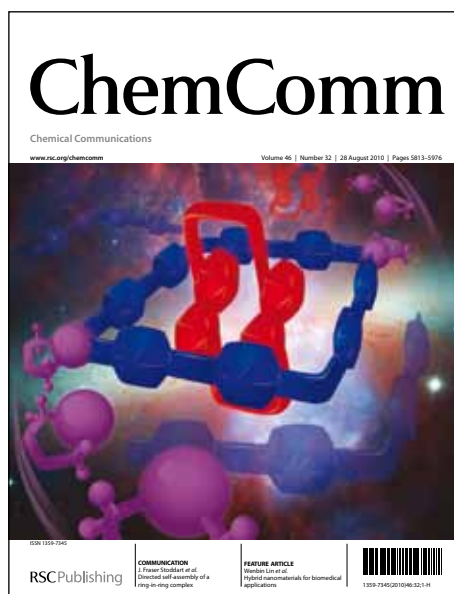# ChemComm

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ARTICLE TYPE

A Green and Facile Approach for Synthesis of Water-Dispersible Reduced Graphene Oxide Based on the Ionic Liquids

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A green and facile route for producing reduced graphene oxide based on ionic liquid has been proposed, by which the as-prepared graphene can be redispersed stably in water (up to 0.6 mg mL^{-1}) after being made into flow-directed solid film.

10 Admitting that the outstanding properties[1] have shown graphene to be a promising material for prospective applications,[2] a persistent challenge is realizing its economical accessibility and easy processibility when targeting the practical implementation in its application. Among various methods proposed in the past, 15 chemical reduction of graphene oxide (GO) in solution[3] is an efficient route to obtain the mass production at low-cost and high-through put. However, the employed toxic agents that would lead to potential environmental hazard during chemical reduction process limit their widespread use. Therefore, some mild 20 deoxidants including reducing sugar,[4] L-ascorbic acid,[5] alcohols,[6] the protein bovine serum albumin (BSA),[7] and so forth have been proposed recently as alternatives from the viewpoint of eco-friendly.

Unfortunately, most of the strategies aimed at large-scale 25 production of graphene have encountered the issue of aggregation and restacking, which is induced by strong π-π effects. To prohibit the irreversible aggregation tendency, stabilizers or surfactants are commonly needed during reduction process. For example, earlier report by Li *et al.*[3a] has demonstrated that the 30 reduction of GO by hydrazine in the presence of ammonia can lead to the water dispersed graphene sheets via electrostatic repulsion mechanism. Han *et al.*[8] dispersed the hydrazine reduced graphene oxide sheets in ionic liquids (ILs) with the aid of a polymerized ionic liquid (PIL).

35 However, as potential commercial products for industrial applications, the graphene suspensions are less attractive than their powder counterparts because the obtained graphene sheets dispersed in given solvents can only be used to fabricate specific composites whose matrices can be dissolved in them, while if 40 dried into powders or films, graphene could be incorporated into different polymers by choosing different solvents to redisperse. Obviously, this invites a new challenge of the redispersibility of graphene powders. In this regard, functionalization strategies have been employed very recently to covalently attach organic 45 groups (e.g. sulfonate ions or alkylamines) to the chemically reduced graphene oxide and facilitate their dispersion in water or organic media. For example, latest work by Kelly *et al.*[9] has shed some light on preparation of water-soluble graphene powder with relatively free of the basal plane defects. Still, when it comes to

50 practical production, the merits of this new approach may be discounted by lengthy process and the harsh sulfonation process in oleum. Therefore, it is still attractive to explore a simple and eco-friendly strategy enabling a production of graphene with desirable redispersibility to be realized.

55 Herein, we present a green and facile routing for synthesis of water-dispersible reduced graphene oxide (RGO) based on 1-Allyl-3-methylimidazolium chloride[10] (AmimCl), which is a imidazolium-based ILs with appreciate dissolvability for cellulose.[11] The outstanding character of the proposed synthesis 60 craft lies in the simply mixing of GO aqueous with ILs at 180°C can subtly bring about a well dispersed RGO in adopted ILs with the synchronous evaporation of water. It is worthy of noting that IL-reduced graphene oxide (IRGO) shows good redispersibility in water (0.6 mg mL^{-1}) after being made into flow-directed solid 65 film. As far as we know, there has been no report on green reduction method based on ILs to obtain RGO with desirable redispersibity in water till now.
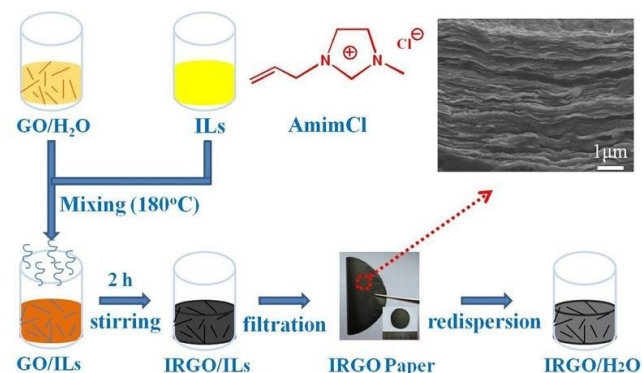
Scheme.1 Illustration of the preparation of IRGO based on ionic liquids.

