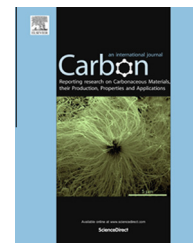


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# Scale-up and purification of graphite oxide as intermediate for functionalized graphene



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## ABSTRACT

High purity graphite oxide (GO) and scale-up of GO synthesis is in high demand for enabling GO applications in catalysis and the synthesis of functionalized carbon nanomaterials. Although Hummers method, which involves oxidizing graphite with  $\text{KMnO}_4$  in sulfuric acid, is highly attractive with respect to its cost-effective raw materials and low energy demand, still purification, scale-up and safety problems prompt numerous challenges in large scale production. Conventional dead-end-filtration (DE) is difficult, owing to the severe plugging of the filters by water-swollen GO, whereas dialysis requires massive amounts of water. Plugging problems are solved when using membrane separation with average membrane pores smaller than the lateral micrometer dimensions of GO nanoplatelets. In contrast to DE and dialysis, a short DE prefiltration of acidified GO dispersions, combined with subsequent cross-flow filtration (CF) enables easy GO scale-up and production of high purity GO. Equipped with on-line monitoring of waste-water, this CF process is automated and enables concentration of GO dispersions in the final stage. In GO purification, pH switching represents the key to removing Mn and S impurities.

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## 1. Introduction

As a single layer of  $\text{sp}^2$  carbon atoms and two-dimensional carbon macromolecule, graphene is attracting significant attention in both academia [1] and industry [2]. Owing to its unique property balance, combining high electrical and thermal conductivity with ultrahigh mechanical strength and barrier resistance, graphene is of interest for advanced carbon and carbon hybrid materials with envisioned applications ranging from molecular carbon composite materials [3,4] to printed electronics [5,6] and catalysis [7–11].

Today, going beyond the IUPAC definition of graphene as a single carbon layer of the graphite lattice [12], the technical

term graphene is often used for few- and multi-layer carbon structures as well as functionalized layered carbon materials [13]. For the sake of clarity, we refer to the functionalized graphene obtained by the reduction of graphite oxide (GO), as reduced graphite oxide (rGO). The presence of functional groups on rGO is essential with respect to improving the interfacial adhesion of rGO to polymers, ceramics and metals, thus enabling the immobilization of nanometer-scaled transition metals and other nanoparticles on graphene. Moreover, the presence of functional groups enhances rGO dispersion in various media without requiring addition of binders and dispersing agents.[14] Two main criteria differentiate rGO materials from pristine graphene: (i) its molecular architecture, and (ii)

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its synthesis. Yet, the precise structures of GO and rGO are rather difficult to identify and subject of on-going debate. In addition to pores and other defects, they contain functional groups, preferably allocated at the edges of graphene layers and its defects [15,16]. Pioneered by Brodie in 1859 [17], the rGO preparation involves a two-step process. In the first step, graphite is oxidized to produce GO. In the second step the thermal or chemical reduction of GO yields rGO. Regarding the use of low cost raw materials, low energy demand, and also its simplicity, this process holds potential for large scale production of functionalized graphene nanomaterials [2,16,18,19]. However, there exist several experimental problems in synthesis and purification of GO, hampering the successful transfer of lab procedures into the industrial scale.

In principle, three different routes enable the preparation of GO from graphite. According to Brodie, fuming  $\text{HNO}_3$  containing  $\text{KClO}_3$  represents an intercalate and highly efficient oxidizing agent for graphite [17]. In contrast to most other methods, this process does not require the use of sulfuric acid, thus producing sulfur-free GO of high purity. However, when chlorate is added to strong acids, highly explosive  $\text{ClO}_2$  gas is formed. Several groups have reported explosions in the lab when trying to reproduce Brodie's GO synthesis [19–23]. Hence, this rather hazardous procedure appears problematic with respect to its scale-up. In 1898, Staudenmaier proposed to use a blend of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in conjunction with  $\text{KClO}_3$  addition. Thereby, the explosion hazard of  $\text{ClO}_2$  gas is combined with the purification problems typical for GO synthesis in the presence of  $\text{H}_2\text{SO}_4$  [24].

