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Low thermal conductivity nitrogen-doped graphene aerogels for thermal insulation

Chenwu YUE, Jian FENG*, Junzong FENG, Yonggang JIANG

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, China

Abstract: Aerogels, like SiO_2 aerogels, Al_2O_3 aerogels and carbon aerogels, have been widely used in thermal insulation. However, graphene aerogels (or reduced graphene oxide aerogels), with similar structure, have never been used in this field. In this paper, the concept of suppressing graphene aerogels' thermal conductivity by introducing defects or doping atoms in graphene was introduced. Nitrogen-doped (N-doped) graphene aerogels with low thermal conductivity were prepared with paraphenylene diamine as bridging and doping agent by CO_2 supercritical drying. With the introduction of doping atoms and bridging agent, the solid thermal conductivity is depressed. Also, with CO_2 supercritical drying, the pore size is reduced and the gaseous thermal conductivity is suppressed. The lowest thermal conductivity of N-doped graphene aerogels is 0.023 W/(m·K), which is nearly 1/2 of that ever reported and which is even lower than that of static air. Meanwhile, the thermal insulation mechanisms were also studied. The low thermal conductivity and low bulk density make N-doped graphene aerogels a potentially useful thermal insulation material that may significantly lighten thermal insulation system.

Key words: graphene, doping, aerogels, thermal conductivity, thermal insulation

* Corresponding author. Tel: +86 0731 84576291. Fax: +86 0731 84576578. E-mail: fengj@nudt.edu.cn.

1. Introduction

With nanoporous structure, high porosity and low density[1], aerogels have been widely used in thermal insulation[2]. Their nanoporous structure suppresses gaseous thermal conductivity[3], low density depresses solid thermal conductivity[4]. For example, SiO_2 aerogels[2], Al_2O_3 aerogels[5] and carbon aerogels[6] et al. Compared with these aerogels, graphene aerogels have similar structure, lower density, higher strength and perfect opacity. The opacity can lower radiant thermal conductivity, hence may further reduced their thermal conductivity. Although with these characters, graphene aerogels have never been used in thermal insulation. The most crucial reason for this should be the superhigh thermal conductivity of graphene.

Graphene is a single atomic layer of sp2 carbon atoms[7,8]. It has received much attention since first obtained by mechanical exfoliation[6] for its excellent electrical[9], thermal[10], optical[11] and mechanical[12] properties. Its measured values of thermal conductivity at room temperature for suspended samples are as high as 2500-5300 W/(m K)[13,14].

However, defects and doping atoms in graphene may significantly impact its thermal conductivity[15,16]. Several groups have studied the effects of different kinds of defects (variety of vacancy[17-19] and doping[20,21]) on its thermal conductivity by computer simulation using force constant method[22], molecular dynamics method[23] and Green's function method[17] et al. They found the thermal conductivity of graphene sharply decreases with the amount of defects or doping atoms increasing. Taking the fact that the thermal conductivity of graphene oxide is only 3.19W/(m K) compared

with graphene (5300 W/(m·K)), the thermal conductivity of graphene can be descended by introducing a great amount of defects or doping atoms.

Zhong[24] reported the thermal conductivity of graphene aerogels (reduced graphene oxide (rGO) aerogels) prepared by hydrothermal reduction and freeze-drying for the first time. The thermal conductivity measured with laser flash technique is as high as 2.183 W/(m·K). Their bulk density and surface area are 227mg/cm^3 and 43m^2/g, respectively. Fan[25,26] studied the effects of thermal treatment on the thermal conductivity of graphene aerogels (rGO aerogels) by infrared microscopy technique. The aerogels were prepared by CO_2 supercritical drying. This reduces their pore size and hence decreases the gaseous thermal conductivity. But the thermal conductivity of graphene aerogels before and after thermal treatment at 450℃ for 5h are still 0.12~0.36 W/(m·K) and 0.18~0.31 W/(m·K), respectively. And their bulk density is 14.1~52.4mg/cm^3 and 16.4~49.0mg/cm^3, respectively. Tang[27] synthesized graphene aerogels (rGO aerogels) with paraphenylene diamine (PPD) as reducing and functionalizing agent in the presence of ammonia ($NH_3 \cdot H_2O$) by freeze-drying, and characterized the thermal conductivity of the aerogels using Hot Disk Techmax TPS1500 thermal meter. The thermal conductivity with bulk density from 1.8mg/cm^3 to 27.2mg/cm^3 is 0.040~0.053 W/(m·K). Since the use of freeze-drying, the pore size of the aerogels is relatively bigger. So the thermal conductivity can be further depressed by reducing the pore size.

