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3D CVDGraphene™ Material Production Scale-up Process using Ni powders

a subsidiary of CVD Equipment Corporation

By Karlheinz Strobl, Mathieu Monville, Subarna Banerjee, Shihsheng Chang,

CVD Equipment Corporation, 1860 Smithtown Avenue, Ronkonkoma, NY 11779, USA

Background

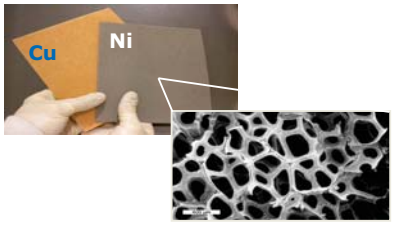
- Graphene, a 2D sp^2-hybridized carbon sheet with one-atom thickness, has attracted increasing attention in recent years because of its unique structure and special properties.
- **CVD graphene** has typically better electrical and other properties than chemically prepared graphene
- Many graphene material applications for making enhanced electrodes for batteries, ultra capacitors, capacitative desalination, etc. need large quantities (g-kg) of graphene

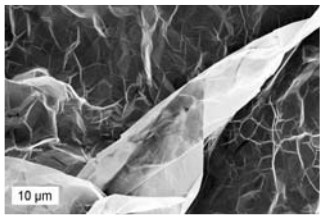
➔ ***THEREFORE there is an need to develop a cost efficient scale-up manufacturing processes for bulk CVD Graphene.***

Prior Work I:

Recently several research publications have described the synthesis of 3D CVD graphene continuous networks[1,2] grown on Ni foam substrates and their utilization for various novel products and application developments such as high sensitive gas sensor[3], electrode or electrode additive for solar cells[4] and ultra capacitors.[5]

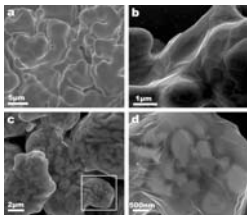
The commercially available Ni foam substrate which is used as a sacrificial template for CVD graphene growth in these publications is typically 1 to 2 mm thick, has a density of ~0.3 g/cm^3 and a surface area in the order of 1 m^2/g.
This results in 0.3 m^2 of CVD graphene per cm^3 of Ni foam used.





Prior Work II:

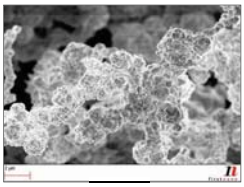
CVD Graphene grown on ≤ 30 µm Ni particles was demonstrated to be capable of "bulk" growth of high-quality mono to few-layer graphene sheets on nickel particles.[6]
This method produced about 2.5% graphene/Ni powder weight. However this paper did not discuss how to scale this idea from 200g (5mg of CVD graphene mass) of Ni powder to larger volumes.



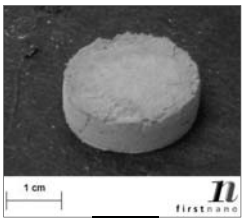
➔ ***Higher density 3D graphene material is desired in applications (sensors, batteries, ultracapacitors, etc.) where more graphene material per mass/volume of active material is required to achieve better performance. This will require g to kg of material per device.***

Summary of our CVD graphene scale-up solution:

We improved on both prior CVD 3D graphene material growth methods to increase the production quantity of CVDGraphene 10-100 times per batch by :
1) Using smaller size Ni powder (to increase surface area and reduce Ni material usage).
2) Processing the material as a "bulk" material to increase the volume of Ni powder processed, i.e. not just increase the surface area, but also the mass
3) Developing a proprietary porous mold method that allowed to created free form of 3D shapes filled with Ni powder
4) Placing multiple powdered filled molds in one CVD reactors to increase the volume utilization of a given size CVD reactor.



[A]



[B]

Process Feasibility Demonstration:

performed on an EasyTube® 3000 CVD research system with a 5" process tube
(manufactured by CVD Equipment Corporation)

[A] To demonstrate the concept to a first level we used a 2-3 µm size, 0.5-0.65 g/cm^3, filamentary T255™ Ni powder (Vale). A more spherical T123™ powder (Vale) with a bulk density of 1.6-3 g/cm^3 was not available in the short time due to export license restrictions, but otherwise would be a more preferable material for this application. Nano size Ni powers might be even more preferable for bulk manufacturing of CVD graphene with this method.

