

# Advanced technology utilising CO<sub>2</sub>-containing methane for production of CNTs and graphene and their applications

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## Summary

Nanotechnology in particular carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene, is both technologically and commercially important. This is clearly seen from the amount of scientific and production activities in the last two decades. Carbon nanomaterials have been portrayed as the materials of the 21<sup>st</sup> century, in a similar manner that Si technology/information technology and petrochemicals have significantly contributed to the worldwide development in the last century. Such enthusiastic outlook with carbon nanomaterials comes from the extraordinary chemical and physical characteristics of the materials, which have inherent high chemical/thermal stability (700°C in air), high surface area (100m<sup>2</sup>/g to greater than 2000m<sup>2</sup>/g), high thermal conductivity (as high as 3000W/mK), high electrical conductivity (as high as 10<sup>7</sup>S/m), and exceptional mechanical properties (Young's Modulus at about 1000GPa). More importantly, many applications utilising these carbon nanomaterials have been widely demonstrated at university labs and by commercial entities. This paper will first outline the method for industrial-scale production of the carbon nanomaterials, CNTs and graphene, including new production methods for CNTs and graphene developed by NTherma Corporation. We will include previous examples for the utilisation of methane gas containing high CO<sub>2</sub> as a feedstock for the production of CNTs. We will discuss a number of applications, including nanocoatings, information technology, and energy. Specific applications in lubricant, anti-corrosive oil pipeline coatings, and Li-ion batteries will be discussed in greater details.

**Key words:** CNTs, graphene.

## 1. Introduction

Carbon nanotubes (CNTs) and graphene are allotropes of carbon with C-C bonds between a single bond and a double bond. Graphene comprises of Sp<sup>2</sup> carbon atoms arranged in a 2D regular array of hexagonal structure as seen in Figure 1. Graphene has a single-atom thickness in the Z-direction. In comparison, CNTs have a tube structure derived from the rolling up of a graphene molecule. When the tube structure is formed by rolling up a single-layer graphene, the CNT is characterised as a single-walled CNT (SWCNT) as seen in Figure 2, with diameter ranging from less than 1nm to 2nm. Another type of CNTs is characterised as multi-walled CNTs (MWCNTs) when the tube structure is formed by rolling up of a multi-layer graphene. The diameter of MWNTs has a range between a few nm to as large as 100nm. CNTs have lengths ranging

from a few micrometres to as long as centimetre and as such the high aspect ratio structure of CNTs exhibits 1D characteristic behaviours.

For over the last two decades, much research and development have contributed to the basic understanding as well as demonstrating the commercialisation potential of these carbon nanomaterials in many applications. The interesting properties of both CNTs and graphene are derived fundamentally from the structure in the hexagonal arrangement of the Sp<sup>2</sup> carbons. The C-C bonds of the Sp<sup>2</sup> carbons in carbon nanomaterials are between a single and a double bond and are called graphitic carbons. The bond dissociating energy of graphitic carbon is about 500 KJ/mol, as compared to 346 KJ/mol for a C-C single bond and 602 KJ/mol for a C=C double bond. As a result, the C-C bonds in graphene and CNTs are very stable as compared to typical C-C bonds in organic and polymeric molecules. These carbon nanomaterials are less chemically reactive and have high thermal stability with a decomposition temperature

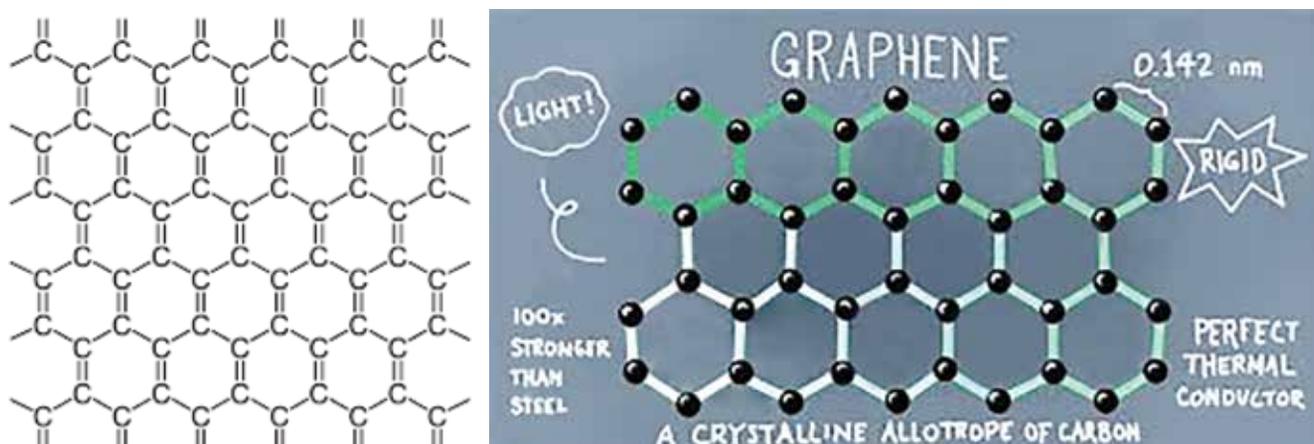


Figure 1. Diagrams representing the structure of 2D graphene and some of their structure and physical characteristics.

