Facile synthesis of polypyrrole/graphene nanosheet-based nanocomposites as catalyst support for fuel cells

Burcu Saner, Selmiye Alkan Gürsel, Yuda Yürüm

Materials Science & Engineering
Faculty of Engineering and Natural Sciences, Sabancı University, Istanbul

ICAM-I2CAM Institute for Complex Adaptive Matter

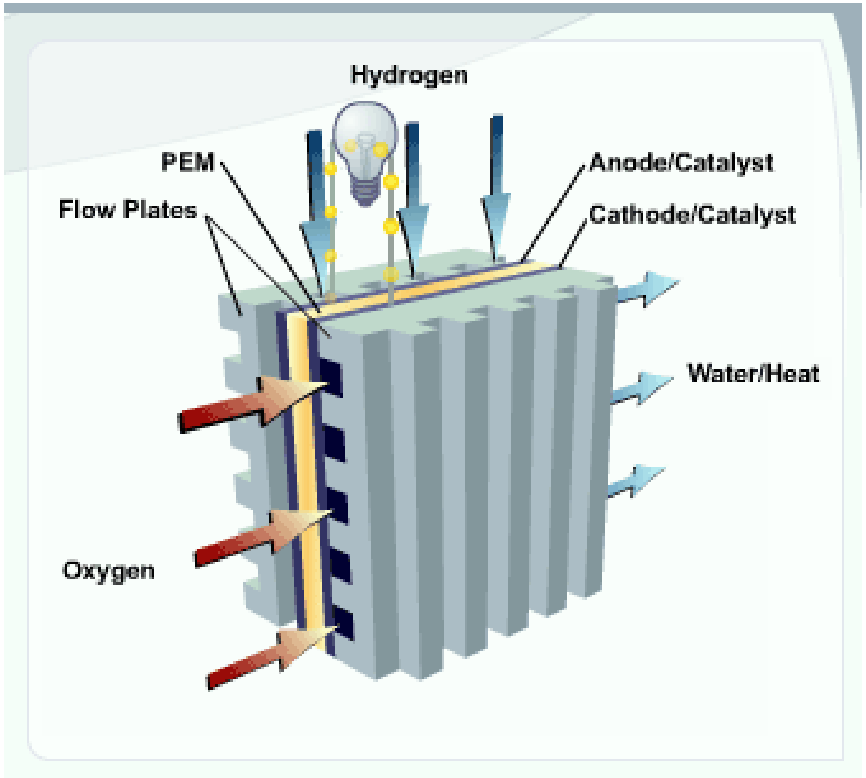
NSF

SABANCI UNIVERSITY Faculty of Engineering and Natural Sciences

2010 MRS FALL MEETING Boston, MA November 29–December 3

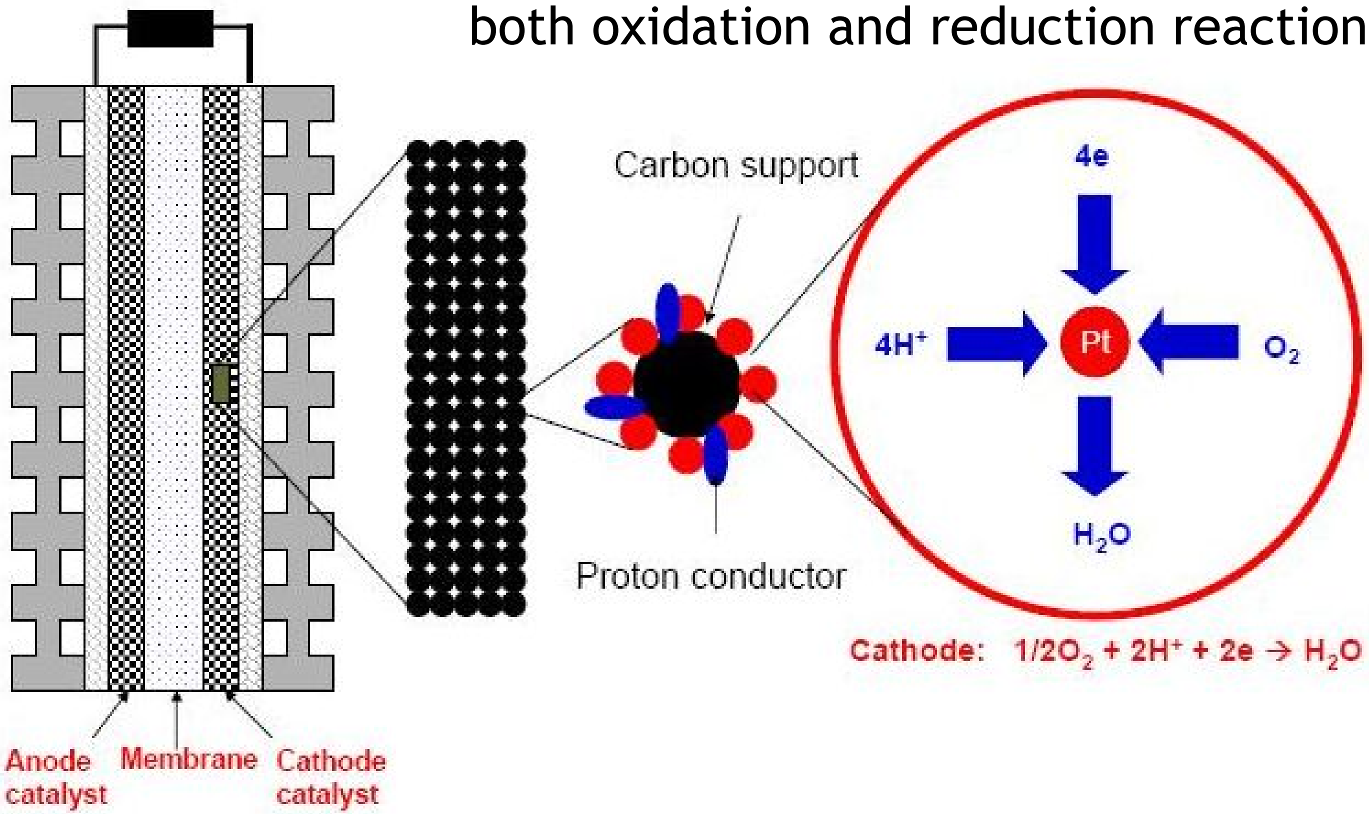
Polymer electrolyte membrane fuel cells

- PEM fuel cells deliver high power density which provides low weight, low cost and low volume.
- In PEM fuel cells, an electrolyte membrane sandwiched between an anode and a cathode.
- Possible limiting factors for the commercialization of PEM fuel cells are the cost of the catalyst materials and poor durability.



