

Graphene: Its role in energy storage devices

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Outline of the talk

- ❖ Graphene – A preamble
- ❖ Methods of preparation
- ❖ Some interesting applications
- ❖ Role of graphene in energy storage devices
 - ✓ Fuel cells
 - ✓ Supercapacitors
 - ✓ Lithium ion batteries
 - ✓ Hydrogen storage
- ❖ Concluding remarks

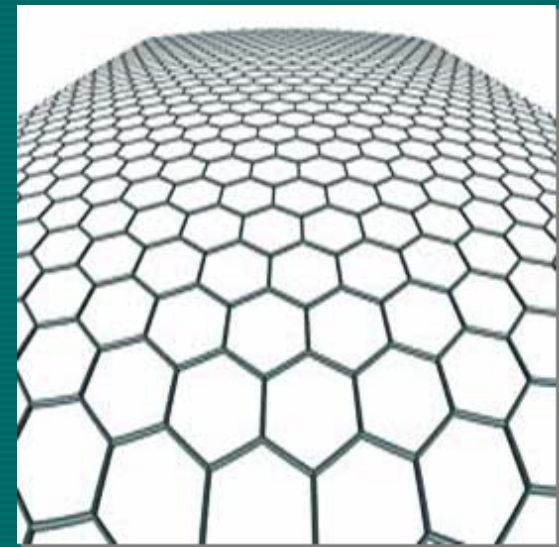
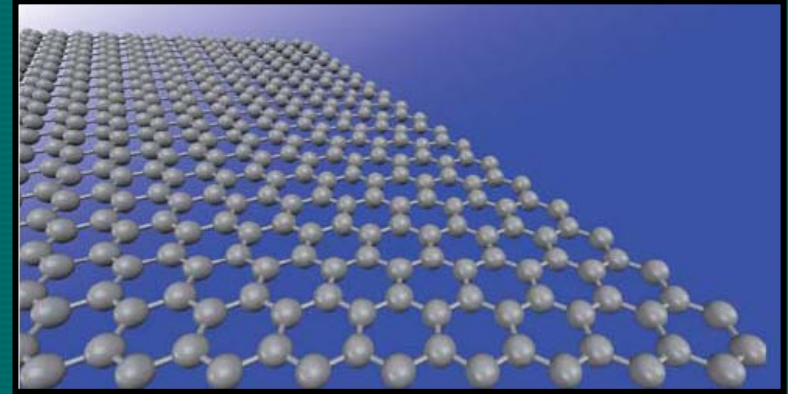


The Nobel Prize in Physics for 2010
was awarded jointly to
Andre Geim and **Konstantin Novoselov**
for their

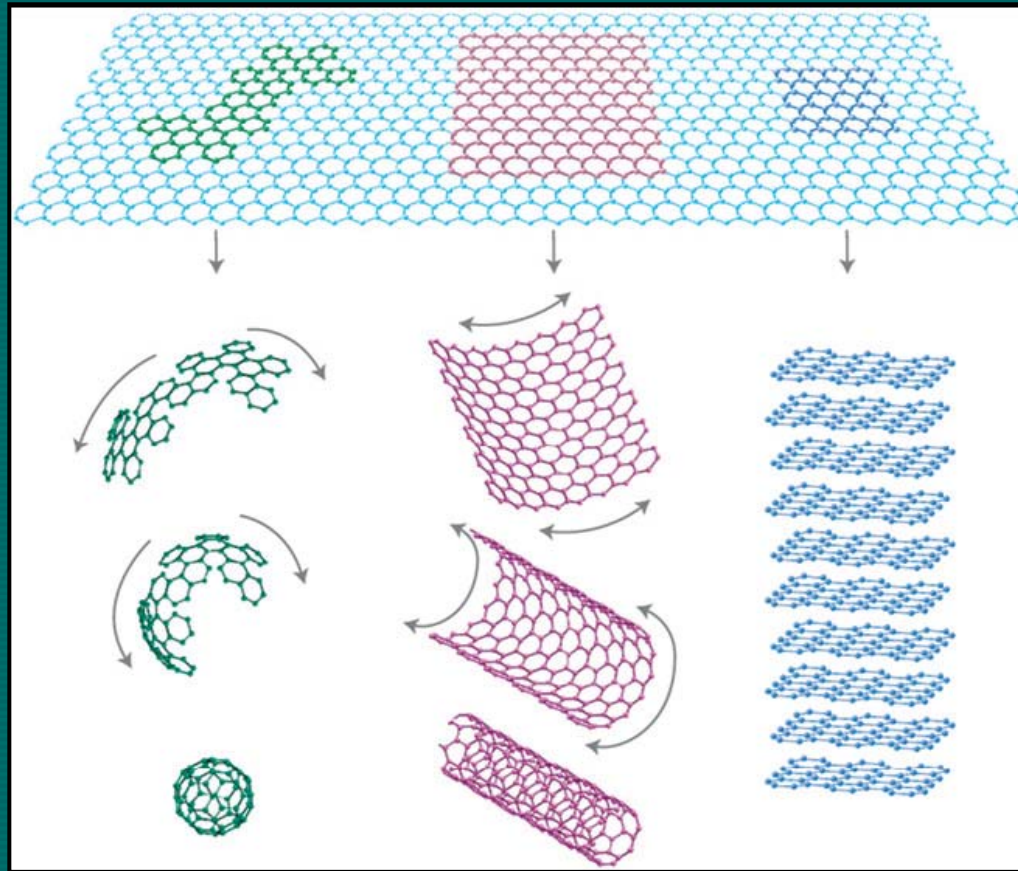
*"groundbreaking experiments regarding
the two-dimensional material graphene."*

Graphene - A preamble

- Graphene is composed of carbon, the building block of all life
- Discovered in 2004 in its full observable and testable form
- The new kid in the block of carbon family - basic building block for graphitic materials of all dimensions
- single sheets of graphite
- a flat monolayer of carbon atoms that are tightly bonded together through covalent bond into a 2D honeycomb lattice

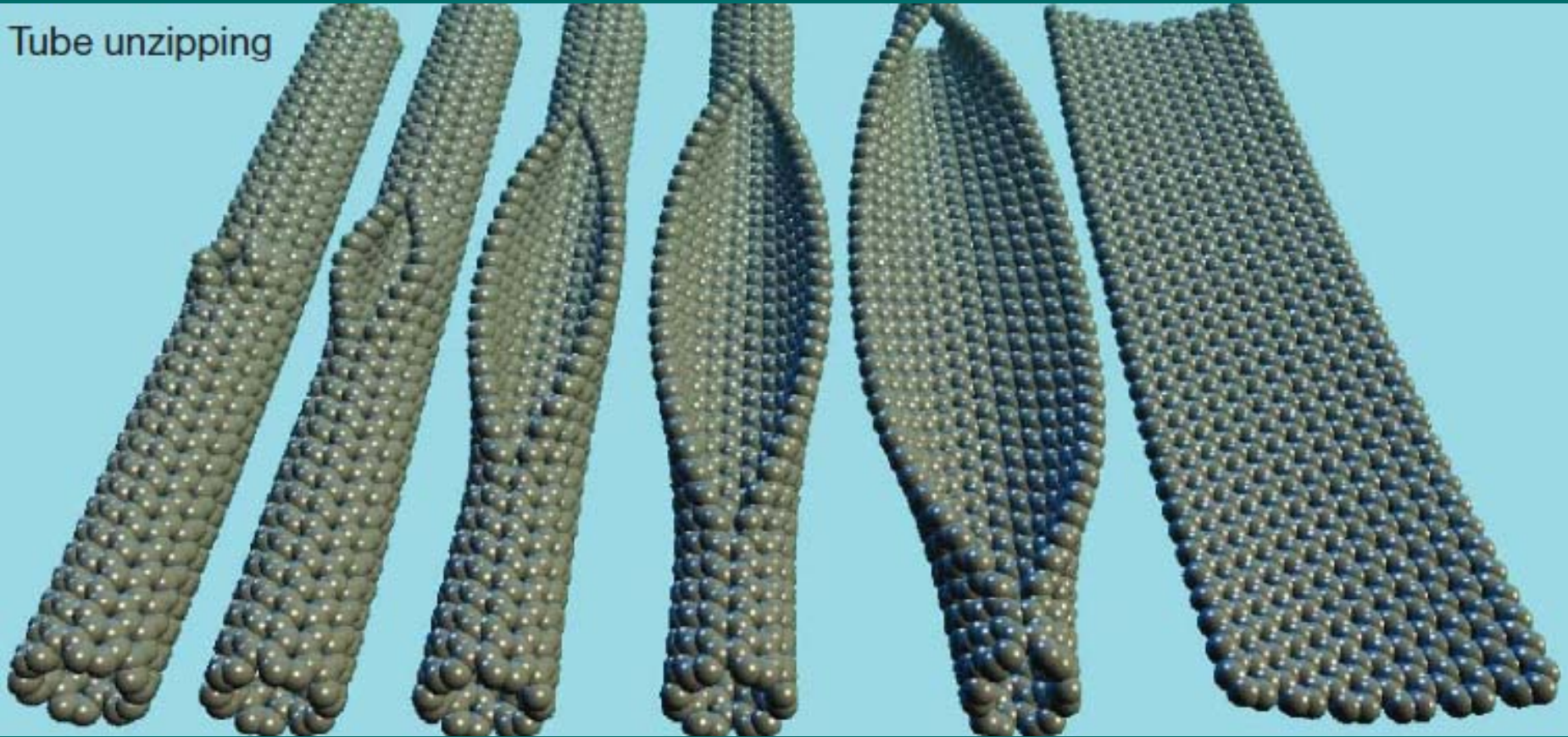


Graphene - Mother of all graphitic forms



Graphitic family: 0-dimensional fullerene, 1-dimensional carbon nanotube, 2-dimensional graphene, 3-dimensional graphite

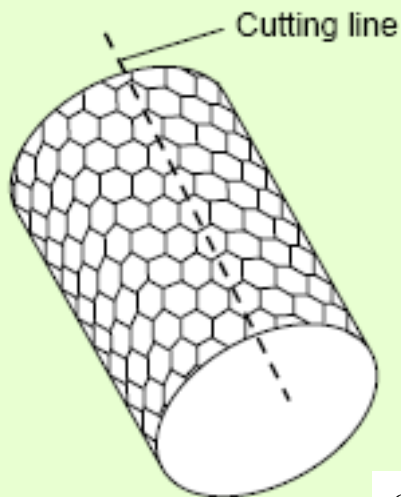
Tube unzipping



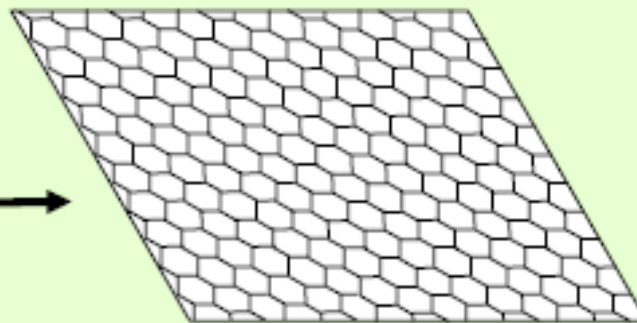
Unzipping the Carbon nanotube to monolayer graphene

Source: Baraton et. al., *Nanotechnology* 22 (2011) 085601

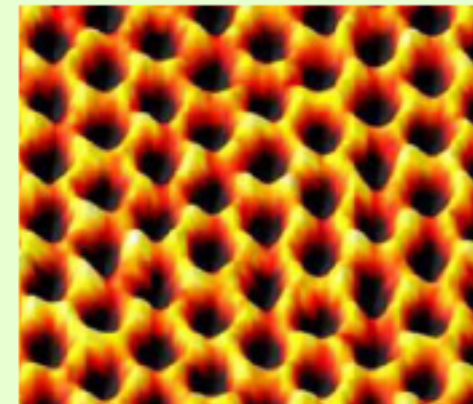
Graphene – The Flat form of CNT



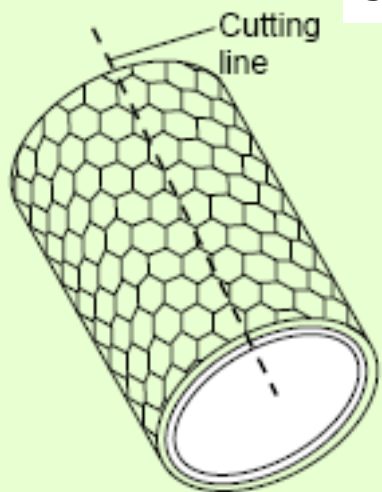
SWCNT



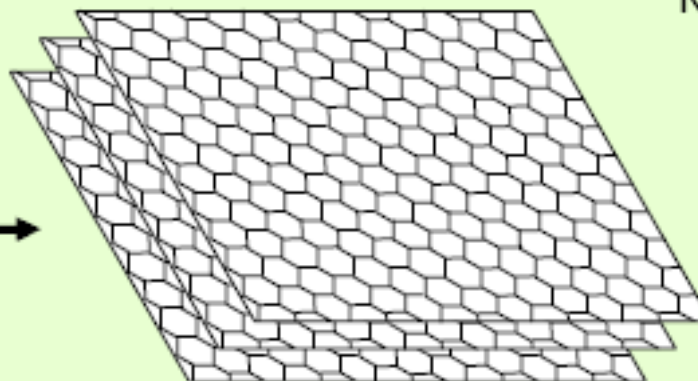
Graphene sheet/NGP



(Image courtesy of
DOE/Lawrence Berkeley
National Laboratory)



MWCNT



multilayered graphene sheets/NGP

Characteristics of graphene

- ✓ thinnest possible material that is ever feasible
- ✓ Highest thermal conductivity (up to $\sim 5,300$ W/m-K), five times that of copper – faster thermal dissipation
- ✓ Electrical conductivity similar to Cu, yet its density is four time lower than Cu – lighter weight components
- ✓ Ultra-high Yong's modulus (approximately 1,000 GPa) and highest intrinsic strength (~ 130 GPa)
- ✓ High specific surface area (up to $\sim 2,675$ m²/g)
- ✓ Outstanding resistance to gas permeation

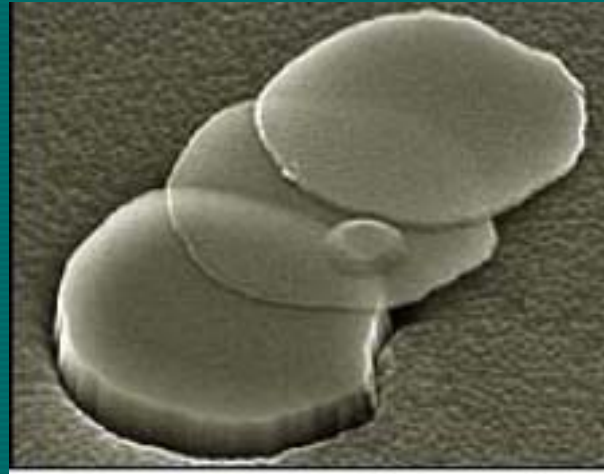
Characteristics of graphene

- ✓ ~200 times stronger than steel
- ✓ "It would take an elephant, balanced on a pencil, to break through a sheet of graphene the thickness of Saran Wrap." - *Researchers at Columbia University's Fu Foundation School of Engineering*
- ✓ Readily surface-functionalizable
- ✓ Dispersible in many polymers and solvents
- ✓ High loading in nanocomposites

Methods of preparing graphene

- Top-down approaches
 - ✓ scotch tape stripping
 - ✓ ion sputtering
 - ✓ pulsed laser deposition
 - ✓ ball milling
 - ✓ arc discharge
- Bottom-up approaches
 - ✓ chemical vapour deposition (CVD)
 - ✓ wet chemistry
 - ✓ ion implantation
 - ✓ pyrolysis

Peeling graphite using “Scotch tape”



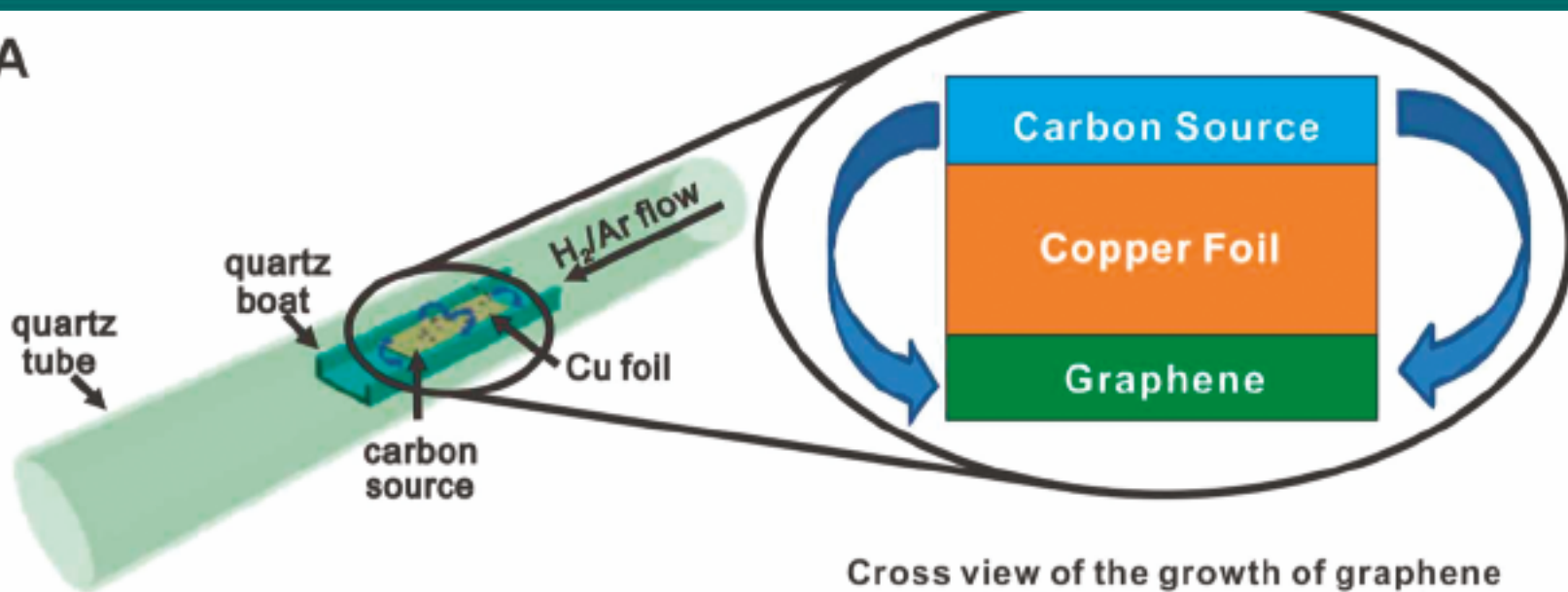
In 2004 - Geim and Novoselov have used a tape to repeatedly peel off graphene sheets from graphite crystals

Large scale production?

