MAY 27, 2020
CONFERENCE ONLINE

Graphene Industrial Forum &2DM 2020

Cost-efficient washing and purification process for graphene oxide manufacturing at industrial scale

GRAFREN AB

Erik Khranovskyy, Reza G. Yazdi, Mykhailo Zhybak, Nathalie Elsässer

LINKÖPINGS UNIVERSITET

MOTIVATION

The issue of graphene quality is a hot topic at present, being raised up and claimed to be responsible for the delayed commercialization of graphene based products. Recent study of the quality of the market available graphene materials has found that most of the samples contained less than 10% of graphene and the rest just graphite powder [1]. Graphene Research Society, headed by National Physics Laboratory, has reacted to the situation and created the first ISO standard on graphene quality [2] which constitutes that graphene can be called two-dimensional crystals of graphite with the thickness up to 10 atomic layers. While other flakes containing more than 10 graphene layers are basically graphite.

FIGURE 1. *Graphene quality issues, raised in the recent literature (left) and illustation fo the complexity of flakes thicknesses in resulting G mixture (right)*

The recently introduced standard was aimed to clarify the mess, existing on the graphene market. However, it does not solve the problem of the material quality by itself. The problem is complexed toward at least two dimensions [3]:

- Mass production of graphene flakes does not allow to control the quality of every flake and no ongoing methods exist for the process quality control on the industrial scale;
- Post-synthesis approaches (such as vacuum filtration or centrifugation) are not applicable for the large volumes of graphene and can not provide economically suitable cost to performance ratio.

Obviously, there is a need for the new post-treatment technologies for improvement of graphene quality. GRAFREN AB team has developed the process for separation of graphene flakes from unreacted species, graphite debris and other impurities via specific mechanical treatment in a water-based dispersion, which provides high material yield at low processing costs [4]. Here, we present the solution for washing and purification for graphene oxide obtained by Hummers method modifications.

METHODS AND CHALLENGES

Main approach for graphene oxide (GO) manufacturing remains still Hummers method, diversely modified in terms of process steps involved, deviation of conditions or chemicals used (see the example below).

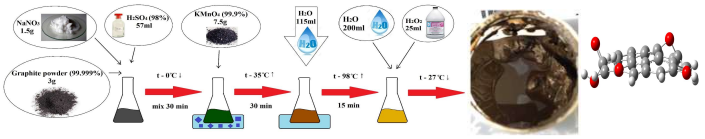


FIGURE 2. *Example of the Hummers modified method, resulting in a sludge of Graphene Oxide (GO). Washing procedure is not included.*

However, still the most resources- and time-consuming step is washing of the as-synthesized sludge of GO and separation of pure graphene flakes from the possible waste of the chemical process. The waste to be removed are **acidic residues, metal ions and unreacted graphite species**, depending on the method modification and chemicals used. Producers are always facing the contradictory choice between larger yield of graphene flakes and the quality of obtained material.

Current methods for separation of pure GO are vacuum filtering or centrifugation, which proved to be applicable for small-scale academy research. However, none of these approaches is applicable for large industrial scale production of GO, due to complexity, low yield, and high labour costs.

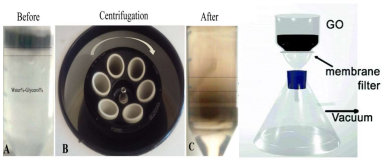


FIGURE 3. *Example of available separation approcahes for GO washing: centrifugation and vacuum filtering (*images are adapted from the web)*

RESULTS

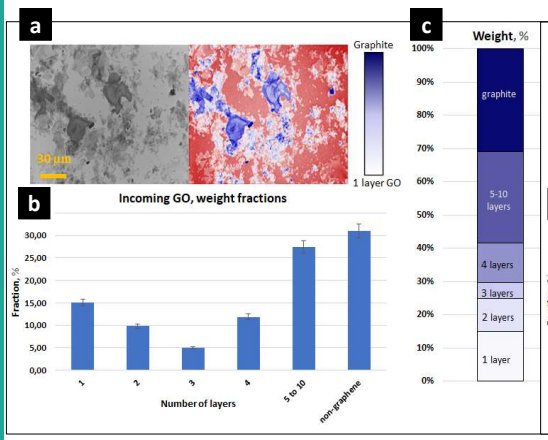


FIGURE 4. *Example of average incoming GO material available on the market (treated according to ISO standard [2] before examination): **a)** SEM image and its color filter processed version; **b)** average weight distribution (calculated from SEM and AFM-mapping analysis, n = 15); **c)** Average weight fraction of the GO sample (calculated from SEM and AFM-mapping analysis, n = 15).*

