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Synthesis of highly concentrated suspension of chemically converted graphene in organic solvents: Effect of temperature on the extent of reduction and dispersibility

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Abstract–We report the effect of temperature on the extent of graphene oxide reduction by hydrazine and the dispersibility of the resulting chemically converted graphene (CCG) in polar organic solvents. The extent of graphene oxide reduction at high temperatures was only slightly higher than at low temperatures (30-50 °C), while the dispersibility of the resulting CCG in organic solvents decreased markedly with increasing temperature. The low dispersibility of CCGs prepared at high temperatures was greatly affected by reduction and influenced by the formation of an irreversible agglomerate of CCG at high temperatures. The reduction of graphene oxide at low temperatures is necessary to prepare highly dispersible CCG in organic solvents. CCG prepared at 30 °C is dispersible in N-methyl-2-pyrrolidone concentrations as high as 0.71 mg/mL. The free-standing paper made of this CCG possessed an electrical conductivity of more than 22,000 S/m, one of the highest values ever reported.

Key words: Chemically Converted Graphene, Graphene Oxide, Hydrazine Reduction, Colloidal Suspension, Dispersibility, Organic Solvent

INTRODUCTION

Graphene and graphene-based materials have attracted significant attention from both science and industry due to their excellent mechanical, electrical, thermal and optical properties, as well as their high specific surface areas [1,2]. Chemical reduction of colloidal suspensions of graphene oxide is considered a scalable and versatile method for producing chemically converted graphene (CCG), which has potential applications in several fields [2-8]. Among the chemical reduction methods, hydrazine reduction is the most popular and effective method to produce high quality CCG [9-12]. However, the major obstacle to the hydrazine reduction of graphene oxide, like other types of chemical reduction, is the irreversible agglomeration of CCG sheets during reduction [9,10]. Stankovich et al. [9] reported that the CCG obtained by hydrazine reduction of an aqueous graphene oxide suspension at 100 °C could not redisperse in water or in any organic solvents. Unfortunately, most of the unique properties of CCG are only associated with individual sheets [10]. Several attempts have been made to disperse CCG in solvent for preparing colloidal suspension of CCG, which is an efficient approach to producing processable CCG in large quantities [10-15]. However, the preparation of high concentrated suspension of CCG, especially in organic solvents, is still a major challenge. A hydrazine reduction of a graphene oxide suspension in a mixture of *N,N*-dimethylformamide (DMF) and water (volume ratio of DMF/H_2O=9) at 80 °C was subsequently diluted 10 times with various organic solvents to create a colloidal suspension of CCG with dispersibility up to 0.03 mg/mL [11]. However, the low concentration of CCG limits its potential applications. An attempt was made to improve the dispersibility of CCG in organic solvents by functionalization with an aryl addend, which resulted in functionalized CCG that readily disperses in DMF at about 0.5 mg/mL [14]. However, the presence of functionalized groups on the surface of CCG sheets is undesirable because they may deteriorate the electrical properties of CCG [15]. Recently, we reported that the CCG obtained by phenylhydrazine reduction of graphene oxide suspension at ambient temperature (CCG-P) could readily redisperse in various organic solvents such as *N,N*-dimethylacetamide, DMF, propylene carbonate (PC), and 1-methyl-2-pyrrolidone (NMP) with a concentration up to 1.0 mg/mL [16]. The high dispersibility of CCG-P is explained by the steric effect of the phenyl group incorporated on the surfaces of CCG-P sheets during reduction. Another reason may be that the phenylhydrazine reduction was carried out at ambient temperature, which may diminish the formation of an irreversible agglomerate of CCG-P sheets during reduction.

Herein, we demonstrate that temperature has a major effect on the dispersibility of CCG in organic solvents during the hydrazine reduction of graphene oxide, while it only slightly improves the extent of reduction. CCG prepared by hydrazine reduction of graphene oxide at ambient temperature was readily re-dispersed in polar organic solvents such as DMF, PC and NMP with a concentration as high as 0.71 mg/mL. This paper demonstrates a simple and efficient approach to produce a highly concentrated colloidal suspension of CCG in organic solvents.

