



Research Article

Environmental impact of the production of graphene oxide and reduced graphene oxide

L. Serrano-Luján¹ · S. Víctor-Román² · C. Toledo⁴ · O. Sanahuja-Parejo² · A. E. Mansour³ · J. Abad⁴ · A. Amassian³ · A. M. Benito² · W. K. Maser² · A. Urbina⁴

© Springer Nature Switzerland AG 2019

Abstract

Reduced graphene oxide (rGO) is widely seen as the most promising route for the low-cost mass production of graphene for many applications ranging from ultrathin electrodes to structural nanocomposites. The Hummers and Marciano methods are the two most successful approaches for producing high-performance rGO, but have been criticized for producing toxic emissions. We have applied life cycle assessment methodology to evaluate the environmental impacts of both production routes for GO and rGO in the context of applications requiring bulk materials or thin coatings. We find no current obstacle to the industrial scale production of graphene arising from its environmental impact. The cumulative energy demand is found to have a cap value between 20.7 and 68.5 GJ/Kg, a relatively high value; impact in other categories (such as human toxicity or resource depletion) is lower, and materials inventory does not include critical/strategic materials other than graphite itself. Our study proposes 1 kg of graphene as functional unit, and an application-specific functional unit normalized by conductivity which show that Hummers production method is far more suitable for bulk applications of graphene, with lower embedded energy per kg of graphene production, while Marciano's production method is better suited for thin film electronic applications.

Keywords Graphene · Graphene oxide · Reduced graphene oxide · Life-cycle assessment · Large production · Potential emissions

1 Introduction

Graphene-based materials have been used in a broad range of applications, extending from electronics and optoelectronic devices [1, 2] to composite materials for building, civil [3, 4], fuel cells [5, 6], water treatment [7–9], lithium-ion batteries [10–13], supercapacitors [14], engineering [15, 16] and medical [17, 18] applications. The use of two-dimensional graphene layers in electronic and

optoelectronic devices requires very little material, on the order of 15 milligrams per m². However, bulk applications where graphene acts as a filler can require the production of 2.4–48 kg of graphene per m³ to realize the desired functionality [19, 20]. To meet the demand for bulk applications, low-cost and mass-production methods are needed to realize the industrialization of graphene manufacturing. To date, graphene oxide (GO), reduced graphene oxide (rGO) and their derivatives have shown promising

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-0193-1>) contains supplementary material, which is available to authorized users.

✉ L. Serrano-Luján, lucia.serrano@urjc.es; ✉ A. Urbina, antonio.urbina@upct.es | ¹Department of Computing Science, King Juan Carlos University, 28933 Madrid, Spain. ²Instituto de Carboquímica (ICB-CSIC), 50018 Zaragoza, Spain. ³KAUST Solar Center (KSC), and Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia. ⁴Departments of Electronics and Applied Physics, Technical University of Cartagena (UPCT), Plaza del Hospital 1, 30202 Cartagena, Spain.

SN Applied Sciences (2019) 1:179 | <https://doi.org/10.1007/s42452-019-0193-1>

Received: 17 October 2018 / Accepted: 18 January 2019

Published online: 25 January 2019

SN Applied Sciences
A SPRINGER NATURE journal

applications in catalysis [21–23], composites [24, 25], energy storage [26, 27], sensing [28–31], water purification [32, 33], supercapacitors [34] and electronics [21, 35] among others.

The production methods of rGO vary in their precursor requirements, chemistry, electrical consumption, environmental impact, scalability, sample properties, and production yield. The choice of the method for industrial application is therefore determined by a careful analysis of the factors just mentioned and the desired performance for the target application. The number of publications dealing with the environmental impact of graphene production is growing, and the main production routes have been analysed, mostly using 1 kg of graphene (often in solution), or 1 cm² of graphene sheet (on different substrates) as the functional units; different impact categories have been analysed in each case making comparison of the different processes from an environmental point of view a challenging task [36–38]. The well-established life cycle assessment (LCA) method can help to address this needed comparison. The LCA method comprises of several steps which can produce meaningful information about the environmental impacts in various categories such as human toxicity (cancer and non-cancer), water contamination, resources depletion or other related to climate change such as green house gases (GHG) emissions or ocean acidification.

Herein, we apply the LCA methodology to evaluate the environmental impact of common processes used in the production of GO as well as various reduction approaches used to produce rGO. First, we compare the impacts of producing GO using the original Hummers method (GO) and the more recent and successful modification of the Hummers method by Marcano et al. (mGO) [22]. We compare the impacts of various reduction strategies, using two different chemical agents, namely hydrazine (hGO) and glucose (gGO), in combination with thermal treatments at different temperatures based on commonly reported methods. Although hydrazine processing has been previously studied [23], glucose processing is included for the first time in an LCA study for graphene production. The results of the LCA are highly dependent on the selection of the functional unit (FU) which must take the performance requisites of the application into consideration. The FU is a metric that relates all emissions and resources used to the desired application (e.g., bulk filler or surface coating) in order to facilitate meaningful comparisons. Exploration towards impact of industrial scale production has been previously performed by Arvidsson et al. for ultrasonication [39, 40] and epitaxial [39, 40] graphene and Cossuta et al. [41]. for several processes, pointing that the least impacting material route remains chemical oxidation followed by thermal reduction, although in terms of cumulative energy demand the ultrasonication exfoliation

has lower energy consumption, but with higher human toxicity [42]. This result confirms the possibility for mass production of graphene with a low environmental impact provided by the laboratory scale analysis presented in the following sections; the results can be considered as a capping limit on the impact for the scaling up of processes towards industrial scale, which should be further reduced.

The article is organized as follows: Sect. 2 explains the scope and boundaries of the LCA study, providing also a description of the experimental procedures carried out at the laboratory. In Sect. 3 the LCA results are presented and in Sect. 4 they are discussed in the context of other studies. Finally, conclusions are provided in Sect. 5.

2 Scope of the assessment

The Life Cycle Assessment presented in this article is based on experimental data taken during laboratory production of GO and r-GO. In this section, a brief overview of production methods and the scope of our assessment is presented.

The most famous method, the mechanical exfoliation of graphite based on the adhesive tape use [28, 43], leads to production of high-quality and high-mobility graphene flakes, but this method is cumbersome, extremely low in yield and it is consequently more difficult to scale-up [44]. Several alternative strategies have been developed since then to achieve scalable production of graphene sheets, including metal ion intercalation [29], liquid phase exfoliation of graphite in organic solvents [24, 45, 46], chemical vapor deposition (CVD) on transition metal catalysts (Ni, Cu, ZnS, Fe) [25–27, 44], vacuum graphitization of silicon carbide (SiC) [47, 48], bottom up organic synthesis of large polycyclic aromatic hydrocarbons (PAHs) [32, 33, 49], and chemical exfoliation/reduction from graphite oxide (GO) [50, 51], resulting in the formation of reduced graphene oxide (rGO). This last approach is considered one of the most promising routes for the large-scale production of graphene, mainly due to its solution-processability and change of properties achieved via inclusion of functional groups during the oxidation/reduction processes. GO is produced by reacting strong oxidants with graphite powder [52, 53]. Hummers developed the most widely used variant for GO production, relying on a mixture of potassium permanganate and sodium nitrate in concentrated sulfuric acid, to produce GO within hours. Several modifications to Hummers' method have been published since, leading to improved oxidation efficiencies [22]. The most common ones rely on increased amounts of potassium permanganate [28, 34, 35, 47, 48, 50, 54, 55] making it possible to obtain large amounts of GO with ease; special mention deserves the process excluding the NaNO₃,

