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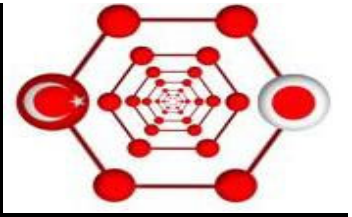

Graphene Manufacture and Utilization

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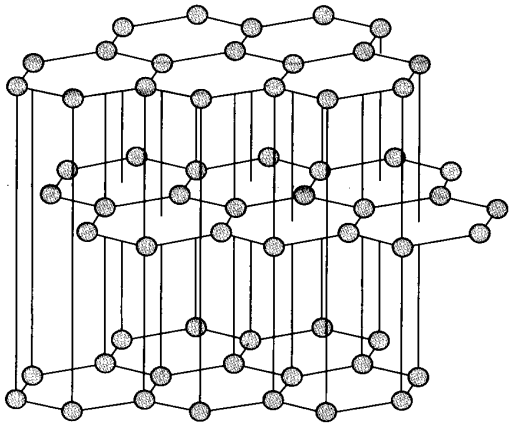
Outline

- Background about graphene and its separation techniques
- Objectives
- The effect of oxidation time on graphite oxide papers
- Chemical procedure for the separation of graphene nanosheets
- Structural, Thermal and Morphological Characterization
- Utilization
- Conlusions

Graphite

- A layered material
- Form by a number of two dimensional graphene stacked along the c-axis with the ABAB… type of stacking sequence.
- Graphene layers couple together by weak van der Waals forces with the distance between layers as 0.335 nm



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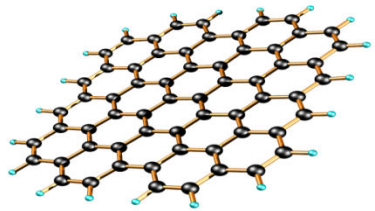
Graphene



- The world's thinnest sheet -only a single atom thick-
- Stable at ambient conditions
- Ripple rather than completely flat in a free standing state.
- High mechanical, thermal and chemical stability because of the strong covalent bonds between carbon atoms
- Electrically conductive
- Tensile modulus and ultimate strength values comparable to those of single-walled carbon nanotubes
- Its theoretical Young's modulus is around 1060 GPa-one of the strongest known materials per unit weight-
- The theoretical surface area of graphene is around 2630 m^2/g

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From graphite to graphite oxide and graphene

- With several surface treatments, graphite is oxidized to graphite oxide (GO), then graphene sheets are separated by the extension of layer-to-layer distance.
- The first graphene sheets were obtained by extracting monolayer from the three-dimensional graphite using a technique called micromechanical cleavage in 2004*.

***Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., Firsov, A. A., Science, 2004, 306: 666**

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Graphite Oxidation

- Brodie in 1859 obtained graphitic oxide by repeated treatment of Ceylon graphite with an oxidation mixture consisting of potassium chlorate and fuming nitric acid **[1]**.
- Staudenmaier in 1898 produced graphitic oxide by the oxidation of graphite in concentrated sulfuric acid and nitric acid with potassium chlorate **[2]**.
- Hummers and Offeman in 1958 oxidized graphite in water free mixture of sulfuric acid, sodium nitrate and potassium permanganate **[3]**.

[1] Brodie, B. C. On The Atomic Weight of Graphite. Philos. Trans. R. Soc. London **1859**, 149, 249.

[2] Staudenmaier, L. Verfahren zur Darstellung der Graphitsaure. Ber. Dtsch. Chem. Ges. **1898**, 31, 1481.

[3] Hummers, W. S. and Offeman, R. E. Preparation of Graphitic Oxide. J. Am. Chem. Soc. **1958**, 80, 1339.

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Objectives

PART 1-GRAPHENE MANUFACTURE

- Tailoring the characteristics of graphite oxide papers via different oxidation times
- Optimization of reactant ratios during oxidation process
- Reduction of the number of layers in the graphite material
- Detail characterization of samples by XRD, SEM, AFM, TGA, Raman Spectroscopy

PART 2-UTILIZATION

- Utilization of graphene nanosheets as fuel cell electrode material

PART 1

GRAPHENE MANUFACTURE

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An improved, safer and mild technique

The exfoliation of graphene nanosheets from graphite was conducted in three major steps as follow:

1: Preparation of Graphite Oxide (GO)
2: Thermal Expansion of GO
3: Reduction of GO and Expanded GO into Graphene based nanosheets

- After each step, sonication process was performed for the homogenous dispersion in water about 1 hr at room temperature.

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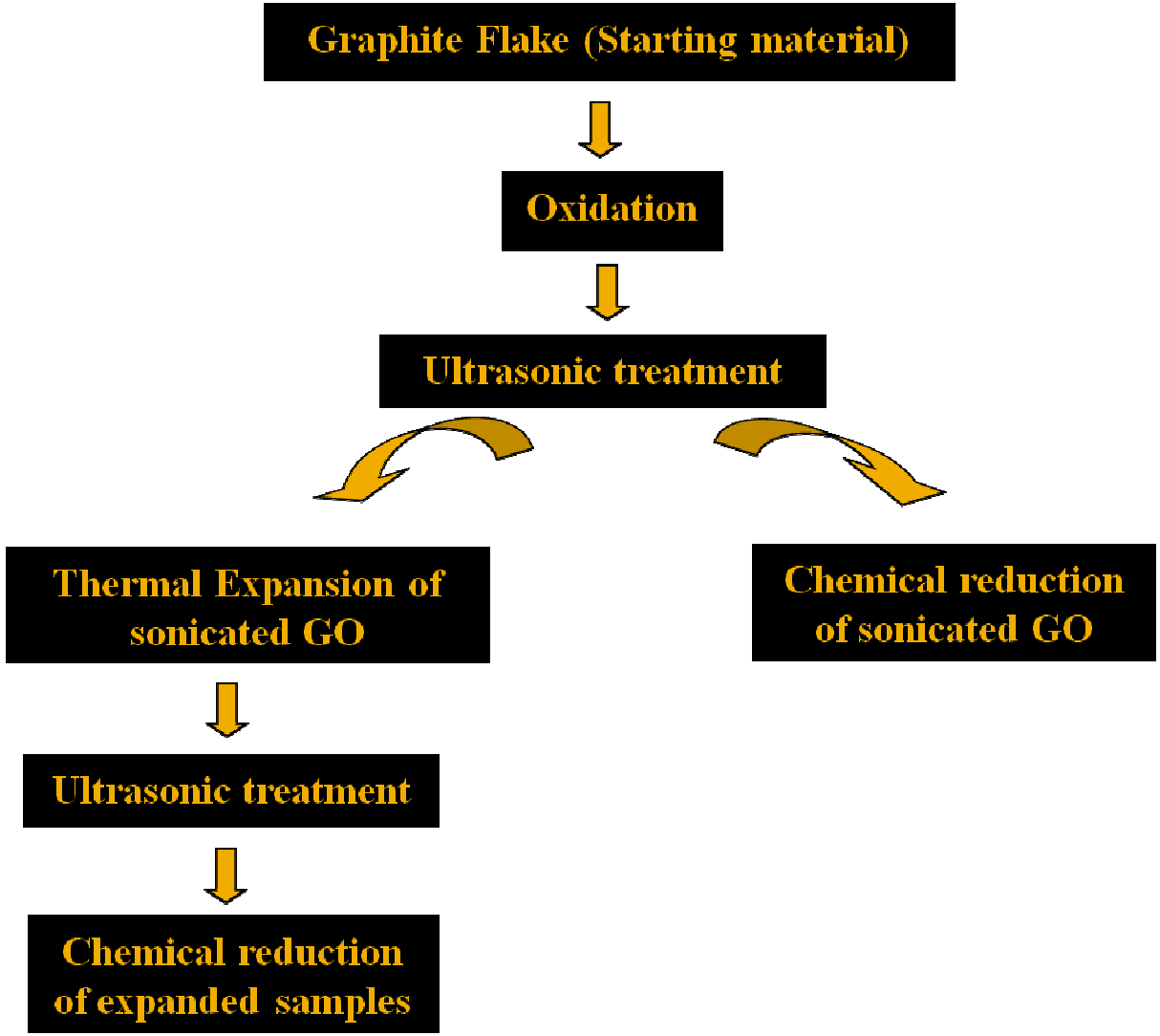
General experimental procedure to separate graphene nanosheets



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Graphite oxidation procedure

- Potassium dichromate/sulfuric acid as oxidant
- Acetic anhydride as intercalating agent.
- Reaction time: 50 min, 6 h, 12 h, 24 h, 48 h, 72 h, 96 h, 120 h, and 10 days
- Reaction temperature: 45°C.

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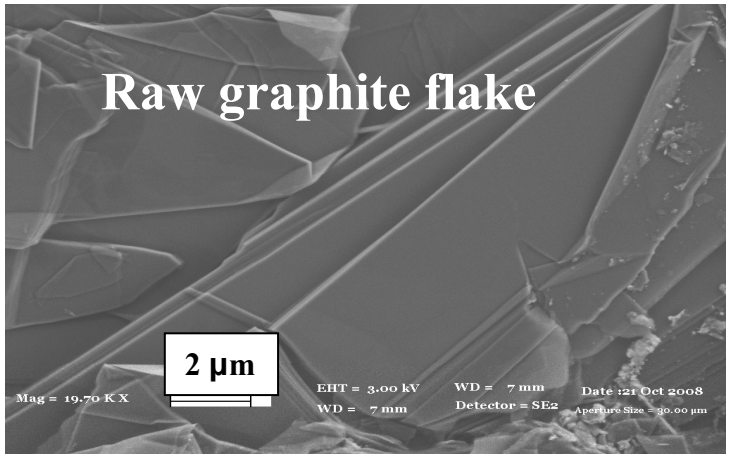
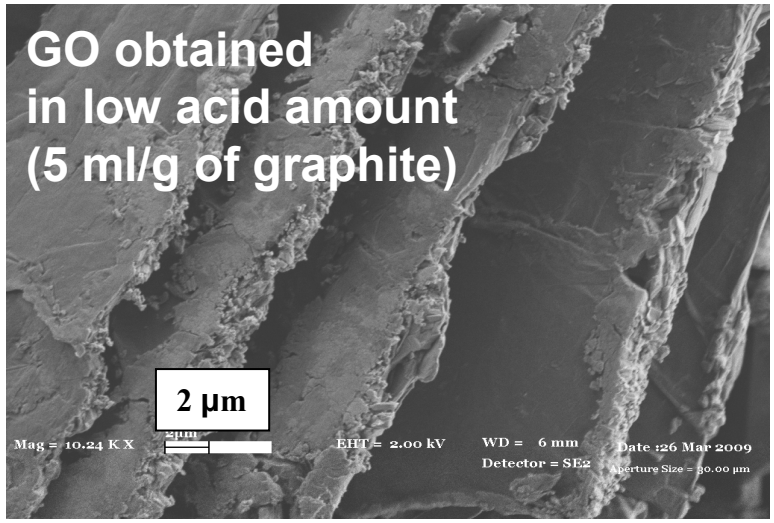
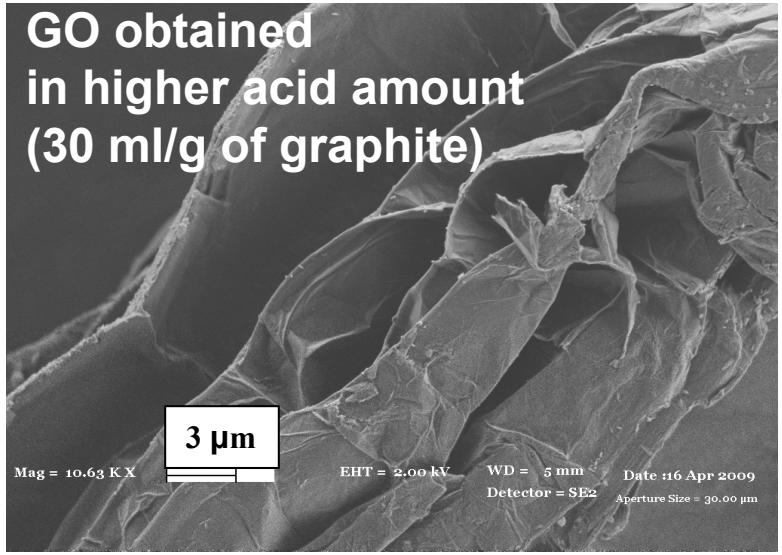
The effect of amount of acid on oxidation process