In this paper, the concept of decreasing graphene aerogels' thermal conductivity by introducing defects and (or) doping atoms to graphene was introduced. By introducing

doping atoms, together with reducing pore size by CO_2 supercritical drying, N-doped graphene aerogels with low thermal conductivity was obtained. These aerogels are potentially useful in thermal insulation for their low thermal conductivity and low bulk density.

2. Experimental section

2.1 materials

Graphene oxide (GO) aqueous suspension (15 mg/ml) was bought from Nanjing Jicang nanotechnology Co. Ltd. GO suspension with other concentration was obtained by diluting the aqueous suspension with deionized water. PPD were purchased from Sinopharm Chemical Reagent Co. Ltd. Ethanol and concentrated $NH_3 \cdot H_2O$ were obtained from Hunan Hengyang Kaixin Chemical Co. Ltd. All the chemicals were used as received without further purification.

2.2 Synthesis of graphene aerogels

100 ml GO suspension (3, 6, 9, 12, 15 mg/ml, for a typical procedure it is 12 mg/ml) was commixed with X g PPD and 2.7 ml concentrated $NH_3 \cdot H_2O$ (The X were 1.2, 2.4, 3.6, 4.8, 6.0, respectively, for a typical procedure it is 4.8). Subsequently, The mixture was heated at 90 ℃ for 8 h to gain N-doped graphene hydrogels. Then the solvent in the hydrogel was exchanged with water and ethanol for 5 times, respectively. Finally, the gel was dried with supercritical CO_2 to form N-doped graphene aerogels.

2.3 Characterization

The bulk density was calculated from the mass and corresponding volume. The microstructure was observed with Hitachi S4800 field emission scanning electron mi-

croscope (SEM). The surface composition was characterized in TESCALAB 250Xi X-ray photoelectron spectroscope (XPS). The nitrogen adsorption-desorption tests were carried out at 77 K in autosorb-1 physical adsorption instrument after 16 hours of sample outgassing in vacuum, and the specific surface area and pore size distribution were calculated by the BET (Brunauer–Emmett–Teller) method and BJH (Barrett–Joyner–Halenda) method, respectively. The thermal conductivity was measured with samples Φ39~42 ×15 mm using Hot Disk TPS2500 apparatus by the 5465 sensor.

3. Results and discussion

During the heat preservation, N-doped graphene hydrogels are obtained by PPD grafting with GO sheets and π-π stacking between reduced graphene oxide sheets[27]. The GO sheets are simultaneously reduced and functionalized by PPD. From the XPS spectra (Fig. 1), N atoms and O atoms respectively account for 13.34 %at and 9.98 %at in the sample (table 1), illustrating the introducing of PPD into as-prepared N-doped graphene aerogels. According to the C 1s XPS spectra (Fig. 1(b)) of as-prepared N-doped graphene aerogels, the peaks at 285.4 eV corresponding to C-N and 286.1 eV corresponding to C(O)N indicate the covalent bonding of PPD to graphene sheets. This can be further proved by the peaks at 399.1 eV and 400.4 eV from N 1s XPS spectra (Fig. 1(c)) and peak at 532.2 eV from O 1s XPS spectra (Fig. 1(d)).

