正確認識石墨烯

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內 容

一、何謂石墨烯?

二、一個錯誤的觀念

三、石墨烯的檢測

四、石墨烯的迷失, 世紀大騙局?

五、石墨烯的應用

何謂石墨烯?

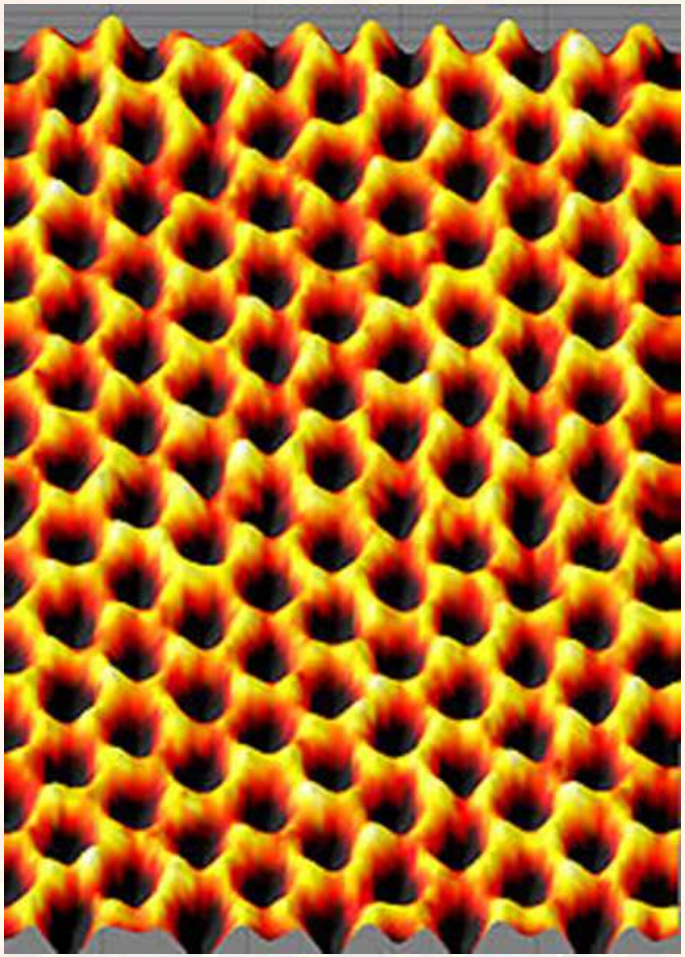
Description

One definition given in a recent review on graphene is:

Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite.[1]

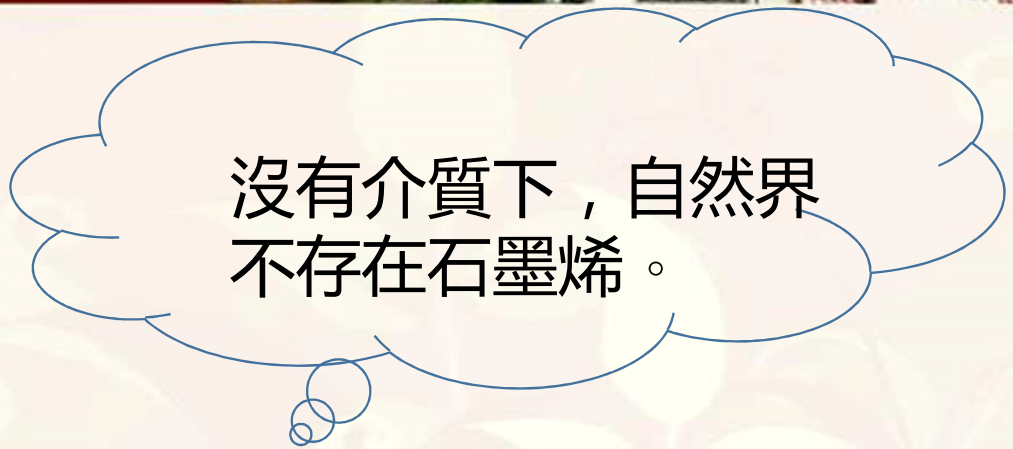
A previous definition is:

A single carbon layer of the graphitic structure can be considered as the final member of the series naphthalene, anthracene, coronene, etc. and the term graphene should therefore be used to designate the individual carbon layers in graphite intercalation compounds. Use of the term "graphene layer" is also considered for the general terminology of carbons.[2]



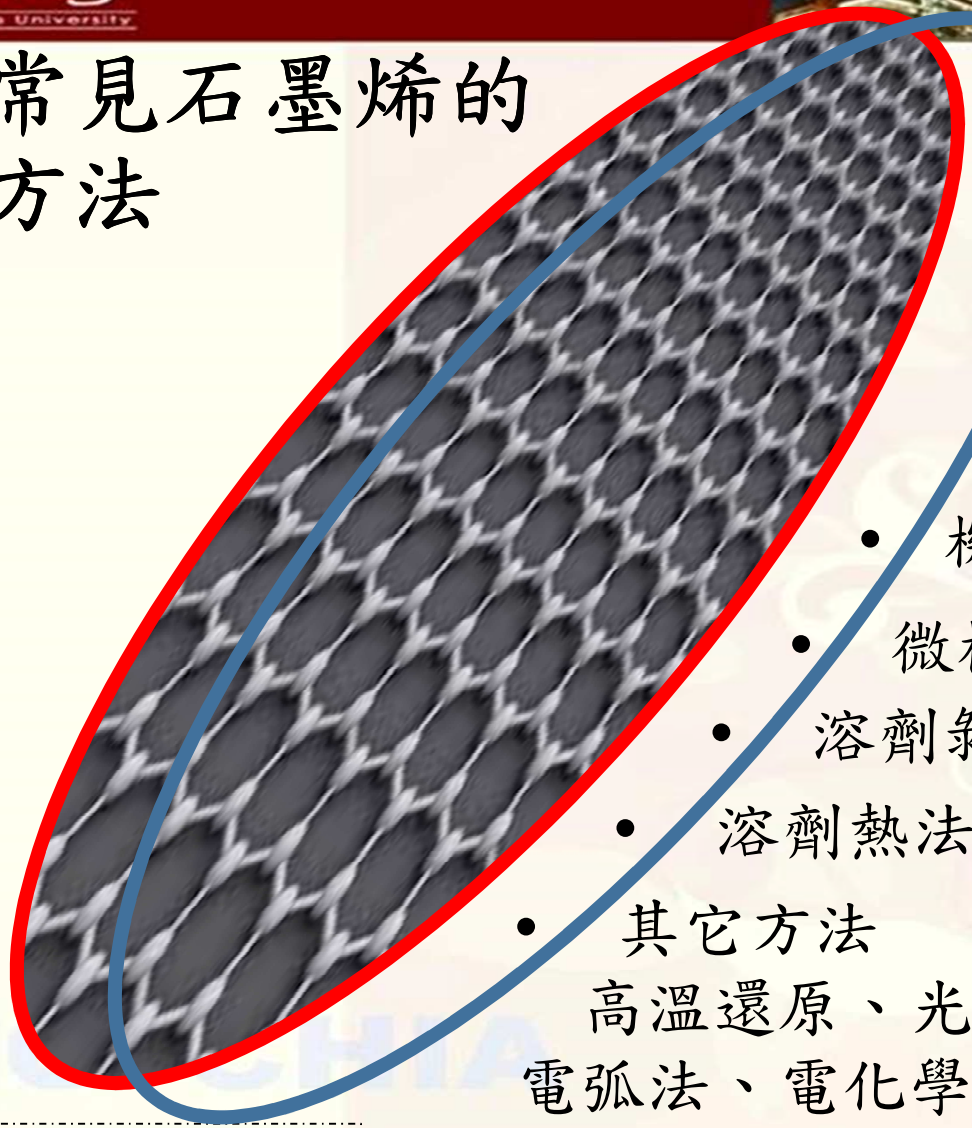
http://en.wikipedia.org/wiki/Graphene

Definition



- Single-layer graphene (SG)
- Bi-layer graphene (BG)
- Few-layer graphenes (≦ 10 layers)
- Graphene odixe (GO)
- Reduced Graphene odixe (RGO)
- Chemically modified graphenes (CMGs).
- Graphene-like