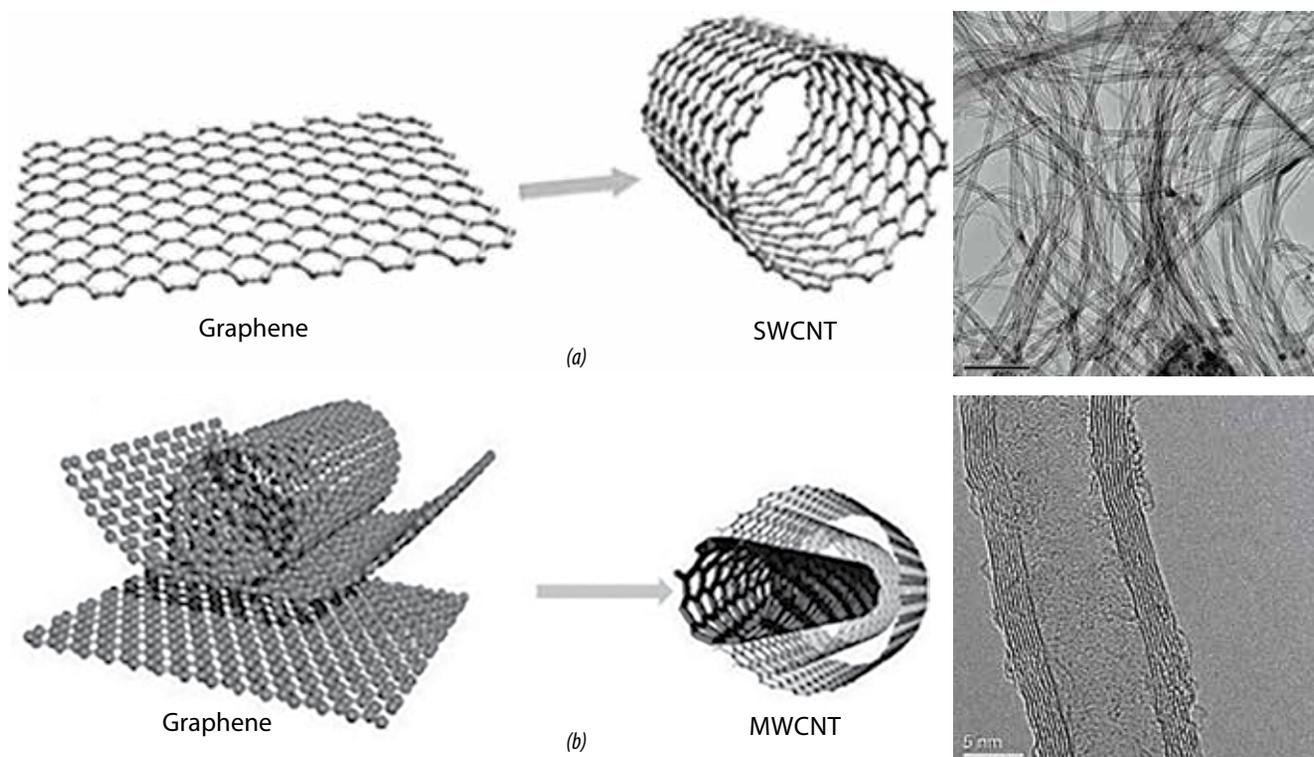


Figure 2. Structures and TEM images of (a). single-walled carbon nanotube (SWCNT) and (b). multi-walled carbon nanotube (MWCNT) as schematic representation from the rolling up of a single-layer and multi-layer graphene, respectively. Scale bars in TEM micrographs are 5nm.

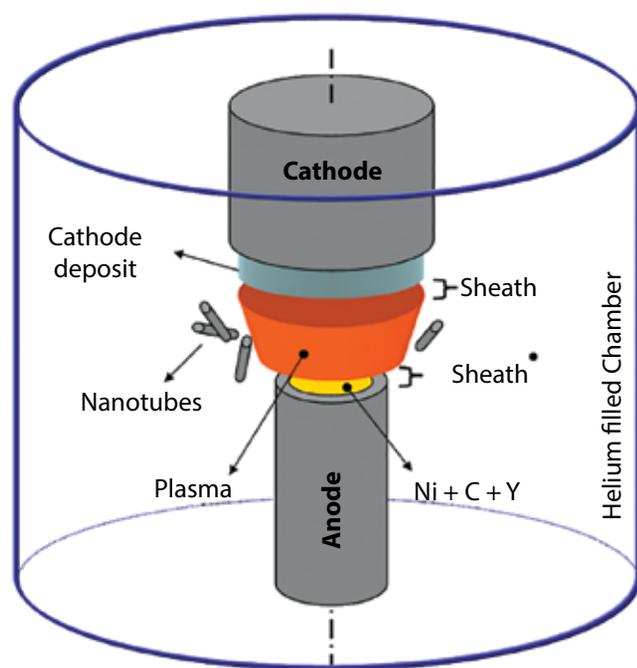
greater than 700°C. The graphitic bonding structure also imparts exceptional mechanical properties. For example, the Young's Modulus of CNTs is higher than 1000Gpa which is about 5X higher than the Young's Modulus of steel. These outstanding mechanical properties and chemical and thermal stability have led to many applications for structural reinforcement such as polymer composites and metal matrix composites.

The fact that these materials are a single- or a few-atomic layer thickness, the specific surface area (SSA) of both CNTs and graphene are very high. The SSA for a perfectly flat single layer graphene is 2630m<sup>2</sup>/g, while

those of SWCNT and MWCNT can be as high as 900m<sup>2</sup>/g and 400m<sup>2</sup>/g, respectively, depending on the diameters of the tubes of the CNTs (Table 1). In addition, the pi-electrons of the Sp<sup>2</sup> carbons in CNTs and graphene are delocalised and thus they give these carbon nanomaterials high electrical conductivity, with values as high as 10<sup>7</sup>σ (S/m) for non-defective CNT and graphene structures. Furthermore, the high ordered C-C bonds in both graphene and CNTs also lead to high thermal conductivity with values as high as 3000W/mK for perfect graphitic carbon structures. In combination, the high SSA and thermal and electrical properties of CNTs and graphene have enabled the

**Table 1.** Physical characteristics of CNTs and graphene in comparison to those of steel

Material	SWCNT	MWCNT	Graphene parallel to surface	Graphene perpendicular	Steel
Young's modulus (Gpa)	1054	1200	1000	N/A	208
Tensile strength (Gpa)	150	150	5	N/A	0.4
Density (g/cm <sup>3</sup> )	~2	2.6	2.2	2.2	7.8
Thermal conductivity (W/mK)	3,000	3,000	3,000	6	50.2
Electrical conductivity $\sigma$ (S/m)	10 <sup>5</sup> - 10 <sup>7</sup>	10 <sup>5</sup> - 10 <sup>7</sup>	10 <sup>7</sup>	10 <sup>2</sup>	2 × 10 <sup>6</sup>
Thermal stability in air (°C)	>700	>700	>700	>700	800
Specific surface area (m <sup>2</sup> /g)	400 - 900	200 - 400	2630	N/A	N/A



**Figure 3.** Schematic representation of a chamber for the production of CNTs by an arc discharge method.

development of these materials for coating applications. For example, a polymeric-CNT composite coating on airplane wing can be applied for de-icing by current induced melting of ice formation on airplane structural surface.

