

## High throughput ionic-liquid-assisted electrosynthesis of graphene microsheets in aprotic media

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### Abstract

In the past few years, electrochemical techniques have been proposed for the synthesis of graphene sheets (GNs).<sup>1</sup> In principle, graphene electrosynthesis employs an ionically conductive solution (electrolyte) and a direct current (DC) power source to induce desired structural changes in the graphitic precursor (e.g. rod, plate, or wire) used as the electrode; which could result in the formation of GNs. This approach offers a number of potential advantages over chemical methods including ease of operation and control over the entire synthesis process by manipulating the applied voltage/current, elimination of harsh oxidizers/reducers, and high mass production potential at ambient pressure/temperature. Presumably, direct exfoliation of the GNs from graphite could overcome the low electronic conductivity of graphene films chemically reduced from graphene oxide (GO) derivatives.<sup>2</sup>

Considering the limitation of water electrolysis in aqueous electrolytes, aprotic solvents are generally employed to provide a wide electrochemical window, enabling more energetic intercalations.<sup>3-4</sup> Among those, ionic liquids have exhibited remarkable tendency to intercalate graphitic electrodes and yield gram-scale quantities of carbon nanostructures (CNS) and GNs.<sup>2</sup> Air- and moisture-stable room temperature ionic liquids (RTILs), salts of large organic cations with relatively bulky inorganic counterions, are molten salts with melting points close to room temperature.<sup>5</sup> Owing to low vapor pressure, high chemical and thermal stability, solvating capability, non-flammability and potential recyclability, RTILs have received pronounced interest as 'green' solvents in organic synthetic processes to replace classic, toxic and volatile molecular solvents.<sup>6</sup> Recently, the reactive nature of some specific RTILs has been explored by several research groups.<sup>7</sup> Accordingly, the possible utilization of RTILs as catalysts or reagents, besides their application as mere solvents, has been proposed.<sup>8</sup>

The first attempt of graphene electrosynthesis using ILs was reported in 2008, producing GNs in 1:1 IL/water volume ratio electrolytes.<sup>4</sup> In this work, a voltage of 10-15 V was applied to an electrochemical cell with graphitic anode and cathode where exfoliation was observed at the anode. This line of research was then pursued by Lu et al., focusing mainly on the complementary role of water during the exfoliation process.<sup>2</sup> The latter authors showed that replacing the graphitic cathode with a platinum wire does not affect the electrosynthesis since the main processes related to GN electrosynthesis occur solely at the anode (similar to illustration in Figure 1). Furthermore, they attributed the wide range of produced nanostructured carbon materials to the electrolyte coloration and fine tuning of the IL/water ratios. In addition, the fluorescence behavior of the product solution was assigned to the presence of carbon nanoparticles and nanoribbons. Consequently, they suggested IL/water ratios of ~1:0.1 for the maximum production of planar structures.<sup>2</sup>

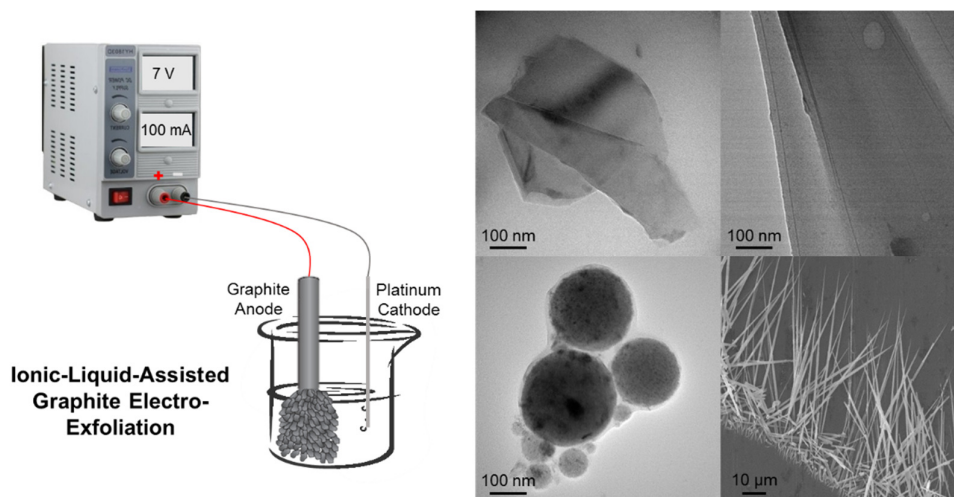


Figure 1: Experimental setup used for graphite anodic exfoliation in the presence of ionic liquids with a variety of product morphologies (planar structures are the majority).<sup>9</sup>