Main challange in fuel cells is catalyst!

Pt is the most common catalyst in PEM fuel cells for both oxidation and reduction reactions.



Catalyst support materials have great influence on the cost, performance and the durability of PEM fuel cells.

Expected features of catalyst support in fuel cells

- high surface area for the enhanced distribution of catalyst metals
- sufficient electrode porosity
- high electronic conductivity
- chemically and mechanically stable under high potential, high acidity, high humidity, and high temperature
- mass producibility
- low cost

*S. K. Natarajan and J. Hamelin, Journal of The Electrochemical Society, 156 (2) B210-B215, 2009.

Graphene nanosheets as nanofillers in conducting matrix

- Graphene nanosheets have high surface area, superior electrical conductivity and excellent mechanical and thermal properties.

- Polypyrrole (PPy) has good electronic and proton conductivity, ease processability and special nanometer structure.

- With the incorporation of graphene sheets as conducting fillers in PPy, graphene sheets act as electron acceptors while PPy serves as an electron donor.

- **Graphene-based composites can be a good alternative to carbon black and utilized as a catalyst support for Pt in PEM fuel cells.**

Objectives

- A mild and safer chemical exfoliation of graphene nanosheets
- Incorporation of graphene nanosheets in conducting polymer matrix to be utilized as catalyst support in PEM fuel cells
- The deposition of Pt catalyst into the graphene-based composites

Chemical exfoliation of graphene nanosheets

Starting Material = Graphite Flake

↓

OXIDATION
Potassium dichromate and sulfuric acid as oxidants
Acetic anhydride as an intercalating agent
The reaction temperature: $45^{o}C$