六種常見石墨烯的製備方法



- 氧化-還原法
- 化學氣相沉積法(Chemical Vapor Deposition，CVD)；物理氣相沉積法 (PVD, Sputtering)
- 機械剝離法(蔡宜壽等)
- 微機械剝離法
- 溶劑剝離法
- 溶劑熱法
- 其它方法

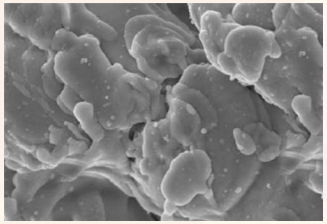
高溫還原、光照還原、外延晶體生長法、微波法電弧法、電化學法等

從天然礦來
Top down

石墨礦

3 D

- 石墨粉
- 插層石墨片(膨脹石墨)
- 熱處理插層石墨片(已膨脹石墨 蠕蟲)

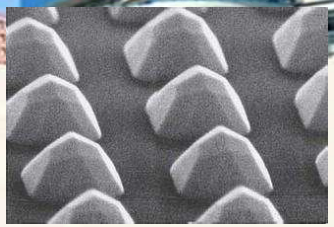


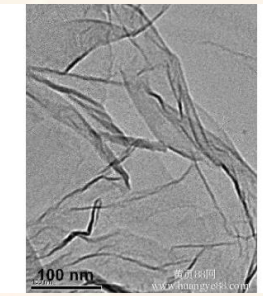
3 D

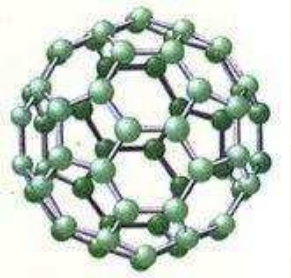
- 單層石墨烯 (2D)
- 多層石墨烯 (小於10層)
- 石墨微片 (小於200層)
- 奈米石墨粉

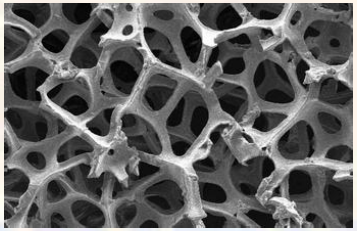
2 D

- 石墨烯量子點(0D)
- 石墨烯片
- 石墨烯球 (0D)
- 3D石墨烯
- 中空石墨烯球(0D)

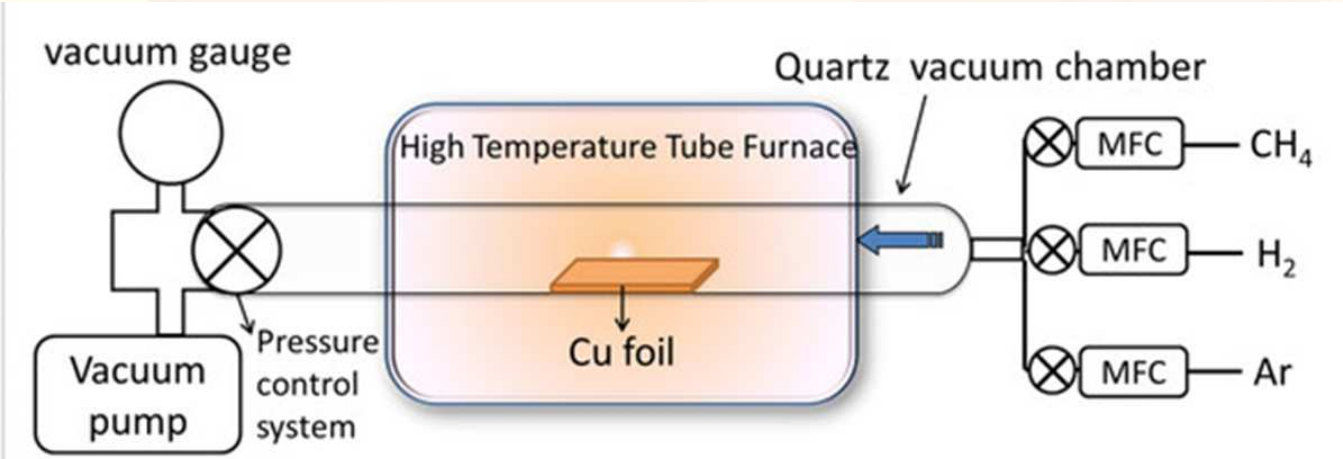








從CVD來 bottom up



一個錯誤的觀念

石墨烯 ≠氧化石墨烯

石墨烯 ≠還原氧化石墨烯

石墨烯、氧化石墨烯、還原氧化石墨烯的區別

區別	石墨烯	還原氧化石墨烯	氧化石墨烯
英文	Graphene	Reduced graphene oxide（RGO）	Graphene oxide（GO）
定義	二維碳材料，是單層石墨烯、雙層石墨烯和少層石墨烯的統稱，不含任何元素和基團，單晶結構，產量少	二維碳材料，表面含沒有被還原完全的基團，表面有缺陷，結晶度差，多晶態，產量高	二維碳材料，表面含有含氧基團（有四種基團），表面有缺陷，結晶度差，多晶態，產量高
層間距離	0.34 nm	0.72 nm	0.68-0.82 nm
親水性	疏水	稍微親水	親水
機械強度	單晶結構，強度非常高，楊氏模量 1100 GPa	存在非晶態，有缺陷，強度比石墨烯差	存在非晶態，有缺陷，強度比還原氧化石墨烯差
導電性	導電性很好，電子遷移率15000 cm2/(v s)	導電率較低	不導電
導熱性	單晶結構，電子運動速度快，傳遞熱量快，導熱性好	存在非晶態，電子運動速度慢，導熱性不及石墨烯	存在非晶態，電子運動速度慢，導熱性不及還原氧化石墨烯
光學性	單層可見光透過率 97.7 %	透光率差	透光率差
主要用途	電池負極材料、航太航空、軍工等	電極材料等	海水淡化，廢水處理、基材、感測器等
主要製備方法	機械剝離、化學氣相沉積法（CVD）、物理氣相沉積法（PVD）	通過化學或熱、光處理等方法不完全去除氧化石墨烯中的含氧官能團（基團）後得到	Brodie法，Staudenmaier法和Hummers法