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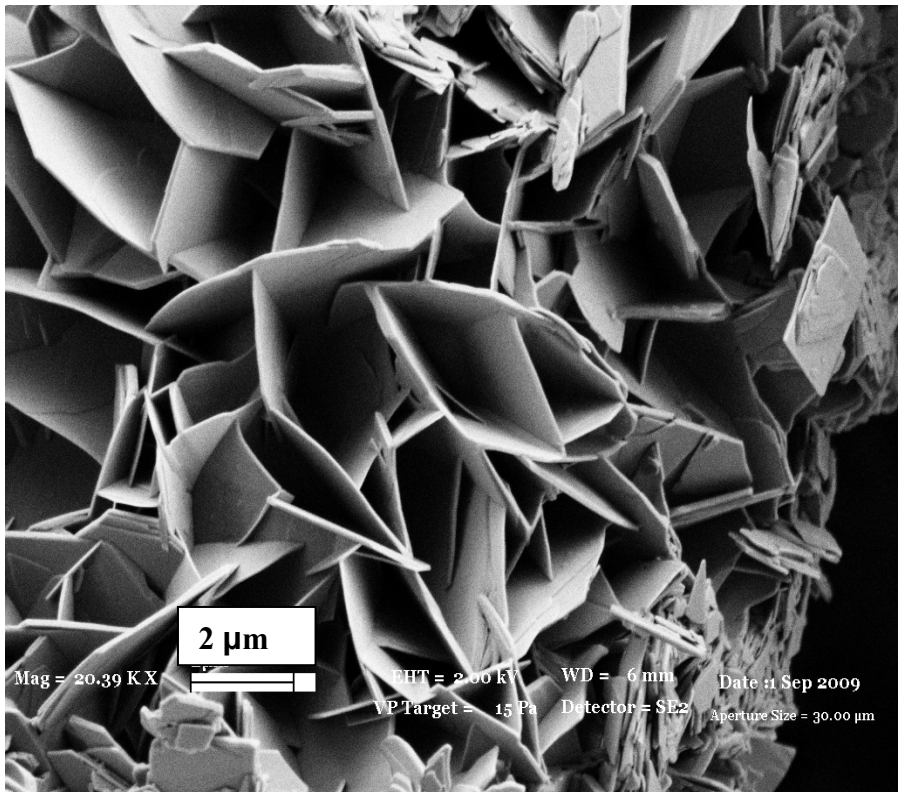
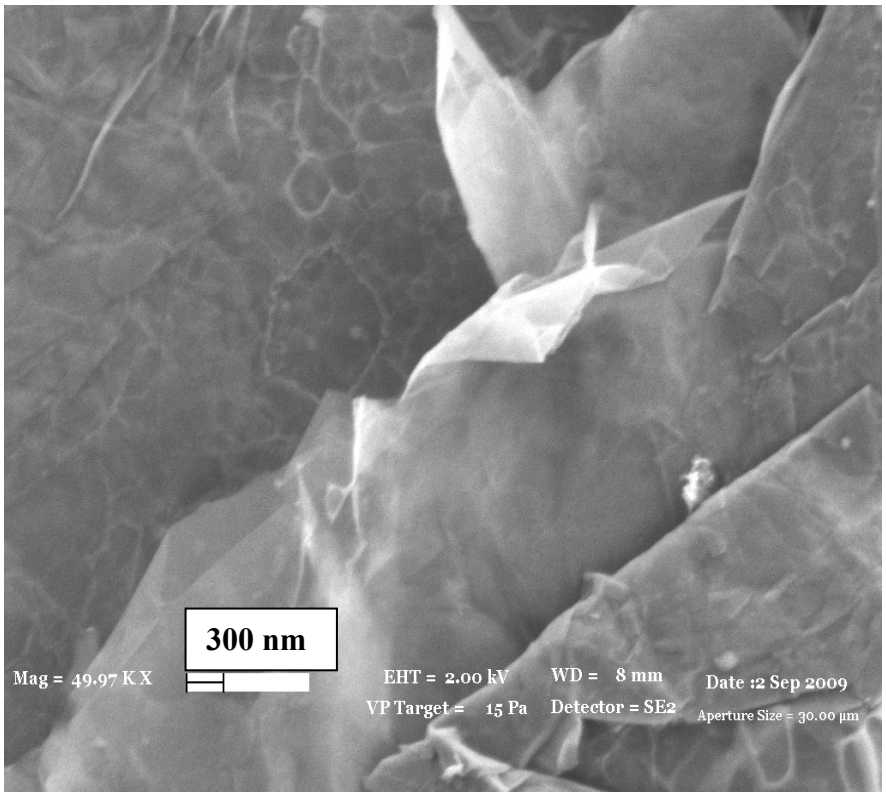
The effect of reaction time on oxidation process

GO-rxn time: 6 hr



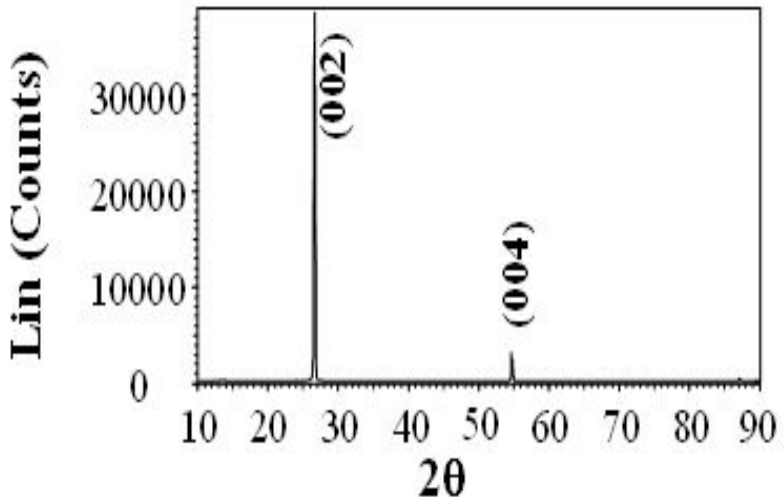
GO-rxn time: 120 hr



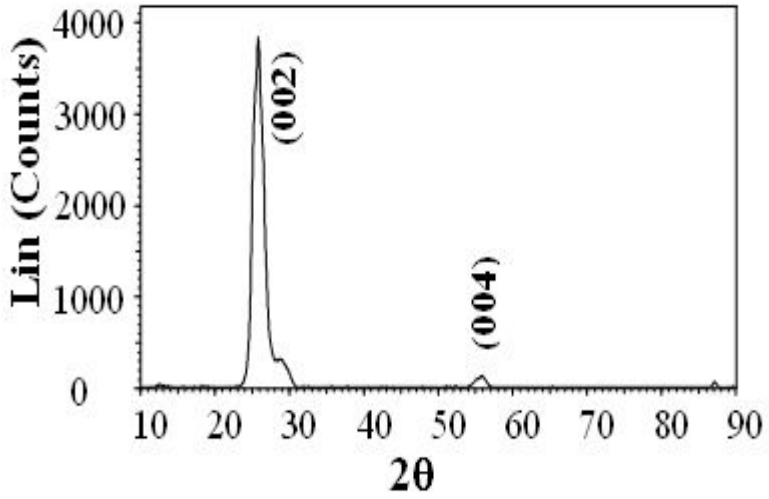
Sheets started to exfoliate at longer reaction times

Structural analysis of GO by XRD

XRD pattern of raw graphite



XRD pattern of GO (partially oxidized)



- Intensity lowers: destruction of structure.
- The shoulder near (002) peak of GO is due to the intercalating agent used in oxidation process

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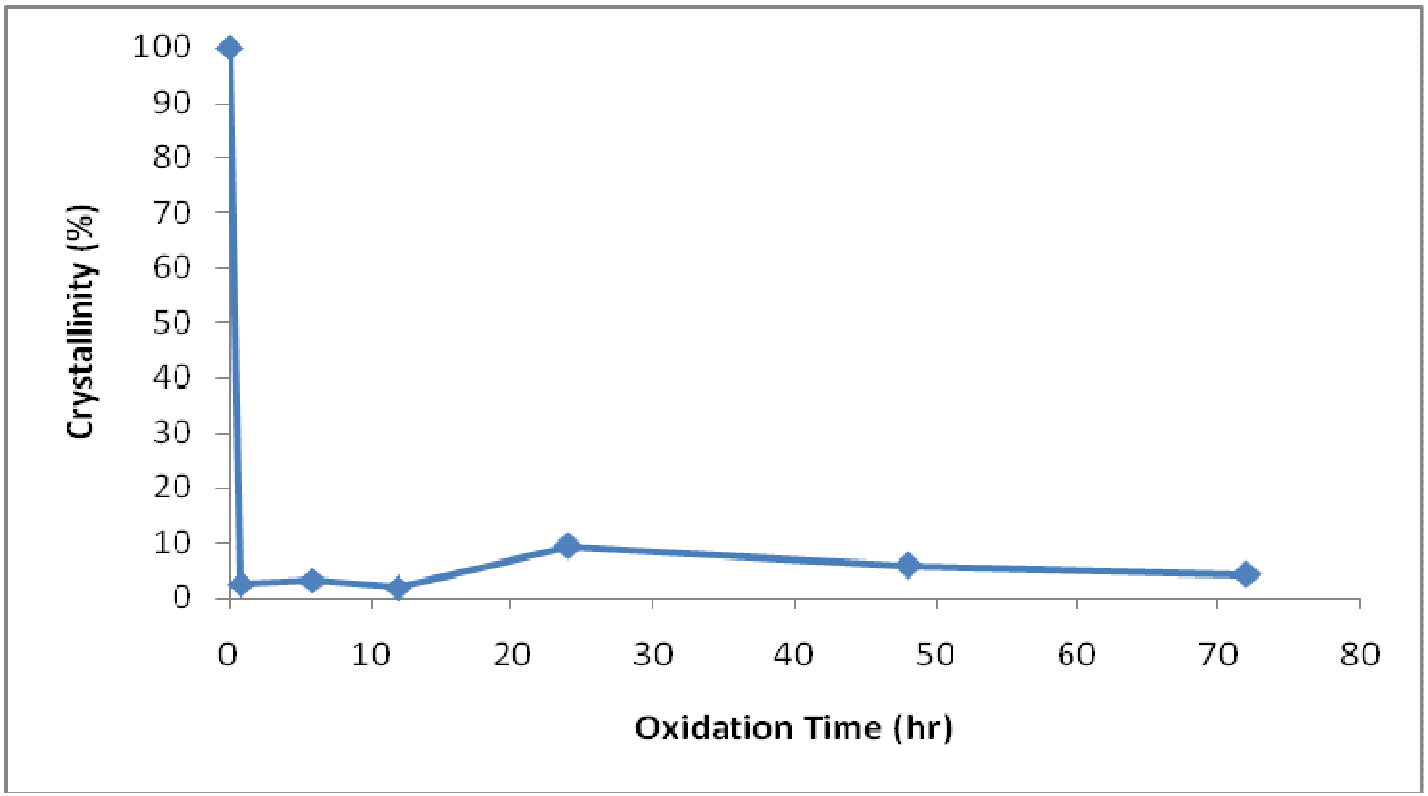
Crystallinity analysis of GO via XRD



Crystallinity of GO samples at different oxidation times obtained from the area under (002) XRD peaks decreases.

