SOLUBLE GRAPHENE AND GRAPHENE HYBRID COMPOSITE (GHC) BY PHYSICAL FUNCTIONALIZATION

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ABSTRACT

We developed soluble graphene and GHC[1] based on solid state carbon source (CS) [2][3] using the physical functionalization. The uniqueness of this process comprises of the microencapsulation of the single molecule of carbon source (CS) onto a template prior to baking process. The precursor was baked in an oven kept under unoxidizing atmosphere.

The pyrolysis product are physically functionalized, showing Raman spectra chart having at least a sharp 2D band and other smaller D, G band depend on the chemical composition of the precursor . The physical functionalization is a process providing functionality to graphene, GHC and related products without going through wet chemical reaction using strong oxidizers and hazardous chemicals .

Key words : physical functionalization, soluble, GHC

PHYSICAL FUNCTIONALIZATION

Graphene oxide (GO) has attracted a lot of attention as it is expected to be the hope for scalling up of graphene by avoiding thin film technique comprising of CH_4 gas CVD on a copper substrate[4] . GO is prepared by Hummers process[5] in which graphite was oxidized with H_2SO_4, $KMnO_4$ and H_3PO_4. GO is converted into reduced graphene oxide (RGO) [6] using some kind of reduction agent and then exfoliated into single layer graphene. Thus GO is the key material for the target of large scale production . The biggest concern of Hummers process is the usage of a large quantity of strong acids which are not environmentally friendly. We are developing new process of making graphene not using hazardous chemicals neither thin film technique. First of all, it is necessary to isolate the CS in the solid state into single molecule using a template and then stabilize it by electrostartic charge generator[7]. This is a microencapsulation process and the isolated single molecule of CS is expected to form single layer of graphene when it get baked in an unoxidizing environment . The pyrollysis products carrying functionality generated by various parameters of baking process as well as chemical composition of the precursor, thus they are called physically functionalized products in order to compare to the known chemical functionalization in the wet chemistry. The microencapsulation utilized in the physical functionalization can be described in the Fig. 1

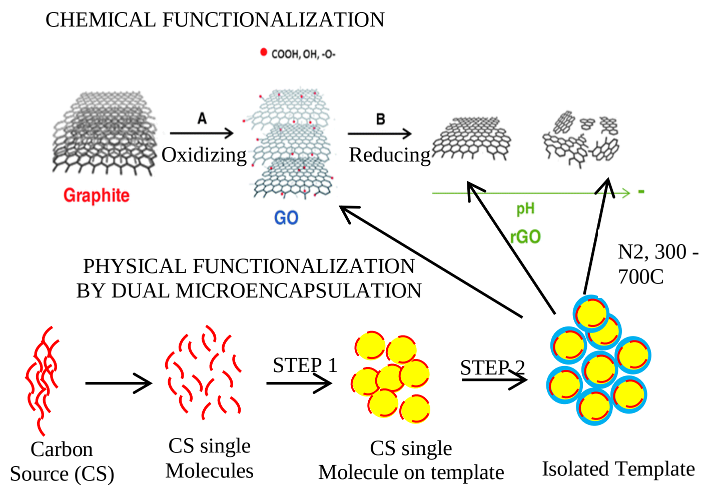


Fig.1 Physical functionalization

Fig.2 is SEM image of the template covered by single molecule of CS by two steps of the dual microencapsulation .