石墨烯的檢測

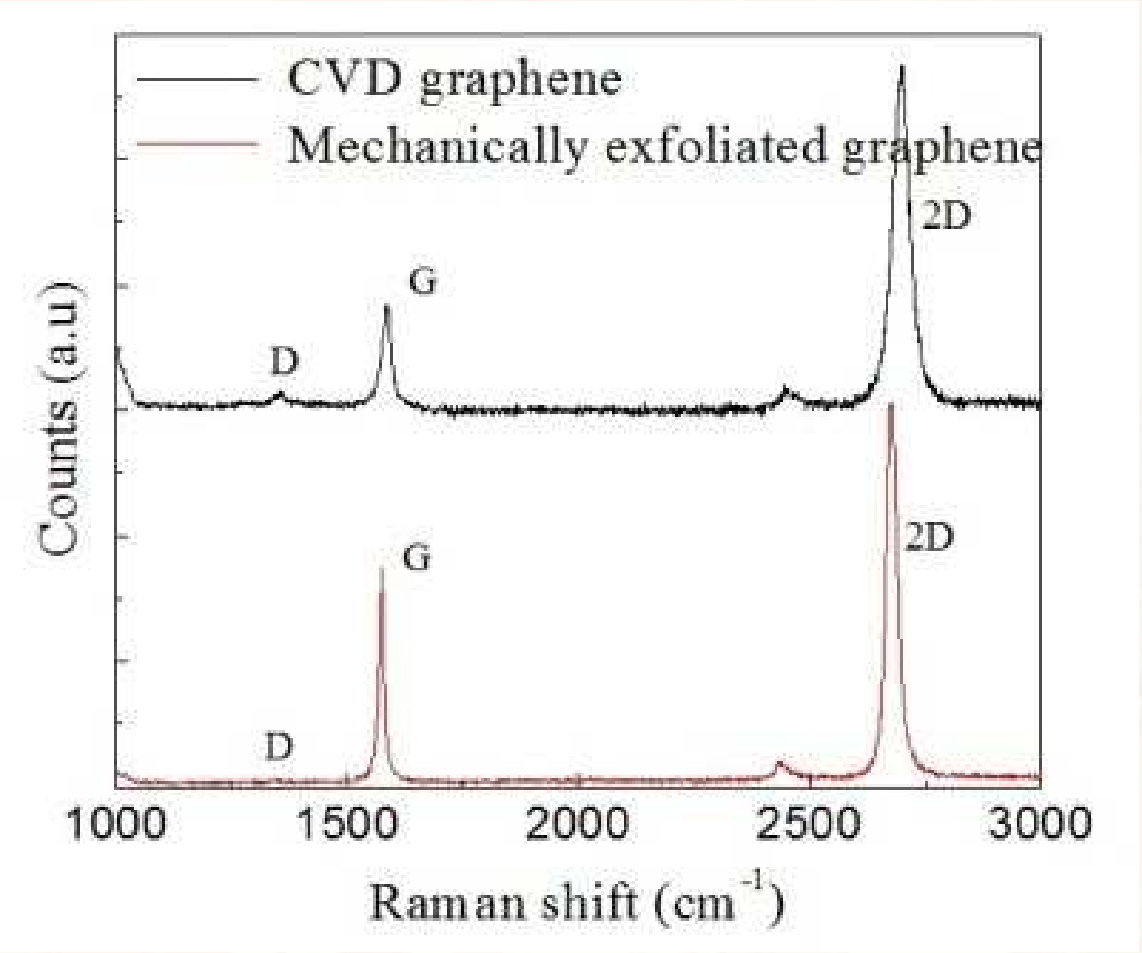
儀器

- 光學顯微鏡
- TEM
- SEM
- AFM
- 拉曼光譜
- X-ray
- XPS (X-ray photoelectron spectroscopy): identify functional groups
- FT-IR(Fourier transform-infrared): identify functional groups
- TGA (Thermogravimetric analysis) : reveals pyrolysis of oxygen-containing functional groups

THE ROLE OF DEFECTS AND STRUCTURAL MODIFICATION ON THE MECHANICAL PROPERTIES

- Various types of defects are possible in graphene and include
  - vacancies,
  - Stone–Wales defects,
  - substitutional impurities (or doping),
  - grain boundaries,
  - adatoms or molecules and various structural modifications or variants.

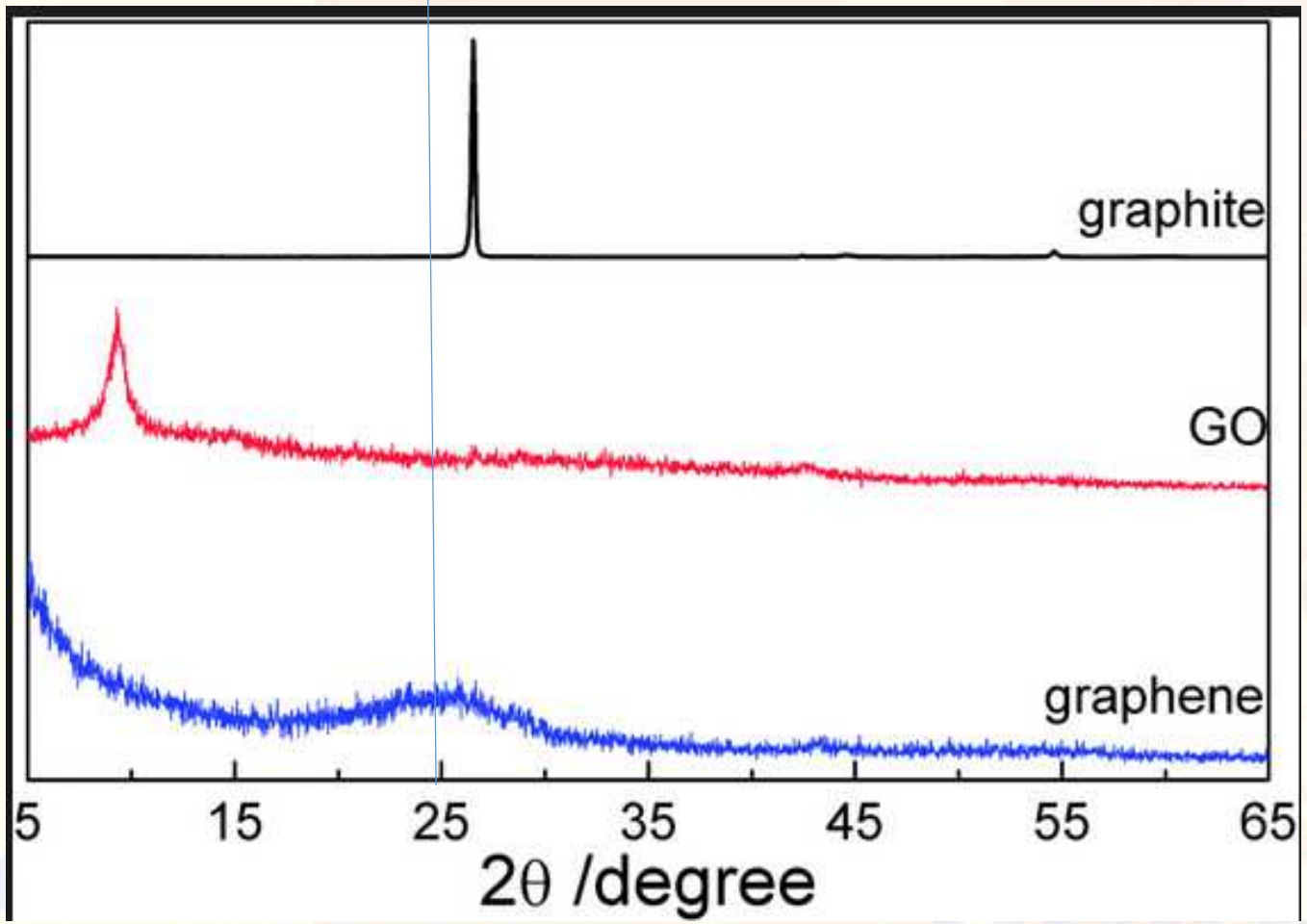
- Right figure shows Raman spectroscopy of the mechanically exfoliated graphene and the CVD graphene.
- The large ratio of the amplitude of the 2D peak to the G peak, and the relatively small amplitude of the D peak indicate that we have high-quality single layer graphene in both types of devices.



Raman spectrum of graphene

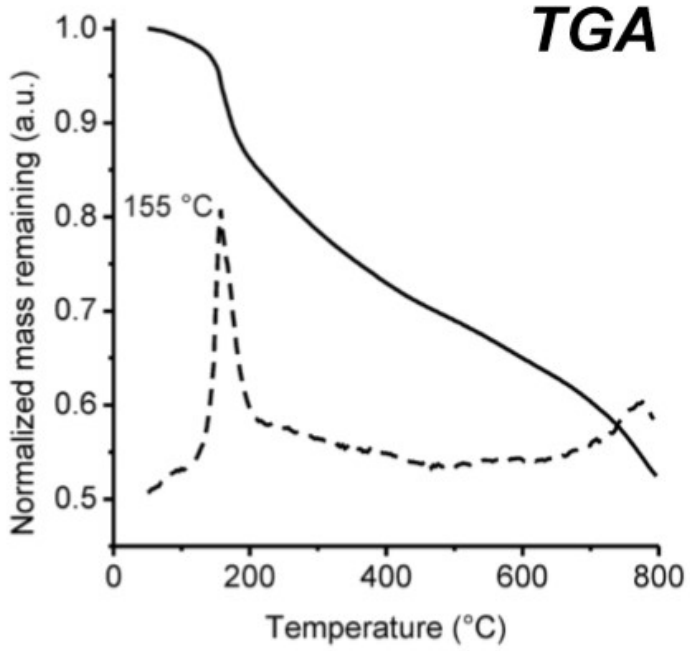
- A typical Raman spectrum of N-doped single-layer graphene.
  - **The D-mode, appears at approximately 1350 cm^{-1},**
  - **The G-mode appears at approximately 1583 cm^{-1},**
  - **The other Raman modes are at 1620 cm^{-1} (D'- mode), 2680 cm^{-1} (2D-mode), and 2947 cm^{-1} (D+G-mode).**