MATERIALS AND METHODS

1. Hydrazine Reduction of Graphene Oxide

Graphene oxide was prepared by a modified Hummers method

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[16,17]. As-synthesized graphene oxide was diluted to a concentration of 4 mg/mL by sonication in an ultrasonic bath (Jeiotech UC-10, 200 W) for 10 minutes to create a homogeneous colloidal suspension. Hydrazine reduction was carried out by adding 4 mL hydrazine hydrate into a 100 mL graphene oxide suspension, which was stirred for 24 h at the desired temperature in the oil bath. The resulting CCG was filtered and washed copiously with DMF, and the CCG filter cake was re-dispersed in DMF, PC and NMP by sonication for 1 h. To determine the dispersibility of CCG in these solvents, 50 mL of CCG suspension was centrifuged at 3,000 rpm for 15 min, after which 20 mL of the upper supernatant was carefully taken, coagulated by adding a few drops of HCl solution (1 M), and filtered. The filter cakes were washed with methanol, dried in a vacuum at 80 °C, and weighed to calculate the dispersibility of the CCG [14].

2. Characterizations

The elemental compositions of CCGs were analyzed by an element analyzer (Flash 2000, Thermo Scientific). The UV-vis absorption spectra of the CCGs dispersed in ethanol were measured with a microplate spectrophotometer (Spectra Max® Plus 384, Molecular Devices). Oxygen functional groups of graphene oxide were analyzed by X-ray photoelectron spectrometer (XPS) with a monochromatic Al K_α radiation (K-alpha, Thermo Scientific). Raman spectra were characterized by using a confocal Raman microscope (Alpha 300S, WITec) with 532-nm-wavelength incident laser light. TGA (Q50, TA Instrument) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min. AFM images were taken using a Veeco Dimension 3100 SPM with a silicon cantilever operated in the tapping mode. X-ray diffraction (XRD) patterns were recorded on a high power X-ray diffractometer (D/MAZX 2500V/PC, Rigaku) at 40 kV and 30 mA with a scan rate of 2°/min. The electrical resistance of a free-standing CCG paper was measured by the four-point probe method (CMT-10 MP, Advanced Instrument Technology). The thickness of the CCG free-standing paper was determined from a cross sectional image obtained by SEM (JEOL, JSM-6500 FE).

RESULTS AND DISCUSSION

1. Effect of Temperature on the Extent of Reduction and Dispersibility of CCG in Organic Solvent

Hydrazine is the most powerful reducing agent for graphene oxide reduction [9-12,14]. Most previous hydrazine reductions of graphene suspensions are carried out at high temperatures, from 80 to 100 °C, to achieve fast and effective reduction [9-11,14]. Unfortunately, the resulting CCGs have very low dispersibility in organic solvents [9, 11,14]. The effects of temperature on the extent of graphene oxide reduction and the dispersibility of the resultant CCG in NMP are shown in Fig. 1 and Table 1. CCGs obtained by hydrazine reduction of graphene oxide at different temperatures are denoted as CCG-x, where x indicates reduction temperature, ranging from 30 to 100 °C. As shown in Fig. 1, the graphene oxide reduction rate strongly depends on temperature. The reduction was almost complete after just 1 h at high temperature, while reduction at low temperature took more than 12 hours. The extent of graphene oxide reduction for 24 h, expressed in terms of C/O atomic ratio, gradually increased with reduction temperature, from 9.58 to 11.46, corresponding to an increase in temperature from 30 to 100 °C. In our work, higher ratios