**2. Production methods for CNTs and graphene**

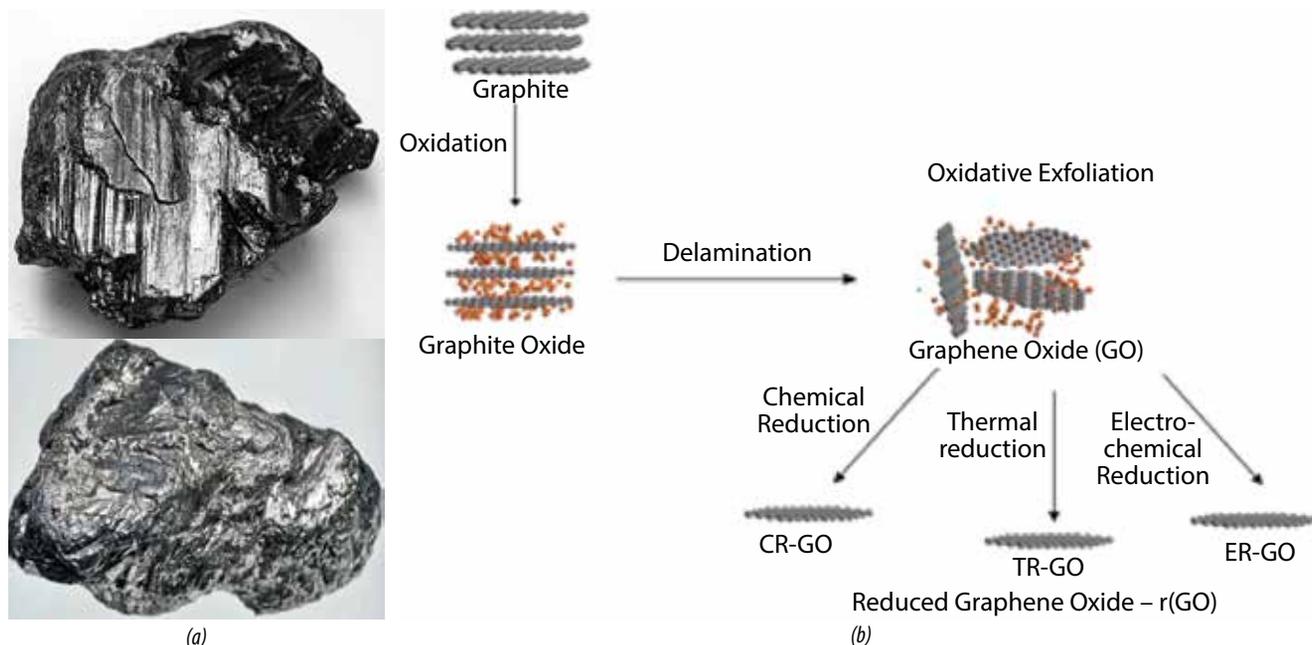
There are many methods for the production of CNTs and graphene that developed over the last decade or two. These methods can be classified based on the two types of starting materials utilised in the production of these nanomaterials:

- Graphite as the source of starting materials;
- Hydrocarbon feedstock as the source of carbon for chemical vapour deposition method.

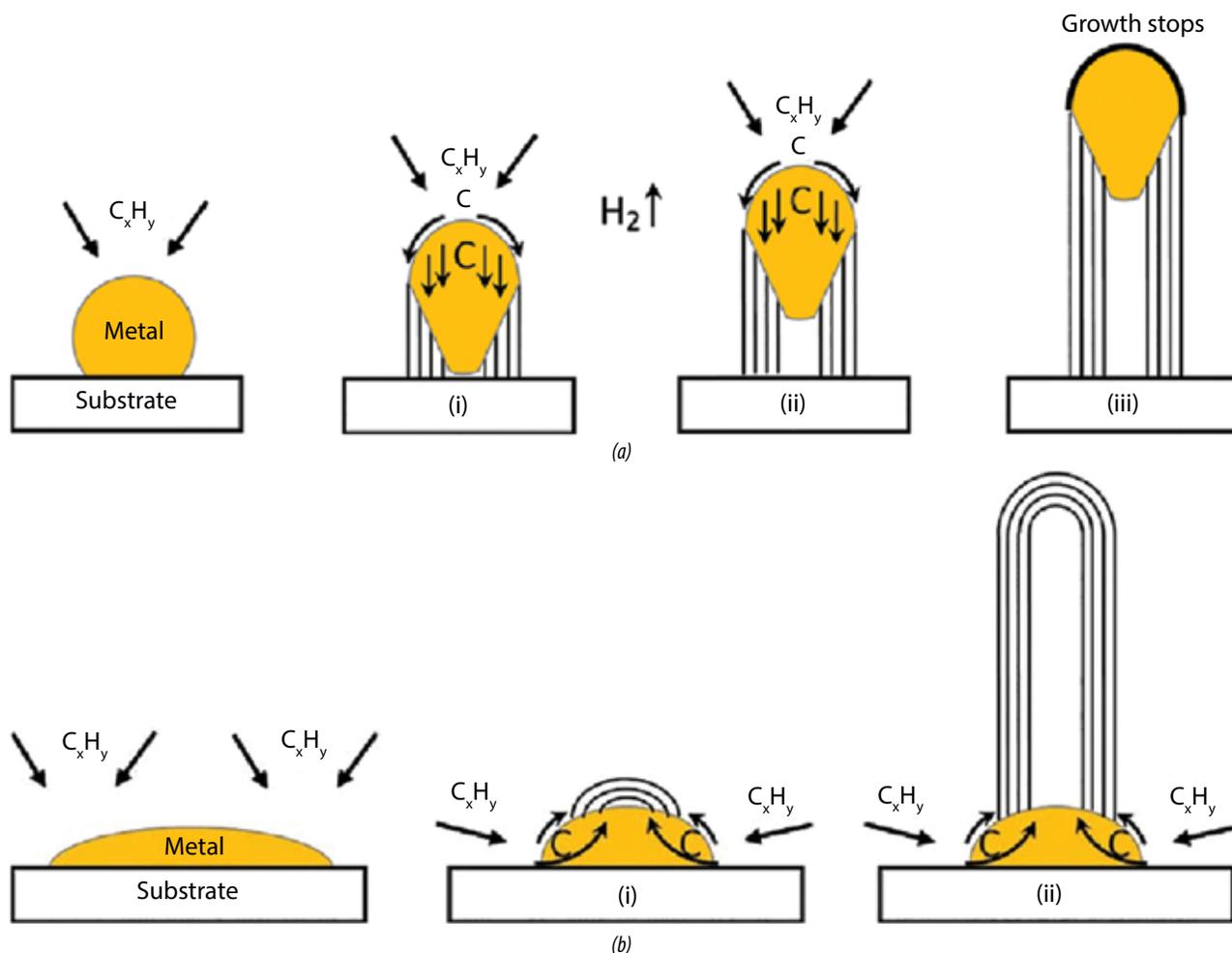
**2.1. Carbon nanomaterials from graphite starting materials**

The production of CNTs from graphite requires a high energy source for the formation of CNTs. The two methods which originally developed in laboratories and produced CNTs for laboratory usage are 1) arc discharge and 2) laser ablation. Arc discharge method is currently being used for the production of small volume of both SWCNTs and MWCNTs (Figure 3). This production method gives amorphous carbons as a side product and requires a purification process.

