



## Cokes of different origin as precursors of graphene oxide



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### ABSTRACT

This study demonstrates that pregraphitic materials (cokes) of different origin (petroleum and coal derivatives) can be used as precursors of graphene oxides. Two carbochemical cokes and a petrochemical one were oxidized and the resultant coke oxides exfoliated by ultrasounds to yield the corresponding graphene oxide materials. These were characterized in terms of the lateral size of the sheets, morphology and chemical composition. The new generation of graphene oxides prepared with coke exhibits similar characteristics to those traditionally obtained from graphite. It is also established that as larger the crystalline structure of the coke is, the higher the graphene oxide yields and the larger the size of the sheets.

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### 1. Introduction

Graphene, a  $sp^2$ -hybridized carbon monolayer, is nowadays used in many research areas due to its unique properties, such as its excellent electronic behavior, its highly aromatic lattice which lends its exceptional mechanical strength and its extraordinary chemical stability in most reaction media [1]. Among the most promising technologies for producing graphene materials, the top-down technologies (i.e. solvent exfoliation or oxidation/exfoliation/reduction) are among the most promising from an industrial point of view, since they can be easily scaled up at a reasonably low cost [2–7]. Most of them use graphite (natural or synthetic) as the primary source of graphene [8–11], thereby making graphite a mineral of considerable strategic importance. However, natural graphite is a limited natural resource located only in a few countries. Synthetic graphite has the advantage that there is a wide variety of commercial precursors (including petroleum and coal) available, but its production requires temperatures of over 2500 °C [10,11] which entails a high energy cost. We recently reported using a pregraphitic material (carbochemical coke) as graphene precursor [12], overcoming the limitations of its partially organized aromatic structure [13]. The advantage of using this material instead of graphite is the production, which requires lower temperatures than graphite (<1100 °C) and therefore is less energy consuming. In addition, cokes are commonly employed at an industrial level, such as in the iron and aluminium industry

[14], which ensures their worldwide supply in the short to mid term.

One important issue still to be addressed before graphene oxide (GO) can be produced on a large scale from pregraphitic materials is the need to ensure a proper control of their characteristics. It is well known that the characteristics of the parent graphite (in terms of purity, crystallinity, homogeneity, etc.) play an important role [15–17]. It has been demonstrated that the size of the graphite crystals affects the oxidation process and the functionalities and sheet size of the resulting GO [18]. This evidences that preferential attack occurs during oxidation at the boundaries of the graphite crystallites and at the defects present in the basal planes [19]. It is expected that a similar process will occur when cokes of different crystallinity are used as a precursor of graphene oxides instead of graphite. As far as the authors are aware no studies have been published on how the characteristics of a coke may affect the properties of the GOs obtained. However, because of their pregraphitic structure (which shows a low structural order and more inherent defects than graphite) and the wide variety of their characteristics due to the versatility of the preparation conditions and precursors used (petrochemical or carbochemical origin, etc.) [20], this issue requires some attention before their use on a large scale to prepare GO.

In this study three cokes of different origin (petrochemical and carbochemical) with crystalline structures of different size were used as raw materials. The GOs were prepared according to a modified Hummers method and were characterized in terms of the lateral size of the sheets and their morphology and chemical composition. These properties were then correlated with the characteristics of the parent cokes.

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## 2. Experimental

### 2.1. Materials used

Three cokes were used as raw materials: a petrochemical premium coke (CkP), a commercial carbochemical coke (CkC) and a third coke obtained from a coal tar fraction at laboratory scale (CkA) [13]. The graphite (Gr) obtained by thermal treatment of CkC at 2800 °C was used for comparative purposes. Parent cokes were characterized by optical microscopy to determine their optical texture, elemental analysis, X-ray diffraction, Raman spectroscopy and particle size distribution (see Supporting Information).

### 2.2. Preparation of coke oxides and coke-based graphene oxides

The GOs were prepared from the cokes (ground and sieved to <75 μm) and graphite by means of a modified Hummers method [21–23]. Concentrated H<sub>2</sub>SO<sub>4</sub> was added to a mixture of the coke and NaNO<sub>3</sub> (1:1), and the mixture was cooled down to 0 °C in an ice bath. KMnO<sub>4</sub> was then added in small doses. The solution was then heated to 35 °C and stirred for 3 h, and then 3% H<sub>2</sub>O<sub>2</sub> was added. The reaction mixture was stirred again for 30 min and, finally, it was centrifuged and the supernatant removed. The remaining solid material was washed with Mili-Q water and centrifuged, this process being repeated until neutral pH. The resulting coke oxides were labelled as CkO-X, where X refers to the parent coke used in each batch (A: synthetic, C: carbochemical and, P: premium). Samples were then ultrasonicated in Mili-Q water for periods of 2, 4 and 8 h. The suspensions were centrifuged, the supernatant was filtered and the solid particles were discarded. The resulting coke-based graphene oxide suspensions were labelled GO-Ck-X, where X again refers to the origin coke used in each batch. The graphite-based graphene oxide suspension was labelled GO-Gr.