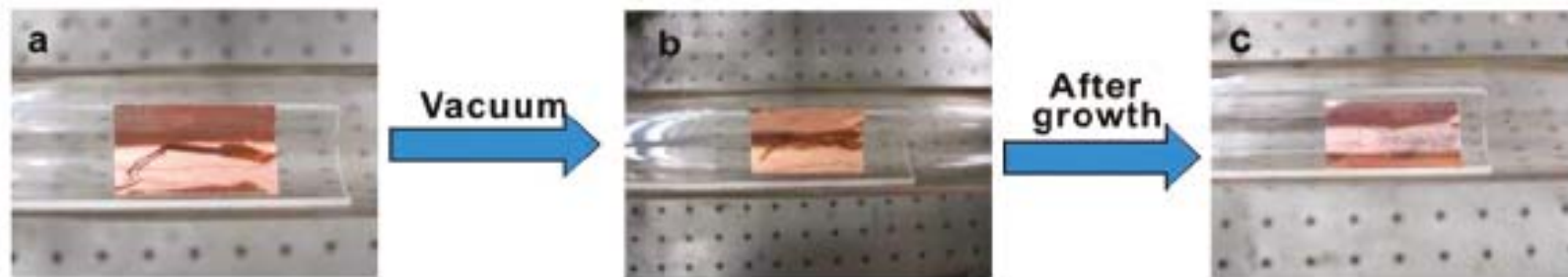
Source: Bor Z. Jang, Wright State University and Aruna Zhamu, AngstromMaterials

Chemical vapour deposition (CVD)

- CVD - One of the promising method of preparation of graphene
- It involves blowing methane over thin sheets of copper
- The carbon atoms in methane form a thin film of graphene
- Accumulation of multilayers of carbon – unusable
- Vacuum condition is necessary

A

10 mTorr for 10 h 1050 °C for 15 min.

B

Carbon source - cookies, chocolate, grass, plastics, cockroaches, and dog feces

Exfoliation of graphite

- ✓ Chemical exfoliation
- ✓ Chemical and thermal exfoliation
- ✓ Electrochemical exfoliation
- ❖ These methods assume significance
 - ❖ ability to prepare graphene in large quantities
 - ❖ cost-effective

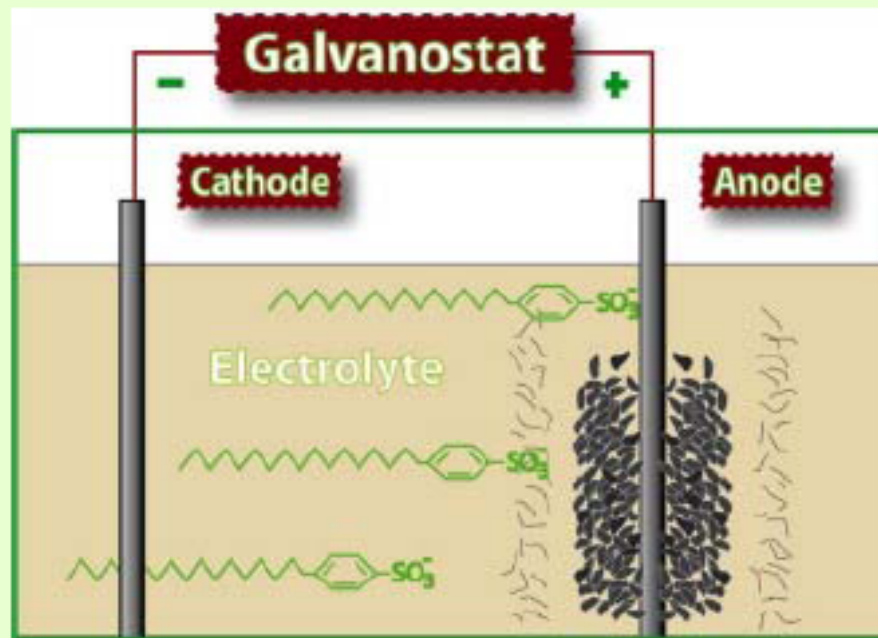
Chemical exfoliation

- Starting material - crystals of natural graphite
- Sonication in dimethyl formamide (DMF) for over 3 h
- DMF “dissolves” graphite - suspension of thin graphitic platelets with large proportion of monolayer graphene flakes
- DMF wets the flakes preventing them from conglomerating
- Centrifuge the suspension at 13,000 rpm for 10 minutes to remove thick flakes. The remaining suspension consists mostly of graphene and few-layer graphite flakes of sub-micrometer size
- The suspension was spray-deposited onto a preheated glass slide or spin coated
- These films were then annealed for 2 h in Ar (90%)-H₂(10%) atmosphere at 250 °C.

Chemical and thermal exfoliation

- ❖ Graphite powder (40 g) is added to a mixture of concentrated HNO_3 (270 ml) and H_2SO_4 (525 ml) with vigorous stirring to disperse the graphite powder
- ❖ Add 330 g potassium chlorate – slow addition to avoid the risk of explosion
- ❖ Allow the reaction to proceed for 120 h at room temperature
- ❖ Extract the graphite oxide (GO) powder from the solution and completely dry it at 100 C in a vacuum oven
- ❖ Thermal exfoliation of GO at high temperature in vacuum

Electrochemical Preparation of Graphene



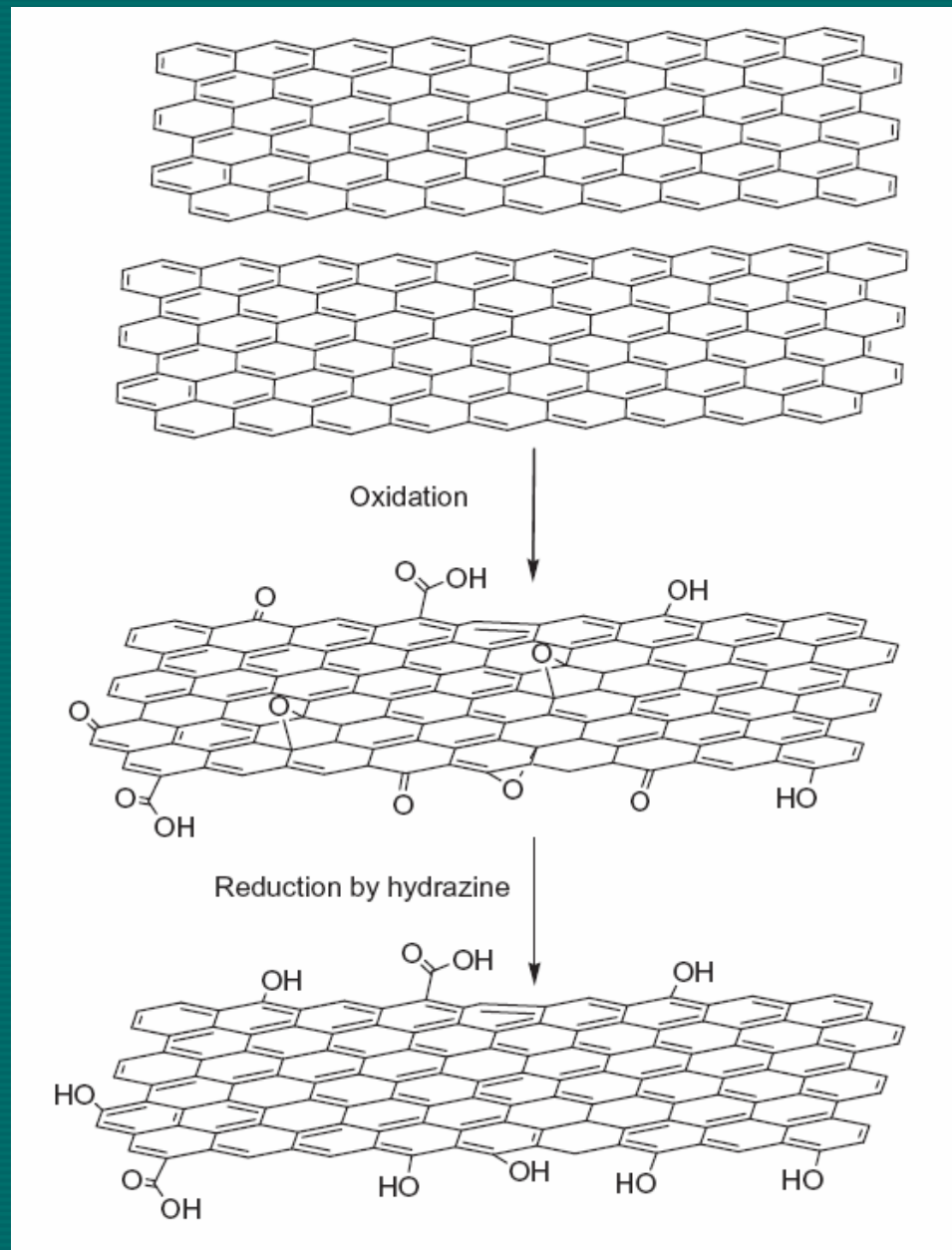
Electrolytic exfoliation

Valles, C.; et al *J Am Chem Soc* **2008**, *130*, (47), 15802-15804.

Tung, V. C.; et al *Nat Nano* **2009**, *4*, (1), 25-29.

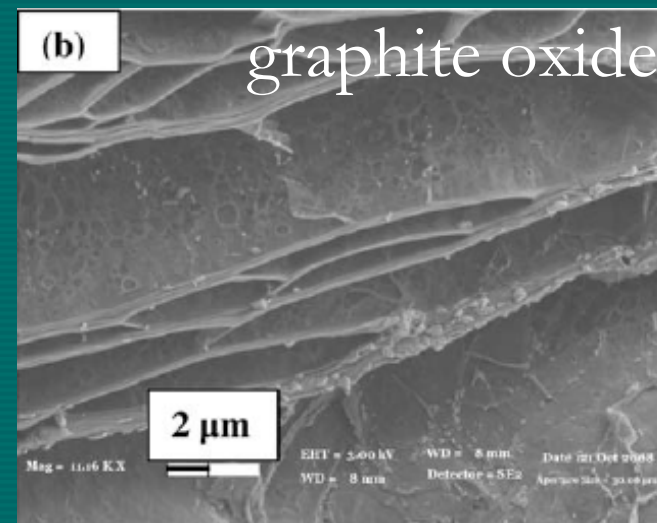
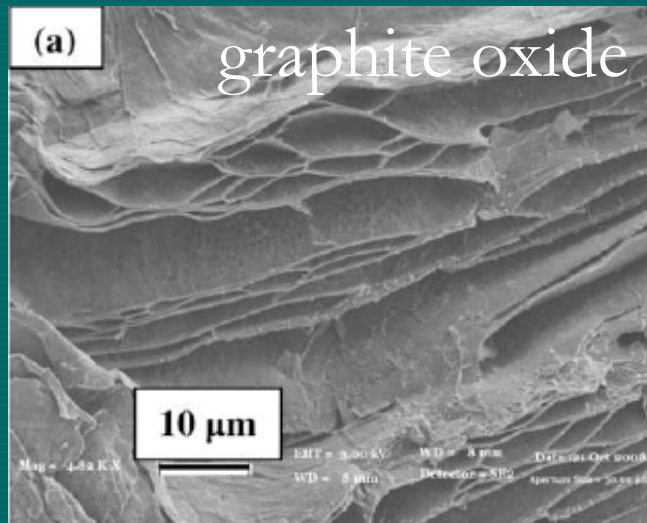
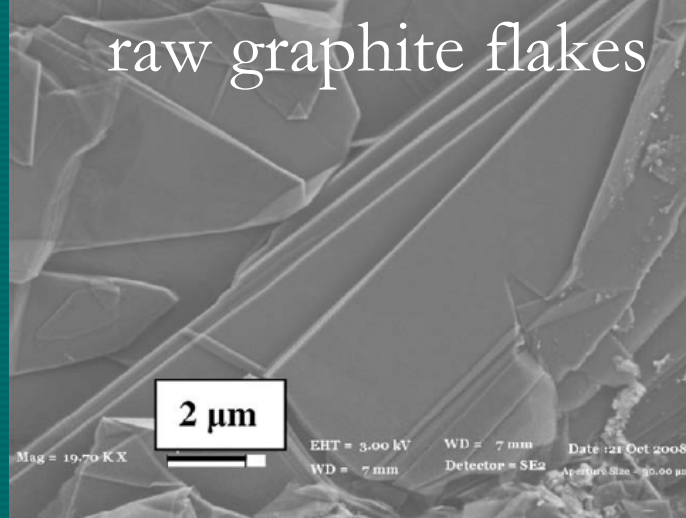
Wang, G.; et al *Carbon* **2009**, *47*, 3242-3246.

Su et al., *ACS Nano*, 2011, 5 (3), pp 2332-2339



Oxidation of graphite to graphene oxide and reduction to reduced graphene oxide

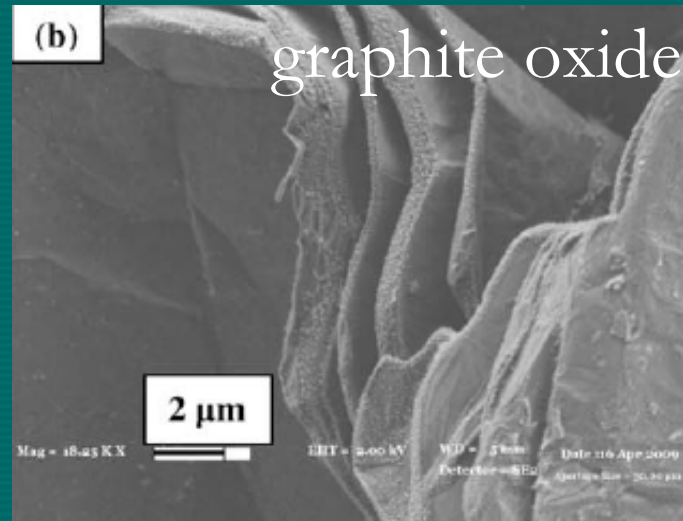
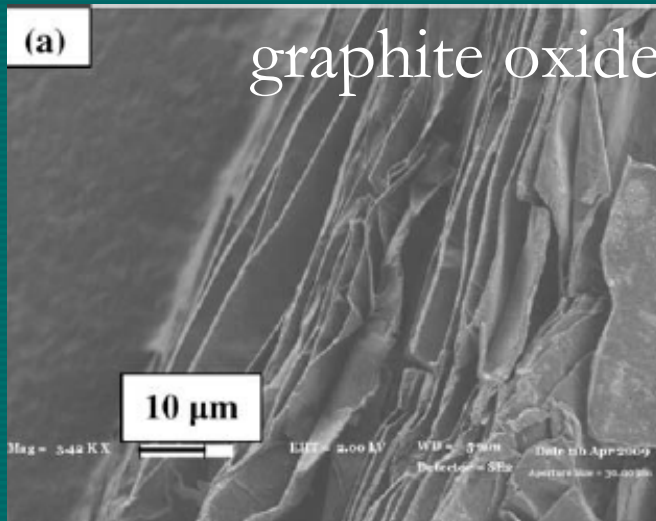
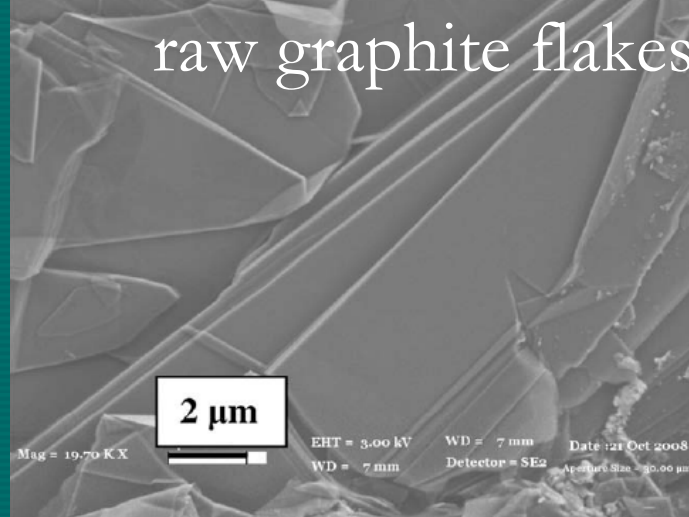
raw graphite flakes



Exfoliation of graphite flakes by chemical oxidation using 1 g of acetic anhydride, 6.2 g of Conc H_2SO_4 and 0.6 g $K_2Cr_2O_7$

