

A possibility to create substantially lighter and tougher composites without radically changing your recipe

Distinguish your product!

Add "graphene" to its title.

You may be able to increase the elastic modulus
of your composites of up to 50%
and extend the breaking strength
(as is the case with synthetic graphene oxide in Dow D.E.R. 331 epoxy resin)

Imagine how your 50% lighter product
would look in the eyes of your customers.

Imagine the acceleration, agility and toughness
provided by a speck of a novel material.

It doesn't take much to achieve this.

Don't change your technology, UPGRADE IT!

Introduce our synthetic graphene oxide (sGO)
in your composition.

Our technology makes it abundant at a fraction of the current price.

Consider to test a sample.

Evaluate what our product can do for your technology.

Graphendo (Jap.: The Graphene Way) is an initiative of Innovatie Centrum Kunststoffen and Z3D Labs. Its mission is to make graphene technology economically feasible for reinforcement of materials.

Graphendo recently started its own GO production. The production happens according to a best standard quality system and statistic process control.

Synthetic Graphene (Hydr)oxide for Reinforcement of Composites

To put this product in context, we convey a quote from J. Sakamoto, et. al. paper "Two-Dimensional Polymers: Just a Dream of Synthetic Chemists ?" in *Angewandte Chemie*, 48, pp. 1030 (2009):

" Although numerous approaches have been reported over the last several decades, the synthesis of a one monomer unit thick, covalently bonded molecular sheet with a long-range ordered (periodic) internal structure has yet to be achieved ... Can one provide reliable and broadly applicable concepts to tackle the synthetic and analytical issues associated with the creation of polymers which meet the structural characteristics of graphene (that is, one repeating unit thick, covalently bonded, and long-range order). Clearly, this would constitute a substantial advance for chemistry in particular, and the molecular sciences in general."

Our company provides a bottom-up synthetic graphene oxide (GO) in large quantities and competitive price. The best use of this two dimensional material is as a reinforcement inclusion in composites.

Graphene Oxide may well compare to the well known Graphene Oxide prepared by treating graphite with oxidizers and acids ("Hummer's method"). But, as our product presumably contains exclusively –OH groups, we could also be speaking of Graphene Hydrxide (GHO). In order to keep the trusted vocabulary, we stick here to the term "Oxide", but it should be noted that our material is presumably unique in its hydroxyl content.

The reinforcement properties of graphene oxide are extraordinary and beyond expectations. Now that its properties are known, please consider using synthetic GO from Graphendo Ltd. in your products. The additional cost is far lower than the improvement this material provides.

The GO fillers can be dispersed into polymers using techniques such as solution mixing, melt blending or mixing in the hardeners. Regardless the method of mixing, superior dispersion of this filler is required in order to achieve the extraordinary reinforcement properties.

Polymer composites with GO-derived graphene materials as filler have shown dramatic improvements in properties such as elastic modulus, tensile strength, thermal stability and breakdown limit. Moreover, these improvements are often observed at low concentrations of the filler evidently due to the large surface area to weight ratio and high aspect ratio (two dimensional) of these materials, requiring small amounts of filler to achieve percolation. [T. Ramanathan et.al., *Nat. Nanotechnol.*, 3, 327 (2008); P. Steurer et.al., *Macromol. Rapid Commun.*, 30, 316 (2009).]. At 0.7 wt% GO concentration, a solution-mixed PVA-graphene oxide composite showed a 76% increase in tensile strength and a 62% increase in Young's modulus; the results were attributed to effective load transfer to the graphene oxide filler via interfacial hydrogen bonding. [J. J. Liang et.al., *Adv. Funct. Mater.*, 19, 2297 (2009).]

Also large shifts in glass transition temperature, T_g are observed [H. J. Salavagione et.al., *J. Mater. Chem.*, 19, 5027 (2009)]. Large increases in Young's modulus and a 30° C shift in T_g at only 0.05 wt% loading of a GO-PMMA composite were attributed to the onset of rheological percolation and to the crumpled morphology of the GO platelets. Composites of GO platelets have shown higher stiffness across all loadings and equal or lower electrical percolation thresholds than carbon black.

