EL GRAFENO. PARTE II: PROCESOS Y VIABILIDAD DE SU PRODUCCION

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GRAPHENE. PART II: PROCESSES AND FEASIBILITY OF ITS PRODUCTION

ABSTRACT:
After the discovery of graphene, a material with properties of high technological interest, the industry seeks to optimize its production mechanisms in order to address a market which is expected to grow strongly. Graphene synthesis can be carried out by various processes, which show differences in quality of the final product. There are two groups of processes: those that are based on carbon atoms to synthesize graphene (bottom-up methods), or those that use more complex structures (top-down methods).
In the first part of this paper a review of the current state of knowledge of the properties of graphene and its possible applications was presented. In this second part, we introduce technologies for its production, in order to determine the feasibility of a plant, from the technical and economic points of view, is presented. Using a multi-criteria analysis, the method of production based on chemical vapor deposition has been selected as the most viable technology. Also, we have estimated the economic feasibility of a plant to produce about 375 m^2 of monolayer graphene per year.

Keywords: graphene; feasibility; production; new material; carbon allotrope

RESUMEN:
Ante el descubrimiento del grafeno, un material con propiedades de gran interés tecnológico, la industria busca optimizar sus mecanismos de producción con el objetivo de abordar un mercado para el cual se prevé un gran crecimiento. La síntesis de grafeno puede llevarse a cabo mediante diversos procesos, si bien para cada uno de ellos se pueden advertir diferencias respecto la calidad del producto final. Entre tales procesos, se distinguen dos grupos: aquellos que parten de átomos de carbono para sintetizar grafeno (métodos *bottom-up*), o aquellos que parten de estructuras más complejas (métodos *top-down*).
En la primera parte de este trabajo se presentó una revisión sobre el estado actual del conocimiento de las propiedades del grafeno y sus aplicaciones posibles. En esta segunda parte se presentan diversas tecnologías para su producción, con el fin de determinar la viabilidad de una planta, desde los puntos de vista técnico y económico. Mediante un análisis multicriterio, se ha seleccionado como tecnología más viable el método de producción basado en la deposición química de vapor. También, se ha estimado la viabilidad económica de un planta que produjera unos 375 m^2/año de grafeno monocapa.

Palabras clave: grafeno; viabilidad; producción; material novedoso; alótropo del carbono

1.- INTRODUCTION

Graphene is a new material with exceptional physical and chemical properties which promise a great impact in various technological areas. While its possible applications are being studied, both the research sector and the industry have shown special interest in graphene.

In the first part of this paper the properties and applications of graphene were presented. In this second part, various technologies for their production, in order to determine the viability of a plant, from both a technical and economic standpoint, will be analysed.

2.- PRODUCTION PROCESSES

The production processes of graphene presented below are those of highest interest at industrial level. Broadly speaking, they can be classified into two groups: top-down methods (those that extract from a precursor what is necessary to produce graphene) and bottom-up methods (those that produce graphene from carbon atoms). Among the

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former are the chemical and mechanical exfoliation and the process of reducing graphene oxide, while among the latter are the chemical vapor deposition and the epitaxial growth on silicon carbide. We will briefly discuss each of them.

2.1.- MECHANICAL EXFOLIATION

It is the process by which mechanical force is applied to separate sheets of graphene from graphite. Usually this is accomplished by adhesion, as Geim and Novoselov demonstrated in 2004 using adhesive tape, or by friction between a source of graphite and other surface (to cause the sliding of one graphene sheet) [1,2,3]. The second step of the process involves deposition of graphene on a substrate – usually SiO_2/Si wafer, to electrically isolate it and facilitate handling. As a source of graphite is very common to use highly ordered pyrolitic graphite (HOPG), because its high purity (impurity levels of about 10 ppm) and its markedly laminar structure [3] .

It is currently the more popular method of manufacturing graphene as it is a relatively simple and versatile process, which also allows the best quality so far (in terms of purity, fewer defects in the structure, fewer sheets of graphene produced from the leaflets, among others), compared to other processes [4,5]. Among its disadvantages, it is relevant to note that the size of the product depends on the source of graphene, and size and number of graphene sheets of each leaflet are variable. Further, mechanical peeling can affect the purity and structure of the sheet produced: by introducing impurities due to exfoliating agents, or inducing stresses, defects, wrinkling or curling. It is not considered an industrially scalable method [5], hence other possibilities are investigated, as discussed in the following sections.

