



Full Length Article

Role of quinoline insoluble particles during the processing of coal tars to produce graphene materials



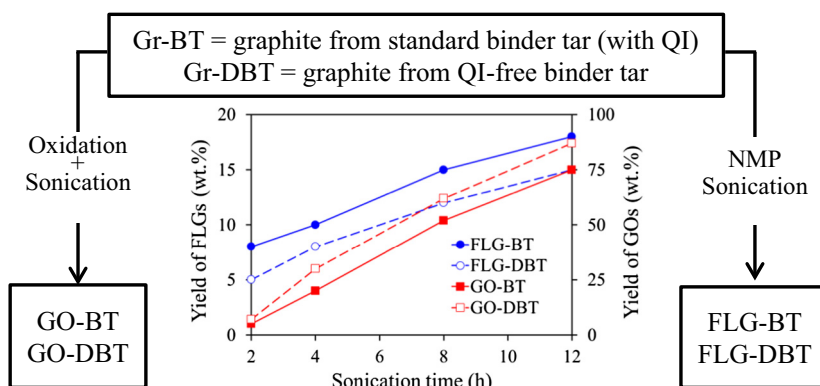
Laura Fernández-García, Patricia Álvarez, Ana M. Pérez-Mas, Clara Blanco, Ricardo Santamaría, Rosa Menéndez, Marcos Granda*

Instituto Nacional del Carbón, INCAR-CSIC, P.O. Box 73, 33011 Oviedo, Spain

HIGHLIGHTS

- QIs in binder tar modify the pathways to produce graphene materials.
- QIs in graphite modify its oxidation behavior to produce GrO.
- Exfoliation yield of GrO with QI is lower and yield GOs with lower sheet size.
- Yield of solvent exfoliation of graphite without QIs is lower.
- FLG sheets from Gr without QIs are larger but with holes at basal planes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 January 2017

Received in revised form 30 May 2017

Accepted 31 May 2017

Keywords:

Quinoline insoluble particles

Binder tar

Coke

Graphite

Graphene oxide

Few-layer graphene

ABSTRACT

This work studies the utilization of a binder grade industrial tar with an inherent content in primary quinoline insoluble particles (QIs) and the correspondent free-QI tar obtained from it by a sedimentation process as raw sources of graphene materials via different preparation procedures. Graphene oxides (GOs) were prepared via the oxidation of binder tar-based graphite and subsequent sonication. The presence of QIs contributes to decreasing both the yield of the oxidation and of the exfoliation steps. This is due to the greater reactivity of QI particles towards oxidation, which modifies the distribution of the oxygen functional groups in the oxidized graphite, impeding its exfoliation. Also, as a consequence of the higher crystallinity of parent graphite without QIs, larger GO sheets were obtained in that case. On the other hand, the presence of QIs in the parent graphite facilitates its solvent exfoliation behavior in N-methyl-pyrrolidone (NMP) to yield few layer graphene (FLG), but contributes to a decrease in the size of the flakes of the graphene materials obtained.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Coal tar (CT) is a by-product obtained in the production of metallurgical coke, the mayor feed stock used in the aluminum and

steel industry and a key part of the energy-intensive manufacturing industry. It accounts for ~3–5 wt% of the total carbon input and its production and characteristics are worldwide maintained [1]. CT is usually processed to prepare coal tar pitch (as the residue of its fractionate distillation) and by modifying its composition two grades of CT with different compositions and applications are industrially produced (binder and impregnation grade CTs). Binder grade tars are usually more aromatic than impregnation grade tars

* Corresponding author.

E-mail address: mgranda@incar.csic.es (M. Granda).

and contain an appreciable amount of insoluble carbonaceous particles called quinolone insolubles (QIs). Both are produced with the specific aim of fulfilling the requirements for binder and impregnations agents in the aluminium and graphite industry (mainly for carbon anodes and graphite electrodes) [2–4]. In an attempt to increase the added value of the tars and pitches these can be transformed into a carbonaceous material, particularly into graphitizable carbons and graphite. Although both types of tars can be used in the fabrication of various advanced carbon materials, such as needle coke [5–7] carbon fibers [8], and mesocarbon microbeads [9], the presence of QIs in binder tars is known to modify their graphitizability by delaying the formation of spheres of mesophase and making difficult for them to coalesce in the process of carbonization [10,11]. As a consequence, binder tars cannot be directly used for manufacturing these materials and usually require the previous elimination of QIs by means of tedious and costly methods such as filtration [12], gravitational settling with a solvent [13–15] or centrifugation (CM) and extraction methods [16]. As an example, it is known that QIs must be eliminated (or reduced in number) to yield needle-coke with a low coefficient of thermal expansion [17,18] or to produce carbon fibers with more uniform mechanical properties [19]. The requirement of this additional step of elimination obviously reduces industrial interest in using binder grade tars as a precursor for the preparation of carbon materials in favor of other coal tar derivatives.

One of the graphite-like materials which has awakened a lot of interest in recent years is graphene. This sp^2 -hybridized carbon monolayer exhibits super electrical and mechanical properties and its applications in everyday life are expected to exponentially grow in a near future, if the supply of graphene materials with controlled characteristics can be guaranteed at a low cost. One of the most promising technologies, from an industrial point of view, for preparing graphene at a low cost uses graphite as raw material [20–23]. Furthermore, several synthetic graphites prepared from coal tars have been studied as precursors of graphene with controlled characteristics, which place the coke industry as a possible supplier of graphene while increasing at the same time its sustainability [23,24]. Among all the examples reported there is no mention of the importance of the presence of QIs in the tar fractions during processing, even though their contribution could determine the suitability of binder tars as precursors of graphene raw material.