↓

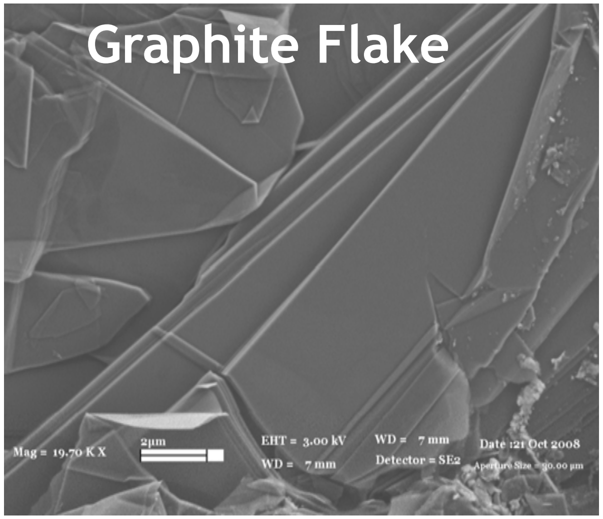
ULTRASONIC TREATMENT

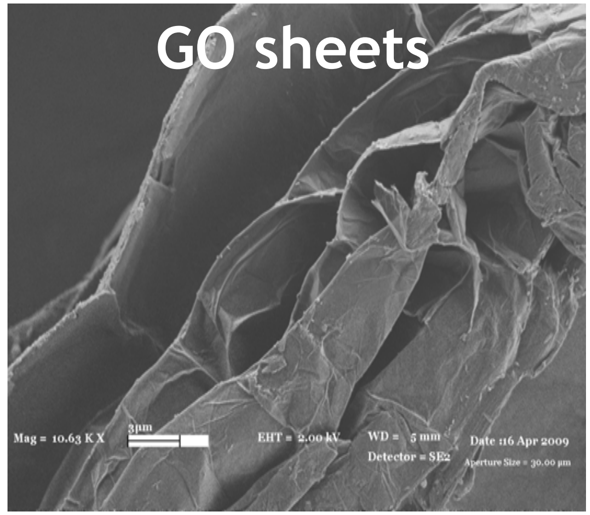
↓

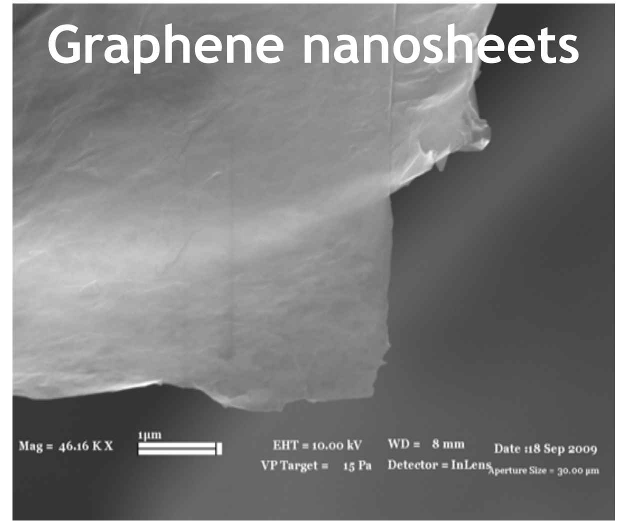
CHEMICAL REDUCTION
by hydroquinone

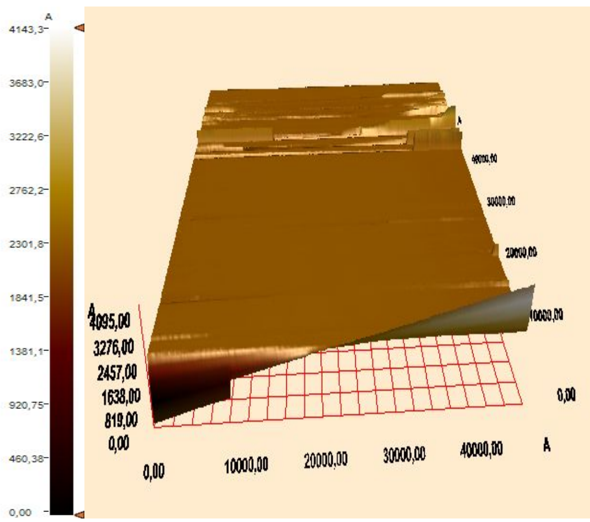
[1]B. Saner, F. Okyay, Y. Yürüm, Utilization of multiple graphene layers in fuel cells. 1. An improved technique for the exfoliation of graphene-based nanosheets from graphite Fuel 89 (2010) 1903–1910.
[2]B. Saner, F. Dinc, Y. Yürüm, Utilization of multiple graphene nanosheets in fuel cells 2. The effect of oxidation process on the characteristics of graphene nanosheets, Fuel (2010), submitted.

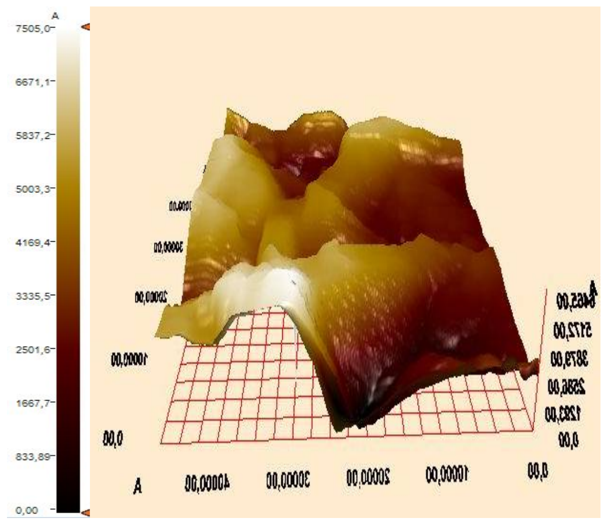
Analysis of surface morphology by SEM (by SE detector) and AFM (by tapping mode)