by increasing the amount of KMnO_4 , and performing the reaction in a 9:1 mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$, which improves the efficiency of the oxidation process, this modified Hummers' method is widely known as Marcano's process [22]. The production of graphene sheets from GO begins with exfoliation, usually by ultrasonic cleavage, to separate and obtain graphene oxide layers. Exfoliation is facilitated by reducing the attraction between graphene layers—made possible by increasing the degree of oxidation of GO—and by enhancing the interaction between graphene sheets and the solvent. As GO contains more than 20 wt% of oxygen, it is hydrophilic and can be easily dispersed in water and other common solvents through further functionalization of oxygen-containing groups [56]. This allows for ease of processing into different types of macroscopic assemblies, such as films or membranes. However, GO is electrically insulating, requiring chemical and/or thermal treatments to restore its sp^2 character by reducing it with the aim of improving its electrical conductivity. The production of rGO can be achieved using different chemical reduction agents [52, 53, 57–59], including hydrazine [51] or glucose, the most commonly used reducing reagent. As chemical treatments alone do not reduce the defects induced by the harsh chemical oxidation of graphite [58], a thermal treatment is also required to improve the conductivity of rGO [60, 61]. In Table 1 we have summarized which processes have been considered in this LCA study.

2.1 Experimental section: preparation of rGO

2.1.1 Synthesis of graphene oxide by the modified hummers method

Graphite oxide was prepared using a modified Hummers method from graphite powder by oxidation with NaNO_3 , H_2SO_4 , and KMnO_4 in an ice bath as reported elsewhere

[53, 61]. In brief, 170 mL of concentrated H_2SO_4 was added to a mixture of graphite flakes (5.0 g) and NaNO_3 (3.75 g), and the mixture was cooled in an ice bath, and stirred for 30 min. KMnO_4 (25 g) was slowly added and stirred for another 30 min. The reaction was then warmed to 35°C and stirred for two more hours. Water (250 mL) was slowly added, and then 30% H_2O_2 (20 mL). The mixture was stirred for an hour, filtered, and the obtained powder was repeatedly washed with 400 mL of $\text{HCl}:\text{H}_2\text{O}$ (1:10), and dried under ambient conditions for 24 h.

Graphene oxide was obtained by mild bath sonication of an aqueous graphite oxide dispersion (1 mg/mL) for 2 h, followed by centrifugation at 4500 rpm for 60 min, leading to a brown-coloured dispersion of exfoliated GO with a final concentration of 0.4 mg/mL.

2.1.2 Preparation of reduced graphene oxide. (hGO, and gGO)

Reduced graphene oxide was prepared by adding excess of reducing agent, hydrazine monohydrate or D-(+)-glucose to the obtained GO dispersion, and refluxing for 1 h. The concentration of reducing agent in each case was 6 μL hydrazine, and 6.4 mg glucose per 1 mL of GO dispersion. Filtration followed by washing with 200 mL of deionized water, and vacuum drying at 80°C overnight afforded the powder-like rGO materials, named as hGO and gGO, respectively.

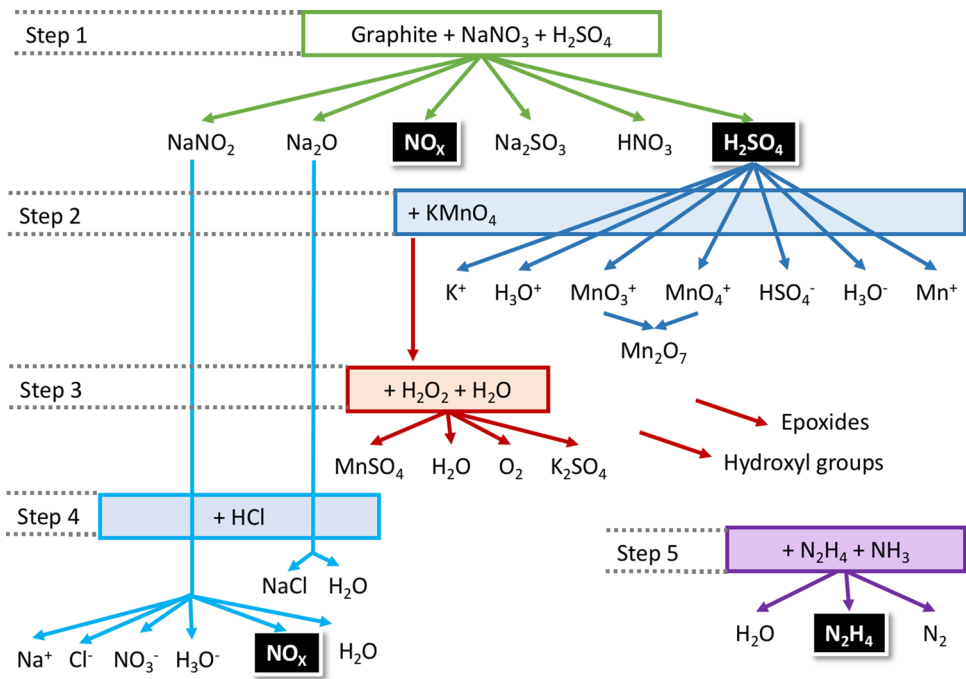
We have identified the reactions occurring during the production of hGO, as Fig. 1 shows in detail. Several of these reactions have been described previously in Ref. [62–64]. We have modelled the reactions to calculate the emissions following the guide provided by Geisler et al. [65]. It should be emphasized that all possible routes have been taken into consideration, where hydrazine emissions have been included.

Table 1 Definition of the cases of study. The columns show the chemicals used during the graphite oxidation, the final processed morphology of the rGO, the reduction agent (H: hydrazine or G:

Glucose) and specific procedure method used (R: reflux, V: vapour, A: annealing), the final conductivity and the thickness

	Oxidation	Structure	Reduction method	σ (S/m)	Thickness (nm)	Case study	Refs
Hummers GO	$\text{KMnO}_4 + \text{NaNO}_3$	Thin-film	H–R	35.45	75	hGO	Hummers and Offeman [53]
			G–R	12.7		gGO	<i>This work</i>
		Paper-like	H–V + A 700°C	3500	10,000	a700-vhGO	Vallés et al. [61]
			A 700°C	8100		a700-GO	
Marcano GO	$\text{KMnO}_4 + \text{H}_3\text{PO}_4$	Monolayer	H–R	10	1	mGO	Marcano et al. [22]
			H–R + A 300°C	35,500		a300-mGO	
			H–R + A 900°C	40,000		A900-mGO	

Fig. 1 Reactions that can take place during the production of the reduced graphene oxide, following the method proposed by Hummers. The chemicals in black background are those that are considered to be emitted in the scenario defined as “worst case” in this study



2.2 Life cycle assessment methodology

2.2.1 Goal and scope

The aim of this study is to assess the environmental impacts of GO and rGO production. We analyze and compare three production routes: first, hydrazine and glucose, which are processes analysed in situ during the laboratory preparation of the materials, and second, we include in the discussion results from literature which use phosphoric acid in order to compare the LCA results [37]. The software SimaPro was used for the calculations (version 8.4.0, licence: analyst).

