

Graphite/Graphene Analytical Index; GG Index

The GG Index is an analytical tool for the characterization and identification of graphite-based carbon materials.

Target materials: natural graphite, artificial graphite and carbon black from petro or coal derivatives, expanded graphite, graphite/graphene oxides, graphene intermediates, graphene, etc.

Required system: SmartLab (9 kW), automated multi-purpose X-ray diffractometer

The discovery of graphite and its industrial use date back to the 16th century, more than 200 years before the first industrial revolution, which took place from the middle of the 18th to the 19th century. The first industrial use of graphite was as pencil lead and fire-retardant materials. It is now used in a variety of high-tech fields such as nuclear energy. More than 1.2 million tons of graphite is produced each year, with an upward trend foreseen in future demand.

Graphite is inexpensive and distributed throughout the world. Sufficient reserves exist to meet demand for hundreds of years, according to verifiable sources. The existing supply of graphite is almost infinite. Once a flake of graphite is peeled off, it becomes a fascinating material called “graphene,” a stunning discovery that did not occur until 2004. Graphene is 1,000 times stronger than iron steel, exhibits more than 10 times higher electrical and thermal conductivity than metals, and is the thinnest and lightest flexible material known today. In 2010, the Nobel Prize in Physics was awarded for this discovery.

Innovative materials and products can potentially be created in various fields using graphene. Therefore, research institutes and companies all over the world conduct research and development for practical application of graphene in almost every industrial field. In the years since its discovery, products such as electronic items, acoustic products, daily commodities, tires, golf balls, sport wears and shoes have been developed making use of graphene for improved impact strength, conductivity characteristics, and so forth.

However, reasonably accurate measurement methods, analytical methods, definitions, standard references etc. have not been developed to identify graphite or graphene qualitatively or quantitatively. Graphite and graphene are currently evaluated in a limited, subjective, speculative way by shape observation using an electron microscope, surface analysis using Raman spectroscopy, a specific surface area measurement by gas absorption and so forth. The purpose of the Graphite/Graphene Analytical Index presented here is to exhaustively identify/characterize graphite, graphite-based graphene intermediates and bulk graphene, and to significantly enhance the efficiency of all the research and development related to these materials. Furthermore, we hope this index accelerates the development of breakthrough products based on graphite and graphene.

The goal of the Graphite/Graphene Index (referred to hereafter as the GG Index) is to elucidate the following items in association with future research.

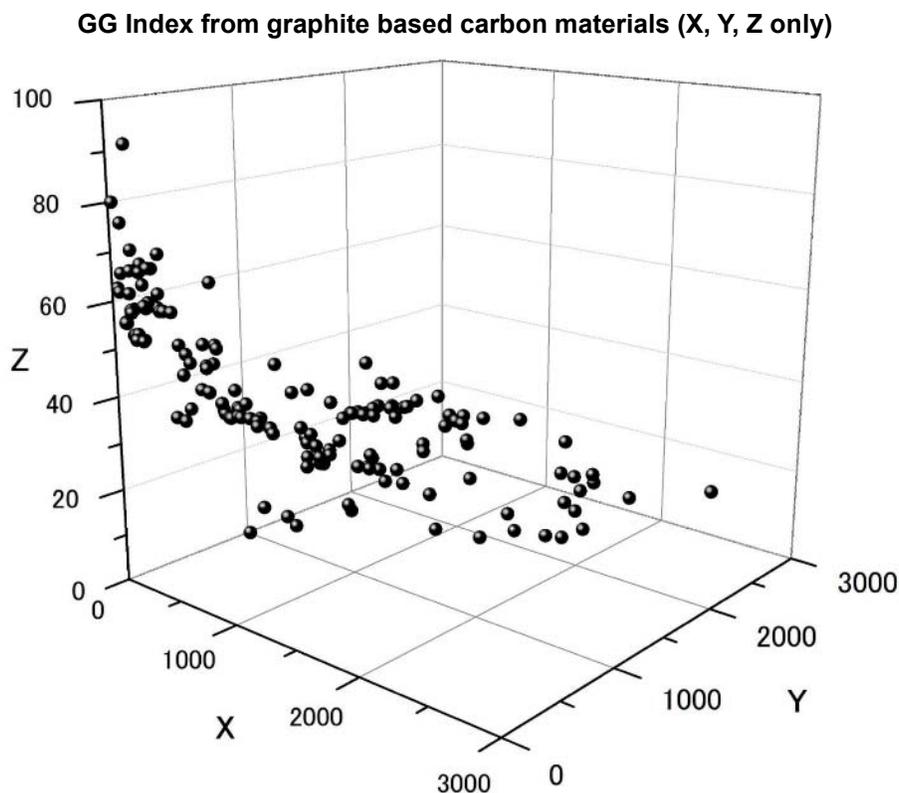
1. Characterization and identification of graphite as raw materials
2. Characterization and identification of graphite, graphene intermediates, and graphene in general
3. Determination of the specifications of graphite, graphene intermediates, and graphene as products
4. Characterization and identification of denaturation of graphite, graphene intermediates and graphene denaturation processed by heat treatment, grinding, chemical treatment, plasma treatment as refining processes
5. Selection of raw graphite and optimization of treatment processes for required graphite or graphene as products based on the four items above

