Thin Coatings of Polymeric Carbon and Carbon Nanotubes for Corrosion Protection

Zafar Iqbal

Department of Chemistry and Environmental Science
New Jersey Institute of Technology
Newark, New Jersey 07102

Collaborators: Graduate students: Chi Yu, Anitha Patlolla
Faculty: M. Sosnowski and H. Grebel
ARDEC: J. Zunino

2009 US Army Corrosion Summit

NJIT New Jersey's Science & Technology University

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
FEB 2009		**00-00-2009 to 00-00-2009**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Thin Coatings of Polymeric Carbon and Carbon Nanotubes for Corrosion Protection	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **New Jersey Institute of Technology,Department of Chemistry and Environmental Science,Newark,NJ,07102**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
2009 U.S. Army Corrosion Summit, 3-5 Feb, Clearwater Beach, FL

14. ABSTRACT

15. SUBJECT TERMS

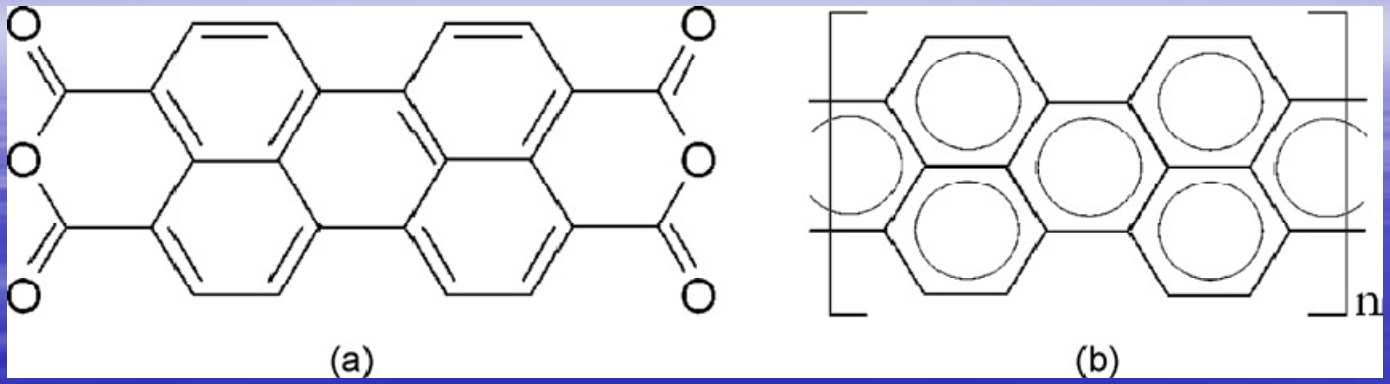
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**16**	

Outline of talk

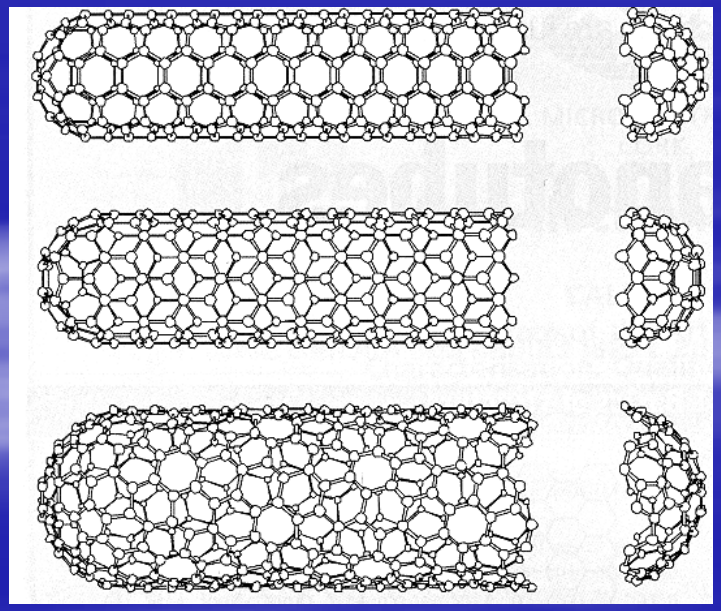
- Introduction – new barrier materials and concepts for corrosion protection
  - Conjugated/conducting polymers
  - Smart-active corrosion protection with carbon nanotube *p-n* junctions
  - Potential corrosion protection in iron-carbon nanotube composites
- Polyperinaphthalene (PPN) results
- Carbon Nanotube approaches and results
- Thermochromic conjugated polymer concepts
- Summary

NJIT New Jersey's Science & Technology University

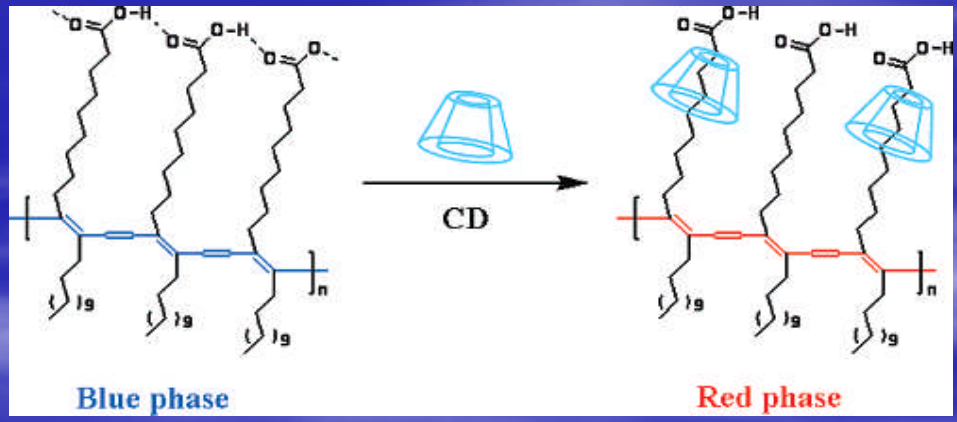
Chemical Structures of Coating Materials



Polyperinapthalene (PPN)



