Smart Functional Nanoenergetic Materials

Graphene as a Reactive Material and Carrier of Energetic Materials

I. A. Aksay, A. Selloni, R. Car, C. Zhang, D. M. Dabbs
Chemical and Biological Engineering and Chemistry
Princeton University, Princeton, NJ 08544

N. Kumbhakarna, S. T. Thynell, R. A. Yetter
Mechanical and Nuclear Engineering
PennState University, University Park, PA 16802

J. B. DeLisio and M.R. Zachariah
Mechanical Engineering
University of Maryland, College Park, MD 20742
Multiscale Processing
Aksay, Eichhorn, Zachariah

Energetic Bridging Molecules

Nanostructured Catalysts

Tetrazine bridge

FGS

Graphene Sponge

AP/nFe₂O₃
RDX/nAl

Metal NPs on FGS

ITO
Graphene
Pt
20 nm

ITO
Graphene
10 nm

Pt
20 nm

ITO
Graphene
Pt

15 µm
4 µm
100 µm
Splitting of Graphite into Single Sheets

- Graphite Oxide by Staudenmaier method (1898) – 4 fold volume expansion
- Thermal expansion (>500 fold) at 1050°C – Boehm (1962)
- SA ~850 m²/g by BET and >1800 m²/g by methylene blue adsorption in solvents
- Disappearance of graphite peaks after oxidation and elimination of all peaks after expansion
- >80% single sheet highly wrinkled functionalized graphene

M.J. McAllister et al., Chem. Materials (2007)
STM Images of FGS & HOPG

Functionalized Graphene Sheets

FGS (C/O=1.85) without vacancy defect

- **FGS**: functionalized graphene sheet
  - Large (>2µm diameter) polycyclic hydrocarbon
  - Commercial production of single sheets (Vorbeck Materials, Jessup, MD)
  - Sheet wrinkling inhibits restacking, maintains surface area

FGS (C/O=1.64) with vacancy defect

- **Lattice defects**
  - Oxygen-decorated carbon vacancies
  - Topological defects

- **Oxygen-containing groups**
  - Epoxides, hydroxides, carboxyls

C. Zhang, 2013
Catalyzed NM Decomposition

Oxygen-decorated vacancy

- Catalytic role of FGS essential to transform nitromethane into more reactive intermediates
  - Once formed, reactions continue within the fluid
- Fast decomposition:
  - After ~14 ps, complete transformation into different species
  - Main combustion products are H₂O, CO₂, and N₂
- Protonation, deprotonation and oxidation reactions promoted by oxygen groups on FGS at carbon vacancies

J. L. Sanbourin et al., submitted (2013)
Tetrazine Decomposition


- 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxide (DAATO\(_{3.5}\))
- 3-amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide (ACTO)
- 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (DATO)

- Low C, H content
- Good oxygen balance
- N-N increases heat of formation
- N≡N produced
- N-O enhances aromaticity, reduces sensitivity

- Tetrazine Based Molecules:
  \[
  \begin{array}{c}
  \text{N-}\text{N} + 2\text{RCN}
  \end{array}
  \]

- Tetrazine-N-oxides Based Molecules:
  (a) N\(_2\)O elimination
  \[
  \begin{array}{c}
  \text{N}_2\text{O} + \text{RCN} + \text{RCNO}
  \end{array}
  \]
  (b) Ring contraction, leading to NO elimination
  \[
  \begin{array}{c}
  \Rightarrow 2 \text{RCN}
  \end{array}
  \]
  (c) Meisenheimer rearrangement, leading to N\(_2\) elimination
  \[
  \begin{array}{c}
  \Rightarrow \text{N-}\text{N}
  \end{array}
  \]
Energetic Scaffolding

- **Chemical modification of FGSs**
  - Planar and edge chemistries for attaching dispersants or binders
  - Joining of FGSs for porous structures