As a reference for these analyses, the GG Index consists of the following four parameters.

X: Crystallite size (unit: Å)	Lateral size in the planar direction of graphite crystallites
Y: Crystallite thickness (unit: Å)	Thickness in the stacking direction of graphite crystallites
Z: Graphenization parameter (unit: %)	The ratio of rhombohedral graphite crystals to the sum of hexagonal and rhombohedral graphite crystals
M: Collapse parameter of graphite crystals (unit: Å ²)	The value related to the structural strain of graphite crystals It indicates the amount of displacement of the carbon atoms from the regular positions in graphite crystals.

The GG Index has the potential to find a correlation between the indices obtained from a number of graphite/graphene samples, as well as to simply analyze one graphite/graphene sample, and to generate a unified analytical method for graphite and graphene. It is desirable that the GG Index will contribute to the creation of requirements or specifications of graphite, graphene intermediates, and graphene required for a variety of products, and to select and optimize various refining processes of graphite and graphene in the future.

Shown below is an example of the GG Index results from about 100 samples of carbon materials obtained from representative manufacturers in the world.



Described below are the following four parameters calculated from the XRD patterns of graphite and graphene powder samples.

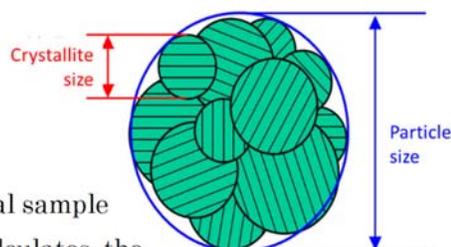
1. X: Crystallite size (unit: Å); Lateral size of graphite crystallites in the planar direction calculated based on a 100 diffraction peak shape
2. Y: Crystallite thickness (unit: Å); Thickness of graphite crystallites in the stacking direction calculated based on a 004 diffraction peak shape

The fundamental parameters (FP) approach is used here. The theoretical diffraction peak shape $f_s^{LN}(k; D_0, \sigma)$ obtained from the following equation is fitted to experimentally obtained 100 and 004 diffraction peak shapes to obtain D_0 as X and Y, respectively.

$$f_s^{LN}(k; D_0, \sigma) = \int_0^{\infty} f_s(k; D) f_{LN}(D; D_0, \sigma) dD$$

k : Scattering vector
 D_0 : Volume-weighted size
 D : Crystallite size
 σ : Standard deviation
 f_s : Peak profile from one crystallite
 f_{LN} : Lognormal distribution
 f_s^{LN} : Peak profile from particles

