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Full Length Article

Peculiarities of the production of graphene oxides with controlled properties from industrial coal liquids

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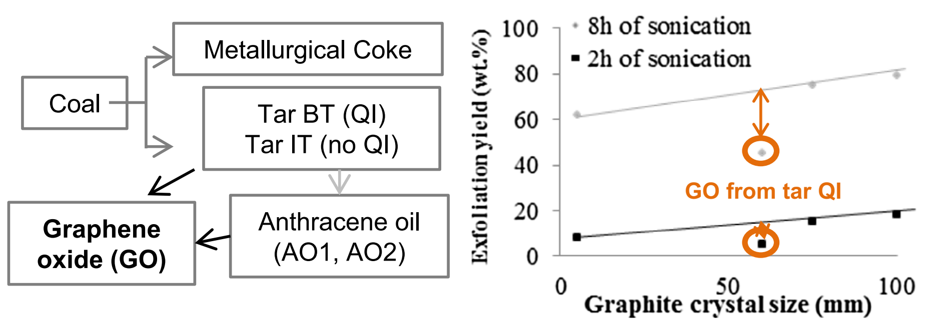
HIGHLIGHTS

- The main industrial coal liquids were evaluated as precursors of graphene.
- Impregnation-grade tar and anthracene oils successfully produce graphene oxides.
- Sheet size and exfoliation yield depend on the crystalline size of parent graphite.
- Quinoline insoluble particles in binder tar modify the graphite oxidation mechanism.
- They also decrease the yield of the graphene oxide.

GRAPHICAL ABSTRACT



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ABSTRACT

The main industrial types of liquid by-products from the metallurgical industry, (impregnation and binder grade tars and anthracene oils) were evaluated as precursors of graphene materials by their graphitization, oxidation and subsequent exfoliation. Impregnation-grade tar and anthracene oils successfully produce graphene oxides with sheet sizes and exfoliation yields which depend on the crystalline size of their parent graphite. Although binder grade tar can also been transformed into graphene materials, the quinoline insoluble particles present in its composition modify the oxidation mechanism of the graphite and the exfoliation of the graphite oxide, decreasing the yield of the graphene oxide prepared from this by-product. These results represent a useful guide for evaluating the conversion of coal liquid residues into a much higher added value product such as graphene.

1. Introduction

The sustainable production of metallurgical coke requires not only the maximization of its quality and yield but also the transformation of the by-products generated into high value-added products [1]. The coke oven gas, produced in ∼15–20 wt% yield, serves mainly as fuel for the same steel installation that produces it [2,3]. The coal-liquids (coal tars) obtained in a ∼3–5 wt%) yield [4] are usually transformed by carbochemical processes into pitches like the distillation residue [5], a process from which other fractions are also obtained, e.g. BTX, carbolic oil, naphthalene oil, wash oil and anthracene oil (the heaviest distillation fraction) [6–8]. Depending on the composition the coal tar (which is determined by the type of processing to which the metallurgical coke is exposed) and processing conditions two main types of pitches are commercialized: binder and impregnation pitches, which are mainly used in the aluminium and foundry industry as binder and impregnating agents for the production of carbon anodes and graphite electrodes. In order to make these by-products

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recyclable and increase the added value of coal tars and pitches, these materials are also employed to produce graphitizable carbons [9]. However, in the worldwide market of carbon materials there is still no driving force for the preparation of graphitizable carbons from coal tars and pitches (i.e. carbochemical cokes and graphites) and this route represents a very small fraction of the total coal-tar pitch market.

In this regard, we have seen in last years a great increase in worldwide interest in graphite-like materials such as graphene. Graphene is a sp^2-hybridized carbon monolayer which exhibits superb electrical and mechanical properties and its applications in everyday life are expected to grow exponentially in the near future, if the supply of graphene materials with controlled characteristics can be secured at a low cost. Among the different preparation procedures reported to date, the most promising from an industrial point of view is the use of graphite as raw material which by solvent exfoliation or oxidation/exfoliation/reduction yields graphene materials at a reasonably low cost. Furthermore, it has been reported that the characteristics of the parent graphite strongly modify the properties of the graphene materials obtained from them [10]. Hence, the sustained production of synthetic graphites with controlled characteristics and different from those of natural graphite (e.g. controlled crystallinity, absence of impurities, etc.) could represent a breaking point for the effective introduction of graphene-based devices in everyday life. The entry of the carbochemical industry into this sector could therefore represent a great opportunity for increasing the added value of metallurgical liquid residues and offer a new market niche with unlimited possibilities for exploration.