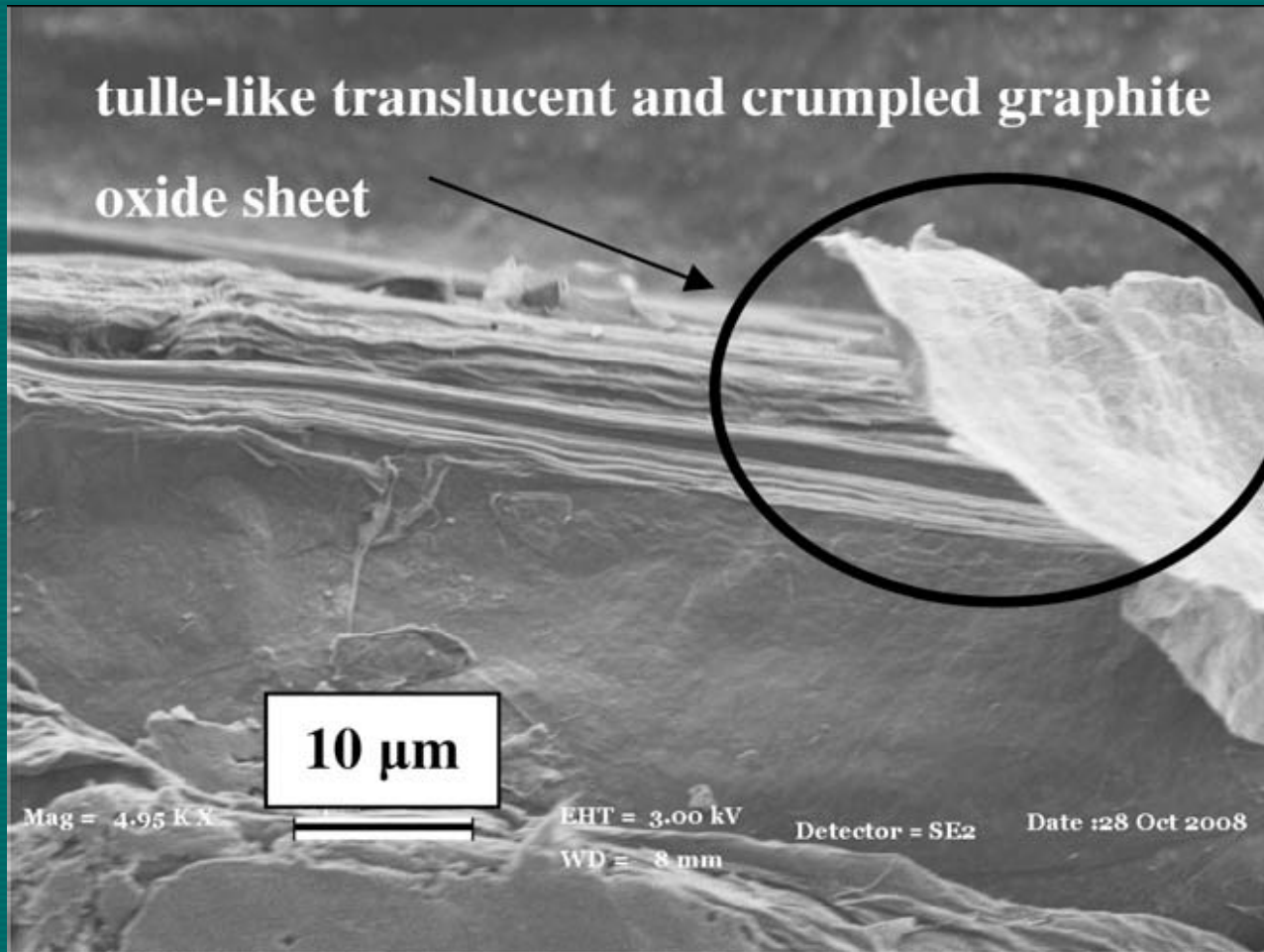
Source: *Saner et al., Fuel, 89 (2010) 1903-1910*

raw graphite flakes



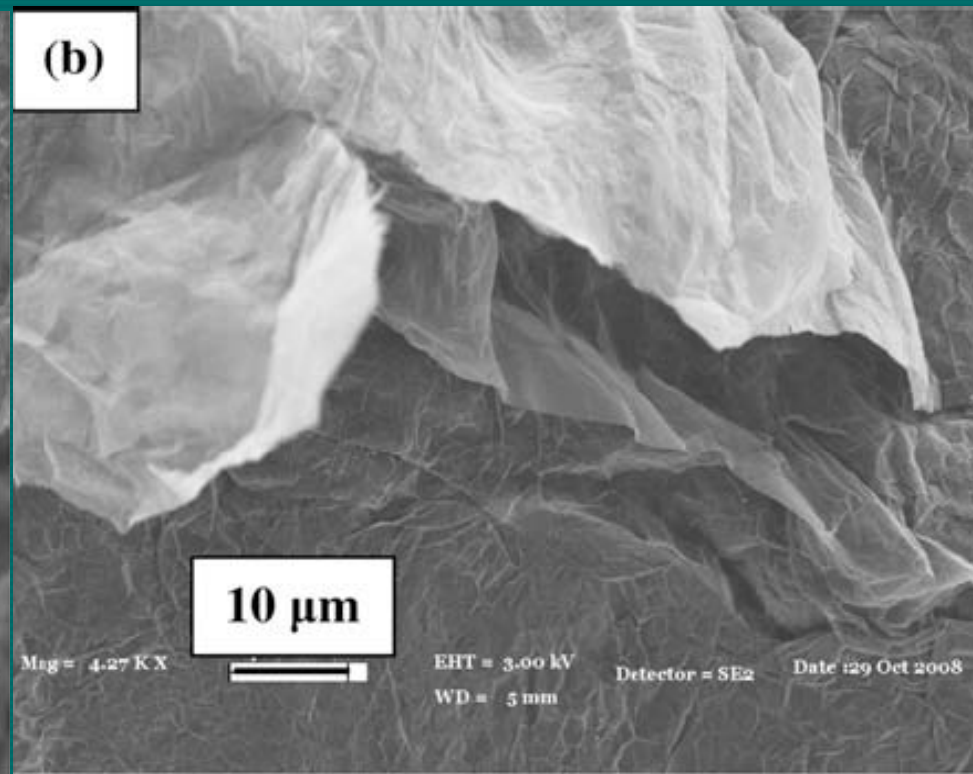
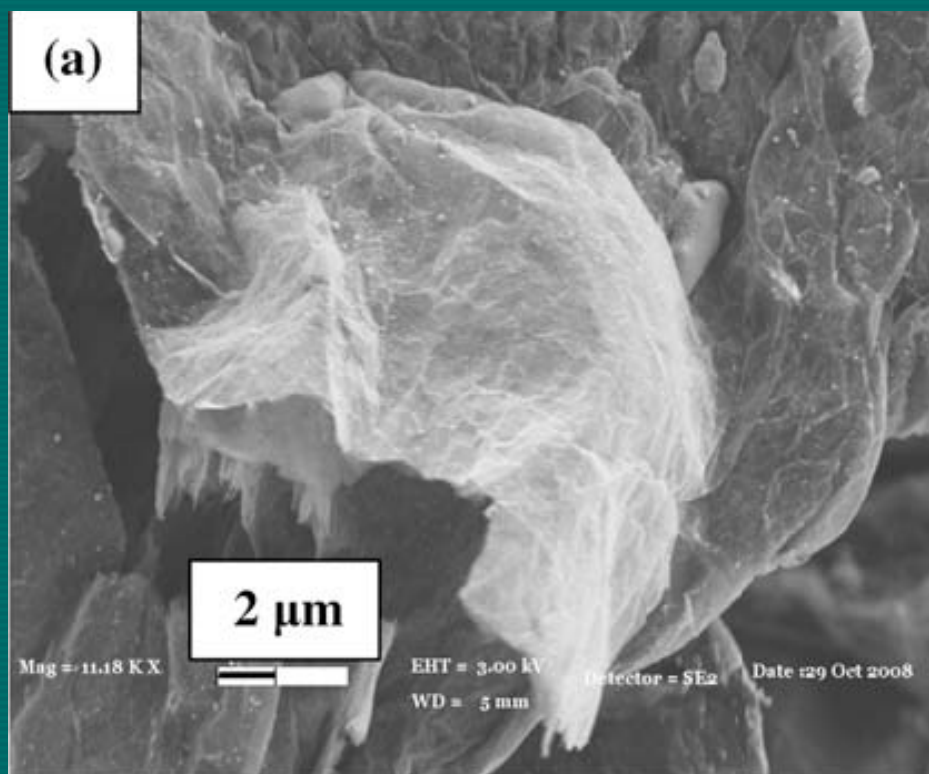
Exfoliation of graphite flakes by chemical oxidation using 1 g of acetic anhydride, 55 g of Conc H_2SO_4 and 2.1 g $\text{K}_2\text{Cr}_2\text{O}_7$

Source: *Saner et al., Fuel, 89 (2010) 1903-1910*

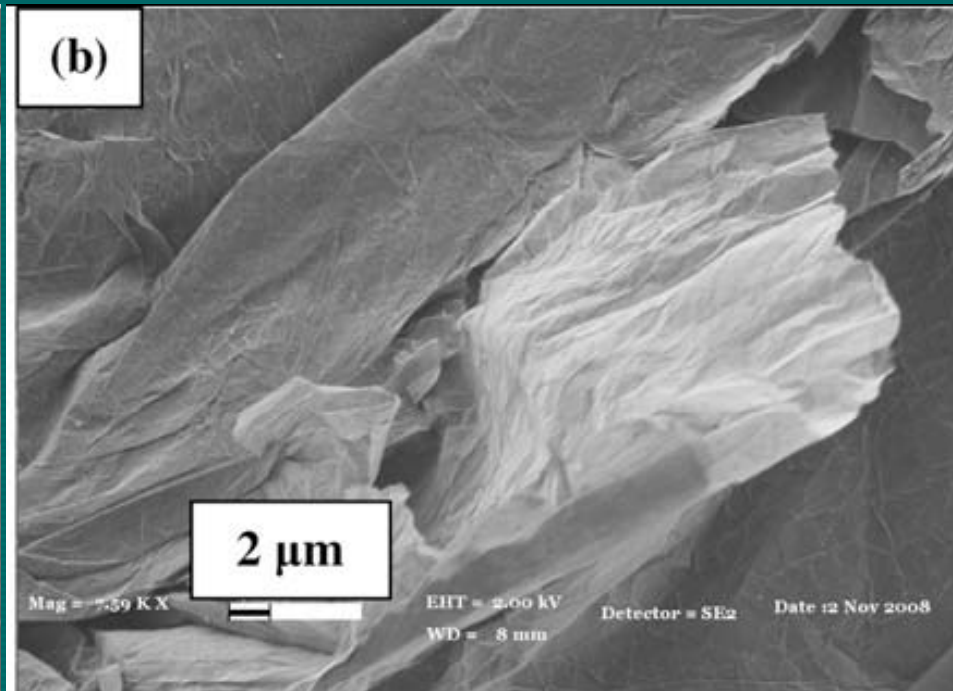
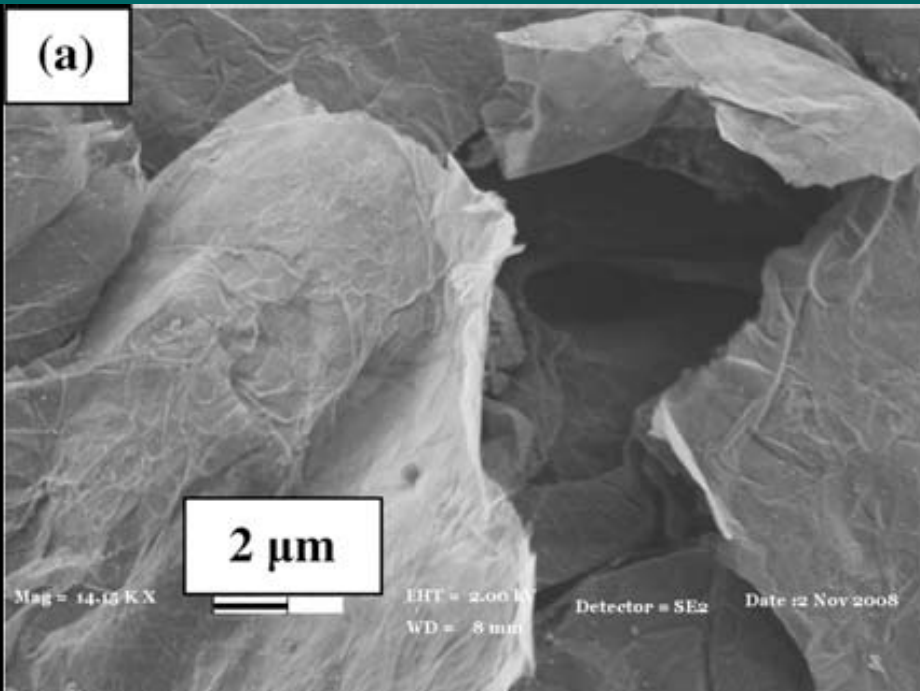


SEM of GO chemically oxidized using 1 g of acetic anhydride, 6.2 g of Conc H_2SO_4 and 0.6 g $\text{K}_2\text{Cr}_2\text{O}_7$ followed by sonication for 1 h at RT

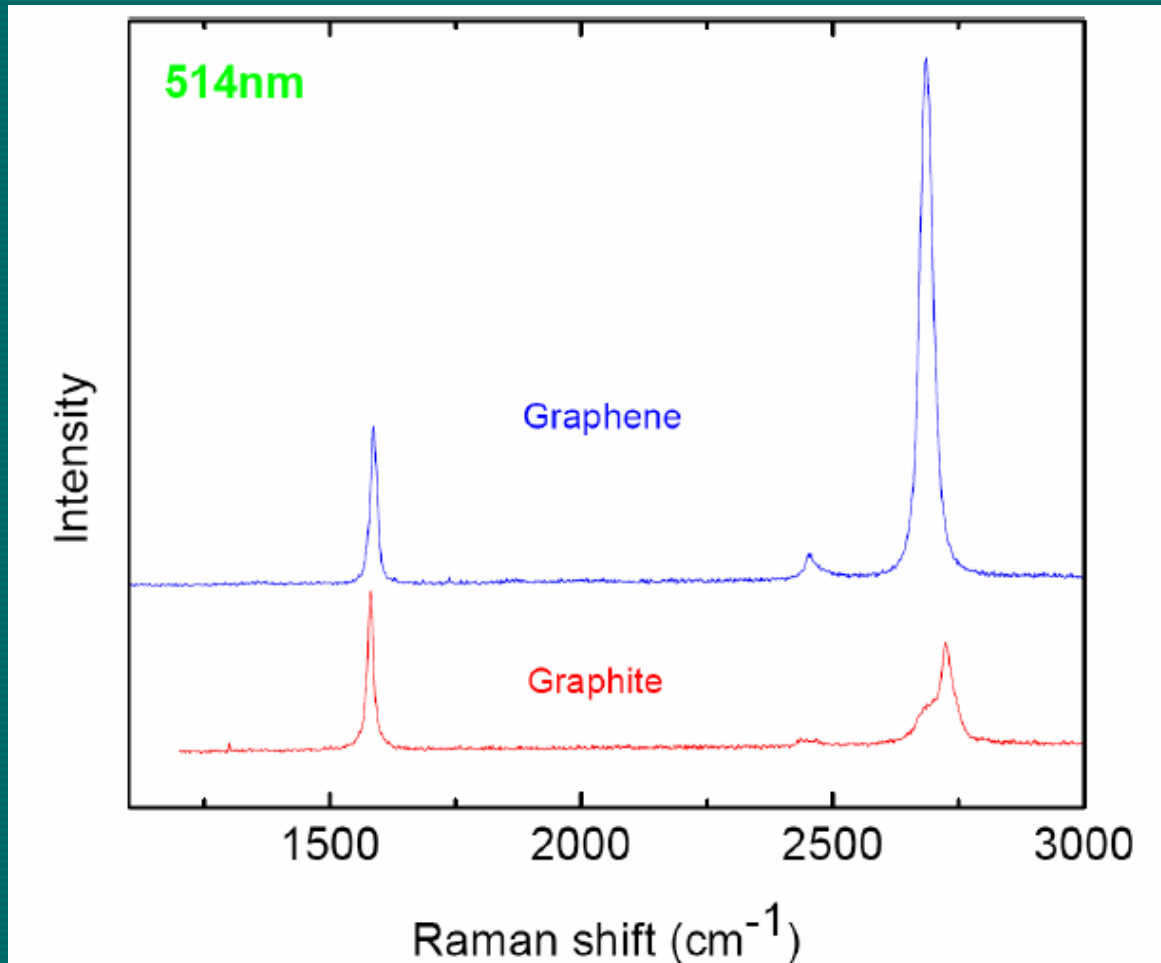
Source: *Saner et al., Fuel, 89 (2010) 1903-1910*



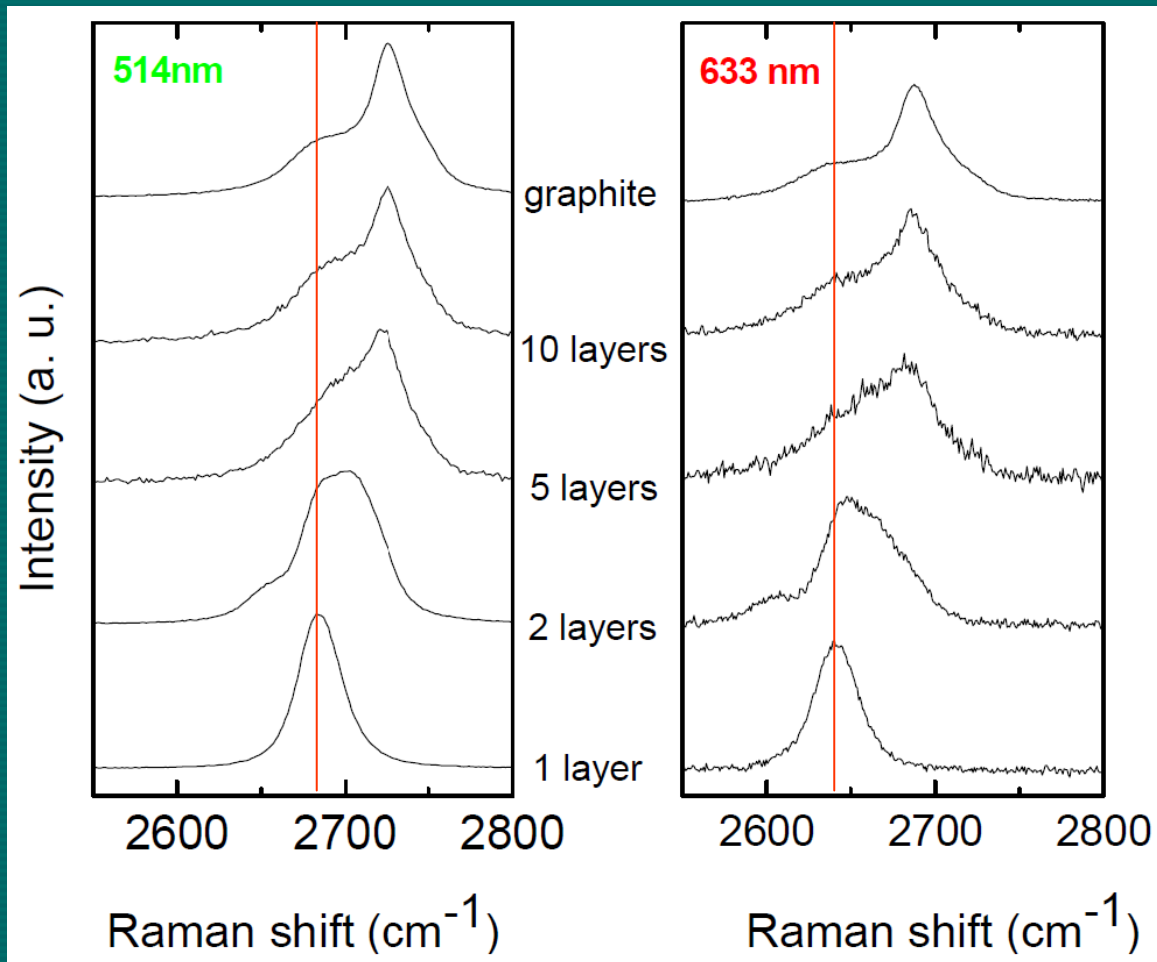
SEM of expanded GO chemically oxidized using 1 g of acetic anhydride, 6.2 g of Conc H_2SO_4 and 0.6 g $\text{K}_2\text{Cr}_2\text{O}_7$ followed by sonication for 1 h at RT and thermal exfoliation at $900\text{ }^\circ\text{C}$ for 15 min.