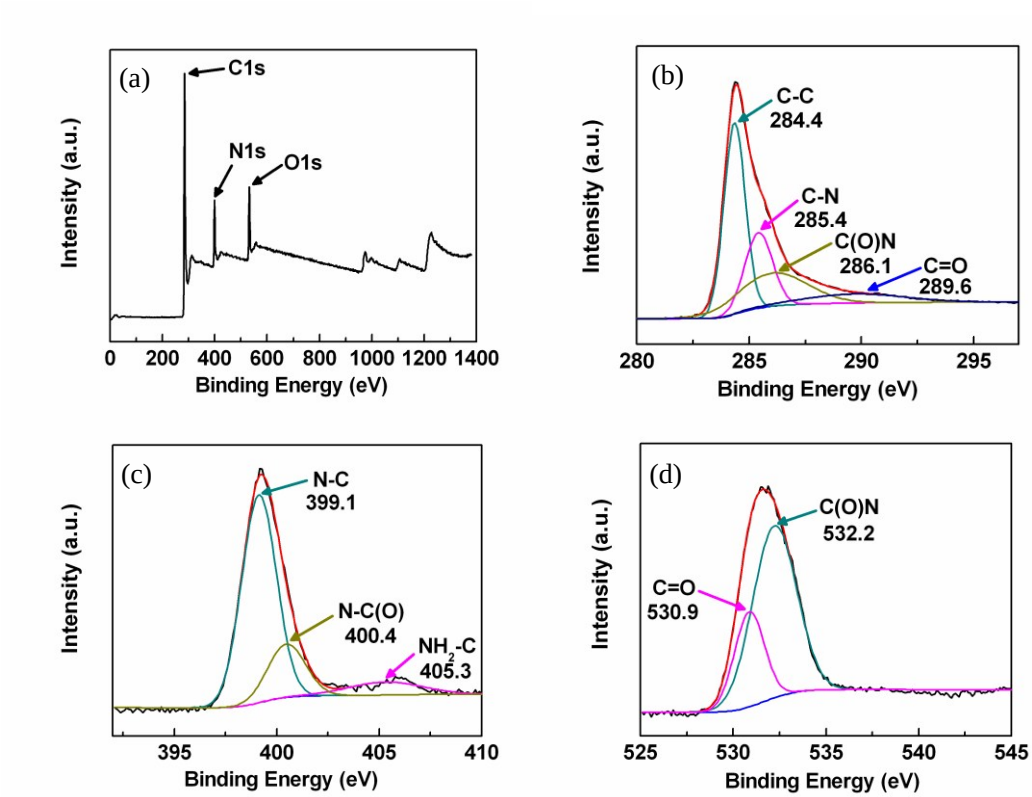


Fig. 1 (a) Broad XPS spectra, (b) C 1s spectra, (c) N 1s spectra and (d) O 1s spectra of as-prepared N-doped graphene aerogels

Table 1 Element percentage of as-prepared N-doped graphene aerogels

Element	C	O	N
Content (%at)	76.68	9.98	13.34

However, different with freeze drying, the porous network is fully preserved after CO_2 supercritical drying. Fig. 2 is the SEM micrograph of as-prepared N-doped graphene aerogels. As shown in the image, the N-doped graphene sheets randomly interconnected with each other, forming pores in several dozens or hundreds nanometers. The size of the pores is much smaller than that of N-doped graphene aerogels prepared by freeze drying (Fig. 3). The microstructure of as-prepared N-doped graphene aerogels

is homogeneous to some extent.