Thermal Exfoliation of GO

GO samples were expanded by heating under an argon atmosphere at different expanding temperatures (900-1100°C) and different expanding times (1-15 minutes) in a tube furnace.

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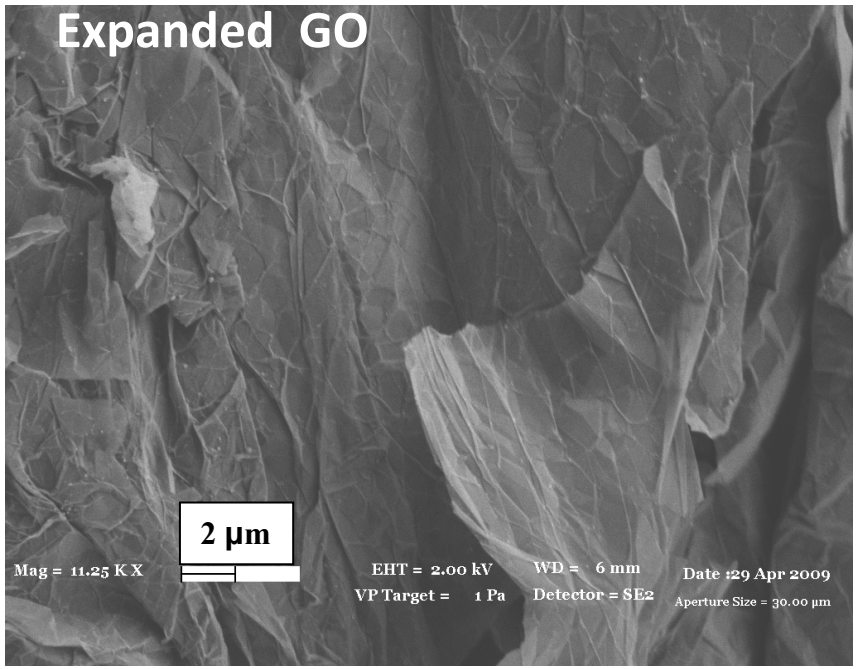
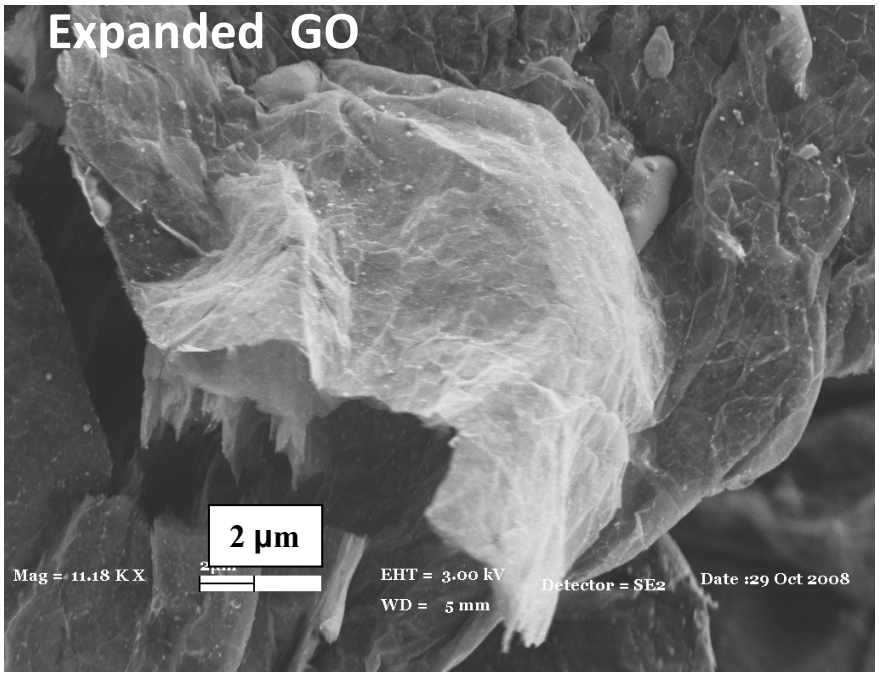
The effect of expansion time

After a short heat treatment period
~1 minute



After a long heat treatment period
~15 minutes



Heat treatment leads to the thermal decomposition of acetic anhydride into CO_2 and H_2O gas which swelled the layered graphitic structure

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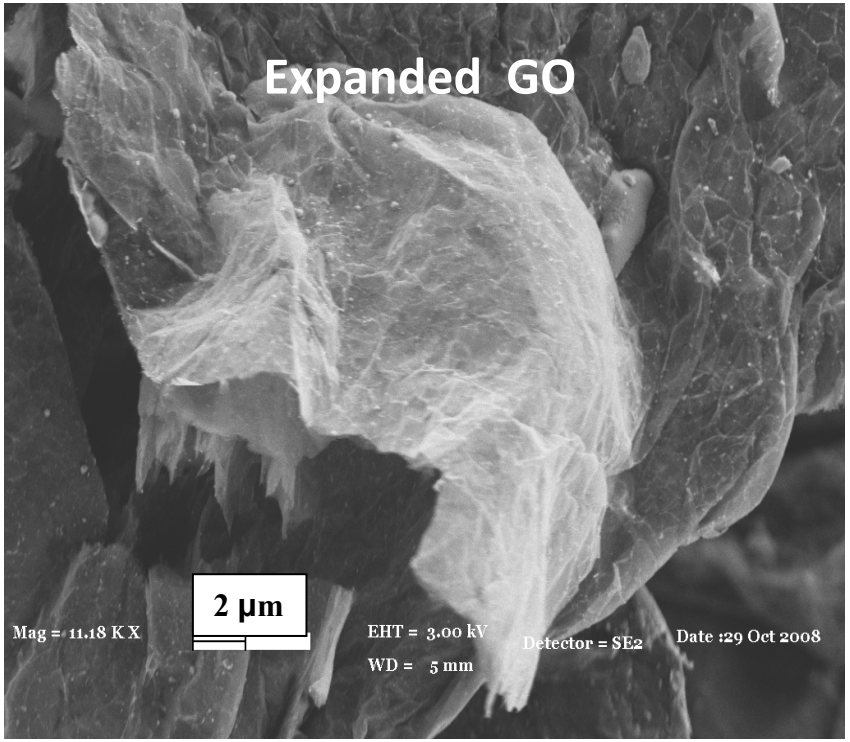
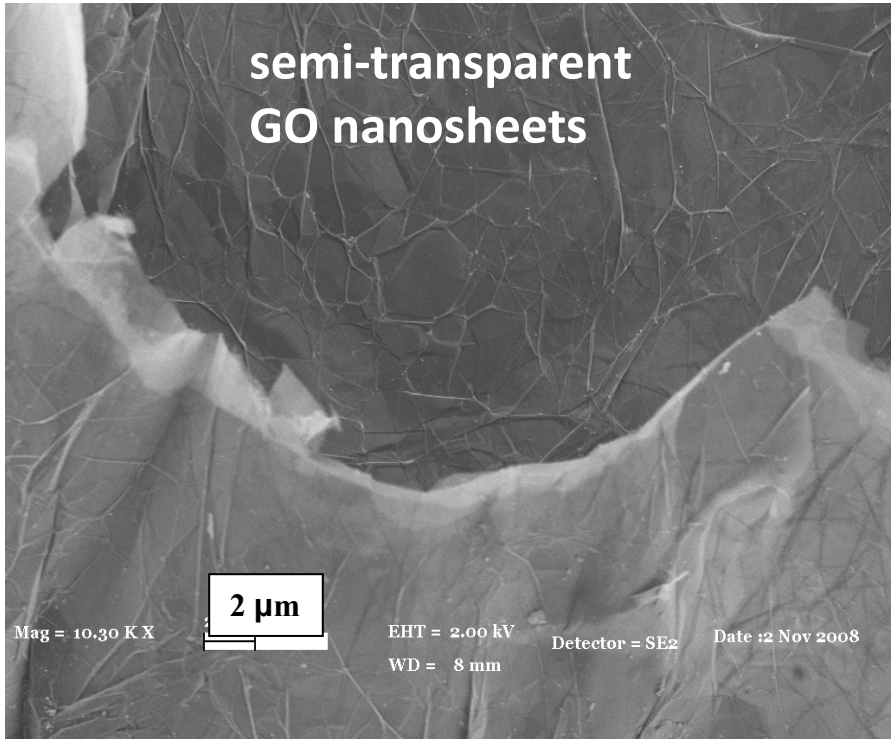
The effect of after sonication process