2.2.- CHEMICAL EXFOLIATION

Graphene sheets that are stacked to form graphite can be separated chemically. To achieve this, van der Waals forces that make these sheets remain stuck must be overcome. Therefore a certain energy (some studies suggest an approximate value of 2 eV/nm^2 [6]) and a method for isolating the material produced are required. Chemical peeling process accomplishes this by the application of sound energy (sonication, for example) to exfoliate graphene leaflets, and a polar solvent (such as water, ethanol, dimethylformamide or N -methyl-2-pyrrolidone [6,7]), respectively. Along with the solvent, it is also common to use surfactants such as dodecylbenzene sulphate to prevent restacking of leaflets [8]. Long sonication times may heat the solvent, leading to undesirable chemical reactions. To avoid this, circulation or cooling systems are used [4].

Chemical exfoliation is ideal for producing large quantities of graphene flakes with better structural quality compared to that produced from graphene oxide. Applied as a solution can be used for conductive coatings, although the flakes would be weakly attached to each other by means of van der Waals forces.

2.3.- REDUCTION OF GRAPHENE OXIDE

Modern methods of reducing graphene oxide start from graphite oxidized, and are based, mostly, in the Hummers method (reported by Hummers and Offeman in 1958 [9]). Graphite is oxidized from a mixture of concentrated sulfuric acid, sodium nitrate, and potassium permanganate.

To exfoliate graphite oxide chemically, thereby achieving graphene oxide, sound energy is transmitted by ultrasonic to precursor dispersed in water or in an organic solvent. It should be noted that the functional groups that adhere during oxidation make blades of graphene oxide highly hydrophilic (this facilitates their dispersion). Once carried out the exfoliation, a subsequent centrifugation would separate the sheets produced from wastes (mainly, graphite oxide not exfoliated). The final reduction of graphene oxide may be performed by reducing agents, heat treatment, or electrochemical reduction [6].

Reduction of graphene oxide is ideal for applications not requiring high quality of the crystal structure, as composites containing graphene, and other mechanical applications. The fact of utilizing graphene oxide involves many defects in the final product. However, an advantage of these defects can be the chemical functionalization of the graphene oxide reduced, a fact that would open the door for biological applications [5].

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2.4.- CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) is one of the most popular methods for manufacturing graphene nowadays. It is a scalable process utilizing a mature technology in industry. Graphene manufactured by CVD, particularly deposited on a metal substrate, enables to obtain a continuous surface and high quality product (electronic and photonic applications, sensors, biomedical applications).

The principle of this production process is as follows [4,10,11]: a precursor that acts as source of carbon atoms has to be deposited on the surface of a catalyst substrate, which must be at a high temperature. Transition metals are used as substrates as they can easily change their state of oxidation, and so provide different routes of low energy in order to trigger the reaction. Once the precursor is decomposed by heat, the carbon is absorbed by the metal. The parameters influencing in a greater extent on the chemical vapor deposition precursor are the type of precursor, the cooling rate, the carbon concentration and the exposure time. The volumetric flow of the gas used and the geometry of the reactor used also play an important role.

Early research on the chemical vapor deposition applied to graphene substrates suggested the use of nickel, but it was noted that offered little control over the homogeneity of graphene on metal surface [5]. Copper, however, facilitates the formation of graphene sheets in a single layer on large surfaces [11]. Before proceeding with chemical deposition, the substrate is usually treated with annealing and hydrogen flow. The control of temperature, exposure time, hydrogen flow and concentration depends on the substrate used. This step reduces the oxidized layer that may have formed on the metal (oxides decrease the catalytic activity). Hydrogen helps to remove impurities [11].

It should be added that the transfer of graphene to other substrates is one of the fundamental problems of the use of CVD as a method of synthesis and currently represents a challenge for the industry.

2.5.- EPITAXIAL GROWTH OF SILICON CARBIDE

The epitaxial growth on silicon carbide (SiC) is an attractive process to produce high-quality graphene process. It places a small sheet of SiC (about 10 x 10 mm^2) in a box having a small orifice. The box is sealed under vacuum or is filled with argon and heated to about 1500°C. Thus, silicon at the surface is sublimed and the remaining carbon atoms are bonded, producing the nucleation and subsequent growth of graphene [12].

This process does not require the use of metals and hydrocarbons, so this is a very clean process. Graphene manufactured through this method results in applications of electronic type (in particular, high frequency transistors), due to its properties: high mobility of charge carriers and large surface. However, it has two major drawbacks: high temperature required and high cost of the precursor (SiC wafers).