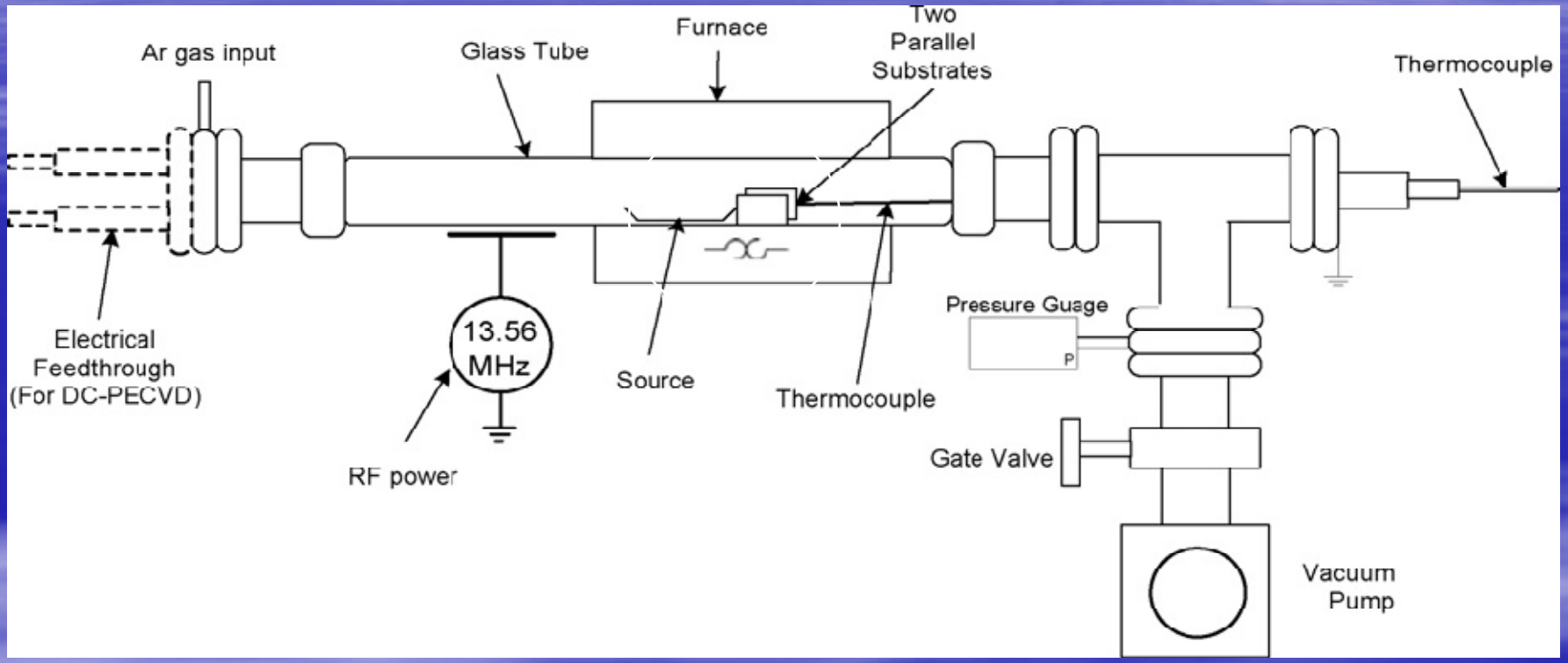
Single wall carbon nanotubes

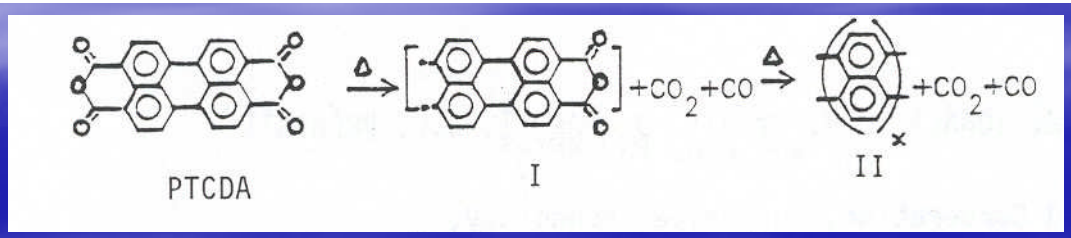


Polydiacetylene: $CH_3(CH_2)_{11}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_8\text{-}COOH$

NJIT New Jersey's Science & Technology University

Apparatus for Plasma-CVD Synthesis and Deposition of PPN

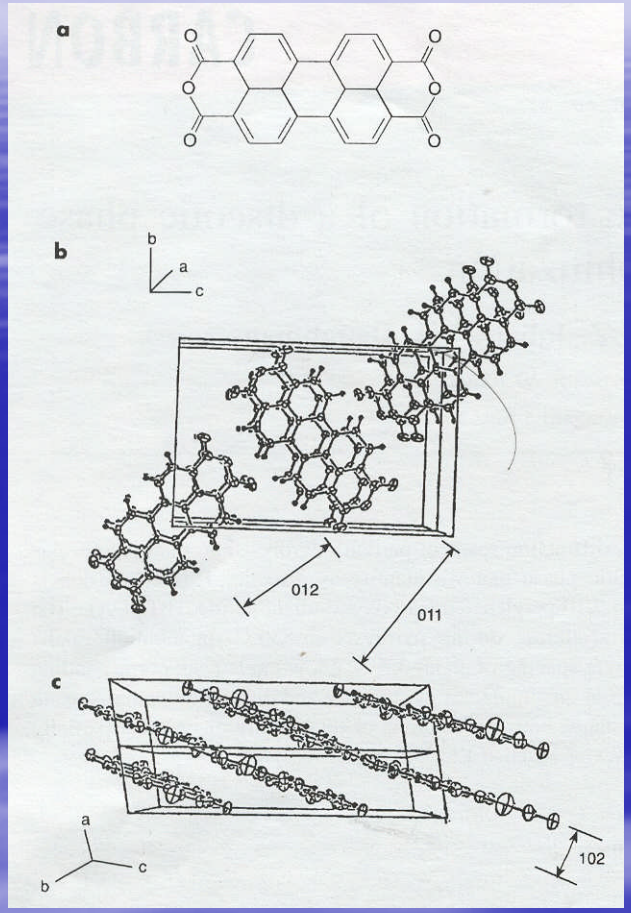




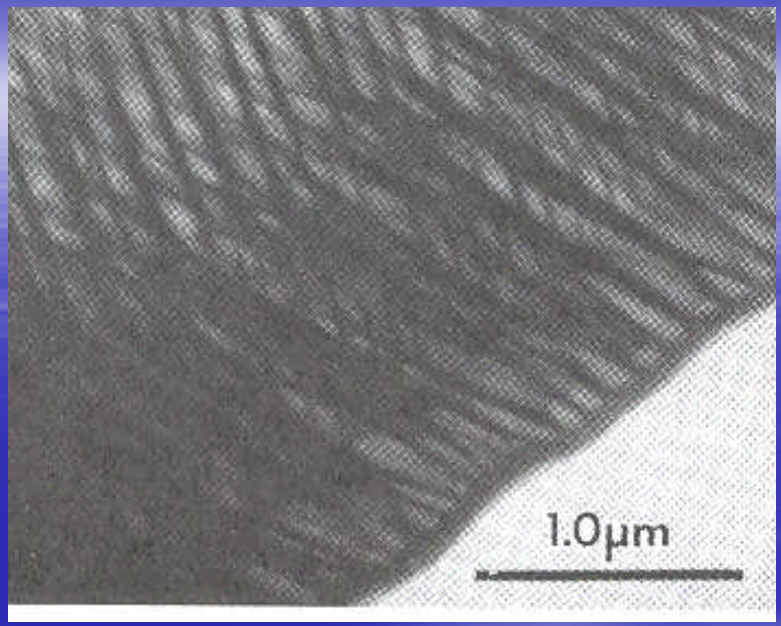
C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals 158*, 425 (2008)