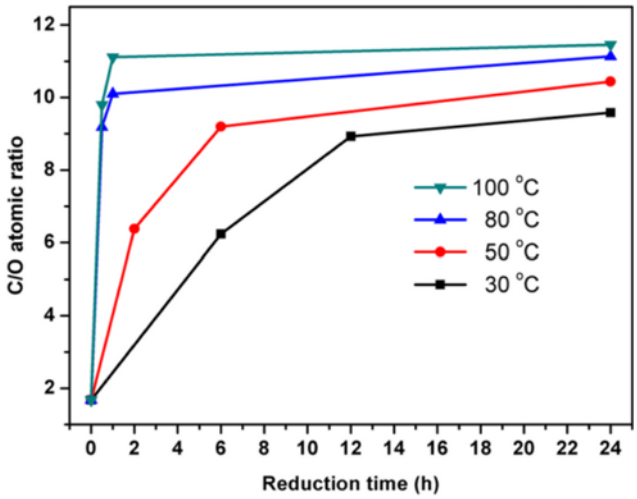

Fig. 1. Effects of reduction temperature on the extent of reduction.

Table 1. Effect of temperature on the extent of reduction and dispersibility of resultant CCGs in NMP

	Reduction time	C/O	C/N	C/(O+N)	Dispersibility in NMP (mg/mL)
Graphene oxide	-	1.68	-	1.68	-
CCG-30	24 h	9.58	40.92	7.76	0.71
CCG-50	24 h	10.44	34.63	8.02	0.28
CCG-80	24 h	11.13	28.45	8.00	0.13
CCG-100	24 h	11.46	26.22	7.97	<0.05

of GO/hydrazine or longer reduction times did not improve the extent of reduction. Higher extents of reduction could only be achieved at higher temperatures. However, it is interesting to note that the amount of nitrogen incorporated into CCG sheets during reduction increased with temperature. As shown in Table 1, the C/N atomic ratio significantly decreased with increasing temperature. Minimal incorporation of nitrogen into CCG during reduction is desirable since incorporated nitrogen is considered an impurity that increases the sheet resistance of the CCG [18,19]. Since nitrogen was incorporated with carbon to create a C-N bond, the C/(O+N) atomic ratio was considered as an alternative for evaluating the extent of graphene oxide reduction to the C/O atomic ratio [20]. According to this evaluation, the extent of reduction at ambient temperature was only slightly lower than that at high temperature. In contrast to the extent of reduction, the dispersibility of the resulting CCG in NMP sharply decreased with an increase in reduction temperature. By increasing the reduction temperature from 30 to 50, 80 or 100 °C, the dispersibility of CCG decreased by approximately 2.5-, 6- or 14-fold, respectively. The apparent reason for the decrease in the dispersibility of CCG in organic solvent is the increase in the extent of reduction. However, we recognized that CCGs prepared at high temperature (80-100 °C) for only 0.5 h were highly aggregated and readily adhered to the surface of a Teflon-coated magnetic bar. On the other hand, these phenomena were not observed when the CCGs were prepared at low temperature for 24 h, even though they exhibited a similar extent of reduction (Fig. 1). To elucidate the reason for the sharp

Table 2. Effect of reduction temperature on the dispersibility of CCGs

	Reduction time	C/O	C/N	C/(O+N)	Dispersibility in NMP (mg/mL)
CCG-30	24 h	9.58	40.92	7.76	0.71
CCG-50	6 h	9.20	60.58	7.97	0.38
CCG-80	30 min	9.18	46.57	7.67	0.26
CCG-100	30 min	9.80	35.21	7.66	0.21