In contrast, the current production technique for graphene relies exclusively on graphite as the starting material (Figure 4). Here layers of graphene in the graphite are the first chemically oxidised to form graphite oxides (GO), which are then exfoliated to one or more layers of GO by ultrasonication. Other techniques for delamination of GO have also been reported, including the use of microwave to separate graphite into layers of GO. Many companies worldwide are claiming to have the capability for producing large quantities of graphene by the tons with this method. The current price for graphene significantly increases with a fewer number of layers, an indication of the difficulty and cost associated with producing graphene with a few layers of graphite. As an example, graphene with 15 layers or more is about USD 1,500 per kg, whereas graphene with one and up to five layers are about USD 50,000 per kg. The challenges of this graphite exfoliation production method come from the lack of control of the graphite oxidation process in order to get uniform and consistent GO and reduced GO (rGO) end product. This lack of control of a number of layers as well as the size and shape of graphene is due mostly to the inherent non-uniformity in the size and shape of the starting graphite materials, which are a product from mining. It should also be pointed out that graphene from



**Figure 4.** (a) Digital images of two graphite lumps showing dissimilarity in sizes and shapes of the mined materials and (b) Schematic representation of production process for graphene from the graphite starting material. Note that the graphene oxide (GO) can be reduced to rGO in the final step by a number of techniques.



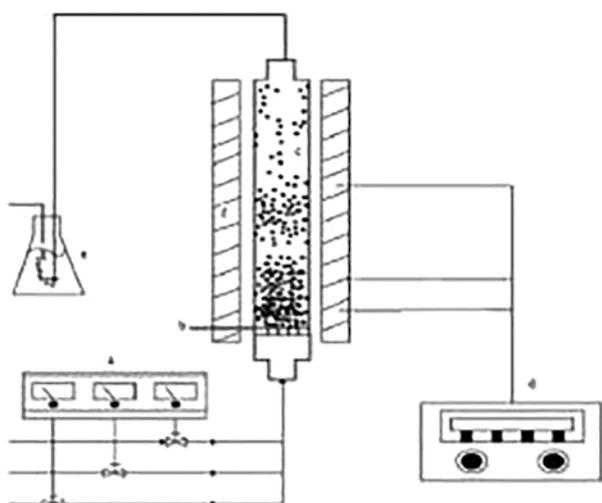
**Figure 5.** Schematic representation of the two growth mechanisms for the CVD production of MWCNTs utilising hydrocarbon feedstock: (a) Tip growth mechanism with catalyst metal particle lifted from the substrate and (b) Base growth mechanism where the catalyst remained attached to the surface of the substrate.

this production method also has impurities as a result of the impurities naturally present in graphite. Therefore, high purity graphene needs additional purification step

and this also adds to the production cost. Furthermore, it is important to note that the rGO is not absolutely like perfect and pristine graphene in that the rGO very likely has defects in structure and thus some physical properties are compromised.

**2.2. Carbon nanomaterials from gaseous starting materials by chemical vapour deposition**

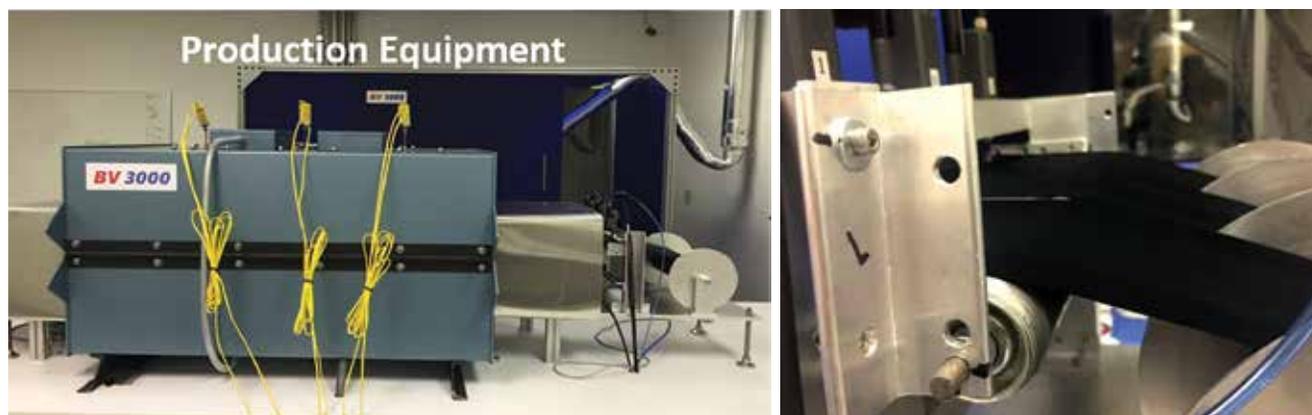
The main method for industrial scale production of CNTs is not derived from graphite starting materials as described above for graphene, instead most of the CNTs are produced by chemical vapour deposition (CVD) with hydrocarbons as the starting materials. CVD method of production is preferred due to high volume and high throughput capability. Figure 5 shows a schematic representation of the CVD growth mechanism of MWCNTs, where hydrocarbon gaseous molecules,  $C_xH_y$ , are broken by either a high temperature or a high energy plasma source in the presence of metal catalyst particles, as seen



**Figure 6.** Diagram of a fluidised bed reactor with the CVD growth of CNTs in the gas phase. Amorphous carbons and CNTs of various lengths are the products of this production process.



**Figure 7.** LG chemical plant for the production of CNTs in South Korea. The cost of the facility was reported to be USD 20M.



**Figure 8.** Digital photographs of the NTherma CNT production tool and a roll-to-roll metal foils, coated with CNTs, exiting the production tool.

in step (i) in Figure 5. The activated carbon species, derived from the breakdown process of the  $C_xH_y$  gas, are then diffused into the metal catalyst particles on the surface of a substrate in the CVD chamber. At this stage when the metal catalyst particles are saturated with the activated carbon species, the CNTs begin to grow from the catalyst particles through what has been termed “nucleation and growth” as seen in step (ii) in Figure 5.

