



One-pot electrochemical gram-scale synthesis of graphene using deep eutectic solvents and acetonitrile



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HIGHLIGHTS

- Ionic liquids and deep eutectic solvents are used for exfoliating graphite.
- Acetonitrile (ACN) is used as the solvent based upon recent reports.
- Type IV deep eutectic solvent gives high graphene yields at low energy consumption.
- Type IV DES in combination with IL gives 1 g of graphene from ACN.
- Simultaneous exfoliation of two graphite rods enhances efficiency.

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ABSTRACT

Interest in the exfoliation of graphite to prepare few layer graphene (FLG) has seen significant growth. The electrochemical procedure has, unfortunately, remained rather elusive to scaling-up options. This work builds on recent results of employing acetonitrile (ACN) as a solvent for reducing the amount of expensive ionic liquids (ILs) used as electrolytes. In order to move towards a more environmentally friendly synthesis route, the yield and energy consumption of graphene exfoliation using the four main types of deep eutectic solvents (DESs) has been investigated. Best performance, in terms of the highest specific yield (graphene weight per unit energy consumed) of 0.307 g/kJ, is observed when Type IV DES is employed as the electrolyte in ACN. Similar results, but with less specific yield, is observed when Type I DES is used (other DESs and the IL, BMPyrrBTA, did not provide high yields of graphene but produced more carbonaceous particles and rolled sheets instead). The physicochemical properties of the DESs also confirm that the best DES for exfoliation is the Type IV variant, which needs further investigation. The quality of graphene produced is excellent (4–5 layers, 80% transparency, specific surface area of 180 m²/g, conductivity of 2.1×10^3 S/m and a contact angle of 94° thereby displaying hydrophobicity) and comparable to most graphene produced via other means. While maintaining high quality, the application of ACN and DES is economically attractive compared to other methods.

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1. Introduction

Since its discovery in 2004, graphene has attracted significant interest for a wide range of potential applications, including renewable energy systems such as solar cells, fuel cells and energy

storage. In this time a range of different methods have been adopted and developed for producing the material in bulk [1–3]. Despite this progress, no single production process is able to comply with all the necessary requirements for the various applications described above [4,5]. In recent years, scalable top-down approaches such as the solution-based exfoliation of graphite precursors have attracted a great deal of interest [5–7]. At the same time, the electrochemical route appears to have lagged behind

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Table 1
Details (including purity as sourced from Sigma–Aldrich) and molar composition of components required to prepare the four categories of DESs (Type III DES has several sub-categories that have also been indicated).

Salt (purity)	Complexing agent (purity)	Category of DES	Molar ratio (Salt:complexing agent)
Choline chloride (>99%)	ZnCl ₂ (99.995%)	Type I DES	1:2
CoCl ₂ ·6H ₂ O (98%)	Choline chloride (>99%)	Type II DES	1:2
Choline chloride (>99%)	Ethylene glycol (99.8%)	Type III DES (ammonium-alcohol)	1:2
Methyltriphenylphosphonium bromide (98%)	Ethylene glycol (99.8%)	Type III DES (phosphonium-alcohol)	1:2
Choline chloride (>99%)	Malonic acid (99%)	Type III DES (ammonium-acid)	1:1
Methyltriphenylphosphonium bromide (98%)	Glycerol (>99%)	Type III DES (glycerol-phosphonium)	1:3
Choline chloride (>99%)	Glycerol (>99%)	Type III DES (NADES)	1:2
Choline chloride (>99%)	Trifluoroacetamide (97%)	Type III DES (ammonium-amide)	1:2
Methyltriphenylphosphonium bromide (98%)	Trifluoroacetamide (97%)	Type III DES (phosphonium-amide)	1:2
ZnNO ₃ ·6H ₂ O (98%)	Urea (Bioreagent grade)	Type IV DES	1:2

Table 2
Physicochemical properties of the different categories of DESs used in this work: (a) as synthesised; (b) dissolved in acetonitrile at a ratio of 1:30 by volume.