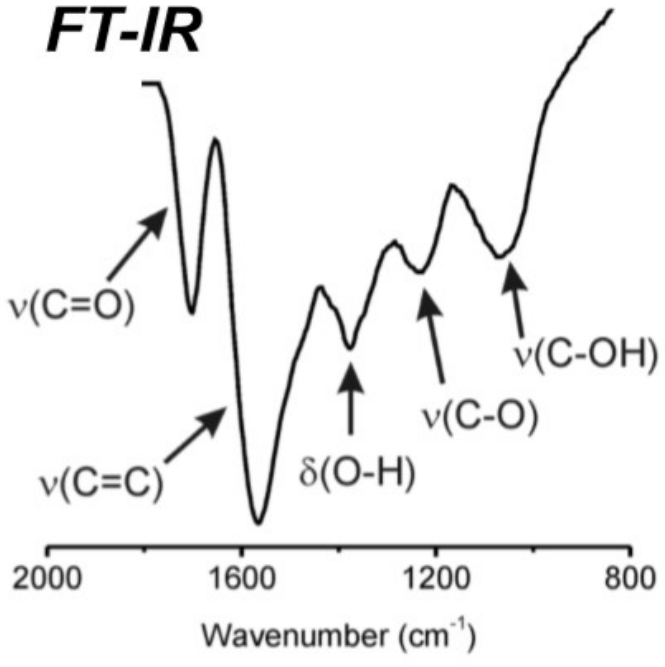
http://cnx.org/contents/f06226c5-c2a4-4798-9c75-b016acea73cd@2/Characterization_of_Graphene_b

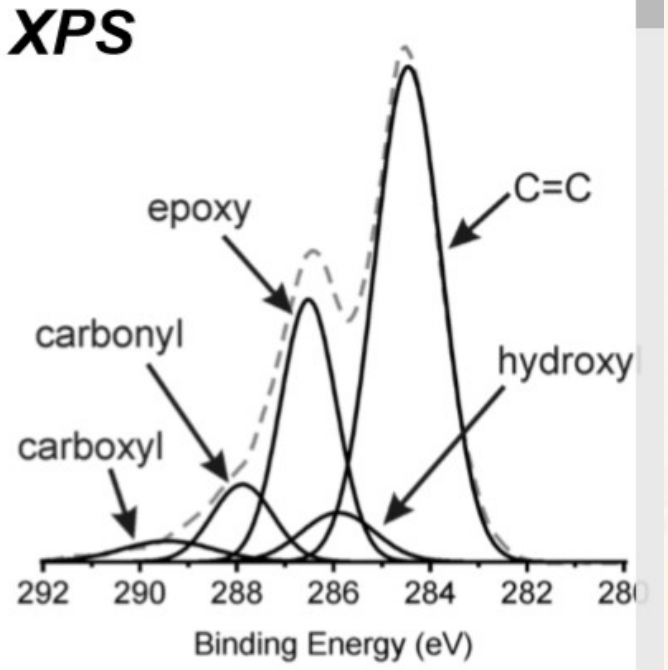

graphite
GO
graphene
5
15
25
35
45
55
65
2θ /degree

graphene

Element	Prominent feature	Sample type	Deconvoluted XPS components (eV)	Possible chemical species
C	C 1s	PS	282.8, 284.5, 285.7, 288.6	Metal carbide, adsorbed carbon, organic impurities & carboxyl group
		GS	285.2, 288.6	sp^2 hybrid carbon & carboxyl
Cr	Cr $2p_{3/2}$	PS	574.2, 575.9, 577.3	Metallic chromium, chromium carbide & CrO
		GS	575.9, 577, 577.9	Chromium carbide, $MnCr_2O_4$ spinel & Cr_2O_3
Mn	Mn $2p_{3/2}$	PS	640.5	MnO
		GS	640.1, 641.3, 642.3, 643.5	Mn_3C, Mn_2O_3, MnO_2 & $MnCr_2O_4$
Fe	Fe $2p_{3/2}$	PS	706.7, 707.9, 709	Metallic Fe, Fe_3C & FeO
		GS	710, 711.1, 712.4	FeO, Fe_3O_4 & Fe_2O_3
Ni	Ni $2p_{3/2}$	PS	852.9	Metallic Ni
		GS	---	


TGA
Normalized mass remaining (a.u.)
1.0
0.9
0.8
0.7
0.6
0.5
155 °C
0
200
400
600
800
Temperature (°C)


FT-IR
ν(C=O)
ν(C=C)
δ(O-H)
ν(C-O)
ν(C-OH)
2000
1600
1200
800
Wavenumber (cm-1)


XPS
epoxy
C=C
carbonyl
hydroxy
carboxyl
292
290
288
286
284
282
Binding Energy (eV)

石墨烯的迷失, 世紀大騙局?

微觀與巨觀

石墨烯是一種二維晶體，是人類已知強度最高的物質，比鑽石還堅硬，強度比世界上最好的鋼鐵還要高上100倍。

人類有能力造出大面積的完美單晶嗎?

不可掌控性

結晶缺陷
平面排列
空間排列
含雜
非炭基團

- - - - - -

天然的石墨烯無法改變，
人類的技術目前可以大
量進行原子搬運嗎?

所以很多物性在宏觀多要大折扣

- 載流子遷移率高、電流密度大
- 強度高
- 導熱率高
- 催化劑
- 吸氫
- 雙極半導體

石墨烯是形容詞嗎?
20年前的納米產品哪去了?

- 石墨烯超越性能的利用率低
  - 石墨烯導熱膠: 石墨烯導熱但膠不導熱
  - 石墨烯導電膠: 石墨烯導電但膠不導電
- 石墨烯的操控技術差
  - Restacking的問題
    - 例如烘乾，噴霧乾燥
    - 例如如何再分散?
- 石墨烯的應用場合不對
  - 微小的器具才是重點
    - 例如電子工業，IC、sensors、量子點
    - 例如冶金，原子互融
    - 例如高分子聚合，結晶插層

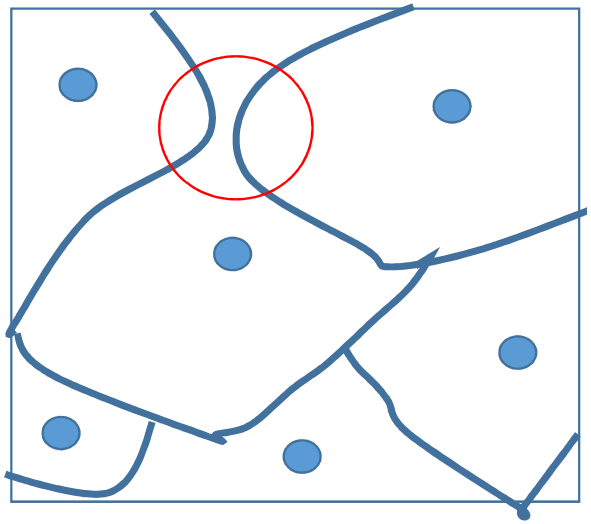
石墨烯真的會改變人類未來嗎?

