GRAPHENE EXPOSED

EXPLOITING THE FULL POTENTIAL OF GRAPHENE

Written by
THE INNOVATION LAB
CARBON WATERS’ TEAM

Approved by
ALBAN CHESNEAU
CEO & CO-FOUNDER
It took 100 years for silicon to be fully exploited. Graphene is younger but more promising than any other material. Its properties are revolutionizing the industry. And now all you have to do is understand its potential and how to use it.
A GRAPHENE MANUFACTURER & FORMULATION DESIGNER

Carbon Waters is a specialty chemicals company designing, developing, and manufacturing the next generation of ready-to-use multifunctional additives.

After 10 years of R&D at CNRS (a top-level French research organization), our team has optimized this breakthrough technology and scaled up production.

MEET OUR TALENTED MEMBERS

The expert team at Carbon Waters consists of PhD experts in graphene-based formulations and production.

We are here to support you at each stage of your project.

- Development Unit
- Process & Production Unit
- Business
- Administration

Our Technology

WE PROVIDE READY-TO-USE GRAPHENE PREMIXES

The value of graphene lies in its ability to robustly transfer its intrinsic properties into dispersions. This creates products that possess specifically and simultaneously enhanced characteristics.

Our engineering team has now acquired a thorough understanding of graphene behavior in a wide variety of chemical environments, so we can continuously propose new graphene premixes as multifunctional additives.
Low carbon impact
Biodegradability
Absence of nanopowders

Both our product and process show a real advantage in term of sustainability:
- Low carbon impact
- Biodegradability
- Absence of nanopowders

Carbon Waters aims to develop solutions for a sustainable world.

Enhancing Performance

<table>
<thead>
<tr>
<th>Polymers &amp; Composites</th>
<th>Coatings &amp; Resins</th>
<th>Other Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>+25%</td>
<td>+35%</td>
<td>+70%</td>
</tr>
</tbody>
</table>

At extremely low concentration

Graphene & Sustainability
The theory that a form of carbon in the structure of graphene should exist, was first postulated in the 40’s by Wallace and later supported by the work of Blakely in the 1960s and 1970s. (1)

For close to 50 years, graphene stayed a theoretical hypothesis until it was isolated by Andre Geim and Konstantin Novoselov in 2004. Together, they were awarded with the Nobel Prize in Physics in 2010 for their groundbreaking work.

This material exhibiting very interesting properties became rapidly a star in many industrial sectors, from electronics and energy storage to bioengineering and nanomaterials and includes composites and coatings.

This popularity has led to high expectations which are long in concretizing. This delay is owed to many reasons. One of them is related to the fact that graphene is not a unique material but a material family, and each member of this family has its own advantages and drawbacks according to applications.

In this context, the main objective of "Graphene Exposed" is to help industrials to perceive differences between each graphene form by answering the following questions:

- What is graphene?
- What are the main production processes?
- How to assess the quality of graphene?
What is graphene?

Graphene is only composed of carbon, like diamond, graphite, and amorphous carbon. However, graphene is a 2D material where one single layer of carbon atoms, is arranged in a honeycomb structure. (2)

This sets it apart from other carbon forms because its unique structure leads to exceptional properties.

- The lightest material known in the world: 0.7mg/m².
- Remarkable mechanical resistance: Young modulus = 1060 GPa & intrinsic strength = 103 GPa. A breaking strength of 42N/m higher than steel one for a similar thickness.
- High thermal conductivity: it outperforms all other known materials.
- High electrical conductivity several dozens KS/m.
- High barrier properties: graphene is so dense, that not even Helium, the gas with the smallest atomic size, can pass through.

Even if graphene is stable and has exceptional properties, functional groups can interrupt the honeycomb structure. This strongly modifies the properties of graphene, e.g. electrical or thermal conductivity.

Even if graphene itself is rather chemically inert, some production processes lead to the introduction of these defects.

Hence, it is important to keep in mind that when certain properties of graphene are desired the production method needs to be chosen wisely.

**INDUSTRIAL GRAPHENE SHOULD NOT BE CONSIDERED AS A UNIQUE SUPER MATERIAL ANSWERING THE NEEDS OF A WIDE RANGE OF APPLICATIONS BUT MORE AS A FAMILY OF MATERIALS WITH A VARIETY OF PROPERTIES.**
Graphene was isolated by the scotch-tape method for the first time in the world. This method proved that graphene was not only a theory, but a reality. The scotch-tape method is absolutely not transferable for an industrial production of graphene.

But it was a stepping-stone, and several different production processes emerged since the first isolation of graphene.