Sonication Process

Ripple sheets → Flat sheets

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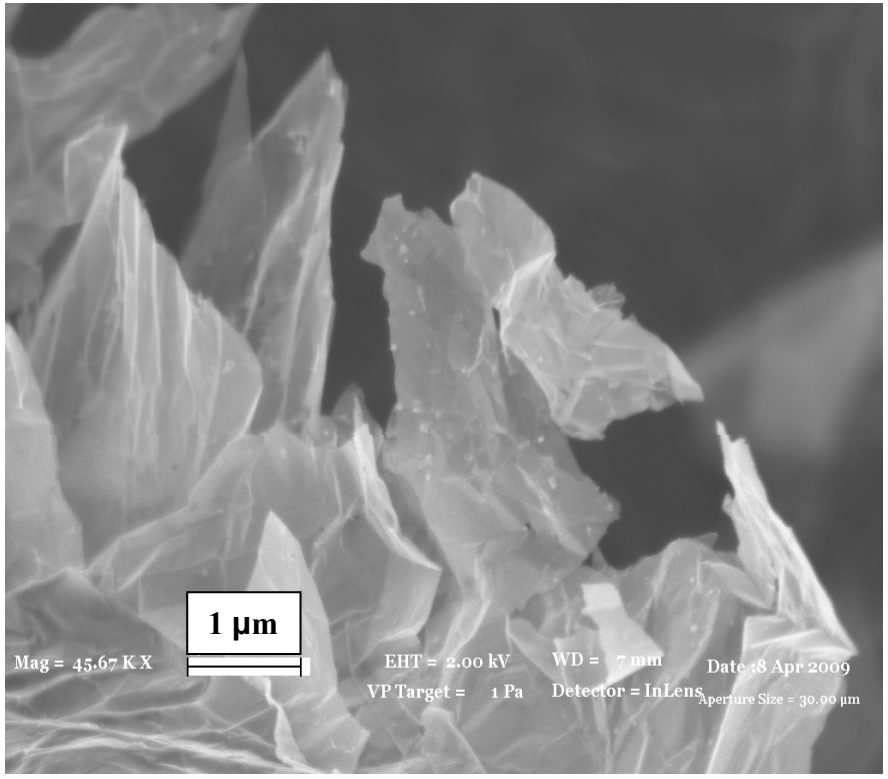
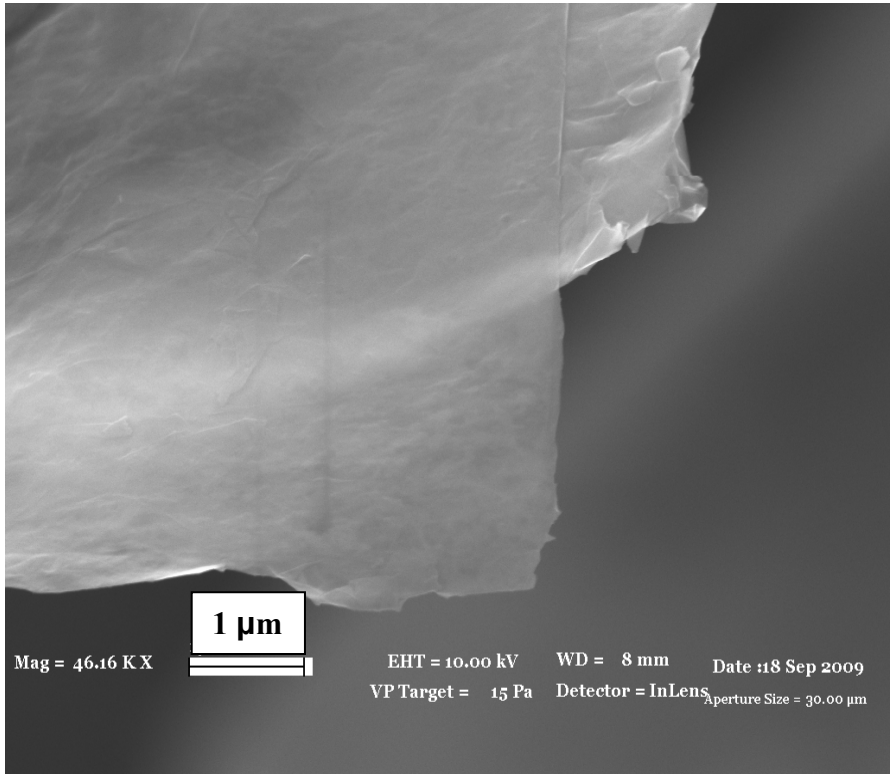
Graphene nanosheets formation after chemical reduction by hydroquinone

Reduction after thermal expansion



Reduction after oxidation process



Both the reaction procedures with expansion and without expansion causes the formation of graphene nanosheets

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Calculation of the number of graphene layers

- **1st way:** By using the data from X-ray diffraction (XRD). Debye-Scherer Equation is applied to calculate the layer number

$$L_a = 0.89\lambda / \beta_{002} \cos\theta_{002}$$

$$n = L_a / d_{002}$$

L_a : stacking height
β : full width half maxima (FWHM)
n: average number of graphene layers
d_{002} : interlayer spacing

- **2nd way:** By using the stacking height value, L_a, from Atomic Force Microscopy (AFM) and interplanar spacing, d_{002} obtained from XRD patterns

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Comparison of layer number with XRD and AFM techniques

Samples	d (nm)	Average number of graphene layers (XRD)	Average number of graphene layers (AFM)
Graphite flake	0.337	86	89
GO-50 min	0.361	17	17
Expanded GO	0.336	30	25
Reduced Expanded GO	0.338	37	17
Reduced GO	0.362	9	11

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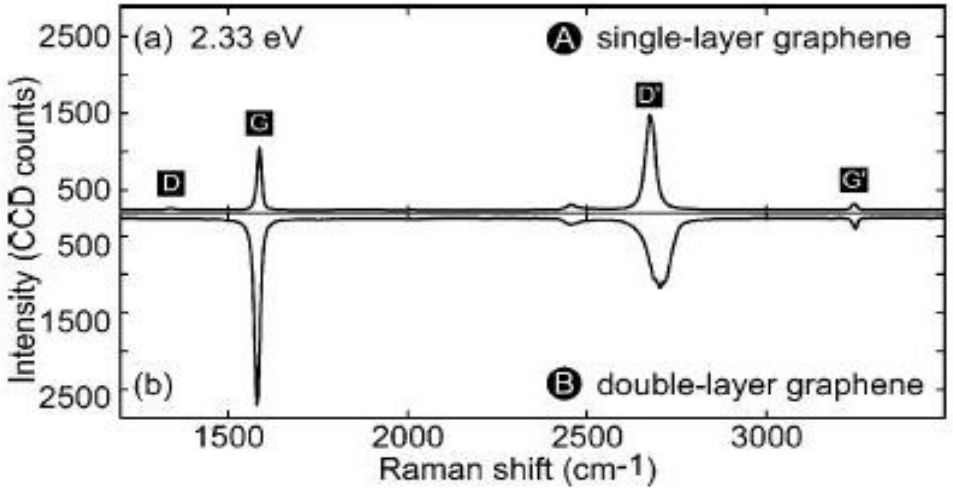
Raman Spectroscopy of single- and few- layer graphene

Raman spectroscopy is a quick and accurate technique to determine the number of graphene layers and to estimate the crystal sizes in disordered carbons.

Raman Spectra of (a) single- and (b) double-layer graphene



- **G band** around 1580 cm^{-1} (Relative intensity enhances with the number of layers)
- **G' band** around 3248 cm^{-1} (Stacking order)
- **D band** around 1360 cm^{-1} (Its intensity depends on the defects of sample)
- **D' band** around 2700 cm^{-1}

D. Graf, *et al*, Spatially Resolved Raman Spectroscopy of single- and few-layer graphene, Nano Letters 7 (2007) 238-242.

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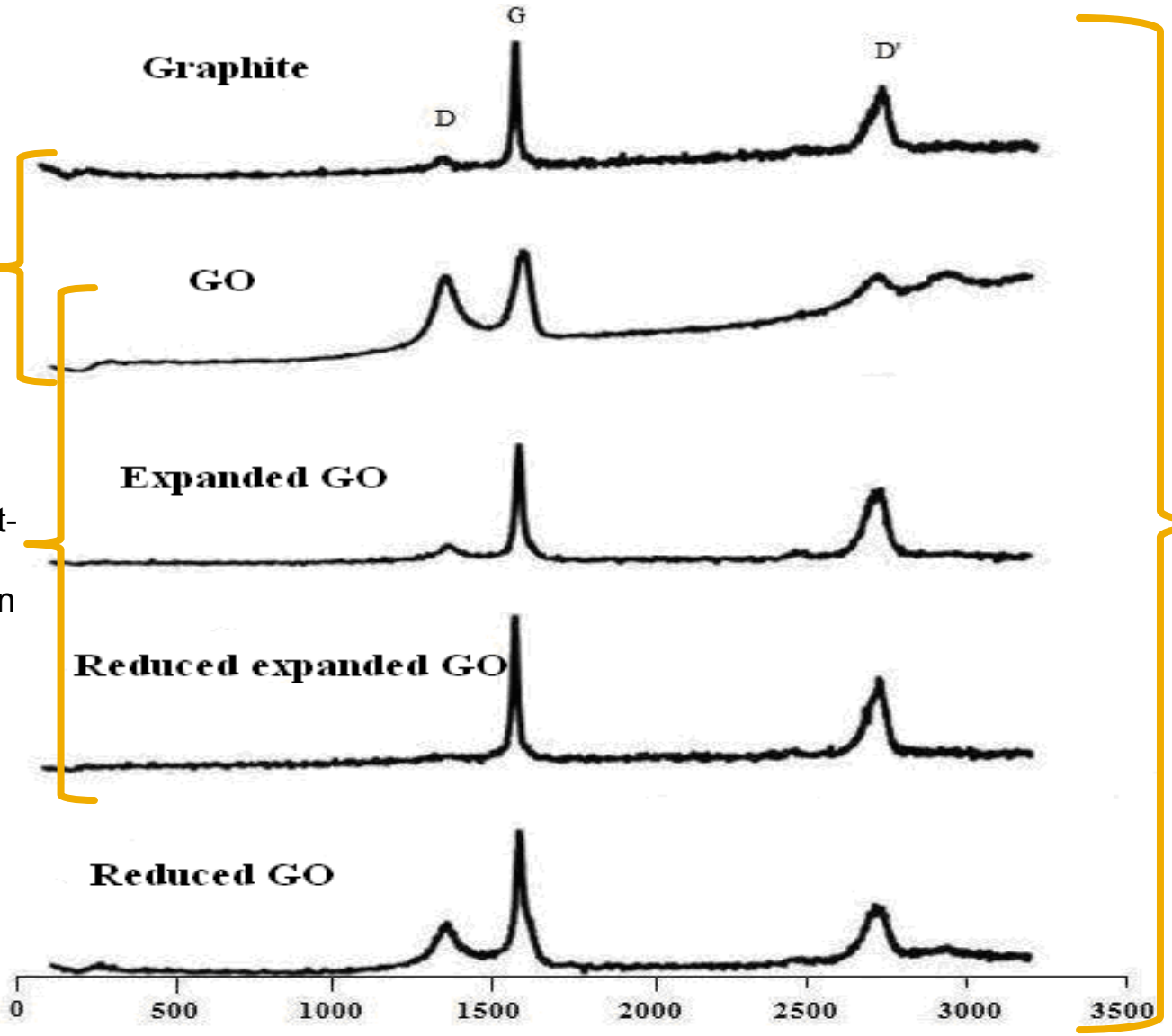
Raman Spectroscopy Characterization

Raman spectra were measured at 514.5 nm excitation

D band intensity increases due to the oxidation

After heat treatment and reduction, defect-free graphene nanosheets formation is observed

Direct reduction of GO leads to decrease of layer number when comparing GO.



Intensity of G band decreases after each step

The experimental results were obtained after 6 hr oxidation.