drop in the dispersibility of CCGs with increasing temperature, the dispersibility of CCGs prepared at different temperatures that had similar C/O atomic ratios was measured. As shown in Table 2, the dispersibility of CCGs with similar C/O atomic ratios significantly decreased with increasing reduction temperature. The CCG-50 and CCG-80 prepared for 6 and 0.5 h, respectively, have a C/O ratio a little lower than that of CCG-30 prepared for 24 h, but they have notably lower dispersibility than that of CCG-30, indicating that higher reduction temperatures are very unfavorable to the dispersibility of CCGs. In comparison to the dispersibility of CCGs prepared at the same temperature, we found that the extent of reduction significantly contributed to the decrease in dispersibility. By increasing the reduction time from 0.5 to 24 h, the C/O ratio of CCG-80 increased from 9.18 to 11.13 and the dispersibility of CCG-80 decreased from 0.27 to 0.13 mg/mL, respectively. However, the temperature was found to be more important than the reduction time. With a similar C/O ratio, the dispersibility of CCGs decreased from 0.71 (CCG-30) to 0.27 mg/mL (CCG-80) as temperature increased from 30 to 80 °C. The decrease in the dispersibility of CCGs prepared at high temperature is attributed to the formation of irreversible agglomeration of the CCG sheets under those conditions. The acceleration of the formation of irreversible agglomerates of CCG sheets at high temperature may be explained by decreases in interactions between CCG sheets and solvent because the strength of hydrogen bonding and dipole-dipole interaction significantly decreases with increasing temperature [21,22].

2. Properties of Highly Dispersible CCG

As shown in Table 1, CCG-30 has relatively high extent of reduction, with a C/O atomic ratio of about 9.58. It is comparable to CCGs described in previous reports [9-12] (Table 3), but it was highly dispersible in organic solvent. In this work, the CCG-30 was chosen for further characterization. The extent of graphene oxide reduction according to reduction time was monitored by UV-vis spectroscopy. Fig. 2 shows the UV-vis spectra of CCG-30 obtained at different

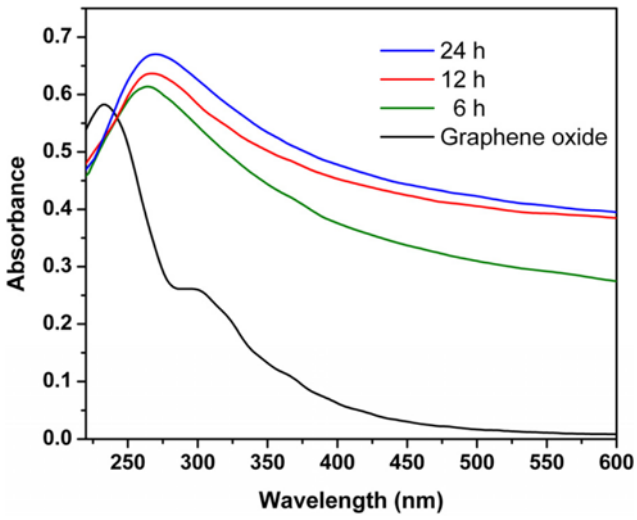

Fig. 2. UV-vis spectra of graphene oxide and CCG-30 obtained at different reduction times.

reduction times, ranging from 6 to 24 h. The UV-vis spectra show that the absorption peak of graphene oxide at 231 nm gradually redshifted to 270 nm, and the absorption in the whole spectrum increased remarkably after a 12 h reduction, indicating restoration of the electronic conjugation within the CCG sheets [10]. Saturation in absorption was observed after a 24 h reduction, suggesting that the reaction was complete.

The removal of oxygen functional groups from graphene oxide during hydrazine reduction was confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3(b), the intensity of the peaks assigned to oxygen functional groups such as hydrogen, peroxide and carbonyl [9] of graphene oxide decreased noticeably after reduction, indicating that most of the oxygen functional groups were removed. In addition, the deconvolution of XPS C1s of CCG-30 shows a new peak at 285.8 eV resulting from the C-N bond due to the incorporation of nitrogen during reduction [9-12]. Raman spectra show a clear redshift of the G peak and an increase in the intensity of the D peak of CCG-30 in comparison with those of graphene oxide (Fig. 4). The intensity ratio I(D)/I(G) increased from 1.07 for graphene oxide to 1.44 for CCG-30. The redshift of the G peak and the increase in the I(D)/I(G) ratio of CCG-30 is attributed to the restoration of sp^2 in the form of new graphitic domains that are small but numerous, which is consistent with previous reports [9,23].