70 We started off with GO aqueous suspension to prepare IL/RGO suspension, with GO prepared from natural graphite by the modified Hummers' method.[12] The key steps of presented synthesis process is illustrated in Scheme 1. First, the GO aqueous solution produced at room temperature was added to the 75 ionic liquids of 180 °C, a temperature which is much higher than the boiling point of water at normal circumstance. To promote heat and mass transfer, stirring is needed in the process. Accompanied by the gradual evaporation of water, the colour of the liquid mixture changed from yellow brown to black, 80 indicating the occurrence of GO reduction. The resulted solution was then stirred continuously at 180 °C for 2 hours to make the reduction and evaporation thoroughly. After that, the homogeneous mixture of ILs and RGO were cooled down to room temperature, at which it can be stable over several months.

By vacuum filtered through a PTFE filter paper (55 mm diameter, 0.22 μm pore size), followed by rinsing with copious deionized water until there was no precipitate in the filtrate if titrated by silver nitrate, indicating there was no free ionic liquids residue in
5 IRGO. A thin layer of filter cake peeled off from the filter paper was vacuum dried for 12 hours to transform into IRGO paper which is free-standing and flexible. Scanning electron microscopy (SEM) analysis reveals that the fracture edges of the papers exhibits a layered structure through the entire cross-
10 section (included in Scheme1), which looks similar to the microstructure obtained for GO paper prepared using the same method.[13] These results indicate that, similar to hydrophilic GO sheets, our IRGO sheets based on ILs can also be assembled to form highly ordered microscopic structures under vacuum
15 filtration induced directional flow. Moreover, the stable RGO/ILs solution as obtained can be used directly to prepare the IRGO /cellulose nanoscomposite as shown in Fig. S1
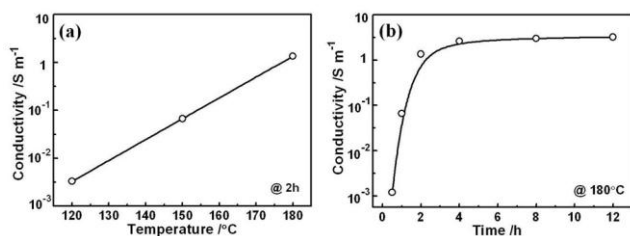

Fig.1 Electrical conductivities of ionic liquids reduced graphene oxide at
20 different temperatures for 2 h (a) and at 180 °C for various times (b).

In general, the reduction   will   give rise to improvement in conductivity of RGO film. The optimum technologic parameters of temperature and time employed in the critical reduction step is therefore identified according to the electrical conductivity of
25 as-produced IRGO paper via a four-point probe method. The correlation of electrical conductivity to temperature and time were plotted as Fig. 1a and 1b, respectively. In our previous tests, the as-prepared film is nonconductive using a temperature close to the boiling point of water (100 °C, normal atmosphere) such as
30 95 °C. So we survey the conductivity at elevated ILs temperature of 120 °C, 150 °C and 180 °C to find that a higher temperature is favourable for GO reduction. We infer that the reduction of GO might be ascribed to thermal reduction in ILs which acts as heating media and provides a circumstance insulated from air.
35 However, further studies are required for clarifying the concrete reduction mechanism of GO in ILs. As Fig. 1b depicted, the conductivity under the temperature of 180 °C increased obviously with reaction time extension in the first 2 hours, then changed little between 2 and 4 hours, and sustained a relatively constant
40 value after 4 hours. Therefore the favourable temperature and time in this experiment is determined as 180 °C and 2 hours. Here, for avoiding ILs degradation at high temperature for a long time, heat treatment time of 2 hours rather than 4 hours is chosen. Of note, the conductivity of as prepared RGO film under
45 optimum condition is comparable to that of the RGO paper from GO reduced by NaOH, while it rises up to nearly 2.5 times bigger once annealed at 200 °C for 30 min.
The reduction of GO is confirmed by FTIR, UV-vis and XPS. As shown in Fig. 2a, the IR spectra[3a,4,6] of GO at room
50 temperature shows strong bands at 3418 cm^{-1} (ν(-OH)), 1735 cm^{-1} (ν(C=O)), 1630 cm-1 (δ(OH)), 1395 cm^{-1} (ν(-OH)) and 1057 cm^{-1} (ν(C-O)). After processed in ILs at 180 °C for 2h, the broad peak at 3418 cm^{-1}, as well as the 1395 cm^{-1} band and the 1057 cm^{-1} band, almost disappears in IRGO, while the ν(C=C) mode occurs
55 indicating the recovery of conjugated structure in this process. UV-vis spectra[3a,4,8] in Fig. 2b shows that the maximum absorption peak at 230 nm corresponding to the π–π* transition of