- “超級電容器”、“觸控式螢幕”、“結構材料”、“感測器”、“高性能電腦”五大領域。
- 鋰電子電池、超級電容、導電油墨、觸控式螢幕、軟性電子、散熱、塗料、潤滑劑、感測器等領域，
- 此外，在高頻電子、環保、光電、聚合物、海水淡化、太陽能電池、燃料電池、催化劑、建築材料等領域，也能發現石墨烯的身影。

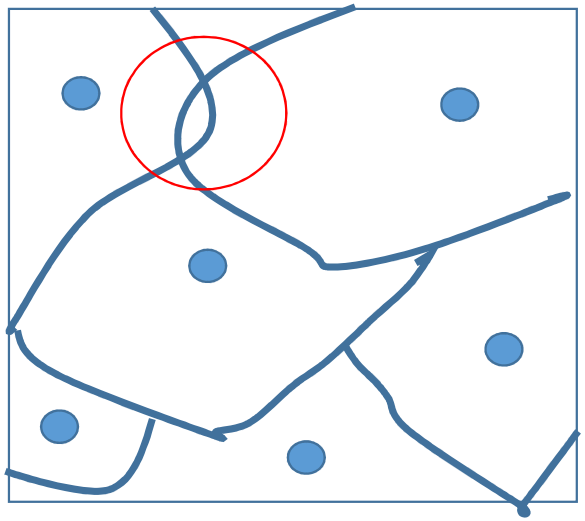
Transparent electrode

- Grain boundary problems

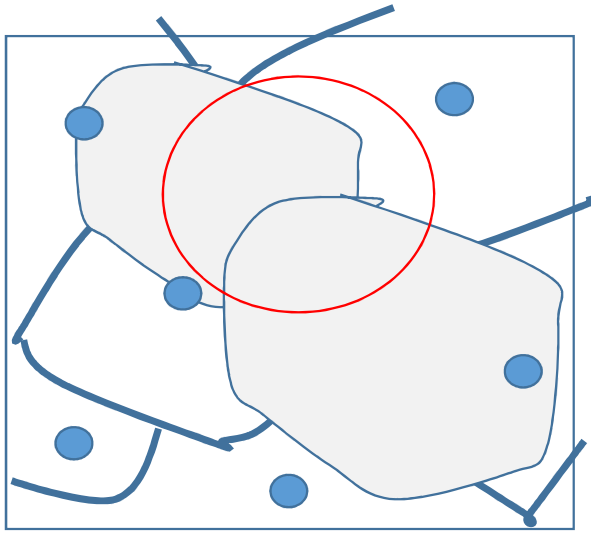
crack



Stack



overlap



華為稱新石墨烯電池性能秒殺市場大部分鋰電池

- 華為此次推出的計畫用於沙漠、陽光直曬等高溫極端環境的移動網路基站，高溫電池中，石墨烯起到的作用是高效散熱，而**非電池的正極或負極材料**。

鋰電池構造

請思考這個問題:

石墨烯負極材料占電池的比例為何?

其實真正的問題是:

- 金屬離子
- 太滑黏不住
- 有孔洞
- 選錯**石墨材料**
- **能量密度不夠**

一些應用例

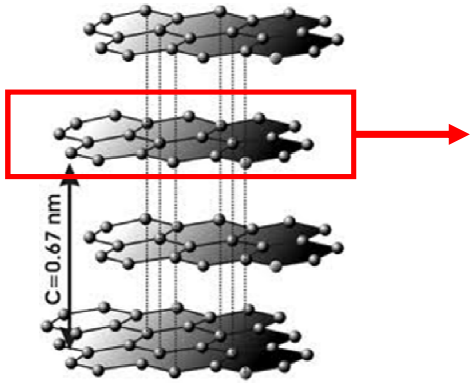
Our Recent Research Works

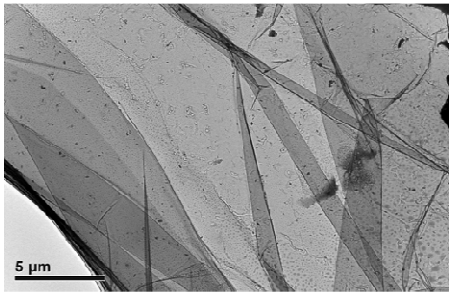
- More industrial applications
- Less academic works

Recent researches (1/8)

- preparation of graphene/graphene oxide powder

graphite





graphene

10-30 μ < 10 layers	**< 1 μ** < 10 layers
	< 1 μ < 3 layers

技術的重點

- 不在於是否能大量做出石墨烯片, 而是
  - 是否能控制你要的層數
  - 是否能控制你要的尺寸大小
  - 是否能控制你要的純度
  - 是否能控制你要的doping 與adatom.

Graphene oxide powder

- Previously, we suffer the acid washing from preparation of graphene oxide by Hummer approach.

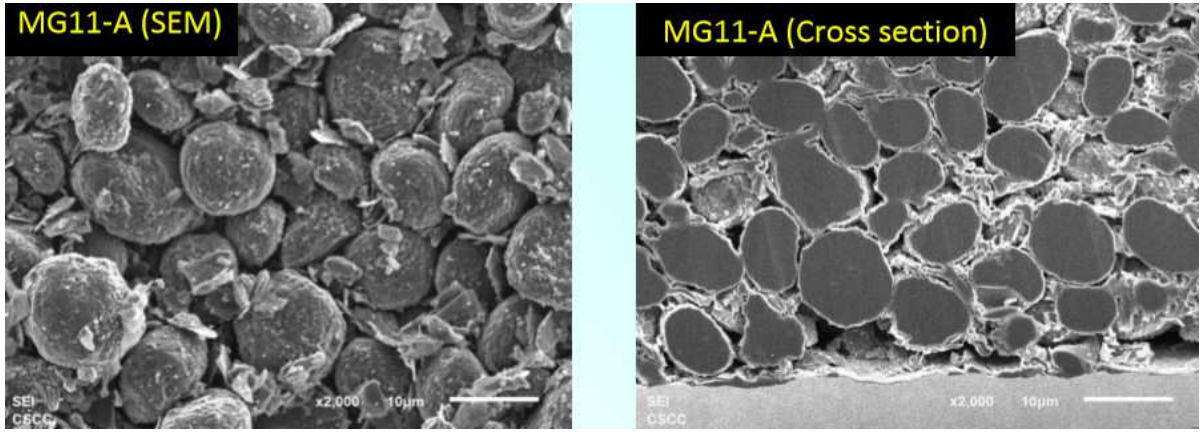
But, now we had successfully solved the problem by using ion-exchange polymer to remove all the added acids.

Recent researches (1/8)

- Battery negative material –
  -- Meso-phase graphite powder

Why?

1-5 μ | 5-10 μ | 10-15 μ



技術的重點

- 不在於是否能大量做出球狀石墨, 而是
  - 是否能控制你要的尺寸大小
  - 是否能控制你要的官能基
  - 是否能控制你要的pH值

Graphene or RGO as Battery negative material

NO!

- We can't find any outstanding advantages in following aspect:

1. Graphene is used sololy as a negative electrode material

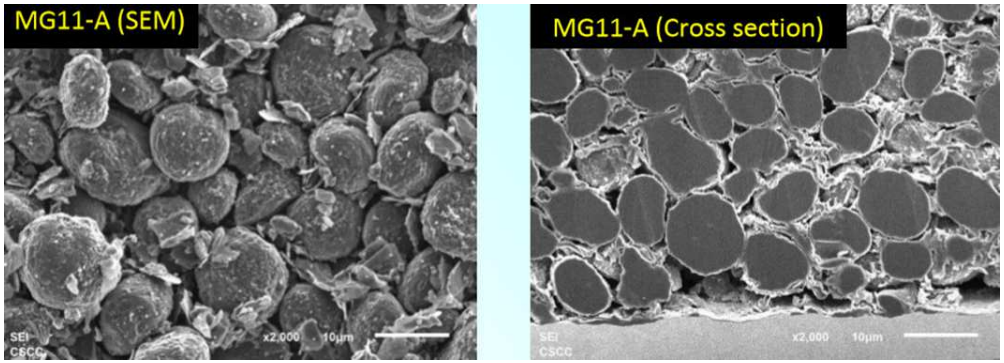
2. With other new negative materials, such as silicon and tin-based materials and transition metal compounds to form composite materials;

3、Negative conductive additive

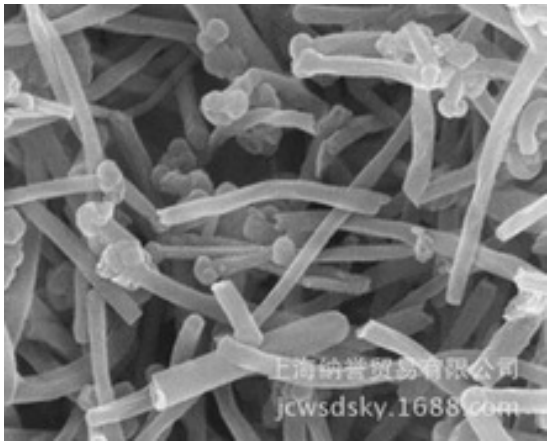
- Comprehensive considerations of
  1. material costs,
  2. production processes,
  3. processability and
  4. electrochemical properties

So, we chosed

- Meso-phase graphite powder is used sololy as a negative electrode material
- Vapor grown carbon fibers (VGDF)）日本昭和電工株式會社 is used as negative conductive additive.