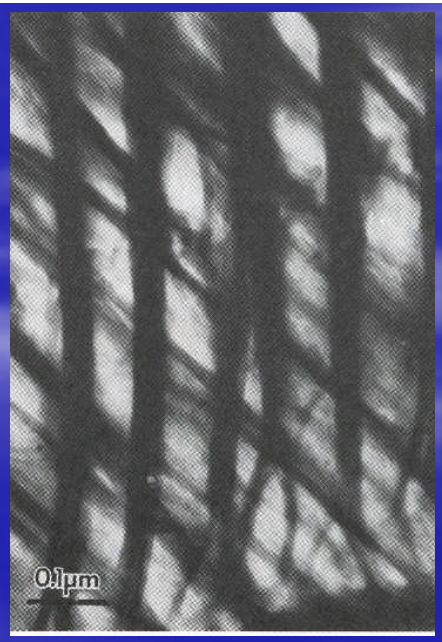
NJIT New Jersey's Science & Technology University

Transition from PTCDA precursor to PPN



Crystal structure of
PTCDA precursor



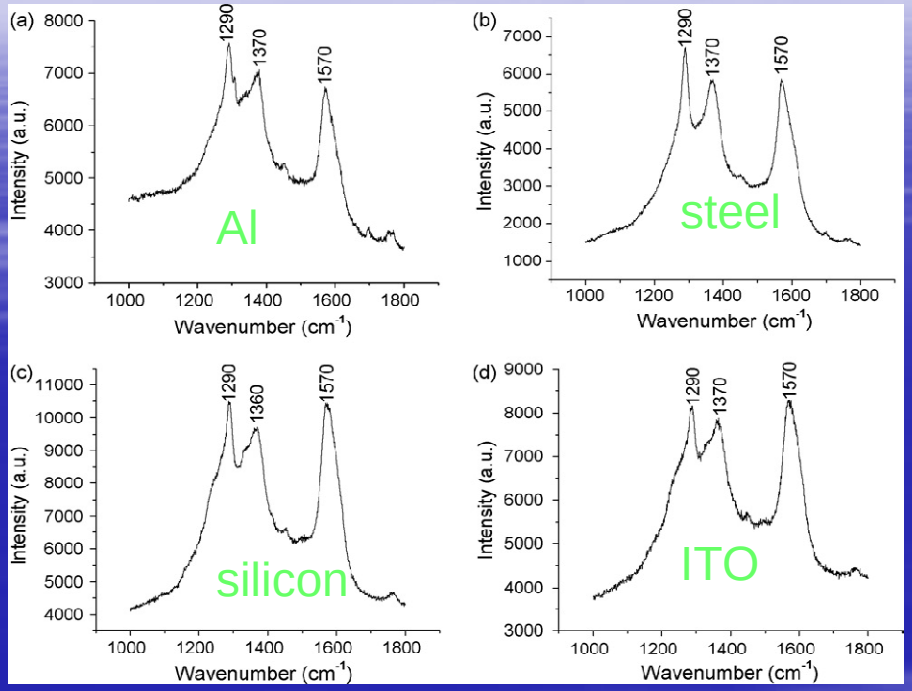


TEM images of PPN

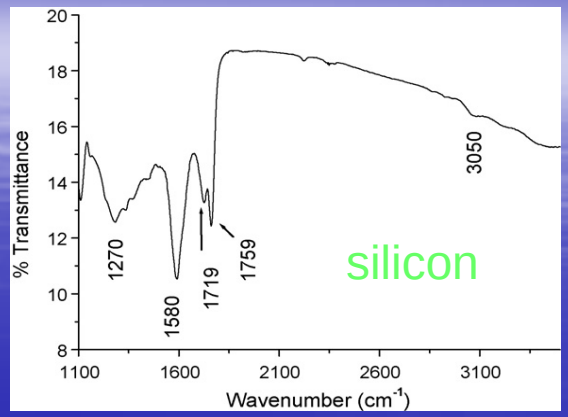
NJIT New Jersey's Science & Technology University

Z.Iqbal, D.M.Ivory, J.Marti, J.L.Bredas and R.H.Baughman, *Mol. Cryst. Liq. Cryst.118*, 103 (1985)