This paper focuses on the feasibility of transforming industrial coal liquid fractions into high value added graphene materials with controlled characteristics. To achieve this, the main coal liquid fractions produced worldwide (i.e. coal-tars) are used as raw materials. In addition, the heaviest distillation fraction produced in the industrial of coal-tar, anthracene-oil, is also investigated as a graphene raw material. The graphites obtained from them are used to prepare graphene oxides by the well-known Hummers method and then subjected to exfoliation by sonication. A detailed charac-

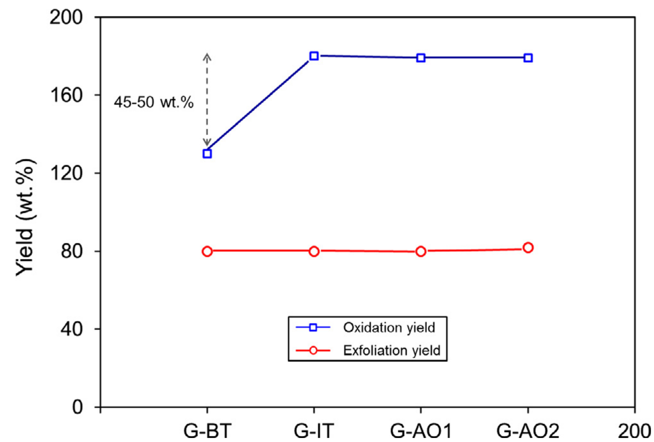

Fig. 2. Graphitization yield and graphite oxidation yield of G-BT, G-IT, G-AO1 and G-AO2.

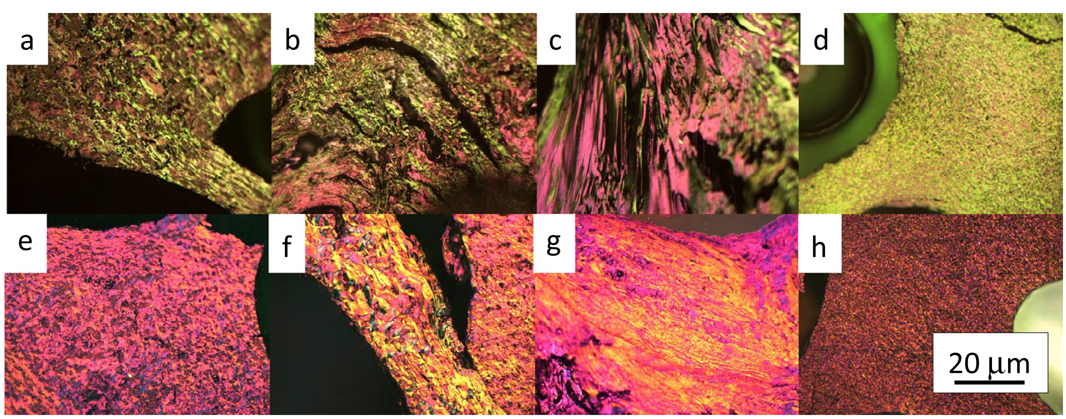

Fig. 1. Optical micrographs of cokes (a–d) and graphites (e–h) from binder tar (a, e), impregnation tar (b, f), anthracene oil tar AO1 (c, g) and anthracene oil AO2 (d–h).

Table 1
Main characteristics of graphites and graphite oxides.

Sample	Elemental Analysis (Wt%)					Raman	XRD (nm)			Optical microscopy (μm)	
	C	H	N	S	O	Id/Ig	d_{00x}[1]	La[2]	Lc[3]	Aw[4]	Al[5]
G-BT	99.7	0.0	0.2	0.0	0.1	0.15	0.337	37	15	10	60
G-IT	99.9	0.0	0.0	0.1	0.0	0.07	0.336	95	51	15	70
G-AO1	99.9	0.1	0.0	0.0	0.0	0.08	0.337	40	15	20	100
G-AO2	99.7	0.3	0.0	0.0	0.0	0.09	0.338	39	15	5	5
GrO-BT	43.8	2.4	0.0	1.9	51.9	0.89	0.907			–	–
GrO-IT	40.7	3.3	0.0	0.2	55.8	0.87	0.949			–	–
GrO-AO1	43.7	2.4	0.0	1.1	52.8	0.90	0.884			–	–
GrO-AO2	45.7	2.3	0.0	0.5	51.5	0.85	0.814			–	–

[1] Measured as d_{002} in the case of graphites and d_{001} in the case of graphite oxides.
[2] Size of the graphitic layer.
[3] Stacking height in the graphitic c-direction.
[4] Average width of the crystalline domains.
[5] Average length of the crystalline domains.