

Fabrication of Graphene/Epoxy Resin Composites with Much Enhanced Thermal Conductivity via Ball Milling Technique

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ABSTRACT: Ball milling is selected to prepare composites of graphene nanoplatelets (GNPs) and epoxy. Much enhanced thermal conductivity was recorded with higher GNP loading, which varied between 5 and 25 wt %. A maximum thermal conductivity of 2.67 W/m·K was found. The prepared composites were characterized by scanning electron microscopy, transmission electron microscopy, and Raman. It was found that KNG180, a commercially available kind of natural graphite, with a thickness of 30 ~ 80 nm were mainly exfoliated into GNPs (<10 layers) with high quality, which were in turn uniformly dispersed in the composites. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40565.

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INTRODUCTION

Polymers have been widely used in electronic industry as plastics and adhesive. However, these insulating materials tend to have very low thermal conductivity, for example, epoxy resin (0.20 W/m·K), making them with poor capability in heat dissipation. Addition of thermal-conductive fillers with high thermal conductivity into polymers is a common practice.¹ Up to now, many types of filler have been used, yet from which graphene stands out as the best, mainly because of its high aspect ratio coupled with a pretty high thermal conductivity (5300 W/m·K).² For example, Connell and his coworkers³ fabricated composite ribbons, loaded with different nanoscale carbon fillers, including multiwalled carbon nanotubes, vapor-grown nanofibers, and commercially available expanded graphite. They found that the expanded graphite was most effective, with in-plane thermal conductivity reaching 6.7 W/m·K (40 wt % loading). Yu et al.⁴ processed natural graphite flakes into graphene nanoplatelets (GNPs) with the thermal-assisted exfoliation. The GNPs thus obtained were dispersed to fabricate composites of epoxy. These GNPs/epoxy composites were found to have thermal conductivities up to 6.44 W/m·K (25 vol % GNPs or 40 wt % loading).

In our research, ball milling method was introduced to fabricate composites. In fact, Zhao,^{5,6} our coworker, has succeeded in preparation of graphene and composites using ball milling method. Here, it would be reported that commercially available KNG180, a kind of natural graphite, could be further exfoliated in ball milling process to produce GNPs (<10 layers), used as fillers in epoxy/composites with maximum thermal conductivity of 2.67 W/m·K

(25 wt % loading). The principle of the mechanically ball milling is that the pure shear among balls of various diameters is able to break the van der Waals interactions among the carbon-atom layers. At the same time, the newly obtained GNPs would be wrapped up by polymer matrix not only preventing GNPs sticking together but also keeping instinct structure of the GNPs perfect. Essentially, ball milling is able to combine the process of the GNPs preparation with the operation of incorporating nanofillers into polymer matrix, which makes the composite preparation more convenient and effective, the most technological characteristic of ball milling compared with another preparation processes reported.^{5,6} Thus, ball milling can efficaciously improve the dispersion, compatibility, and interfacial interaction of GNPs in polymer matrix. Thereby, two issues existing with the use of GNPs as thermal-conductive fillers in polymer composites⁵ would be efficiently settled down: (i) GNPs tend to aggregate when dispersed in polymers matrix due to strong intrinsic van der Waals interactions, making it difficult to achieve full potential in enhancement of the thermal conductivity and (ii) there is interfacial thermal resistance caused by the phonon mismatch at the interface between GNPs and polymer matrix, resulting in severe phonon scattering and finally a drastic reduction in thermal transport. In addition, the thermal transport of GNPs by phonons will be strongly hindered by the gaps between adjacent sheets.⁷

EXPERIMENTAL

Materials

Graphite nanoplatelets (KNG180, Xiamen Knano Graphite) were placed in a desiccator prior to use. Acetone, epoxy resin,

and ethylenediamine were purchased from Xilong Chemical Reagent, Jiangsu Sanmu chemical industry, and Aladdin reagent, respectively. Other raw materials were used as received.

Preparation of GNP/Epoxy Composites

The different mass fractions (the range of 5–25 wt % loading) of KNG180 were dispersed in acetone solution containing 15 wt % epoxy resin with the help of sonication for 0.5 h at room temperature. The suspension was placed in a stirring basket ball milling machine and mixed at a speed of 300 rpm at room temperature for the corresponding hours (the range of 6–36 h), after which the mixture was heated to 60°C to remove acetone solvent, followed by drying in a vacuum oven. Afterward, the ethidene diamine (1 g) was used as curing agent and the mixture was stirred for 10 min before poured into polytetrafluoroethylene (PTFE) molds, which finally cured at room temperature for one day and postcured at 80°C for 24 h.