SEM images of graphene like nanosheets



The Raman signatures for graphene and graphite employing a 514 nm laser wavelength in the Raman spectrometer



Raman spectra recorded at 514 nm and 633 nm laser wavelengths excitation for different number of graphene layers and graphite

Graphene: *Will it Change the Way We Live?*

Some interesting applications

Graphene Materials and Applications



Flexible/Transparent Displays/Touch Panels

Transparent Electrodes

Printable Inks



Printed Electronics, EMI shields

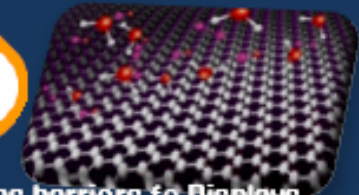
Large-Scale CVD Graphene + Graphene Nanoplatelet Composites

Semi-conductors

Gas Barriers



Ultrafast Transistors, RFIC, Photo/Bio/Gas Sensors



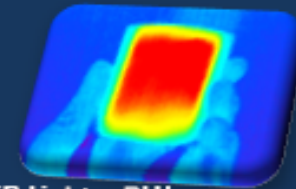
Gas barriers for Displays, Solar Cells

Energy Electrodes

Heat Dissipation



Super Cap./Solar Cells
Secondary Batteries
Fuel Cells



LED Lights, BLU
ECU, PC ...

Composites

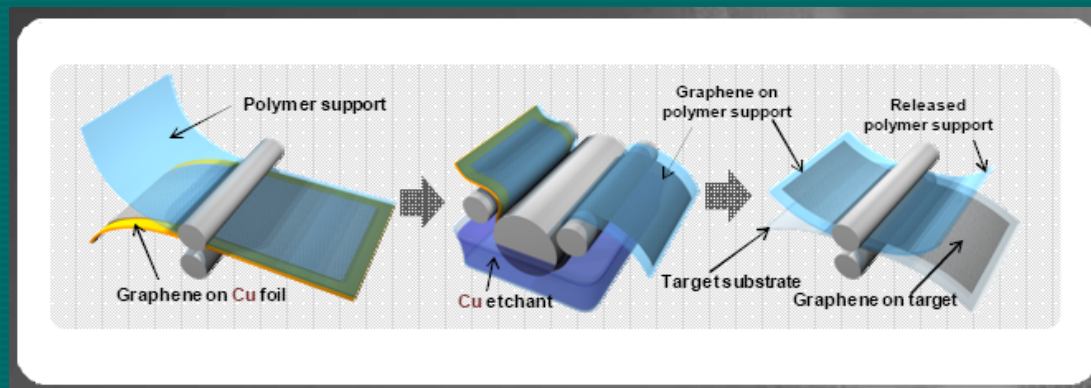


Cars,
Aerospace
Applications

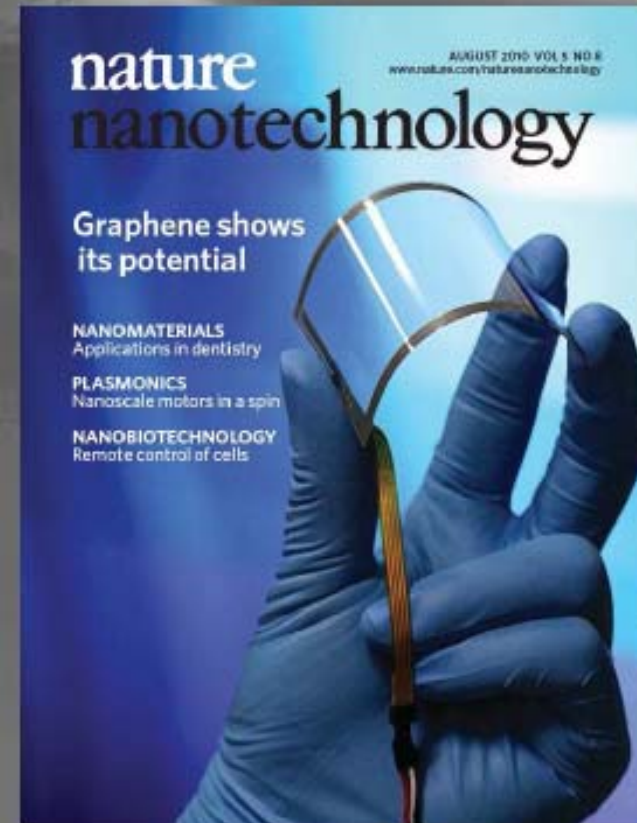
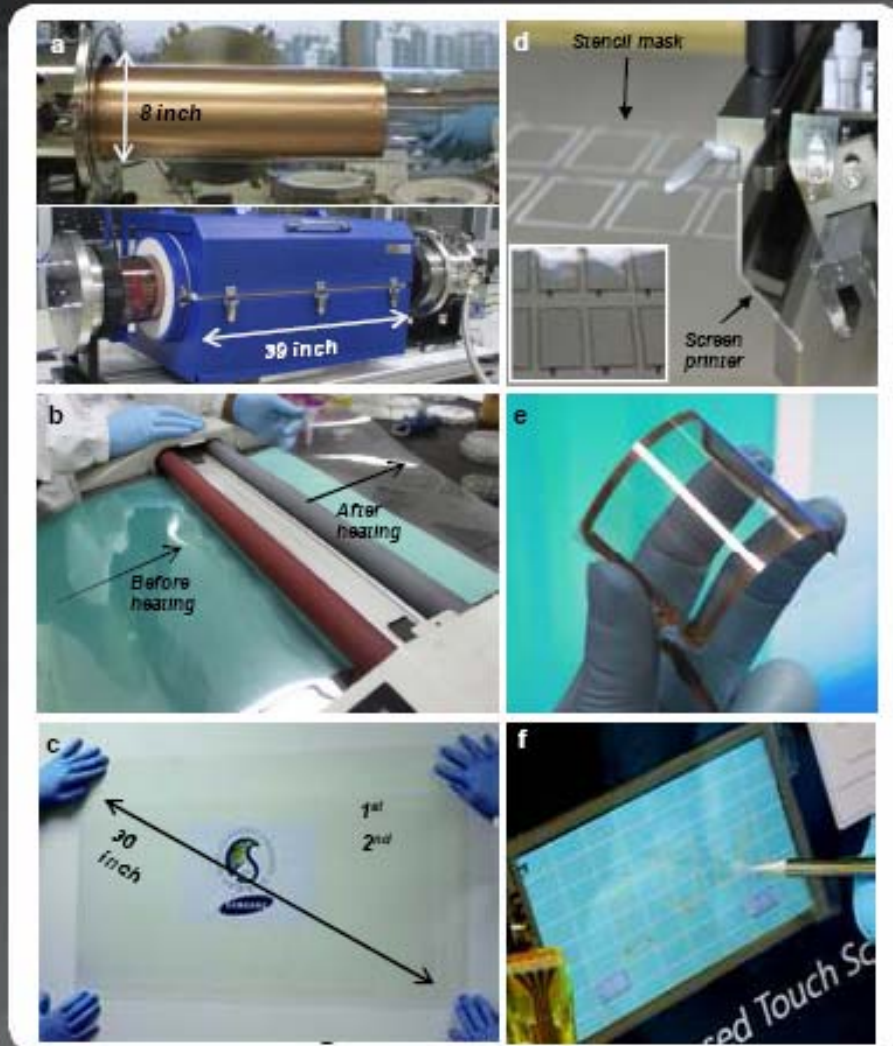
Images: Royal Swedish Academy

Market size: \$5-10 billion by 2013

Roll-to-Roll Production of Ultra-Large-Scale Graphene Films



Roll-to-Roll Production of Ultra-Large-Scale Graphene Films



S. Bae et al. (2010)

Courtesy: Byung Hee HONG, SKKU, South Korea

Flexible OLED



Transparent OLED



Graphene – A replacement for Si?

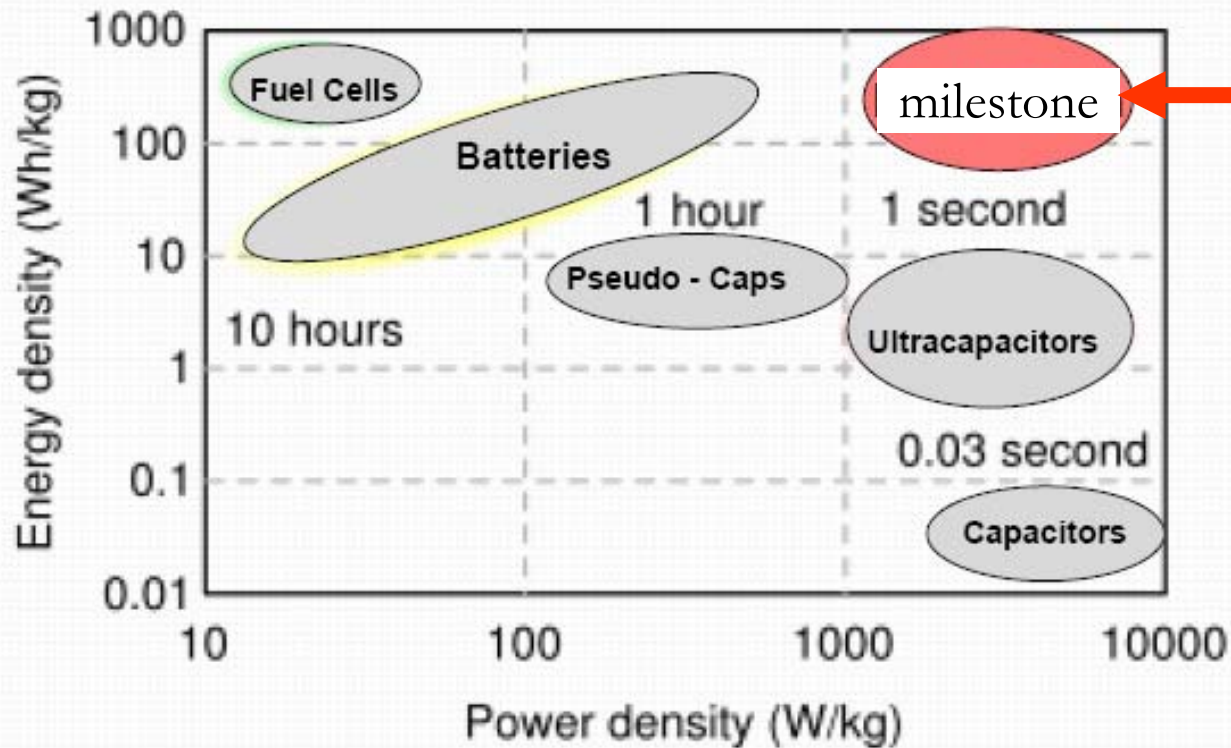
- Electronic chips – Silicon
 - Achieve more power and much smaller without increase of temperature
 - development of graphene transistors would run at much faster speeds and be able to ultimately battle the heat at a microscopic scale
 - IBM has already demonstrated a 100 GHz graphene-based transistor and stated that a 1THz processor is on the horizon
 - Graphene – Will it replace silicon in transistors?

Other interesting applications

- ✓ Optoelectronic devices
- ✓ Energy storage devices
- ✓ Dye-sensitized solar cells
- ✓ Photovoltaic devices
- ✓ Neural implants - Alzheimer's and Parkinson's disease
- ✓ Electrochemical sensors, Biosensors
- ✓ Sensors - oil exploration, TNT detection
- ✓ Chemically modified electrodes
- ✓ Thinnest solid lubricant
- ✓ Lubricant additive
- ✓ Graphene – TiO_2 composite - Photocatalyst

Role of graphene in energy storage devices

Energy Storage Today



Energy Density = The ability to store energy
Power Density = The ability to release energy

How graphene could/would help in reaching this mile stone?

Applications of graphene in energy storage devices

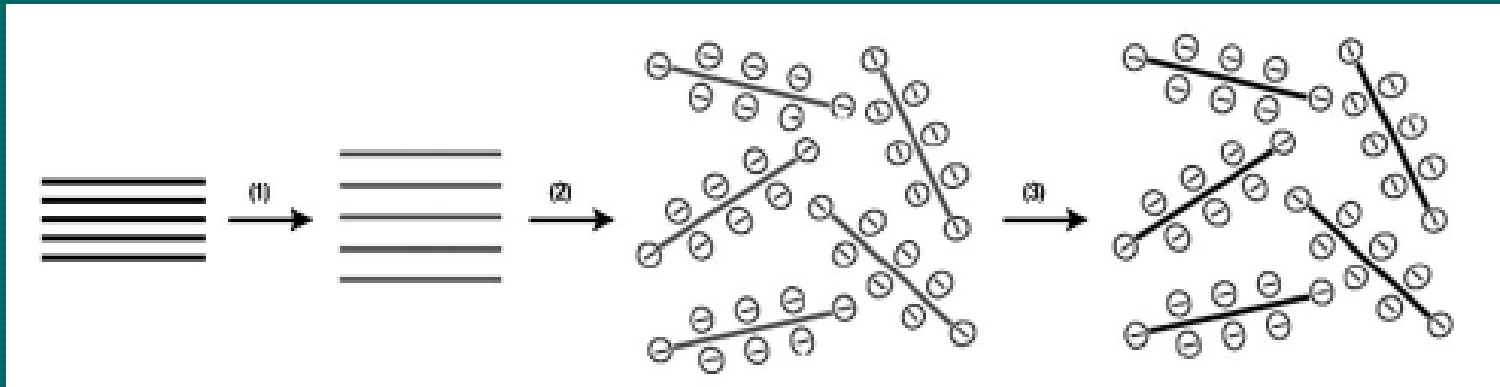
- ❖ Fuel cells
 - ✓ Catalyst support
 - ✓ Bipolar plate
- ❖ Supercapacitors
 - ❖ Electrode materials
- ❖ Li-ion Batteries
 - ✓ Anode active material
 - ✓ Hybrid active material
 - ✓ Electrode conductive additives
- ❖ Hydrogen storage material

Fuel cells

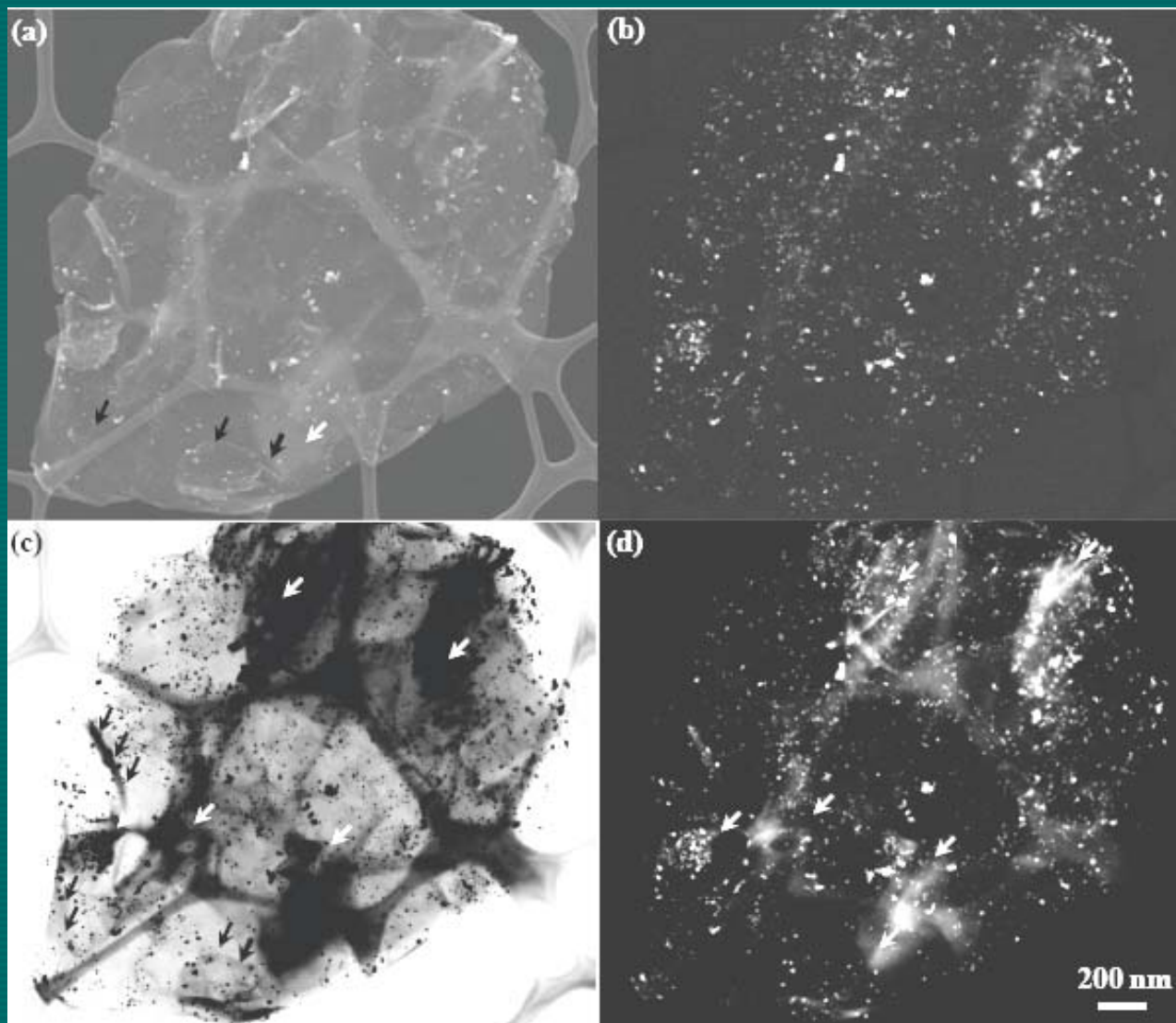
Role of Graphene in fuel cells

- Direct ethanol and direct methanol fuel cells –
 - 👍 high energy density
 - 👍 low pollutant emission
 - 👍 low operating temperature
 - 👍 ease of handling liquid ethanol/methanol fuel
 - 👎 low electrocatalytic activity of anode/cathode
 - 👎 high cost of platinum (Pt)-based catalysts
 - 👎 low DMFC power density
 - 👎 low CO toleration
 - 👎 short cycle life
- Graphene – good electrical conductivity and large specific surface area – how we can use it?