Fig. 5 shows a thermal gravimetric analysis (TGA) and the derivative of thermogravimetric (DTG) curves for graphene oxide and

Table 3. Elemental compositions of CCG-30 in comparison with those given in previous reports

Sample	C (wt%)	O (wt%)	H (wt%)	N (wt%)	C/O (atomic ratio)	C/N (atomic ratio)	C/(O+N) (atomic ratio)	Ref.
Graphene oxide	54.53	43.29	2.18	0	1.68	-	1.68	Present work
Reduced GO	-	-	-	-	10.3	16.1	6.28	[9]
CCG	82.92	13.72	0.11	3.25	8.06	29.8	6.34	[10]
HRG	-	-	-	-	11.0	25.27	7.66	[11]
HG (after annealing)	80.53	8.92	-	5.67	12.02	17.14	7.06	[12]
CCG-30	84.53	11.76	1.30	2.41	9.58	40.92	7.76	Present work

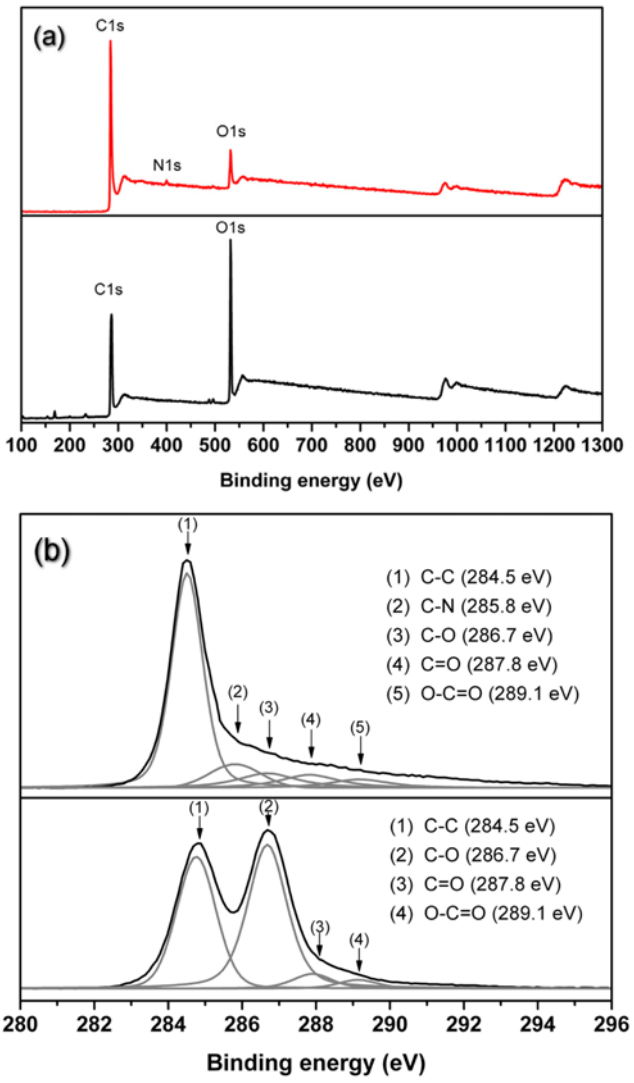

Fig. 3. (a) XPS survey spectra and (b) XPS C1s of graphene oxide (bottom) and CCG-30 (top).