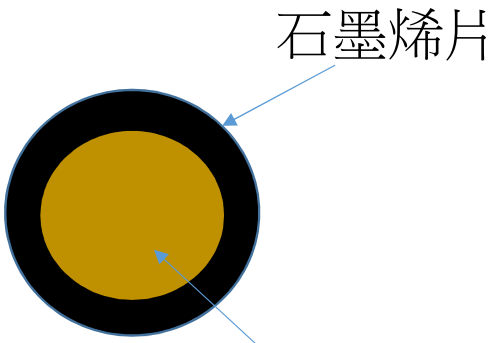
More compact and dense



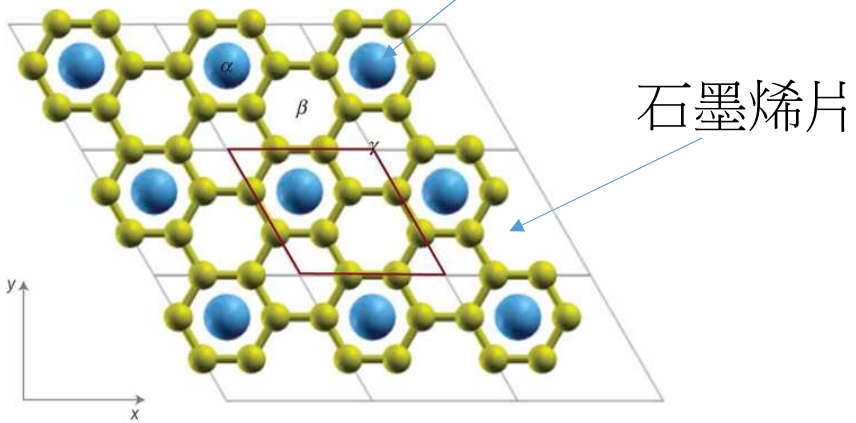
Courtesy: 日本昭和電工

鋰電負極__解決之道

初期：石墨烯片包覆微米/次微米 硅

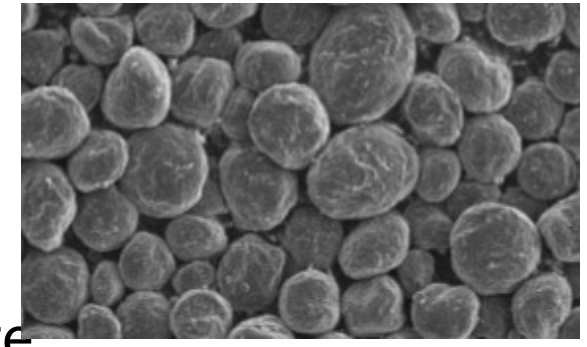


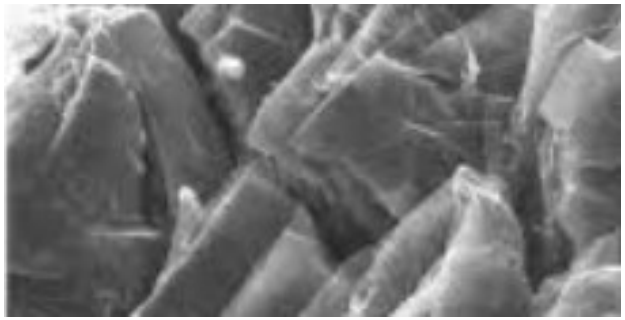
- 未來: 硅原子填入石墨烯片中



Recent researches (1/8)

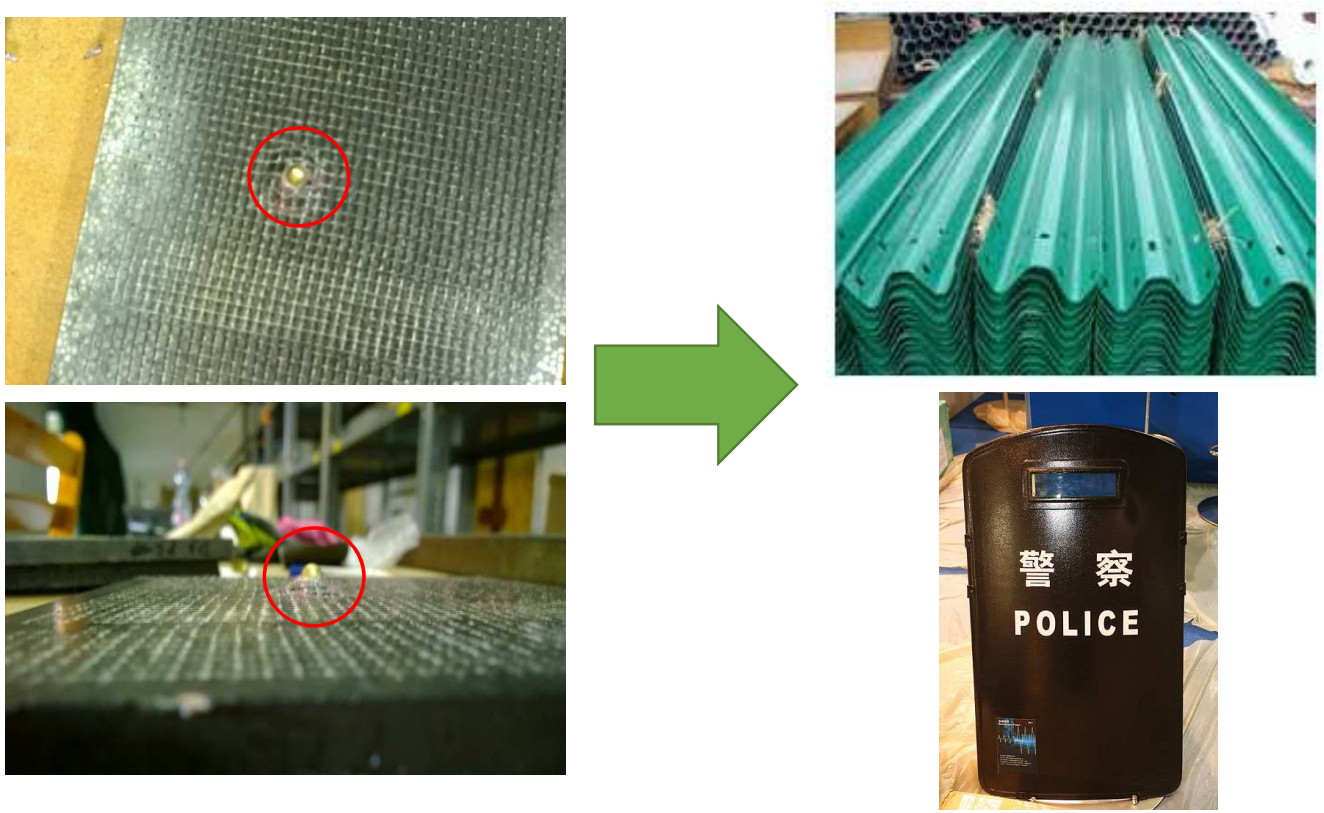
- Fillers for textile spinning filaments
  - Submicron meso-phase graphite powder
  - Submicron expandable graphite powder
  - Of course, submicron multilayer graphene