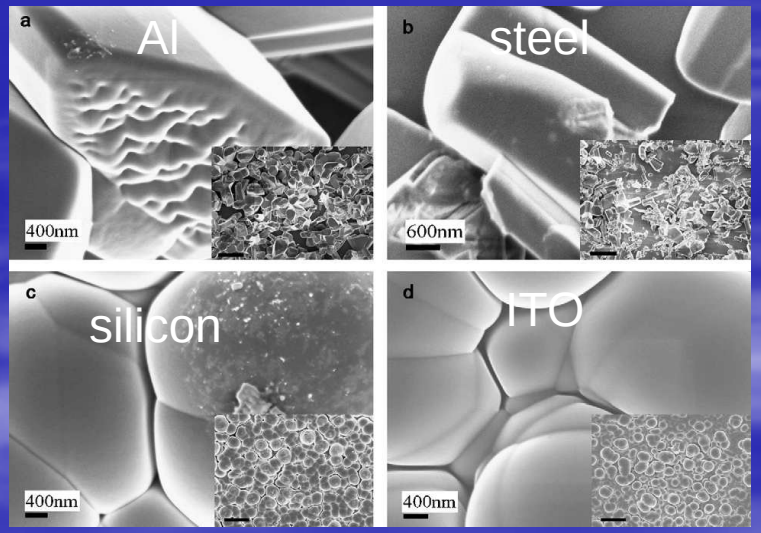
PPN Coating Characterization



Raman



FTIR

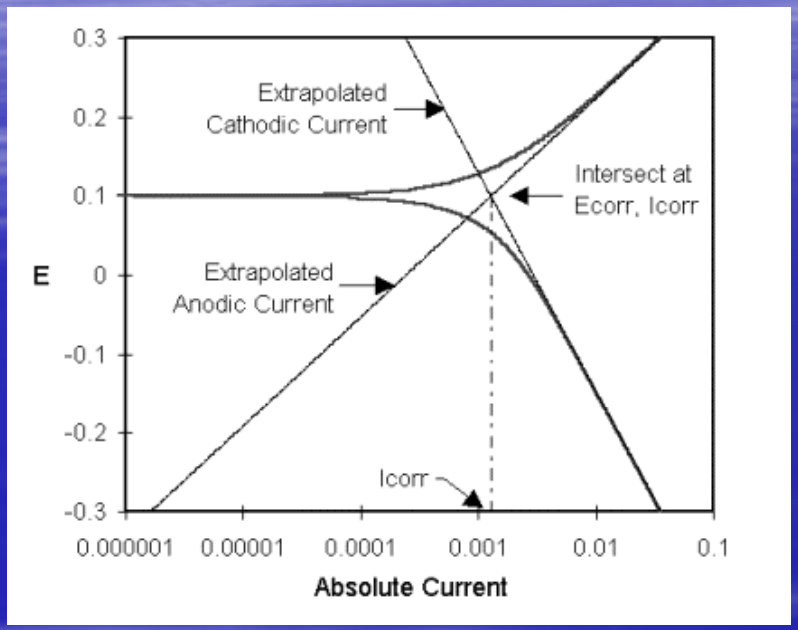


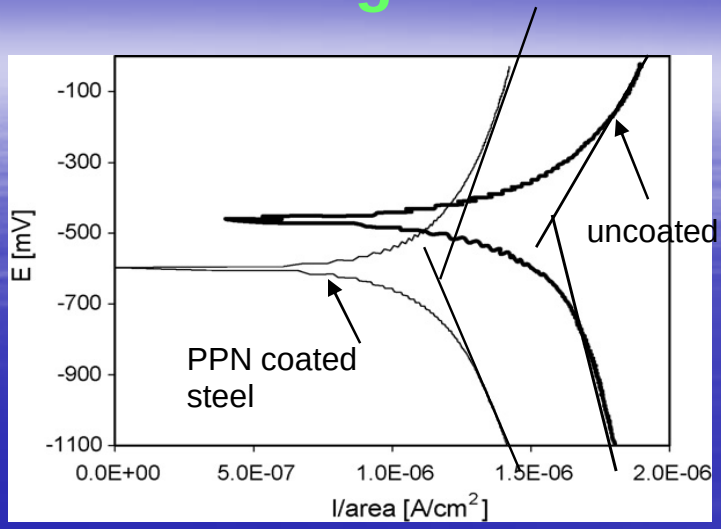
SEM on different substrates

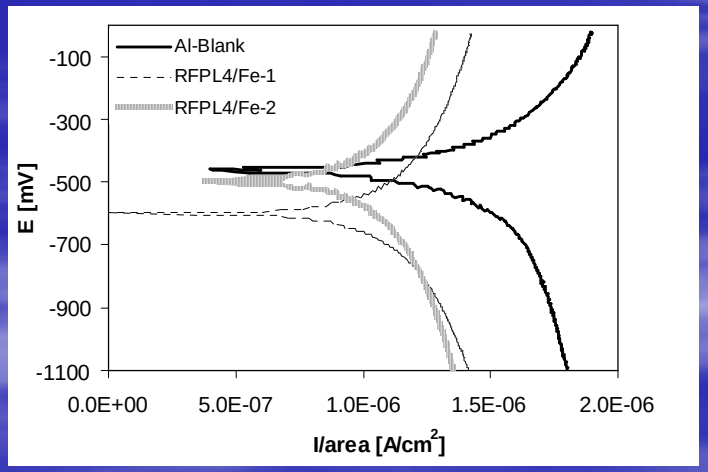
C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals 158*, 425 (2008)

NJIT New Jersey's Science & Technology University

Potentiodynamic Corrosion Testing Tafel Plots







Applications:

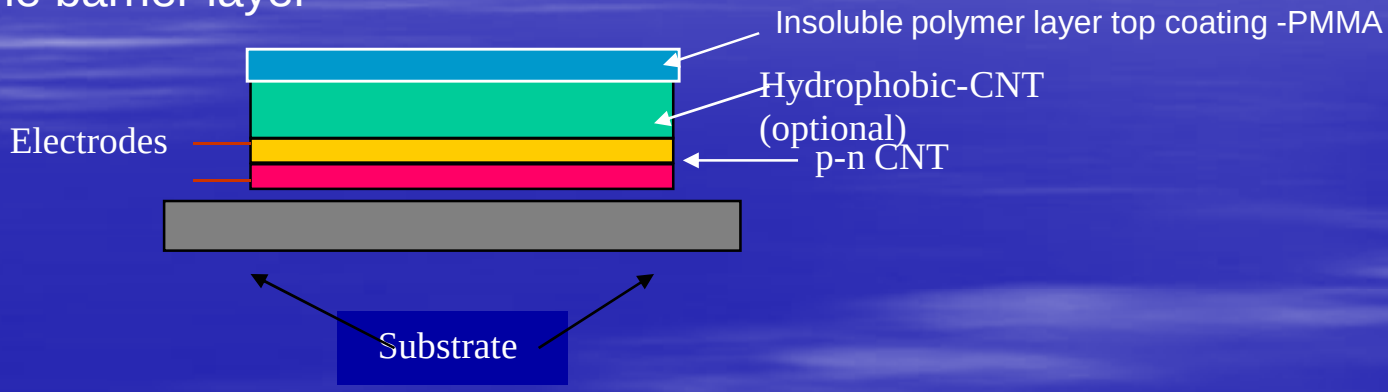
- Corrosion protection for inaccessible device components
- Corrosion protection for fuel cell current collecting bipolar flow-field plates ["Corrosion Resistant Coated Fuel Cell Plate with Graphite Protective Barrier and Method of Making the Same", Z. Iqbal, T. Rehg, J. Guiheen and D. Narasimhan – US Patent 6,864,007 (2005) *Honeywell-GE Power Systems*].

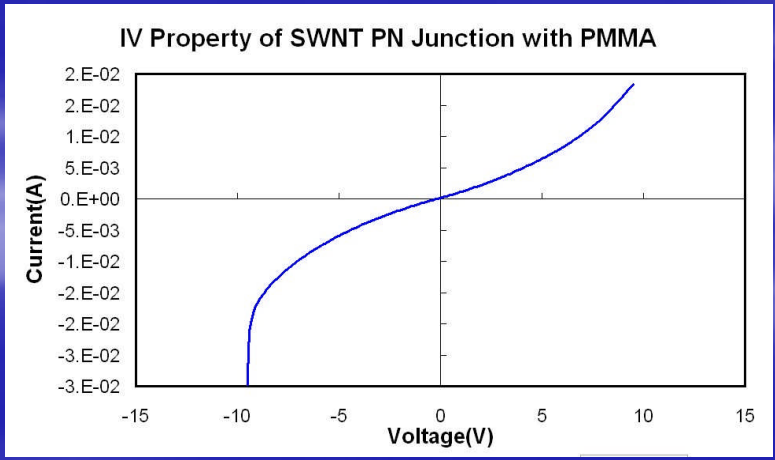
C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals 158*, 425 (2008)