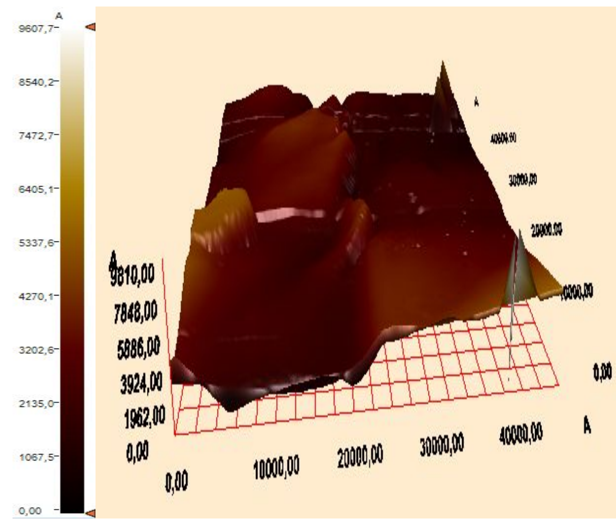










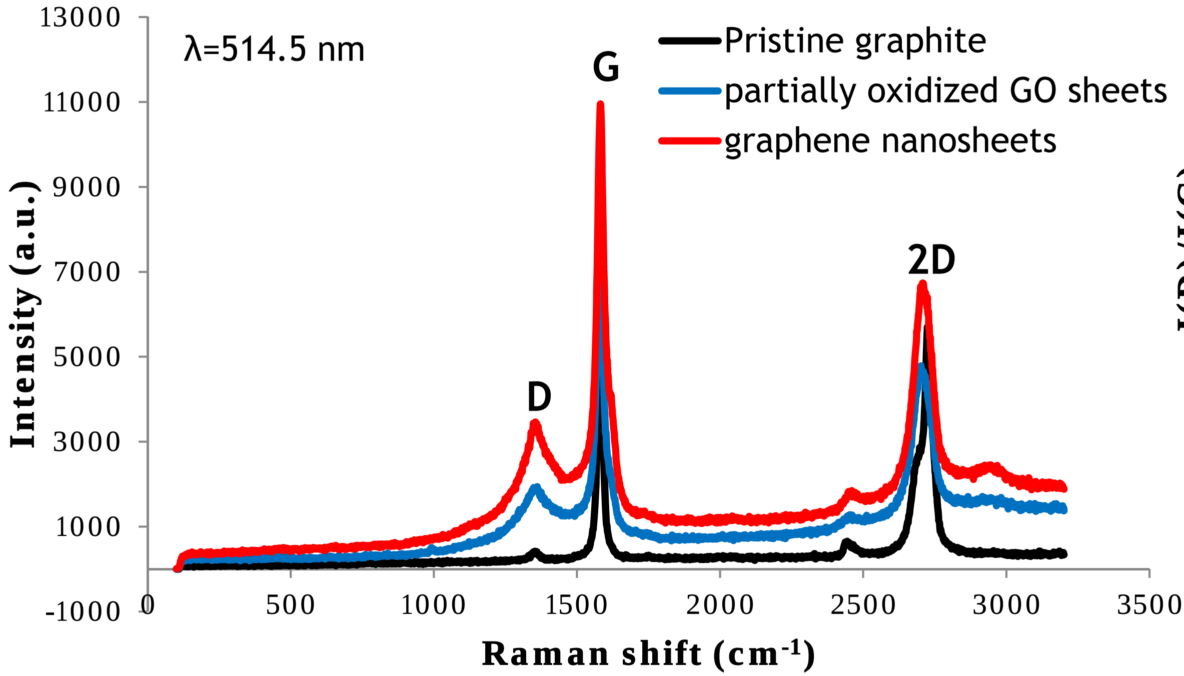


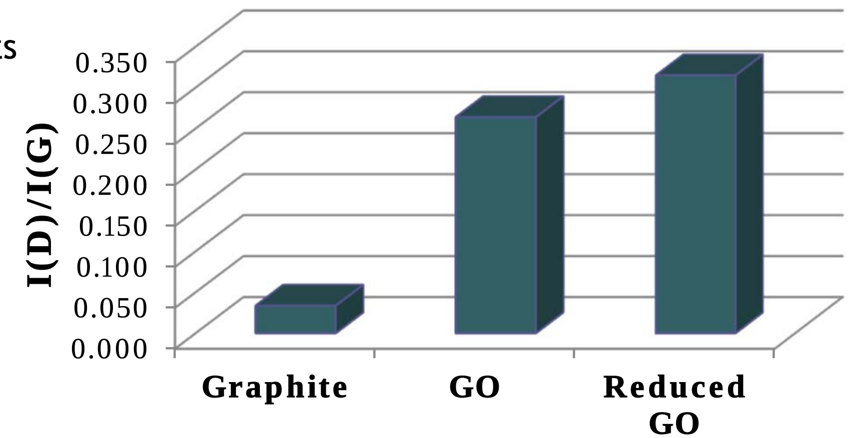
Rigid and condensed layers

Ripple layers

Flatter layers

Comparison of Raman Spectroscopy Results with XRD results





As I(D)/I(G) increases, flake thickness decreases*[1].

Average Layer number was calculated from XRD data by using Debye Sherrer Equations*[2]:

Samples	Average number of graphene layers	d(Å)
Graphite	86	3.37
GO sheets	21	3.39
Graphene nanosheets	19	3.42

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

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

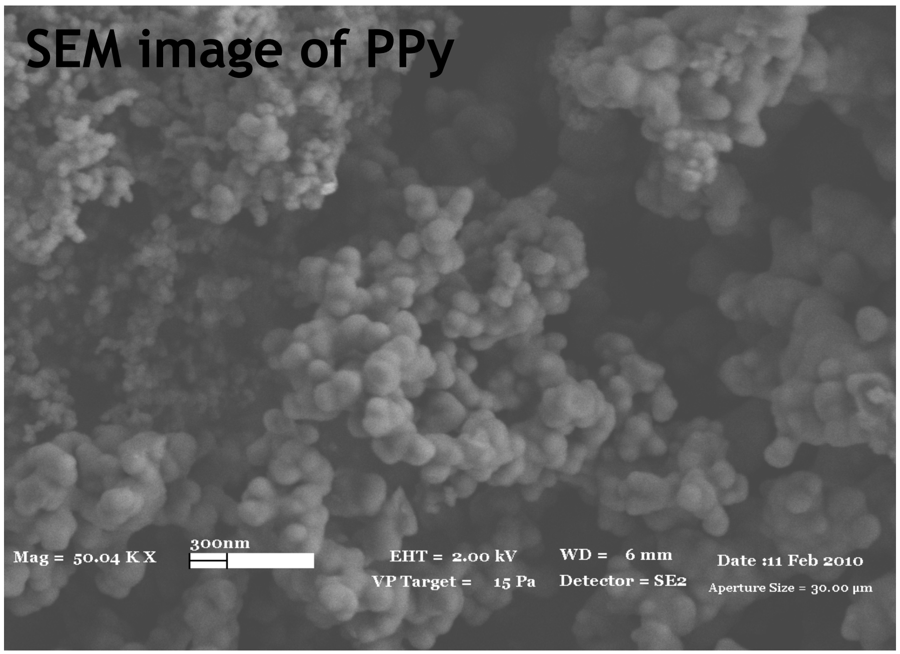
L_a : stacking height
β : full width half maxima (FWHM)
n: average number of graphene layers
d_{002} : interlayer spacing

*[1]A. C. Ferrari, *Nano Lett.*, 9 (2009) 1433-1441.

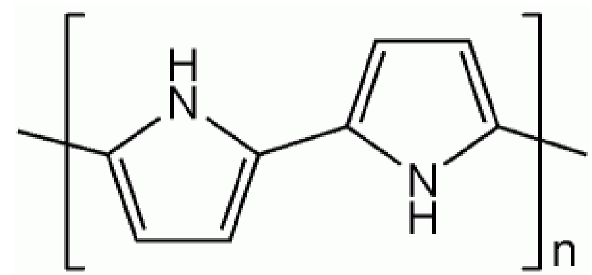
*[2]B. Sakintuna, S. Cetinkaya, Y. Yürüm, *Energy Fuels*, 18 (2004) 883-8.

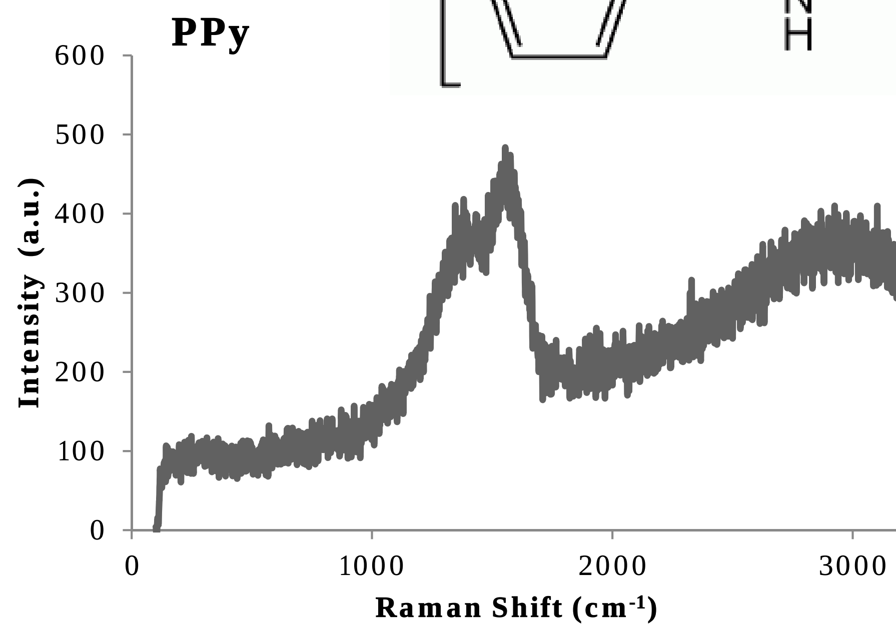
Synthesis of Polypyrrole by *in situ* polymerization