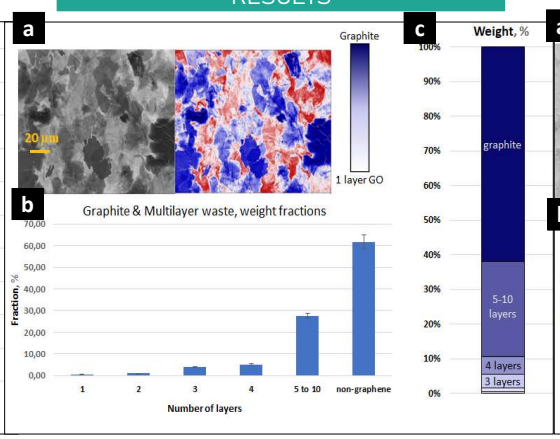


FIGURE 5. *Example of average separated waste fraction of GO material after 1 run of Grafren purification process (treated according to ISO standard [2] before examination): **a)** SEM image and its color filter processed version; **b)** average weight distribution (calculated from SEM and AFM-mapping analysis, n = 15); **c)** Average weight fraction of the GO sample (calculated from SEM and AFM-mapping analysis, n = 15).*

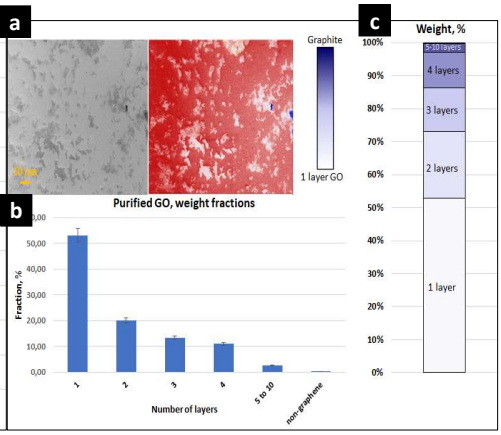
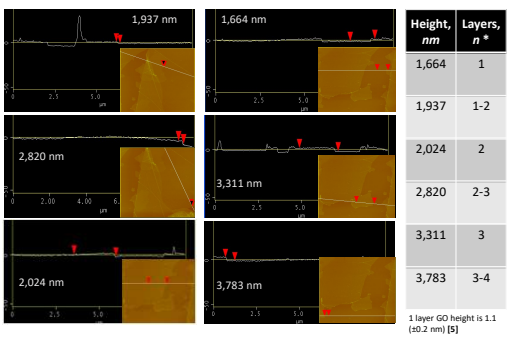


FIGURE 6. *Example of average purified GO fraction after 1 run of Grafren purification process (treated according to ISO standard [2] before examination): **a)** SEM image and its color filter processed version; **b)** average weight distribution (calculated from SEM and AFM-mapping analysis, n = 15); **c)** Average weight fraction of the GO sample (calculated from SEM and AFM-mapping analysis, n = 15).*



Height, *nm*	Layers, *n* *
1,664	1
1,937	1-2
2,024	2
2,820	2-3
3,311	3
3,783	3-4

1 layer GO height is 1.1 (±0.2 nm) **[5]**

FIGURE 7. *Examples of AFM examination of GO samples.*

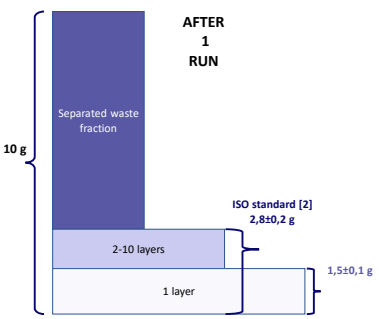


FIGURE 8. *Examples of weight yieald of the process after 1 run for specific GO paste sample.*

SUMMARY

- The innovative procedure for washing graphene oxide sludge and separation of flakes is suggested.
- The process allows separation of GO flakes of the thickness/size, required by the ISO Standard for Graphene and 2D Materials.
- The process can be run several times, aiming on fine separation of the flakes, potentially reaching 100% single flakes composition.
- Process is scalable and flexible, being potentially used by both GO manufacturers as well as GO users as a tool for quality assurance.
- Process is independent on the quality of incoming material and can be potentially expanded for other 2D materials with quality issues.

CONTACT PERSON

Dr. Erik Khranovskyy, PhD
ceo@grafren.se
+46700895814
www.grafren.se

REFERENCES

[1] P. Bögild, The war on fake graphene, Nature 562, 502-503 (2018)
[2] ISO. Nanotechnologies-Vocabulary-Part 13: Graphene and Related Two-Dimensional (2D) Materials www.iso.org/standard/64741.html (2017).
[3] A. Kovtun et al. Benchmarking of graphene/based materials: real commercial products versus ideal graphene, 2D Materials, 6 025006 (2019).
[4] Patent Appl. No. 1950819-1 "Method for redistributing a flake material into at least two flake size fractions" (filed 28 June 2019).
[5] C. Gómez-Navarro et al. Electronic transport properties of individual chemically reduced graphene oxide sheets, Nano letters 7(11) 3499 (2007).

Graphene Industrial Forum &2DM 2020