Similarly, the different mass fractions (the range of 5–25 wt % loading) of KNG180 were disposed in acetone solution containing 15 wt % epoxy resin with the assistance of sonication for 24.5 h. The resulted mixture was heated to 60°C to remove acetone solvent, followed by drying in a vacuum oven. Afterward, ethidene diamine (1 g) was added into the resulted mixture which was poured into PTFE molds, and finally cured at room temperature for 1 day and postcured at 80°C for 24 h.

Besides, the dimension of all of prepared composite samples was about $50 \times 50 \times 4 \text{ mm}^3$.

Characterization

The thermal conductivities of the samples were measured using C-therm TCi thermal conductivity analyzer operated at room temperature under normal atmosphere. The samples of about $50 \times 50 \times 4 \text{ mm}^3$ in size were measured on the inductive probe with one surface (facing the inductive probe) polished with sand paper. At least three frequencies were used in the measurement of each sample, and the testing values were averaged for the given specimen.

Scanning electron microscopy (SEM) was performed using S-4800 (II) FESEM instrument (HITACHI) and operated at a voltage of 5 kV. High-resolution transmission electron microscopy (HRTEM) images were acquired on microtomed composite slices using JEM-2010 JEOL microscope. Raman spectra were received by irradiating samples with 532 nm laser and data recorded with Labram spectrometer (Super LabRam II system, Dilor, France).

RESULTS AND DISCUSSION

Thermal Conductivity

Thermal conductivities of composites measured by C-therm TCi thermal conductivity analyzer were affected by the GNPs quality, dispersion, loading, and thermal resistance of the interface between GNPs and polymer matrix. Figure 1 showed the thermal conductivities of our GNPs/epoxy composites. Clearly, the thermal conductivities increased linearly with the increase of the mass loading of the filler, independent of the mixing strategy. Although largely the same, there were differences between these two processes. For example, the two changing curves of thermal

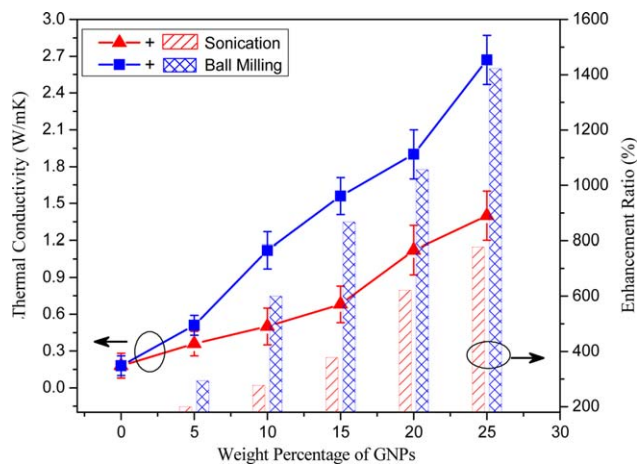


Figure 1. Thermal conductivity of epoxy composites prepared via two different methods as a function of filler percentage (x). These samples were prepared subjected to treatment for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity had obvious different turning points (5 and 15 wt % for ball milling and sonication). For sonication mixing, the thermal conductivities showed a slow-growth (0.2–0.36 W/m-K) before the turning points (15 wt %), rose faster with the increase of filler loading and reached the maximum of 1.40 W/m-K; while for ball milling, the thermal conductivities quickly reached the turning point (5 wt %), then increased from 0.51 to 2.67 W/m-K (the max enhancement ratio up to 1422% with 25 wt % filler). Besides, for the composite samples with 10 wt % or higher loading of filler, the thermal conductivities of the composites prepared by ball milling, were double that of the composites prepared by other method. Three reasons are proposed to explain this much enhancement: (i) the better homogeneous dispersion of GNPs in polymer could possess better thermal conductance, revealed by the SEM. (ii) The high quality and better exfoliation degree of GNPs could promote better thermal conductance. TEM and Raman results showed that KNG180 were effectively exfoliated into GNPs with super-large surface area skillfully preserved by polymer in ball milling, resulting in the increased contact surface area between GNPs and polymer improving the phonon transport in composite. (iii) The better interfacial interaction between GNPs and epoxy was essential in enhancing thermal-conductive property. In ball milling, mechanochemistry advanced the interfacial interaction between filler and matrix, leading to the homogeneous dispersion and perfect adhesion of fillers into polymer matrix, reducing the thermal interfacial resistance effectively and improving the phonon transport in composites.

