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Understanding Irreducible and Reducible Oxides as Catalysts for Carbon Nanotubes and Graphene Formation

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Understanding irreducible and reducible oxides as catalysts for carbon nanotubes and graphene formation

Alicja Bachmatiuk
Introduction

History of sp$^2$ carbon formation through oxide catalysts

Irreducible and reducible oxides for sp$^2$ carbon formation

Carbothermal reduction of SiO$_2$

Theoretical studies

Summary
sp² carbon allotropes

0D – FULLERENES
1D – CARBON NANOTUBES
2D – GRAPHENE

sp² hybridization

Overlapping of Sigma Bonds in a Single Graphene Layer
Properties of graphene and CNTs

CARBON NANOTUBES
- Remarkably high electron mobilities at room temperature
- Young’s modulus 1000-5000 GPa
- Metallic or semiconducting properties
- Easy to functionalize

GRAPHENE
- Young’s modulus 1060 GPa
- Semi-metal with unique electronic properties
- Easy to functionalize

Graphene nanoribbons (GNR)
- GNR properties depend on ribbon width and chirality
Application for electronics

Conventional synthesis with metals

drawbacks:
- transfer required
- difficulties with purification

Synthesis from SiC

drawbacks:
- high temperature
- interaction with SiC

New synthesis using metal oxides

drawbacks:
- no transfer required
- no purification needed
- low temperature possible

FETs with graphene
Carbon nanotubes formation using metal catalysts

- Metal catalysts required (transition metals)
- Metal catalysts are argued to fulfil various roles:
  - Catalytic decomposition of carbon feedstock (CVD)
  - Catalytic nucleation and growth of CNT

CNT growth catalyzed by a Ni


Vapor-Liquid-Solid (VLS) mechanism:

Drawbacks for electronic applications:
- difficulties with purification
- transfer required
Carbon nanotubes formation through oxide catalysts

**SWCNT from MgO, PbO$_2$, In$_2$O$_3$**


**Carbon nanofibres from SiO$_2$**

Bachmatiuk, et al., ACS Nano, 3 (2009) 4098

**SWCNT from NPs: SiO$_2$, Er$_2$O$_3$, Al$_2$O$_3$, TiO$_2$**


**SWCNT and MWCNT from ZrO$_2$**

Carbon nanotubes formation from hybrid catalysts

MWCNT growth from $\text{Al}_2\text{O}_3$ substrate


- Catalyst lies entirely within tube at its base
- Graphitic walls stem from the oxide support
- Metal catalyst nucleates the CNT
- Oxide causes CNT growth

Oxides are active catalysts for carbon nanotube formation

WHY NOT GRAPHENE?
Graphene formation through oxide catalysts

Graphene growth on MgO, Al₂O₃, Ga₂O₃, TiO₂


Graphene growth on MgO and ZrO₂

Scott, et al., APL, 98 (2011) 073110

Graphene growth on sapphire


NO metals

Nanographene growth on different substrates

Graphene synthesis by surface diffusion

MgO, cyclohexane, 875 °C

ZrO₂, acetylene, 480 °C

MgO, acetylene, 325 °C

Irreducible oxides

Step site nucleation and growth

- Low temperatures (< 500 °C), small nano-islands
- Reaction stops once nano-crystals are encapsulated
- Graphene layers root into step sites

Scott, et al., APL, 98 (2011) 073110
Theoretical studies of surface diffusion

$\text{C}_2\text{H}_2$ adsorption sites on MgO (100)

- $\text{C}_2\text{H}_2$ adsorption on surface is weak
- $\text{C}_2\text{H}_2$ adsorption at step site is stronger
- Step sites play very important role

In collaboration with TU Dresden

Scott, et al., APL, 98 (2011) 073110
Possible growth route

Hydrogen diffuses, Carbon remains
Temperature influence on graphene domain size

Sapphire substrates

\[ \text{C}_2\text{H}_5\text{OH}, \ 850 \degree \text{C} \]

\[ \text{C}_3\text{H}_8, \ 1350 \degree \text{C} \]

Low temperature \(\Rightarrow\) smaller domains \(\Rightarrow\) more defects


In collaboration with Cornell University
sp\textsuperscript{2} carbon formation from oxide catalysts

**Irreducible oxides**
(MgO, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, TiO\textsubscript{2}, Ga\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2})

![Graphs showing C 1s and Zr 3d intensities](image)

- After H\textsubscript{2} exposure
- During CNT growth C\textsubscript{2}H\textsubscript{2}:H\textsubscript{2} 1:5 525°C
- Cool down under vacuum 200°C

Scott, et al., APL, 98 (2011) 073110

**Reducible oxides**
(SiO\textsubscript{2})

![Graphs showing Si 2p and O 1s intensities](image)

- Normalized intensity
- Binding energy (eV)

Bachmatiuk, et al., ACS Nano, 3 (2009) 4098
Bachmatiuk, et al., Carbon, 48 (2010) 3175

- No zirconium or zirconium carbide is observed
- No silicon or silicon carbide is observed
GOAL:

Formation of sp$^2$ carbon via carbothermal reduction of Si$_x$O$_y$

\[ 3C + SiO_2(s) \rightarrow SiC(s) + 2CO(g) \] – endothermic process (below 1000 °C)

\[ C + SiO_2(s) \rightarrow SiO(g) + CO(g) \]

\[ 2C + SiO(g) \rightarrow SiC(s) + CO(g) \]

- SiC results from the direct reduction of SiO by solid carbon
Carbothermal reduction

- Stacked-cup CNTs are formed by precipitation
- SiC particles are present at roots
- Oxide particles are reduced during the process
- Local EDS of the particles shows only Si & C

Bachmatiuk, et al., ACS Nano, 3 (2009) 4098
Bachmatiuk, et al., Carbon, 48 (2010) 3175
Spectroscopic study

- SiC and O$_x$Si-H$_y$ are observed

- No silicon or silicon carbide is observed


Proposed mechanism

- SiO$_2$ is reduced via a carbothermal reaction forming SiC
- SiC particles coalescence and then the carbon nanofibres grow by precipitation

Theoretical studies of carbothermal reduction

Carbothermal reduction of SiO$_2$ in presence of CH$_4$

- Formation of SiC occurs on the surface/subsurface layers of the SiO$_2$ nanoparticle

Graphene synthesis by bulk diffusion

- sp² carbon formation via a precipitation mechanism from SiₓOᵧ
Graphene synthesis by bulk diffusion

- Formation of graphene at 1000 °C from SiO – early steps
- Where and how is the graphene formed? FIB cross-sectional studies
Evidence for SiC formation

In collaboration with AFRL
Summary

- Oxides are alternative systems for growth of sp² carbon
- Two different routes are possible
- Step sites are crucial for graphene growth (irreducible oxides)
- Precipitation process occurs (reducible oxides)
- Domain size depends on the process temperature
- Low temperature synthesis (<500 °C) is possible
Thank you for your attention!