Soluble Graphene and Printing

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Abstract

We are developing graphene derivatives by physical functionalization. The products are believed to be composed of graphene core surrounded by functional groups which are helping out the solubility of material in certain kind of solvents. These functional groups are cleavage under high heat and or irradiation to render pure graphene. The differentiated physical properties of the graphene precursor under energy sources could be used for printing technologies.

Soluble graphene

Many printing technologies are associated with wet applications and large scale production. Pure graphene [1] produced by conventional gas CVD is very inert to solvents and lacking of wet application capability. We will discuss in the present study the potential applications of soluble graphene for printing.

Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex [2]. It is the basic structural element of other allotropes, including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. In recent years, graphene is attracting a lot of attention from all over the world, more likely, in the field of microelectronics due to its substantially high electron mobility [3] over the known materials such as GaAs, single-walled carbon nano tube (SWNT) and considered as non-rusted metal. Graphene also meets applications in energy storage, due to its extraordinarily large surface area.

While scientists had theorized about graphene for decades, it was first produced in the lab in 2003. Andre Geim and Konstantin Novoselov at the University of Manchester won the Nobel Prize in Physics in 2010 "for groundbreaking experiments regarding the two-dimensional material graphene." Conventionally, graphene is fabricated by CVD process of methane gas CH_4 at a relatively low temperature (300C) on a Cu foil substrate. The graphene products are also called pristine graphene, showing sharp 2D band and smaller G band in Raman chart indicating monolayer structure. The thin film of graphene from CVD process can be isolated by pressure transfer into a targeted substrate. The thin film process as well as transfer process, actually, are not straight forward and thus restrict large scale production. Graphene is very inert material and thus limits many wet applications. Conventional graphene process utilizes gas phase carbon source, and actually is ***a physical process***. On the other hand, other approach with ***chemical process*** to resolve the issue of large scale is the world known GO which is prepared by the exfoliation of graphite after oxidation process with strong oxidizers [4] such as H_2SO_4, HNO_3, H_3PO_4, $KMnO_4$, raising concern of environment. The GO is a ***chemically functionalized product***.

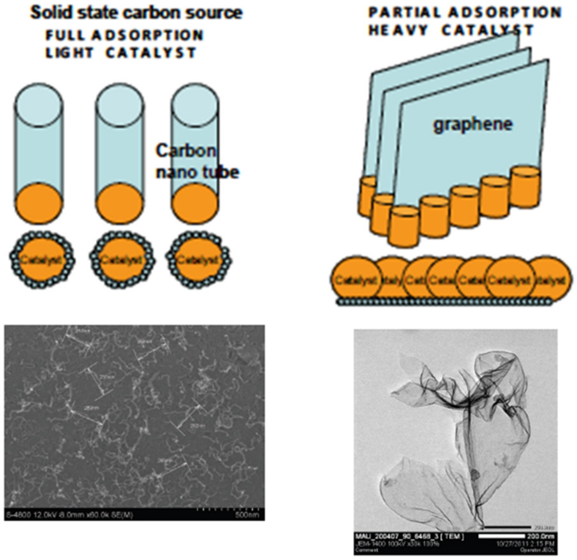

Figure 1. Suggested graphene forming mechanism in CVD process utilizing solid state carbon source

Recently, we developed another way of fabricating graphene using CVD process of solid state carbon source (CS) instead of gas phase CS [5]. Solid state CS is more easily handled than the gas phase CS in this pyrolytic process and offers better control of catalyst amount in the reaction forming nano carbon materials. We had found that at low portion of catalyst, for example, MS/CS weight ratio lower than 0.1, always multi-walled carbon nanotube (MWNT) was observed when reaction temperature exceeds 1000C in N2 whereas at a very high portion of catalyst such as MS/CS > 2, flaky shape materials of graphene are frequently obtained in the same baking condition. This could be explained by the assumption that at low portion of catalyst, CS molecules tend to fully adsorbed on the surface of catalyst and grow into a tube shape. On the other hand, at very high portion of catalyst, CS molecules can partially adsorbed on catalyst surface and grow into flaky sheet of graphene, confirmed by Raman spectroscopy and TEM image (Figure 1). Based on these observations, we studied baking parameters of process at the relatively low baking temperature and discovered that, a group of chemical having graphene core surrounded by soluble functional groups is achieved. The functionalized graphene in this case is called physically functionalized graphene and the process is called physical functionalization which is different from chemical functionalization above described as no need to use chemicals for functionalization.