Low loadings of exfoliated GO platelets in epoxy reduce the coefficient of thermal expansion (up to 32% at 5 wt%) [S. R. Wang et.al. *Macromolecules*, 42, 5251 (2009).] and increased the critical buckling strength (by 52% at 0.1 wt%) versus the neat polymer. [M.A. Rafi ee et.al., *Appl. Phys. Lett.*, 95, 3 (2009).]

Why use our synthetic GO in your composite?

Benefits for your composite product if it incorporates synthetic GO:

- at miniscule amounts it could improve the elastic modulus by over 50%
- increases the breaking limit over multiple times the breaking limit of pristine material
- creates mechanism to prevent crack formation and propagation
- chemically and physically inert it improves the life-expectancy of the composite, since rendering it impenetrable to light and thus less apt to aging.
- improved dispersibility/solubility guaranteeing perfect blending and need of miniscule amounts
- distinguishes the product by adding "graphene" to its title and composition
- marks the product as "hi-tech" since it incorporates truly two dimensional crystal reinforcement
- improvement comes about at miniscule amounts used of the order of or less than 1%
- given the miniscule amounts needed, the added cost does not scare customers of your products away

Drawbacks for your composite product if it incorporates synthetic GO:

- adds cost, which should be justifiable given the improved properties in your application
- colours the composite, adds a dark tint due to light absorption/scattering by dispersed GO sheets

CHARACTERIZATION OF GRAPHENDO'S sGO

This TEM images of a **graphene oxide** flakes bottom-up synthesized in a two dimensional polymerization contains a SAED superimposed on the upper left side. The SAED image confirms the successful two dimensional polymerization of a carbon hexagonal lattice. The interplanar spacings are

$$d_{10}=2.50 \pm 0.27 \text{ \AA} \text{ and } d_{11} = 1.47 \pm 0.13 \text{ \AA}$$

The theoretical ratio $d_{10}/d_{11}=3^{1/2}$ for this lattice is confirmed by the experiment $d_{10}/d_{11}=1.70$

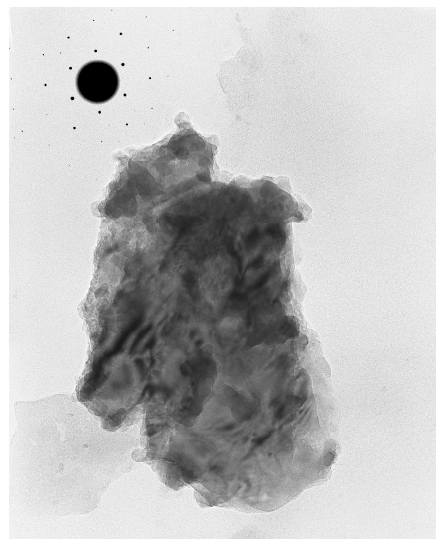


Figure 1. SAED analysis superimposed on a TEM image of sGO.

The identification is a result of the material characterization of the product which properties turn out to be identical with the prior art on graphene oxide.

Fig.1 contains the low magnification TEM image (x100 000) of the synthetic graphene oxide flakes. The layered and folded structure typical of two dimensional crystals such as graphene and graphene oxide is obvious.

The proof of the crystalline order of the synthetic graphene oxide a number of materials' characterization methods are employed such as Raman spectroscopy, Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction (SAED) and X-Ray Diffractoscopy (XRD). The results are conveyed on Figures 2,3,4 and 5.

The expected Raman spectra signatures measured at laser excitation $\lambda = 632.8 \text{ nm}$ are the D, G, 2D and D + D' peaks. In our spectrum in Fig. 2, the G peak shows hardening and reaches the highest position of 1600 cm^{-1} and D peak appears at 1370 cm^{-1} . The second order of the D peak, 2D (or G') peak position is usually observed in the range $2640 - 2700 \text{ cm}^{-1}$ depending on the number of layers and the D + D' peak at 2940 cm^{-1} is due to the defect activated combination of phonons. Additionally, a peak centered at 1450 cm^{-1} is modulating the spectrum. Its origin is attributed to a C-OH mode (phenol -OH group) and is characteristic band of the hydroxyl group covered carbon hexagonal lattice of graphene (hydr)oxide.