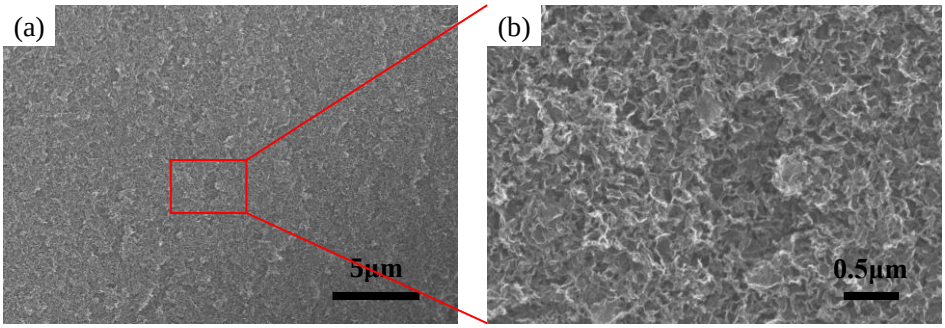


Fig. 2 SEM micrograph of as-prepared N-doped graphene aerogels

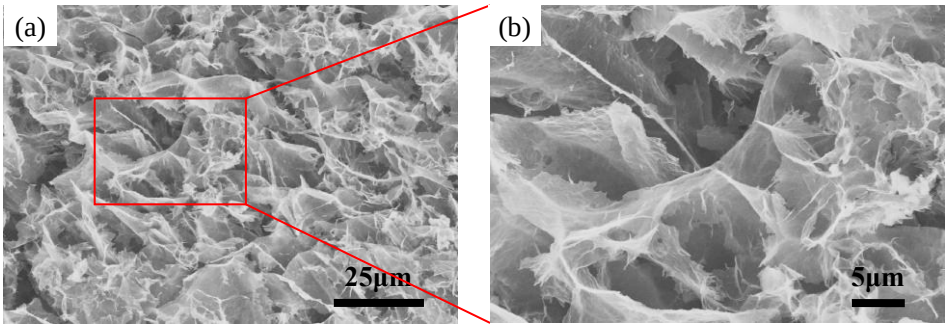


Fig. 3 SEM micrograph of as-prepared N-doped graphene aerogels by freeze drying

The N_2 adsorption-desorption isotherm curve and BJH pore size distribution of as-prepared N-doped graphene aerogels with bulk density 34.5 mg/cm^3 are shown in Fig. 4. The isotherm curve belongs to typical type Ⅲ adsorption-desorption isotherm[28], revealing plenty of pores with size more than 5 nm and wide range of pore sizes. The result is consistent to the result of SEM micrograph. Also, the adsorption capacity is really large, showing the great pore volume. According to the BJH pore size distribution, most of the pore diameter is larger than 10 nm, which reaches their maximum at 49 nm. This can further prove the result from SEM micrograph. The pore volume see downward tendency with the pore diameter increasing to 140 nm, but the volume of pore with sizes bigger than 140 nm is still great. Those pores cannot be ex-

plored by N_2 adsorption-desorption test but can be observed from the SEM micrograph. According to the bulk density of as-prepared N-doped graphene aerogels (11.1~35.0 mg/cm^3, Table 2), the pore volume may be 28~89 cm^3/g compared with 3.26~5.88 cm^3/g by BJH method based on N_2 adsorption-desorption isotherm curves.

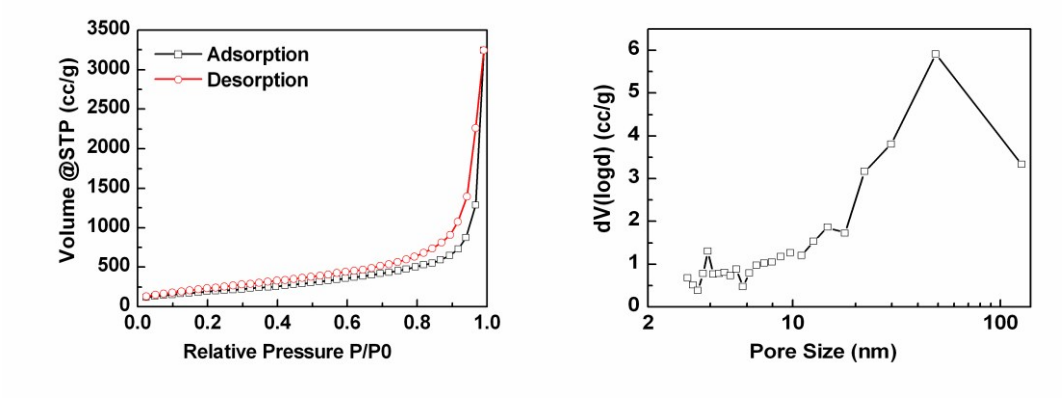


Fig. 4 N_2 adsorption-desorption isotherm curve and BJH pore size distribution of as-prepared N-doped graphene aerogels

Table 2 The textural properties of as-prepared N-doped graphene aerogels with varied bulk density

GO concentration (mg/ml)	Bulk density (mg/cm^3)	BET surface area (m^2/g)	Pore volume (cm^3/g)
3	11.1±0.7	568.7	3.26
6	19.9±0.6	705.5	4.93
9	24.7±1.1	802.4	4.90
12	34.5±1.0	891.7	5.88
15	35.0±1.1	751.7	4.15

At the same time, shrinkage of 1 %~8 % in sample diameter with the variation of GO

concentration was observed during CO_2 supercritical drying. That may attribute to the surface tension during drying, although which is relatively weak due to the super-critical state of resolve. But the shrinkage does not impact the structure and appear-ance of as-prepared N-doped graphene aerogels, without crack being noted from the photograph (Fig. 5) and the micrograph (Fig. 2).