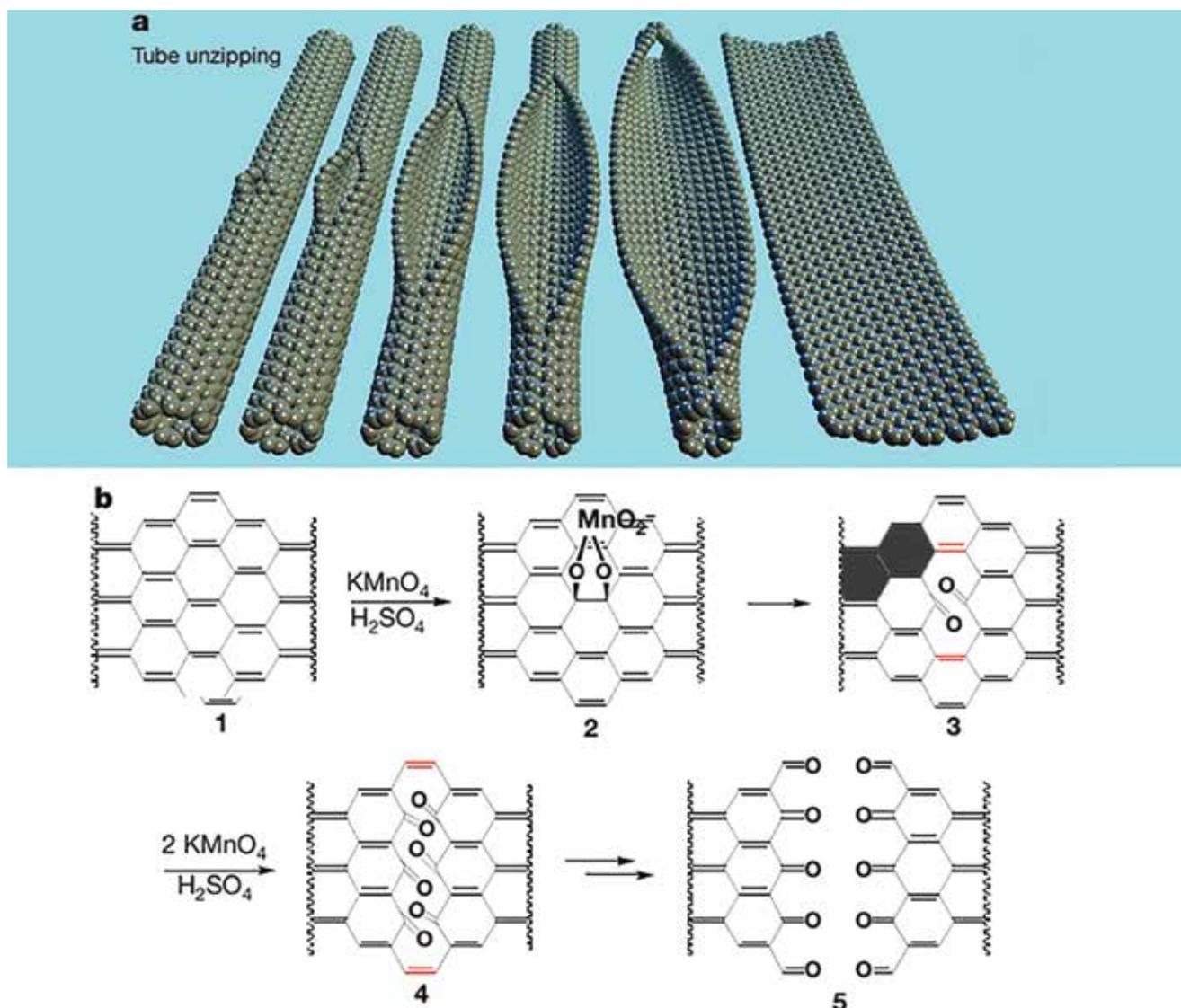
The hydrocarbon gas molecules can be methane, acetylene, ethylene, and ethanol, just to name a few examples. The type of hydrocarbon gas coupled with the type of metal catalyst and the CVD processing conditions are the main determining factors as to the types of CNTs one can produce, whether it is SWCNTs or MWCNTs. It is important to note that there are two mechanisms of CNT growth as shown in Figure 5, a tip growth mechanism and a base growth mechanism. To a large degree, the type of growth mechanism is determined by the force of interaction between the metal catalyst with the surface material on the substrate. The strong adhesive force between the metal particles and the surface of a substrate prevents the metal from physically lifting off the substrate and therefore base growth is the resulting mechanism. The tip growth mechanism is, on the other hand, a result of poor adhesive force between the metal particle and the surface material of the substrate. The typical substrate for the CVD growth of CNTs is a Si wafer with a thin film of either  $Al_2O_3$  or  $SiO_2$  coating as this was initially developed in many university labs in the 1990s.

This method of CVD growth using a Si substrate for supporting metal catalyst particles was not widely used for the production of CNTs due to it being limited to only a batch process production and thus only able to produce low volume at a low throughput rate. For large industrial



**Figure 9.** Digital photograph of the continuous extraction process for CNTs grown on the surface of a metal foil. The CNTs have greater than 99% purity and will not require any additional purification process.

scale production, the method of choice is the use of a fluidised bed reactor, as seen in Figure 6, from the initial stage of commercialisation of CNTs. Here the formation of the metal catalyst particles and the ‘nucleation and growth’ process is more in the gas phase and not supported on a surface of a substrate. It is important to point out that this has been the main method for large industrial scale production of CNTs for more than a decade. Even with a great number of efforts in the development of metal catalysts and CVD processing gases and processing conditions over these many years, the inherent issues of impurities and control of structural uniformity such as length remained elusive. Because of this reason, high purity CNTs are much more expensive due to the required purification step being very expensive from both equipment and operation terms. For example, 95% pure MWCNTs with the length of less than 50 microns are priced at above USD 9K per kg, whereas 60% purity MWCNTs are priced less than USD 400 per kg. A typical chemical plant

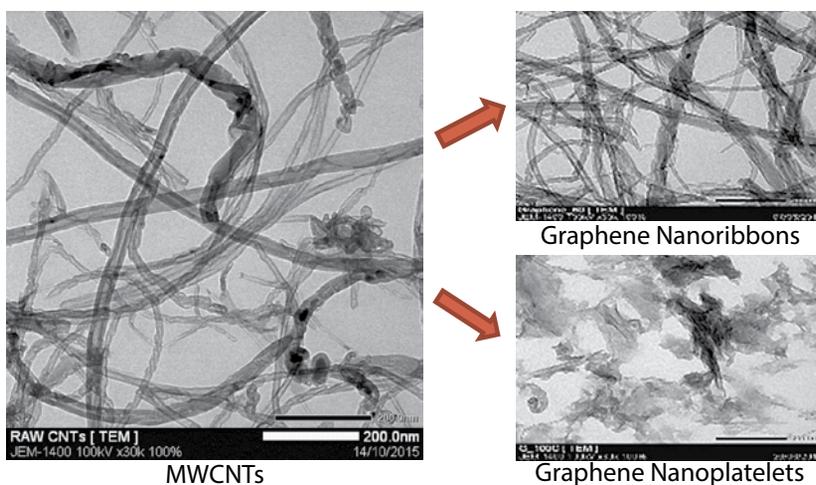


**Figure 10.** Schematic representation of (a) the chemical unzipping process of CNTs to produce graphene nanoribbons and (b) the chemical mechanism of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  reagents in the oxidation of CNTs and unzipping C-C bonds along the length of CNTs.

for the production of CNTs is shown in Figure 7 and it is reported to cost USD 20M for production volume of tons of CNTs per year.