The template was baked in a quartz tube filled with N2 . The pyrollysis products are physically functionalized graphene, graphene hybrid composite (GHC) , graphene oxide confirmed by Raman spectroscopy charts illustrated in Fig. 3, 5 and 7 . It is recognized in Fig. 3 that Raman spectrum of a physically functionalized product shows a major 2D band at approximately 2650 cm^{-1}, a minor G band at approximately 1575 cm^{-1}, and an intensity ratio of 2D band over G band greater than 1. Fig. 4(A) shows FtIR chart of the same product having Raman spectroscopy chart illustrated in Fig. 3. It is observed from Fig. 4(A) that a large content of C=C aromatic stretch was shown at wave number 1471 cm^{-1}, 1541 cm^{-1}, 1617 cm^{-1} and very minor C-Cl stretch at wave number of 720 cm^{-1}. This FtIR chart reveals a large content of monolayer functionalized graphene [8][9]. Generally speaking, multilayer graphitic carbon such as graphite , carbon black shows more major stretch in the vicinity of wave number zone below 1000 cm^{-1} . Next, Fig. 4(B) shows FtIR chart of the same product baked at longer time and one can see more C=O stretch appeared at wave number $1702cm^{-1}$, as well as aliphatic stretch appeared at 936 cm^{-1}, CN stretch at 1311 cm^{-1} ,indicating the increased oxide product with longer baking time. It should be noted that eventhough the reaction chamber was filled with N2, it might contain some portion of oxygene from the atmosphere, which would cause the oxidation of the new pyrolysis product . Fig. 5 exhibits Raman spectroscopy chart of physically functionalized product which had been oxidized into graphene oxide (GO) and no 2D band shown. Fig. 6 shows FtIR chart of physically functionalized GO with C=O, CN, =CH stretch similar to what observed in Fig. 4(B) . Fig. 7 exhibits Raman spectroscopy chart of a physically functionalized GHC showing major 2D band and minor G and D band . Fig.8 exhibits FtIR chart of a physically functionalized GHC product, in which one can see major aromatic stretch –C=C, carbonyl stretch –C=O , aliphatic stretch –C=H, -CN, C-Cl stretches. It could be concluded that the physically functionalized products are normally monolayer or very few layer of oxide products and graphene is only formed at very short bake time depend on chemical composition of the precursor.

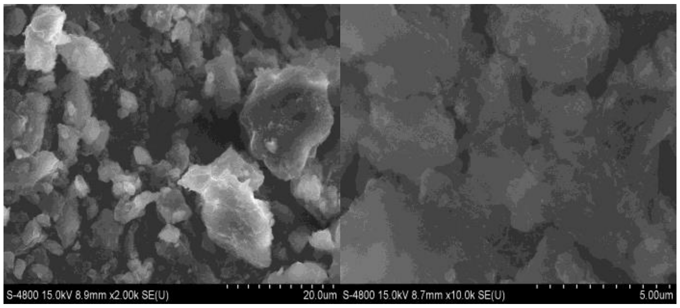
Next, Fig. 9 shows solutions of physically functionalized products in tetrahydrofuran (THF) and alkaline . It is observed that some products are soluble in strong polar organic solvents and some are soluble in alkaline . The solubility in alkaline solution could become the evidence of oxide product containing carboxylic –COOH group from –C=O stretch showns in above mentioned FtIR chart. Finally, Fig. 10 shows the process of purification . The baked product can be smply purified using organic solvents such as IPA, THF, DCM to eliminate catalyst and other microencapsulation additives due to the solubility of main product in solvent and there is no need to use strong and hazardous acids .

CONCLUSION

The physically functionalized products by dual microencapsulation are monolayer functionalized graphene, graphene oxide and/or GHC. These materials are usefull for production of graphene in large quantity without using unfriendly chemicals and appropriate for multiple applications , especially thin, thick film , powder, wet coating . They can be converted into pure graphene and pure GHC using conventional process including heat, light, reduction agent. The physically functionalized graphene and GHC should be suitable for large scale production of graphene, GHC .

REFERENCES

[1] Khe C. Nguyen, US2013/0116114 A1
[2] Khe C. Nguyen, US 2010 0247419 A1
[3] Khe C. Nguyen, US 2010 0278715A1
[4] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. (2004). *Science* **306** (5696): 666–669.
[5] Hummers, W. S.; Offeman, R. E. (1958). "Preparation of Graphitic Oxide". *Journal of the American Chemical Society* **80** (6): 1339
[6] http://www.graphenea.com/pages/graphene-oxide
[7] US Patent application pending, March 2014
[8] J. Chil. Chem. Soc. vol.58 no.3 Concepción set. 2013 http://dx.doi.org/10.4067/S0717-97072013000300030
[9] http://www.intechopen.com/books/carbon-nanotubes-from-research-to-applications/syntheses-of-carbon-nanotube-metal-oxides-composites-adsorption-an



