Research paper

Highly efficient reduction of graphene oxide by sub/supercritical water and their application for thermal interface materials

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Highlights
- A green and efficient way to the reduction of GO is investigated.
- The mechanism of reduction of GO by sub/supercritical water is confirmed by experiment.
- RGO as a filler of TIMs, it significantly enhances the thermal conductivity of composites.

Abstract
Heat transfer in the electronics industry has become a critical problem for the progress of miniaturizing device components. As a filler for thermal interface materials (TIMs), graphene has attracted great attention owing to high thermal conductivity and low Kapitza resistance. Therefore, how to obtain high quality and large-scale graphene has become a key issue. In this report, we suggest an approach, which is simple, fast, efficient and eco-friendly, to reduce graphene oxide by sub/supercritical water from 200 to 400 °C. The reduction of graphene oxide is caused by higher temperature and the unique characteristic of water in this temperature range. This hypothesis is verified by X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman, thermal gravimetric analysis (TGA) results and comparison experiments. Furthermore, we used the reduced graphene oxide as a filler for graphene-epoxy composites. As a result, the thermal conductivity of the composites significantly increased compared to the pristine epoxy.

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1. Introduction
Heat transfer in the electronics industry has become a critical problem for the progress of miniaturizing device components. As a result, it has created an urgent need to improve the performance of thermal interface materials (TIMs) in modern chip. The TIMs is the thermal channel between hot source and heat sink. As TIMs, high thermal conductivity is the essential prerequisite for improving the power of heat transfer. Conventional TIMs are based on polymers filled with high thermal conductivity particles such as alumina, silica, and silver, which require high volume fractions of filler (50–70 vol.%) to achieve thermal conductivity values of 1–5 W/mK [1–4]. Years ago, carbon nanotube has been used as a filler [5] for TIMs due to high thermal conductivity. However, the thermal conductivity of carbon nanotube–polymer composites has not improved substantially because of the high Kapitza resistance of...
carbon nanotube [4]. Recently, graphene has attracted great attention as a filler [6–12] for TIMs owing to high thermal conductivity and low Kapitza resistance. Therefore, how to obtain high quality and large-scale graphene has become a key issue.

Nowadays, many methods have been proposed to prepare single-layer and multi-layer graphene [13], such as, micro-mechanical exfoliation of graphite [14], chemical vapor deposition [15,16], epitaxial growth [17], liquid phase exfoliation [18,19] and reduction of graphene oxide (GO). However, the reduction of GO is the most promising way of achieving mass production of graphene. GO can be converted to reduced graphene oxide (RGO) by using chemical reduction agents or other reduction means, such as hydrazine [20], hydroquinone [21], L-ascorbic acid [22], vitamin C [23], sugar [24], aluminum powder [25], zinc powder [26], iron powder [27] and heat treatment. Among them, the heat treatment is environmentally safer to a large extend. In general, the heat treatment methods include low temperature solvothermal reduction (lower than 200 °C) [28–30], high temperature annealing (higher than 1000 °C) [31] and supercritical fluid reduction (about 200 °C–400 °C) [32]. The low temperature solvothermal reduction is time-consuming (about 20 h) and the reduction process is incomplete. The condition of high temperature annealing is rigorous. Some researches [32] suggest that supercritical CO2 and alcohol can be used for reducing GO, and other research [33] reports that mixed solution of sulfuric acid and organic solvent can improve solvothermal reduction of GO. However, the sulfuric acid and organic solvent cause serious pollution to the environment. Therefore, we can make full use of the higher temperature and H+ catalyzed dehydration to improve reduction of GO, and to avoid serious pollution to the environment. Fortunately, water shows these excellent properties in the temperature range from 200 to 400 °C [34–36]. It can produce large amounts of H+, which means that GO can be reduced by acid catalyzed dehydration [29,33]. Certainly, water is friendly to the environment. Besides, there are few reports about the thermal properties of reduced graphene oxide — epoxy composites.

In this paper, firstly, we suggest a way to reduce GO by sub/supercritical water in the temperature range from 200 to 400 °C. It is simple, green and fast. Secondly, we do the comparative experiment of reducing GO by solvothermal (N, N-dimethylformamide (DMF)) under the same condition, and explore the mechanism of the reduction of GO by sub/supercritical water. Thirdly, we use the RGO as a filler for TIMs and study its thermal properties.