**2.3. Carbon nanotubes by NTherma's new production method**

In the last few years, NTherma Corporation demonstrated a new approach for the production of 99.5+% purity of CNTs, with absolute control of CNT lengths ranging about 10 microns to 250 microns, and at a much lower production cost. This is achieved by having the CVD CNT growth process



**Figure 11.** TEM images showing the conversion of MWCNTs to graphene nanoribbons and graphene nanoplatelets by chemical unzipping process.

with the metal catalyst on the surface of a moving substrate in a continuous fashion. The substrate for supporting metal catalyst particles is a thin stainless-steel metal foil and thus this production method is achieved as a roll-to-roll process for high volume and high throughput production rate. Images of NTherma's equipment for CNT production and rolls of stainless-steel metal foil coated with CNTs exiting the production tool are shown in Figure 8. The nature of the CVD growth of CNTs with metal catalyst particles supported on the physical surface of a substrate affords CNTs of highly uniform lengths. This is one technological advantage of this method as compared to the conventional fluidised bed CVD method currently used in production worldwide.

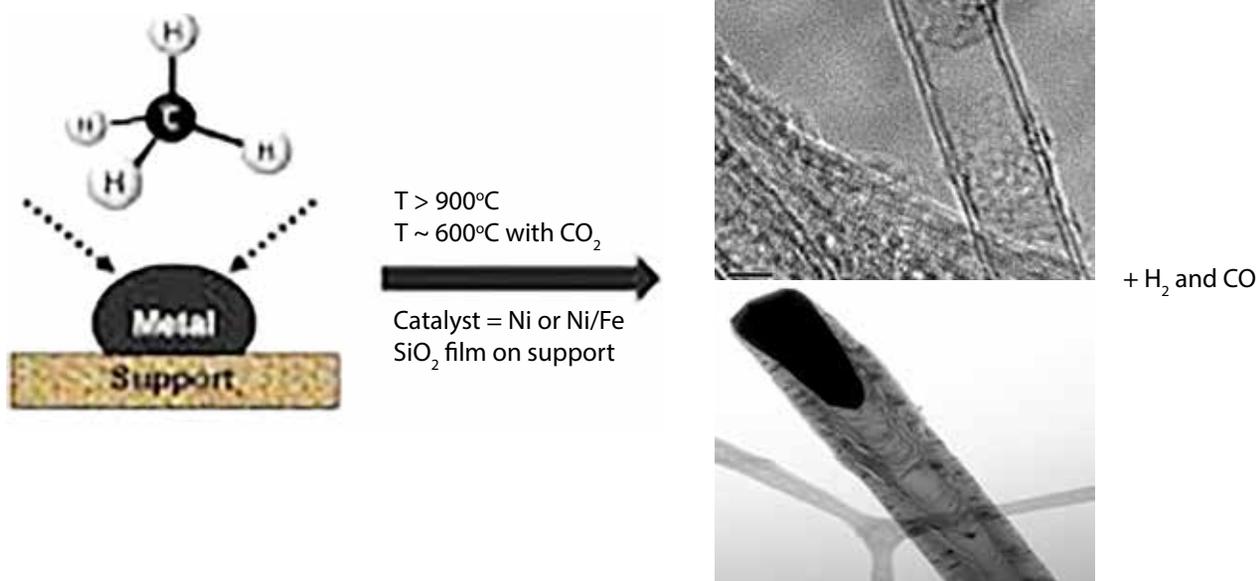
Another advantage of NTherma's new production method is the ability to produce CNTs with 99+% purity without requiring any costly purification process. The CNTs produced in this roll-to-roll method can be completely extracted from the metal substrate by physically scraping with a knife edge or by ultrasonication, also in a continuously automated fashion, as demonstrated by the photograph seen in Figure 9. It should also be pointed out that because a purification process with strong oxidation chemicals is not needed, the structure integrity such as lengths and crystallinity of the as-grown CNTs is maintained, and thus purity higher than 99+% and CNTs longer greater than 50 microns are available only from NTherma production method. This type of high quality

MWCNTs may offer opportunities for end users to be able to better optimise performances in various applications.

### 2.4. Chemically unzipping CNTs for the production of graphene

As discussed above, the oxidative exfoliation of graphite as a method to produce graphene still has many challenges, namely inconsistent quality and high cost for high quality graphene with a fewer number of layers (less than 5). Using NTherma's high quality CNTs and opening up the CNTs by well demonstrated chemical unzipping process offers a very practical solution to produce high quality graphene at a lower cost. The unzipping of CNTs is achieved with the common chemicals,  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$ , where the oxidation of CNTs occurred along the length of the CNTs causing the CNTs to open and resulting in the formation of graphene. The process is schematically represented in Figure 10, in which the unzipping chemistry introduces oxide groups along the basal plane of the graphene.

The graphene produced from the unzipping of CNTs can be tailored to two types: graphene nanoribbons and graphene nanoplatelets. As the name implied, the nanoribbons are long strips of graphene with a high aspect ratio structure. The length of the graphene nanoribbons is predetermined by the length of the starting CNTs, which is controlled by NTherma's unique production method and thus gives the absolute ability



**Figure 12.** CVD growth of CNTs using methane and  $\text{CO}_2$ . TEM images of various carbon nanomaterials, including large diameter double-walled CNTs (top image) and carbon nanofiber (bottom image).



**Figure 13.** (a) Diagram showing various applications of carbon nanomaterials, with polymer composite currently being the largest users of CNTs, at almost 50%; and (b) A very low weight bicycle frame fabricated from a carbon nanomaterial composite.

to produce graphene nanoribbons of any desirable lengths. Moreover, the oxidative chemistry for unzipping can be extended to produce graphene nanoplatelets by simply increasing the time or temperature of the reaction and with more oxidising reagents. Figure 11 shows the resulting TEM images of both graphene nanoribbons and graphene nanoplatelets as products from the unzipping of MWCNTs under different reaction conditions, wherein the nanoplatelets are produced in reaction conditions that have higher oxidative chemical reagents and at a higher temperature of reaction. It is important to note that graphene produced using high purity CNTs is also of high purity since the chemical reagents and the end products are easily dissolved away with water. Thermal Gravimetric Analysis data show 100% mass lost with almost 100% attributed to graphitic carbons at decomposition temperature greater than 600°C (data not shown), and specific surface area measurements by BET show more than doubling of values consistent with the opening of CNTs to more surface area graphene.