DES category	Viscosity (mPa s)		Density (g/cm ³) at 25 °C		Conductivity in ACN (mS/cm)	Surface tension (mN/m)	
	(a)	(b)	(a)	(b)		(a)	(b)
Type I DES	85,000	12.70	1.7573	0.8281	0.199	H ^c	37.9
Type II DES	S ^b	0.50	1.239	0.8053	S ^b	H ^c	21.3
Type III DES (ammonium-alcohol)	37	0.05	1.1164	0.7979	7.61	50.76	25.1
Type III DES (phosphonium-alcohol)	45	0.20	1.2462	0.8002	1.47	54.6	33.2
Type III DES (ammonium-acid)	1108	0.38	1.37	0.7926	0.64	H ^c	30.5
Type III DES (glycerol-phosphonium)	12,500	7.31	1.3063	0.8031	0.12	64.8	33.1
Type III DES (NADES)	259	0.34	1.1911	0.7986	1.33	66.3	25.4
Type III DES (ammonium-amide)	S ^b	0.37	1.3317	0.837	1.16	76.9	32.0
Type III DES (phosphonium-amide)	S ^b	0.58	S ^b	0.995	S ^b	H ^c	34.8 ^a
Type IV DES	11,200	6.39	1.7025	0.843	5.98	H ^c	39.0

^a This is the same as the surface tension of pure acetonitrile.
^b S = solidified so impossible to determine physical properties.
^c H = surface tension too high to measure.

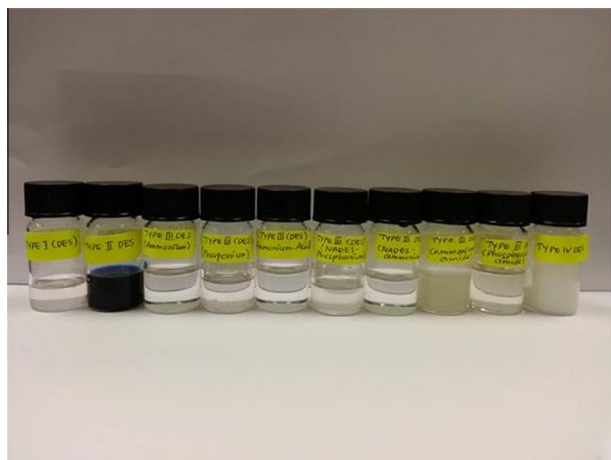


Fig. 1. A digital image of ten different types of DESs is shown here prior to their use for electrochemical exfoliation experiments of graphite rods. From left to right, the order of DESs is Type I, Type II, Type III-ammonium (alcohol), Type III-phosphonium (alcohol), Type III-ammonium (acid), Type III-glycerol (phosphonium), Type III-NADES, Type III-ammonium (amide), Type III-phosphonium (amide) and Type IV.

[8], despite the promise of relatively simple scale-up options [9,10]. Only a few studies have addressed the bulk production of graphene using this technique [8,11,12]. As a result, information on process conditions, especially economic considerations directly related to the amount of electrical energy consumed to make the process viable, is severely lacking.

The electrochemical method [8,11–13], involves a graphite working electrode that is intercalated by cations [14], anions [15]

or both (via oxidation–reduction cycling) [16] depending upon whether the graphite functions as an anode or a cathode, respectively. Three-electrode configurations using aqueous-based surfactants have been reported to produce monolayers successfully [17]. However, yields appear to be low in comparison to organic solvent-based electrolytes [14]. Recently, acetonitrile (ACN) has been employed as a solvent to exploit the advantages of ionic liquids (ILs) and high yields have been reported [18]. The selection of a ratio of 1:50 by volume for IL to ACN, was aimed at reducing costs. In previous studies that ratio was reported at an IL concentration of 0.1 M [19–21].

Acetonitrile has many advantages as an organic solvent but its high vapour pressure and toxic nature is a source of concern [19]. It is primarily used to limit the quantity of IL in solution (to reduce costs) [18] but practical solutions may require more environmentally friendly alternatives. In this work, four types of deep eutectic solvents (DESs) are investigated with the aim of reducing the quantity of organic solvent required for graphene production.

DESs are environmentally friendly IL alternatives that are cheaper than common ILs by an order of magnitude [22]. They come in four types and the third can be further sub-categorized into ammonium, phosphonium, amide, alcohol or acidic alternatives [23]. Type III DESs have recently been used for exfoliating graphite in aqueous solutions but the energy consumption is in the order of 2 MJ [24]. In comparison, the use of ACN in combination with a commercially available IL (BMPyrrBTA) only consumes about 10 kJ of energy and produces high quantities of few layer graphene (FLG) [18]. In this investigation, a single representative of all four types of DESs (along with sub-representatives of the different variants of Type III DESs that include natural DESs or

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