Two different strategies can be applied:

1-Bottom Up: Graphene produced from gases by Chemical Vapour Deposition (CVD)

2-Top Down: Graphene produced from graphite by exfoliation

- Chemical exfoliation
- Liquid exfoliation
- Oxidative exfoliation
Different graphene forms

We can segment the graphene family in 2 ways:
- Thickness of the material
- Degree of functionalization

1- THICKNESS OF THE MATERIAL

Graphene is limited to 10 layers, so less than 3nm thick. Nowadays, very few companies are able to produce such a graphene. (3)

- SLG: Single Layer Graphene (1 Layer)
- FLG: Few Layer Graphene (2-5 Layers)
- MLG: MultiLayer Graphene (<10 Layers)
- GNP: Graphite NanoPlates (<250 Layers)

---

Different graphene forms

We can segment the graphene family in 2 ways:
- Thickness of the material
- Degree of functionalization

2- DEGREE OF FUNCTIONALIZATION

FUNCTIONAL GROUPS, EVEN IN LOW QUANTITY, DECREASE THE PERFORMANCE AS ANTICORROSION AGENT OR THERMAL AND ELECTRICAL CONDUCTOR. THE DEGREE OF FUNCTIONALIZATION AND THEREFORE THE LEVEL OF DEFECT, DEPENDS STRONGLY ON THE METHOD OF PRODUCTION!

**CVD GRAPHENE**
SLG or FLG with nearly no functional groups or defects

**CHEMICALLY EXFOLIATED GRAPHENE**
FLG or MLG with very low amount of functional groups and defects

**LIQUID EXFOLIATED GRAPHENE**
FLG, MLG or GNP with some functional groups

**REDUCED GRAPHENE OXIDE**
SLG, FLG, MLG or GNP with some functional groups

**GRAPHENE OXIDE**
FLG, MLG or GNP with many functional groups
Production processes

CHEMICAL VAPOR DEPOSITION (CVD)

CVD is the only bottom-up production method for graphene which is used in an industrial environment.

Here, carbon containing gases are brought in contact with a metal surface under high temperatures (1000°C) and high pressure.

Subsequently, the graphene honeycomb structure is formed on the metal substrate which serves as a catalyst.

Even though the quality of the so produced graphene is high, being mostly SLG graphene with very little functional groups or defects, this production method has major drawbacks.

Firstly, current industrial technology is still limited in the size of the graphene surface produced. Secondly, the obtained graphene needs to be transfer from the metal surface to the target substrate.

Methods commonly used involve wet chemical transfer processes that can contaminate the product. Nowadays, a lot of research is still focused in improving these techniques.

Graphene obtained by chemical vapor deposition shows very good properties, it is however limited in size and versatility.

Its integration into specific applications is still very challenging.
Production processes

LIQUID EXFOLIATION

This method was first described in 2008 in order to answer the needs for a scalable production method to produce graphene.

This top-down method requires mechanical energy in order to exfoliate graphite. Most commonly, techniques like sonication or high-shear-mixing are utilized. However, the efficiency of exfoliation is difficult to control.

Consequently, this method usually leads to a large distribution of graphene flakes in size and thickness.

"Choose wisely the additives or solvents for an optimized graphene formulation"
For this exfoliation method, graphite is commonly oxidized under harsh conditions to obtain graphite oxide. This bulk material can be dispersed by sonication in polar solvents, e.g. water, to form graphene oxide.

The oxidation introduces a large amount of oxygen containing functional groups which allows the exfoliation to even obtain SLG and ensures the stability in dispersion without the need of further additives.

Therefore, this family of graphene materials can have lowered thermal or electrical conductivity.

In order to resolve this problem, graphene oxide is most commonly reduced with agents, like hydrazine, or through electrochemical approaches to form so-called reduced graphene oxide (rGO).

However, this reduction process is never 100% complete and can even introduce holes into the carbon lattice.

Even if rGO is still slightly oxidized compared to pristine graphene it has been used for the development of many applications and has shown its convenience.
This top-down approach to obtain graphene in dispersion from graphite is mastered by Carbon Waters. The resulting aqueous dispersion of graphene is extremely stable without the need for surfactants or organic solvents.

The production route takes advantage of the fact that potassium intercalation compounds dissolve spontaneously in polar solvents.

Chemical exfoliation leads to a solution of charged graphene flakes, merely stable under inert conditions.

This major drawback was recently solved by a CNRS* team thanks to simple, but beautiful transfer into water under specific conditions.