2.2.2 Definition of the cases of study: functional units

This study focuses on the production of GO and rGO for its use as a semitransparent electronic conductor. In order to reflect this application of graphene in the functional unit, and due to the final uses of the reduced graphene oxide, the functional unit should be related to its conductivity and transmittance. Therefore, two functional units have been defined:

- Functional Unit 1 (FU1): the production of 1 kg of reduced graphene oxide, this FU1 provides an easy way to compare with most LCA studies which use the same FU and is most used for bulk applications of graphene.
- Functional Unit 2 (FU2): this second functional unit attempts to link the production of the material with

the final application. Thus, looking at the conductivity and thickness of the reported material, FU2 is defined as the mass of material required per 1 m² layer divided by its conductivity (mg S-1m-1) being the final units in terms of milligrams divided by S·m, or milligrams per surface and conductivity and it is independent of the thickness of the layer under consideration. Other studies proposed 1cm² of graphene, pointing to electronic applications, but without normalization by conductivity [38].

The density considered in this study is 2 g/cm³, as an average of densities reported in literature and producers technical sheets. [60, 61, 66].

The processes description required during the production and the Spanish-2015 electricity mix that has been considered and are presented in Tables S2 and S3 in Supplementary information respectively. The selection of this electricity mix is due to fact that the experimental data have been measured at a Spanish laboratory, the results can be tuned for other electricity mixes (for other countries or for an evolution of the Spanish mix); for example, results for China, Korea, USA, Germany and Sweden are also included in the supplementary information (Figure S5) where the limited change of the CED calculation with electricity mix is shown.

In Table 1 a definition of the different cases of study are provided and the labels used in all figure are linked to the different routes. These labels are used throughout all the article.

2.2.3 System boundary

Figure 2 shows the boundaries of this study, which includes all inputs and outputs from the cradle to the gate; from the extraction of the materials and production of the ingredients, until the production of the final reduced graphene oxide. From all the cases of this study defined in Table 1, the chemicals that could be emitted during the reduction of the graphene oxide have been considered for the hydrazine-based reduction of GO (see Figure S5). This *worst-case* scenario has been studied, and the potential emissions are included since other studies point this recipe out as a disadvantage of the hydrazine reduction. End-of-life and recycling procedures are out of the scope of this study due to the lack of information in this regard.

2.2.4 Life cycle impact assessment (LCIA) and cumulative energy demand (CED) methodology

In order to estimate the potential hazards from chemical emissions, we have defined a scenario where all the potential emissions are considered. From all the potential chemicals that could be emitted, we have selected those of highest toxicity, being hydrazine the substance of significant toxic concerns.

Life cycle impact assessment (LCIA) methods are applied to get Cumulative Energy Demand (CED) of the products, and the related environmental impacts of the functional units. We emphasize that the international reference life cycle data system (ILCD) method is also applied, as recommended for the characterisation steps in LCIA [67]. Normalised LCIA results give, for each impact topic on midpoint level, or area of protection on endpoint level, the relative share of the impact of the analysed system in the total impact of this category per average citizen or globally, per country, etc.... When displaying the normalised LCIA results of the different impact topics next to each other, it can hence be seen

to which impact topics the analysed system contributes relatively more and to which less. In this article, the inputs in the inventory of the reduced graphene oxide were translated into environmental impact categories scores, by the application of life cycle impact assessment methods. The scores shown in Fig. 4 are normalized, that means the different characterized impact scores are related to a common reference, e.g. the impacts caused by one person during 1 year, in order to facilitate comparisons across impact categories.

3 Results

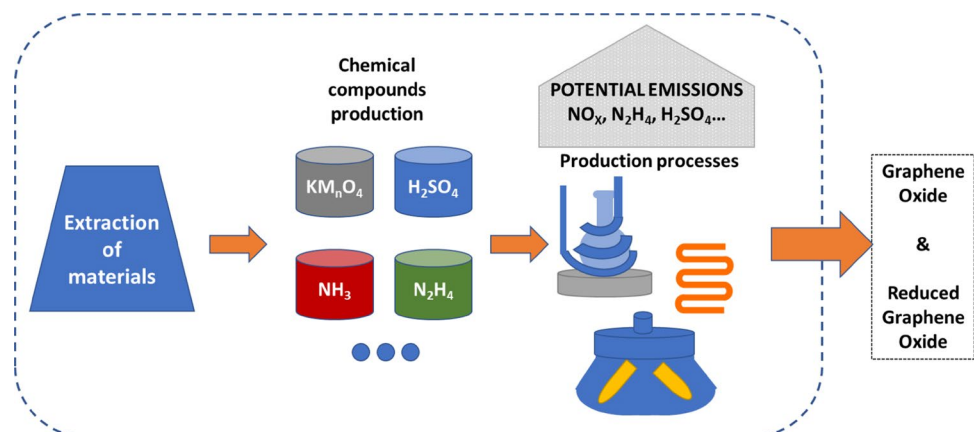
3.1 Impacts of the production methods of rGO

The various production methods of rGO can be classified as being derived directly from the Hummers method of GO production or from modifications of this method. The most widely used modification is that of Marcano, and to which we refer as Marcano's method (mGO), as summarized in Table 1.

The comparative LCA study is applied to two popular Hummer's production methods of rGO, namely hydrazine-reduced (hGO), described in Ref. [49], and glucose-reduced rGO (gGO), as well as to three variations of mGO method, which are summarized in Table 1 along with other protocols mentioned in the literature.

We have assessed in situ, in the laboratory, the impact of all the steps associated to the experimental protocols of gGO, and identified all potential emissions during the production and their environmental impact. The inventories of required materials, electricity and emissions for hGO and gGO based on the Hummers method were obtained directly from laboratory work compilation, while the modified Hummers recipe (Marcano's method) inventory was completed following the article from Marcano et al. [22].

Fig. 2 Cradle-to-gate system boundary for the application of LCA methodology to the cases of study: production of reduced graphene oxide following Hummers recipe, glucose-based reduction, and modified recipe proposed by Marcano. We compare the cumulative energy demand and the environmental impacts whether the rGO is finally annealed or not. Use phase, end of life and recycling processes are not included in the scope of the study



3.2 Life cycle inventory

The outcomes of this study are classified in two main groups. First, the life cycle inventory (LCI) which has been built from the Ecoinvent database (version 3.4) [23]. Tables S1–S13—Supplementary Information—show the processes and materials related to the production of a kilogram of dried reduced graphene oxide, assuming a density of 2 g/cm³. As glucose is not included in the Ecoinvent database, details for its production were obtained and summarized in Supplementary Information.