NJIT New Jersey's Science & Technology University

Multilayer Smart Carbon Nanotube Coating

- Paints of 3 types of carbon nanotubes prepared as paints or inks in polymers
- p-n doped layer functions as a transistor to monitor the health of the coating
- Top layer functionalized with hydrophobic (e.g. fluorine-containing) groups functions as the barrier layer

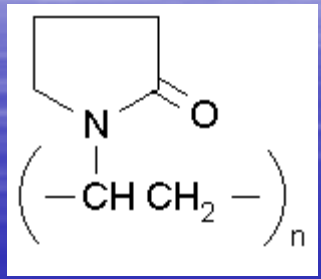




NJIT New Jersey's Science & Technology University

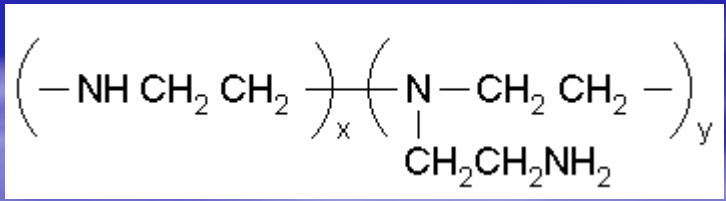
Carbon Nanotube Functionalization/Doping

A) *p*-Doping



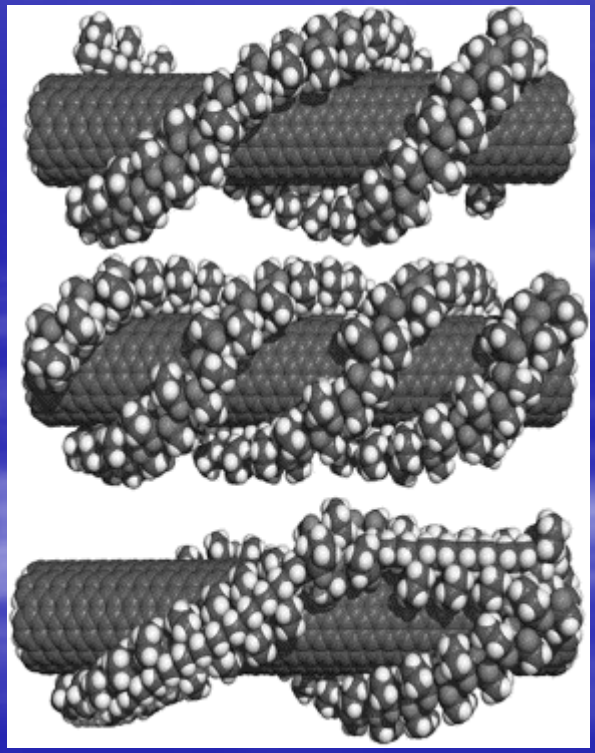
Polyvinylpyrrolidone (PVP)

B) *n*-Doping



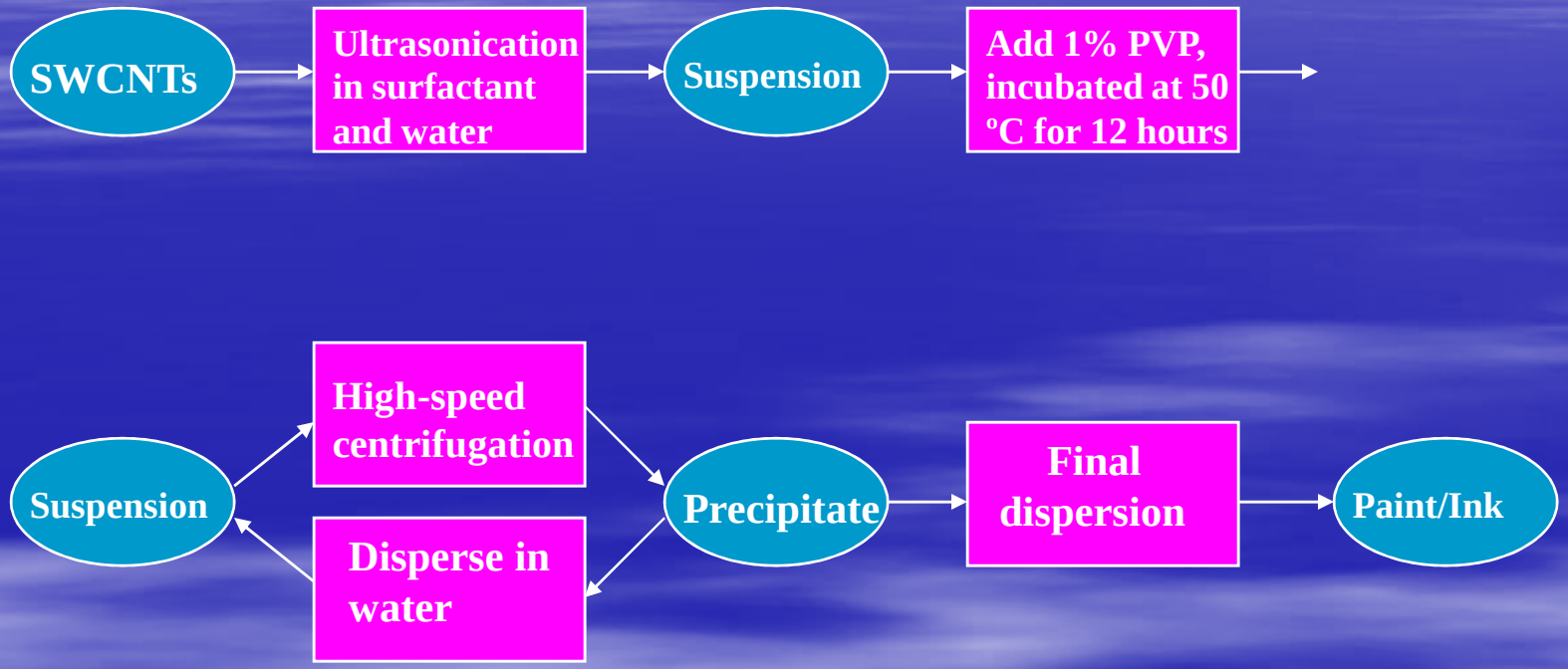
Polyethyleneimine (PEI)

C) Polymer Wrapping Model



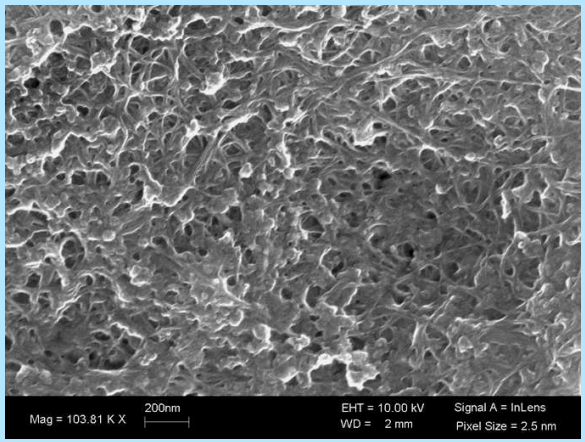
NJIT New Jersey's Science & Technology University