aromatic C-C bonds in GO is red-shifted to 265 nm in IRGO, It also suggests that GO is reduced and the π-conjugation network is
60 restored. For further proving the formation of reduced graphene oxide in ionic liquids (IRGO), X-ray photo electron spectroscopy (XPS)[3c,4,5a,7] is employed to characterize the elemental compositions. Fig.2c is the C1s deconvolution spectra of GO and IRGO. The C1s peak of GO is composed of four components
65 including C-C (284.5 eV), C-OH (285.6 eV), C-O (287.1 eV) and C=O (288.3 eV). After reduction in ionic liquids at 180 °C for 2 hours, the intensities of all oxygen-containing functional groups are removed remarkably while the intensity of C-C bond increases dramatically. The data is in accordance with previous
70 report.[3a,3c,4,5a,6-8] indicating the GO is successfully reduced to IRGO from the viewpoint of chemical structure.
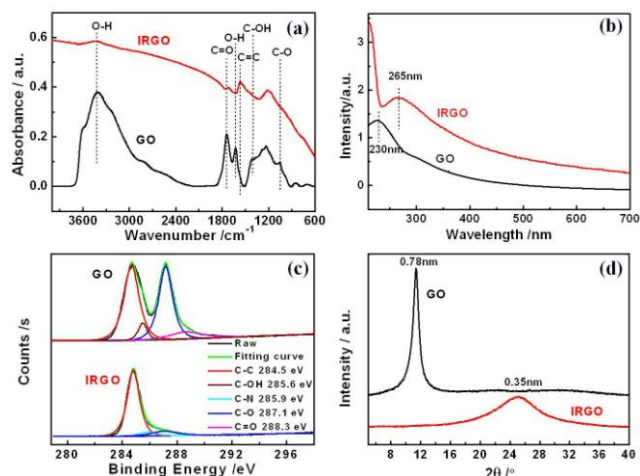

Fig.2 FTIR spectra (a), UV-Vis absorbance spectra (b), C1s XPS spectra (c) and XRD patterns (d) of GO and IRGO.

75 Furthermore, the physical structure of GO and IRGO is also analysed. Fig. 2d shows the X-ray diffraction (XRD) patterns[2b,4,5b] of the GO and IRGO. GO paper exhibits a sharp diffraction peak at $2\theta = 11.38°$, corresponding to the interlayer d-spacing of 0.78 nm, which is larger than that of the graphite (0.34
80 nm) due to the oxygen-containing groups located on the graphene sheets. After reduced in ionic liquids at 180 °C for 2 hours, this sharp diffraction is replaced with a broad diffraction peak at $2\theta = 25.2°$, corresponding to the interlayer d-spacing of 0.35 nm. The remarkable drop of interlayer d-spacing compared with GO (0.78
85 nm) confirms that the introduced oxygen functional groups are removed in the reduction process and the close aggregation of graphene in IRGO paper takes place.[2b,4,5b]

The redispersibility is of particular importance for graphene processability and applications, because most of their unique
90 properties are only associated with individual graphene sheets. The as-prepared free-standing IRGO paper was redispersed into water and other organic solvents with a nominal concentration of 0.1 mg mL^{-1} to survey the solubility. As shown in Fig. 3a, IRGO shows good dispersibility in water, N, N-dimethylformamide
95 (DMF), N-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO) and 2-propanol via sonication, except for toluene, tetra-hydrofuran (THF) and chloroform. Of note, stable dispersions can be gained in water and DMF even when left quiescent for half a month at room temperature. Herein, it is of particular interest to
100 notice that the as-prepared paper can be easily redispersed in water to form stable IRGO aqueous, which is rarely reported about this phenomenon before. Therefore, dynamic light scattering (DLS) is employed to identify whether the IRGO could be dispersed well in water. Fig. 3c shows the distribution of
105 hydrodynamic radius (Rh) for IRGO aqueous by DLS. The Rh

