Cross section SEM image of part a. (c) SEM image of the electrospun nanogrooved PI fibers. (d) Enlarged SEM image of the porous spheres in part b. Inset: TEM image of a porous PI sphere.

A simple sacrificial template method, which has been illuminated in our previous work,[31] was utilized to produce porous structure for electrosprayed PI spheres and nanogroove structure for the electrospun PI fibers. Two different concentrations of the mixed solutions consisted of sacrificial template polystyrene (PS) and poly(amic acid) (PAA, the precursor of PI, as shown in Scheme S1 in the supporting information†) were prepared. The high-viscosity solution was first electrospun into fibers layer on the collected electrode, and the low-viscosity solution was then electrosprayed into spheres layer on the fibers. At last, another fibers layer was prepared to cover the spheres, generating a FSF sandwich structure. During the fabrication process, the sacrificial PS could distribute in the composite fibers and spheres uniformly. After a following thermal imidization process, the PS would be decomposed, so that numerous nanogrooves and pores could be left behind on the fibers and spheres respectively (see ESI† for details experimental procedures). Namely, a sandwiched PI fabric composed of porous spheres and nanogrooved fibers was obtained. The whole fabrication process was shown in Figure 1.

The optical and cross section morphologies of the sandwiched PI fabric was shown in the Figure 2. An around 7×7 cm fabric was produced, and it presented good behaviour at the room temperature (as shown in Figure 2a). Looking from the SEM image of cross section, we could clearly observe a sandwiched structure, two fiber-layers on both sides and one sphere-layer in the middle, which had no interspace between fiber-layer and sphere-layer. Obviously, the electrospun PI fibers got numerous nanogrooves on the surface by sacrificial PS, and the electrosprayed PI spheres got nanometer pores both on the surface and inside uniformly (as shown in inset TEM image of Figure 2). The porous PI spheres possessed an average diameter of about 1.6 ± 0.2 μm (as shown in the Figure S1a†), and accumulated with each other tightly. Moreover, it was worth to be mentioned that the thermal imidization process not only could decompose the sacrificial PS, but fuse the interface between fibers and spheres in some degree to obtain a freestanding material.