In our opinion, milling time is one of most important factors influencing the dispersion, the exfoliation degree, the quality of GNPs, and so on, further effecting the enhancement in thermal conductivity. The thermal conductivities of our fabricated epoxy composites containing 10 wt % (red line) or 20 wt % (blue line) GNPs were examined as a function of the ball milling time which was shown in Figure 2. For these two kinds of composites, the change in the thermal conductivity was similar, reaching maximum performance after 18 or 24 h and then slightly

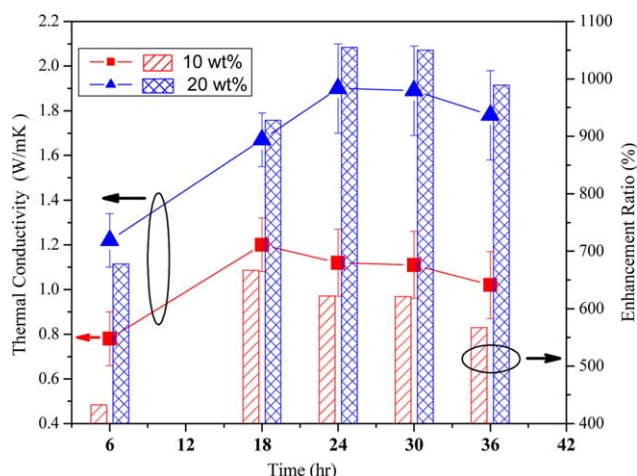


Figure 2. Thermal conductivity of epoxy composites prepared by ball milling as a function of milling time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reducing. It was obvious that the thermal conductivities of composites with more fillers needed more time to reach to the maximum value. The reasons of the phenomenon are as follows: with the extension of ball milling time, the percentage of GNPs advanced. However, extensive shearing would generate structural defects of GNPs in composites,⁶ limiting a further improvement in properties. For instance, the size of GNPs could be much smaller, which was bad for thermal conductivity enhancement.

In summary, the theoretic performance of GNPs would be reduced significantly due to the GNPs aggregation and poor compatibility with polymer, the critical issue in relation to the potential of GNPs in polymer composites.⁷ Consequently, ball milling can exfoliate KNG180 into GNPs with high specific surface area, wrapped up epoxy, finally leading to homogeneous dispersion and good incorporation.

SEM and TEM

Figure 3(a,b) showed SEM of epoxy composites prepared by both methods. Figure 3(a) showed that GNPs interconnecting with each other were dispersed uniformly inside polymer matrix. In contrast, much graphite sheets were indicated in the form of aggregates in Figure 3(b). The inside structure of composites prepared by ball milling as shown in Figure 3(a) was so harmonious and consummate that phonon scattering processes especially GNPs and epoxy matrix were effectively minimized.

To gauge the morphology and dimension of our GNPs in composites, part of the mixture (before curing) was washed with acetone, dried, and characterized by SEM and TEM. The specimens were prepared by loading the microtomed epoxy composite slices of GNPs onto standard TEM grids. Figure 4(a) showed SEM image of GNPs having a great tendency to restack to form graphitic structure. Thus, layered GNPs were also present, because of due to the van der Waals interactions or the surplus epoxy. TEM images of the specimens shown in Figure 4(b,c) revealed the cross-sections of the obtained GNPs. Figure 4(b) showed that few of long black lines existed, surrounded by much more shorter lines, implying that the sizes of the most GNPs were homogeneous and had lateral dimensions on the

submicron scale. Obviously, the number of layers could be visualized directly from the Figure 4(c), suggesting a successful achievement of GNPs. Individual single atomic carbon layers (corresponding to monolayer graphene sheets) dominated by one dark line with a thickness of 0.5 nm could be readily identified, suggesting that composites contained a number of single-layer graphene. Besides, in Figure 4(d), some multilayer graphite sheets extracted from mixture prepared by ball milling for 6 h existed, from which we could infer that plenty of GNPs would not appear until enough ball milling time.