PPy was synthesized by using $FeCl_3$ as an oxidant in the mixture of H_2O and ethanol as 1:1 (by volume).



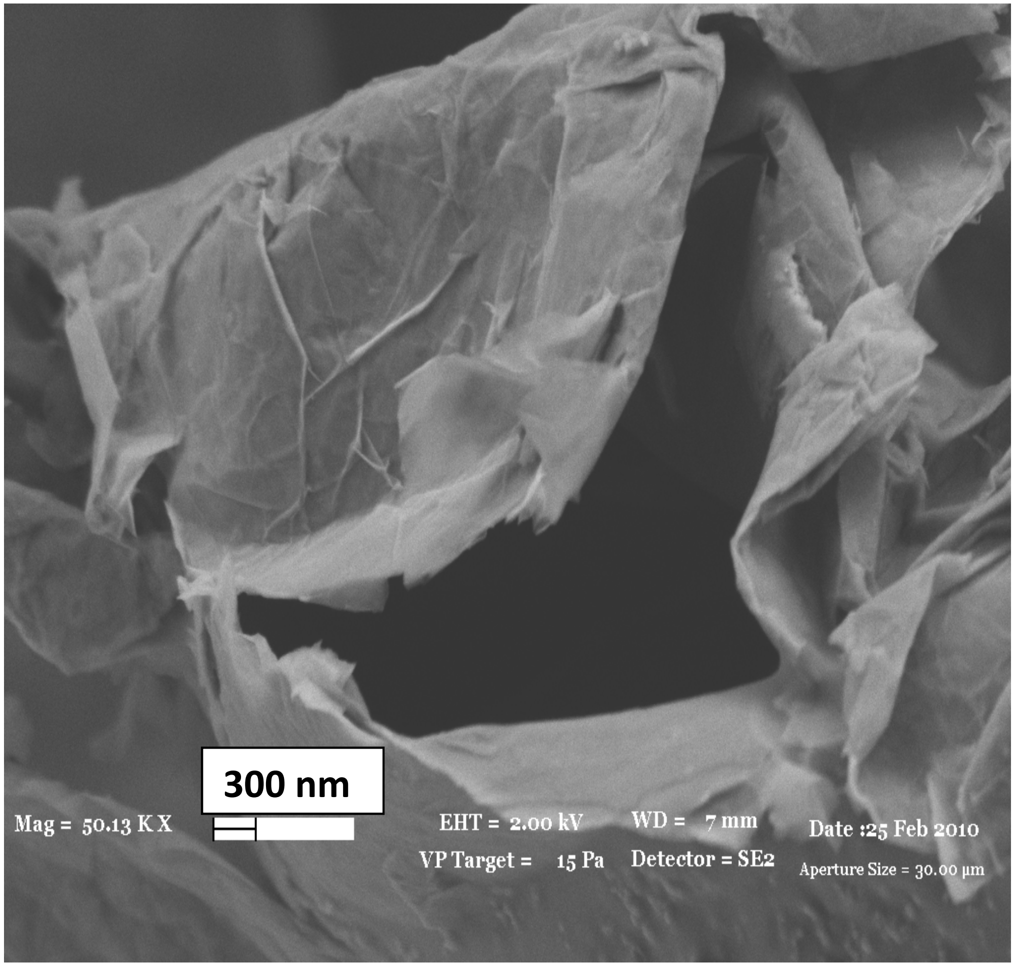
irregular sphere-like particles



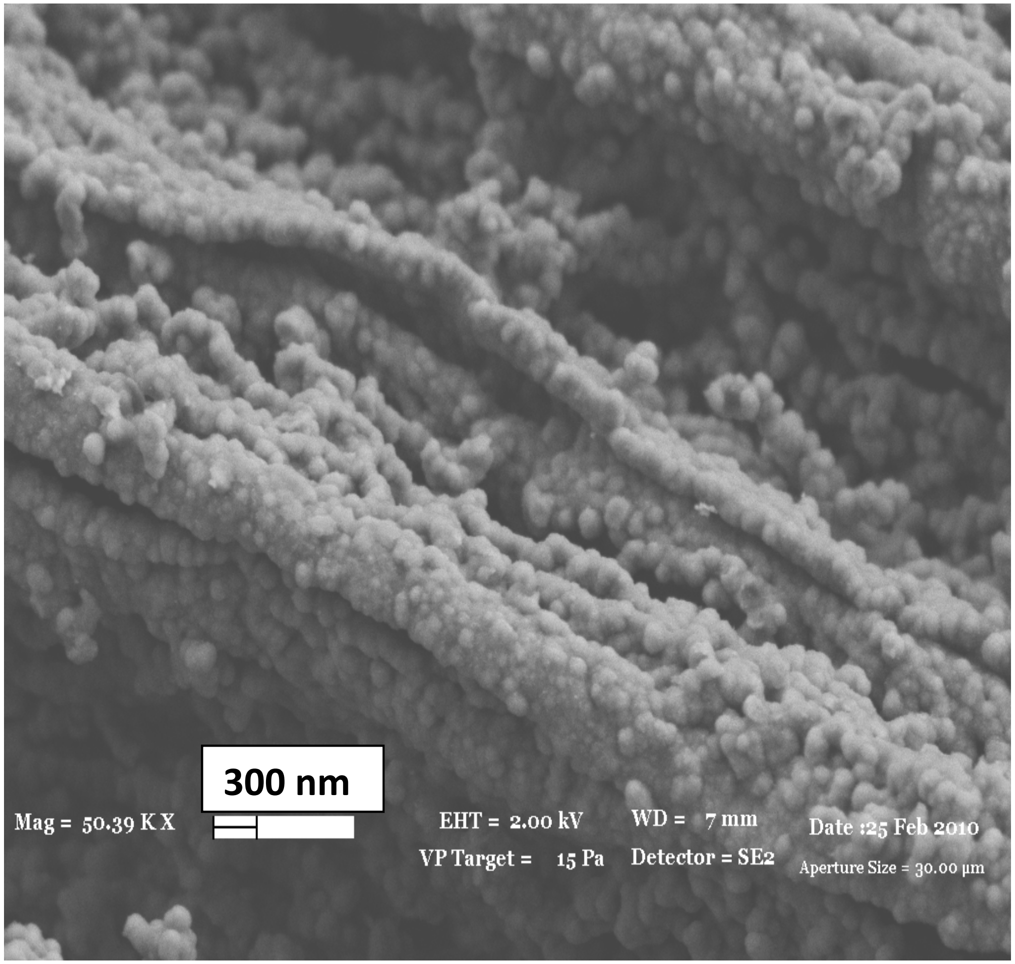


- ➢The band at ~1580 cm^{-1} due to C=C backbone stretching of PPy
- ➢The band at ~1350 cm^{-1} due to the ring stretching of PPy

Polypyrrole coated graphene nanosheets via *in situ* polymerization