3.- COMPARISON OF PRODUCTION PROCESSES

Let us compare the graphene manufacturing processes previously mentioned, according to various criteria referring to the quality of the final product, the method, and market information. These criteria are:

- Dimension: it refers to the average size of the graphene samples (largest dimension). Some applications require larger graphene surfaces, while others may use small size flakes.
- Grain size: size of the crystal grains is a measure of the crystallinity of the structure. A larger grain size implies a higher electrical conductivity (because the grain boundaries prevent movement of the electrons), but a smaller grain size increases the strength of the material (grain boundaries impede movement of dislocations).
- Number of layers: it is a measure of the homogeneity of the manufactured material. The product may have a single layer of graphene or more. While there are applications where the use of monolayer graphene is not necessary, high variability of this number implies variability of properties (which is unwanted).
- Electronic mobility: this is one of the most important characteristics, since many of the applications of graphene are in fields related to electronics. In principle, the higher electron mobility the better is the final product; however, not all applications require this property (for example, mechanical applications). Electron mobility is compared to room temperature.
- Precursor: the precursor used in each production process will also be assessed.

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- Process temperature: some processes require high temperatures in some of their phases.
- Scalability: based on the current state of technology, the manufacturing methods have been assessed as function of their possible scalability (ie, be able to be replicated on an industrial scale).
- Transfer: it indicates if the process requires a transfer phase of graphene produced to a given substrate. It is recalled that for some applications it is necessary, for example, an insulating substrate. It is relevant to compare the different methods according to this approach since the transfer phase can induce defects in the product.
- Applications: for each production process, the groups of applications that could potentially cover are listed.
- Market share: for each production process, the current market shares covering the fields of applications are added.

Each criterion was rated, from the information in Table 1, with integer values between 1 and 4, so that 1 is the worst and 4 the best value. On the other hand, Table 1 also contains the individual scores for each of the criteria, for each method of manufacture, and the weights that have been given to the comparison criteria, giving priority to the quality shown by the graphene produced by each alternative, scalability of the method of manufacture, and market information.

The results can be seen graphically in Fig. 1. The manufacturing process that would be more interesting for industrial scale production is the chemical vapor deposition on a copper substrate. As justification, first, non-scalable processes were discarded. For example, mechanical exfoliation, although giving the best quality graphene, would be economically convenient only to small production scales. It is therefore the ideal method for manufacturing in research sector. The latter, although it is the most important sector of the current demand of graphene, could be reduced as theoretical studies would progress. Regarding the epitaxial growth on silicon carbide it has not only discarded by its little current scalability, but also because provides a product of poorer quality than, for example, CVD. Moreover, we estimate that the market share for which it is better positioned is smaller than that of the other processes. This decision is also justified if the cost of the precursor, which is very high, is analyzed. Production costs by epitaxially grown on SiC are greater than those for CVD, and this difference is expected to increase in the future. Second, chemical exfoliation and reduction of graphene oxide use technologies that already exist in the industry, and are therefore scalable processes. However, the quality of the product does not allow them to access electronic or photonic applications (one of the factors affecting their quality is the number of impurities in the final product due to the chemical reactions involved in the process), which are the markets of greater importance in relation to the various applications of graphene. In addition, both have the disadvantage of the possible use of pollutants and toxic organic solvents (although this does not have taken into account in the scoring table). These two processes are widely used for the manufacture of composite materials; however, as mechanical reinforcement, graphene competes directly with carbon fiber technology, currently well developed.

CVD also uses technology already available in the industry. It should be added that main drawbacks of this process are the high temperature required in the process (about 1000ºC), the high cost of copper used as substrate, and the need for a transfer step to other substrates if required. Furthermore, as it produces graphene surfaces and not flakes, the product will be unsuitable for use in composite materials and coatings.

4.- FEASIBILITY OF PRODUCTION

It is estimated that world production of graphene in 2010 was 28 tons, and is expected to grow to 573 tons in 2017 [17]. We conducted a study [18] to determine the feasibility of launching a company to work with a plant for an annual production of about 375 m^2 graphene (about 290 mg/year). In comparison, the pilot plant that Graphenea multinational has installed in San Sebastián (Spain) produces 5 m^2 graphene per year [19]. The investment of the proposed plant would be about 180,000 €; the most expensive element would be the reactor. A CVD reactor appropriate for this production costs approximately 90,000 €. With respect to operating costs, they would be about 450,000 €/year. Market prices of graphene are highly variable. For reference, the price of a 10 mm x 10 mm sheet of commercial monolayer graphene ranges between 9 € on copper substrate to 44 € on SiO_2/Si substrate; however, a wafer of 4 inches in diameter on copper is priced at 299 €, ie 4 €/cm^2 [17]. If, using a scale factor, we assume a sale price equal to 5% of the least of these, ie, 0.2 €/cm^2, production costs would be amortized after selling about 225 m^2 of graphene on copper substrate, that is to say, just seven months after the start of production. It is easy, therefore, to intuit a more than acceptable technical and economic feasibility of such production. In the cited study [18] the reader can find more details on these estimates.