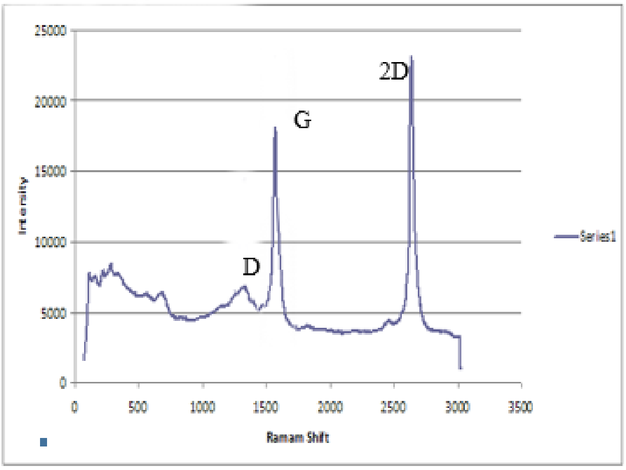

Figure 2. Raman spectroscopy of physically functionalized graphene.

In a summary, we can make graphene precursor by isolating the solid state CS into single molecules then let them partially adsorbed on particulate substrate which is catalyst. The composite (CS/MS) is slowly baked in an unoxidizing environment to nucleate functionalized aromatic network. This step is called soft bake. Then, the soft baked products are soluble and needed to be quickly thermally treated (Rapid Thermal Annealing, RTA) to form destination products, for example, conductive ink, transparent conductor, microelectronic devices, energy storage devices, biomedical devices, 2D and 3D printing media... With various soluble functionalities, the physically functionalized graphene can play a key role in large scale production and wet applications that pure graphene is missing. We also found that the physically functionalized graphene can be converted into pure graphene by high heat or irradiation, especially, UV such as blue LED, UV laser, UV light (Figure 3). The converted product is also very hydrophobic as one can see from FtIR spectrum (Figure. 4)

Typically, the physically functionalized graphene is the graphene precursor showing Raman spectrum almost identical with that of pure graphene (Figure 2). In our works, there are two different kinds of precursors obtained by different raw materials and different manufacturing process. The 1st type of precursor is soluble in organic solvents, showing aliphatic stretch -CH and plenty of aromatic stretch from FtIR spectroscopy, suggesting a graphene core carrying aliphatic groups. The 2nd type of precursors exhibits solubility in alkaline solution, showing –CO stretch besides aromatic –C=C and aliphatic –CH stretch from FtIR spectroscopy (Fig.1) suggesting a graphene core carrying aliphatic groups and carboxylic acid –COOH and it could be graphene oxide (GO). Both types of precursors are insulative, hydrophilic and become highly conductive at least 10 million time under heating or UV exposing, suggesting a cleavage of functional groups along with a reconnection of aromatic network into large plane (Fig.2).

So the major features of phys. func. graphene are:

a) Product of CVD process of solid state CS.at low temperature
b) Soluble in solvents and alkaline solution..
c) Gaining electrical conductivity and hydrophobicity when soluble functional groups are removed.
d) The removal of soluble functional group can be carried out by heat, UV and chemical.