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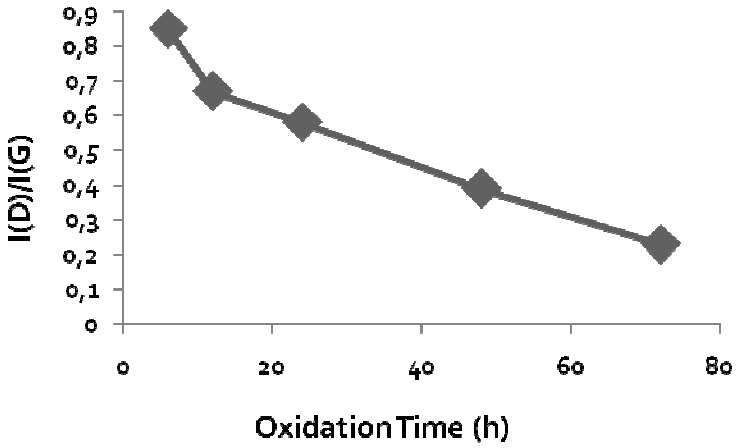
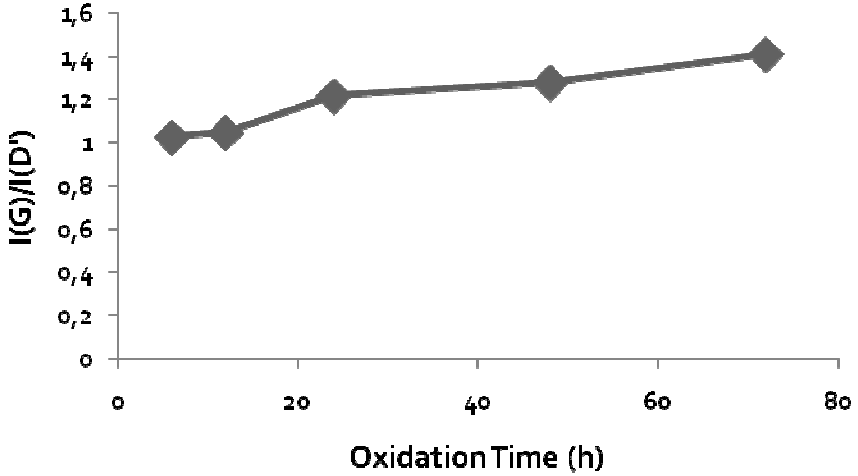
Raman Spectroscopy Characterization of GO sheets

- The intensity of D band depends on any kind of disorder defects in sample*
- The intensity of the G band increases almost linearly as the stacking height increases
- When moving from graphite to nanocrystalline graphite and graphene, I(D)/I(G) varies inversely with the size of crystalline grains or interdefect distance*



I(D)/I(G) decreases as oxidation time increases

As I(D)/I(G) decreases flake thickness increases



As I(G)/I(D') increases layer number increases

*A. C. Ferrari, *Nano Lett.*, Vol. 9, No. 4, 2009

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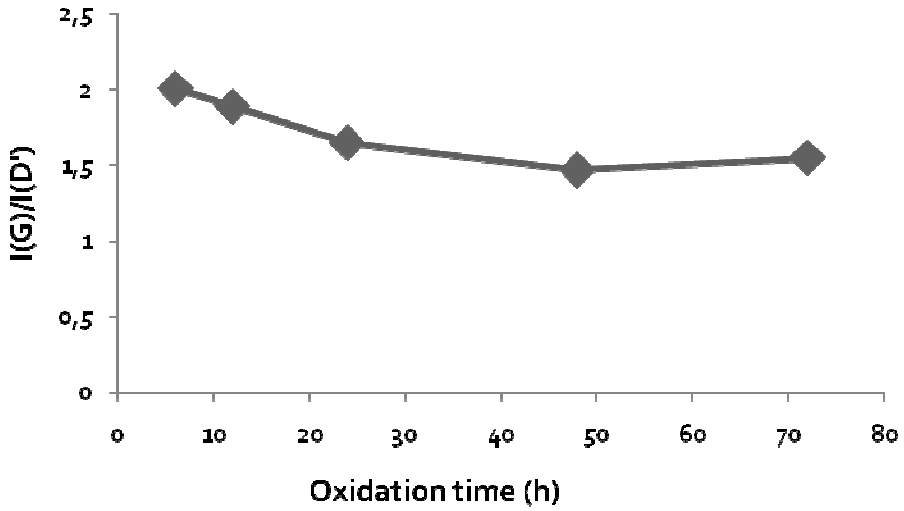
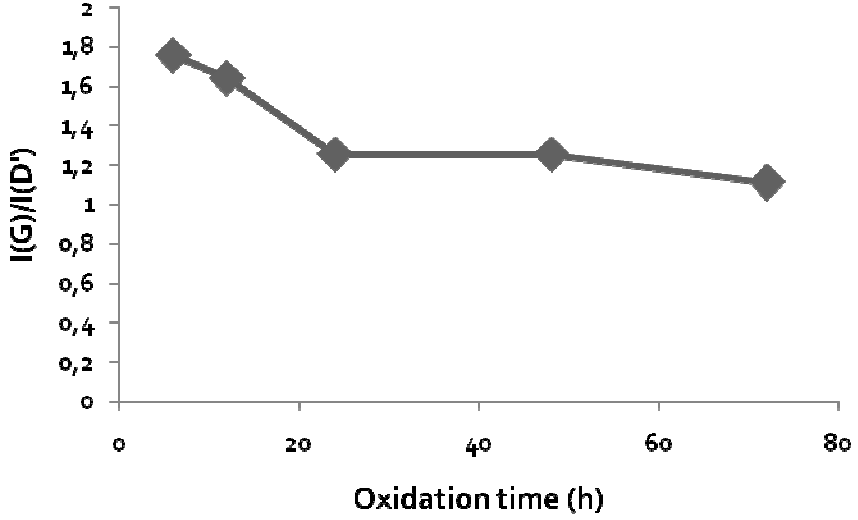
Raman Spectroscopy of reduced graphene sheets

Reduced GO



Reduced Expanded GO



As I(G)/I(D') decreases layer number decreases. Therefore stacking height decreases.

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Atomic Force Microscopy (AFM) Characterization

- AFM is a significant tool for the characterization of sheet thickness and the surface morphology.
- All AFM characterization was performed in tapping mode using a silicon cantilever probe.

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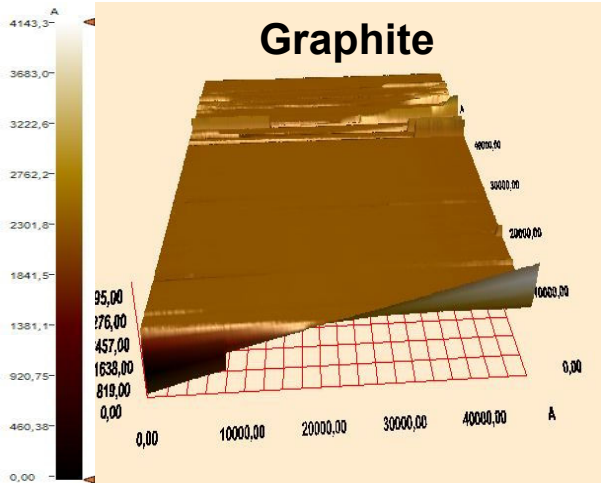
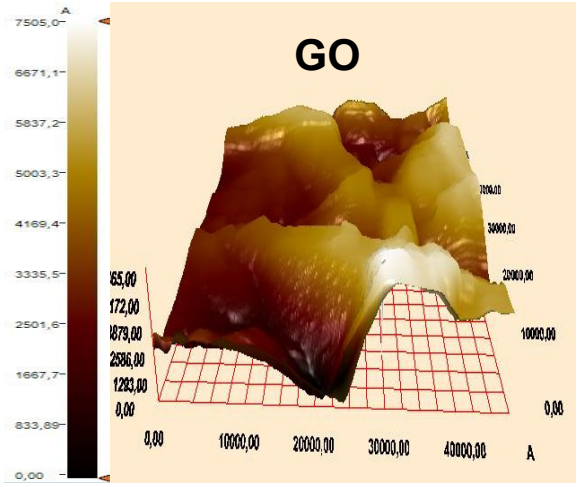
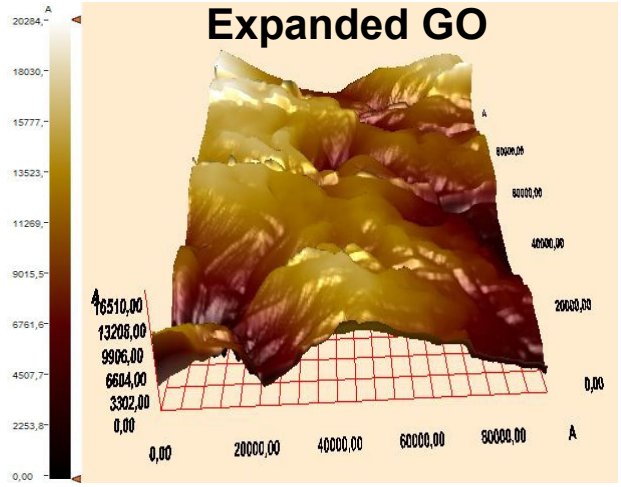
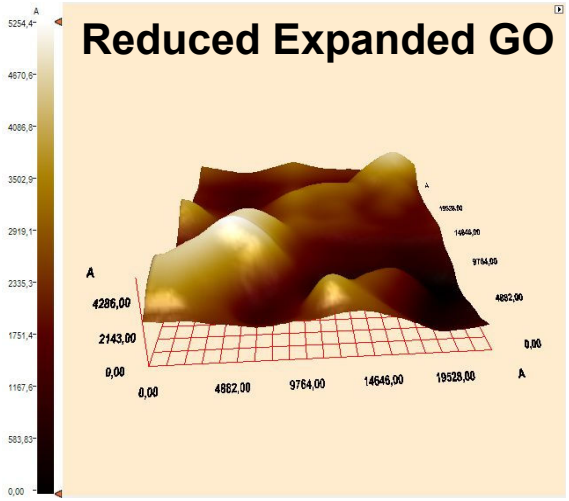
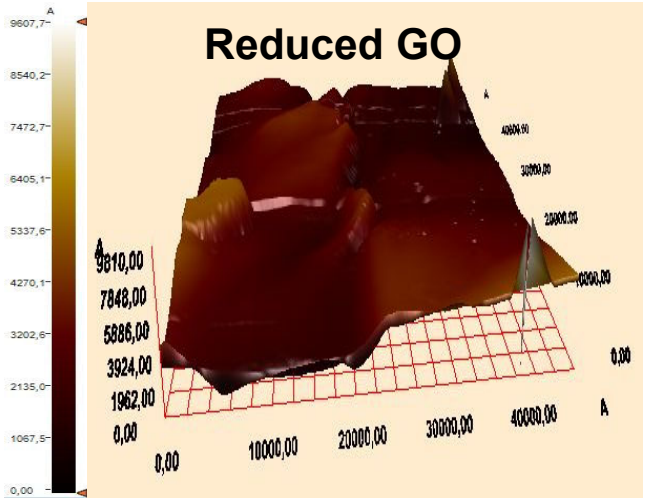
AFM 3D Views-Surface Analysis by tapping mode