3.3 Cumulative energy demand (CED)

In Fig. 3 we show the CED values for the cases of study. The detailed shares of CED are shown for FU1 using stacked bars where each contribution is graphically show. For the FU2 a dot is superimposed for each method (right axis of Fig. 1, detailed numbers are provided in the supplementary information). For rGO production methods based on Hummers' method, the electric consumption is the primary share of the CED, representing a share of 83%, 95%, 77% and 92% for hGO, gGO, a700-vhGO and a700-GO respectively. For Marcano's method, use of methanol required for its reduction has an embedded energy share of 60%, 47% and 40% for mGO, a300-mGO and a900-mGO respectively, of which the electric consumption share is 10% and 23% for last two cases due to the electricity required during the annealing process.

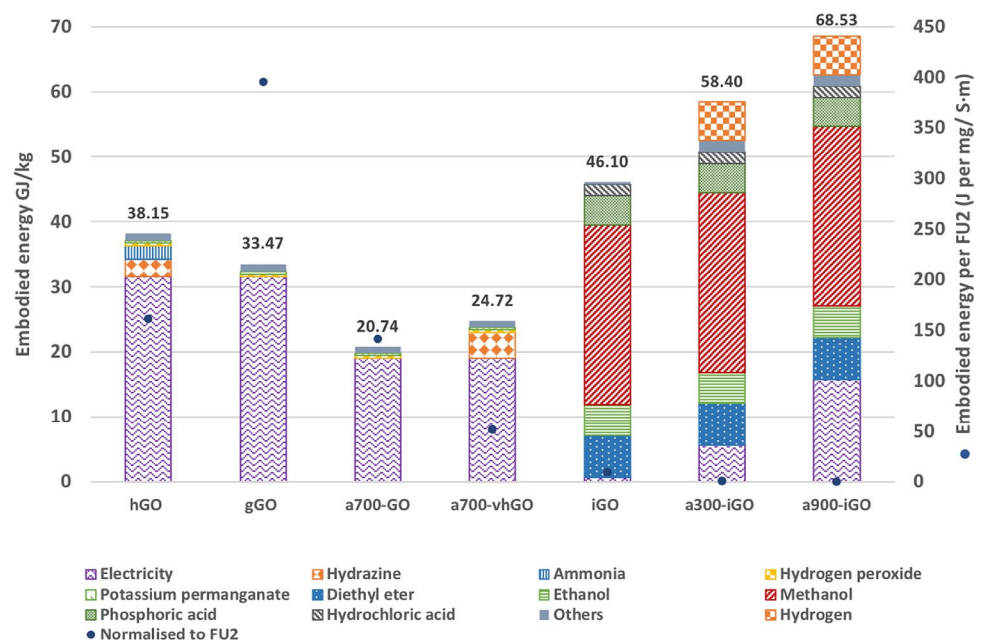
The CED in Marcano's rGOs are higher than in Hummers' ones when FU1 is considered. However, when results are translated into FU2, where the final properties of films are

considered (required amount of product per m² and its conductivity), the situation changes considerably as can be seen in Fig. 3. From these results, we conclude that the additional annealing process required to produce rGO is more than compensated by the improvement of conductivity of the final product made possible by the modified approach. In some cases, deposition process on glass or silicon require the use of molecular anchors or additional reduction steps, which have not been taken into consideration in the calculation, it will produce a minor modification of impacts in comparison with the annealing process. Table S14 in Supplementary Information summarizes the CED for FU1 and FU2, as well as for non-reduced GO. Due to the higher yield of Marcano's recipe and its reduced energy use, graphene oxide has 2.1 times less embodied energy than Hummers' GO recipe.

3.4 Environmental and health impacts

We apply the ILCD methodology to assess the environmental impact of the production of rGO. The compilation of inputs to produce rGO results in electricity consumption and pollutant emissions are translated into impact indicator scores. In this study, the impacts produced into three categories that showed the largest scores were studied in detail, namely (i) *human toxicity cancer*, (ii) *human toxicity non-cancer effects* and (iii) *freshwater ecotoxicity*. The scores are shown in Fig. 4. The share of the chemicals and electricity into the scores are shown in Figure S4, and the final scores for all impact categories of ILCD methodology are shown in Tables S15 and S16, in the Supplementary Information.

Fig. 3 Cumulative energy demand (GJ) for FU1 (1 kg—stacked bars) showing the different contributions and for FU2 (mg/S·m—dots, right axis) of reduced graphene oxide by different routes



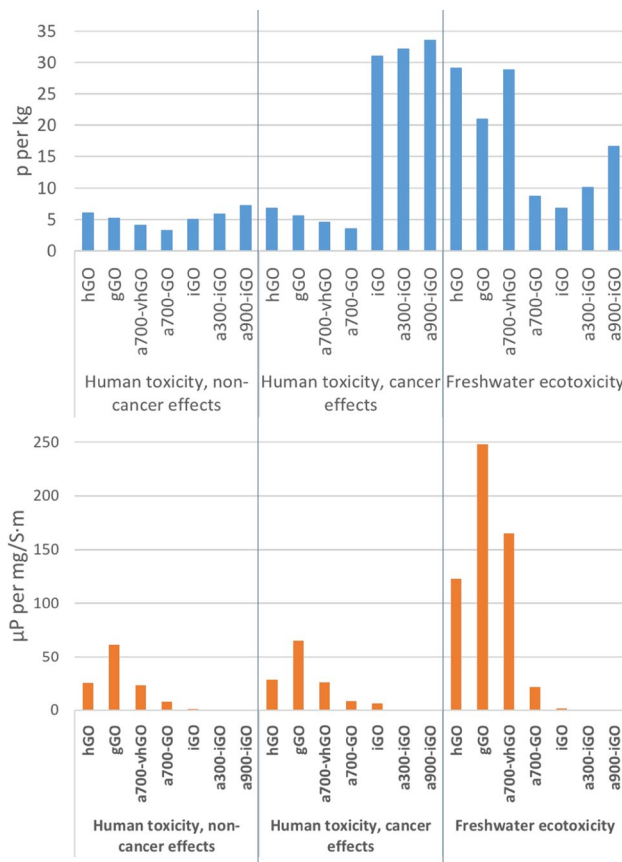


Fig. 4 Normalized environmental impacts of reduced graphene oxide production routes, applying ILCD methodology as implemented in the SimaPro software for five impact categories. Results for two functional units are shown for each process. Details of the contribution of each subprocess is provided in figure S3 in the supplementary information

Looking at the FU1 (production of 1 kg of rGO), the environmental impacts for rGO produced by Marcano's recipes have greater environmental impacts in all categories for applications requiring bulk utilization of graphene, mainly due to the use of phosphoric acid, except for *freshwater ecotoxicity*. In this case, the recipes that use hydrazine in large amounts result in higher impacts (hGO and a700-hvGO). The case study on a700-GO reveals lowest final scores for all categories and thus can be considered as the type of rGO with lowest impact in its production process, but for *Freshwater ecotoxicity*, with a 1.8 points of interval. Nevertheless, looking at FU2 (values normalised to amount of product per area and conductivity), Marcano-based routes emerge as the route with lowest environmental impact, due to the large conductivity of graphene produced by this method and the small amounts of material needed in the form of thin coatings in electronic and optoelectronic applications.

