Domino Reaction for the Controlled Functionalization of sp² Carbon Allotropes

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Innovative Sustainable Chemistry and Materials and Proteomics Group
Chemistry from biobased C-3 platform

\[
\begin{array}{c}
\text{HO-} \quad \text{OH} \\
\text{HO-} \quad \text{OH}
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
\text{HO-} \quad \text{NH}_2 \\
\text{HO-} \quad \text{OH}
\end{array}
\]
Chemistry from biobased C-3 platform

\[
\text{HO-CH}_2-\text{CH(OH)-OH} \quad \rightarrow \quad \text{HO-CH}_2-\text{CH(OH)-OH} \quad \text{NH}_2
\]

\[
\text{HO-CH}_2-\text{CH(NH}_2)-\text{OH} + \text{CH}_3\text{C(O)CH}_2-\text{COOH} \rightarrow \text{C}_5\text{H}_9\text{O}_2\text{N} \quad -2\text{H}_2\text{O} \rightarrow \text{HO-CH}_2-\text{CH(OH)-OH}
\]

- **Yield**: at least 96%
- **Atom efficiency**: 85%
- **Easy procedure**
- **No solvent**
- **By product**: H$_2$O
Serinolpyrrole: *Janus* molecule
Carbon fillers from a layer of sp²-bonded carbon atoms

- Graphene
  - Stacked
  - Wrapped

- Stacked graphene layers
  - Randomly arranged
  - With different shape anisotropy

- Carbon black
- Graphite, nano-graphite, graphene
- CNT
Characterization of carbon allotropes (CA)

CB

CNT

FEW LAYERS GRAPHENE
Characterization of carbon allotropes (CA)

- TGA, Elemental Analysis: carbon purity
- BET: surface area, activity
- Infrared, XPS: functional groups
- Raman, X-ray: bulk structure
- TEM, HRTEM: morphology
Facile functionalization of carbon materials

Carbon allotrope

Mixing, energy, air

Oxygenated functional groups on carbon allotrope surface

Bulk structure substantially unaltered

Facile functionalization of carbon materials

Mixing, energy, air

Oxygenated functional groups on carbon allotrope surface

Bulk structure substantially unaltered

High yield functionalization!

Yield: 86 %  
BET Surface area: 77 m$^2$/g

97 %  
275 m$^2$/g

98 %  
300 m$^2$/g
High yield functionalization!

Yield: 86 %  
97 %  
98 %

BET Surface area: 77 m²/g  
275 m²/g  
300 m²/g

HSAG water suspensions from 1 to 0.01 mg/mL

High surface area graphite HSAG
Mechanistic investigation

Model compound
Mechanistic investigation

Model compound

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & &
\end{align*}
\]

In air

Thermal energy

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & &
\end{align*}
\] + HSAG

In air

Thermal energy
1,2,5-Trimethylpyrrole (TMP)

- Out of plane C-H bending
- C=C stretching cyclic alkene

Absorbance (a.u.) vs. Wavenumbers (cm$^{-1}$) at 25°C
TMP from 25° to 150°C

C=C stretching cyclic alkene

out of plane C-H bending

Increasing temperature
TMP + HSAG cat. - from 25 to 150°C

\[
\text{\begin{align*}
\text{H}_3\text{C} & \text{N} \text{CH}_3 \\
\Delta, \text{Air} & \\
\text{H}_3\text{C} & \\
\text{HSAG as cat.}
\end{align*}}
\]

C=C stretching cyclic alkene

out of plane C-H bending

Increasing temperature

Absorbance (a.u.)

2000 1800 1600 1400 1200 1000 800

Wavenumbers (cm\(^{-1}\))

TMP + HSAG 1%
80°C

TMP
TMP + HSAG cat. - from 25 to 150°C

\[ \text{H}_3\text{C} - \text{N} - \text{CH}_3 \quad \Delta, \text{ Air} \quad \text{HSAG as cat.} \]

C=C stretching cyclic alkene

out of plane
C-H bending

Absorbance (a.u.)