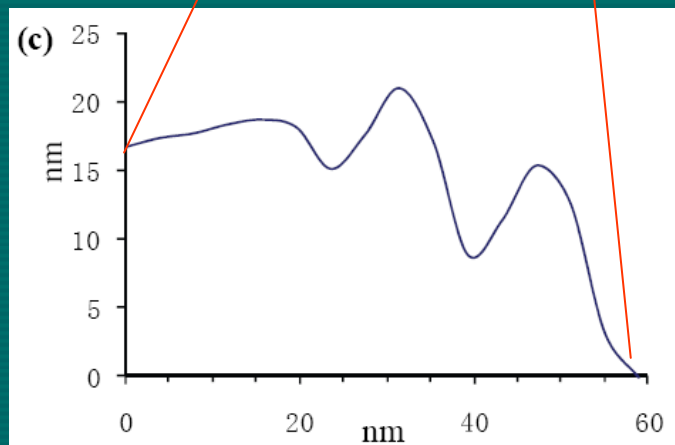
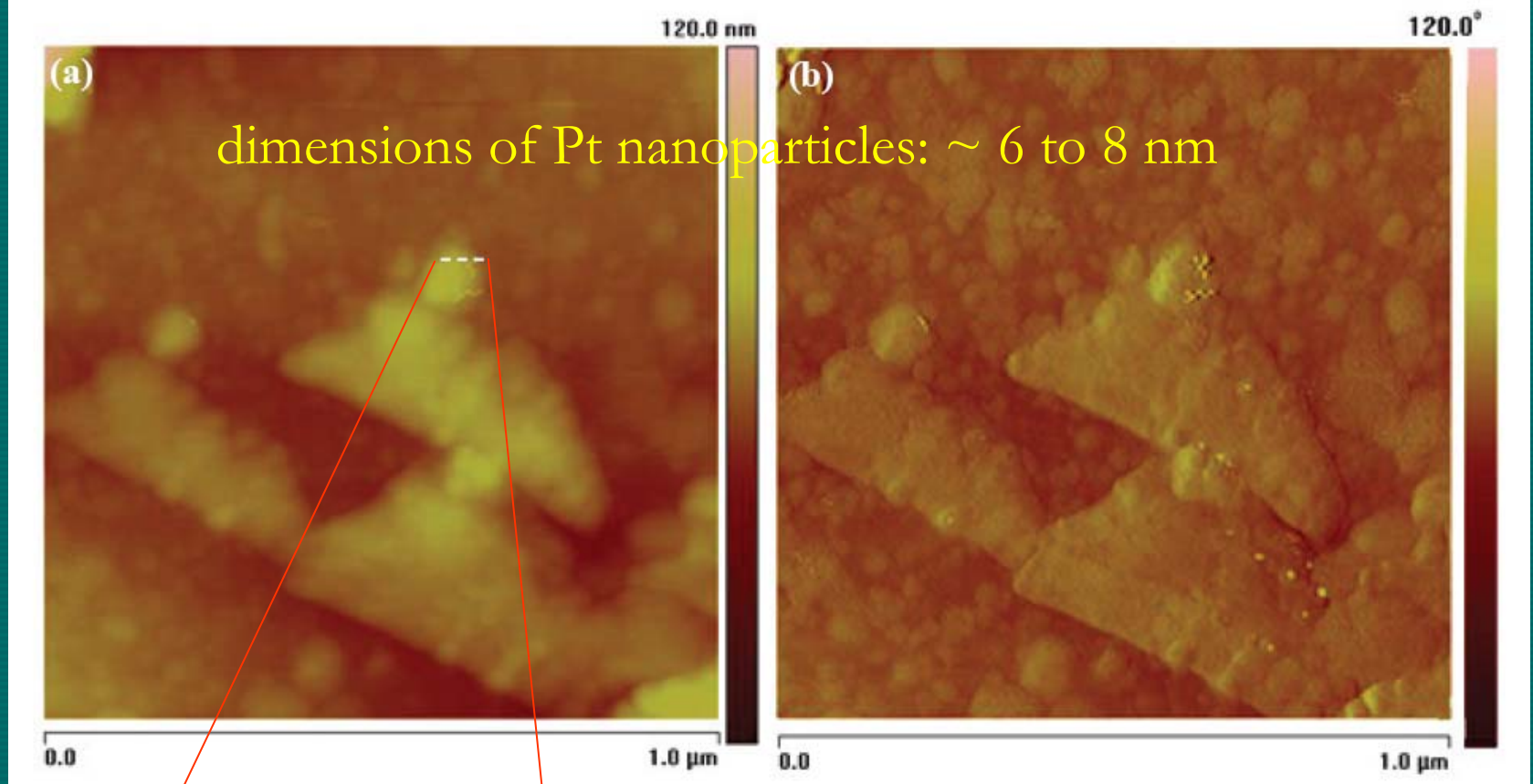
Schematic route for anchoring of Pt/Pt-Ru nanoparticles on graphene to prepare Pt/Pt-Ru-graphene nanocomposites



- ❖ Water-ethylene glycol is used as the medium
- ❖ oxidation of graphite to graphite oxide (GO);
- ❖ exfoliation of GO to graphene oxide sheets by sonication in water;
- ❖ attachment of Pt/Pt-Ru particles on the graphene oxide sheets;
- ❖ chemical reduction of graphene oxide sheets

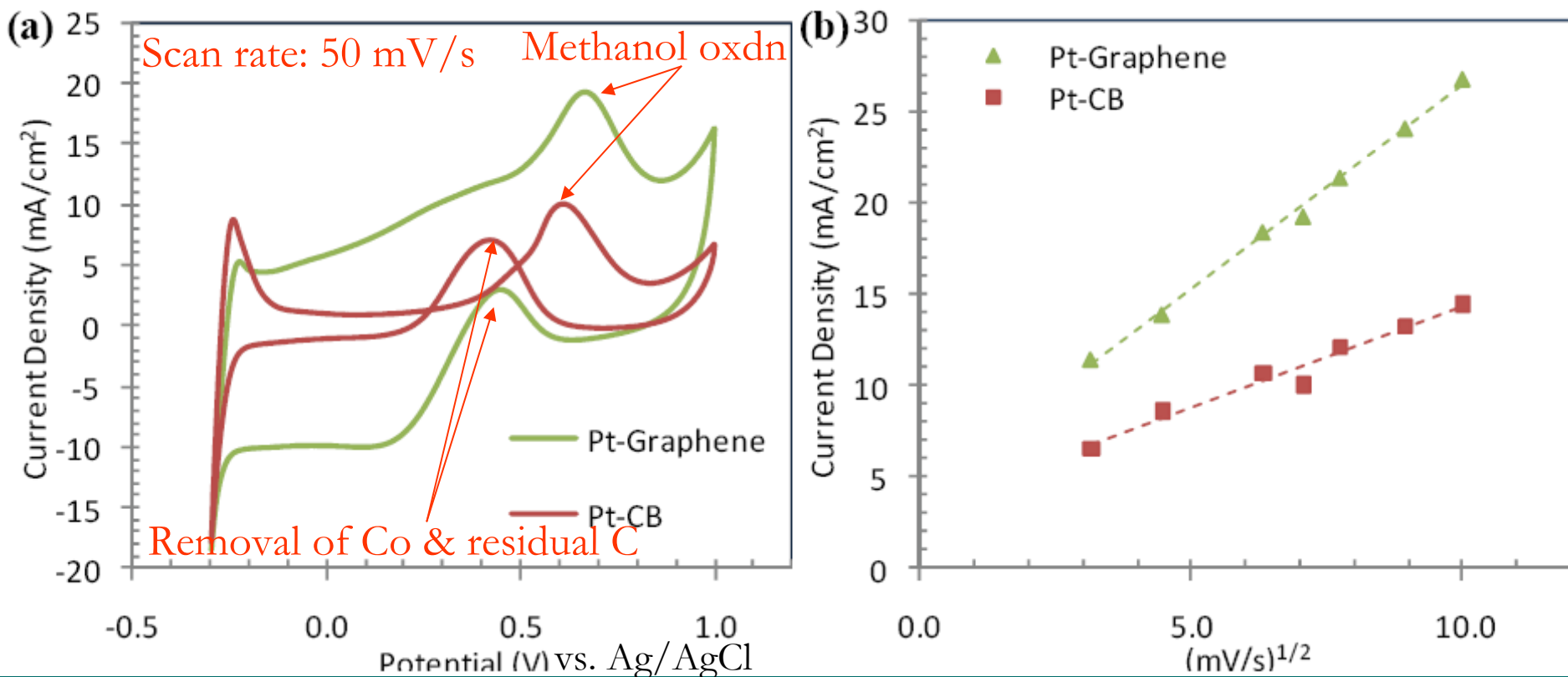


Pt nanoparticles supported on graphene sheets simultaneously imaged with (a) SE; (b) BSE (b); (c) STEM-BF; and (d) STEM-HAADF detectors



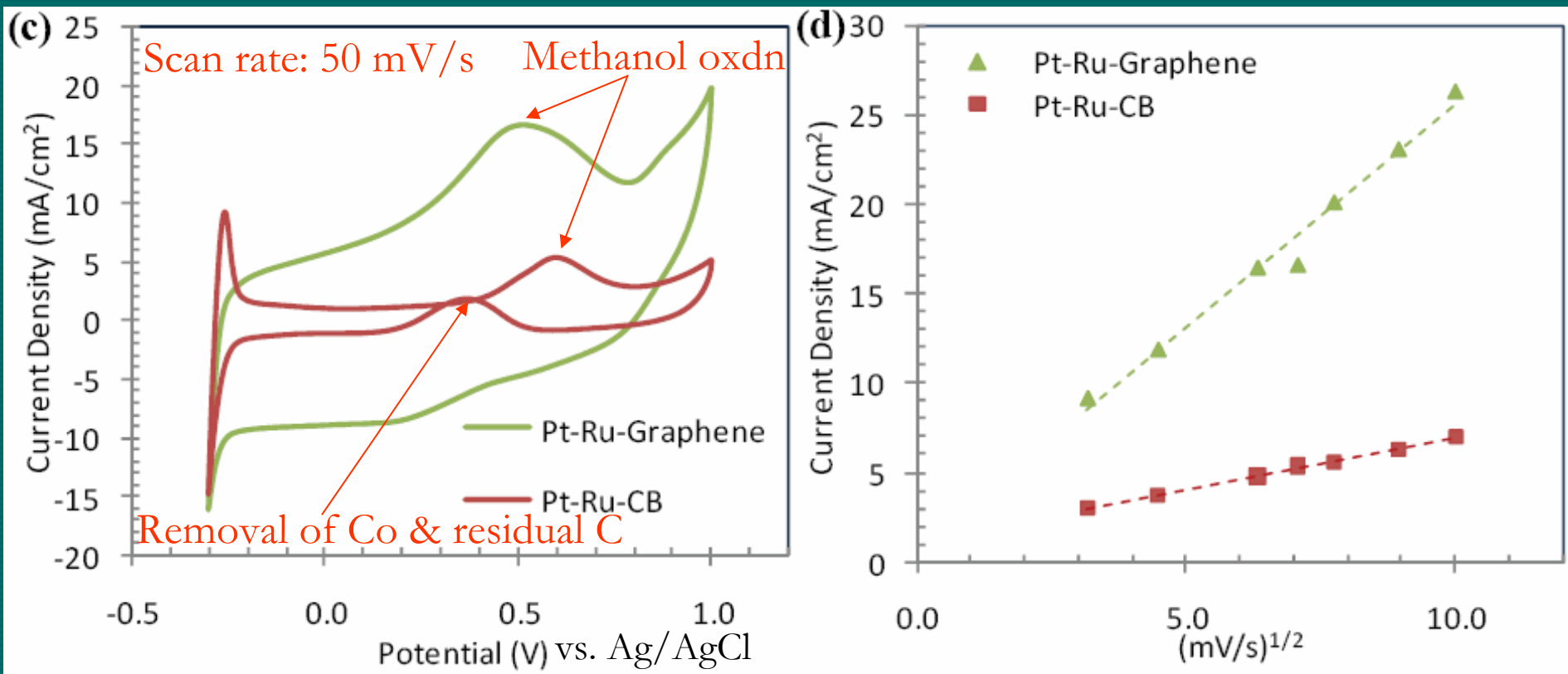
AFM topography (a) and phase (b) images of Pt nanoparticles supported on graphene sheets

Electrocatalytic activity of graphene and Vulcan XC-72R carbon black-supported Pt nanoparticles for methanol oxidation



CV's (5th): 1 M CH₃OH/0.5 M H₂SO₄ Peak current density vs. scan rate

Electrocatalytic activity of graphene and Vulcan XC-72R carbon black-supported Pt nanoparticles for methanol oxidation



CV's (5th): 1 M CH₃OH/0.5 M H₂SO₄ Peak current density vs. scan rate

Comparison of electrocatalytic activity of methanol oxidation on graphene and carbon black-supported Pt and Pt-Ru nanoparticles

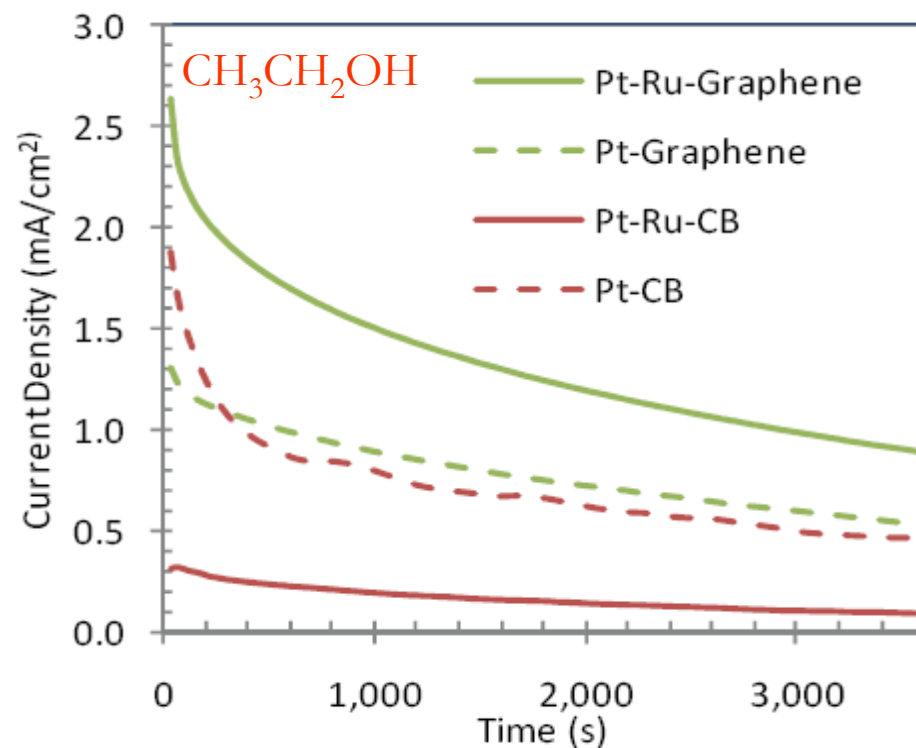
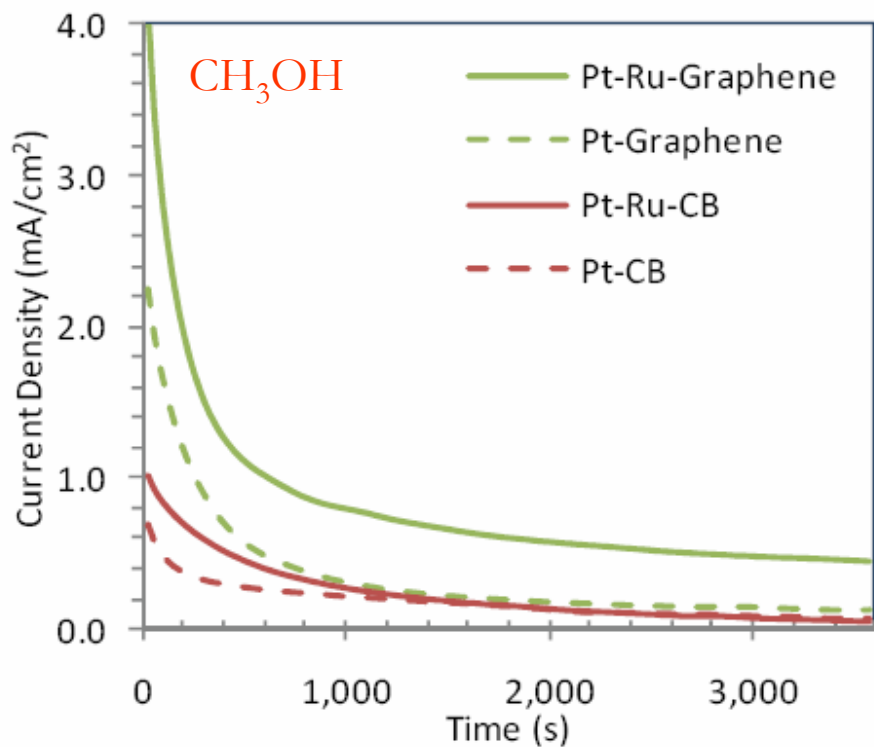
Electrode	Forward Sweep		Reverse Sweep		I_F/I_R Ratio
	E (V)	I_F (mA/cm ²)	E (V)	I_R (mA/cm ²)	
Pt-graphene	0.65	19.1	0.46	2.93	6.52
Pt-CB	0.59	9.76	0.43	7.01	1.39
Pt-Ru-graphene	0.50	16.5	-	-	-
Pt-Ru-CB	0.58	5.23	0.36	1.51	3.46

- ✓ Current in the forward sweep - directly proportional to the amount of methanol oxidized at the electrode
- ✓ Current in the reverse sweep - removal of CO and other residual carbon species formed on the electrode in the forward sweep.
- ✓ I_F/I_R -tolerance of Pt/Pt-Ru catalysts to CO and other carbonaceous species – retained even after 50 cycles – good stability
- ✓ Graphene-supported Pt/Pt-Ru nanoparticles - higher activity for methanol oxidation and a better tolerance to CO

Comparison of electrocatalytic activity of methanol oxidation on graphene and carbon black-supported Pt and Pt-Ru nanoparticles

Electrode	Forward Sweep		Reverse Sweep		I _F /I _R Ratio
	E (V)	I _F (mA/cm ²)	E (V)	I _R (mA/cm ²)	
Pt-graphene	0.72	16.2	0.48	4.43	3.66
Pt-CB	0.65	13.8	0.46	15.3	0.90
Pt-Ru-graphene	0.66	18.1	0.46	5.23	3.46
Pt-Ru-CB	0.64	7.50	0.36	4.93	1.52

- ✓ IF/IR -tolerance of Pt/Pt-Ru catalysts to CO and other carbonaceous species – good stability
- ✓ Graphene-supported Pt/Pt-Ru nanoparticles - higher activity for ethanol oxidation and a better tolerance to CO



Chronoamperometric curves for graphene- and carbon black-supported Pt and Pt-Ru nanoparticles in 1 M CH₃OH or CH₃CH₂OH/ 0.5 M H₂SO₄. The potential was 0.4 V vs. Ag/AgCl.

