Simultaneous Reduction of Graphene Oxide and Polyaniline

Doping-Assisted Formation of a Solid-State Charge-Transfer Complex

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General Structure of PANI

Mixed oxidation state polymer

Pernigraniline

Emeraldine Base (EB)

LeucoEmeraldine (LE)
DOPING CHEMISTRY

Emeraldine base (EB)  Leucoemeraldine (LE)
Non-conducting

Protonation

Emeraldine salt (ES)
doped state ((highly) conducting)
**PANI NANOFIBRILAR MORPHOLOGY**

**1D: PANI nanofibers**

Intrinsic morphology of PANI: easy and direct synthesis
D. Li, R.B. Kaner, JACS, 2006, 128, 968

nf-PANI

High specific surface area
High dispersibility

Nf-PANI/MWNT (50 wt%)
In water (10mg/mL)

nf-PANI/MWNT

Graphene Oxide
- Ease of synthesis (large scale)
- Water solubility
- Control of conductivity (reduction)
- Large surface area

Graphene Oxide & nf-PANI
- Many similarities
- Highly compatible

SYNERGETIC EFFECTS
SYNTHESIS GO-PANI & R(GO-PANI)

GO-PANI & R(GO-PANI)

Step 1: *In-situ* polymerization

- **GO in H$_2$O**
  - 1M HCl aq.
  - 0.5 mg/mL

- **APS**
  - 1M HCl aq.
  - Sonication 80W; 1.5h

- **GO-PANI**

**nf-PANI conditions**
- Temperature: 15-18 °C
- Acidity pH: ≈ 1.5
- Reactant conc.: 0.5 mg/mL
- Oxidant / Aniline: 0.31
- Reaction volume: 100 mL
- Sonication power: 80 W

**GO : aniline = 1 : 1**
**SYNTHESIS GO-PANI**

**GO-PANI & R(GO-PANI)**

*Step 1: In-situ polymerization*

1. Add 1M HCl aq. to GO in H₂O to obtain 0.5 mg/mL.
2. Add APS in 1M HCl aq. Sonication 80W; 1.5h.
3. Filtr Wash. to obtain GO-PANI.

*Step 2: Reduction*

1. Add 6μL/mL of hydrazine hydrate to GO POW
2. Sonication 80W; 1.5h
3. Stirr T 90 °C 4.5h
4. Filtr Wash. to obtain R(GO-PANI)

**Parameters**

<table>
<thead>
<tr>
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<th>Value</th>
</tr>
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<td>Temperature</td>
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**GO : aniline = 1 : 1**
GO sheets: **TEMPLATE** for aniline nucleation and polymerization
GO-PANI: **THIN LAYER COATING** of GO by PANI (for 1:1 GO/aniline)
R(GO-PANI): **THIN LAYER COATING** RGO by PANI maintained

**MORPHOLOGY = f(SYNTHESIS CONDITIONS)**

<table>
<thead>
<tr>
<th>Elemental Analysis</th>
<th>Calculated wt% PANI/Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-PANI</td>
<td>0.85</td>
</tr>
<tr>
<td>R(GO-PANI)</td>
<td>1.01</td>
</tr>
</tbody>
</table>
### PROPERTIES COMPOSITE

<table>
<thead>
<tr>
<th></th>
<th>GO/PANI</th>
<th>R(GO/PANI)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conductivity</strong></td>
<td>300 S / m</td>
<td>2600 S / m</td>
</tr>
<tr>
<td><strong>Thermal stability:</strong></td>
<td>520 ºC</td>
<td>570 ºC</td>
</tr>
<tr>
<td>(TGA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Morphology:</strong></td>
<td>Laminar (thin coating)</td>
<td>Laminar (thin coating)</td>
</tr>
<tr>
<td><strong>Dispersability:</strong></td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>
| (in water)             | **•** Stable, homogeneous  
**•** Easily (re-)dispersible |
**GO-PANI:** Superposition GO and PANI (ES)

**R(GO/PANI):** PANI in a partially reduced oxidation state between ES and LE

**STABLE!** No change of features with time

**SPECTROSCOPY: IR**

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1140 cm$^{-1}$</td>
<td>shift to 1130 cm$^{-1}$ (NH$^+$)-vibration</td>
</tr>
<tr>
<td>1305 cm$^{-1}$</td>
<td>decr. intensity C-N str.</td>
</tr>
<tr>
<td>1486 cm$^{-1}$</td>
<td>shift to 1470 cm$^{-1}$ C=C, quinoid rings</td>
</tr>
<tr>
<td>1724 cm$^{-1}$</td>
<td>incr. intensity carbonyl</td>
</tr>
</tbody>
</table>