(A) step 1 **(B) step 2**

FIG. 2 SEM image of the template carrying single molecule of CS during the dual microencapsulation

GHC4_SMS 7438(5) _NF300_0.17

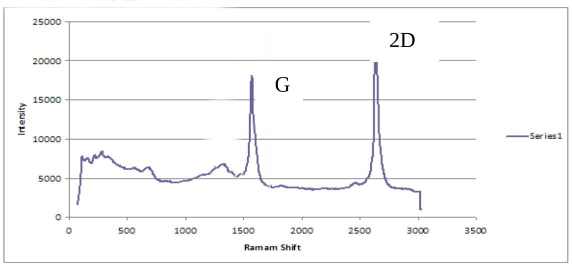


FIG. 3 Raman spectroscopy chart of a physical functionalized product

OXD GHC4 SMS7419(5)_NF300_0.5_L5

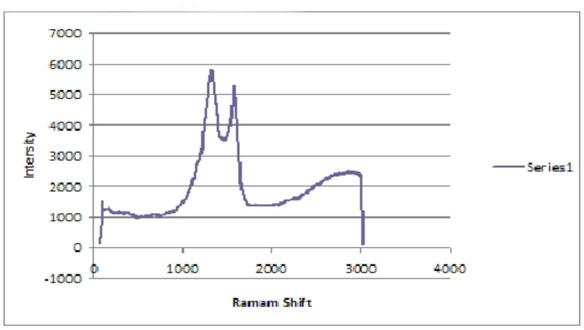
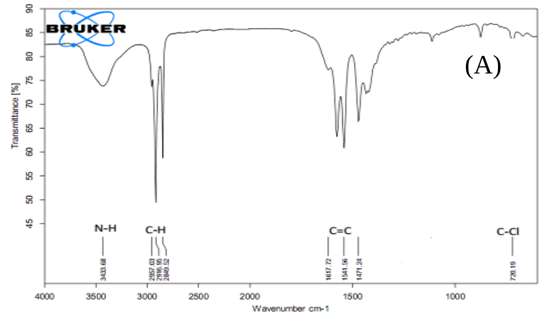


FIG. 5 Raman spectroscopy chart of physically functionalized product which had been oxidized into graphene oxide (GO)

GHC4 SMS7438(5)-NF300-0.17



GHC4 SMS 7438(5)_NF300_0.25

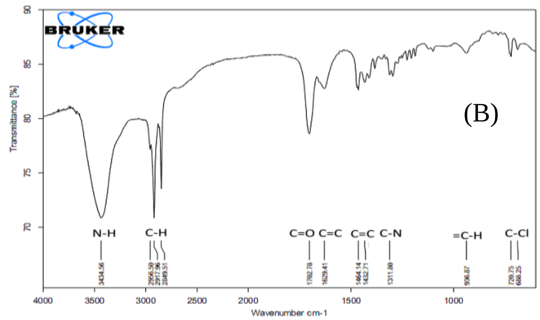


FIG.4 FtIR charts **of the** physically functionalized product prepared at different bake time . A) bake time=0.17 factor B) bake time=0.25 factor .