- **Spacers**
  - Long chain bridging molecules
  - In collaboration with ENS Cachan (France)

Fabien Miomandre and Pierre Audebert, École Normale Supérieure de Cachan, France

AFOSR/MURI
August 21, 2013
Synthesis of Modified Tetrazines

Fabien Miomandre and Pierre Audebert,
École Normale Supérieure de Cachan, France

Dichloro-\(s\)-tetrazine (TzCl\(_2\))
Tetrazines and Tz-FGS

Pure tetrazines

JL4

JL40

JL41

JL37

Tetrazines attached to FGS (Tz-FGS)

JL25: JL4 attached to FGS

JL24: JL40 attached to FGS

JL43: JL41 attached to FGS

JL38: JL37 bridging 2 FGSs
Tetrazine Electrochemistry

\[ \text{Cl-Tz-Cl} \]

- \( \pi \) bond: resonance effect, \( e^- \) donating
- \( \sigma \) bond: inductive effect, \( e^- \) withdrawing

For \( \text{TzCl}_2 \), inductive effect is much stronger than the resonance effect, making tetrazine ring electron deficient and redox peaks more positive.

Inductive effect from electron-donating groups: tetrazine ring becomes electron rich compared to ring in \( \text{TzCl}_2 \).
Dichlorotetrazine and FGS

TzCl$_2$ does not bind to FGS

- Confirmed by FTIR and thermal analysis
- TzCl$_2$ can react with solvent, catalyst
- Ab-initio model shows TzCl$_2$ physisorption on FGS energetically favored over chemisorption
Tetrazines Bound to FGS

B

\[
\text{Cl-}N=N-O-\text{CH} \rightarrow + \text{FGS2} \rightarrow \text{N=N-O-CH}
\]

C

\[
\text{CH}_3-(\text{CH}_2)_3-O-Tz-\text{Cl} + \text{FGS2} \rightarrow \text{N=N-O-CH}
\]

Current A

Potential V

-3,0\times 10^{-6}

-2,0\times 10^{-6}

-1,0\times 10^{-6}

0

1,0\times 10^{-6}

2,0\times 10^{-6}

3,0\times 10^{-6}

-1,5, -1, -0, 0, 0, 5, 1, 0, 1, 5

Potential V

-1,5, -1, -0, 0, 0, 5, 1, 0, 1, 5

-1,5\times 10^{-6}

-1,0\times 10^{-6}

0

1,0\times 10^{-6}

1,5\times 10^{-6}

-1,5, -1, -0, 0, 0, 5, 1, 0, 1, 5

-3,0\times 10^{-6}

-2,0\times 10^{-6}

-1,0\times 10^{-6}

0

1,0\times 10^{-6}

2,0\times 10^{-6}

3,0\times 10^{-6}

-1,5, -1, -0, 0, 0, 5, 1, 0, 1, 5

-1,5\times 10^{-6}

-1,0\times 10^{-6}

0

1,0\times 10^{-6}

1,5\times 10^{-6}

-1,5, -1, -0, 0, 0, 5, 1, 0, 1, 5

Binding visible as shift in redox peaks for FGS and tetrazine

- Redox peaks of tetrazines shift to negative after grafting (FGS acts as e⁻ donating group)
- Redox peaks of FGSs shift to positive after grafting (tetrazine acts as e⁻ withdrawing group)
Infrared Spectra of Pure Tetrazines

- Strong C-N (aromatic) stretch between 1400-1500 cm\(^{-1}\)
- C-H stretch from substituent groups (2800-3000 cm\(^{-1}\))
- Ether bridge between substituent and tetrazine ring \(\sim 1200\) cm\(^{-1}\)
FGSs Bridged by Tetrazine

Redox peaks of JL 37, FGS shift as with other Tz-FGS products

Shifts in redox peaks roughly equivalent for all Tz-FGS products, regardless of type of tetrazine grafted onto FGS