The result of the indexed SAED of a synthetic graphene oxide flake is conveyed in Fig. 3. The diffraction pattern is unequivocal – it confirms the two dimensional hexagonal carbon lattice belonging to the space group $p31m$. The interplanar spacings are $d_{10} = (2.50 \pm 0.27) \text{ \AA}$ и $d_{11} = (1.47 \pm 0.13) \text{ \AA}$ and coincide with the expected for graphene oxide. The theoretical ratio $d_{10}/d_{11} = \sqrt{3}$ for this lattice is confirmed by the experiment.

Fig.4 depicts the high magnification TEM image (x1 500 000) of the surface of the synthetic graphene oxide flakes. The black dots in the image are the oxygen atoms of the hydroxyl groups attached to the underlying carbon hexagonal lattice. The characteristic spacings in their order are indicated. One clearly sees the angle the grooves form which is characteristic of the symmetry and coincides with the structures previously seen on graphene oxide.

The table on Fig. 5 shows the results of the 2θ [deg] peaks of the XRD at Cu K α (1.54 \AA) of the synthetic graphene oxide (left column) compared to the peak lists of commercial rGO by NanoInnova

and Ruoff's group graphene oxide both produced in a "top-down" fashion. The results of the comparison are conveyed in the right column where a deviation of 0,5 [deg] is marked "close", a deviation of less than 0,5 [deg] is marked "ok" and no deviation is marked "perfect." The absence of the "top-down" graphene oxide peak in the range of 10-12 deg assigned to (002) plane confirms the true two dimensional nature of the synthetic graphene oxide. Standard "top-down" procedures of producing graphene oxide are unable to fully exfoliate graphite and few layer crystallites are always present thus peaks from (00n) planes are strong. The synthetic graphene oxide produced via the two dimensional polymerization must not have peaks associated with (00n) planes and (002) plane in particular. The coincidence for other 2θ [deg] peaks is sufficient alone to claim that the product of the two dimensional polymerization is identical to graphene oxide.

The conveyed experimental data shown on the figures qualify the offered sGO, as graphene oxide.

The offered synthetic graphene oxide has a high potential as reinforcement in composite materials, resins, engineering polymers, coatings and adhesives.

As the use of GO for the reinforcement of polymers and composites is a widely unexplored field, you may be well ahead of your competition if you implement this promising technology in your designs.

Is your demand higher than we could supply on short terms? Then let us operate your own Graphene Oxide plant and produce any amount you want for yourself.

We are eager to cooperate with you in order to gather new insights and invent new applications.

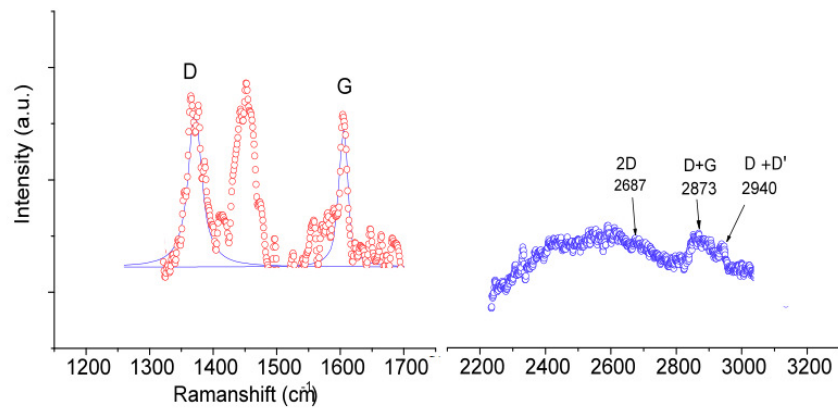


Figure 2. Raman spectrum of synthetic graphene oxide.

