Carbon Nanofibers and Graphene for the Corrosion Protection of Steel

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Electronic structure mapping of graphene and chemical bonding at graphene interfaces

Finite-size effects on phase transitions of binary and ternary vanadium oxides

Graphene nanocomposites for anti-corrosion and EMI shielding applications

Non-hydrolytic metal—organic syntheses of early transition metal oxides and lanthanides
Graphene & Carbon Nanotubes: The New Carbon Age

Growing Graphene & Carbon Nanofibers on Low Alloy Steels

Graphene Polymer Nanocomposites: Protecting the Rust Belt!

Scanning Transmission X-ray Microscopy as a Tool for Studying Carbon Interfaces
Graphene

- Synthesized in 2004 through mechanical exfoliation a.k.a. “scotch tape” method (Nobel Prize in Physics, 2010)
- Single and bi-layer graphene are semimetals
- Conceptualized as the building block of graphite, carbon nanotubes and fullerenes
- Itinerant massless Dirac fermions
- High mobility charge carriers
- Room temperature half-integral quantum Hall effect

Can be visualized as perfectly seamless cylinders formed by rolling up a graphene sheet.

Single-walled nanotubes are really a family of large molecules — each sample has a wide variety of diameters and chiralities.

Single-walled nanotubes can be metallic or semiconducting.
Applications: A Different Flavor Each Time

More than Moore Microelectronics
Flip chip transistors
Ultrafast electronics
Electrical interconnects

Ultrahigh mobilities & Ballistic conduction

Eliminating Defects
Introducing Bandgap
Large-Area Fabrication

Criteria for applications very unforgiving with respect to defect tolerance

Applications: A Different Flavor Each Time

- Composites and Coatings
  - ITO Replacement
  - EMI Shielding
  - Corrosion Protection
  - High-Strength Polymer and Metal Composites

Reasonable conductivity
Flexibility
High Strength

Inexpensive, largescale syntheses
Bonding to Matrix Dispersion
Scalable Synthetic Routes to Graphene

Chemical Vapor Deposition

Oxidation of Graphite Followed by Exfoliation and Reduction

Solution-Phase Exfoliation of Graphite
CVD Growth of Graphene

- **Precursors**
  - Methane
  - Ethanol bubbler
  - Acetylene

- **Parameters**
  - Cooling rate (quenched)
  - Gas flow/ partial pressure (Ar = 300 sccm, H₂ = 10 sccm, CH₄=98 ppm)
  - Temperature (980°C)
  - Time (10-30 min.)

SLG on Cu
Direct Carbon Nanofiber & Carbon Nanotube Growth onto Steel

Reducing the Carbon Footprint of the Steel Industry

Europe Steel Industry Can't Meet EU Carbon Emissions Target - Eurofer

Steel lobby says EU CO2 targets require technology breakthroughs

LONDON: European steelmakers need new, breakthrough technology to be able to meet the EU's proposed target of cutting their carbon emissions by about 90 per cent by 2050 from 1990 levels, industry body Eurofer said.

Such levels of abatement would require as a minimum condition for their achievement yet unproven or breakthrough technologies to be commercially available at competitive prices.
In Situ CNT Growth on Steel from Blast Furnace Effluent Gases
Time Course Study of CNT Growth on Steel
Efficacy of Growth as a Function of Process Parameters

CO: H$_2$ 1:1

650°C

Carbon Fiber Growth from Realistic Blast Furnace Effluent Stream
In Situ Carbon Nanofiber Growth on Steel
Carbon Nanotube & Nanofiber Growth on Different Steel Substrates

Growth catalyzed by incipient carbide particles formed at steel surfaces
Corrosion – deterioration of a material due to reactions with its surrounding environment

- Requirements for rust formation
  - Iron
  - Oxygen
  - Water
  - Electrolytes
  - Iron oxide does not form passivating layer
- Degrades mechanical strength

\[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \]
\[ 2 \text{Fe} \rightarrow 2 \text{Fe}^{2+} + 4 \text{e}^- \]
\[ 2 \text{Fe} + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe(OH)}_2 \]
\[ 2 \text{Fe(OH)}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 \]
Corrosion Costs


Zanowicz, R. Army Corrosion Office an Overview; Picatinny, NJ, 2005.
Active-Passive Approach to Corrosion Protection