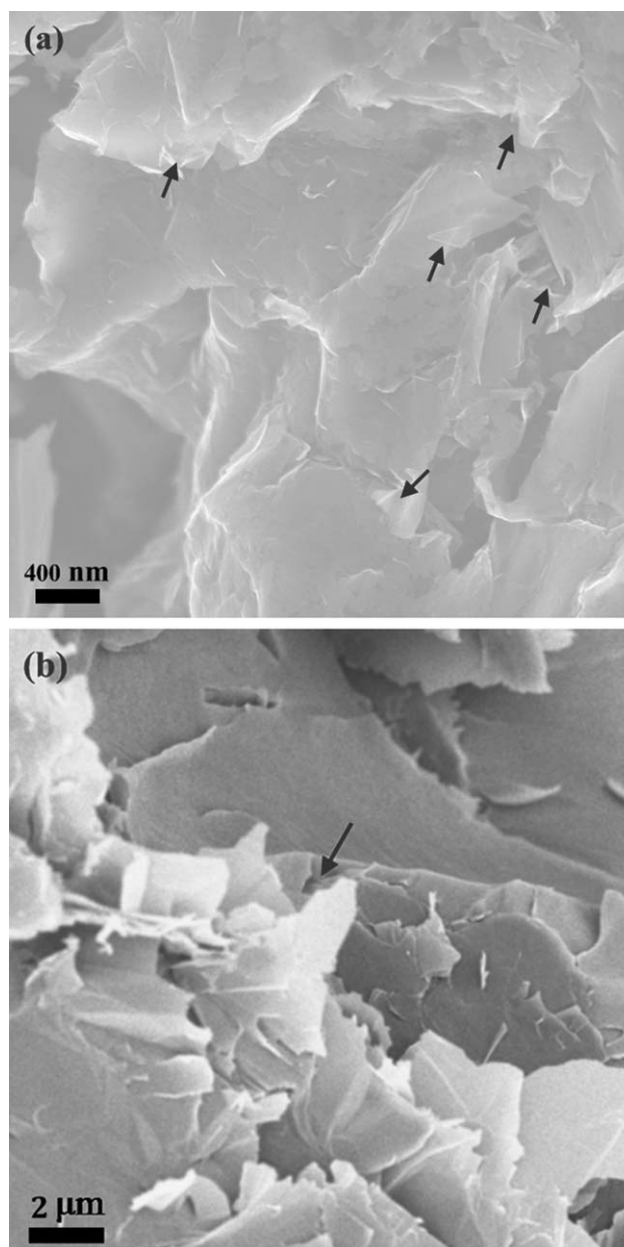


Figure 3. SEM images of fractured nanocomposites prepared from (a) ball milling induced exfoliation; and (b) sonication. These samples (25 wt % loading) were prepared subjected to treatment for 24 h. Arrows indicate the location of the fillers.