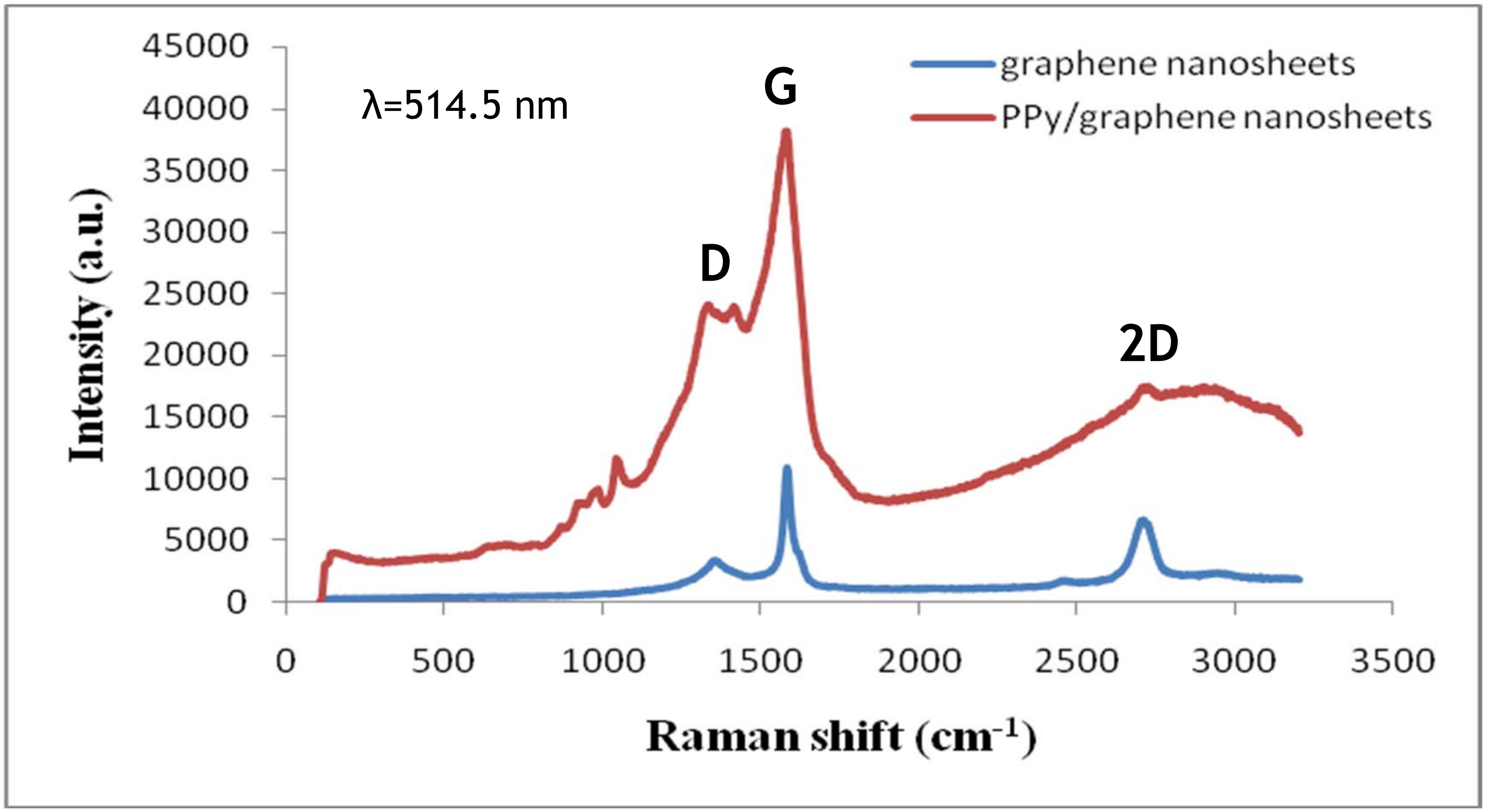
Graphene nanosheets obtained after chemical reduction of GO



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

B. Saner, S. Alkan-Gursel, Y. Yürüm, Synthesis and characterization of polypyrrole/graphene nanosheet composites as the potential catalyst support materials for fuel cells, Energy & Environmental Sciences, 2010, submitted.