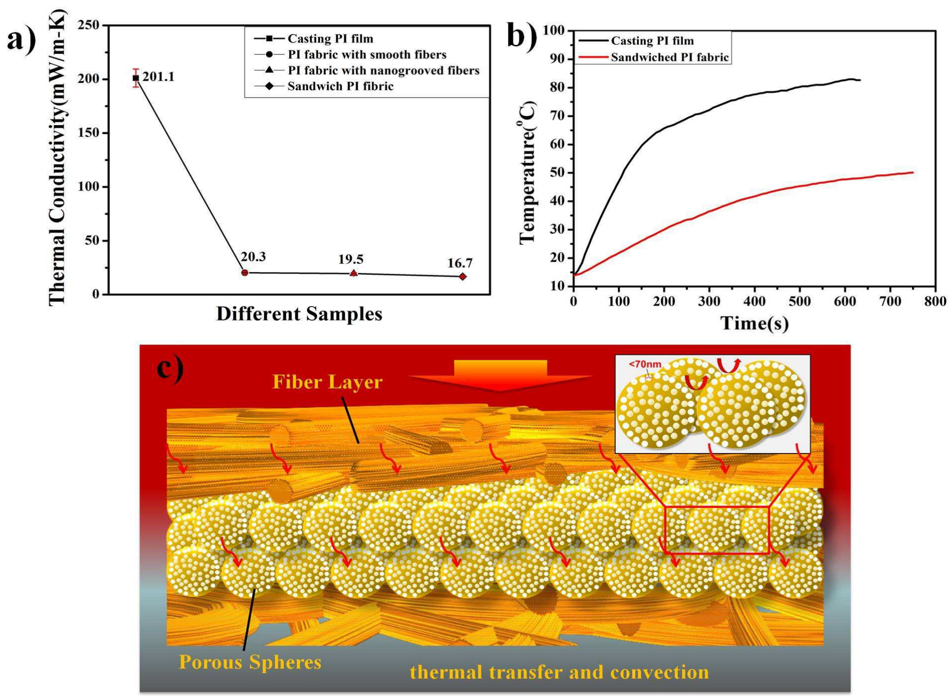


**Figure 3.** Characterizations and mechanism of thermal insulation performance. (a) Thermal conductivities and (b) apparent thermal insulation performance of the casting PI film, PI fabric with smooth fibers, PI fabric with nanogrooved fibers and sandwiched PI fabric. (c) Schematic diagram of the heat transferring mechanism of the sandwiched PI fabric.

Thermal conductivities and intuitionistic thermal insulation performance of the prepared sandwiched fabric were measured at room temperature. For comparison, other one casting PI film and two electrospun PI fabrics with smooth and nanogrooved fibers, were tested under the same conditions. As shown in Figure 3, the original conductivity of casting PI film was as high as 201.1 $mW \cdot m^{-1} \cdot K^{-1}$. After the introduction of nanogrooved fibers and porous spheres, the thermal conductivity of the FSF sandwiched PI fabric dropped sharply to 16.7 $mW \cdot m^{-1} \cdot K^{-1}$, which was even in the same order of magnitude with that of silica aerogel (<20 $mW \cdot m^{-1} \cdot K^{-1}$). On the other hand, in the comparison with the other two electrospun fabrics, the introduction of nanogroove structure and porous spheres could both reduce the thermal conductivities, confirming that the unique sandwich structure and hierarchical micro/nanometer structures could decrease the heat transferring effectively. Furthermore, an apparent heat insulation performance was measured at room temperature (as described in the experimental section). As the time progressed, the cryosurface temperatures of the casting PI film and sandwiched PI fabric could hold an approximate 30 °C gap (as shown in Figure 3b). In order to display the thermal-insulation property visually, the sandwiched fabric was placed onto a heated metal plate, and water droplets were dripped on the surface of fabric and metal plate, respectively. After a few seconds, the water on metal plate was boiled and evaporated violently. While the sandwiched fabric could protect the water droplet from boiling, showing a great heat-proof performance (seen the movie 1 in ESI†). This excellent thermal insulation performance of sandwiched PI fabrics could be explained as follows: when the heat flow come across the fiber-layer, the nanogroove structure on the fibers could largely increase the heat transfer path, resulting in a low conduction transfer. The average diameter of fibers was around 0.75 μm (as shown in the Figure S1b), and this nanometer electrospun fibers could absorb, scatter and eliminate most of radiation transfer. As the heat flow was slowed down by fiber-layer, the compact porous PI spheres could play an important role in the thermal insulation. For the porous PI spheres, the pores size was mostly around 50 nm (as shown in the Figure S1c), which was smaller than the average free path of air molecules, so that it could limit the collision of air molecules and reduce the heat convection. Thus, the combination of porous structure, nanogroove structure and sandwich structure endowed this PI fabric with a ultra-low thermal conductivity and excellent thermal insulation performance.