Current status and future prospects

- As catalyst supports, graphene can more effectively enhance the electrocatalytic activity of Pt and Pt-Ru nanoparticles for the oxidation of methanol and ethanol into CO_2 .
- A next step will be the exploration of a facile and efficient method to synthesize graphene-supported Pt and Pt-Ru nanoparticles with controlled properties:
 - 👉 formation of nanoparticles on defined locations
 - 👉 the density of nanoparticles located on graphene sheets
 - 👉 the size of nanoparticles, and the size and thickness of graphene sheets

Role of graphene in fuel cells

- Platinum - one of the best catalysts for the electrochemical oxygen reduction reaction (ORR) – Fuel cells
 - 👉 Expensive
 - 👉 Exhibit time-dependent drift due to the poisoning
 - 👉 deactivation of the Pt surface with carbon monoxide
- Nitrogen-doped graphene - metal-free electrode
 - 👉 Offers enhanced electro-catalytic activity
 - 👉 long-term operation stability
 - 👉 tolerance to crossover effect than Pt for ORR oxygen reduction via a four-electron pathway in alkaline solutions producing water as a product

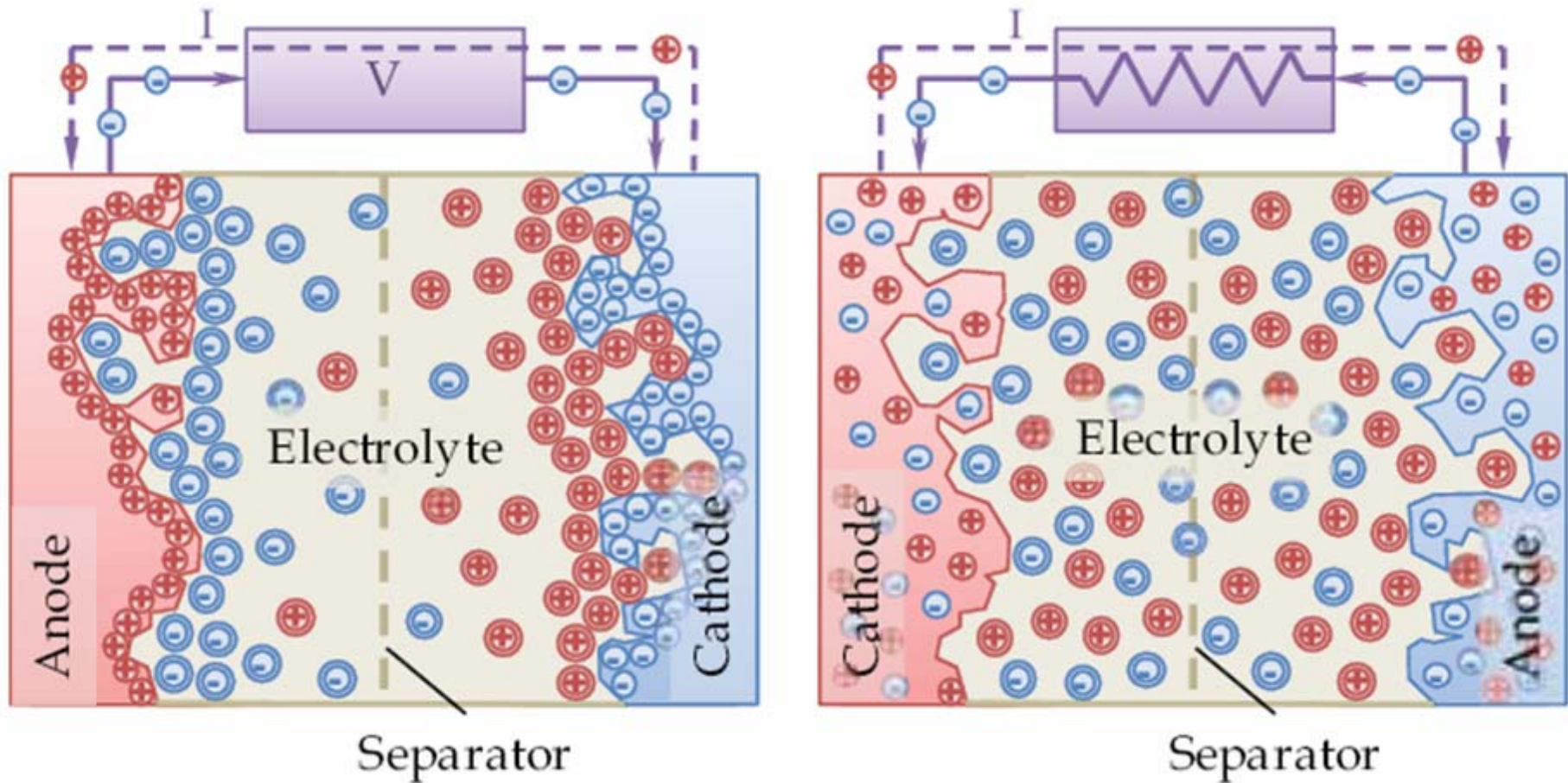
Role of graphene in fuel cells

- In proton exchange membrane fuel cells (PEMFCs) Pt based electro-catalysts are widely used as anode and cathode electrocatalysts for hydrogen oxidation and for ORR, respectively.
- Graphene nanosheets (GNS) and nitrogen doped-GNSs can serve as the catalyst support for Pt nanoparticles for ORRs in PEMFCs.
- Nitrogen doping
 - ❖ creates defects, which could act as anchoring sites for the deposition of Pt nanoparticles
 - ❖ increase the electrical conductivity
 - ❖ improve carbon-catalyst binding

Supercapacitors

Supercapacitors – A preamble

- ❖ There has been an ever increasing demand for environmentally friendly high-performance energy-storage systems
- ❖ Supercapacitors - high power capability, long cyclic life (> 100 000 cycles), low maintenance, and fast dynamics of charge propagation
- ❖ Application in portable electronic devices, electric vehicles and hybrid electric vehicles (HEVs) – Suitable?
- ❖ Most of the commercially available supercapacitor products have a specific energy density < 10 Wh/kg, which is 3 to 15 times lower than batteries
- ❖ How to increase the energy performance of supercapacitors to be close to or even beyond that of batteries?



Schematic diagrams of an electrochemical double layer type capacitor charged (left) and discharged (right) states

Cathode and Anode: AC; Electrolyte: H_2SO_4

Mechanism of energy storage in supercapacitors

- The mechanism by which a supercapacitor stores energy is, in principal, based on two types of capacitive behaviors:
 - ❖ the electrical double layer (EDL) capacitance from pure electrostatic charge accumulation at the electrode-electrolyte interface and the
 - ❖ pseudo-capacitance due to fast and reversible surface redox processes at characteristic potentials
- These two mechanisms can function simultaneously, depending on the nature of the electrode material

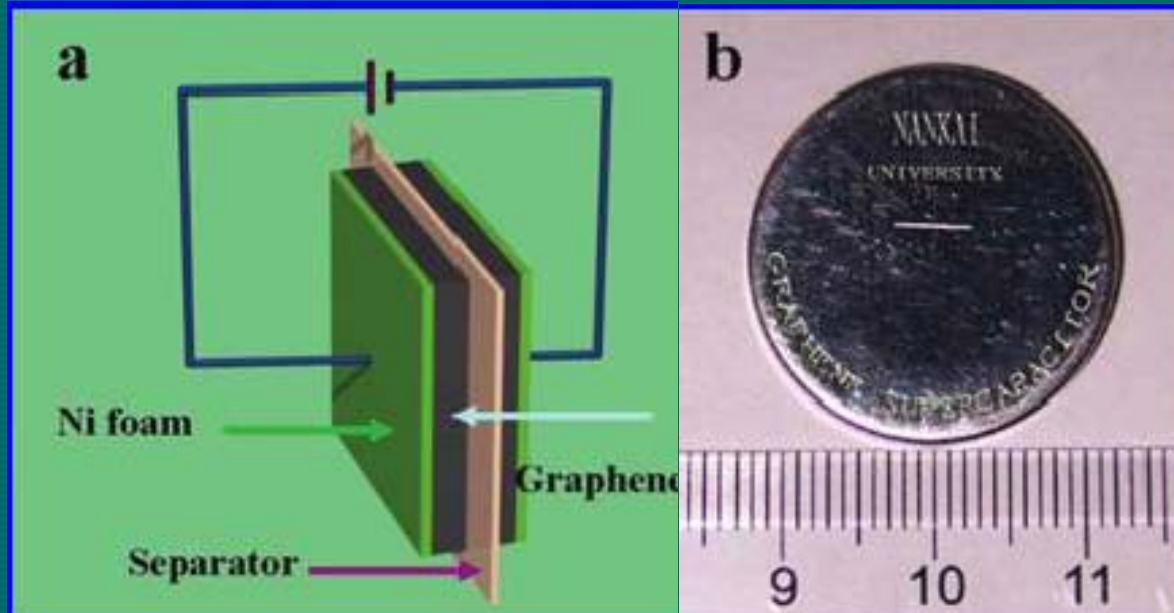
Important requirements of electrode materials for supercapacitors

- ✓ Good electrical conductivity
- ✓ High surface area
- ✓ Chemical and mechanical stability
- ❖ Currently used electrode materials
 - Activated carbon – low cost, easy process
 - Capacitance: 50-130 F/g
 - Pores are too small for electrolyte entry
 - Other forms of carbon
 - Carbon nanotube
 - Transition metal oxides – RuO_2 , MnO_2 , NiO
 - Conducting polymers – PANI, PPY,

Supercapacitor

- The performance of a supercapacitor is evaluated on the basis of the following criteria:
 - ♥ power density substantially greater than batteries with acceptably high energy densities ($> 10 \text{ Wh/kg}$)
 - ♥ an excellent cycle ability (> 100 times of batteries)
 - ♥ fast charge-discharge processes (within seconds)
 - ♥ low self-discharging
 - ♥ safe operation; and
 - ♥ low cost

Graphene based materials for supercapacitors



Cathode and anode: Graphene + 10% PTFE

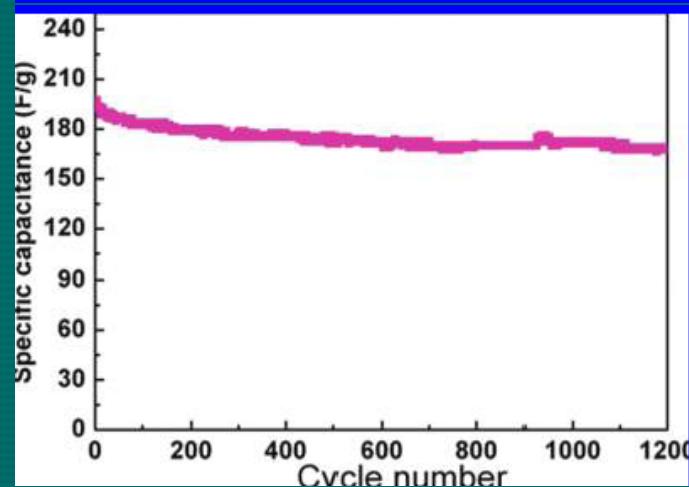
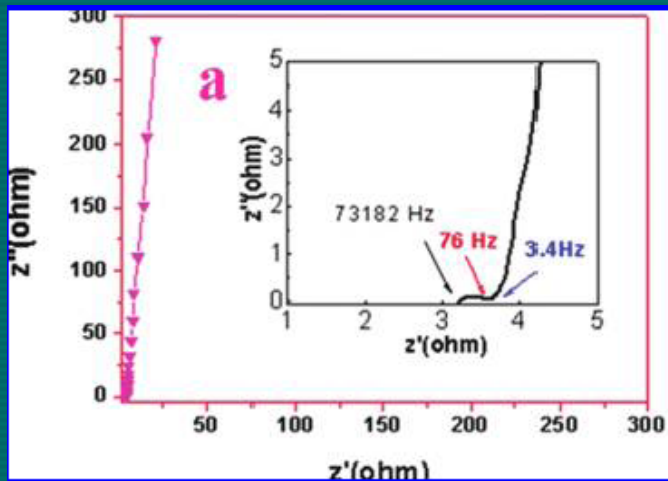
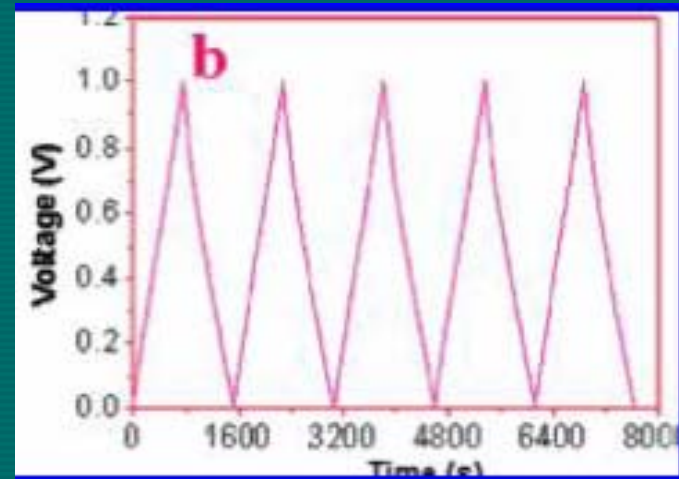
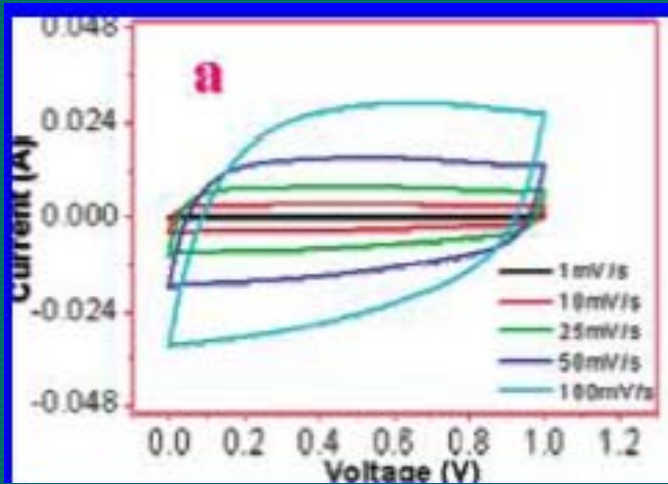
Electrolyte: 30% KOH

Separator: Polypropylene film

Current collectors: Ni foam

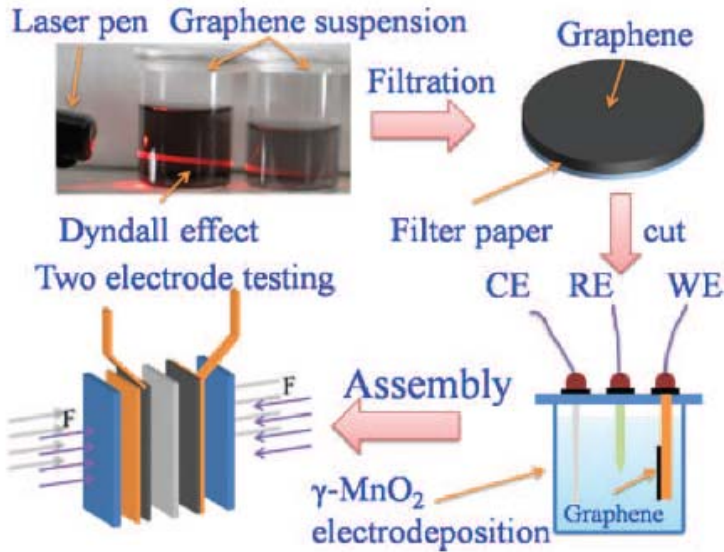
Source: Wang et al., *J. Phys. Chem. C* **2009**, *113*, 13103–13107

Electrochemical performance

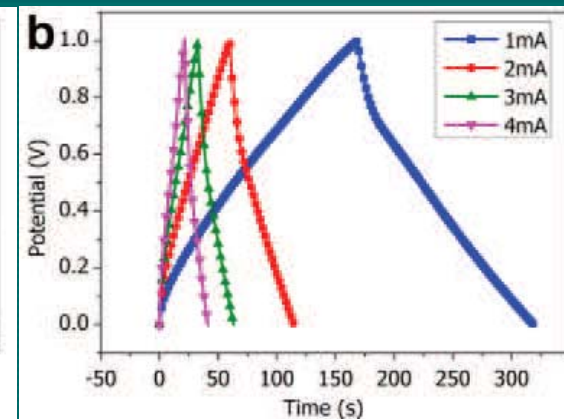
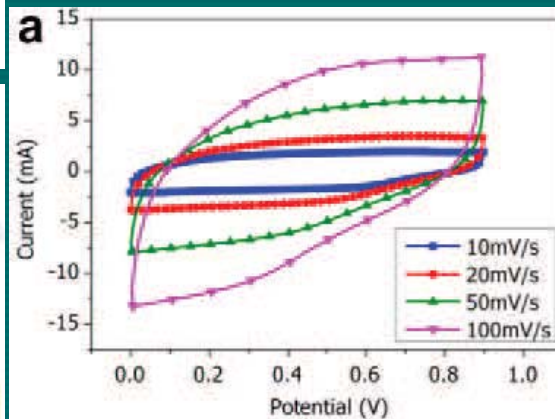
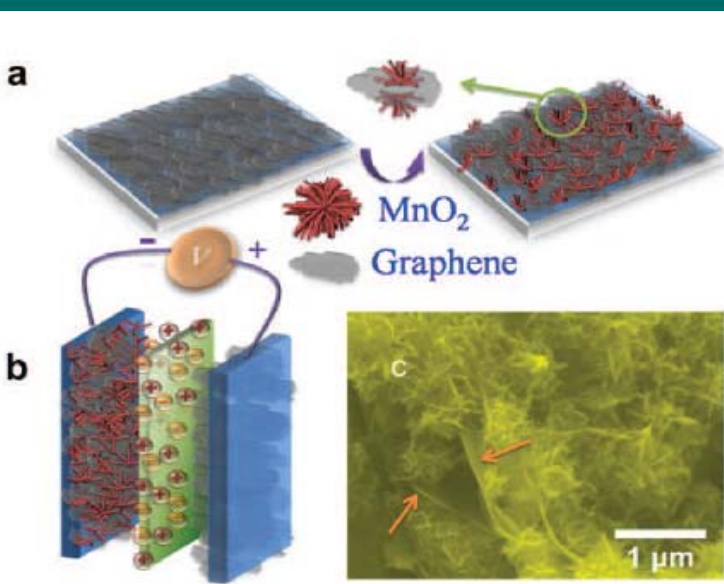


