Graphene: first and forthcoming industrial applications

MARIO PAGLIARO
Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Palermo, Italy

***Mario Pagliaro** is a chemistry and energy scholar based at Italy's Research Council in Palermo, Italy, where he leads a research group focusing on nanochemistry, solar energy and the bioeconomy. Co-author of 22 books and of 250 research articles, he ranks amongst Italy's most cited scientists in nanotechnology, materials science and organic chemistry. Dr Pagliaro serves on the advisory and editorial boards of several internationally recognized journals, including Chemical Society Reviews.*

"Now that low cost chemical routes to produce graphene have become available" we wrote in a study published in 2015 (1), "three important technologies, namely cost-effective electricity storage, polymer nanocomposites and environmental remediation" will emerge as the first applications of the atomically thin carbon films known as graphene (a single plane of sp^2 carbon bonded atoms in a honeycomb hexagonal lattice) beyond specialty niche markets.

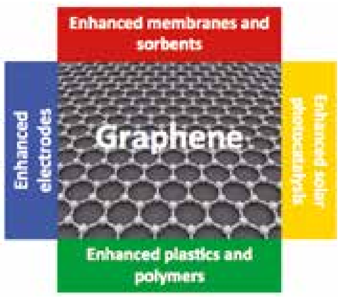

Figure 1. Three main commercial uses for graphene, followed in the near future by enhanced solar photocatalysis, were forecasted in a 2015 *Chemical Communications* study: enhanced composites, enhanced electrodes, and sorbent materials.

First isolated by Geim, Novoselov and co-workers in 2004 repeating the use of adhesive tape to exfoliate graphite (2), today graphene is manufactured on small industrial scale using widely different graphite exfoliation routes affording graphene and related materials (GRM), chiefly in the form of black, solid powders. Products manufactured in Europe on industrial scale have either low defectivity (percentage of sp^2 bonds >95%) featuring low surface area (<200 $m^2 g^{-1}$), or are highly exfoliated but show higher defectivity (3).

Yet, the authors of the benchmark study concluded, "the actual quality of several industrial GRM is clearly good enough for many applications", (3) and -- most importantly -- graphene companies are no longer selling graphene by the gram, but rather on multi kilogram scale. The market includes two main GRM product classes:
highly expensive graphene obtained via chemical vapour deposition of a carbon-rich gas precursor, and much cheaper graphene powders obtained via graphite exfoliation (4).

Our 2015 forecast turned out to be at least partly true. Graphene-polymer composites produced adding 1% wt GRM in polymer resin obtaining composites of significantly improved flexural strength and modulus are now a commercial reality appreciated by skiers and tennis players, for example, as skis and tennis rackets manufactured using graphene composites are lighter, stronger and more flexible. Similarly, a 250% improvement in service life, a 35% increase in the resistance to the passage of vehicles, and a 46% reduction of the track left by tires and higher resistance to deformation was lately verified in Italy during the first real-life test of an asphalt concrete modified with industrially manufactured graphene (5).

Furthermore, once laid, the asphalt concrete containing graphene-based modifier is easily and entirely recycled, dramatically reducing the environmental impact of producing bitumen and extracting aggregates from quarries (5).

Commercialization of the first graphene-based air filters is now in sight, after Tour and his team lately reported that not only bacteria and allergens but also large molecules such as pyrogens, mycotoxins, nucleic acids and prions can be completely deactivated by simply functionalizing commercial vacuum air filtration systems with porous graphene foam which first traps airborne contaminants, and then destroys them by periodically heating up to a temperature of 350°C as a result of electricity passing through it (6).

Due to their intrinsic safety, low cost, longevity, and absence of toxic and expensive cobalt, lithium iron phosphate (LFP) cathodes remain the industrially preferred cathode technology to manufacture Li-ion batteries on today's huge industrial scale (7).

Added at just 2 wt% amount on the surface of commercial carbon-coated lithium iron phosphate cathode, graphene is well known to enhance the energy density of the resulting LFP battery by close to 40% (8). With low cost "bulk" graphene now available at relatively low cost thanks to green chemical and electrochemical exfoliation routes, expect battery companies in China – where most of the world's lithium battery manufacturing is located – to launch soon graphene-modified LFP lithium batteries.
To avoid graphene layer re-agglomeration and self-assemble back to graphite, graphene obtained via exfoliation directly at battery companies which already consume large amounts of graphite used to produce the battery anodes, will be used immediately after production.

"Graphene" we wrote in the conclusions of the 2015 study (1), "will not remain a laboratory curiosity resulting in the publication of some 40 research papers per day."

Subsequent developments have shown that this has been the case.

REFERENCES

1. R. Ciriminna, N. Zhang, M.-Q. Yang, F. Meneguzzo, Y.-J. Xu, M. Pagliaro, Commercialization of Graphene-Based Technologies: A Critical Insight, Chem. Commun. 51 (2015) 7090-7095.
2. K. S. Novoselov , A. K. Geim , S. V. Morozov , D. Jiang , Y. Zhang , S. V. Dubonos , I. V. Grigorieva, A. A. Firsov, Electric Field Effect in Atomically Thin Carbon Films, Science 306 (2004) 666-669.
3. A. Kovtun, E. Treossi, N. Mirotta, A. Scidà, A. Liscio, M. Christian, F. Valorosi, A. Boschi, R. J Young, C. Galiotis, I. A Kinloch, V. Morandi, V. Palermo, Benchmarking of graphene-based materials: real commercial products versus ideal graphene, 2D Mater. 6 (2019) 025006.
4. T. Barkan, Graphene: the hype versus commercial reality, Nat. Nanotechnol. 14 (2019) 904-910.
5. Directa Plus, Successful First Road Surface Trial Results, ft.com, 1 April 2019. See at the URL: https://markets.ft.com/data/announce/detail?dockey=1323-14022451-0OAKAL2F5ALH0HT69AJQCQS5OP.
6. M. G. Stanford, J. T. Li, Y. Chen, E. A. McHugh, A. Liopo, H. Xiao, J. M. Tour, Self-Sterilizing Laser-Induced Graphene Bacterial Air Filter, ACS Nano 13 (2019) 11912.
7. M. Pagliaro, F. Meneguzzo, The driving power of the electron, J. Phys. Energy 1 (2019) 011001.
8. L.-H. Hu, F.-Y. Wu, C.-T. Lin, A. N. Khlobystov, L.-J. Li, Graphene-modified $LiFePO_4$ cathode for lithium ion battery beyond theoretical capacity, Nat. Commun. 4 (2013) 1687. ■