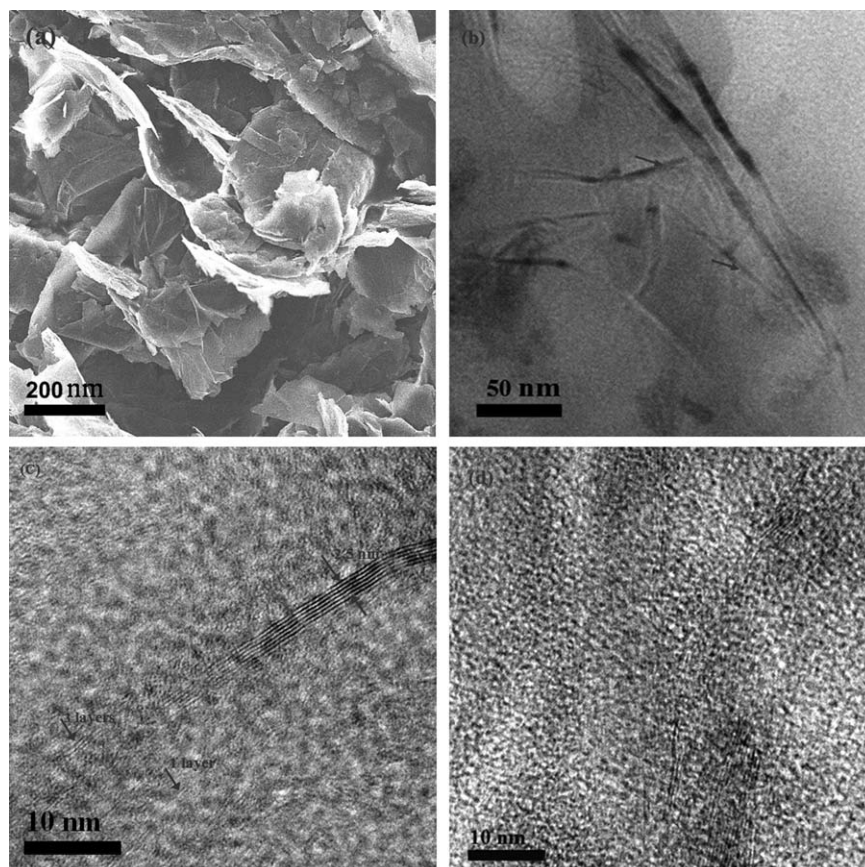


Figure 4. (a) SEM image of our graphene in solid state and (b,c) HRTEM images of GNPs embedded in epoxy resin slice. These samples (25 wt % loading) were prepared subjected to treatment for 24 h (a,b,c) and 6 h (d). Arrows indicate the location of the fillers.

Raman Spectroscopy

The degree of exfoliation is measured by Raman spectroscopy.⁸ Generally, there are three main peaks, that is, a *D* peak at 1350 cm^{-1} , a *G* peak at 1580 cm^{-1} , and a *2D* peak at 2700 cm^{-1} . The intensity of the *D* peak which is characteristic of sp^3 carbon atoms of defects and disorders¹² has allowed one to determine the quality of graphene.⁹ The shape and shift of the *2D* peak have been used to judge the number of layers in a multilayer graphene.⁹ The width of the *G* band which is related to the vibration of sp^2 -bonded carbon atoms in a two-dimensional (2D) hexagonal lattice has allowed us to study the level of doping of a sample.^{10,11} Figure 5 compared the Raman spectra of comparative graphene, KNG180, and various of GNPs prepared by ball milling. The two most intense features are the *G* peak at 1580 cm^{-1} and a *2D* peak at 2700 cm^{-1} , the second most prominent band always observed in graphite samples.¹¹ Obviously, the various results of GNPs displayed a main *2D* peak maximum located at 2676 cm^{-1} in the low frequency region (which was 29 cm^{-1} lower than that of pristine KNG180 located at 2705 cm^{-1}), which was consistent with the monolayer feature of graphene sheets.^{12,13} Besides, the shape of *2D* peak was sharp and symmetrical which was similar to the thin graphene data reported previously.^{12,13} The phenomenon of the red-shift of the *G* peak of these products relative to KNG180 (1577 cm^{-1}) has been reported.¹⁴ The vibration of sp^2 -bonded carbon atoms in a 2D hexagonal lattice probably modify

significantly because of the doping effects in thinner graphene sheets.¹⁴ What is more, the small *D* peak and a sharp *G* peak confirmed the sp^2 type bonding of the carbon atoms in the basal plane.¹⁵ The ID/IG ratios were used as a measure of carbon nanosheets edge quality¹⁶ (relative edge roughness/defect