### 2.3. Characterization of the coke-based graphene oxides

The coke-based graphene oxides (GO-Ck-X) were characterized by Raman spectroscopy using the same experimental conditions as those used to characterize the parent cokes (see Supporting Information).

The GO-Ck-X samples were also characterized by atomic force microscopy (AFM) using a Nanotec Electronica™ atomic force microscope. Suspensions were deposited on mica substrates by drop casting. All the samples were imaged under identical conditions. Nanosensor™ PPP-NCH PointProbe Plus microcantilevers were used to image the GO-Ck-X sheets in an attractive regime amplitude-modulated mode.

XPS analyses of the samples were carried out in a VG-Microtech Mutilab 3000 device. The C/O atomic ratio was calculated from the general XPS spectra of the samples. The XPS C1s peak was analysed using a peak synthesis procedure that combines Gaussian and Lorentzian functions [24] to identify the functional groups and

their respective percentages. The binding energy profiles were deconvoluted and classified as follows: undamaged structures of sp<sup>2</sup>-hybridised carbon (284.5 eV), damaged structures or sp<sup>3</sup>-hybridised carbon (285.5 eV), C–O groups (286.5 eV), C–O groups (287.7 eV) and COO groups (288.7 eV).

## 3. Results and discussion

### 3.1. Characterization of the parent cokes

The cokes were characterized by means of elemental analysis (Table 1). All the cokes have a carbon content >96 wt.%, which obviously is lower than that typical of graphite (around 99.6 wt.

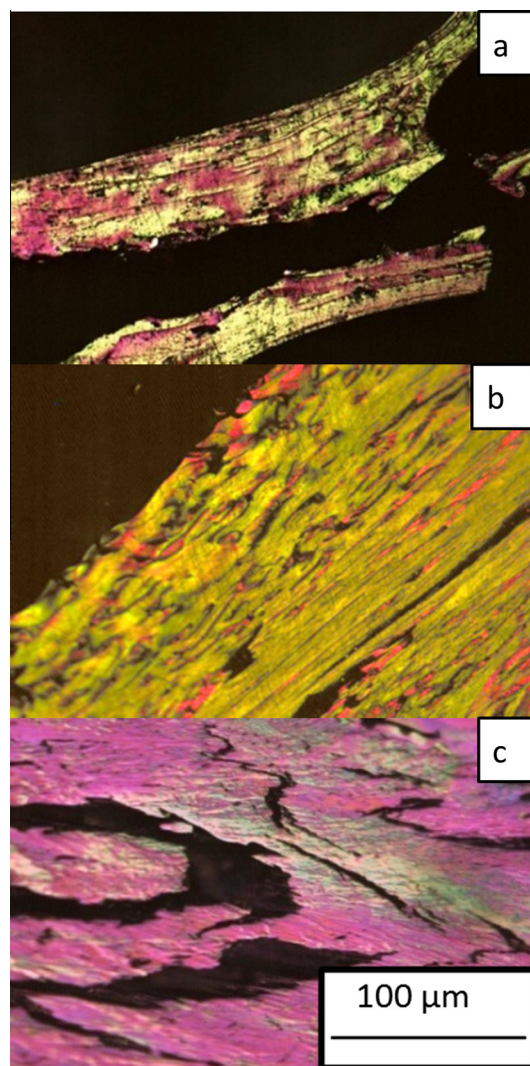


Fig. 1. Optical images of cokes (a) CkA, (b) CkC and (c) CkP.

Table 1

Main characteristics of the cokes (CkA, CkC and CkP) and graphite (Gr).

Sample	Optical texture (μm)		Elemental analysis (wt.%)						XRD (nm)			Raman spectroscopy		
	W	L	C	H	N	S	O	Ash	<i>d</i> <sub>002</sub>	<i>L</i> <sub>c</sub>	<i>L</i> <sub>a</sub>	<i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub>	<i>W</i> <sub>D</sub> (cm <sup>-1</sup> )	<i>W</i> <sub>G</sub> (cm <sup>-1</sup> )
CkA	20–50	100–200	96.5	1.0	1.4	0.3	0.8	–	0.345	3.7	4.7	0.91	1352	1587
CkC	50–70	200–300	98.4	0.1	0.9	0.3	0.3	0.3	0.346	4.2	10.6	0.82	1349	1580
CkP	50–100	500–700	99.0	0.2	0.3	0.4	0.1	0.8	0.346	5.4	7.9	0.88	1352	1590
Gr	10–20	100–200	99.5	0.1	0.2	0.0	0.2	0.1	0.336	5.3	70.7	0.15	1350	1580

W = Microcrystallite width, L = Microcrystallite length.

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