SWCNT Paint/Ink for Coatings

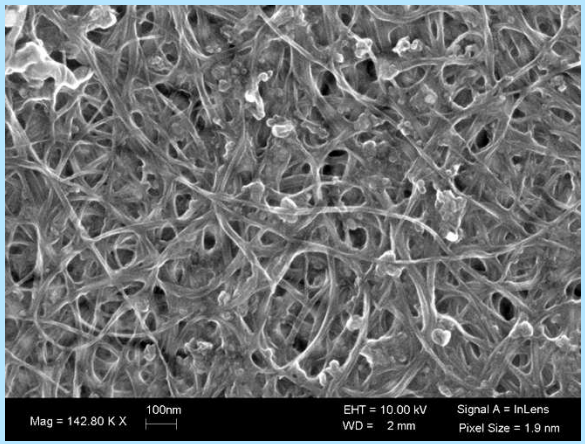


NJIT New Jersey's Science & Technology University

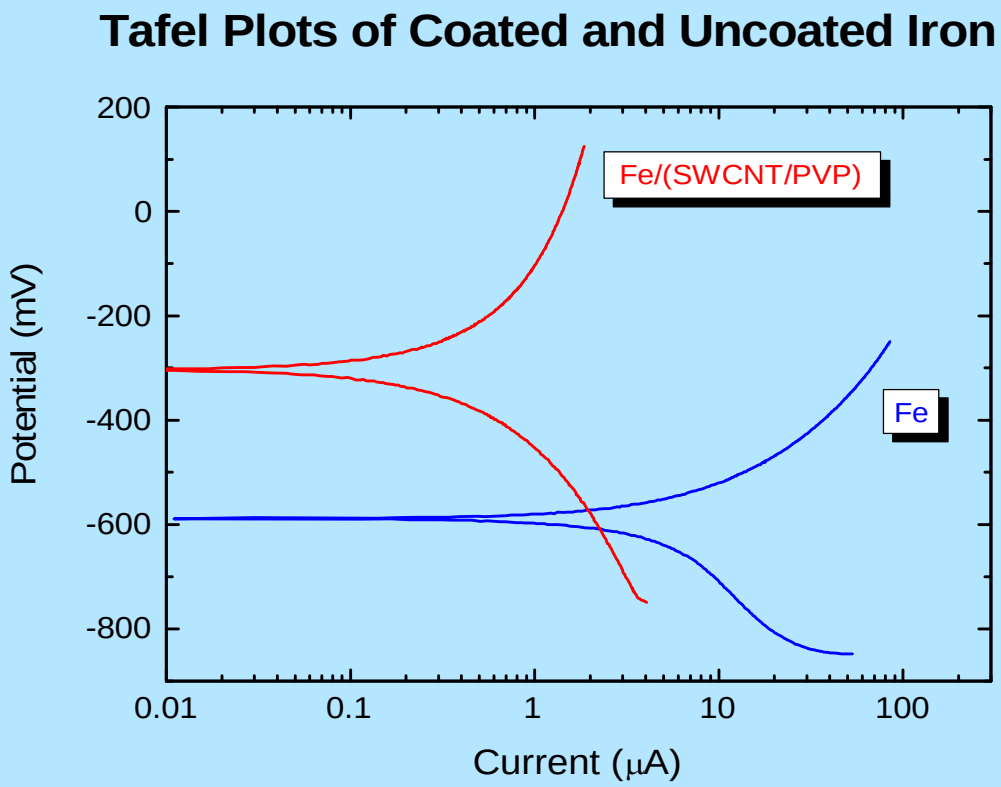
Multilayer Smart Carbon Nanotube Coating



p-doped SWCNTs PVP



n-doped SWCNTs PEI

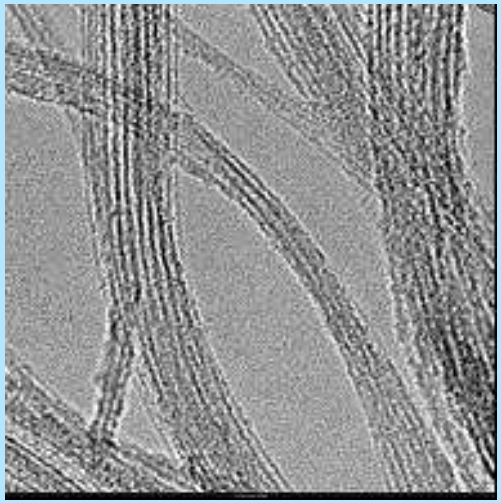


Corrosion current decreases with nanotube coating- thus improved corrosion protection

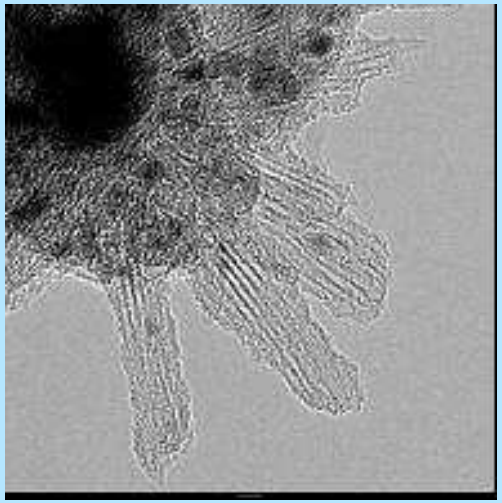
NJIT New Jersey's Science & Technology University