- Indicates similar bonding behavior (e.g., proximity of tetrazine ring to FGS through bridging ether)
Infrared of Tetrazines on FGS

- Tetrazine association with FGS indicated by C-H (2800-2950 cm⁻¹) and C-N (~1600 cm⁻¹) stretching frequencies not seen on native FGS
  - Ether bridge masked by multiple absorption bands in 1000-1300 cm⁻¹ region
  - C-H and C-N bands disappear after heating Tz-FGS to high temperature (>400°C)
Modeling Tetrazine Binding to FGS

Optimized Structures for FGS$_2$ and Dichloro-s-Tetrazine

FGS$_2$ mixed with TzCl$_2$

TzCl$_2$ covalently bound to FGS$_2$

vibrational mode corresponding to 3047 cm$^{-1}$
### Energy Difference: Products and Reactants

Unit cell \(7.77 \times 8.78 \times 30 \text{ Å}^3\); Cubic cell \(30 \times 30 \times 30 \text{ Å}^3\) with MP correction

<table>
<thead>
<tr>
<th></th>
<th>E (Ry) - PBE</th>
<th>E (Ry) - PBE-vdW</th>
<th>E (eV) - vdW</th>
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</thead>
<tbody>
<tr>
<td>Dichloride-Tz (~6 Å)</td>
<td>-162.1805122731</td>
<td>-162.186631801034</td>
<td>-0.049</td>
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<tr>
<td>FGS(_2)</td>
<td>-697.9309461955</td>
<td>-698.110388095506</td>
<td>-2.500</td>
</tr>
<tr>
<td>FGS(_2) - dichloride-Tz (physi)</td>
<td>-860.1229108453</td>
<td>-860.330779074904</td>
<td>-2.865</td>
</tr>
<tr>
<td>FGS(_2) - dichloride-Tz (chemi)</td>
<td>-828.8369113821</td>
<td>-829.051351415406</td>
<td>-2.975</td>
</tr>
<tr>
<td>HCl</td>
<td>-31.2146620615</td>
<td>-31.216230021156</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\[ \text{FGS}_2 + \text{dichloro-Tz} \rightarrow \text{FGS}_2 - \text{dichloro-Tz} \text{ (physisorbed)} \]

\[ \Delta E_{\text{PBE}} = -0.156 \text{ eV} \quad , \quad \Delta E_{\text{PBE-vdW}} = -0.459 \text{ eV} \]

\[ \text{FGS}_2 - \text{dichloro-Tz (physi)} \rightarrow \text{FGS}_2 - 1\text{-oxy, 4-chloro-Tz (chemisorbed)} + \text{HCl} \]

\[ \Delta E_{\text{PBE}} = 0.966 \text{ eV} \quad , \quad \Delta E_{\text{PBE-vdW}} = +0.860 \text{ eV} \]

**Covalent bond energetically unfavorable!**
Optimized Structures for JL40 and JL24

JL40

FGS₂ mixed with butoxy-Tz (JL40)

JL24

Butoxy-Tz (JL40) covalently bound to FGS₂

Vibrational mode corresponding to 2969 cm⁻¹

d_{OH-N} = 1.72 Å
d_{OH-C} = 2.83 Å
**Energy Difference: Products and Reactants**

Unit cell $7.77 \times 8.78 \times 40 \, \text{Å}^3$; Cubic cell $30 \times 30 \times 30 \, \text{Å}^3$ with MP correction