Recent researches (2/8)

2.2 Plastic/multi-layers graphene composites



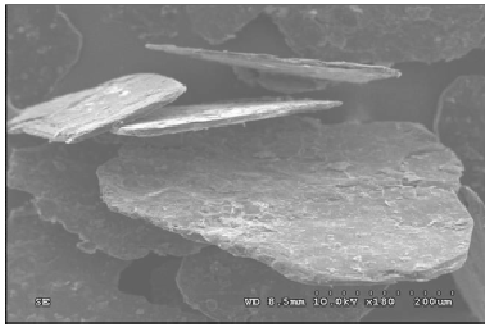
多層石墨烯片/(發泡)高分子複合材料

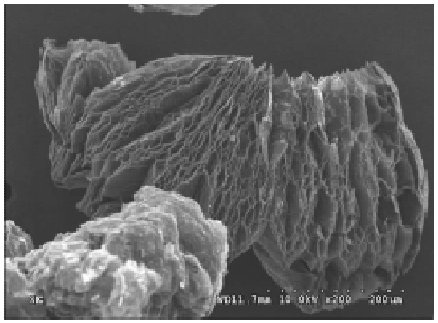
- 特性:
  - 剛性、強度提升
  - 防火性能提升
  - 抗靜電提升
  - 耐衝擊提升
  - 硬度提升
  - 質輕
- 。
- 防水
- 耐鹽水
- 耐酸鹼、化學藥品
- 導熱性提升
- 抗紫外線性能提升
- 遮蔽電磁波性能提升
- 用途:
  - 建築（三合板、模板、梁柱、地板、.....）
  - 土木(防波堤、高速路防撞欄杆、
  - 家俱
  - 交通(汽車車體、船甲板、車船內裝__)
  - 其他

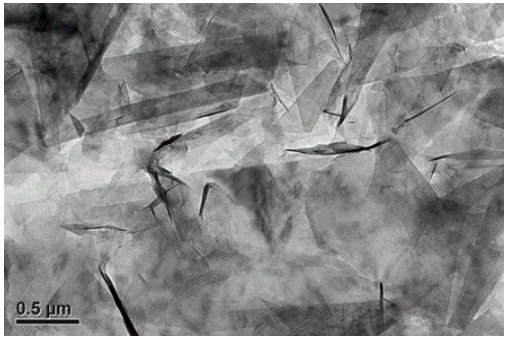
Preparation of Material

immersing in a bath of chromic acid,
then concentrated sulfuric acid,

Non-Chemical exfoliation







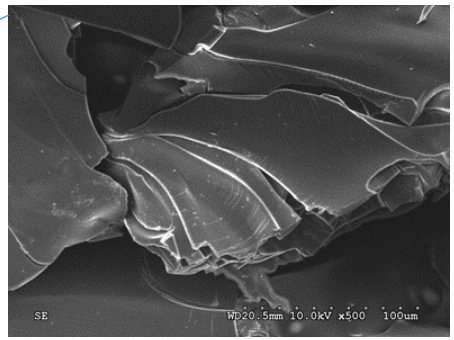
natural flake graphite

Expanded graphite

graphene

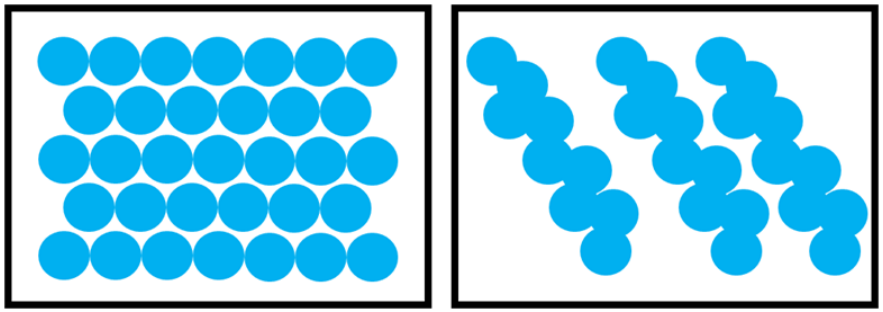
encapsulation

pallets



Recent researches (4/8)

STF (Shear Thickening Fluid)



- TEOS >> hydrolysis >> nanoSiO_2 + PEG + dispersants
- Graphene balls + PEG + dispersants

Recent researches (5/8)

Metal Porous Plates for flame retardant and heat insulation

Aluminum

Stainlees stell + glass fibers

Tungsten steel

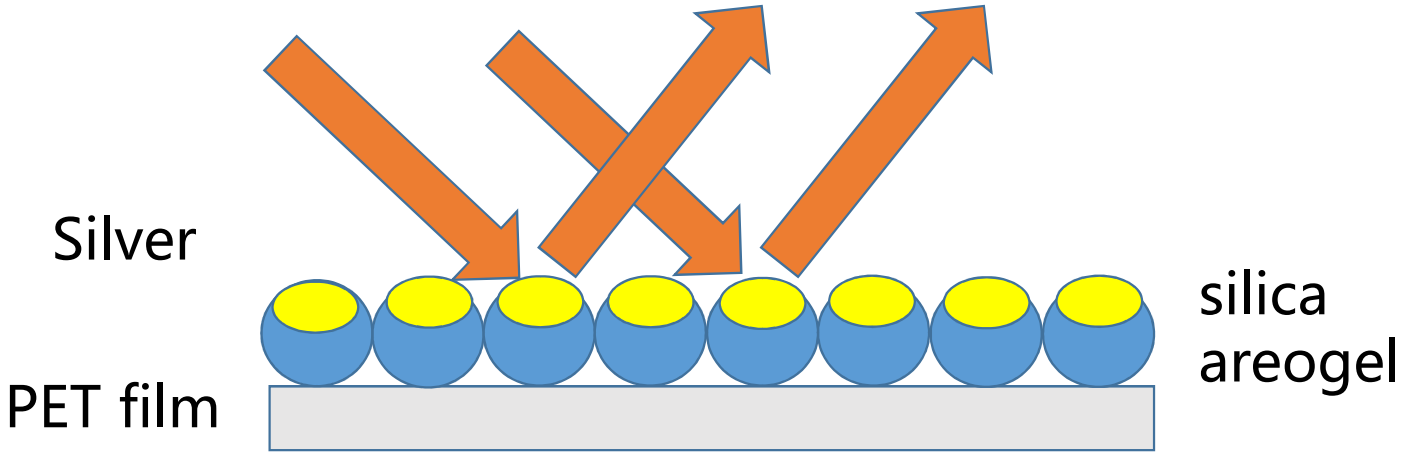
Metal Porous Plates for flame retardant and heat insulation

石墨烯合金 graphene/Cu; graphene/Al....

- 多層石墨烯片/多孔不銹鋼複合材料
  - 特性:
    - 防火、絕熱、散熱
    - 模具成型，可做成不同形狀
  - 用途:
    - 軍事用途
    - 煉鋼、冶金
    - 其他

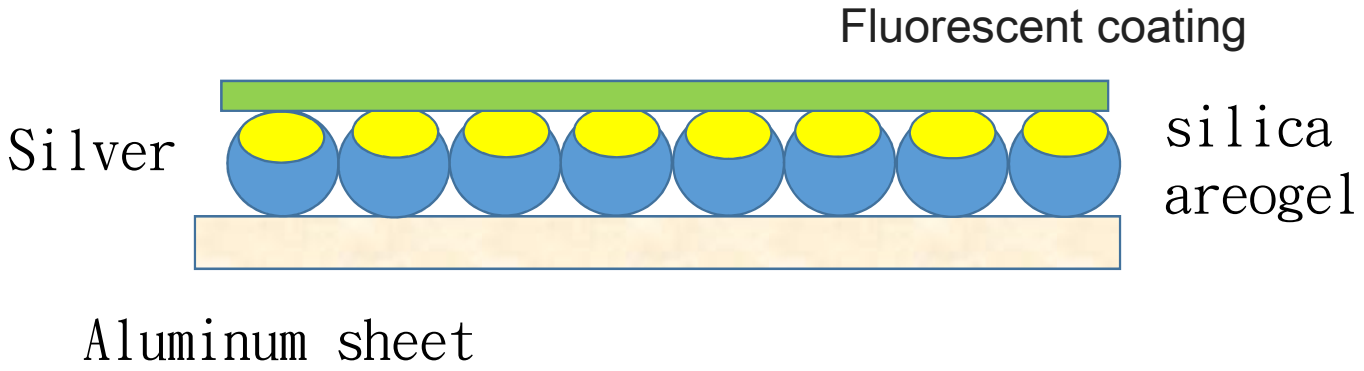
Recent researches(6/8)

heat Insulation film



Recent researches(6/8)