Multilayer Smart Carbon Nanotube Coating

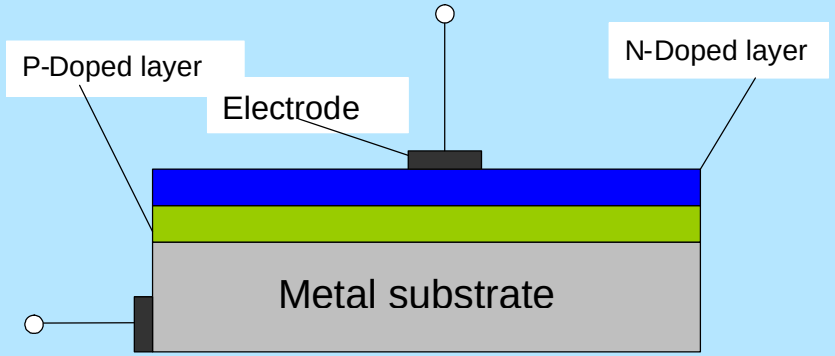
TEMs

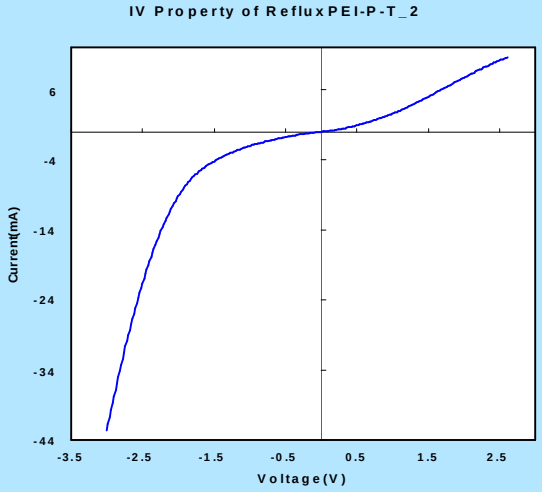


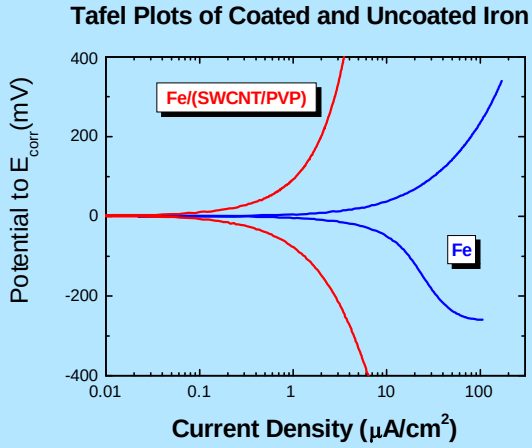
As-prepared SWCNTs



n-doped SWCNTs PEI

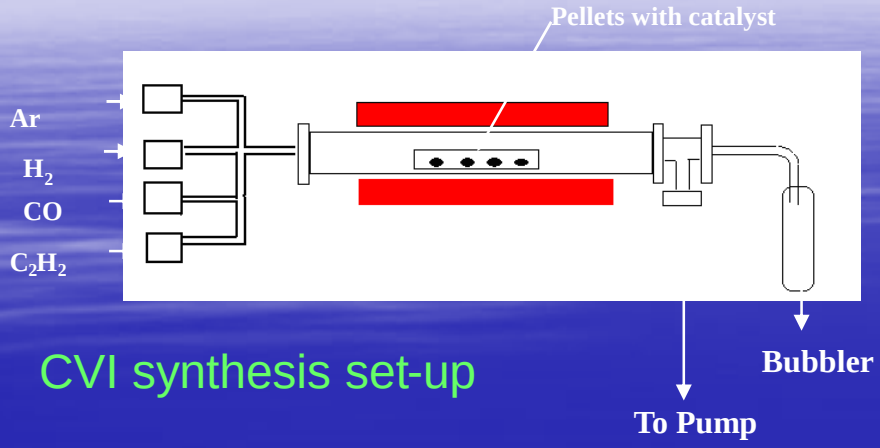






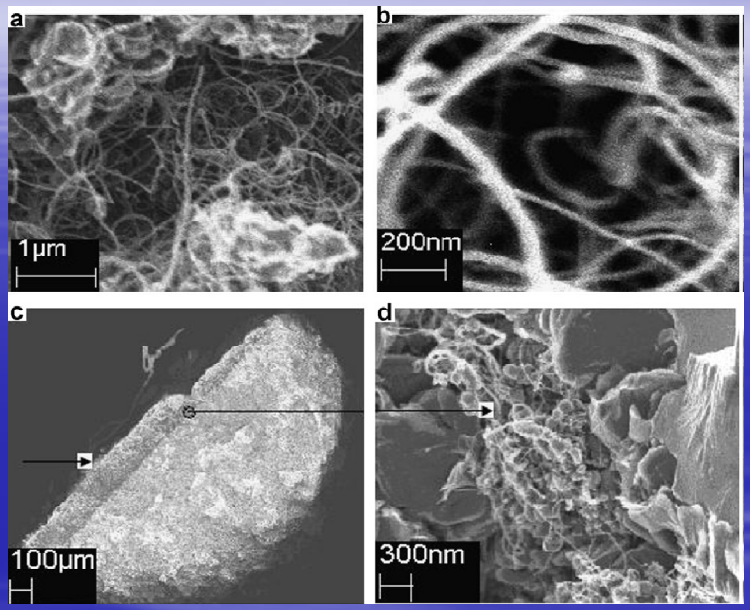
NJIT New Jersey's Science & Technology University

Potentially corrosion-resistant high strength bulk iron-carbon nanotube composites

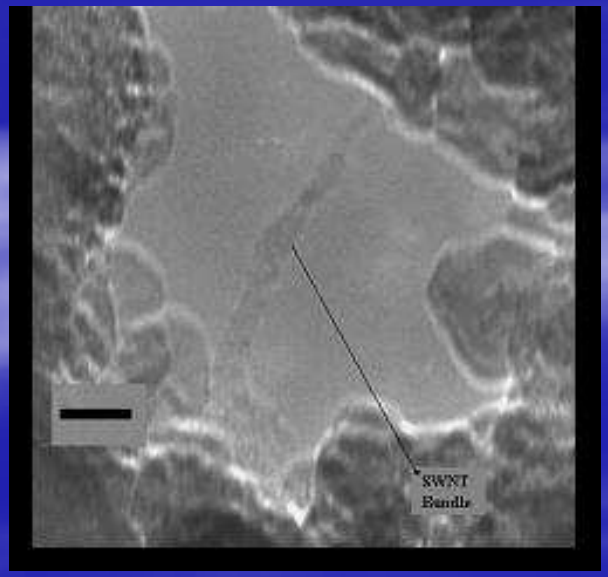


CVI synthesis set-up

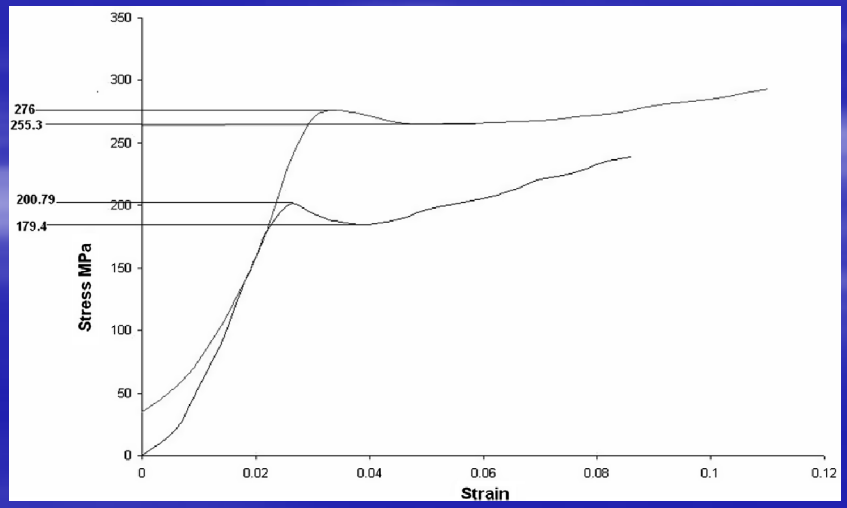
SEM



TEM



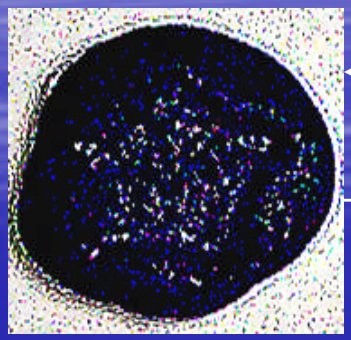
45% increase in yield strength relative to iron