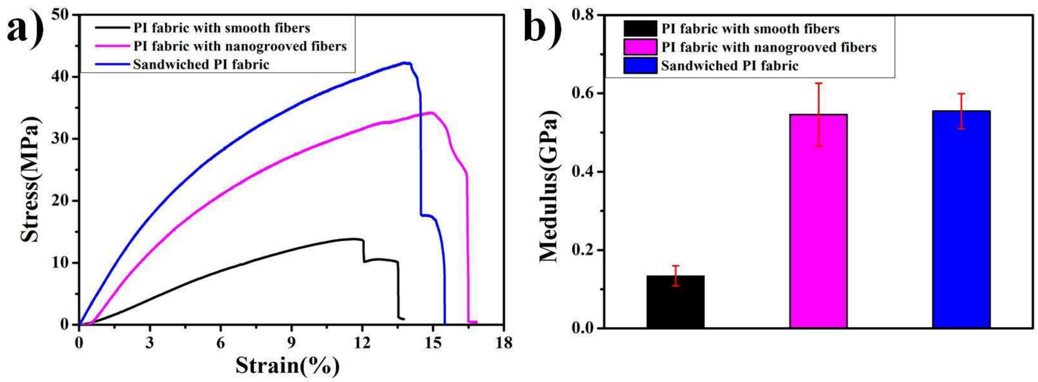


**Figure 4.** Mechanical properties of the PI fabric with smooth fibers, with nanogrooved fibers and the sandwiched PI fabric. a) Stress-strain curves and b) Young modulus of the three fabrics.

The further highlight of this sandwiched super-insulation PI fabric is its excellent mechanical property. As a comparison, other two PI fabrics with smooth fibers and nanogrooved fibers were both measured under the same conditions (as shown in Figure 4). The tensile strength of sandwiched PI fabric could reach 42±3 MPa, and the Young Modulus was as high as 555±45 MPa, which is simultaneously 3 and 4.1 times higher than that of smooth fibers fabric with 14±2 MPa and 134±26 MPa, respectively, indicating a good tensile property. This result could be explained as follows: During the drawing process, the electrospun fabric would go through two loading stages: the rubbing action between fibers and tensile action of fibers. For the smooth fibers, the interaction between fibers is a kind of point to point weak contact, which can only provide little rubbing action. Nevertheless, the introduction of nanogroove structure can increase the contact area between fibers largely, which leads to an improvement of interfacial interactions. This kind of interfacial action can make much contribution to the rubbing actions, so that the tensile strength could be increased multiply. So, this sandwiched fabric have a good tensile strength and elongation at break (＞10%), which was much important for insulation materials.

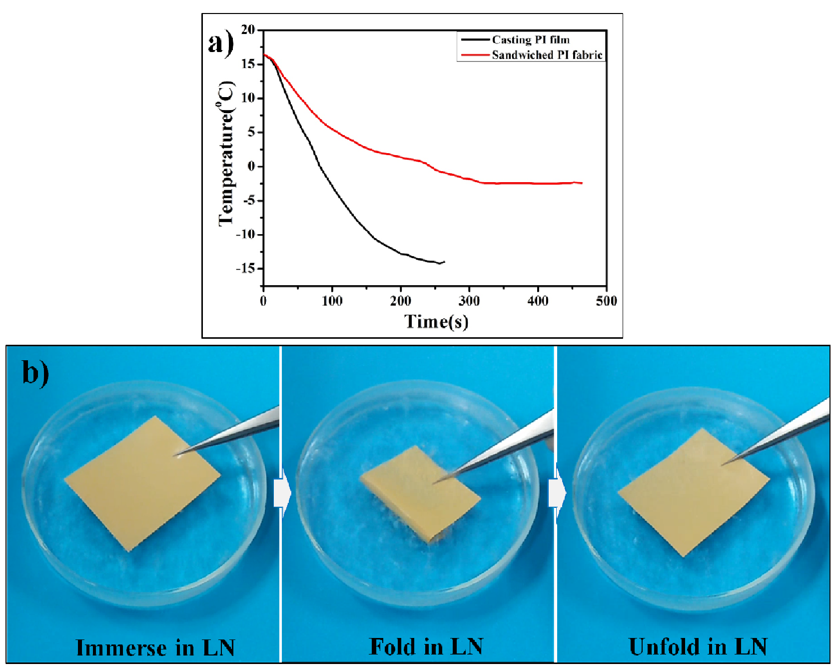


**Figure 5.** Cryogenic insulation and resistance performances of the sandwiched PI fabric. a) Apparent cryogenic insulation performance of the casting PI film and sandwiched PI fabric. b) The prepared sandwiched PI fabric could hold a great flexibility and even be folded in liquid nitrogen.