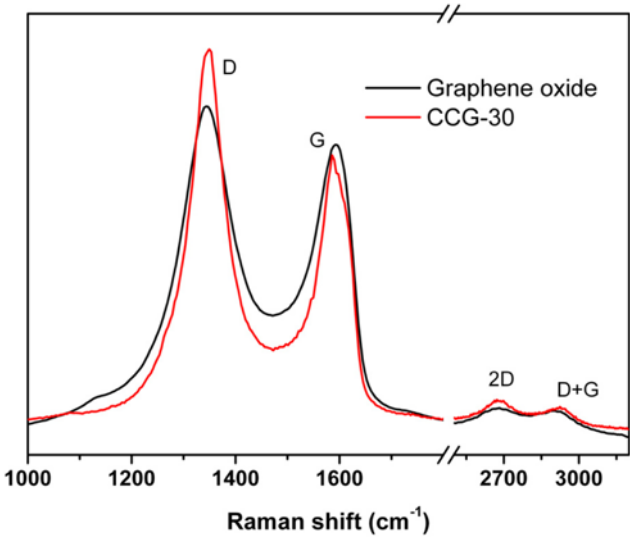

Fig. 4. Raman spectra of graphene oxide and CCG-30.

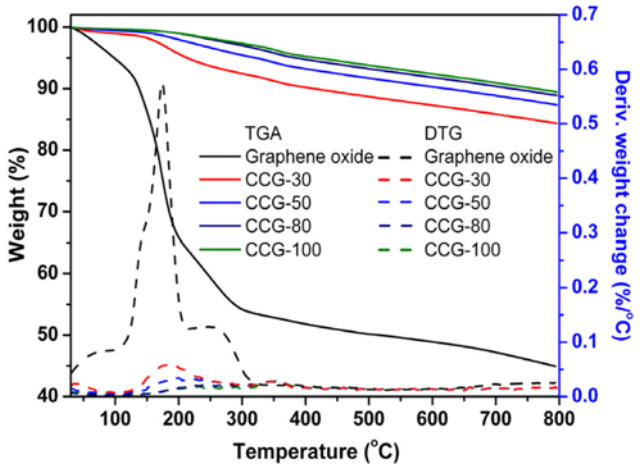

Fig. 5. TGA and DTG curves of graphene oxide and CCGs.

CCGs characterized under a nitrogen atmosphere. CCGs exhibited high thermal stability in comparison with graphene oxide. The mass loss, up to 800 °C, was only around 15.6, 12.6, 11.1 and 10.5 wt% for CCG-30, CCG-50, CCG-80 and CCG-100, respectively, compared with 55 wt% mass loss of graphene oxide. The main mass loss occurred from 150 to 250 °C, due to the decomposition of labile oxygen functional groups such as hydroxyl, epoxy and carbonyl [9, 15]. The DTG curves of CCGs show that the intensity of the decomposition peaks at 175 °C and significantly decreases with increasing reduction temperature, indicating that heat enhances the removal of labile oxygen functional groups.

CCG-30 was readily redispersed in polar organic solvents such as DMF, PC and NMP with mild sonication (Fig. 6(a)). These suspensions were stable for at least one month without noticeable precipitation. The dispersibility values of CCG-30 in DMF, PC and NMP were 0.64, 0.66 and 0.71 mg/mL, respectively, all of which are at least two times higher than that of CCG obtained by hydrazine reduction of graphene oxide in a DMF/water (9/1) system [11], and even higher than that of an aryl addend functionalized CCG [14]. A free-standing paper of CCG-30 prepared by filtration shows a layer-by-layer structure (Fig. 6(b) and 6(c)), indicating that the CCG sheets were well dispersed in the solvent. The individual CCG-30 sheets characterized by atomic force microscopy (AFM) exhibited a thickness of approximately 1.1 nm, which is thicker than that of CCG generated under basic conditions (1 nm) [10] or in a DMF/water system (0.7-0.8 nm) [11].