In 1958, Hummers and Offeman introduced the process for GO and rGO synthesis that is most popular today. They used  $\text{H}_2\text{SO}_4$  and  $\text{NaNO}_3$  for graphite intercalation and added  $\text{KMnO}_4$  in order to oxidize graphite [20]. In the absence of chlorate no explosive  $\text{ClO}_2$  is formed. However, it should be noted that there exist other hazards relating to the powerful oxidizing agent dimanganese heptoxide ( $\text{Mn}_2\text{O}_7$ ), which is formed as intermediate when  $\text{MnO}_4^-$  reacts with  $\text{H}_2\text{SO}_4$  [16,25]. In its pure form, the highly reactive  $\text{Mn}_2\text{O}_7$  oxidizes most organic compounds including acetone and even alcohols [26]. Moreover, it decomposes and can cause severe explosions at elevated temperatures exceeding  $95^\circ\text{C}$  [25]. In spite of the high  $\text{Mn}_2\text{O}_7$  dilution in sulfuric acid typical for Hummers method, special safety precautions require careful temperature control and the absence of organic compounds in order to prevent explosion hazards. Quantitative removal of residual  $\text{Mn}_2\text{O}_7$  is imperative for the subsequent use of GO together with organic media. It should be noted as well that GO is a strong oxidizing agent and is an explosive. Exposure to bright light can trigger highly exothermic, explosive GO decomposition [27,28].

When  $\text{H}_2\text{SO}_4$  is present during graphite oxidation, sulfates are formed. In addition to sulfate ions, some sulfates are covalently attached to GO [29]. Even trace amounts of sulfur impurities are detrimental to GO and rGO applications in catalysis, in which sulfur can severely poison many catalytic sites. In a recent advance aiming at enabling industrial GO scale-up, Tour et al. have improved Hummers method by excluding the  $\text{NaNO}_3$ , while increasing the amount of  $\text{KMnO}_4$  and using a 9:1 mixture of  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  [30]. They claim significant advantages with respect to Hummers process, namely reduced

exothermicity, no evolution of toxic gases, higher yield of well-oxidized hydrophilic GO, and the formation of cyclic phosphate groups resulting from the reaction of vicinal diols with phosphoric acid. Although the removal of phosphate impurities is not addressed, they see their modified Hummers process as promising route to the large scale production of GO [30]. In addition to sulfur, potassium salts represent another problematic source of impurities, which were reported to dramatically increase the flammability of GO and can even cause its violent, explosive combustion [31]. As a consequence, the GO purification is an important prerequisite for GO scale-up and for achieving high GO product quality together with assuring safety regarding GO storage and handling.

In literature, standard procedures for GO purification involve filtration [32], centrifugation [18,33] and dialysis [33,34]. The main challenge, especially with respect to filtration and centrifugation processes, is the massive swelling of GO in water, as encountered with progressing purification. Highly swollen and viscous GO suspensions tend to plug the pores of most conventional filters. Moreover, they severely impair the GO sedimentation in a centrifuge [31]. Two strategies have been proposed to minimize GO swelling: washing GO (i) with an acid, most commonly HCl [19], or (ii) with an organic solvent [29,31]. However, both strategies have severe shortcomings. Washing with an acid requires additional washing with water in order to remove residual acid. The absence of acid is essential in GO processing, since especially HCl represents a serious corrosion hazard to any steel device such as the oven for thermal GO reduction or the polymer compounders used in melt processing of GO, respectively. According to Dimiev et al., washing with an organic solvent fails to improve GO purity, since removal of sulfate ions and also of manganese and potassium salts require washing with water [29].

In our research, we explore the dead-end filtration, dialysis, and cross flow membrane-mediated filtration (CF) in conjunction with pH switching during washing cycles in order to enable the scale-up of the Hummers GO process. Moreover, both GO product quality and safety are improved by efficiently removing sulfur, manganese and potassium salt impurities. Although CF is widely applied in protein purification and other biotechnology processes [35] as well as water purification [36], it is used for the first time in GO purification. High purity GO is essential for the subsequent formation of rGO by thermal and chemical GO reduction, thus enabling tailoring of functionalized graphene nanomaterials.

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## 2. Experimental

### 2.1. Synthesis of GO

GO was synthesized according to the procedure described by Hummers and Offeman [20]. Two different batch sizes starting with 60 and 120 g of graphite have been used. Graphite (60 g/120 g, KFL99.5, Graphit Kropfmühl AG, Hauenberg Germany) was dispersed in  $\text{H}_2\text{SO}_4$  (95%, 1.4 L/2.8 L, VWR International GmbH, Darmstadt, Germany). Then  $\text{NaNO}_3$  (30 g/60 g, Merck KGaA, Darmstadt, Germany) was added and the resulting mixture was stirred overnight. After cooling to  $0^\circ\text{C}$  using an ice bath,  $\text{KMnO}_4$  (180 g/360 g, Grüssing, Filsum Germany)

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