2. Experimental

2.1. Materials

Natural graphite powder (SP), potassium permanganate (KMnO4) (AR), concentrated sulfuric acid (H2SO4) (98%, AR), hydrogen peroxide (H2O2) (30%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Epoxy resin (6002) and curing agent (5772) were purchased from Shanghai resin Co., Ltd (Shanghai, China). They were used as received. Deionized water was used throughout the experimental procedure.

2.2. GO synthesis

GO was prepared from natural graphite powder via the modified Hummers method [37]. 50 ml H2SO4 was added into a flask and cooled to 0 °C by ice bath. 2 g natural graphite powder was added into flask and stirred. 7 g KMnO4 was added gradually during stirring and cooling. Low temperature (below 10 °C) mixture was maintained for 30 min. The reaction temperature was raised to 35 °C by heating and maintained for 2 h. 700 ml deionized water was added to the mixture and the temperature increased drastically, keeping the high temperature reaction lasting for 30 min. In addition, H2O2 was added until the gas evolution ceased. The product was collected by filtering with glass filter, washing repeatedly with deionized water and drying under vacuum conditions at 50 °C overnight.

2.3. Reduction of GO by sub/supercritical water

The reduction of GO by sub/supercritical water was performed in a 15 ml sealed stainless-steel reactor. 20 mg graphite oxide was placed into a container and dispersed in 10 ml water by sonication (180 W, 40 KHz, DS-3510 DTH, Sonxi Ultrasonic, Shanghai, China) for 2 h. Then the GO suspension was transferred into the stainless-steel reactor. The reactor was heated up to preset temperatures (200 °C, 300 °C, 400 °C) within 40 min in a tube furnace and all the reaction temperature retains for the same time (1 h). The sub/supercritical experiments were finished by placing the hot reactor into an ice-cold water bath. The RGO was collected by filtering, washing repeatedly with deionized water and drying under vacuum conditions.

2.4. Preparation of graphene-epoxy composites thermal interface materials

Graphene-epoxy composites are prepared as follows: The graphene suspension was obtained by dispersing RGO in acetone with sonication (2 h). Epoxy was added to graphene suspension, then subjected to 30 min of high-wear mixing. The acetone was dried at 80 °C in a vacuum oven (30 min). Meanwhile, curing agent was added with continuous stirring with the weight ratio of epoxy to curing agent of 4:1. The homogeneously dispersed mixture of epoxy and RGO was loaded into a custom Teflon mold, degassed and heated in vacuum for curing. Composites were cured at 80 °C for 6 h to complete the curing cycle. The composites with different RGO loadings varying between 2 and 10 vol.% were prepared from the same above procedure.

2.5. Characterization

Fourier transform infrared spectroscopy (FTIR) was used to verify the functional groups of samples. The FTIR spectra (Nicolet 6700, ThermoFisher, USA) of GO and RGO were recorded in the wavenumber range of 4000–400 cm⁻¹ using the KBr pellet technique. X-ray Diffraction (XRD) was used to confirm the crystal structure. The XRD experiments were carried out using a Bruker D8 ADVANCE with Cu Ka radiation (Bruker, Germany). The XRD measurements were operated with acceleration voltage of 40 kV and acceleration current of 20 mA. Thermal gravimetric analysis (TGA) was performed in Q600 Simultaneous DSC-TGA (TA Instruments, USA), with a scan rate of 20 °C/min from room temperature to 600 °C under nitrogen atmosphere. Atomic Force Microscopy images (AFM) were obtained by a Nanoscope Ilia in tapping mode. The thermal conductivity of graphene-epoxy composites was measured by a heat flow method (DRL-2, Xiang Ke, China), its accuracy is higher than 97%. The diameter of sample is 12 mm and the thickness of sample is 2 mm (see supporting information Fig. S1).