- heat Insulation film



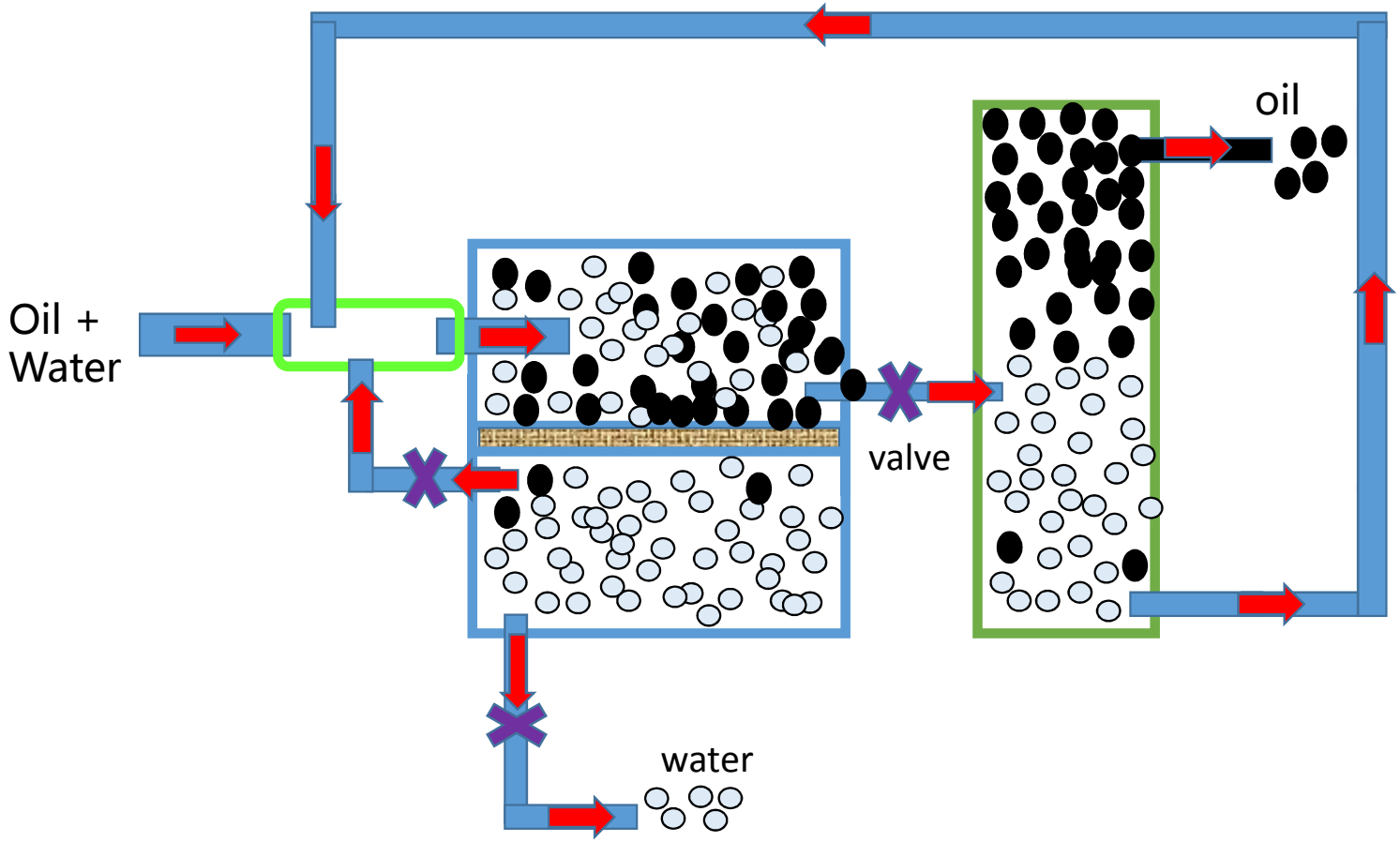
New Project

- Grinding and Polishing Wheel for SiC Wafers

油水分離

- Experimental

installation



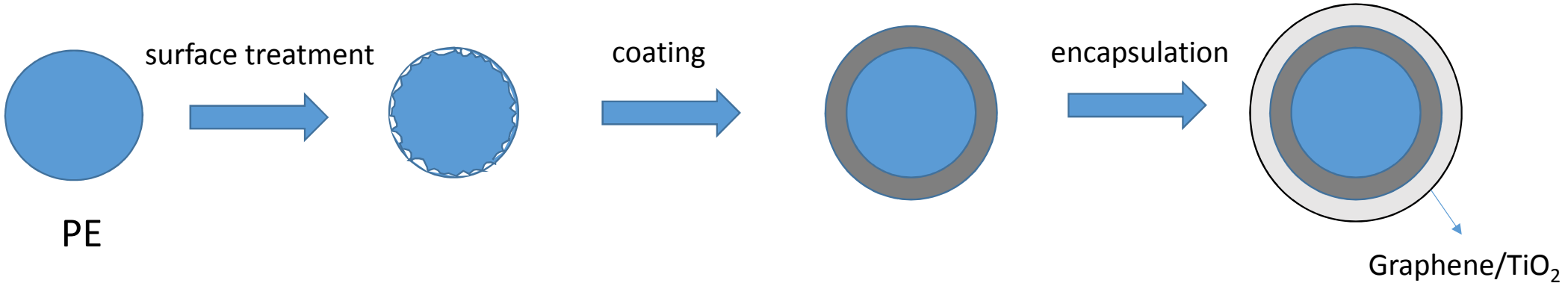
石墨烯氣凝膠

石墨烯氣凝膠在固體材料中是獨一無二的，具有非常低的密度(其體積高達95 %是空氣)，因此未來將會突破新的應用層面，如超級電容器、吸附材、催化載體，以及氣體感應器等。

投資與技轉項目
--CNH油品(润滑油/机油)

- 特性:
  - 分散性佳
  - 修护金属受损表面
  - 润滑性好、
  - 阻力小、
  - 抗磨性好、
  - 温升低、
  - 抗氧化、
  - 寿命長.....
- 用途:
  - 車輛
  - 船舶
  - 航空器
  - 機械
  - 其他

顆粒狀_石墨烯/二氧化鈦@聚乙烯粒



光觸媒__用於除色、除臭、滅菌

石墨烯防鏽塗料

- Before




石墨烯/磷酸鹽

After





石墨礦基石墨烯應用

- 汽車：車架、外殼、防銹、機油、電池、超級電容、防撞檔板、貼紙、高速路防撞檔板
- 環保：容器、管道、海水淡化、去離子、油水分離
- 電子：高頻電子、感測器、基板、導電油墨、散熱塗料、 OLED、IC、 發熱膜、耐大電流開關
- 能源：太陽能電池、燃料電池、鋰電子電池、超級電容
- 建築：防銹散熱塗料、裝潢板、木條、模板、智慧玻璃
- 其他如防彈盾牌、防彈衣、3D印表機材料、納米藥物運輸系統、生物檢測、腫瘤治療、防護墊

- Various types of defects are possible in graphene and include
  - vacancies,
  - Stone–Wales defects,
  - substitutional impurities (or doping),
  - grain boundaries,
  - adatoms or molecules and various structural modifications or variants.

本世紀是石墨烯時代,但距離本世紀末還有82年，

所以科技還有一大步努力空間。

謝 謝 聆 聽!

願意回答任何問題!