<table>
<thead>
<tr>
<th></th>
<th>E (Ry) - PBE</th>
<th>E (Ry) - PBE-vdW</th>
<th>E (eV) - vdw</th>
</tr>
</thead>
<tbody>
<tr>
<td>butoxy-Tz ($\sim10 , \text{Å}$)</td>
<td>-220.4648826439</td>
<td>-220.478220728922</td>
<td>-0.193</td>
</tr>
<tr>
<td>FGS$_2$</td>
<td>-697.9309345403</td>
<td>-698.110388095506</td>
<td>-2.500</td>
</tr>
<tr>
<td>FGS$_2$ - butoxy-Tz (physi)</td>
<td>-918.4079033041</td>
<td>-918.621008247310</td>
<td>-2.972</td>
</tr>
<tr>
<td>FGS$_2$ - butoxy-Tz (chemi)</td>
<td>-887.1673536470</td>
<td>-887.427812619112</td>
<td>-3.639</td>
</tr>
<tr>
<td>HCl</td>
<td>-31.2146620615</td>
<td>-31.216230021156</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**FGS$_2$ + Butoxy-Tz $\rightarrow$ FGS$_2$ - butane-Tz (physi)**
\[ \Delta E_{\text{PBE}} = -0.164 \, \text{eV} \quad , \quad \Delta E_{\text{PBE-vdW}} = -0.441 \, \text{eV} \]

**FGS$_2$ - Butoxy-Tz (physi) $\rightarrow$ FGS$_2$ - 1-oxo, 4-butoxy-Tz (chemi) + HCl**
\[ \Delta E_{\text{PBE}} = 0.352 \, \text{eV} \quad , \quad \Delta E_{\text{PBE-vdW}} = -0.313 \, \text{eV} \]

*Covalent bond energetically favorable!*
Under slow thermal ramp (10°C/min) dichlorotetrazazine sublimes but JL 40 melts. JL 40 vaporizes and does not decompose under experimental heating conditions.
JL 40 and JL 24

- Low molecular weight substituent sufficient to yield stable liquid phase
- Slow thermal ramp shows only desorption of tetrazine when associated with FGS
Energetics of Tetrazines and Tz-FGS

- In standard thermal analysis, condense phase may vaporize during slow thermal ramp
- Confined Rapid Thermolysis (CRT)/FTIR
  - Rapid heating rate 2000K/s to 1,000psig
  - 50Hz sampling
  - 2cm⁻¹ resolution
  - Sample allowed to decompose under isothermal conditions
  - Very sensitive to decomposition occurring in condensed phases
Enhanced Decomposition of Tetrazines on FGS

- Evolved gas analysis during CRT shows JL 37 and JL 40 decompose at 335°C.
- Decomposition of tetrazine (JL 37) is more extensive when bound to FGS (JL 38).
  - No tetrazine vapor apparent, higher amounts of decomposition products formed.
- In comparison, dichlorotetrazine goes into vapor phase with no decomposition.
T-Jump Time-of-Flight Mass Spec

- 0.003" diameter Pt wire is coated with sample of interest.
- Wire is rapidly heated at $10^5$ K/s within the extraction region of a linear TOF mass spectrometer.
- Time resolved spectra are acquired during a single reaction event.
- Electrical characteristics of the wire are monitored to determine wire temperature at any given time during heating.
- A data sampling rate of 10 kHz was used.

Decomposition of pure tetrazine (JL 37) is delayed when attached to FGS (JL 38)

- Significant decomposition of JL 37 at 0.6 ms (597 K), delayed to 1.4 ms on FGS (840 K)
- No large mass fragments in JL 38: more complete decomposition of tetrazine
Dielectric Elastomers with Stiff Electrodes

Voltage as a function of stretch
(electrodes: 3 wt. % FGS22-SE;
elastomer: VHB, H2/H1=0.2)
Adaptive Materials (Nanocomposites)

Summary

- Developed synthesis methods to construct nanocomposite fuels using functionalized graphene sheets as (i) nucleation templates and stabilizer for energetic particles, polymeric nitrogen molecules, embedded nitrogen; and (ii) carbocatalysts.
- Covalent attachment of tetrazines is confirmed by CV, FTIR, thermal analysis, and quantum mechanical modeling to understand the fundamental mechanisms of energetic functions.
- High surface area, hierarchically structured graphene-tetrazine networks will be developed for controlled energy release.