Wavenumbers (cm\(^{-1}\))

Increasing temperature
TMP + HSAG cat. - from 25 to 150°C

C=C stretching cyclic alkene

out of plane C-H bending

Absorbance (a.u.)

Wavenumbers (cm⁻¹)

Increasing temperature
TMP + HSAG 1/1 - from 25 to 150°C

C=C stretching cyclic alkene
C-H bending

Increasing temperature

Absorbance (a.u.)

Wavenumbers (cm\(^{-1}\))

1800 1600 1400 1200 1000 800
TMP + HSAG 1/1 - from 25 to 150°C

\[
\text{H}_3\text{C} \quad \text{N} \quad \text{CH}_3
\text{H}_3\text{C} \quad + \text{HSAG} \quad \Delta_{\text{Air}}
\]

C=C stretching cyclic alkene

Oxidation

Out of plane
C-H bending

Increasing temperature

Absorbance (a.u.)

Wavenumbers (cm\(^{-1}\))

<p>|</p>
<table>
<thead>
<tr>
<th>1800</th>
<th>1600</th>
<th>1400</th>
<th>1200</th>
<th>1000</th>
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<tr>
<td>TMP</td>
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<tr>
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<td>TMP+HSAG 1/1</td>
<td>130°C</td>
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</tbody>
</table>
TMP + HSAG 1/1 - from 25 to 150°C

C=C stretching cyclic alkene

Oxidation

C-H bending

out of plane

Increasing temperature

Wavenumbers (cm⁻¹)

Absorbance (a.u.)
Mechanistic path

Paal-Knorr reaction

Paal-Knorr Reaction

HSAG

1
Mechanistic path

Carbocatalyzed benzyl oxidation

Carbocatalyzed Oxidation

Paal – Knorr Reaction
Mechanistic path

* Structure confirmed by means of NMR spectroscopy
Mechanistic path

* Structure confirmed by means of NMR spectroscopy
Mechanistic path
Model reaction and DFT calculation

\[
\begin{align*}
&\text{H}_3\text{C} & \quad\quad & \text{O} \\
&\text{H}_3\text{C} & \quad\quad & \text{N} \\
&\text{C} & \quad\quad & \text{H} \\
\text{H}_3\text{C} & \quad\quad & \text{C}_6\text{H}_6
\end{align*}
\]

\[
\text{Structure confirmed by means of FT-IR and NMR spectroscopy}
\]

\[
\text{DFT (B3LYP/6-311++G(d,p))}
\]
Model reaction and DFT calculation

* Structure confirmed by means of FT-IR and NMR spectroscopy
Model reaction and DFT calculation

\[ \text{TMP} + \text{Anthracene} \quad 150^\circ \text{C} \]

\[ \text{Abs} \quad 1250 \quad 1300 \quad 1350 \quad 1400 \quad 1450 \quad 1500 \quad 1550 \quad 1600 \]

Wavenumbers (cm\(^{-1}\))

\[ \text{DFT (B3LYP/6-311++G(d,p))} \]
Facile functionalization of carbon materials

Hypothesis for the mechanism

Paal – Knorr Reaction

Carbocatalyzed Oxidation

Diels-Alder reaction

[Image of reaction mechanisms]
Facile functionalization of carbon materials

Functional group:
from few % to 20%

Functionalization yield:
from 85% to quantitative

Covalent bond
between functional group
and graphene layer

Bulk structure of graphitic materials:
substantially unaltered

M. Galimberti, V. Barbera, Italian Patent 102016000113012 (2016)
M. Galimberti, V. Barbera, Italian Patent 102016000113070 (2016)
Nano-carbon Up

Polyol dispersions

Monolithic aerogel

Latex dispersions

Rubber nanocomposites

Carbon papers

Conductive ink

Polyurethane

Conductive coating
Thanks for the Attention