Goyal, Wiegand, Owens, Iqbal Chemical Physics Letters 442 (2007) 365–371

NJIT New Jersey's Science & Technology University

Multilayer Smart Polydiacetylene Paint Coating



PCDA blue

ZnO

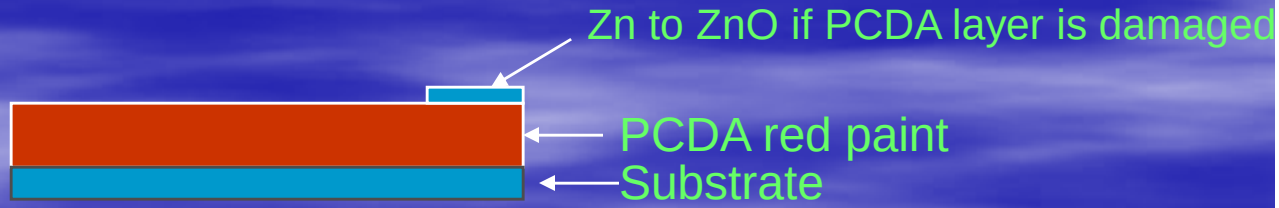
at ambient T

185 F

irreversible

PCDA red

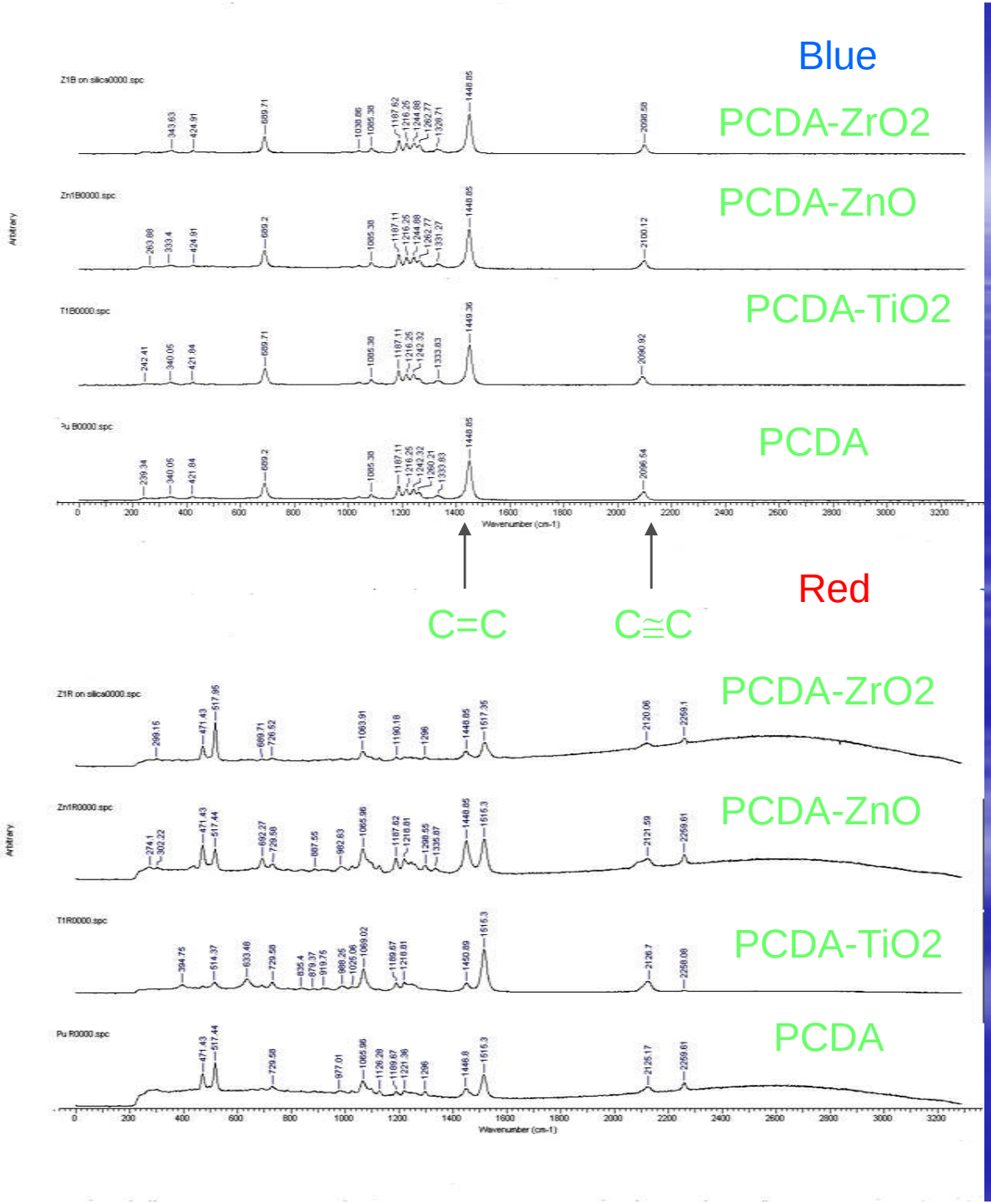
- If PCDA red layer is damaged, oxygen from the corroding substrate will react with Zn strip to form ZnO
- In presence of ZnO PCDA will undergo red to blue conversion – Raman data next slide



NJIT New Jersey's Science & Technology University

Monitoring blue and red PCDA phases in presence or absence of ZnO, ZrO_2 and TiO_2 by Raman scattering

Also note: Red phase is highly fluorescent



NJIT New Jersey's Science & Technology University

Summary

- Three types of nanotechnology-based passive and smart barrier coatings for corrosion protection discussed
  - Plasma-deposited conducting carbon polymer PPN can be used to protect small device or engine components and has been demonstrated to protect PEM fuel cell current collecting bipolar metal plates
  - Carbon nanotube paints/inks can form smart protective coatings via p-n junction layers which can electrically sense coating damage due to corrosion
  - Semiconducting, thermochromic polydiacetylene paints undergo irreversible color changes which can become reversible in the presence of chemical reactions induced by corrosion

NJIT New Jersey's Science & Technology University