- Coating serves as a barrier to water permeation and ion channels to the surface
- Create a passivation layer to prevent the electrochemical reactions from occurring at the metal surface

Polyetherimide (PEI)

- Hydrophobic
- Low moisture permeation/water uptake
- Solvent resistant
- Temperature resistant
- Formable
- Flexible
- Great adhesion to the steel surface
- Good mechanical strength
PEI/CNF Composite Coatings on Low-Alloy Steels

> 30 days protection under accelerated salt spray testing

Towards a closed loop process for value addition to steel while reducing the carbon footprint of the steel industry.
Synthesis of Graphene

1. Milling of graphite
2. Ultrasonication of milled graphite into NMP
3. Centrifugation to collect dispersed graphene
4. Redispersion within THF or NMP
Unfunctionalized Graphene

- Tata natural flake graphite
- Purity: 99.5 wt.%
Nanocomposite solutions

- Sonication of graphite into NMP
- Synthesis of polyamic acid using UFG/NMP solution
- Coating of UFG/polyamic acid onto cleaned steel
- Imidization/curing

Coatings

Coating thickness: 15-20 µm

Steel

20 wt.% UFG & 2 wt.% MWCNT

PEI

20 wt.% UFG
Coating Characterization

Steel

PEI

2 wt.% UFG/MWCNT/PEI

20 wt.% UFG/PEI
Tafel Plot Analysis

Day 10

1.7% wt. UFG PEI 1.3% wt. UFG Blank Steel 1.0% wt. UFG

Day 14

1.7% wt. UFG PEI 1.3% wt. UFG Blank Steel 1.0% wt. UFG
Weight-Loss Measurements

- Standardized by ASTM G1
- Samples are exposed to 3.5% NaCl solution until sufficient rust formation allows for determination of weight lost to corrosion
- Corrosion rate (CR) can be calculated from
  \[ CR = 87.6 \left( \frac{W}{DAT} \right) \]
  - 87.6: constant
  - W: weight loss in g
  - D: density in g/cm³
  - A: surface area in cm²
  - T: time in h
- CR in mm/yr
## Corrosion Rate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanized Steel</td>
<td>$3.87 \times 10^{-2}$</td>
</tr>
<tr>
<td>Uncoated Low-Alloy Steel</td>
<td>$1.22 \times 10^{-1}$</td>
</tr>
<tr>
<td>PEI Coating</td>
<td>$9.24 \times 10^{-3}$</td>
</tr>
<tr>
<td>2 wt.% UFG/MWCNT/PEI Coating</td>
<td>$5.52 \times 10^{-4}$</td>
</tr>
<tr>
<td>20 wt.% UFG/PEI Coating</td>
<td>$8.46 \times 10^{-4}$</td>
</tr>
</tbody>
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Near-Edge X-ray Absorption Fine Structure Spectroscopy

Element specific probe of local and global electronic structure - peak positions and lineshapes directly related to density of states

Energy density of the final state

$$\sigma = \frac{4\pi\hbar^2e}{m^2\hbar c}\sum \zeta(E_f)|\phi_f|e\cdot p|\phi_i|\delta(h\omega + E_i - E_f)$$

Dipole matrix term

Delta function for the conservation of energy

remove core e⁻

Auger e⁻

Canadian Light Source
XAS Spectrum of Single-Layered Graphene

Manifestation of Dirac physics depends sensitively on defects: rippling, adsorbates, interfacial hybridization.
Ab-initio Calculated X-ray Absorption Spectra

- \( a=b=24.20 \, \text{Å} \), \( c=15.0 \, \text{Å} \)
- 200 Carbon atoms
- C K-edge XAS

Mapping the $\pi^*$ cloud with STXM

- Extended defects on the micron scale
- Folds and ripples distort the anisotropy of transferred graphene

$\pi^*$ region (285.7 eV)
Closed loop process allow fabrication of carbon nanofibers and carbon nanotubes from blast furnace gases onto low alloy steels.

Nanocomposite protective coatings developed using carbon nanofibers and graphene in conjunction with PEI.

X-ray absorption spectroscopy and imaging tools enable rippling of graphene and functionalization patterns to be directly imaged.
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