3. Results and discussion

3.1. The reduction of GO confirmed by XRD, FTIR and TGA measurements

Fig. 1 shows the typical AFM image of RGO (Other image see supporting information Fig. S2). It indicates graphene sheets with
an average thickness of 0.9 nm. As calculation, the specific surface area of RGO is 234 m²/g (see supporting information Fig. S3). It is lower than the theoretical specific surface area of graphene, which due to the agglomeration of the GO upon reduction. Fig. 2a, b, c shows the XRD results of GO is treated by sub/supercritical water in different temperature (200 °C, 1 h; 300 °C, 1 h; 400 °C, 1 h). We can observe that the GO peak (001) disappears and the graphene peak (002) occurs. Furthermore, the intensity of graphene peak (002) increases with the enhancement of treated temperatures. This phenomena confirms that GO was reduced by sub/supercritical water and that higher temperature improved the reduction of GO. The reduction of GO by sub/supercritical water treated was also demonstrated by FTIR spectroscopy, as shown in Fig. 3. Fig. 3a exhibits that there are a large number of oxygen-containing functional groups presence in GO [38–41], such as, 3401 cm⁻¹ (stretching vibration of –OH), 1762 cm⁻¹ (stretching vibration of C=O on the edges of the layer planes of conjugated carbonyl groups), 1628 cm⁻¹ (vibrations of the adsorbed water molecules and skeletal vibrations of unoxidized graphitic domains), 1412 cm⁻¹ (vibrations of O–H), 1224 cm⁻¹ (stretching vibrations of C–OH), 1052 cm⁻¹ (vibration of C–O). Fig. 3b, c, d shows the FTIR spectra of RGO by sub/supercritical water at 200 °C, 300 °C, 400 °C, respectively. It indicates the majority of oxygen-containing functional groups (O–H, C=O) have been removed. Moreover, the content of other remaining oxygen-containing functional groups (C=O, C–OH) decreases with the enhancement of reduction temperature. The FTIR results also prove that GO can be reduced by sub/supercritical water and higher temperature promote reduction.

Fig. 4 illustrates the TGA curves of GO and RGO. The TGA curve of GO has a weight loss of 62 wt% that is caused by the removal of oxygen-containing groups. It shows that GO posses a large numbers of functional groups. However, the RGO by supercritical water (400 °C, 1 h) has a weight loss of 6 wt%, indicating little functional groups in RGO. The decrease of functional groups suggests that GO has been reduced by supercritical water.

Raman spectroscopy is a nondestructive method for characterizing GO and RGO. Raman spectra of GO and RGO are shown in Fig. 5. As depicted in Fig. 5a, the D/G intensity ratio (I_D/I_G) of GO is about 0.91, supercritical treatment at 400 °C for 1 h increased the I_D/I_G to 1.08 (Fig. 5c). This agrees well with the Raman spectrum of the RGO by other method [42], indicating the reduction did take place. The XRD results, FTIR spectra, Raman and the TGA curves verify GO can be reduced by sub/supercritical water.

3.2. The reasons for the reduction of GO by sub/supercritical water

Which causes the reduction of GO by sub/supercritical water in the temperature range from 200 to 400 °C? It may be caused by the
reduction temperature. Therefore, GO is treated by water (160 °C, 1 h). The XRD result of the GO treated by water (160 °C, 1 h) (see supporting information Fig. S4) shows there is only GO peak (001) but not graphitic peak (002). The peak (001) of GO slightly shifts into high angle, which as a result of the removal of water molecules between the interlayer. The FTIR spectra of the GO treated by water (160 °C, 1 h) (see supporting information Fig. S5) indicates the oxygen-containing groups have not changed compared to that of GO. The FTIR spectra are concordant with the XRD result and prove that the GO can not be reduced at 160 °C (1 h). Therefore, it suggests that the temperature is an important factor for the reduction of GO by sub/supercritical water.

Are there any other factors affect on the reduction of GO by sub/supercritical water? In order to explore this, the GO is treated by DMF under the same condition (200 °C, 1 h; 300 °C, 1 h; 400 °C, 1 h). Fig. 2d, e, f shows the XRD results of the RGO by DMF under different conditions. In all cases, the GO peak (001) disappeared and the graphitic peak (002) occurred. However, the intensity of graphitic peak is lower than that from the RGO by sub/supercritical water under the same conditions. The XRD result confirms that the degree of reduction for GO by sub/supercritical water is higher than that by DMF under the same condition. The FTIR spectra of the GO treated by water (160 °C, 1 h) (see supporting information Fig. S5) indicates the oxygen-containing groups have not changed compared to that of GO. The FTIR spectra are concordant with the XRD result and prove that the GO can not be reduced at 160 °C (1 h). Therefore, it suggests that the temperature is an important factor for the reduction of GO by sub/supercritical water.