Fig. 5 Photograph of as-prepared N-doped graphene aerogels

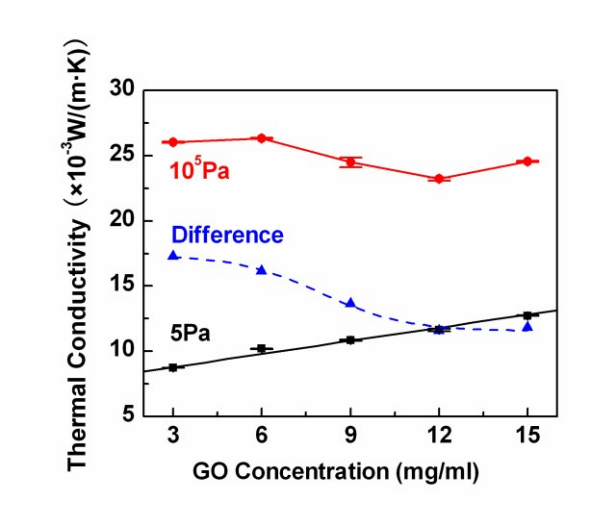


Fig. 6 Thermal conductivity of as-prepared N-doped graphene aerogels

Fig. 6 shows the thermal conductivity of as-prepared N-doped graphene aerogels with varied GO concentration. With the GO concentration increasing from 3 mg/ml to 12 mg/ml, the thermal conductivity of as-prepared N-doped graphene aerogels at room temperature (25 ℃) and atmospheric pressure (10^5 Pa) shows decrease tendency. But

with the GO concentration continues to increase to15 mg/ml, the thermal conductivity increases a little. When the GO concentration is 12 mg/ml, the thermal conductivity is only 0.023 W/(m K). The thermal conductivity at room temperature and 5 Pa see a different trend. The thermal conductivity almost linearly increases with the GO concentration increasing. The higher GO concentration increases the bulk density of as-prepared N-doped graphene aerogels. This reinforces the juncture of graphene sheets and magnifies the solid content in unit volume. Since graphene sheets are the carrier of heat transmission, the solid thermal conductivity increases. With the radiant thermal conductivity at this temperature and the gaseous thermal conductivity at 5 Pa both negligible, the thermal conductivity at room temperature and 5 Pa is mostly consist of solid thermal conductivity. So, the thermal conductivity of as-prepared N-doped graphene aerogels at 5Pa increases with the increasing of GO concentration. Differently, the difference between thermal conductivity at atmospheric pressure and that at 5Pa narrows down. The difference matches very well with the inverse S-curve. The reason for that is the difference mainly makes up of gaseous thermal conductivity. The enhancement of bulk density caused by the increase of the GO concentration decreases the pore size of as-prepared N-doped graphene aerogels (Fig. S11, Fig. 2). Hence the gaseous thermal conductivity was restrained more thoroughly. When the GO concentration is relatively low (< 6 mg/ml), the pore size is relatively great. Its restrain to gaseous thermal conductivity is not so significant. Meanwhile, when the GO concentration is relatively high (> 12 mg/ml), the effect of GO concentration on bulk density diminishes. Hence, the relationship between GO concentration and gas-

eous thermal conductivity lighten. So, with the increase of the GO concentration, the difference (namely, gaseous thermal conductivity) shows an inverse S-curve. Logically, the linear increase of the thermal conductivity at 5Pa and the nonlinear decrease of the difference (the gaseous thermal conductivity) inducing the variation of the thermal conductivity of as-prepared N-doped graphene aerogels at atmospheric pressure.

Table 3 Thermal conductivity of rGO aerogels

author	Bulk density (mg/cm^3)	BET surface area (m^2/g)	Thermal conductivity ($W/(m·K)$)	Reference
Yajuan Zhong	227	43	2.183	[24]
Zeng Fan	14.1~52.4	-	0.12~0.36	[25], [26]
Gongqing Tang	1.8~27.2	-	0.040~0.053	[27]
Chenwu Yue	11.1~35.0	568~892	0.023~0.026	This work

Compared with that from public articles (Table 3), the thermal conductivity of as-prepared N-doped graphene aerogels is significantly lower, which is nearly half of the minimum value ever reported. Four reasons may contribute to this result.

First, just as reported by Fan[26] et al, the defects in graphene and the relatively small size of graphene sheets limit the transmission of heat, and hence reduces the thermal conductivity of as-prepared N-doped graphene aerogels to some extent.