Here, we investigated the room temperature electrochemical exfoliation of iso-molded graphite anodes in a novel electrolyte composed of IL and acetonitrile (~1:50 vol. IL/solvent ratios) using four different IL structures. Figure 1 depicts the experimental setup used for this purpose with a variety of product morphologies. Our approach provides three main advantages compared to the previously published methods using IL/water electrolytes: i) cost efficiency due to low IL content, ii) extended electrochemical stability in the aprotic electrolytes, and iii) much higher exfoliation yields caused by the more effective anionic intercalation within the graphitic layers.<sup>9</sup> Thus, we achieved up to 86% exfoliation in 4 hours using BMPyrr BTA/acetonitrile electrolytes (Figure 2). The major products of the graphite exfoliation, for all the four tested ILs, were crumpled and folded graphene sheets. In addition, carbonaceous particles and rolled sheets were isolated but in much smaller quantities (Figure 1). Furthermore, we demonstrated the complementary role of sonication after electrosynthesis for improving the overall quality of the graphene-based products inferred from Raman spectra analysis.

Importantly, using control experiments (i.e. replacing graphite anode by a platinum wire), we revealed that the reactions of the IL moieties with the electrodes are mainly responsible for the reported fluorescence behavior rather than carbon nanostructures.<sup>9</sup> Furthermore, the cathodic reduction of the cationic moieties such as imidazolium rings generates carbene species that are reactive with the graphite anode and interfere with the anionic intercalation. On the other hand, this provides the opportunity for in-situ functionalization of the graphene sheets via species produced during electrosynthesis process. The resulting functionalized GNs could be used for a variety of applications as a competitive material in energy storage/generation, environmental remediation, biomedical areas and so forth. In any case, via facile post-treatment techniques, any functional group can be removed from the products if not desired. Finally, the research presented here paves the way for future studies on ionic-liquid-assisted electrochemical production of GNs in large scales.

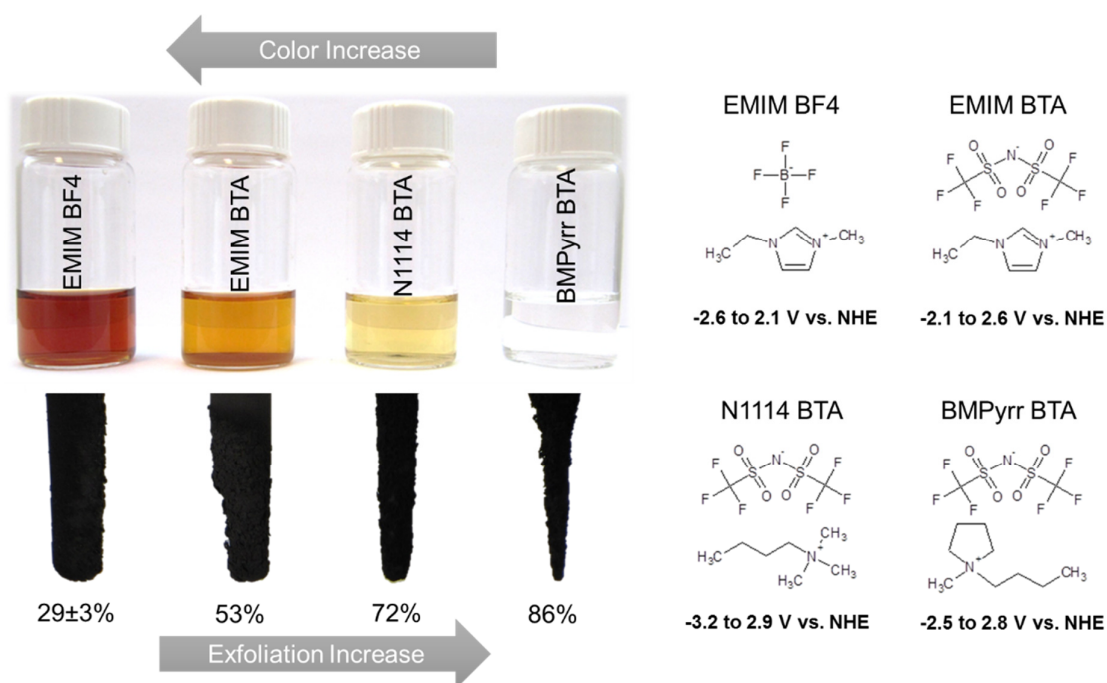


Figure 2: Electrolyte color changes and the exfoliation yield after 4 hours of ionic-liquid-assisted electrochemical graphite exfoliation at 7 V using 0.1 M IL/acetonitrile (~1:50 IL/solvent vol. ratio) at 293 K (the  $\pm$  shows 95% confidence interval from 3 experiments). Numbers below the investigated ILs show their respective electrochemical stability window on platinum at 293 K versus normal hydrogen electrode (NHE).<sup>9</sup>

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