### 2.5. Utilisation of high CO<sub>2</sub>-containing methane for production of CNTs by CVD

More recently, the utilisation of methane and CO<sub>2</sub> mixed gases for the growth of CNTs has successfully demonstrated. There are several advantages for this method, the most obvious being the utilisation of CO<sub>2</sub>, a greenhouse gas, for the production of high value-added carbon nanomaterials. Methane gas has been widely used previously for the production of CNTs, mainly for SWCNTs both in the labs and in industrial production.

Metal catalyst requirements are more stringent and the temperature is higher for thermal CVD in order to produce SWCNTs with methane gas. CO<sub>2</sub> in a mixture with CH<sub>4</sub> has also been demonstrated in the CVD growth of CNTs. It has been reported that the temperature required for the CVD process is significantly lower, from greater than 900°C to as low as 600°C. Also, Ni or Ni/Fe catalyst was reported to be more efficient in the growth of CNTs with fewer defects. Figure 12 shows a reaction involving CH<sub>4</sub> and the CVD conditions for growing large diameter double-walled CNTs and carbon nanofibers.

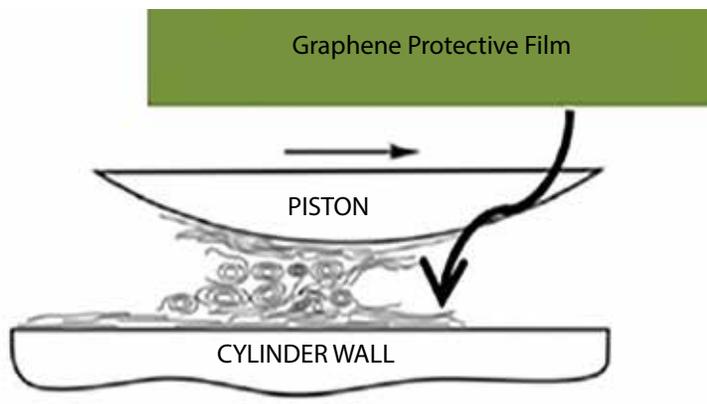
Clearly, the CVD process for the production of CNTs utilising CO<sub>2</sub>-containing CH<sub>4</sub> gas has been demonstrated and the CNTs can be utilised in various applications. It should be pointed out that the chemical unzipping of these CNTs, as briefly discussed in Section 2D, for producing graphene of different structures, will also find uses in applications where the structural requirement of graphene is altogether different from the existing graphene derived from the unzipping of MWCNTs. There are still many parameters to be investigated for optimal CNT growth utilising CO<sub>2</sub>-CH<sub>4</sub> gas mixture as the feedstock. These are exciting opportunities. For example, the ability to grow SWCNTs with CO<sub>2</sub>-CH<sub>4</sub> mixed gas feedstock at large industrial scale and low cost is without a doubt a game changer.

### 3. Applications of CNTs and graphene

Currently, the amount of CNTs being produced worldwide is valued at more than USD 4.5B and according to a projected market growth of higher than 15%, the size of the market will be close to USD 10B in 2023. In



(a)



(b)

**Figure 14.** (a) Digital photograph comparing motor oil with and without graphene at 25 mg/L concentration; (b) a diagram showing the coating of graphene on the surface of piston and cylinder as the proposed working mechanism of graphene additive to oil.

comparison, the market size of graphene is smaller due to a later start of development and it is expected to grow by more than 40% per year. Even with all the technical and productisation challenges currently faced by these materials, there are clear market opportunities for both CNTs and graphene, particularly for materials with higher quality and lower cost.

The main reason for such a high rate of market growth for CNTs and graphene is the wide array of applications with high market potential. Therefore, it stands to reason why carbons have been considered to be the materials for the 21<sup>st</sup> century. Figure 13 shows a diagram of many applications for CNTs and graphene that have been reported scientifically and in some cases, have been adapted by industries. Many of these applications have high economic and technological impacts. Currently, the biggest use of CNTs and graphene is for polymer composites mainly in the sport equipment market, such as a lightweight bicycle frame as seen in Figure 13. Other applications in composites are in late stage development with high end applications facing technical problems such as inconsistency in CNT and graphene quality, high prices, lack of availability required structures for high performance, or combination thereof. There is a saying that “not all CNTs are the same” and it could be said for graphene as well. Moreover, specific applications will require specific sets of physical characteristics from the CNTs or graphene, whether the applications are to exploit the mechanical, chemical, thermal, electrical or high surface area properties of these materials. Therefore, each different application will require a different type of CNT and graphene and the ability to tailor the structure of these materials will allow one to optimise for best performance.