Ripple sheets → Flatter sheets

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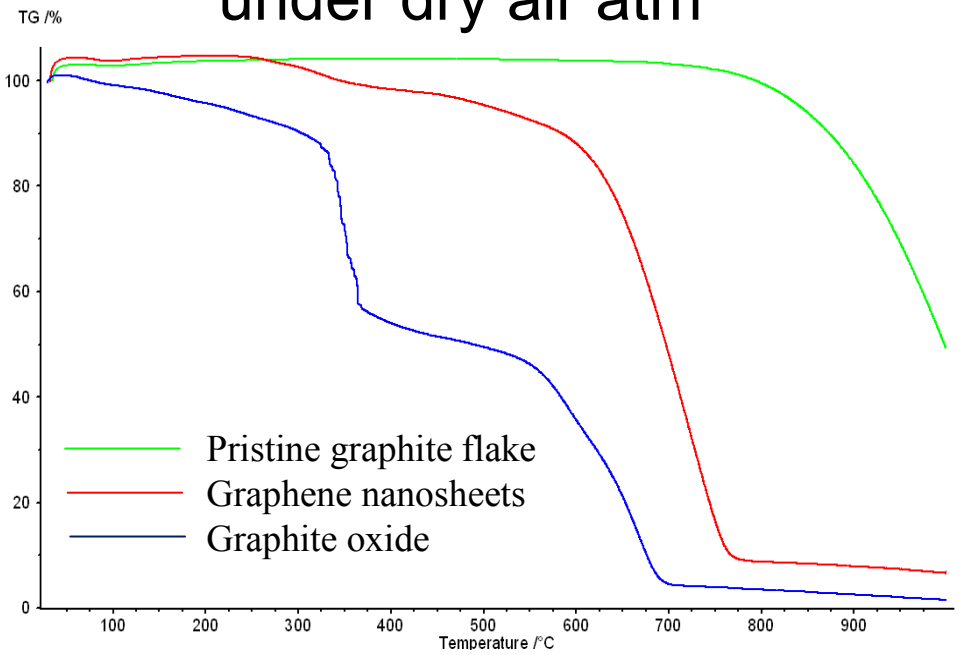
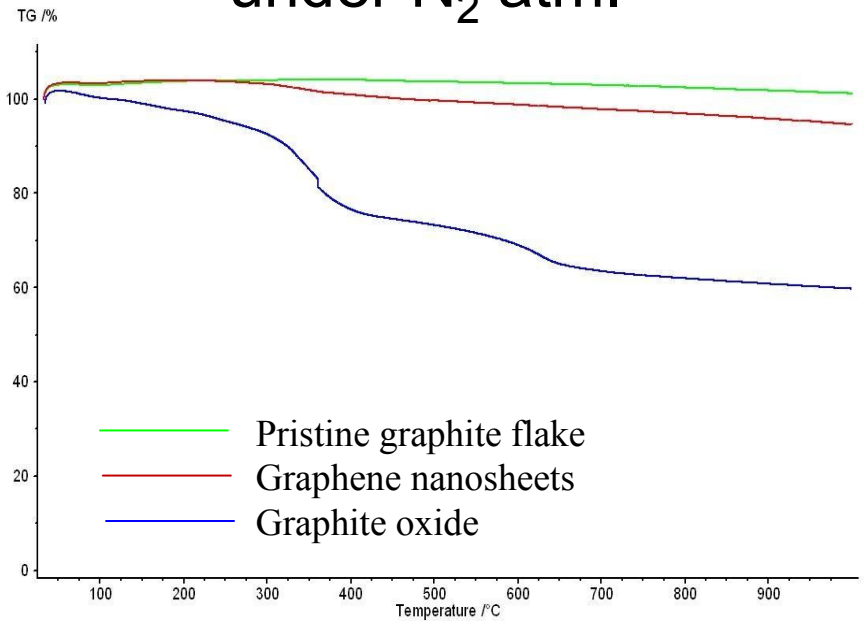
Thermal Behaviour Investigation by TGA

under dry air atm



- Pristine graphite flake starts to lose mass around 750°C due to the carbon dioxide evolution.
- The thermal decomposition of GO in two steps around 300°C and 550°C due to the removal of oxygen functional groups and carbon dioxide evolution.
- Reduced graphene oxide sheets exhibit a weight loss at about 240 °C.

under N_2 atm.



The weight percentage of GO sample is still about 60% after thermal treatment under N_2 atm, but there is no loss in the weight percentage of reduced graphene sheets.

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Findings

Morphological Analyses

- *SEM* images indicated the existence of rippled graphene layers rather than completely flat layers in a free standing state.

- *AFM* images in 3D view supported the formation of rippled graphene layers and effect of reaction in each step

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Findings

Crystal Structure Analyses

- *Raman* spectra indicated that there is a linearly decrease in graphene layers with respect to the decrease in G band intensity.
- Formation of D band after oxidation process was an evidence for the success of the reaction procedure.
- After heat treatment and reduction processes, quasi-defect-free graphene sheets were formed.
- As I(G)/I(D') decreases after chemical reduction layer number decreases.
- *Also, XRD* results indicated reduction of the average number of graphene layers steadily from raw graphite to graphene nanosheets by stepwise chemical procedure
- The average number of graphene layers calculated from AFM and XRD analyses were consistent.

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Conclusions

- Graphene-based nanosheets were produced in moderate quantities by improved, safer and mild chemical route applied in the present work.

- The shorthest and most exfoliated (minumum number of graphene layers) method is graphite oxidation, ultrasonic treatment and chemical reduction of GO samples.

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Conclusions

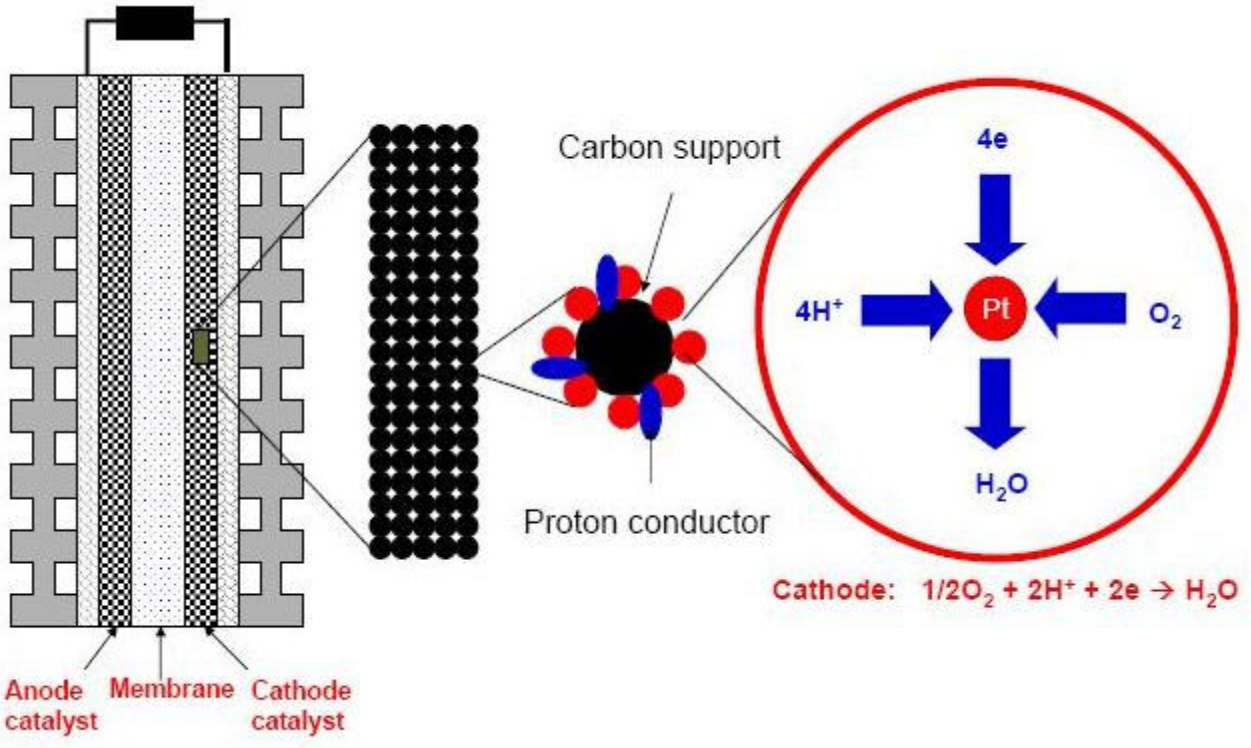
Characterization Techniques	Results
SEM	Graphene layers can exist by being rippled rather than completely flat in a free standing state
AFM	3D views of samples were evidence for reaction process in each step
XRD	Change of interplanar spacings also explained how each step in the proposed procedure affected the morphology of graphite
TGA	The thermal stability of graphene nanosheets is much lower than pristine graphite flake
Raman Spectroscopy	The formation of partially ordered graphitic crystal structure of graphene nanosheets
Calculation of layer number with XRD andAFM	**(1)** the average number of graphene layers reduced steadily from raw graphite to graphene-nanosheet samples by stepwise chemical procedure **(2)** The average number of graphene sheets can be reduced upto 7 by chemical reduction process
Crystallinity analysis by XRD	GO samples became amorphous and the percent crystallinity decreases upto 2%

PART 2
UTILIZATION

Utilization of graphene nanosheets

- Fuel cells are emerging as an attractive power source due to their inherently clean, efficient and reliable service.
- Polymer electrolyte membrane fuel cells still cannot compete commercially in several utilizations owing to the high cost, the poor durability and reliability.

Main drawback in fuel cells is catalyst



The interaction between the carbon support and Pt catalyst has significant importance on the electrode performance.

The characteristic properties for the catalyst support materials

- high specific surface area required for the enhancement of the dispersion and narrow distribution of catalytic metals
- low combustive reactivity under both dry and humid air conditions at low temperatures (150 °C or less)
- high electrochemical stability under fuel cell operating conditions
- high conductivity
- easy-to-recover Pt in the used catalyst.

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Fabrication of Polypyrrole/graphene based electrodes for fuel cells

- Polypyrrole (PPy) is one of the most significant conducting polymers due to its relatively easy processability, electrical conductivity, and environmental stability.
- Geometric structures affect the performance of electrodes (Mass Transport, Charge Transport and 3 point contact of gas, catalyst and PEM).
- Graphene nanosheets have potential applications in energy storage devices like supercapacitors, fuel cells or other power source systems due to free standing layers having high electrical conductivities and large surface area.