These properties could be used for printing applications:

a) Xeroprinting, is a printing process based on the principle of xerography, which was investigated almost two decades ago but never reached the goal of one million copies from one master print due to short life of persistent latent image and thus did not reach the commercialization. Xeroprinting research activities had been pursued with photochemistry and/or photoconductivity of organic salts in Eastman Kodak Research Lab and at Imaging Science lab of Tokyo Institute of Technology in Japan. Today, with the advanced graphene technologies, xeroprinting can be revisited due to the absolute persistency of electrostatic charge master. The writing head can be a heat mode of a laser or a UV laser

b) Digital off-set printing plate making.

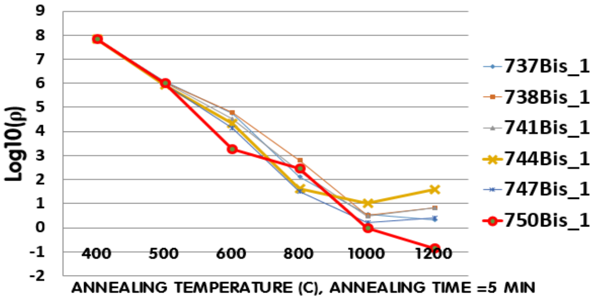

Figure 3. Bulk electrical resistivity of phys. func. graphene annealed at different temperature for 5 minutes

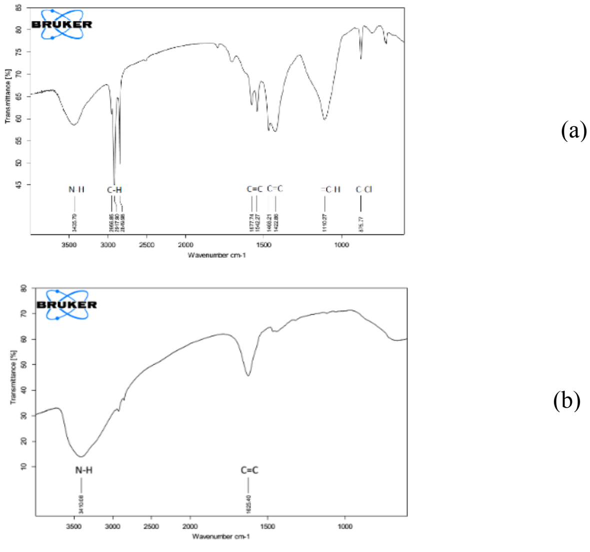

Figure 4. FtIR spectrum of a) phys. func. graphene and (b)converted product . (a) shows aliphatic stretch –CH, carbonyl stretch –CO besides aromatic stretch –C=C, while (b) shows only aromatic stretch –C=C

Soluble graphene precursor is coated on an anodized Al plate (hydrophilic). After being dried, the latent image is formed by thermal writing head or UV light as above mentioned. The image area becomes hydrophobic and the non-image area is washed out with solvent or alkaline developer. The visible image is developed with hydrophobic off-set ink.

c) Digital gravure printing plate making

Soluble graphene precursor can be made into thick film with or without the aids of appropriate polymer on an anodized Al plate (hydrophilic) to form thick gravure plate suitable for gravure ink (aqueous).

d) 3D printing

Soluble graphene precursor can form a solid rock by evaporating solvent. Under writing sources of heat or UV, a 3D solid will be formed after the unexposed parts get washed out by solvent leaving behind 3D solid image

e) Conductive ink

A permanently stable liquid ink is formulated from soluble graphene precursor due to the solubility of graphene precursor molecule. After being printed, the ink is thermally treated or UV treated to become conductive for printed electronics.

Conclusion

Overall, soluble graphene precursor just unveils wet and large scale applications that the conventional graphene products are not able to. More details will be discussed in the presentation.

References

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Author Biography

Khe Nguyen received his PhD in Material Science from Tokyo Institute of Technology (1982). Since then, he had worked in Research Lab of Dainippon Ink& Chemical in Japan (1982), Research Lab of Eastman Kodak in Rochester NY (1989), Research Lab of Hewlett-Packard in Palo Alto (1992), Research Lab of Saigon Hitech Park (2002). Now, he is Chairman and Founder of HK Lab in Vietnam