Specific capacitance of 205 F/g; Energy density of 28.5 Wh/kg;
Power density of 10 kW/kg

Graphene and nanostructured MnO₂ composite electrodes for supercapacitors



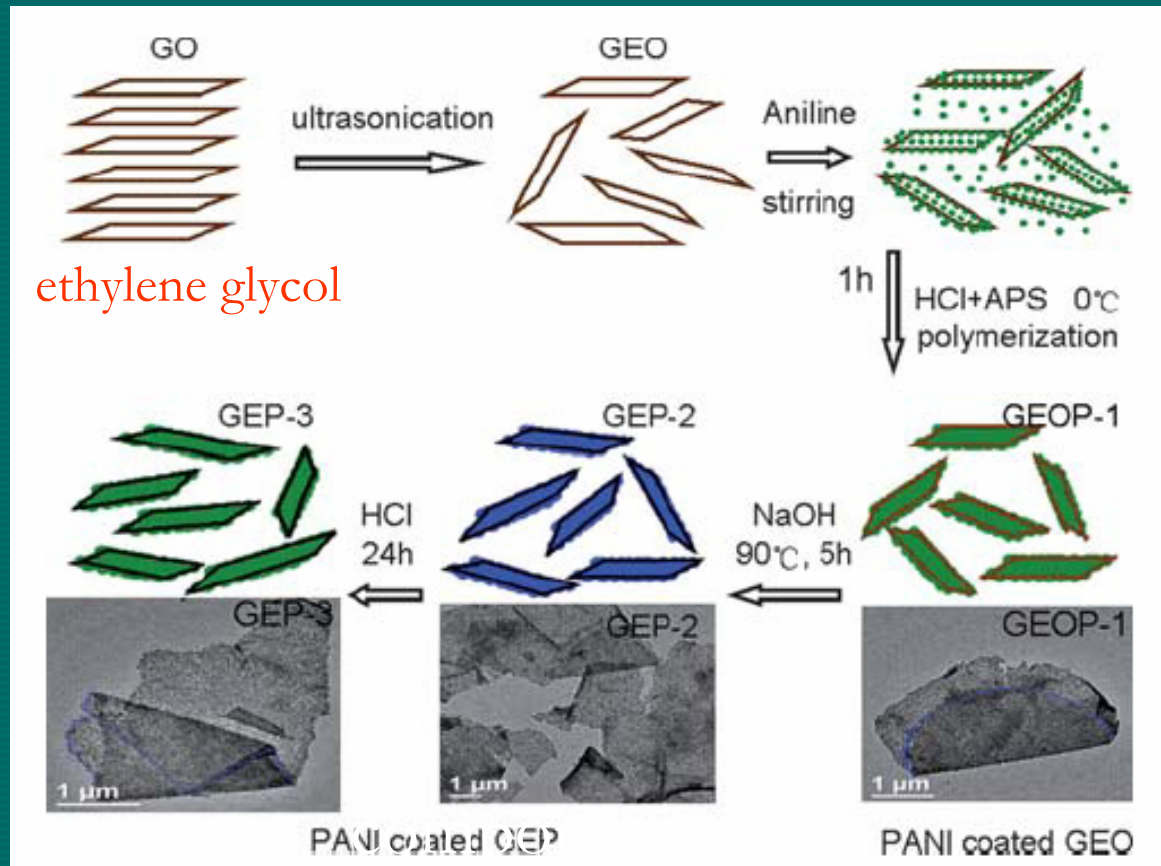
Anode: pure graphene;
Cathode: MnO₂-coated graphene
Electrolyte: 1 M KCl;
Separator: Polypropylene film
Current collector: high purity Ti



Excellent capacitive behavior & low contact resistance
Capacitance: 150 F/g; Max. storage energy: 5.2 Wh/kg

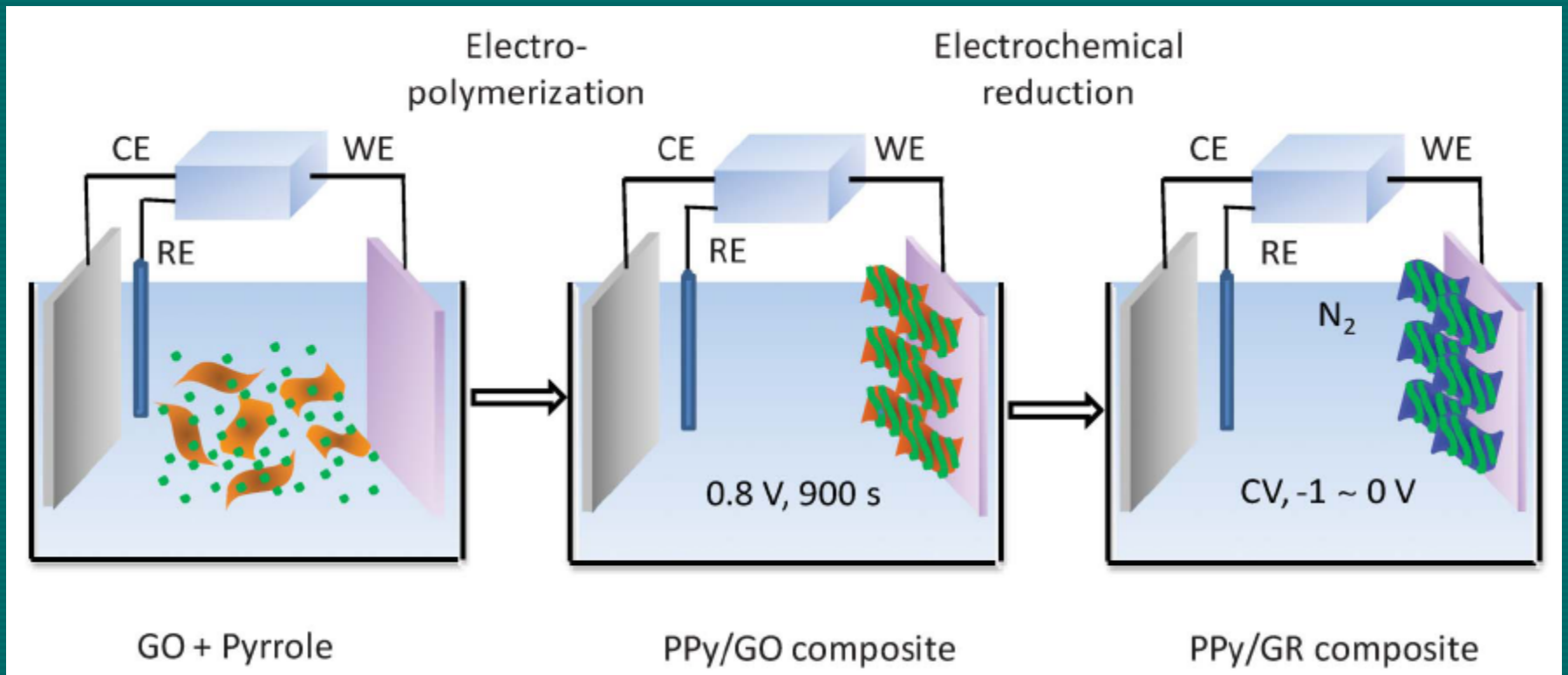
Source: Cheng et al., *Carbon*, 49 (2011) 2917

Graphene/PANI hybrid material for supercapacitors

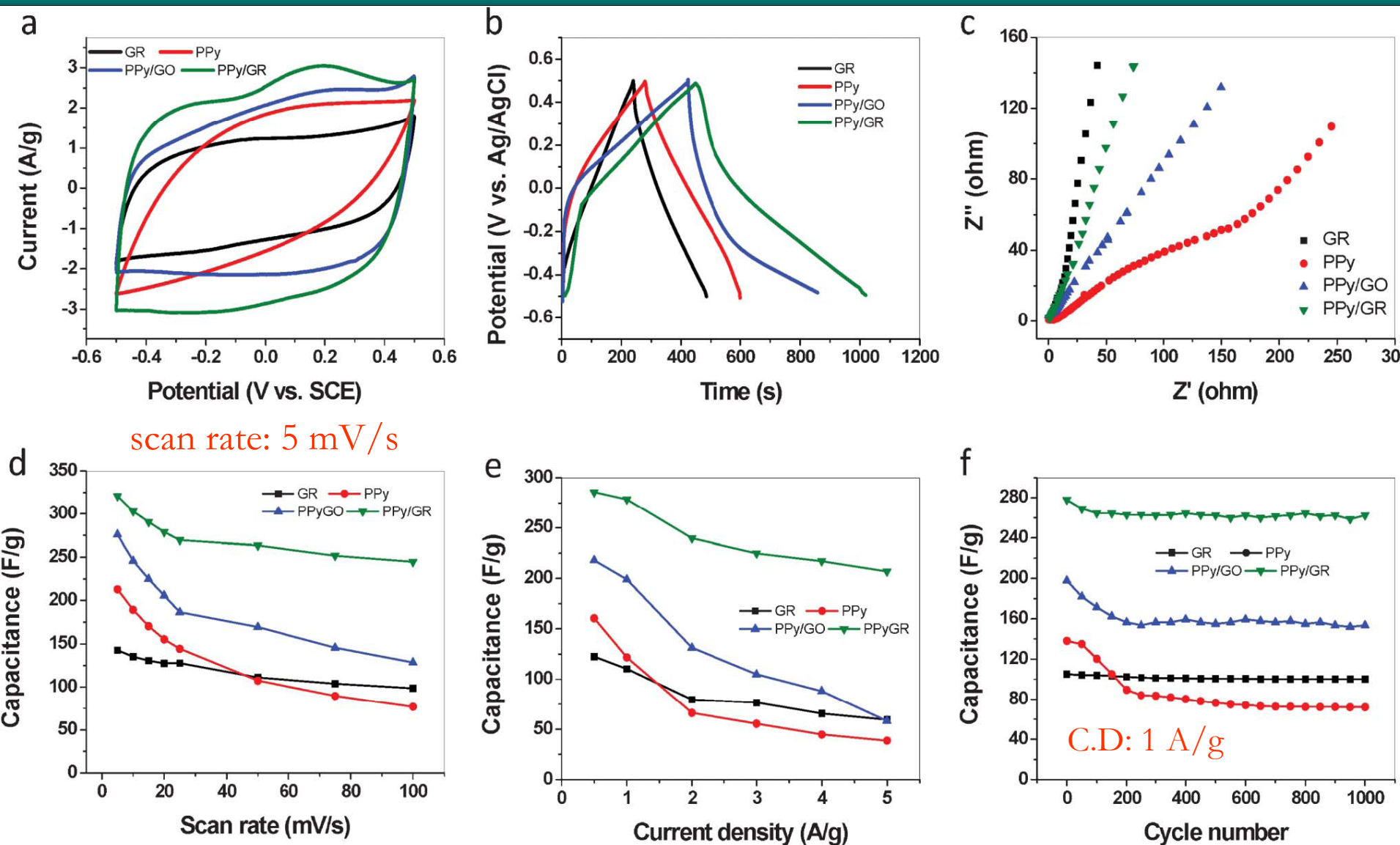


- *in situ* polymerization-reduction/dedoping-redoping process
- A high specific capacitance of 1126 F/g with a retention life of 84% after 1000 cycles

Polypyrrole/Graphene nanocomposites for supercapacitors



Polypyrrole/Graphene nanocomposites for supercapacitors



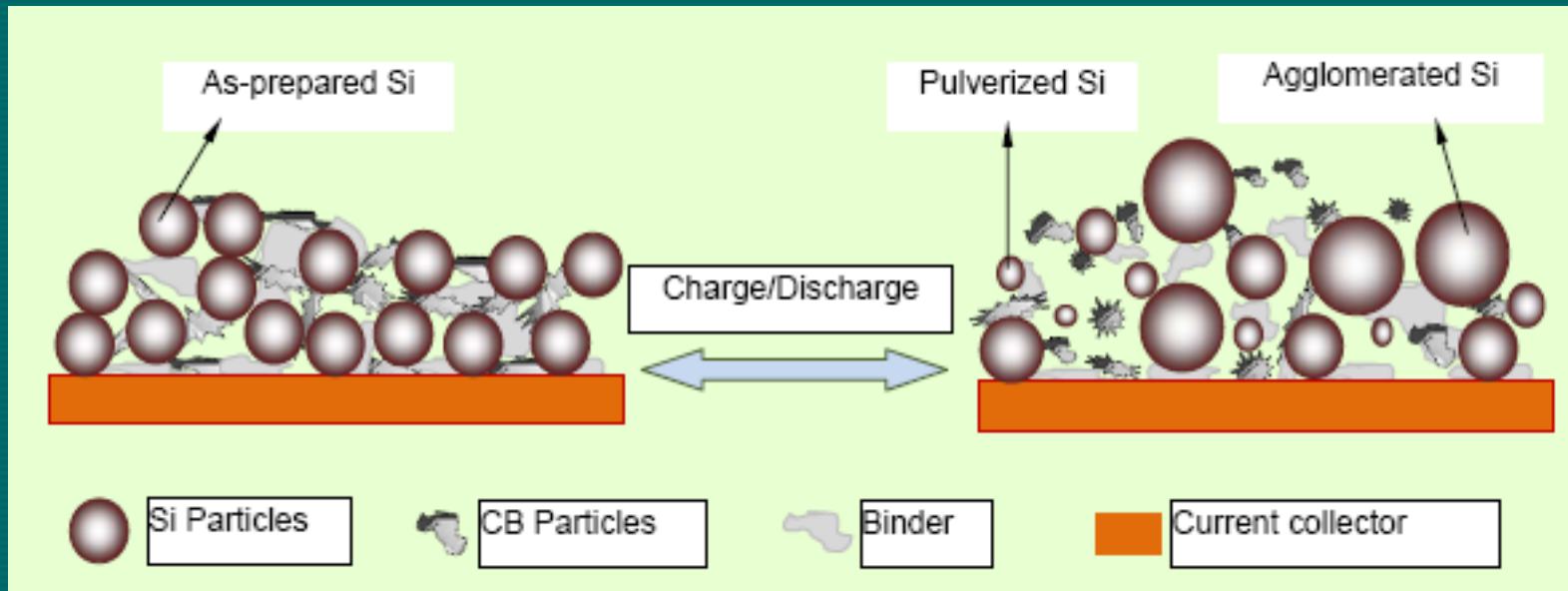
Electrochemical properties of GR, PPy, PPy/GO, PPy/GR 0.5 M Na_2SO_4

Graphene based supercapacitor materials

Material	Specific Capacitance (F/g)	Energy density Power density
Chemically reduced GO	135	
Graphene-hydrous RuO ₂ (38.3 wt%)	99 570	20.1 W h/kg at 100 mA/g 10 kW/kg at 4.3 W h/kg
Graphene (2675 m ² /g)	550	
Graphene (microwave assisted reduction of GO)	191	At 150 mA/g discharge current
Thermal reduction in propylene carbonate	120	
Graphene (hydrazine reduced GO)	205	28 W h/kg 10 kW h/g
Graphene-PANI (50:50 wt%) (microwave-solvothermal)	408	
Graphene-PANI (in situ anodic electro-polymerization of PANI film on graphene paper)	233	
Graphene-PANI	1046	
Graphene-MnO ₂	216	
Polymer modified graphene sheet + MWCNT	120	
Curved Graphene Sheets	100–250 at current density 1 A/g	85.6 W h/kg at 1 A/g
Thermally reduced graphene	75 F/g	31.9 W h/kg
MnO ₂ nanowire-graphene	117 F/g 31 F/g	– 30.4 W h/kg

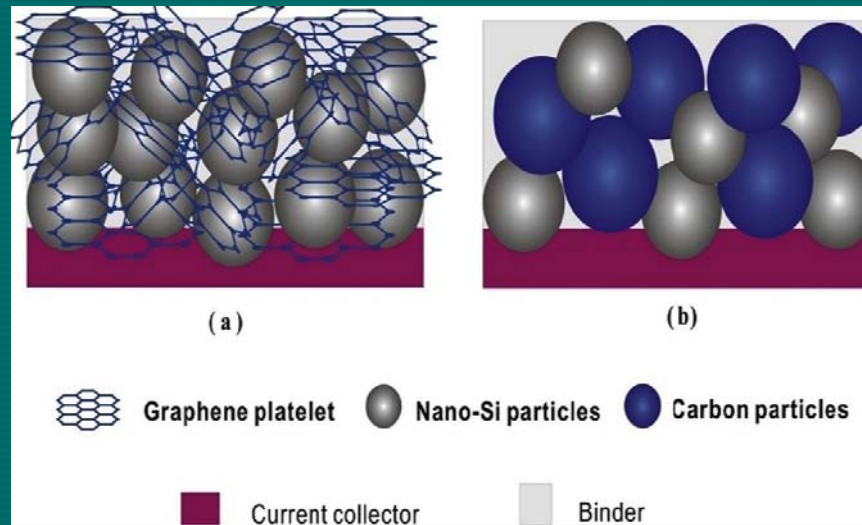
Lithium batteries

Graphene as a conductive additive



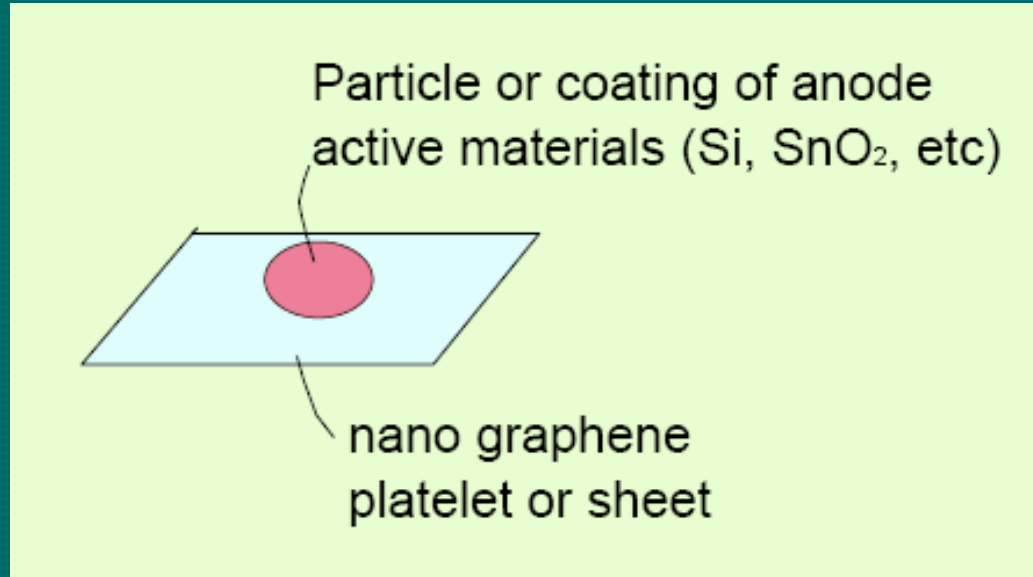
- ❖ Si - highest Li storage capacity (4,200 mAh/g)
- ❖ During charge/discharge cycles
 - ❖ High volume expansion/shrinkage (320-380%)
 - ❖ Pulverization of Si particle or thin film;
 - ❖ Fragmented particles lose contact with the conductive additive and current collector - significant capacity decay