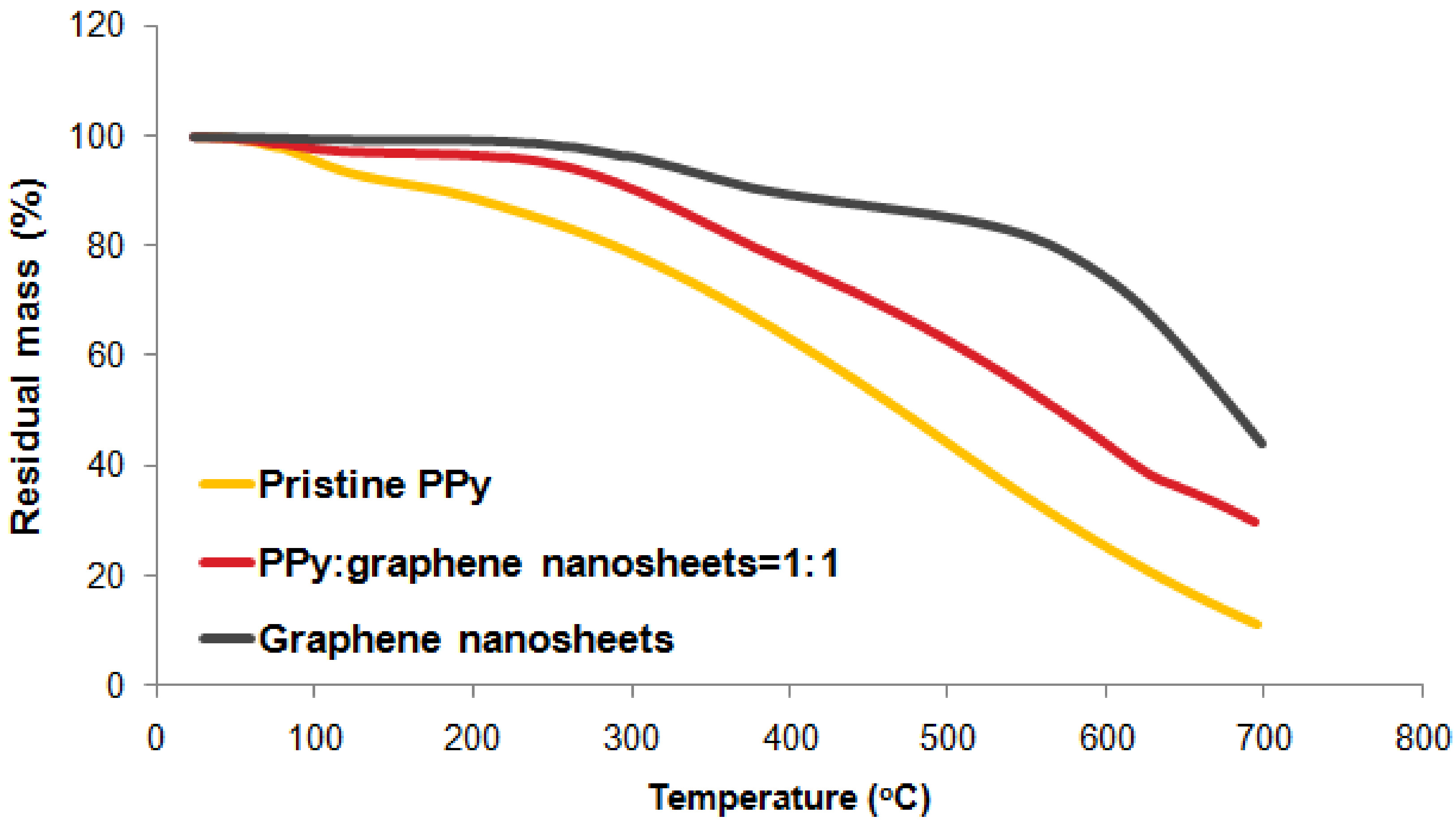
Raman spectroscopy characterization



G band intensity is directly proportional to crystallite size, L_a*.
This indicated that the flake thickness was increased due to coating.

*K. Sato, R. Saito, et al., *Chemical Physics Letters* **427**, 117–121, 2006.

Thermogravimetric analysis of PPy/Graphene nanosheet composites



The amount of weight losses of pristine PPy, graphene nanosheets and Py:graphene nanosheets=1:1 at 700 °C were about 88%, 56%, and 70%, respectively.

Conductivity and surface area results

Samples	Conductivity (S/cm) by four-probe method	Surface area (m^2/g) According to BET theory
Pristine PPy	**7.6×10^{-4}**	**-**
Graphene nanosheets	**3.96**	**507**
PPy/Graphene nanosheets	**0.13**	**290**