In addition to the outstanding thermal insulation performance and mechanical property, this sandwiched PI fabric also presented cryogenic resistance behaviour and self-extinction performance. Similar to the method of testing apparent heat insulation, an apparent cold insulation measurement was taken. As shown in Figure 5a, compared with casting PI film, the sandwiched fabric could hold an approximate 12 $^{O}$C temperature difference on the surface. It was because that the numerous nanogrooves and pores would greatly increase the transfer path of cold air, so that the sandwiched PI fabric could present a better apparent cryogenic insulation performance than the casting PI film. Also, the advanced PI material could allow this sandwiched fabric to keep a great flexibility and even be folded in liquid nitrogen (LN, -196 $^{O}$C), endowing it with a wide operating temperature range (as shown in Figure 5b, also seen the movie 2 in ESI†). What is more, the sandwiched PI fabric possessed superior fire-resistance property, making it an excellent candidate in fire safety field (as shown in Figure S2†). Actually, the decomposition temperature of this fabric could reach 500 $^{O}$C (as shown in Figure S3†), which was much higher than most common polymer. Thus, this unique PI fabric showed a great integrated performance and could satisfy various application environments, such as cryogenic engineering and aerospace.

## Conclusions

In summary, a flexible high-performance sandwiched super-insulation PI fabric has been designed and fabricated by using simple electrohydrodynamics jet technology. This unique sandwiched PI fabric with nanogroove and porous structure possessed a ultra-low thermal conductivity (16.7 $mW\cdot m^{-1}\cdot K^{-1}$), excellent mechanical property and wide operating temperature range. Moreover, the fabric also had some other multifunction, such as cryogenic resistance, self-extinction and thermal stability. Therefore, such sandwiched super-insulation PI fabric with excellent integrated performance would have a potential application in some harsh conditions, such as the insulation layer of aircraft or space suit, cold-protective for cryogenic storage and so on.

## Acknowledgements

The work is financially supported by the National Natural Science Foundation of China (Grants 51373007 and 51003004), the Beijing Natural Science Foundation (Grant 2142019), the National Basic Research Program of China (Grants 2010CB934700 and 2012CB933200), the Fundamental Research Funds for the Central Universities, and the SRF for ROCS, SEM. The authors truly thank Rui Ma for her technical assistance.