Second, the CO_2 supercritical drying sharply diminishes the pore size in as-prepared N-doped graphene aerogels. According to the computation by BJH method based on N_2 adsorption-desorption curve, most of the pores centralize on 49 nm. It is shorter

than the mean molecule freedom path (~70 nm[3]) at room temperature and atmospheric pressure, and hence can obviously depress the gaseous thermal conductivity. The research of Feng[29] et al shows that the gaseous thermal conductivity will be crucially suppressed, if only the pore diameter smaller than 2 times of the mean molecule freedom path (namely 140nm at room temperature and atmospheric pressure). So the gaseous thermal conductivity is reduced. Besides, the 2-dimension structure of graphene sheets may effectively block off the transfer of gas molecules like the wall compared with other aerogels (such as SiO_2 aerogels, Al_2O_3 aerogels, carbon aerogels et al) with 3-dimension open-cell network structure (Fig. 7). Hence graphene aerogels can greatly suppress the gaseous heat transmission through gas molecular collision. With these 2 mechanisms the gaseous thermal conductivity of as-prepared N-doped graphene aerogels is significantly depressed.

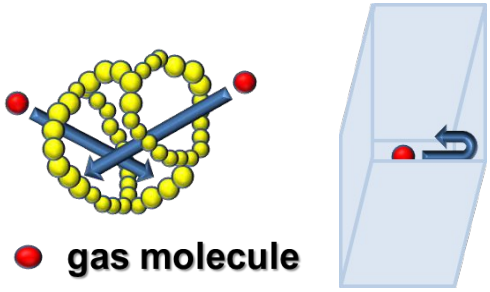


Fig. 7 Schematic diagram of aerogels with open-cell network structure (left) and as-prepared N-doped graphene aerogels (right)

Third, the introduction of doping atoms turns sp2 carbon to sp3 carbon, destroying the perfect π-electron conjugated structure and crystal structure, which are the main path heat transmitting through graphene. Phonons are the main carrier of heat delivering in

graphene, which transfer heat by lattice vibration. With the introduction of doping atoms, the crystal structure of doping graphene is divided into smaller pieces by sp3 carbon atoms (namely carbon chemically linked with doping atoms (Fig. 1(b), the peaks at 285.4 eV and 286.1 eV)). The scattering of phonons on these obstacles together with the defects and edge can significantly minish the amount of heat passing through the doping graphene (Fig. 8). Meanwhile, electrons are the other carrier of heat delivering in graphene, which transfer heat by electron travelling. With the doping atoms introduced, the intactness of π-electron conjugated structure is broken, the resistance of electron motion boosting. As a result, the heat transferred through electron travelling is reduced. By this way, the solid thermal conductivity of as-prepared N-doped graphene aerogels is further debased. Fig. 9 is the thermal conductivity (5 Pa) of as-prepared N-doped graphene aerogels (GO is 12 mg/ml) with varied PPD mass. When PPD mass is no more than 4.8 g, the thermal conductivity at 5 Pa decreases with the increasing of PPD mass. Since the increasing of PPD mass increases the amount of N doped to the sample, the as-prepared N-doped graphene aerogels with more PPD show better thermal insulation performances at 5 Pa.