In light of what has been said, this paper aims to study the influence of the QIs present in industrial binder coal tars during their processing on the production of graphene materials. To this end, an industrial binder coal tar and the tar resulting from the removal of its QIs by sedimentation were used as graphene raw material. The graphites obtained from them were transformed into graphene materials by two known methodologies: i) by means of their oxidation and subsequent exfoliation to yield graphene oxide (GO) and ii) by their solvent exfoliation in NMP to yield few-layer graphene (FLG). A detailed characterization of the graphites, graphite oxides and graphene materials by means of X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), elemental analysis and X-ray diffraction (XRD) as well as a detailed analysis of the yields obtained in each of the processing steps allowed an analysis of the problems of using a binder coal tar containing QIs as a precursor of graphene. It is hoped that the results obtained will encourage binder-grade coal tar producers to evaluate its potential for the production of graphene on a large scale.

2. Materials and methods

2.1. Preparation of graphites

Two graphites were prepared from an industrial binder tar with a 4.7 wt% of QI content (BT) and the corresponding derived free-QI

tar in which QI particles were removed by a sedimentation process (DBT). Both tars were produced by Nalonchem S.A. The graphitization of the samples was achieved in several steps using standard procedures [25]. Briefly, an initial carbonization at 650 and 1000 °C under nitrogen at atmospheric pressure yielded two cokes labelled as Ck-BT and Ck-DBT. The resultant powders were graphitized at 2800 °C in a graphite furnace for 45 min under argon flow to provide the graphites Gr-BT, Gr-DBT. The heating rates selected were 50 °C min^{-1} from room temperature to 700 °C, 100 °C min^{-1} from 700 °C to 1000 °C, 20 °C min^{-1} in the interval of 1000–2000 °C and 10 °C min^{-1} from 2000 °C to 2800 °C.

2.2. Preparation of graphite oxides (GrOs) and graphene oxides (GOs)

The GrOs were synthesized from the synthetic graphites by the modified Hummers method. This method makes use of the Hummers reagents with additional amounts of NaNO_3 and KMnO_4 . Concentrated H_2SO_4 (360 mL) was added to a mixture of synthetic graphite (7.5 g) and NaNO_3 (7.5 g), and the mixture was then cooled down to 0 °C using an ice bath. KMnO_4 (45 g) was added slowly in small doses to keep the reaction temperature below 20 °C. The solution was heated to 35 °C and stirred for 3 h, at which point 3 % of H_2O_2 (1.5 L) was added slowly, giving rise to a pronounced exothermic effect up to 98 °C. The reaction mixture was stirred for 30 min and, finally, the mixture was centrifuged (3700 rpm for 30 min), any supernatant being discarded. The remaining solid material was then washed with 600 mL of water and centrifuged again, this process being repeated until neutral pH to yield the graphite oxides GrO-BT and GrO-DBT. Colloidal suspensions of individual graphene oxide sheets in purified water (1 mg/mL) were prepared in 1-L batches by subjecting the GrO suspensions to sonication up to a period of 12 h. At selected intervals (2 and 12 h) the suspensions were centrifuged (3700 rpm for 30 min), the supernatant was filtered over cellulose, and the solids were discarded to yield the graphene oxides (GO-BT-t and GO-DBT-t, where t indicates the sonication time in hours).

2.3. Preparation of few layer graphenes (FLGs) by solvent exfoliation

Gr-BT and Gr-DBT were dispersed in N-methyl pyrrolidinone (NMP, spectroscopic grade, Aldrich) at a concentration of 1 mg mL^{-1} (200 mL, round-bottomed flask). These dispersions were then sonicated (Bransonic Ultrasonic 5510-MTH, 135 W-42 kHz) for 2–12 h. During the experiment, the temperature of the bath was kept below 60 °C. After sonication, the dispersions were transferred to vials and centrifuged at 1500 rpm for 60 min (Sigma 2-16P). The samples obtained were labelled FLG-BT (few-layer graphene exfoliated from Gr-BT) and FLG-DBT (few-layer graphene exfoliated from Gr-DBT).

2.4. Characterization of graphite and graphene samples

The optical texture of the cokes and graphites was determined by means of polarized light microscopy under a Zeiss Axioplan microscope, equipped with an adjusted ocular (10 \times), an oil-immersion objective (20 \times , 50 \times and 100 \times), a polarizer and a one-wave retarder plate to generate interference colours. Prior to the analysis, the samples were embedded in an epoxy resin, then polished and finally examined using polarized light.

X-ray diffraction of the samples was performed using a Bruker D8 Advance diffractometer. The radiation frequency used was the $\text{K}\alpha_1$ line from Cu (1.5406 Å), with a power supply of 40 kV and 40 mA. The crystallite size along the c-axis (L_c) was obtained from the (002) reflection of the XRD patterns, which were recorded at steps of 0.01° and intervals of 6 s per step, using the Scherrer

Download English Version:

<https://daneshyari.com/en/article/4768555>

Download Persian Version:

<https://daneshyari.com/article/4768555>

[Daneshyari.com](https://daneshyari.com)