[B] To demonstrate the scalability of the concept, a multi-unit porous mold holding eight of the same cylindrical pockets was prepared. A compact Nickel powder pellet covered with a graphene skin was obtained after the CVD graphene processing. After CVD graphene processing, all eight pockets presented similar CVD graphene mass yields.

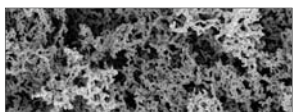
[C] Low magnification SEM images after CVD graphene processing show the filamentary Ni power sintered into a coral-like open cellular material structure.

[D] Ni powered elements fused together into a mechanically and electrically interconnected network with a relatively smooth, facetted surface, with pores in the 1-10 µm range.

Using the non optimal T255™ (Vale) Ni powder, close to 3-4% mass yield of CVD Graphene was obtained.

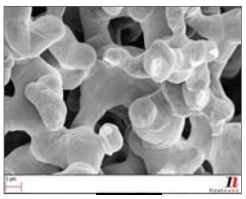
A 5" process tube for an Easytube® 3000 system has a usable inner process volume of about 2,600 cm^3.

- Assuming a minimum of 30-50% usable optimized mold space (rest is used for gas transmission and fixturing) we obtain **800-1,300 cm^3 usable production volume for CVD3^{D}Graphene™**
- If the total available mold space is filled with high density Ni powder (T123™ or smaller size nano powder) the **CVD3^{D}Graphene™ mass per batch could be in the range of 32 to 150 g.**



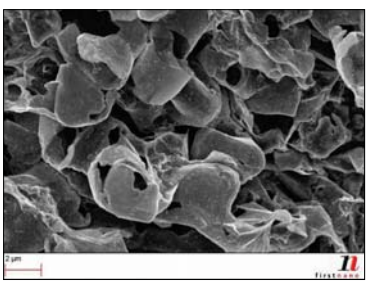
[C]

Multi layered **CVD3^{D}Graphene™** *covering the sintered Ni cellular material substrate made from Ni powder.*



[D]

To harvest the **CVD3^{D}Graphene™** we etched the Ni in $FeCl_3$ solution (1M) and obtained the 3D CVD graphene pellets shown on the left image immersed in water. The right image shows the SEM image of the resulting dried CVD 3D graphene network.
If desired this 3D graphene network can be further processed by sonication, vacuum filtration etc. It can also be used for sensor and other means in an as made format with customized mold shapes.
Supercritical drying methods can also be used to make graphene aerogel-like structures with less mechanical damage due to surface tension of drying liquids.



Future Work

Use the smaller size Ni powder to increase mass yield and reduce the etching time.
Create novel free forms shapes of 3D CVD graphene networked material for composite, sensors and other applications
Mixing small and larger size, filamentary and/or spherical Ni powers to obtain a controllable porous Ni foam structure for targeted applications.

References:

[1] Chen Z., Ren W., Gao L., Liu B., Pei S., Cheng H-M., Nature Materials **10** (2011), 424-428.
[2] Monville M.R., Strobl K., Stolyarov D., Polyakova E., MRS Fall (2011), Poster AA5.15.
[3] Yavari F., Chen Z., Abhay V.T., Ren W., Cheng H-M., Koratkar N., Scientific Reports **1** (2011), #166. [4] Bi H., Huang F., Liang J., Tang Y., Lü X., Xie X., Jiang M., J. Mater. Chem. **21** (2011) 17366-17370.
[5] Cao X., Shi Y., Lu G., Huang X., Yan Q., Zhang Q., Zhang H., Small **7** (2011), 3163-3168.
[6] Chen Z., Ren W., Liu B., Gao L., Pei S., Wu Z-S, Zhao J., Cheng H-M., Carbon **48** (2010) 3543.

CVD Materials Corporation | 1860 Smithtown Avenue | Ronkonkoma, NY 11779 | Tel: 631.981.7081 | Fax: 631.981.7095 | www.cvdmaterialscorporation.com