- (1) “Crystallite” here is the part regarded as a single crystal.
- (2) The single crystal is one crystalline particle where atoms are arranged with a three-dimensional regularity. Even if defects exist (where some 6-membered rings turn to 5- or 7-membered rings or some carbons have an sp^3 hybridized orbital due to the addition reactions of hydrogens or hydroxy groups), the part where the atoms are arranged with a roughly three-dimensional regularity can be regarded as a single crystal.
- (3) The thickness of the crystallite is the amount of layers stacked.
- (4) The crystallite size calculated based on the hkl diffraction peak shape is the single crystal size along the hkl direction. In the case of graphite, the $\langle 100 \rangle$ direction means the planar direction, and the $\langle 001 \rangle$ direction (calculated based on the 004 diffraction peak shape) means the stacking direction.
- (5) Normally, one recognizable particle in powder consists of several crystallites (see right). For example, the $\langle 001 \rangle$ direction of one of the adjacent two crystallites differs from that of the other.
- (6) Although the crystallite sizes and thicknesses of a real sample have size distributions, the GG Index software calculates the volume-weighted average values.
- (7) According to the accuracy of the XRD peak shape analysis, the analyzable maximum size is now around 1,000 Å. The possibility and benefit to obtain larger than 1,000 Å as the crystallite size should be discussed in future.



3. Z(R): Graphenization parameter (unit: %)

According to the following formula¹, the ratio of rhombohedral graphite contained in the graphite crystalline sample is calculated based on the integrated intensities of 101 diffraction peaks of hexagonal graphite 2H and rhombohedral graphite 3Rh. The obtained ratio is what we call the “graphenization parameter”.

$$R = \frac{I_{3Rh_{101}}}{I_{2H_{101}} + I_{3Rh_{101}}}$$

The stacking manner of the hexagonal crystallites is different from that of the rhombohedral crystallites. The larger the ratio of rhombohedral graphite is, the easier the layers are peeled off or the exfoliation has already been progressing². In general, graphene, graphene intermediates, and some graphite show a high trend in terms of R values.

4. $M(B_{eff})$: Collapse parameter of graphite crystals (unit: \AA^2)

The effective Debye parameter B_{eff} calculated based on the following formula is affected by the amount of displacement of the carbon atoms, which are supposed to be arranged with a 3-dimensional regularity, from the regular positions in graphite crystals³.

$$\ln\left(\frac{I_{obs}}{I_{calc}}\right) = \ln k - 2B_{eff} \cdot \left(\frac{\sin \theta}{\lambda}\right)^2$$

B_{eff} : Effective Debye Parameter
 I_{obs} : Observation Intensity
 I_{calc} : Calculated Intensity

B_{eff} is almost zero for ideal crystals; however, atomic positions in real crystals are displaced slightly from their regular positions due to thermal vibrations and lattice defects. The larger B_{eff} is, the larger the thermal vibrations and the amount of lattice defects are. In other words, B_{eff} can be regarded as the degree of crystal collapse.

The targeting material is graphite only; therefore, the thermal atomic vibrations are the same regardless of samples if the temperature is the same. The difference between obtained B_{eff} values is considered to be attributed to the difference in the amount of lattice defects; i.e., to the structural strain.

M	< 1.0	Crystalline state of graphite is maintained in a very good condition.
	1.0~3.0	Crystalline state of graphite is maintained.
	> 4.0	Crystalline state is largely destroyed.

¹ Structural Change of Graphite with Grinding Michio INAGAKI, Hisae MUGISHIMA, Kenji HOSOKAWA(1973 Volume 1973 Issue 74 Pages 76-82)

² US Patent: US9428393, UK Patent: GB2528381

³ Characterization of Powders by Effective Debye Parameter INAGAKI Michio, NAKA Shigeharu (1978 Volume 27 Issue 298 Pages 604-609)