OXD GHC4 SMS7419(5)_NF300_0.5_L5

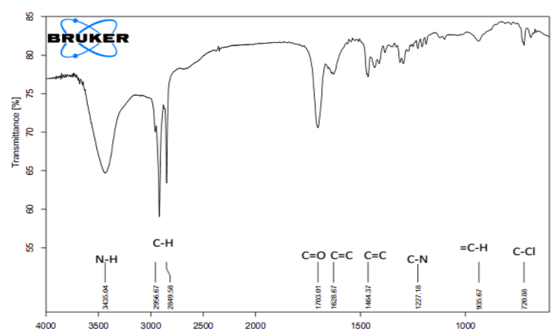


FIG. 6 FtIR chart of oxidized physically functionalized product

GHC4(4)_1 SMS7449_NF304_0.33

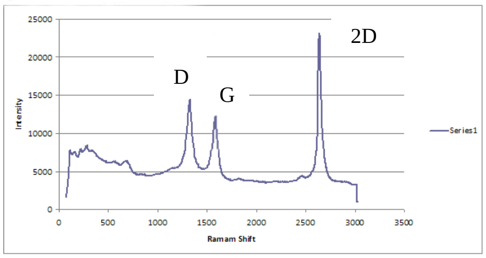


FIG.7 Raman spectroscopy of a physically functionalized GHC

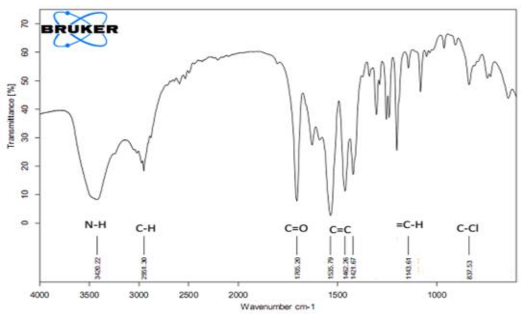


FIG. 8 FtIR chart of physically functionalized GHC

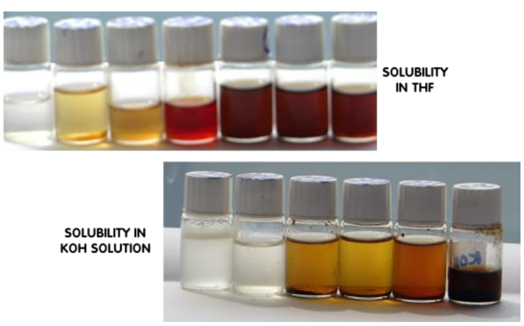


FIG. 9 Solutions of physically functionalized graphene, GHC and GO in THF and in alkaline solution

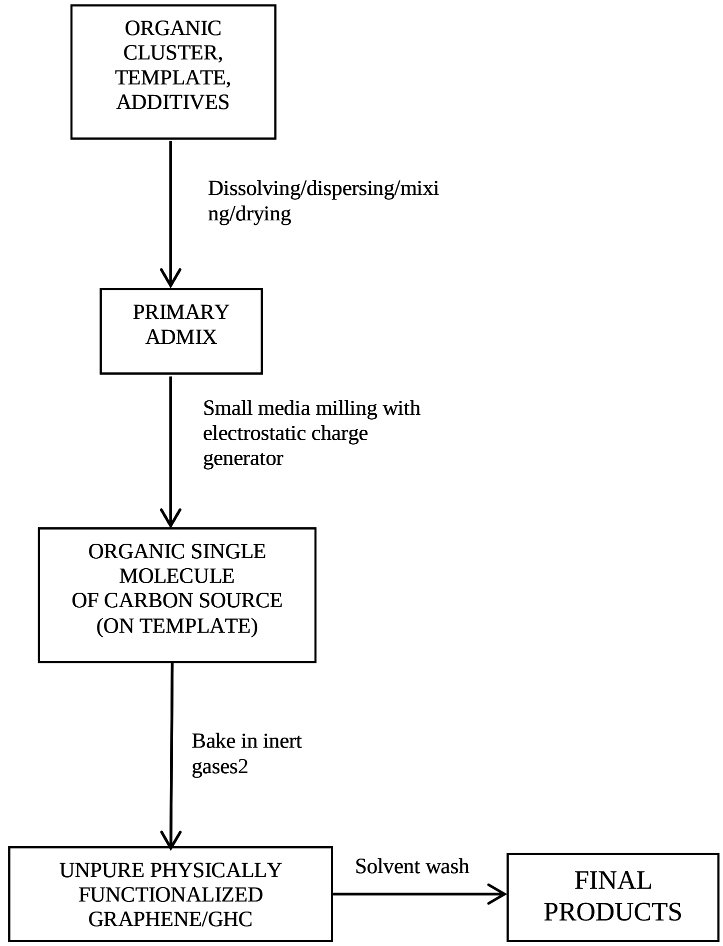


Fig. 10 Schematic diagram of process of making physically functionalized products