higher than that from RGO by sub/supercritical water under the same conditions (see supporting information Fig. S6). The FTIR result also proves that the degree of reduction for GO by sub/supercritical water is higher than that by DMF under the same condition. The TGA curve of the RGO by DMF (400 °C, 1 h) is shown in Fig. 4b. The RGO by DMF (400 °C, 1 h) has a weight loss of 19 wt%, which is lower than that of GO (62 wt%) and higher than that from RGO by supercritical water (6 wt%). It indicates that the content of oxygen-containing functional groups of RGO by DMF is lower than that of GO, and higher than that of RGO by supercritical water. The TGA curve demonstrates that the degree of reduction of GO by sub/supercritical water is higher than that by DMF under the same condition, too. The XRD, FTIR results in accordance with TGA and prove that the reduction of GO by sub/supercritical water is affected not only by the temperature, but also the unique feature of water at this temperature range. The reason is that water is a typical protic solvent, and it can produce large amounts of H⁺ in temperatures ranging from 200 °C to 400 °C [34–36]. But DMF, as a typical non-prootic solvent, can’t produce H⁺ under high temperature and high pressure conditions. The GO can be reduced by acid catalyzed dehydration [29,33,42]. As a result, the reduction of GO by sub/supercritical water is a joint contribution of both the higher temperature and the unique performance of water.
3.3. Application in TIMs

Fig. 7 shows the thermal conductivity of graphene-epoxy composites, and the RGO obtained by sub/supercritical water conditions. The obtained values for the pristine epoxy was $k = 0.192$ W/mK at room temperature, which is in agreement with the epoxy vendor's specifications. The thermal conductivity of graphene-epoxy composites (10 vol.%, reduction temperature 400 °C, supercritical water) can achieve 1.263 W/mK, which is slightly lower than other method (see Table 1.), but it can be mass produced at low cost. Moreover, it indicates that thermal conductivity increases with the addition of graphene and also increases with the enhancement of reduction temperature. Because graphene possesses high thermal conductivity and the degree of reduction of GO enhances with the increment of reduction temperature. Fig. 8 shows the thermal conductivity of graphene-epoxy composites, the RGO obtained by solvothermal (DMF) conditions. The thermal conductivity of composites is much higher than that of pristine epoxy. Furthermore, it exhibits the thermal conductivity of composites lower than that from sub/supercritical water reduction under the same temperature. As a result, it confirms that the reduction power under sub/supercritical water is better than under solvothermal (DMF), and the sub/supercritical water reduction is an efficient way.

4. Conclusions

In conclusion, we have demonstrated an efficient and green approach to the reduction of GO. The GO can be reduced by sub/supercritical water in the temperature range from 200 to 400 °C. It requires only 1 h, which is quicker than using the low temperature solvothermal conditions (about 20 h). The mechanism of reduction of GO by sub/supercritical water is proved by comparison experiment, to be specific, the higher temperature conditions and the unique characteristic of water. Water at this temperature range can produce large amounts of H+, which significantly improve the reduction of GO. These findings are confirmed by the XRD results, FTIR spectra and TGA curves. In addition, we have used the RGO as filler for the graphene-epoxy composites, which substantially increases the thermal conductivity of TIMs with lower volume fraction.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.applthermaleng.2015.07.011.

Table 1. Thermal conductivity enhancement in TIM composites.

<table>
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<tr>
<th>Filler</th>
<th>Thermal conductivity</th>
<th>Fraction</th>
<th>Matrix material</th>
<th>Method</th>
<th>Reference</th>
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<td>Graphene (2 nm)</td>
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<td>5.4 vol.%</td>
<td>Epoxy</td>
<td>Thermal shock</td>
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<tr>
<td>Graphene – MLG</td>
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<td>10 vol.%</td>
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<td>Liquid-phase-exfoliation</td>
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<td>non-covalent functionalized</td>
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<td>4 vol.%</td>
<td>Epoxy</td>
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<td>8</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>1.26</td>
<td>10 vol.%</td>
<td>Epoxy</td>
<td>Supercritical water</td>
<td>This work</td>
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References