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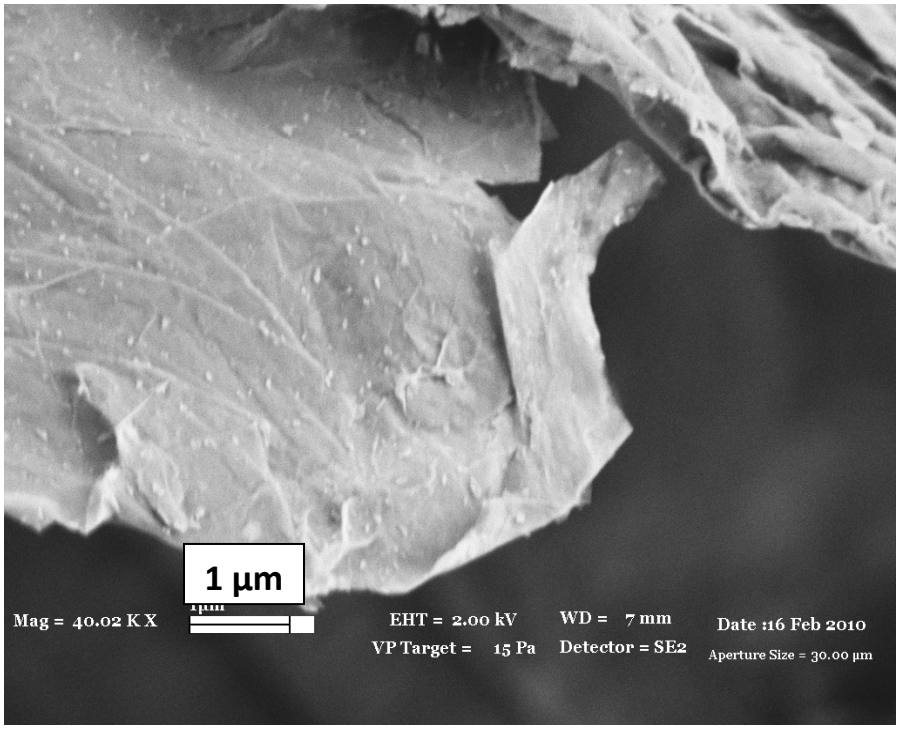
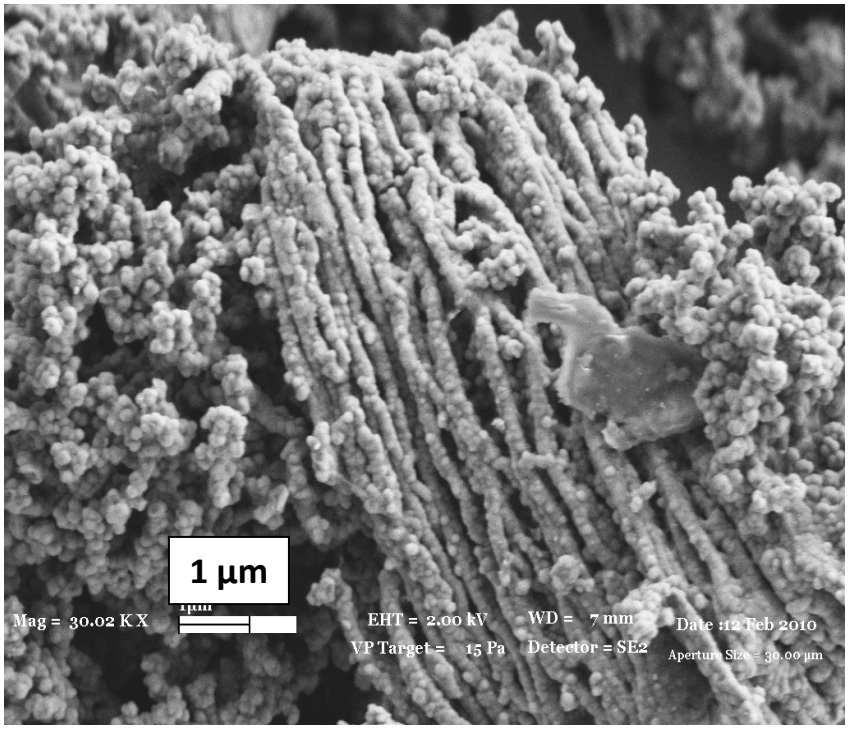
Polypyrrole coated GO nanosheets *in situ* polymerization



GO nanosheets after 10 days oxidation



PPy coated GO nanosheets
(Pyrrole/GO nanosheets 1:1 by weight)

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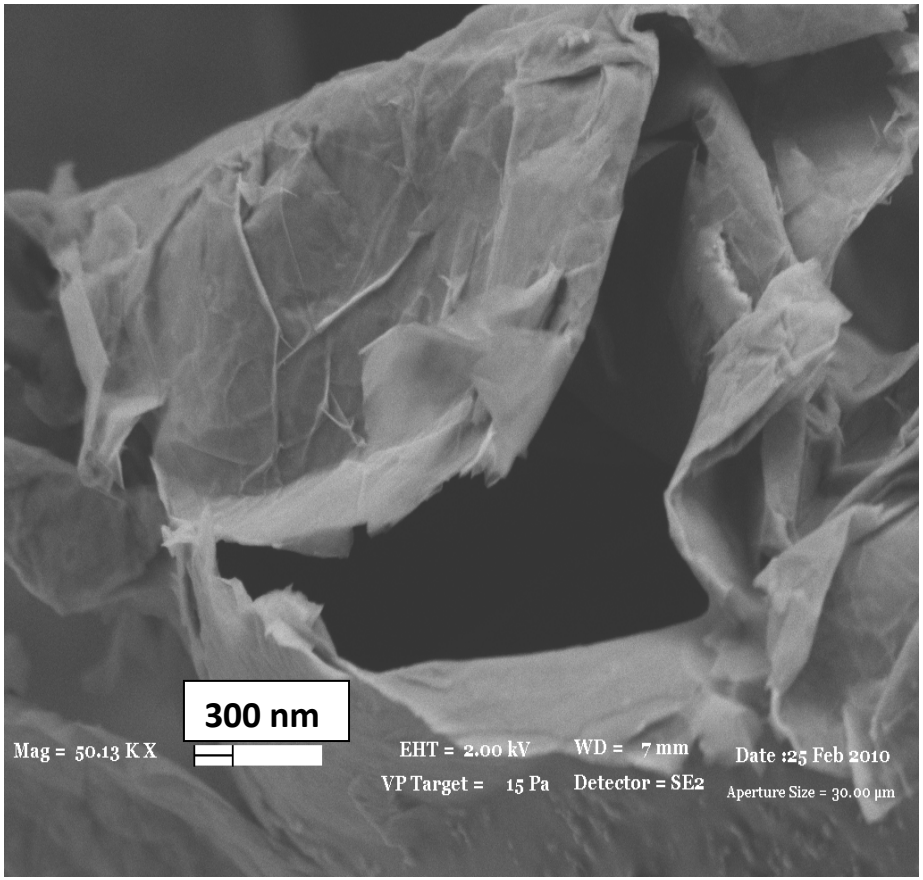
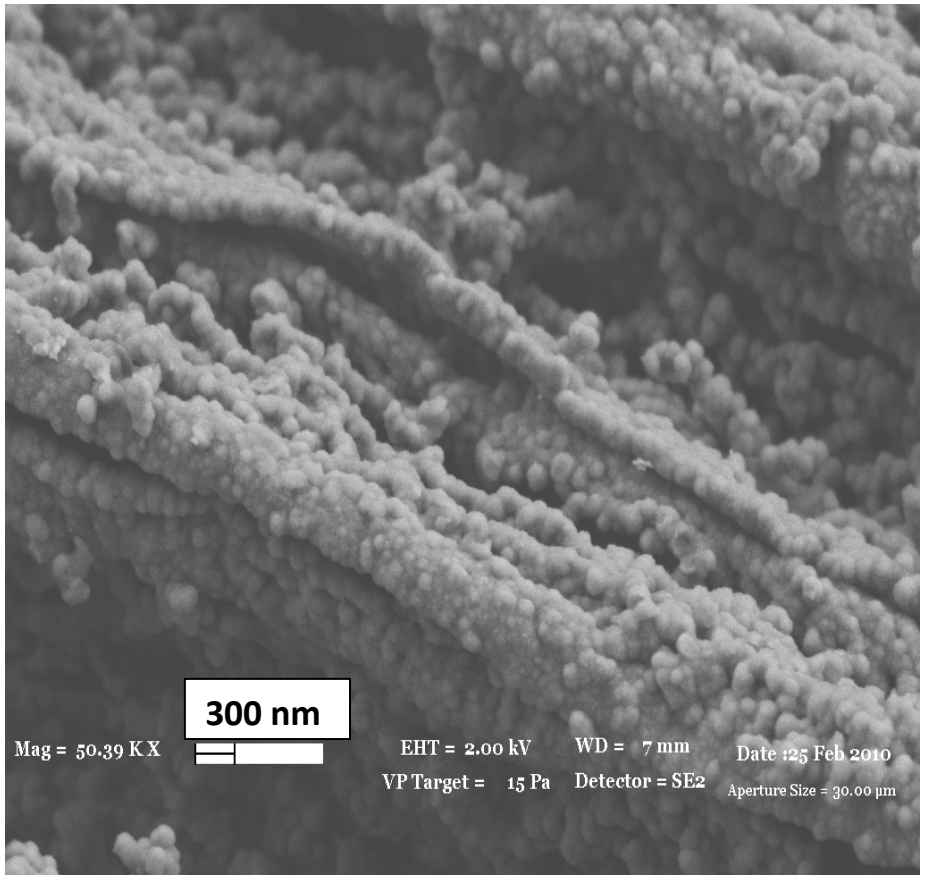
Polypyrrole coated graphene nanosheets *in situ* polymerization



Graphene nanosheets obtained after chemical reduction of GO



PPy coated graphene nanosheets (Pyrrole/graphene nanosheets 1:1 by weight)

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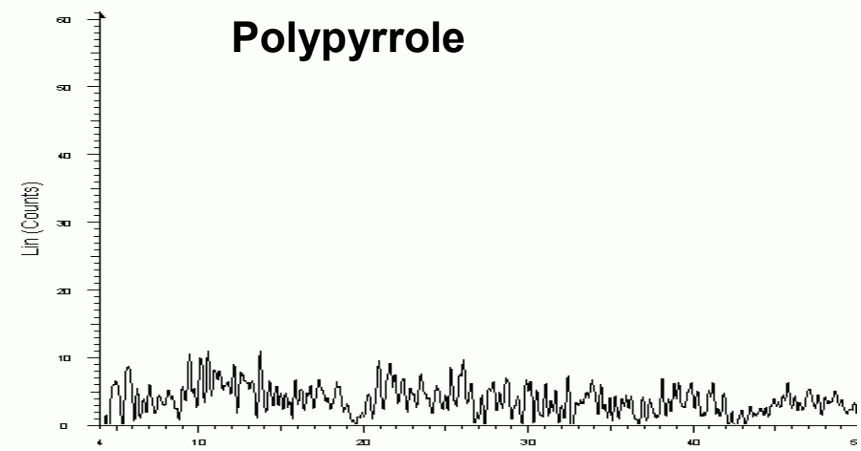
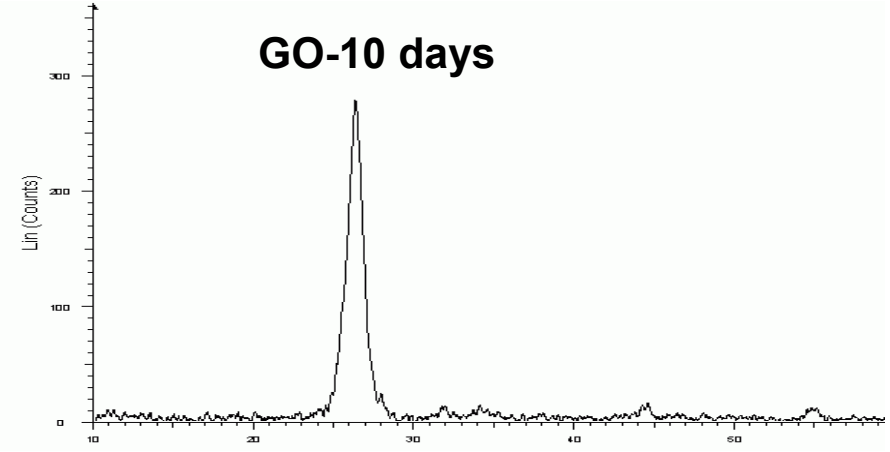
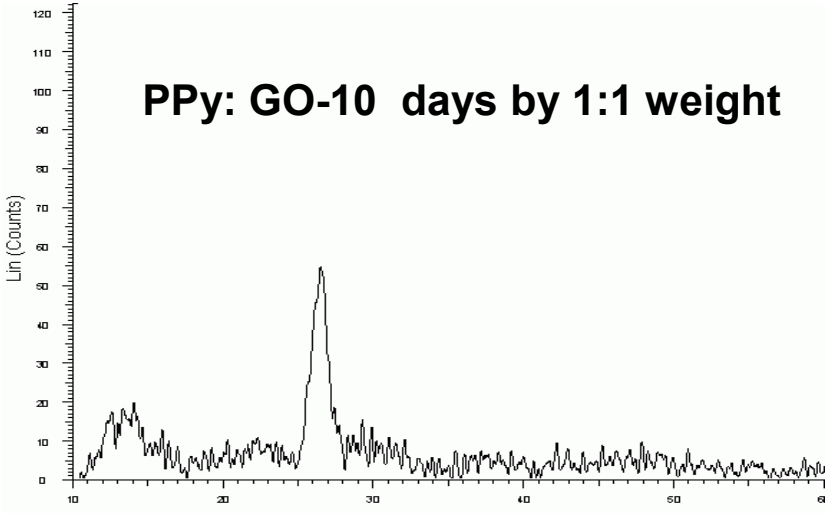
XRD characterization