Looking at the potential emissions stemming from the production of rGO from Hummers' method, we consider the worst case, where the chemical substances identified as concerning are released into the environment. Table S1 (in the Supplementary Information) shows the potential impacts of these emissions into several impact categories and methodologies. Hydrazine is the most concerning chemical, with an important impact on *human toxicity* and *cancer effect* impact categories, followed by the potential emissions of NO_x , that impacts *photochemical ozone formation*, *acidification*, *terrestrial eutrophication* and *marine eutrophication*. The final environmental impacts are summarized in Fig. 5, where they are presented for the different categories, and in the inset the contribution of each chemical to the categories is added to provide its global contribution to the final score.

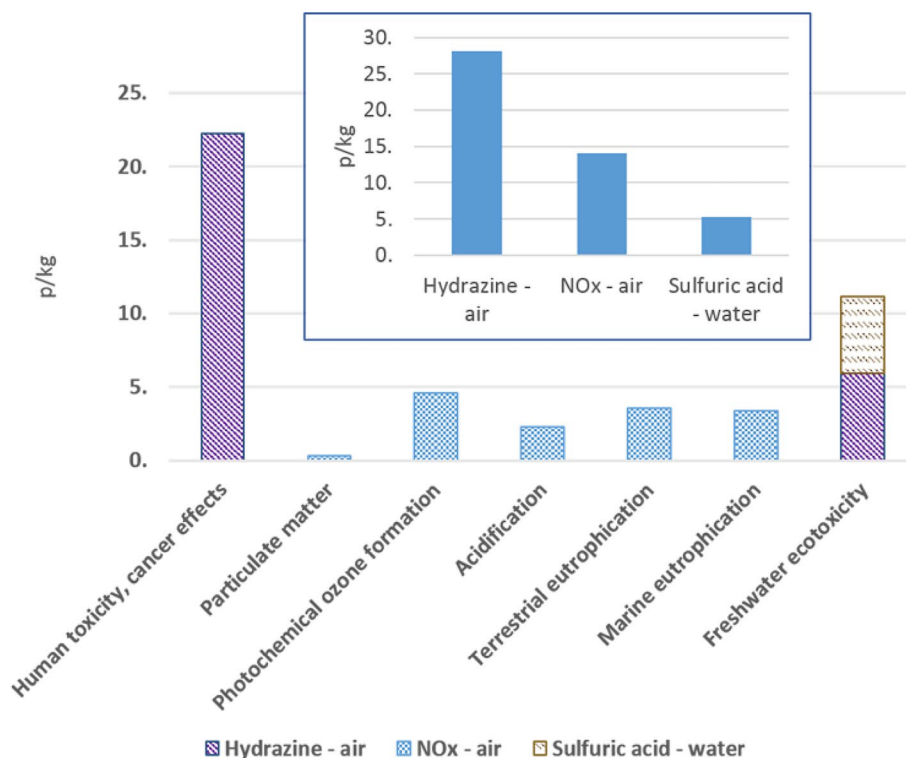
The emissions of hydrazine and sulfuric acid produce the largest impact on *freshwater ecotoxicity*, and on *cancer effects* under *human toxicity* attributed to the hydrazine. The remaining categories are impacted by the NO_x emissions. This strongly indicates that controlling or curbing the emissions during the production of graphene by Hummers' recipe will be crucial to achieving a rGO production with lower environmental impacts. The potential damage caused by other compounds and ions such as chloride and nitrate are negligible when compared to the ones shown in this section.

4 Discussion

The environmental impact of seven production routes for reduced graphene oxide have been studied using life cycle assessment methodology. Two main groups of results are obtained depending on whether the recipe is based on Hummers' method (using hydrazine or glucose in the process), or if it is based on modified Hummers' methods.

We have considered the worst-case scenario for the potential emissions, cost in energy terms and environmental impact of production for hGO. The results for 1 kg of 4 types of hGO do not present a large difference from mGO, with values in the range 46–38 GJ/kg [37]. Nevertheless, when the results are normalized by a performance factor for the use in electronic applications (evaluated as FU2 in this article), the modified recipe (Marcano method) proves to be the most efficient one from an environmental impact stand point, justifying finally the use of an alternative to Hummers' recipe, such as the Marcano's method. The environmental impacts associated to Hummers' recipe are lower than those associated to the improved recipe, although the higher conductivity achieved by the latter, as well as the lower required thickness of the layer and overall amount of

Fig. 5 Normalized environmental impacts of the potential chemicals emitted during the production of 1 kg of reduced graphene oxide, following Hummers recipe (hGO case study), applying ILCD methodology as implemented in the SimaPro software. In the inset, the graph shows the contribution of each chemical to the normalized impact for 1 kg of reduced graphene oxide



material needed to achieve the same conductivity, make Marcano's recipes more suitable for applications involving high quality GO such as semi-transparent electrodes for electronic devices.

If we consider the potential gas emissions from hGO production, the emissions of hydrazine and nitrogen oxide are the main concerns for the large-scale production. Previous studies pointed out the solvent recovery during the production as a key factor in order to get a cleaner rGO production, since the Hummers' method is more toxic as compared with phosphoric acid-reduced method by Marcano [22], while on the other hand, a detailed LCA analysis including the use of phosphoric acid performed by Arvidsson et al. [39] increases impacts and show that the ultrasonication route has lower energy and water use, but higher human and ecotoxicity impacts, compared to the chemical reduction route. It must be emphasized that in the study by Arvidsson et al. the environmental impacts from background systems such as energy production were not included, and they always contribute significantly to LCA results, especially regarding electricity consumption and associated impacts, such as embedded energy and emissions. Also, in our study the use of H_2SO_4 during production has been taken into account (see Table S1); LCA of H_2SO_4 has been thoroughly studied in the past, and the results taken into account for the assessment presented in this article and included in the evaluation of impacts for each category presented in Fig. 2 [68].

As a summary of results, we emphasize the following main points:

Cumulative energy demand (CED) of the processes studied ranges between 20.7 and 68.5 GJ/Kg, which is a value higher than other previously reported for any kind of graphene production [69], and particularly four times higher than similar methods based on chemical reduction, which ranged from 0.9 to 10 GJ/Kg (in this case for a FU of 1 kg of graphene *in solution*, so further processing for a dry kg is not included in the calculation). It should be emphasized that the calculations presented in this article are based in laboratory experimental data, where use of equipment is not optimized, i.e., real factor of use of equipment is lower than 1, thus providing an upper limit for CED and leaving room for a more efficient use of equipment. Comparing with other published LCA results, it is worth to mention that processes using less energy have higher human toxicity impact (for example ultrasonication exfoliation), an indicator that reduction in environmental impacts usually require additional processing, thus increasing the energy consumption (mostly electricity, which the subsequent increment in GHG emissions if renewable energies are not the principal component of the energy mix of the country's grid) [37].

Climate change impact measured as emissions of CO_{2eq} move in a range between 1.06×10^3 kg and 2.36×10^3 kg of CO_{2eq} respectively for mGO and hGO for the production of 1 kg of graphene. In this category of impact, the influence

of choosing an electricity mix is limited, as shown by changing the country (five examples are provided in the supplementary information, Figure S5). As expected, processes with higher contribution of electricity consumption to final CED are more affected by the change of electricity mix, but always in a limited way.