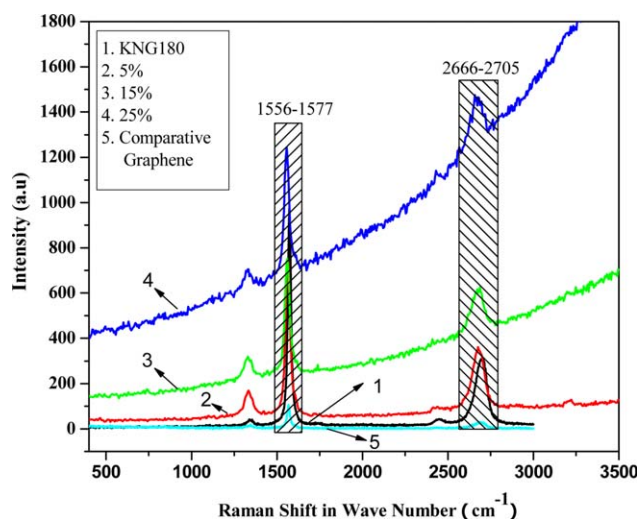


Figure 5. Raman spectra of kinds of carbon nanoplatelets product in different wt % mixture, KNG180 and comparative graphene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density, including dangling bonds and crystallographic randomness¹⁶). The ID/IG ratios ranged from 0.23 to 0.34 (0.21 for the comparative graphene) for the GNPs and rose with the increasing of the mass loading of fillers which agreed with the fact that during ball-milling process, the new required GNPs could not be well protected because of the higher and higher weight loading KNG180, bringing about more and more damage.

CONCLUSIONS

Based on the characterization and analysis earlier, GNPs/epoxy composites with high thermal conductivity have been successfully prepared using ball milling which also has completely displayed its advantages contrasted to another methods. The significant increment in thermal-conductive property of GNPs/epoxy composites could be mainly attributed to the homogenous dispersion of GNPs in matrix. Although the thermal conductivity improvement in composites does not reach the theoretically predicted value dominantly due to the presence of thermal interface resistance at the nanoplatelets/polymer or nanoplatelets/nanoplatelets boundaries, ball milling offer optimistic feasibility of preparing composites or even large scale GNPs in the premise of low-cost, easy-operating, and high-efficiency.

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REFERENCES

1. Huang, X. Y.; Zhi, C. Y.; Jiang, P. K. *J. Phys. Chem. C* **2012**, *116*, 23812.
2. Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E. P.; Nika, D. L.; Balandin, A. A.; Bao, W.; Miao, F.; Lau, C. N. *New J. Phys.* **2009**, *11*, 095012.
3. Ghose, S.; Watson, K. A.; Delozier, D. M.; Working, D. C.; Connell, J. W.; Smith, J. G.; Sun, Y. P.; Lin, Y. *Polymer* **2006**, *8*, 961.
4. Yu, A.; Ramesh, P.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C. *J. Phys. Chem. C* **2007**, *111*, 7565.
5. Zhao, W. F.; Fang, M.; Wu, F. R.; Wu H.; Wang, L. W.; Chen G. H. *J. Mater. Chem.* **2010**, *20*, 5817.
6. Wu H, Zhao W, Chen G. One pot in situ ball milling preparation of polymer/graphene nanocomposites. *J. Appl. Polym. Sci.* **2012**, *125*, 3899.
7. Han, Z. D.; Fina, A. *Prog. Polym. Sci.* **2011**, *36*, 914.
8. Dresselhaus, M. S.; Jorio, A.; Hofmann, M.; Dresselhaus, G.; Saito, R. *Nano Lett.* **2010**, *10*, 751.
9. Ferrari, A. C. *Solid State Commun.* **2007**, *143*, 47.
10. Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K. S.; Krishnamurthy, H. R.; Geim, A. K.; Ferraria, C.; Sood, A. K. *Nat. Nanotechnol.* **2008**, *3*, 210.
11. Huang, M.; Yan, H.; Chen, C.; Song, D.; Heinz, T. F.; Hone, J. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 7304.
12. Kudin, K. N.; Ozbas, B.; Schniepp, H. C.; Prud homme, R. K.; Aksay, I. A.; Car, R. *Nano Lett.* **2008**, *8*, 36.
13. Calizo, I.; Balandin, A. A.; Bao, W.; Miao, F.; Lau, C. N. *Nano Lett.* **2007**, *7*, 2645.
14. Geng, J.; Kong, B. S.; Yang, S. B.; Jung, H. T. *Chem. Commun.* **2010**, *46*, 5091.
15. Al-Mashat, L.; Shin, K.; Kalantar-zadeh, K.; Plessis, J. D.; Han, S. H.; Kojima, R. W.; Kaner, R. B.; Li, D.; Gou, X. L.; Ippolito, S. J.; Wlodarski, W. *Phys. Chem. C* **2010**, *114*, 16168.
16. Casiraghi, C.; Hartschuh, A.; Qian, H.; Piscanec, S.; Georgi, C.; Fasoli, A.; Novoselov, K. S.; Basko, D. M.; Ferrari, A. C. *Nano Lett.* **2009**, *9*, 1433.