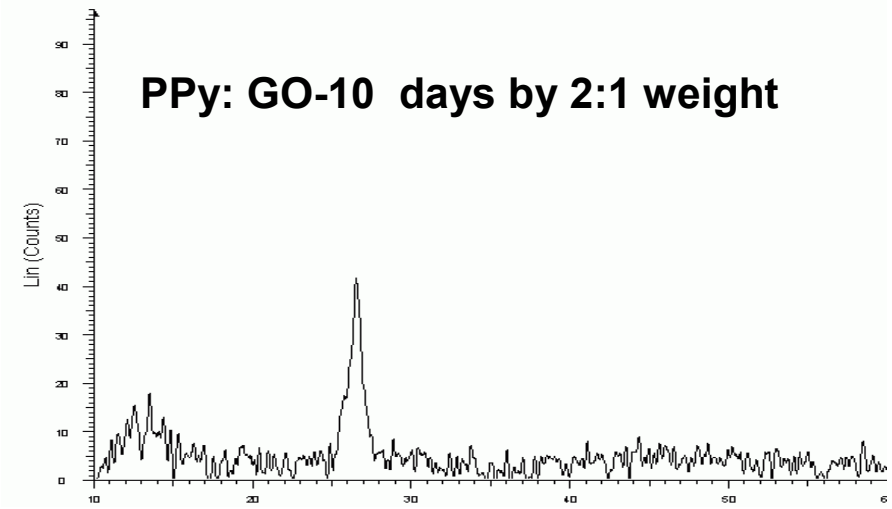




GO-10 days-max intensity of 002 peak is 274 cps



GO-10 days-max intensity of 002 peak is 53.1 cps



GO-10 days-max intensity of 002 peak is 40.6 cps

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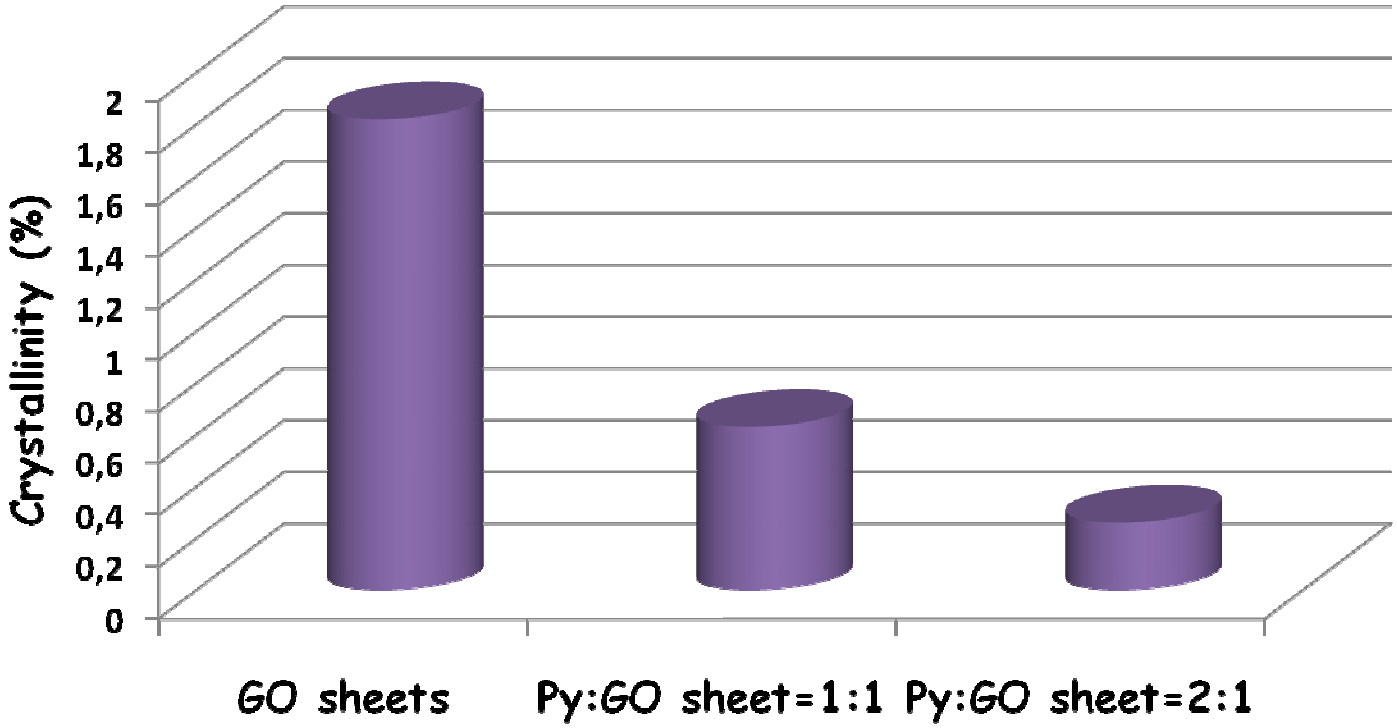
Crystallinity change



Crystallinity of Graphite (%)=100
Polypyrrole=amorphous

As pyrrole amount increases, crystallinity decreases.

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Measurement of electrical conductivities

preliminary data

- Pellet electrodes were prepared under adjusted pressure by using graphene nanosheets
- Electrical properties of electrodes were estimated in through between two gold plates at room temperature by voltameter according to the feed ratio of PPy to GO nanosheets, their thickness, resistance and conductivity values.

Samples	Electrical Conductivity (S/cm)
PPy	$1.1*10^{-6}$
GO nanosheets	2.900
PPy:GO nanosheets 1:1 by mechanical stirring	0.039
PPy:GO nanosheets 2:1 by mechanical stirring	0.029
PPy:GO nanosheets 1:1 by in situ polymerization	0.018
PPy:GO nanosheets 2:1 by in situ polymerization	0.009

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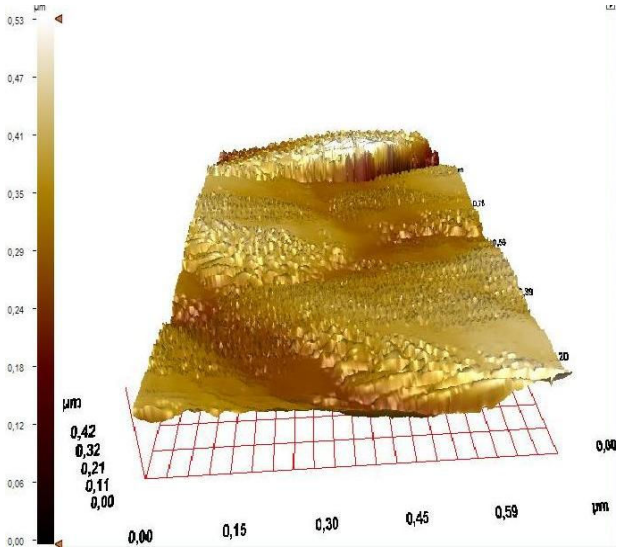
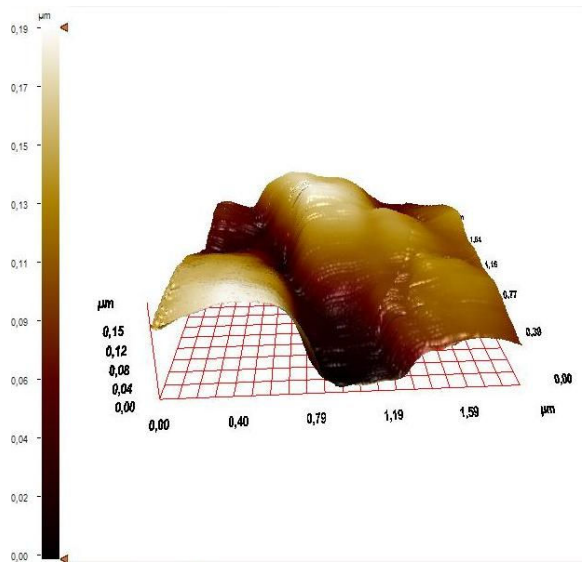
AFM analyses of electrodes

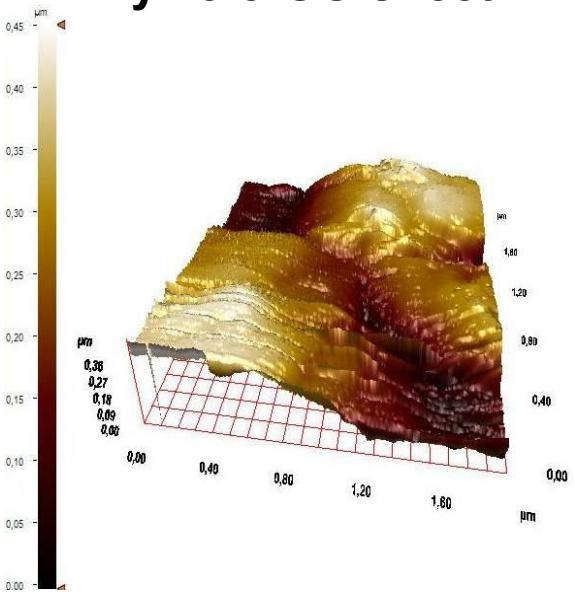
Polypyrrole



Pyrrole:GO sheet=1:1



Pyrrole:GO sheet=2:1



- As pyrrole concentration increases, the electrode surface becomes smoother.
- As GO sheet amount increases, the height difference of surface increases due to ripples in GO sheets.

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Conclusions

- The electrical conductivity of PPy-GO nanosheet based composites was slightly decreased with the increase of the feeding mass ratio of pyrrole to GO nanosheets due to percolative behaviour.

- Functionalized graphene sheets could potentially lead to a more stable, efficient, and lower-cost fuel cell. Therefore, PPy/Graphene-based nanocomposites as fuel cell electrodes have a dramatic effect on fuel cell performance.

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Thank you for your attention