Furthermore, the chemical exfoliation is highly efficient. This aqueous graphene dispersion combines the advantages of different families of graphene materials: high quality of graphene while maintaining the versatility of a dispersion.

This key innovation in the field of producing graphene via exfoliation methods opens possibilities to use graphene for industrial applications, e.g. as additives for paints or composites.

Carbon Waters’ ongoing achievement is to transpose this process to an industrial scale.
Graphene quality

Graphene has neither global standard nor reference material

A KEY FACTOR

Technical data delivered by graphene manufacturers does not easily allow a comparison of the different forms of graphene. Firstly, the type of analysis methods differ a lot and secondly it can be questionable if the analysis is systematic.

Research conducted by the National University of Singapore (NUS) proposes a protocol to analyse and to compare the quality of graphene.

The quality of graphene from 60 manufacturers was analysed with the conclusion that the graphene is generally low quality and non-optimal for many applications.

It tends to show that most graphene manufacturers produce graphite micro-platelets.

Nowadays several local initiatives are taking shape, in order to develop programs for the verification of graphene quality. In Europe, this work is settled up in cooperation with the LNE* and INERIS**.
With only absorbing 2% of the visible light, one layer of graphene is transparent to the human eye. Graphene absorbs however at a very characteristic wavelength in the ultraviolet range. It is well described in the literature that pristine graphene exhibits a characteristic absorbance peak at 269 nm. This peak can be attributed to transitions of the carbonyl groups typical of graphene oxide. The shoulder found at 300 nm is described in the literature as transitions of aromatic C bonds.

Graphene oxide on the other hand has many defects and functional groups interrupting electronic conjunction within honeycomb structure. UV-Vis spectroscopy is a very simple tool to get a first idea of the quality of a graphene dispersion and to investigate the stability over time.
When discussing the quality of graphene, Raman spectroscopy is the technique that needs to be taken into consideration. (6)

Since the first isolation of SLG in 2004, it is an ongoing effort by many research groups to decipher the Raman spectrum of graphene in order to extract the integrality of information available. Meaning the higher the intensity the thinner the material. This is especially evident in comparison to the Raman spectrum of graphite.

This is not a simple undertaking and expertise is required to interpret correctly the information. The Raman spectrum of graphene oxide is evidently different compared to graphene, due to the presence of numerous functional groups.

The G mode is the reference of all comparison because it represents the carbon honeycomb structure of graphene.

The D mode induced through sp³ via functional groups or edges.

The 2D mode is very sensitive to the thickness of the graphene.

It is important to remember that the efficiency of graphene in different applications relies directly on its structure and properties as shown on the figure presented above.

INTERESTED IN A SPECIFIC APPLICATION? BE CAREFUL TO SELECT THE RIGHT TYPE OF GRAPHENE
The main goal for the years to come will be to scale-up an industrial and energy-efficient process as well as producing few or even no waste.

Graphene would then answer to a very modern and urgent need: ally a high performance for the industry with a neutral or positive impact on the environment.
Meet our expert team

PEOPLE BEHIND THE INNOVATION LAB

ALBAN CHESNEAU
CEO & CO-FOUNDER

CHARLOTTE GALLOIS
ACCOUNT MANAGER

JULIA HOF
PROCESS ENGINEER

THOMAS BOTTEIN
R&D ENGINEER

HÉLOÏSE DELPOUVE
R&D ENGINEER

NEED ADVISES?
Working with graphene relies on several steps:

1. Select the right graphene form according to your application.
2. Conduct tests and validate the potential of graphene for your product.
3. Optimize the performance and the process of incorporating graphene to your product.
4. Scale-up the production process and make industrial qualification.

GET IN TOUCH WITH OUR EXPERT TEAM
contact@carbon-waters.com
The purpose of "GRAPHENE EXPOSED" is to explain the subtleties of this incredible material. Since its discovery, many industrialists have tried to produce and apply graphene in different ways. We hope this e-book has given you a better understanding of graphene and how it can be applied to your needs.

The writers behind GRAPHENE EXPOSED: Alban Chesneau, Charlotte Gallois, Julia Hof, Thomas Bottein.

The designer of GRAPHENE EXPOSED: Dia-adine Hamoudi, Marketing & Communication Manager

Approved by Alban Chesneau, CEO & Co-founder of Carbon Waters

We thank you for reading our e-book "GRAPHENE EXPOSED". If you have any questions do not hesitate to contact us.

Contact

Carbon Waters
14 Avenue Pey Berland
33607 Pessac FRANCE

www.carbon-waters.com
contact@carbon-waters.com
Carbon Waters
@CarbonWaters