for IRGO in the aqueous solution is about 400 nm, smaller than that of GO sheets in water. On the other hand, the perfect and symmetrical curve suggests that IRGO sheets can be dispersed well in water to form a colloidal aqueous. The colloidal nature of the resulting IRGO dispersions is further confirmed by zeta potential. The average value of the zeta potential of the IRGO aqueous is +39.07 eV. According to Riddick[14] the solution can be stably dispersed if the value of zeta potential is above 30 eV, while the solution is much more stable once the value is exceeded 40 eV. Herein, the zeta potential value of IRGO is quite close to 40 eV, that is to say, the graphene reduced by ILs can be dispersed steadily in water.
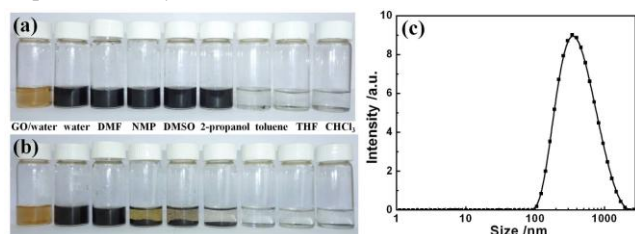

Fig.3 Solubility of IRGO in different solvents and GO in water for comparison purpose with a concentration of 0.1 mg mL^{-1}, (a) Fresh prepared and (b) after preparation for 36 h (c) DLS profiles of RGO aqueous.

In order to know the solubility of IRGO in water in a quantitatively way, UV-vis spectra[3a,4,8] as shown in Fig.4A were measured for IRGO aqueous solutions with different concentrations. The plot of the absorbance versus concentration is shown as dots in Fig. 4B. The straight line is a linear fit to the data with a correlation coefficient of 0.998, which manifests a preferable linear relation exists between the maximal absorption at 265 nm and the concentrations in the range of 0.05 to 0.6 mg mL^{-1}. It is found that the absorbance at the nominal concentration above 0.7 mg mL^{-1} severely deviate from Beer's law because of heterogeneous dispersion. We therefore experimentally infer that the maximum concentration of our IRGO aqueous is about 0.6 mg mL^{-1}.
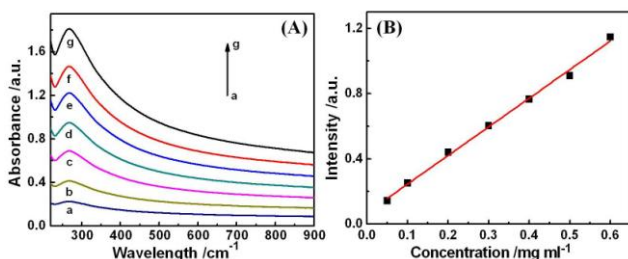

Fig.4 (A) UV-vis spectra of IRGO in water at different concentration (a to g) of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mg mL^{-1}, respectively. (B) The plot of the absorbance intensity versus concentration.

On the origin of the water-dispersable for IRGO, we notice that there is a C-N XPS peak (285.9eV) in the XPS spectrum of IRGO as shown in Fig. 2c. To further confirm the origination of N element, elemental analysis is applied to quantify the content of N element in IRGO. The relatively high content of nitrogen suggests that a portion of ILs cations is left in the IRGO paper. Since Hu et al.[15] have demonstrated that collective van der Waals forces between ILs and graphene are able to describe both the short-ranged cation-π interaction and the long-ranged dispersion interaction through a combination of a quantum mechanical calculation on the level of density functional theory. In addition, Han et al.[8] reported that there is the π-π interaction between the graphene layers and aromatic ILs cation. We hence speculate that the cations bound to ILs may play an essential role in the

stabilization of aqueous of the as-prepared IRGO, which also provides reasonable explanation of the unusual positive zeta potential of the prepared solution.

In conclusion, we developed a green and facile route to prepare reduced graphene oxide based on ILs. The merit of this approach lies in the simply mixing of GO aqueous with ILs at high temperature can subtly bring about a well dispersed RGO in adopted ILs (IRGO) with the synchronous evaporation of water. Furthermore, the filtering scrubbed IRGO shows good redispersibility in water (0.6 mg mL^{-1}) after being made into flow-directed IRGO solid film. We believe that the obtained IRGO which is dispersible in AmimCl and water will open up possibilities for compounding of graphene into cellulose or water soluble polymers in green solvents to exploit the advantages of graphene.

Notes and references

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† Electronic Supplementary Information (ESI) available: SEM images of IRGO/cellulose nanocomposites. See DOI: 10.1039/b000000x/

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