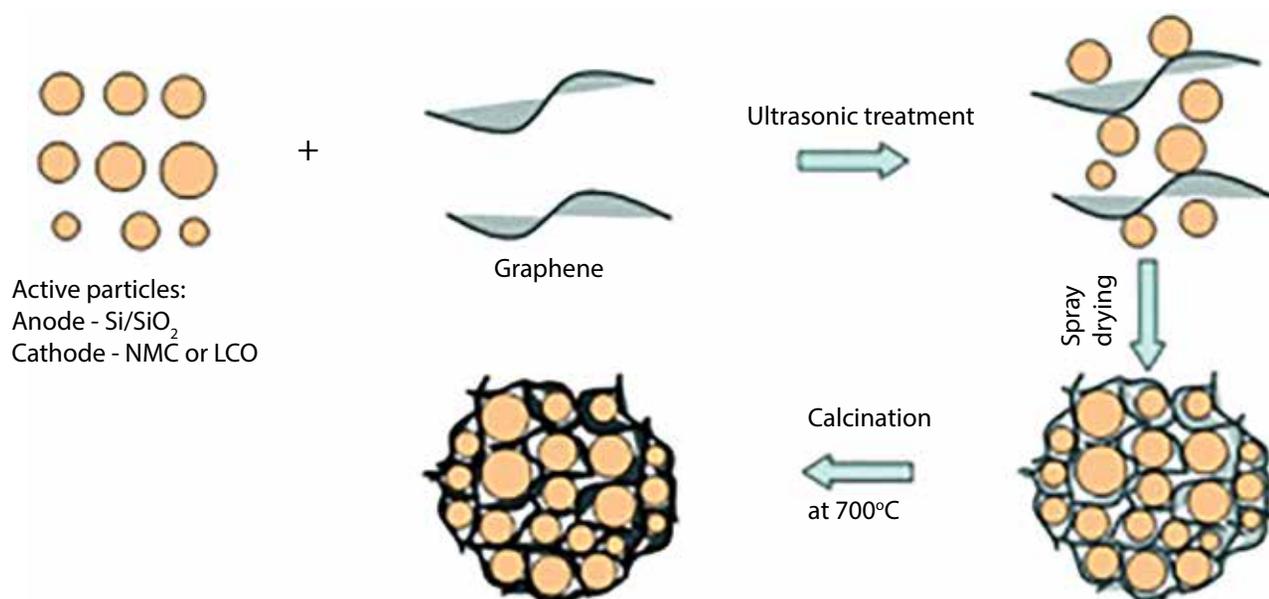


**Figure 15.** Digital photographs showing CNT coating of metal nut and bolt in preventing oxidation when exposed to high concentration salt water.

A discussion with all the important details on any one of these applications would be beyond the scope of this paper, instead, we will briefly survey a number of applications related to the oil industry and energy. These applications include: 1) graphene oil additive, 2) nanocoating for anti-corrosive oil and gas pipelines, and 3) Li-ion battery.

### 3.1. Graphene as an oil additive

The lubricity characteristic of the long chain carbon molecule, i.e. oil molecule, is well known and therefore it is not very surprising that graphene and CNTs also exhibit lubricant behaviour. Many scientific publications have demonstrated the lowering of the coefficient of friction by SWCNTs and graphene when added to motor oil or mineral oil. The key issue for fully realising this application is the ability to form a stable solution of graphene or CNTs in oil, which many university labs and industrial R&D centres have not been fully able to achieve. A stable suspension of an oil additive is required to have at least a 6-month shelf-life as a requirement of the oil industry, as seen in Figure 14a. We found that by chemically unzipping high purity MWCNTs less than 20 microns in length to produce graphene, the solution stability is achieved with NTherma’s graphene. Testing in laboratory under a controlled environment for both physical characteristics



**Figure 16.** Schematic representation of the wrapping of graphene around active particles in Li-ion battery. The results are faster charging, higher cycle life and improve safety.

as well as testing in a lab engine were done for comparison of oil samples with and without graphene addition. Results show great performance characteristics for oil with graphene additive for reduction of coefficient of friction by 50% in a four-ball tribology tester. Scar sizes on the balls for tribological testing equipment were also smaller for oil with graphene which indicated an anti-wear characteristic of graphene. Figure 14b shows a diagram of graphene coating the metal surfaces of the piston and cylinder wall as the working mechanism of the graphene additive.

An increase in fuel efficiency of up to 15% was also observed for testing in an engine in the lab. It is important to point out that the efficiency is highly dependent on the running conditions of the engine and whether it was under a load. In addition, vehicle testing on normal road conditions was also carried out for small passenger cars, buses, and container trucks. As compared to vehicles using oil without graphene, there was an increase in fuel efficiency ranging between 5% to 19% with some correlation to the type of vehicles. Similar to the data from the lab test, a wide range of data results from the road testing in vehicles can be attributed to driving conditions, engine sizes, the age of vehicles, and the load on vehicles. These are extremely promising data and the commercialisation of graphene oil additive is underway.

### 3.2 Anti-corrosive coatings with graphene for oil and gas pipeline

Corrosion of metal is a big problem in many industries, particularly for metal that interacts with a corrosive

environment such as seawater or crude oil as are the cases for seagoing vessels and oil/gas pipelines, respectively. Graphitic carbons such as those in CNTs and graphene have strong resistance to chemical oxidation and therefore it stands to reason that a coating containing graphene or CNTs would have an anti-corrosive characteristic. Many examples demonstrating this characteristic for CNTs and graphene have been reported. Figure 15 demonstrates the coating of CNT-polymer thin film for anti-corrosive effect on exposure to salt water. It is clearly seen that the coating of CNT-containing film protects the metal nut and bolt from oxidation by the salt water.

Many examples of anti-corrosive data have been reported for both graphene and CNTs coating on steel pipes and other steel surfaces. Graphene nanoplatelet-epoxy composite coating of a metal substrate has been showed to inhibit diffusion of molecules from solution to the metal substrate by EIS (Electrochemical Impedance Spectroscopy). In order to achieve highly reliable anti-corrosive protection, consistency in graphene quality and structure is absolutely needed to fully realise the oil pipeline coating application. This is a very promising application with high economic impact on the oil industry.

### 3.3. Graphene balls and conductive graphene for improved li-ion battery performance

As electric vehicles are becoming more mainstream, there is a real need for better performing batteries. Graphene and CNTs are currently used extensively in

batteries as a replacement of carbon blacks in order to improve the electrical conductivity at both the anode and cathode. Recent development has now moved beyond just replacement of carbon black but rather actively wrapping active particles with graphene in order to further improve electrical connectivity and conductivity of the active particles on both the anode and cathode. Figure 16 shows an example of a method for actively wrapping active particles with graphene nanoplatelets. The formation of graphene balls for use in Li-ion batteries for both anode with Si particles and cathode with LiCoO particles have been demonstrated.

Recently Samsung Electronics has demonstrated the concept of graphene balls for cathodes in Li-ion battery and showed that this improved the rate of charging by 5X while still maintaining high capacity and long cycle life. It was also demonstrated that the wrapping of graphene on LiCoO (LCO) active particles for the cathode also increase the safety of Li-ion battery. Oxygen gas was not released when the LCO particle was covered by graphene nanoplatelets thus the highly exothermic reaction of

O<sub>2</sub> with Li metal was minimal and thermal runaway was prevented. The study attributed graphene high thermal conductivity as the mechanism to keep the LCO particles from becoming overheated and thus prevent any release of O<sub>2</sub> and hence improve the safety of Li-ion batteries. This application of graphene is also economic importance to the EV and battery industry.

#### 4. Conclusions

Carbon nanomaterials such as CNTs and graphene are an important class of material. The application space for both CNTs and graphene is wide and will have high economic impact. Applications such as coatings, additive to oil and battery will continue to grow as these industries adapt the new technology. The use of CO<sub>2</sub>-containing CH<sub>4</sub> gas for the CVD growth of CNTs has been demonstrated to be feasible. This gas mixture combine with the new method for producing high quality CNTs and graphene in a high throughput roll-to-roll fashion has a high chance to be a game changer to CNTs and graphene development in many applications and industries