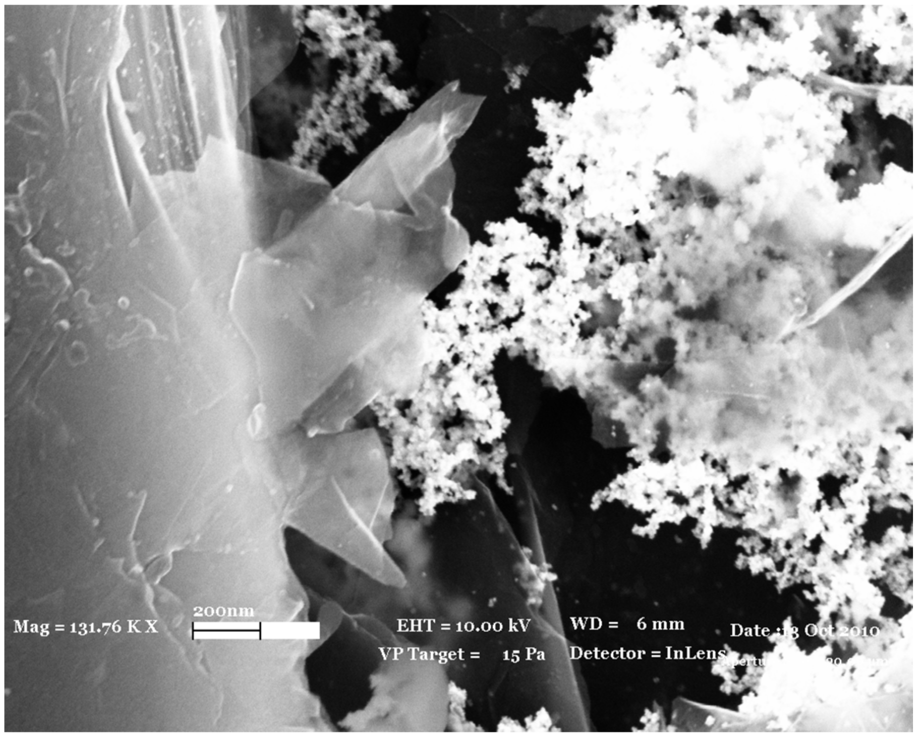
- After PPy was coated onto the surface of graphene nanosheets, the conductivity of the composite was improved due to the better compactness and structure of PPy in the composite than in pure PPy.

- High surface area has a significant influence on the dispersion and distribution of catalytic metals on catalyst supports.

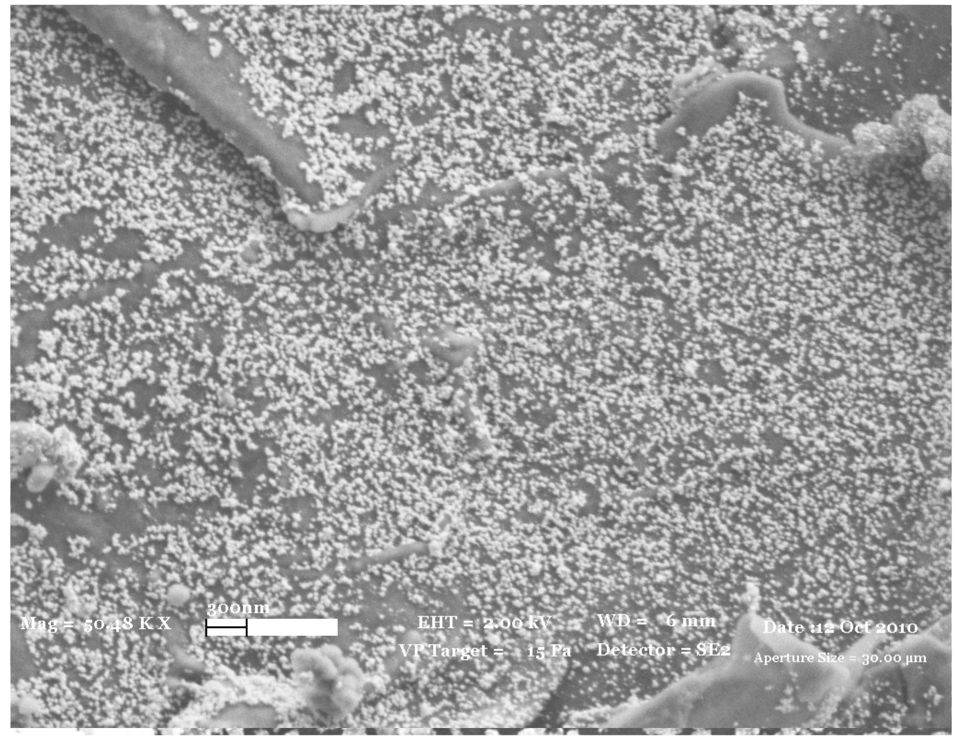
Surface area measurement of graphene nanosheets via nitrogen gas absorption yielded a BET value of 466 m^2/g*.
*S. T. Nguyen , R. S. Ruoff, et. al., Carbon 45 (2007) 1558–1565

Pt deposited PPy/Graphene nanosheet-based nanocomposites

Pt (8 % H_2PtCl_6 solution) deposition on the surface of graphene sheets was performed by using 1M $NaBH_4$ as a reducing agent by sonication technique about 2 hr at room temperature*.



- ➢Some Pt particles were aggregrated and some of them were dispersed uniformly on the surface of graphene nanosheets
- ➢Pt nanoparticle size: 6-20 nm



- ➢Pt particles were uniformly dispersed on the surface of nanocomposites.
- ➢Pt nanoparticle size: 20-30 nm

*B. Saner, A. Yurum, S. Alkan-Gursel, Y. Yurum, Investigation of Pt catalyst deposition on polypyrrole/graphene nanosheet composites for PEMFC, *in preparation.*

Conclusions

- ✓ Graphene nanosheets were exfoliated from graphite by applying a mild, safer and cost effective chemical route including oxidation, sonication and reduction.
- ✓ Graphene nanosheets were coated uniformly by conducting PPy by *in situ* polymerization of pyrrole monomer.
- ✓ Sonication process provided the best exfoliation and dispersion of both Pt nanoparticles and graphene nanosheets.
- ✓ PPy/Graphene nanosheet-based nanocomposites having enhanced thermal stability, and electrical conductivity, and high surface are promising catalyst supports for to prevent the corrosion of catalysts and to provide long-term durability in PEM fuel cells.

Acknowledgment

- Thanks to Assoc. Prof. Mustafa Çulha and PhD student Mehmet Kahraman from Yeditepe University for their permission to use their Raman Spectroscopy.

- Thanks to Prof. Dr. Levent Toppare from Middle East Technical University for his help in four probe measurements.

- Thanks to
  - NSF grant number DMR-0844115
  - ICAM-I2CAM, 1 Shields Avenue, Davis, CA 95616

  for their travel support to attend MRS conference.

Thank you!