Graphene production does not require the use of any of the materials included in the list of strategic substances, other than graphite itself which has been recently included in the list of critical materials by de European Commission [70], and therefore there is no risk of important depletion of resources even if the manufacture is upscaled at industrial level. On the other hand, electricity consumption is high, but can be compatible with an electricity generation demand to be covered by renewable energy resources.

The comparative study of the three production methods has shown that gGO (use of glucose) produces the least environmental impact, and that the impact on human health for hGO is in the highest range and therefore resources should be devoted to minimizing this impact by acting on the production steps, which mostly contribute to this impact category: the use of hydrazine (hGO and a-700GO) or the use of phosphoric acid (mGO).

The production of rGO based on Hummers' recipe has been widely criticized because of the potential toxic emissions of NO_x groups and the yield of this route is inferior to others. The control of the emissions emerges from this study as the most important pathway to minimizing the potential emissions.

Assessment of the various methods confirm that, as expected, different processes have different impacts, with large differences in some categories (such as human toxicity) and some crossed balances (for example: lower energy consumption correlates with higher human toxicity, a result which has also been found for ultrasonication process [37]). Our results emphasize the future lines of research that should be prioritized, such as the glucose-reduced GO route. The glucose method presents lower impacts than hydrazine Marcano method for rGO, especially to reduce impact in the category *Human health—cancer effects*.

The annealing process is known to be key to the production of rGO. The balance between quality of rGO and environmental impacts of production is directly linked to the annealing temperature which impacts electricity consumption.

The final application type, bulk versus surface coating, should be considered when designing the industrial route for graphene mass production. Total global graphene capacity has increased from 120 tons/yr in 2012 to 910 tons/yr in 2018 [71], driven largely by Chinese capacity expansions, with graphene market set for 40% annual growth, reaching \$305 Million in 2025 [72]. The balance

between the environmental impacts and benefits for society depends on the function that graphene will perform and, as a positive feedback process, the improvement on manufacturing processes and the development of a wider application's map will affect the rate of commercialization of graphene.

5 Conclusions

The demand for GO and rGO for very different applications, ranging from its use as fillers in composites in order to enhance the electrical or mechanical properties, to advanced functional electronic coating materials, requires the optimization of production routes in order to minimize potential toxic emissions and energy consumption while achieving the best technical outcome.

Our analysis identifies the critical steps in the fabrication route and points to realistic approaches to industrialize production of graphene from small scale laboratory processes to large scale manufacturing processes; after a detailed evaluation and comparison of the environmental impacts of the Hummers and related production routes for GO and rGO, no current obstacle to the industrial scale production of graphene has been found.

The route towards industrialization of graphene production will not find obstacles from the point of view of strategic mineral depletion or from large energy consumption. The studied production routes, namely Hummers' and Marcano's methods, do not require the use of any of the materials included in the list of strategic substances other than graphite itself, and therefore there is no risk of important depletion of resources even if the manufacture is upscaled at industrial level. When different production methods are compared, the production of rGO following Hummers' recipe results in lower energy consumption compared to modified methods, making this more suitable for bulk applications; the cumulative energy demand ranges between 20.7 and 38.2 GJ/Kg, depending on the specific reduction route. However, when results are translated into a functional unit which is focused on advanced functional applications for electronic devices, where the final properties of films are considered (and evaluated by calculating the required amount of product per m^2 divided by its conductivity), the additional annealing process required to produce rGO by Marcano's process (up to a range between 46.1 and 68.5 GJ/Kg) is more than compensated by the improvement of quality of the final product made possible by the modified Hummers approach for production (in this article we used Marcano's as the representative of such alternative routes).

Once this main conclusion is established, a detailed analysis of different modifications of the main processing

routes, such as the use of different thermal annealing processes or the use of hydrazine or glucose for the reduction method, provides some additional conclusions: the electric consumption is the primary share of the cumulative energy demand of the production process, representing a share of 83%, 95%, 77% and 92% for hGO, gGO, a700-vhGO and a700-GO respectively for Hummers method; while for Marcano's method, the use of methanol required for the reduction of GO has an embedded energy share of 60%, 47% and 40% for mGO, a300-mGO and a900-mGO respectively, of which the electric consumption share is 10% and 23% for last two cases due to the electricity required during the annealing process. Finally, we emphasize that the glucose method presents lower impacts than hydrazine method for rGO, especially when the *Human health—cancer effects* impact category is analyzed. This study showed the competition between different routes of graphene production. In the future, the benefits of the use of graphene in competition to alternative materials for the same function should also be analyzed from a life cycle assessment perspective, and work must be devoted to the quantification of impacts in a scaled-up industrial production, following preliminary analysis by Cossuta et al. [41], which points that the chemical oxidation process followed by thermal reduction is the least impacting route to produce large quantities of graphene and showing that almost all processes benefit from a scale-up activity.

Acknowledgements This work was supported by Projects ENE2016-79282-C5-1-R and ENE2016-79282-C5-5-R funded by MINECO-Spain (including EU FEDER funds), Project 19882-GERM-15 funded by F. Séneca (Región de Murcia, Spain), and DGA Grupo Reconocido T03_17R by Gobierno de Aragón (including EU FEDER funds). L. S.-L. and C. T. are also grateful to F. Séneca for postdoctoral grant Ref. 19759/PD/15, and predoctoral grant Ref.19768/FPI/15 respectively. SVR thanks Spanish MINECO for her PhD grant (BES2014-068727 and associated EU Social Funds).

Compliance with ethical standards

Conflicts of interest There are no conflicts to declare.