Performance - Graphene vs. Carbon



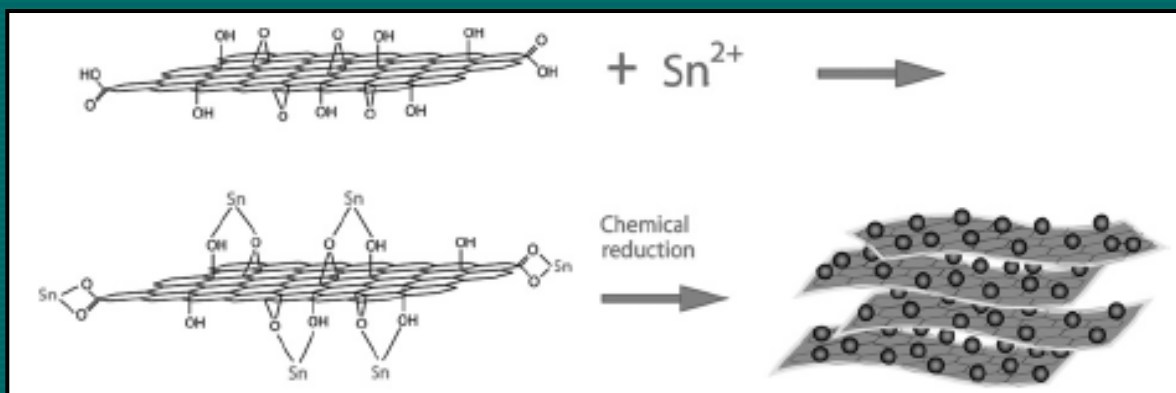
- ❖ Increased electrode conductivity due to a percolated graphene network;
- ❖ Dimensional confinement of active material particles by the surrounding graphene sheets limits the volume expansion upon lithium insertion;
- ❖ SnO_2 – graphene nanocomposite form a stable 3D architecture.
- ❖ Graphene sheets prevent aggregation of nanoparticles during Li charge/discharge process.

Graphene composite – anode active material for Lithium ion batteries



- Aruna Zhamu and Bor Z. Jang, US Patent Appl. No. 11/982,672 (11/05/2007)
- SnO₂ and Co₃O₄ coated graphene nanosheets can be used as an anode materials in Li ion batteries

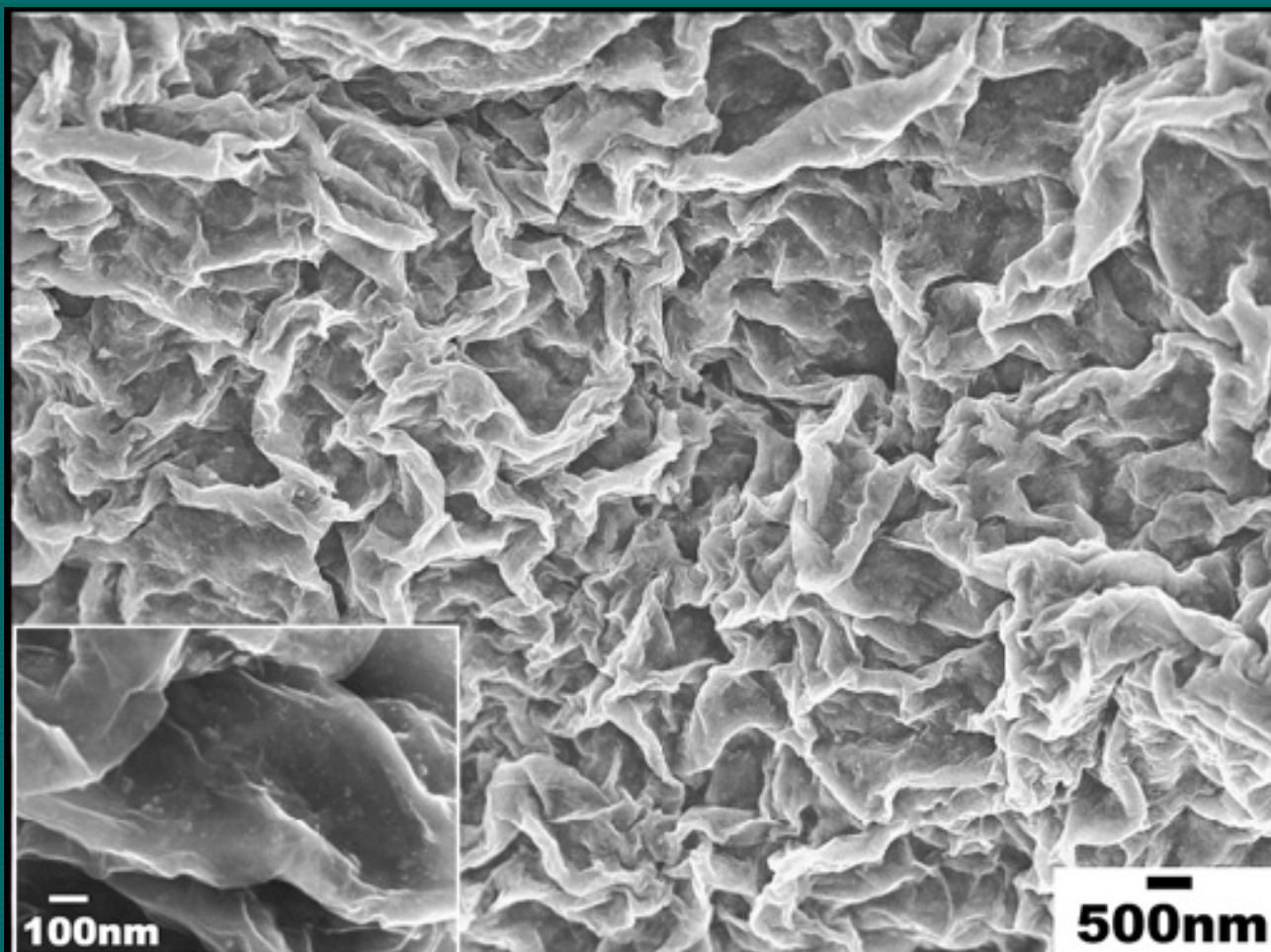
Graphene-Sn composite as anode active materials for Li ion batteries



Synthesis of the Sn/graphene nanocomposite with a 3D architecture

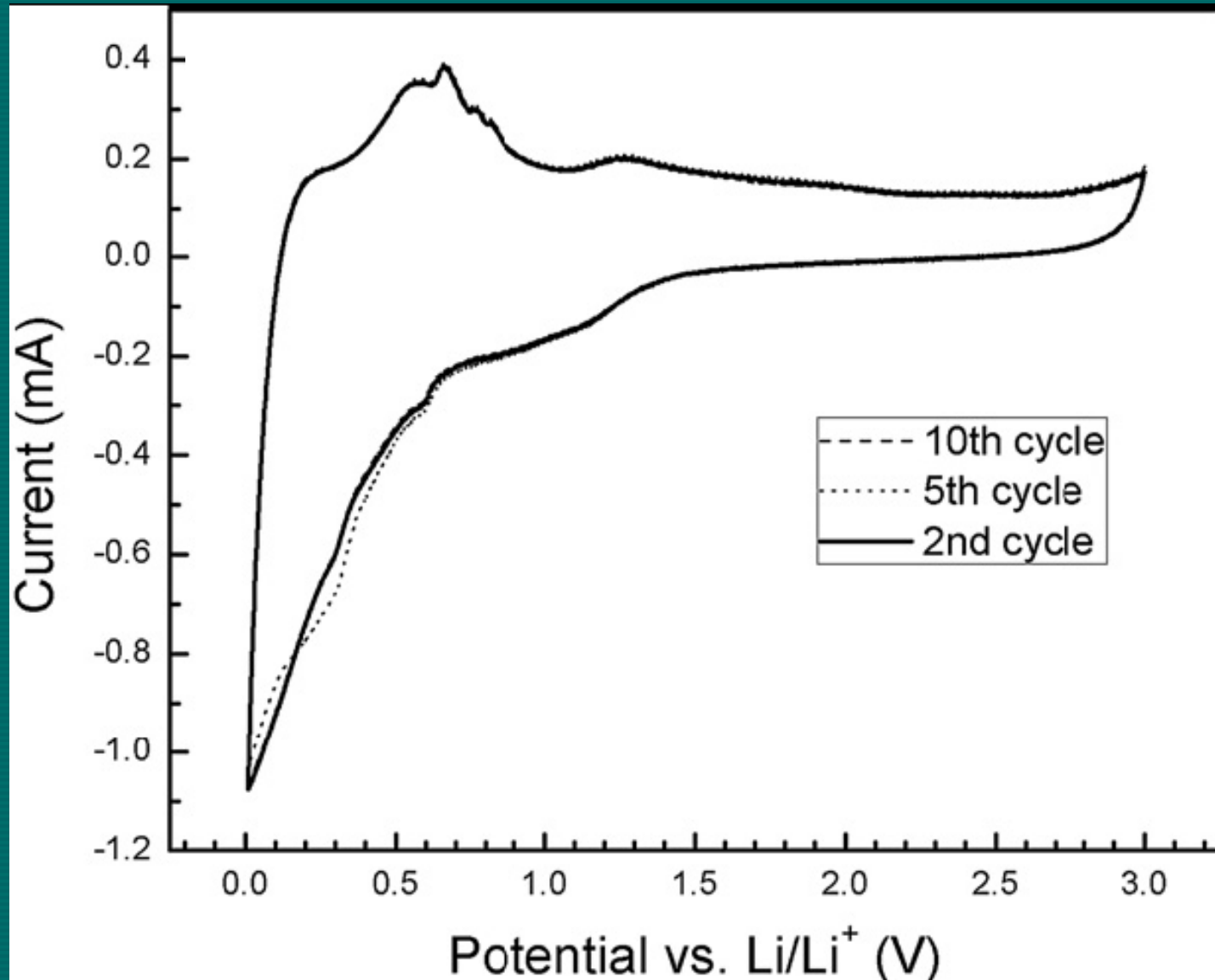
- ❖ Graphene oxide nanosheet – Dispersed in deionized water by ultrasonication
- ❖ Addition of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and citric acid
- ❖ Purge with Argon
- ❖ Addition of NaBH_4 to reduce Sn^{2+} to Sn and graphene oxide nanosheets to graphene nanosheets
- ❖ The mixture was stirred at $0\text{ }^\circ\text{C}$ (ice bath) for 3 h
- ❖ Filtration, washing in DI-water, drying in vacuum at $40\text{ }^\circ\text{C}$
- ❖ To improve the crystallinity - annealed at $200\text{ }^\circ\text{C}$ for 15 h in Ar atmosphere

Source: Wang et. Al., *J. Mater. Chem.*, 2009, 19, 8378–8384



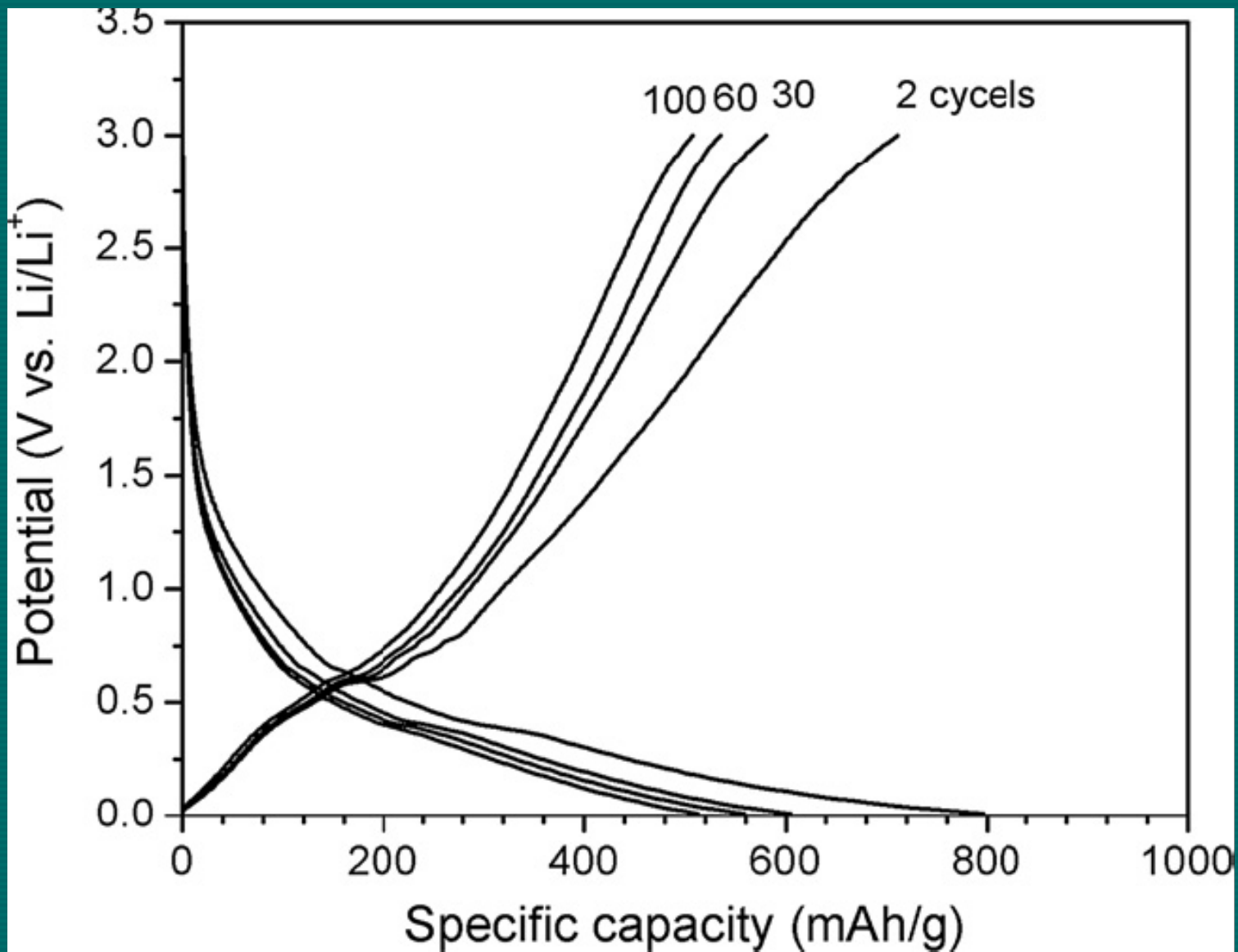
FESEM image of Sn/graphene nanocomposite

Source: Wang et. Al., *J. Mater. Chem.*, 2009, 19, 8378–8384



Cyclic voltammograms of the Sn/graphene electrode

Source: Wang et. Al., *J. Mater. Chem.*, 2009, 19, 8378–8384



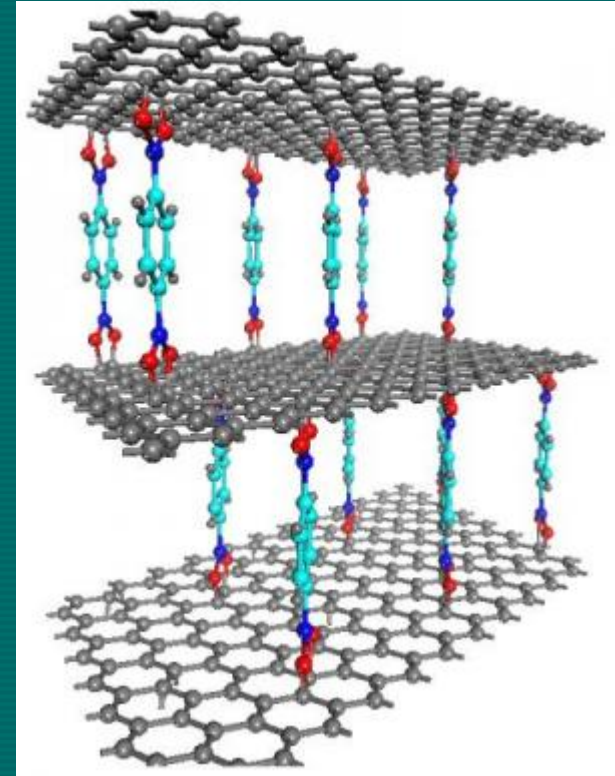
Charge/discharge profiles of Sn/graphene electrode in lithium-ion cells

Source: Wang et. Al., *J. Mater. Chem.*, 2009, 19, 8378–8384

Hydrogen storage

Layered graphene oxide framework (GOF) for H₂ storage

- GOF - Stacking up of oxidized graphene sheets like a multilevel parking lot can accumulate H₂ in greater quantities
- GO layers are connected by boron carboxylic molecules - link the GO layers with one another and also maintain space between them
- GOFs can hold at least a hundred times more H₂ than ordinary graphene oxide
- GOFs might be used both to store hydrogen and to release it when it is needed -fundamental requirement in fuel cell applications



A graphene-oxide framework (GOF) connected by boron-carboxylic “pillars”

Graphene – Yesterday – Today and Tomorrow



2004



2011



In the coming years?

Thank you