## Notes and references

1 J. P. Randall, M. A. B. Meador, S. C. Jana, *ACS Appl. Mater. Inter.*, 2011, **3**, 613-626.
2 N.Leventis, C. Chidambareswarapattar, A. Bang, C. Sotiriou-Leventis, *ACS Appl. Mater. Inter.*, 2014, **6**, 6872-6882.
3 G. Zu, J. Shen, W. Wang, L. Zou, Y. Lian, Z. Zhang, B. Liu B, F. Zhang, *Chem. Mater.*, 2014, **26**, 5761-5772.
4 A. J. Hunt, *Materials Engineering Congress.*, 1992, 398-403.
5 K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada, *Adv. Mater.*, 2007, **19**, 1589-1593.
6 U. F. Ilhan, E. F. Fabrizio, L. McCorkle, D. A. Scheiman, A. Dass, A. Palczer, M. B. Meador, J. C. Johnston, N. Leventis, *J. Mater. Chem.*, 2006, **16**, 3046-3054.
7 S. Mulik, C. Sotiriou-Leventis, G. Churu, H. Lu, N. Leventis, *Chem. Mater.*, 2008, **20**, 5035-5046.
8 M. A. B. Meador, C. M. Scherzer, S. L. Vivod, D. Quade, B. N. Nguyen, *ACS Appl. Mater. Inter.*, 2010, **2**, 2162-2168.
9 A. Katti, N. Shimpi, S. Roy, H. Lu, E. F. Fabrizio, A. Dass, L. A. Capadona, N. Leventis, *Chem. Mater.*, 2006, **18**, 285-296.
10 M. A. B. Meador, L. A. Capadona, L. McCorkle, D. S. Papadopoulos, N. Leventis, *Chem. Mater.*, 2007, **19**, 2247-2260.
11 Z. Wang, Z. Dai, J. Wu, N. Zhao, J. Xu, *Adv. Mater.*, 2013, **25**, 4494-4497.
12 L. Li, B. Yalcin, B. N. Nguyen, M. A. B. Meador, *ACS Appl. Mater. Inter.*, 2009, **1**, 2491-2501.
13 J. Cai, S. Liu, J. Feng, S. Kimura, M. Wada, S. Kuga, L. Zhang, *Angew. Chem.*, 2012, **124**, 2118-2121.
14 C. Huang, S. Chen, D. H. Reneker, C. Lai, H. Hou, *Adv. Mater.*, 2006, **18**, 668-671.
15 G. Gong, J. Wu, J. Liu, N. Sun, Y. Zhao, L. Jiang, *J. Mater. Chem.*, 2012, **22**, 8257-8262.
16 C. Chidambareswarapattar, Z. Larimore, C. Sotiriou-Leventis, J. T. Mang, N. Leventis, *J. Mater. Chem.*, 2010, **20**, 9666-9678.
17 N. Leventis, C. Sotiriou-Leventis, D. P. Mohite, Z. J. Larimore, J. T. Mang, G. Churu, H. Lu, *Chem. Mater.*, 2011, **23**, 2250-2261.
18 H. Guo, M. A. Meador, L. McCorkle, D. J. Quade, J. Guo, B. Hamilton, M. Cakmak, *ACS Appl. Mater. Inter.*, 2012, **4**, 5422-5429.
19 M. A. B. Meador, E. McMillon, A. Sandberg, E. Barrios, N. G. Wilmoth, C. H. Mueller, F. A. Miranda., *ACS Appl. Mater. Inter.*, 2014, **6**, 6062-6068.
20 M. A. B. Meador, C. R. Aleman, K. Hanson, N. Ramirez, S. L. Vivod, N. Wilmoth, L. McCorkle, *ACS Appl. Mater. Inter.*, 2015, **7**, 1240-1249.
21 L. Zhang, J. Wu, X. Zhang, G. Gong, J. Liu, L. Guo, *RSC Adv.*, 2015, **5**, 12592-12596.
22 J. H. Moon, G. R. Yi, S. M. Yang, D. J. Pine, S. B. Park, *Adv. Mater.*, 2004, **16**, 605-609.
23 A. Greiner, J. H. Wendorff, *Angew. Chem.*, 2007, **46**, 5670-5703.
24 P. W. Gibson, C. Lee, F. Ko, D. Reneker, *J. Eng. Fiber Fabr.*, 2007, **2**, 32-40.
25 H. Wu, J. Fan, X. Qin, G. Zhang, *Mater. Lett.*, 2008, **62**, 828-831.
26 B. Wang, Y. D. Wang, *Adv. Mater. Res.*, 2011, **332-334**, 672-677.
27 N. Sabetzadeh, H. Bahrambeygi, A. Rabbi, K. Nasouri, *Micro & Nano Letters*, 2012, **7**, 662-666.
28 A. K. S. Chauhan, A. Mishra, U. Pandey, S. J. Pawar, *International Journal of Engineering Research*, 2013, **2**, 2793-2798.
29 R. Arambakam, H. V. Tafreshi, B. Pourdeyhimi, *Mater. Design*, 2013, **44**, 99-106.
30 J. Wu, N. Wang, Y. Zhao, L. Jiang, *J. Mater. Chem. A*, 2013, **1**, 7290-7305.
31 F. Bai, J. Wu, G. Gong, L. Guo, *ACS Appl. Mater. Inter.*, 2014, **6**, 16237-16242.

Journal of Materials Chemistry A




Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

# Communication