References

- Solis-Fernández P, Bissett M, Ago H (2017) Synthesis, structure and applications of graphene-based 2D heterostructures. *Chem Soc Rev* 46:4572–4613. <https://doi.org/10.1039/C7CS00160F>
- Zhang Y, Mori T, Niu L, Ye J (2011) Non-covalent doping of graphitic carbon nitride polymer with graphene: controlled electronic structure and enhanced optoelectronic conversion. *Energy Environ Sci* 4:4517–4521. <https://doi.org/10.1039/C1EE01400E>
- Lv S, Ma Y, Qiu C et al (2013) Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites. *Constr Build Mater* 49:121–127. <https://doi.org/10.1016/j.conbuildmat.2013.08.022>
- Chuah S, Pan Z, Sanjayan JG et al (2014) Nano reinforced cement and concrete composites and new perspective from graphene oxide. *Constr Build Mater* 73:113–124. <https://doi.org/10.1016/j.conbuildmat.2014.09.040>
- Lin J-S, Kumar SR, Ma W-T et al (2017) Gradiently distributed iron oxide@graphene oxide nanofillers in quaternized polyvinyl alcohol composite to enhance alkaline fuel cell power density. *J Membr Sci* 543:28–39. <https://doi.org/10.1016/j.memsci.2017.08.045>
- Zhang Y, Liu L, der Bruggen BV, Yang F (2017) Nanocarbon based composite electrodes and their application in microbial fuel cells. *J Mater Chem A* 5:12673–12698. <https://doi.org/10.1039/C7TA01511A>
- Upadhyay RK, Soin N, Roy SS (2013) Role of graphene/metal oxide composites as photocatalysts, adsorbents and disinfectants in water treatment: a review. *RSC Adv* 4:3823–3851. <https://doi.org/10.1039/C3RA45013A>
- Zeng X, Wang G, Liu Y, Zhang X (2017) Graphene-based antimicrobial nanomaterials: rational design and applications for water disinfection and microbial control. *Environ Sci Nano*. <https://doi.org/10.1039/C7EN00583K>
- Liu P, Yan T, Shi L et al (2017) Graphene-based materials for capacitive deionization. *J Mater Chem A* 5:13907–13943. <https://doi.org/10.1039/C7TA02653F>
- Srivastava M, Singh J, Kuila T et al (2015) Recent advances in graphene and its metal-oxide hybrid nanostructures for lithium-ion batteries. *Nanoscale* 7:4820–4868. <https://doi.org/10.1039/C4NR07068B>
- Sun Y, Tang J, Zhang K et al (2017) Comparison of reduction products from graphite oxide and graphene oxide for anode applications in lithium-ion batteries and sodium-ion batteries. *Nanoscale* 9:2585–2595. <https://doi.org/10.1039/C6NR07650E>
- Liu J-Y, Li X-X, Huang J-R et al (2017) Three-dimensional graphene-based nanocomposites for high energy density Li-ion batteries. *J Mater Chem A* 5:5977–5994. <https://doi.org/10.1039/C7TA00448F>
- Cai X, Lai L, Shen Z, Lin J (2017) Graphene and graphene-based composites as Li-ion battery electrode materials and their application in full cells. *J Mater Chem A* 5:15423–15446. <https://doi.org/10.1039/C7TA04354F>
- Scalia A, Bella F, Lamberti A et al (2017) A flexible and portable powerpack by solid-state supercapacitor and dye-sensitized solar cell integration. *J Power Sources* 359:311–321. <https://doi.org/10.1016/j.jpowsour.2017.05.072>
- Zhang X, Fan X, Yan C et al (2012) Interfacial microstructure and properties of carbon fiber composites modified with graphene oxide. *ACS Appl Mater Interfaces* 4:1543–1552. <https://doi.org/10.1021/am201757v>
- Yavari F, Rafiee MA, Rafiee J et al (2010) Dramatic increase in fatigue life in hierarchical graphene composites. *ACS Appl Mater Interfaces* 2:2738–2743. <https://doi.org/10.1021/am100728r>
- Sun X, Liu Z, Welsher K et al (2008) Nano-graphene oxide for cellular imaging and drug delivery. *Nano Res* 1:203–212. <https://doi.org/10.1007/s12274-008-8021-8>
- Gan T, Hu S (2011) Electrochemical sensors based on graphene materials. *Microchim Acta* 175:1. <https://doi.org/10.1007/s00604-011-0639-7>
- Valles Romero JA, Cuaya-Simbro G, Morales Maldonado ER (2016) Optimizing content graphene oxide in high strength concrete. *Int J Sci Res Manag IJSRM* 4:4324–4332
- Devasena SM, Karthikeyan K (2015) Investigation on strength properties of graphene oxide concrete. *Int J Eng Sci Invent Res Dev* 1:307–310
- Yao P, Chen P, Jiang L et al (2010) Electric current induced reduction of graphene oxide and its application as gap

- electrodes in organic photoswitching devices. *Adv Mater* 22:5008–5012. <https://doi.org/10.1002/adma.201002312>
22. Marcano DC, Kosynkin DV, Berlin JM et al (2010) Improved synthesis of graphene oxide. *ACS Nano* 4:4806–4814. <https://doi.org/10.1021/nn1006368>
 23. Swiss Centre for Life Cycle Inventories (2013) Ecoinvent Database. <http://www.ecoinvent.org/database/>. Accessed 23 Sep 2013
 24. Stankovich S, Dikin DA, Dommett GHB et al (2006) Graphene-based composite materials. *Nature* 442:282–286. <https://doi.org/10.1038/nature04969>
 25. Cano M, Khan U, Sainsbury T et al (2013) Improving the mechanical properties of graphene oxide based materials by covalent attachment of polymer chains. *Carbon* 52:363–371. <https://doi.org/10.1016/j.carbon.2012.09.046>
 26. Wang H, Cui L-F, Yang Y et al (2010) Mn₃O₄–graphene hybrid as a high-capacity anode material for lithium ion batteries. *J Am Chem Soc* 132:13978–13980. <https://doi.org/10.1021/ja105296a>
 27. Jiang Y, Wei M, Feng J et al (2016) Enhancing the cycling stability of Na-ion batteries by bonding SnS₂ ultrafine nanocrystals on amino-functionalized graphene hybrid nanosheets. *Energy Environ Sci* 9:1430–1438. <https://doi.org/10.1039/C5EE03262H>
 28. Novoselov KS, Geim AK, Morozov SV et al (2004) Electric field effect in atomically thin carbon films. *Science* 306:666–669. <https://doi.org/10.1126/science.1102896>
 29. Viculis LM, Mack JJ, Kaner RB (2003) A chemical route to carbon nanoscrolls. *Science* 299:1361. <https://doi.org/10.1126/science.1078842>
 30. Coleman JN, Lotya M, O'Neill A et al (2011) Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* 331:568–571. <https://doi.org/10.1126/science.1194975>
 31. Hernandez Y, Nicolosi V, Lotya M et al (2008) High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat Nanotechnol* 3:563–568. <https://doi.org/10.1038/nnano.2008.215>
 32. Aghigh A, Alizadeh V, Wong HY et al (2015) Recent advances in utilization of graphene for filtration and desalination of water: a review. *Desalination* 365:389–397. <https://doi.org/10.1016/j.desal.2015.03.024>
 33. Ning F, Shao M, Xu S et al (2016) TiO₂/graphene/NiFe-layered double hydroxide nanorod array photoanodes for efficient photoelectrochemical water splitting. *Energy Environ Sci* 9:2633–2643. <https://doi.org/10.1039/C6EE01092J>
 34. Li R-Z, Peng R, Kihm KD et al (2016) High-rate in-plane micro-supercapacitors scribed onto photo paper using in situ femtosecond laser-reduced graphene oxide/Au nanoparticle microelectrodes. *Energy Environ Sci* 9:1458–1467. <https://doi.org/10.1039/C5EE03637B>
 35. Eda G, Fanchini G, Chhowalla M (2008) Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nat Nanotechnol* 3:270–274. <https://doi.org/10.1038/nnano.2008.83>
 36. Cai J, Ruffieux P, Jaafar R et al (2010) Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* 466:470–473. <https://doi.org/10.1038/nature09211>
 37. Wang G, Yang J, Park J et al (2008) Facile synthesis and characterization of graphene nanosheets. *J Phys Chem C* 112:8192–8195. <https://doi.org/10.1021/jp710931h>
 38. Mei X, Zheng H, Ouyang J (2012) Ultrafast reduction of graphene oxide with Zn powder in neutral and alkaline solutions at room temperature promoted by the formation of metal complexes. *J Mater Chem* 22:9109–9116. <https://doi.org/10.1039/C2JM30552F>
 39. Arvidsson R, Kushnir D, Sandén BA, Molander S (2014) Prospective life cycle assessment of graphene production by ultrasonication and chemical reduction. *Environ Sci Technol* 48:4529–4536. <https://doi.org/10.1021/es405338k>
 40. Arvidsson R, Molander S (2017) Prospective life cycle assessment of epitaxial graphene production at different manufacturing scales and maturity. *J Ind Ecol* 21:1153–1164. <https://doi.org/10.1111/jiec.12526>
 41. Cossutta M, McKechnie J, Pickering SJ (2017) A comparative LCA of different graphene production routes. *Green Chem* 19:5874–5884. <https://doi.org/10.1039/C7GC02444D>
 42. Du Q, Zheng M, Zhang L et al (2010) Preparation of functionalized graphene sheets by a low-temperature thermal exfoliation approach and their electrochemical supercapacitive behaviors. *Electrochim Acta* 55:3897–3903. <https://doi.org/10.1016/j.electacta.2010.01.089>
 43. Novoselov KS, Jiang D, Schedin F et al (2005) Two-dimensional atomic crystals. *Proc Natl Acad Sci* 102:10451–10453. <https://doi.org/10.1073/pnas.0502848102>
 44. Novoselov KS, Geim AK, Morozov SV et al (2005) Two-dimensional gas of massless Dirac fermions in graphene. *Nature* 438:197–200. <https://doi.org/10.1038/nature04233>
 45. Xiang Q, Yu J, Jaroniec M (2012) Graphene-based semiconductor photocatalysts. *Chem Soc Rev* 41:782–796. <https://doi.org/10.1039/C1CS15172J>
 46. Cano M, Benito AM, Urriolabeitia EP et al (2013) Reduced graphene oxide: firm support for catalytically active palladium nanoparticles and game changer in selective hydrogenation reactions. *Nanoscale* 5:10189–10193. <https://doi.org/10.1039/C3NR02822D>
 47. Berger C, Song Z, Li X et al (2006) Electronic confinement and coherence in patterned epitaxial graphene. *Science* 312:1191–1196. <https://doi.org/10.1126/science.1125925>
 48. Choi W, Lahiri I, Seelaboyina R, Kang YS (2010) Synthesis of graphene and its applications: a review. *Crit Rev Solid State Mater Sci* 35:52–71. <https://doi.org/10.1080/10408430903505036>
 49. Hernández R, Vallés C, Benito AM et al (2014) Graphene-based potentiometric biosensor for the immediate detection of living bacteria. *Biosens Bioelectron* 54:553–557. <https://doi.org/10.1016/j.bios.2013.11.053>
 50. Gilje S, Han S, Wang M et al (2007) A chemical route to graphene for device applications. *Nano Lett* 7:3394–3398. <https://doi.org/10.1021/nl0717715>
 51. Stankovich S, Dikin DA, Piner RD et al (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45:1558–1565. <https://doi.org/10.1016/j.carbon.2007.02.034>
 52. Brodie BC (1859) On the atomic weight of graphite. *Proc R Soc Lond* 10:11–12. <https://doi.org/10.1098/rspl.1859.0007>
 53. Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. *J Am Chem Soc* 80:1339. <https://doi.org/10.1021/ja01539a017>
 54. Tomović Ž, Watson MD, Müllen K (2004) Superphenalene-based columnar liquid crystals. *Angew Chem Int Ed* 43:755–758. <https://doi.org/10.1002/anie.200352855>
 55. Treier M, Pignedoli CA, Laino T et al (2011) Surface-assisted cyclodehydrogenation provides a synthetic route towards easily processable and chemically tailored nanographenes. *Nat Chem* 3:61–67. <https://doi.org/10.1038/nchem.891>
 56. Wang Y, Xie L, Sha J et al (2011) Preparation and chemical reduction of laurylamine-intercalated graphite oxide. *J Mater Sci* 46:3611–3621. <https://doi.org/10.1007/s10853-011-5277-2>
 57. Staudenmaier L (1898) Verfahren zur Darstellung der Graphitsäure. *Ber Dtsch Chem Ges* 31:1481–1487. <https://doi.org/10.1002/cber.18980310237>
 58. Mattevi C, Eda G, Agnoli S et al (2009) Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films. *Adv Funct Mater* 19:2577–2583. <https://doi.org/10.1002/adfm.200900166>