Electrical conductivity is another property, besides C/O atomic ratio, used to evaluate the quality of CCG. The sheet resistance of a free-standing paper of CCG-30 was characterized by using the four-point probe method, and the thickness of the free-standing paper was determined from an SEM image (Fig. 6(c)). As shown in Table 4, the electrical conductivity of a free-standing paper of CCG-30 dried at 50 °C for 12 h was 5,160 S/m, which then increased to 22,100 S/m after further drying at 150 °C for 12 h. The high electrical conductivity of the free-standing paper of CCG-30, compared with other CCGs reported in previous publications [10,11], can be explained by the low amount of incorporated nitrogen [18,19] and the difference in the starting material, graphene oxide. In this work, graphene oxide was synthesized by the modified Hummers method using

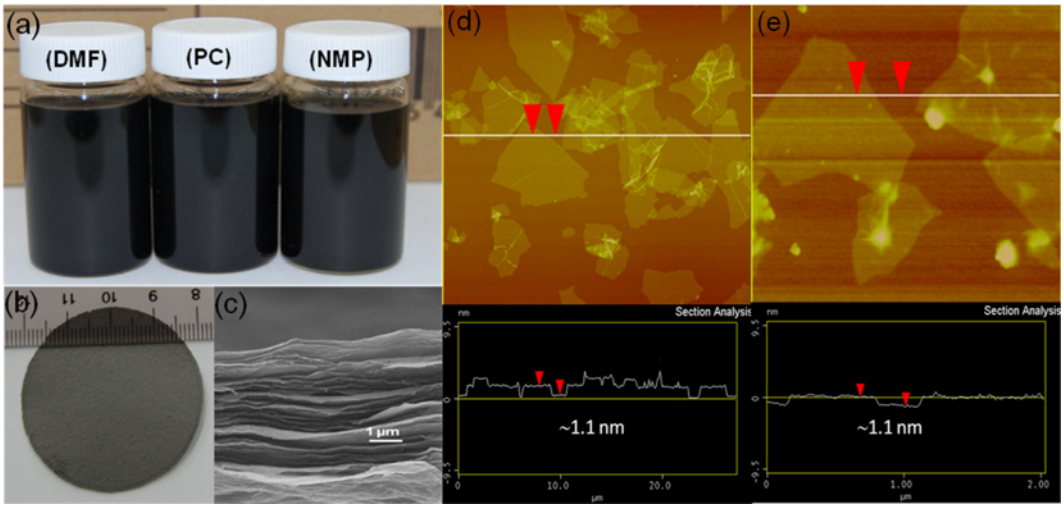

Fig. 6. (a) Dispersion of CCG-30 in polar organic solvents. (b) Free-standing paper of CCG-30 and its SEM cross-section image (c). AFM image of graphene oxide (e) and CCG-30 (d) with its height profile.

Table 4. Electrical conductivities of free-standing papers of CCGs

	Solvent	Drying temperature	Electrical conductivity (S/m)
CCG[5,19]	Water	in air	7,200
		at 220 °C	11,800
		at 500 °C	35,100
HRG[6]	DMF	in air	1,700
		at 150 °C	16,000
CCG-30	DMF	at 50 °C	5,160
		at 150 °C	22,100

microwave-assisted, thermally expanded graphite as the starting material, which has been proven to be a good method for obtaining macroscopic graphene sheets (Fig. 6(d)) with high-quality electrical properties [17].

CONCLUSIONS

The effect of temperature on the extent of graphene oxide reduction by hydrazine and the dispersibility of the resulting chemically converted graphene (CCG) in organic solvents were investigated. The rate of hydrazine reduction of graphene oxide was accelerated by temperature, while the degree of reduction slightly increased with temperature. In contrast, the dispersibility of CCG in organic solvents remarkably decreased with increasing temperature. The low dispersibility of CCGs prepared at high temperatures was attributed to the high extent of reduction and the formation of irreversible agglomerates of CCG at high temperature. The reduction of graphene oxide at low temperatures is a key factor that prevents CCG sheets from forming irreversible agglomerates or restacks. The CCG prepared at 30 °C has dispersibility in NMP as high as 0.71 mg/mL and its free-standing paper exhibited an electrical conductivity of more than 22,000 S/m, one of the highest values ever reported. We believe that highly concentrated suspensions of CCG in organic solvents will facilitate the fabrication of graphene-based materials such as polymer-graphene composites, hybrid materials, conductive inks, and thin films by solution processing techniques.

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