The graph shows the infrared spectra of GO-PANI and R(GO-PANI), with arrows indicating the wavenumbers and their corresponding assignments.
GO-PANI: Superposition of GO and PANI (ES)
R(GO-PANI): PANI in a partially reduced oxidation state between ES and LE
STABLE! No change of features with time
SPECTROSCOPY: UV-VIS

GO-PANI: ES slightly deprotonated: due to carboxylate groups at GO
R(GO/PANI): PANI in a partially reduced oxidation state between ES and LE
STABLE! ALSO IN LIQUID PHASE!

<table>
<thead>
<tr>
<th>Wavenlength (nm)</th>
<th>Absorbance (a.u.)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>incr. intensity</td>
<td>π-π*, benzenoid rings</td>
</tr>
<tr>
<td>430</td>
<td>incr. intensity</td>
<td>polaron-π*</td>
</tr>
<tr>
<td>800</td>
<td>shift to 860nm low. intensity</td>
<td>π-π*</td>
</tr>
<tr>
<td>260</td>
<td>shift to 275 nm not visible</td>
<td>π-π* graphene</td>
</tr>
<tr>
<td>300</td>
<td>not visible</td>
<td>n-π*, carbonyl moieties</td>
</tr>
<tr>
<td>260</td>
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Absorbance (a.u.)

Wavenlength (nm)

GO-PANI
R(GO-PANI)
nf-PANI
Intermediate oxidation state does not reoxidize into the ES state. Stabilization of an anomalous oxidation state of PANI in between ES and LE.
CURIOSITIES

R(GO-PANI)

• Thin PANI layer coating RGO → favors interactions at extended RGO-PANI interface

• Stable intermediate oxidation state in between ES and LE → Charge-transfer processes are involved

• High environmental degradation stability, in solid and liquid state

• Improved conductivity

• Dispersibility in aqueous media → Involvement of charges

Graphene (GO, RGO): excellent electron acceptor
Formation of a donor (LE) - acceptor (RGO) solid-state charge-transfer complex

Double role of RGO: electron acceptor & large counterion of ES

\[
\text{RGO}^{\delta^-} \text{- PANI (ES-LE)}^{\delta^+}
\]
CONCLUSIONS

In-situ polymerization of PANI and GO + simultaneous reduction

- Easy, one pot synthesis route (under ambient conditions)
- Thin PANI coating on GO or RGO
- Stabilization of intermediate PANI oxidation state (ES-LE). Solid & Liquid state

Formation of a Solid-state Charge-Transfer Complex R(GO-PANI)

- Donor-Acceptor interactions at interface RGO-PANI (ES-LE)
- RGO dual role:  i) electron acceptor of PANI (LE)  
  ii) large anionic counterion of doped PANI (ES)
- Equilibrium partially charged system \( RGO^{5^-} - PANI \) (ES-LE)\(^{5^+}\)

ENHANCED MATERIALS PROPERTIES R(GO-PANI)

- Conductivity: 2600 S/m (due to RGO)
- Environmental (chemical and thermal degradation) stability
- High hydrophilicity for both, GO-PANI and R(GO-PANI)
- Excellent water dispersibility for both, GO-PANI and R(GO-PANI)
OUTLOOK

FUNCTIONAL AND PROCESSABLE (GO – PANI) materials

MACROSCOPIC ASSEMBLY INTO FUNCTIONAL MATERIALS/DEVICES BASED ON GRAPHENE AND ICPS

Direct processing
• Coatings
• Casting
• Printing
• Impregnation

Combining with other polymers
• Coatings
• casting
• spinning

• Flexible conducting films and circuits,
• Flexible electrochemical materials/devices

• Conducting fibers
• Membranes,….

FLEXIBLE PLASTIC AND WEARABLE ELECTRONICS
MESSAGE

GRAPENE OXIDE & POLYANILIE
THE PERFECT FOILS

J. Phys. Chem C online. DOI: 10.1021/jp201791h
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(PG4 RGO papers)

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www.icb.csic.es/index.php?id=g-cnn

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