59. Chen J, Yao B, Li C, Shi G (2013) An improved Hummers method for eco-friendly synthesis of graphene oxide. *Carbon* 64:225–229. <https://doi.org/10.1016/j.carbon.2013.07.055>
60. Acik M, Lee G, Mattevi C et al (2011) The role of oxygen during thermal reduction of graphene oxide studied by infrared absorption spectroscopy. *J Phys Chem C* 115:19761–19781. <https://doi.org/10.1021/jp2052618>
61. Vallés C, David Núñez J, Benito AM, Maser WK (2012) Flexible conductive graphene paper obtained by direct and gentle annealing of graphene oxide paper. *Carbon* 50:835–844. <https://doi.org/10.1016/j.carbon.2011.09.042>
62. Sorokina NE, Khaskov MA, Avdeev VV, Nikol'skaya IV (2005) Reaction of graphite with sulfuric acid in the presence of KMnO₄. *Russ J Gen Chem* 75:162–168. <https://doi.org/10.1007/s11176-005-0191-4>
63. Dreyer DR, Park S, Bielawski CW, Ruoff RS (2009) The chemistry of graphene oxide. *Chem Soc Rev* 39:228–240. <https://doi.org/10.1039/B917103G>
64. Cao N, Zhang Y, Cao N, Zhang Y (2015) Study of reduced graphene oxide preparation by Hummers's method and related characterization. *J Nanomater J Nanomater* 2015:e168125. <https://doi.org/10.1155/2015/168125>
65. Geisler G, Hofstetter TB, Hungerbühler K (2004) Production of fine and speciality chemicals: procedure for the estimation of LCIs. *Int J Life Cycle Assess* 9:101–113. <https://doi.org/10.1007/BF02978569>
66. Kuila T, Bose S, Khanra P et al (2012) A green approach for the reduction of graphene oxide by wild carrot root. *Carbon* 50:914–921. <https://doi.org/10.1016/j.carbon.2011.09.053>
67. Hauschild MZ, Goedkoop M, Guinée J et al (2012) Identifying best existing practice for characterization modeling in life cycle impact assessment. *Int J Life Cycle Assess* 18:683–697. <https://doi.org/10.1007/s11367-012-0489-5>
68. Silva GA, Kulay LA (2003) Application of life cycle assessment to the LCA case studies single superphosphate production. *Int J Life Cycle Assess* 8:209–214. <https://doi.org/10.1007/BF02978473>
69. Arvidsson R (2017) Review of environmental life cycle assessment studies of graphene production. *Adv Mater Lett* 8:187–195. <https://doi.org/10.5185/amlett.2017.1413>
70. European Commission (2013) Critical raw materials for the EU: Report of the Ad-hoc Working Group on defining critical raw materials. <https://ec.europa.eu/growth/tools-databases/eip-raw-materials/en/community/document/critical-raw-materials-eu-report-ad-hoc-working-group-defining-critical-raw>. 8 Nov 2013
71. Zurutuza A, Marinelli C (2014) Challenges and opportunities in graphene commercialization. *Nat Nanotechnol* 9:730
72. Fisher E (2013) Graphene market set for 40% annual growth. *Lux research*. <http://www.luxresearchinc.com>. 17 Jan 2013

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.