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	Final product				Process				Market information	
	Dimension (mm)	Grain size (µm)	Number of layers	Electronic mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	Precursor	Process temperature (ºC)	Scalability	Transfer	Applications	Market share (%)
Criterion weight (%)	*10*	*10*	*15*	*10*	*5*	*5*	*15*	*5*	*15*	*10*
Mechanical exfoliation	> 1	> 1000	1 – 10	> $2 \cdot 10^5$	Graphite (*HOPG*)	-	No	Yes	Research	55
Score	*2*	*4*	*1*	*4*	*2*	*4*	*1*	*1*	*1*	*4*
Chemical exfoliation	Microns (infinite as foil of overlapping flakes)	≤ 0,1	1 – 2	100 (for foil of overlapping flakes)	Graphite	-	Yes	Yes	Composites, coatings, energy storage, biomedicine	21
Score	*1*	*1*	*4*	*2*	*2*	*4*	*3*	*1*	*3*	*2*
Reduction of graphene oxide	Microns (infinite as foil of overlapping flakes)	~ 100	1 – 2	1 (for foil of overlapping flakes)	Graphite oxide	100 (chemical reduction)	Yes	Yes	Composites, coatings, energy storage, biomedicine	21
Score	*1*	*2*	*4*	*1*	*2*	*3*	*3*	*1*	*3*	*2*
Chemical vapor deposition	~ 1000	1000	1	10000	CH_4	1000	Yes	Yes	Electronics, photonics, energy generation, sensors, biomedicine	24
Score	*4*	*3*	*4*	*3*	*3*	*2*	*3*	*1*	*3*	*2*
Epitaxial growth on SiC	100	50	1 – 4	10000	SiC	1500	Not yet	No	Electronics, photonics	13
Score	*3*	*2*	*2*	*3*	*2*	*1*	*2*	*4*	*2*	*1*

Table 1. Comparison of different processes of graphene production according to various criteria [2,3,13,14,15,16]. The weight of each criterion and assigned individual scores (before applying the weighting coefficients) between 1 and 4 (1 is the worst and 4 the best value) are indicated.

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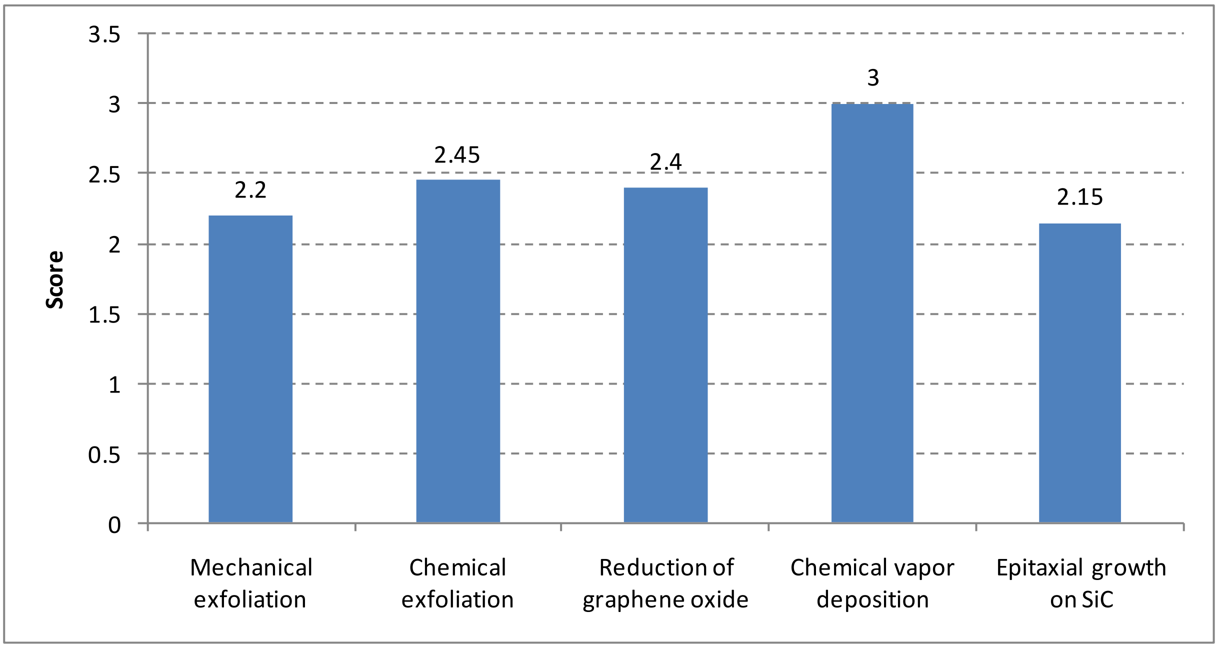

Fig. 1. Total scores for the production processes that were compared

TO KNOW MORE

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