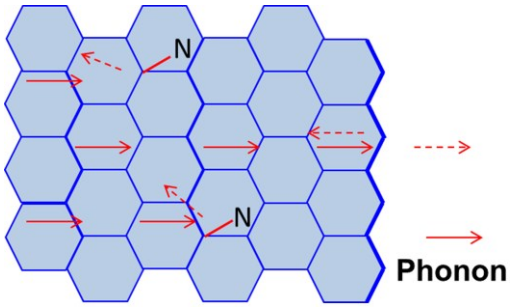


Fig. 8 Schematic diagram of as-prepared N-doped graphene aerogels

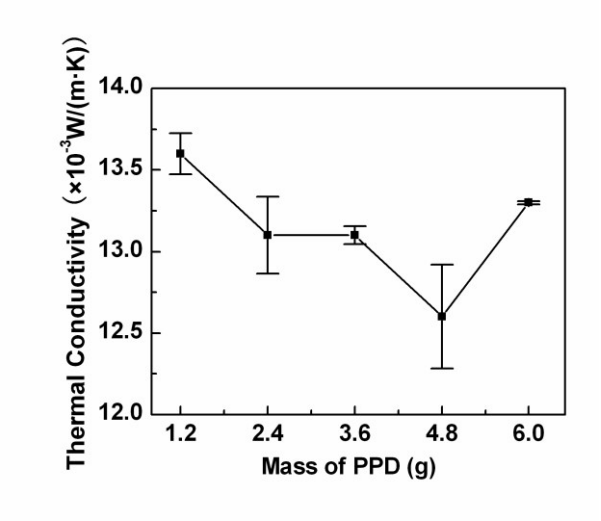


Fig. 9 Thermal conductivity (5Pa) of as-prepared N-doped graphene aerogels with varied PPD mass

Fourth, PPD also plays a role like bridging agent. It linked doping graphene with each other. With the introduction of bridging agent, the heat transferring between the graphene is significantly limited even if that through graphene could have been greater. The bridging agent crucially restricts the heat flux like bottleneck. Therefore, the heat pass through the as-prepared N-doped graphene aerogels is reduced and the solid thermal conductivity ulteriorly gets fallen. According to Fig. 9, the increasing of thermal conductivity (5 Pa) when PPD mass is 6.0 g illustrates the increase of the amount of 'bridges' accelerating the heat transfer to some extent.

With the above four reasons, the thermal conductivity of as-prepared N-doped graphene aerogels is really low, which is even lower than that of static air (0.026 W/(m·K))[30]. The low thermal conductivity (0.023~0.026 W/(m·K)) and low bulk density (11.1~35.0 mg/cm^3) are crucially important for the use of N-doped graphene aerogels in thermal insulation. And the use of this material may significantly lighten the weight of thermal insulation system. Meanwhile, the gaseous thermal conductivity

of N-doped graphene aerogels still takes up a great proportion among the thermal conductivity. That may because the percentage of pore with relatively bigger size (>140 nm) is still considerable. So the thermal conductivity of N-doped graphene aerogels may be further depressed by ulteriorly narrowing the pore size.

4. Conclusion

We introduced the concept of lowering the thermal conductivity of graphene aerogels by introducing defects or doping atoms in graphene, and prepared low-thermal-conductivity N-doped graphene aerogels using PPD as bridging and doping agent by CO_2 supercritical drying. The PPD is anchored in graphene sheets during reaction. By CO_2 supercritical drying, the pore sizes of as-prepared N-doped graphene aerogels are much smaller than that by freeze drying. Remarkably, the lowest thermal conductivity of as-prepared N-doped graphene aerogels is only 0.023 W/(m ·K), even lower than that of static air, showing good thermal insulation performances. The reasons are: (1) The transmission of heat is limited by the defects in graphene and the relatively small size of graphene sheets; (2) The relatively smaller pore size and 2-dimension structure of graphene sheets suppress the gaseous thermal conductivity; (3) The introduction of doping atoms boosting the scattering of phonon, greatly depresses the solid thermal conductivity; (4) The bridging agent restricts the heat flux like bottleneck, further lowering the thermal conductivity. With low bulk density (11.1~35.0 mg/cm^3) and low thermal conductivity (0.023~0.026 W/(m ·K)), the as-prepared N-doped graphene aerogels are potentially useful in thermal insulation,

and may significantly lighten the weight of thermal insulation system.

Acknowledgements

Thanks for the support from National Natural Science Foundation (51172279, 51302317) of China, Aid Program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province and Aid Program for Innovative Group of National University of Defense Technology.

References

[1] N. Hüsing and U. Schubert, Angew Chem Int Ed, 1998, **37**, 22-45;

[2] J. Feng, Q. Gao, J. Feng and Y. Jiang, Journal of National University of Defense Technology, 2010, **32**, 40-44;

[3] X. Lu, M. C. Arduini-Schuster and J. Kuhn, Science, 1992, **255**, 971-972;

[4] S. N. Schiffres, K. H. Kim, L. Hu, A. J. H. McGaughey, M. F. Islam and J. A. Malen, Adv Funct Mater, 2012, **22**, 5251-5258;

[5] Q. Gao, C. Zhang, J. Feng, W. Wu, J. Feng and Y. Jiang, Chinese Journal of Inorganic Chemistry, 2008, **24**, 1456-1460;