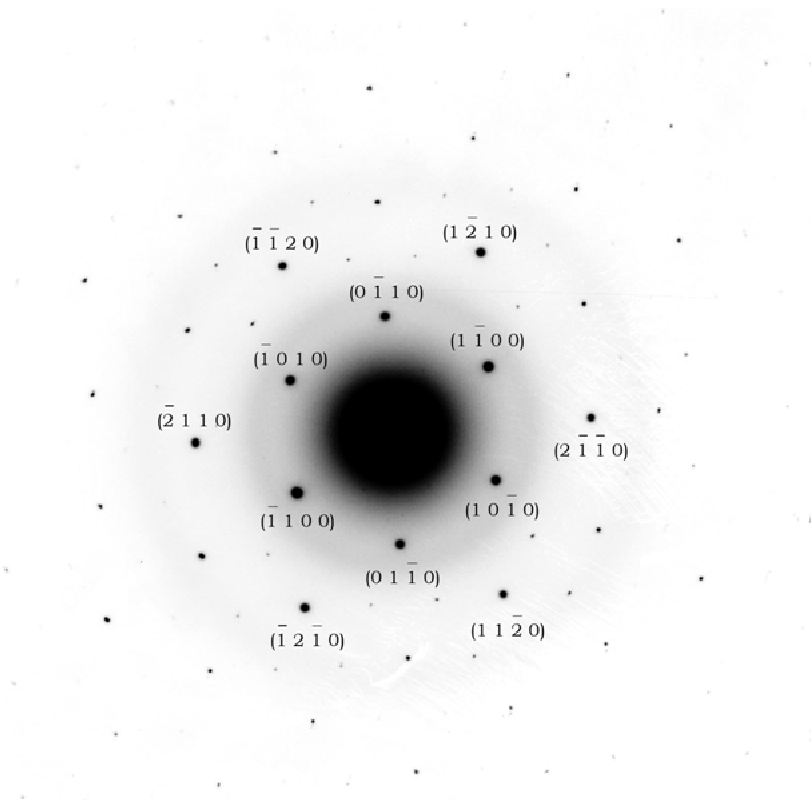


Figure 3. An indexed electron diffraction pattern (SAED) of synthetic graphene oxide flake.

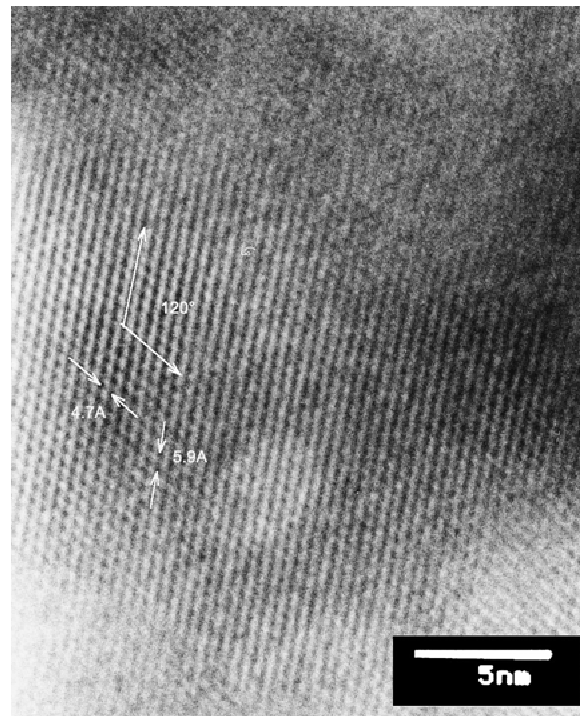


Figure 4. The surface of a graphene oxide flake at 1 500 000 times magnification in TEM.

synthetic GO	NanoInnova rGO	Ruoff's group GO	match
n.a.	n.a	10	n.a.
16.2	n.a.	15.5	close
20.4	20.4	20.3	perfect
22.4	23.7	n.a.	close
25.9	25.9	n.a.	perfect
28.6	n.a.	28.9	close
30.2	30.3	30	ok
33.0	32.1	33.1	ok
38.7	n.a.	n.a.	n.a.
40.8	n.a.	40.4	close
broad	-	-	-
42.5 - 43.4	43.4	42.5	ok

Figure 5. The 2θ [deg] peaks in the XRD at Cu K α (1.54 Å) of the synthetic graphene oxide and comparison with prior art.



Consider to test it for yourself!

Evaluate yourself what our product can do for your technology.

Lighter?
Cost saving?
At last made possible at all?
More durable?
Quantum leap?

We could also do research work for you, e.g. at our partner institute, the Academy of Sciences in Bulgaria, Sofia University or Hogeschool Rotterdam.

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