[6] J. Feng, J. Feng and C. Zhang, J Porous Mater, 2012, **19**, 551-556;

[7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A Firsov, Science, 2004, **306**, 666-669;

[8] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, B. A. Lawrence, L. Wei and M. T. James, ACS NANO, 2010, **8**, 4806-4814;

[9] D. Basu, M. Gilbert, L. Register, S. Banerjee and A. MacDonald, Appl Phys Lett, 2008, **92**, 042114;

[10] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, NANO Letters, 2008, **8**, 902-907;

[11] M. Liu, X. Yin, E. Ulin-Avila, B. Geng, T. Zentgraf, L. Ju, F. Wang and X. Zhang, Nature, 2011, **474**, 64-67;

[12] A. K. Geim, Science, 2009, **324**, 1530-1534;

[13] S. Ghosh, W. Bao, D. L. Nika, S. Subrina, E. P. Pokatilov, C. N. Lau and A. A. Balandin, Nat Mater, 2010, **9**, 555-558;

[14] W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi and R. S. Ruoff, Nano Lett, 2010, **10**, 1645-1651;

[15] P. Yang, X. Wang, P. Li, H. Wang, L. Zhang and F. Xie, Acta Phys Sin, 2012, **61**, 076501;

[16] W. Yu, H. Xie and X. Wang, Journal of Engineering Thermophysics, 2012, **33**, 1609-1611;

[17] H. Zhang, L. Geunsik and C. Kyeongjae, Physical Review B, 2011, **84**, 115460;

[18] H. Justin, K. Alper, S. Cem, S. H^aldun, C. Gianaurelio and C. Tahir, ACS NANO, 2011, **5**, 3779-3787;

[19] Y. Y. Zhang, Y. Cheng, Q. X. Pei, C. M. Wang and Y. Xiang, Physics Letters A, 2012, **376**, 3668-3672;

[20] L. Wang and H. Sun. J Mol Model, 2012, **18**, 4811-4818;

[21] Z. Hui, P. He, Y. Dai and A. Wu, Acta Phys Sin, 2014, **63**, 074401;

[22] K. Hossein, N. Neophytos, P. Mahdi and K. Hans, J Comput Electron, 2012, **11**, 14-21;

[23] N. Khosravian, M. K. Samani, G. C. Loh, G. C. K. Chen, D. Baillargeat and B. K. Tay, Computational Materials Science, 2013, **79**, 132-135;

[24] Y. Zhong, M. Zhou, F. Huang, T. Lin and D. Wan, Solar Energy Materials & Solar Cells, 2013, **113**, 195-200;

[25] Z. Fan, D. Z. Y. Tng, C. X. T. Lim, P. Liu, S. T. Nguyen, P. Xiao, A. Marconnet, C. Y. H. Lim and H. M. Duong, Colloids and Surfaces A: Physicochem Eng Aspects, 2014, **445**, 48-53;

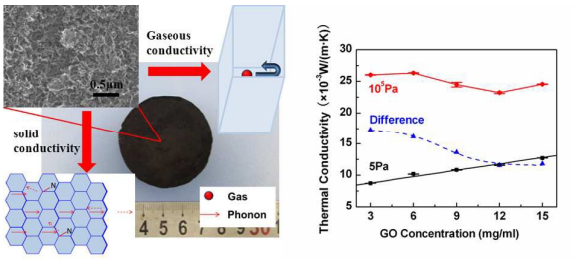
[26] Z. Fan, A. Marconnet, S. T. Nguyen, C. Y. H. Lim and H. M. Duong, International Journal of Heat and Mass Transfer, 2014, **76**, 122-127;

[27] G. Tang, Z. Jiang, X. Li, H. Zhang, A. Dasari and Z.Yu, CARBON, 2014, **77**, 592-599;

[28] F. Rouquerol, J. Rouquerol and K. Sing, Adsorption by powders and porous solid, principles, methodology and applications, Academic Press, 1999;

[29] J. Feng, J. Feng, Y. Jiang and C. Zhang, Aerospace Materials & Technology, 2012, **42**,1-6;

[30] R. Singh and H. S. Kasana, Appl Therm Eng, 2004, **24**, 1841-1849.



N-doped graphene aerogels with low thermal conductivity were prepared for the first time