Mass Production of Graphene Material and Its Industrial Applications

Dr. Cheng-Yu Hsieh
Enerage Inc.

2013.11
Product

graphene

Lithium Iron Phosphate

graphene based supercapacitor

Li-ion battery separator
Graphene (2004)


Graphene

- Thermal Conductivity => 5300 W/m • K
- Specific Surface Area => 2630 m²/g
- Resistivity => 10⁻⁶ Ω • cm
- Electron Mobility => 2 • 10⁵ cm²/V • s
- Transparency => 97.7%
- Young’s Modulus => 1050 GPa

Applications

Graphene Markets, Technologies and Opportunities 2013-2018

*Graphene Markets, Technologies and Opportunities 2013-2018*
USA Patent Applications

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**Synthesis**

**Bottom - Up**

**SiC Epitaxial**

![Diagram of SiC Epitaxial Synthesis](image)


**CVD**

![Diagram of CVD Process](image)

*C. Mattevi et al., J. Mater. Chem., 21, 3324 (2011)*
**Synthesis**

**Top - Down**

**Scotch tape exfoliation**


**Ball milling**

* V. Leon et al., Chem. Commun., 47, 10936 (2011)
Top - Down

Graphite oxide reduction

\[ \text{Graphite} \rightarrow \text{Graphite-OX} \rightarrow \text{Graphene-OX} \]

- i) Thermal or chemical reduction
- ii) Ultrasonication
- iii) Reduction with NaBH₄
- iv) Reduction with \(-E (V)\)

* A. Bonanni et al., TrAc Trends in Analytical Chemistry 37, 12 (2012)
Synthesis

- Thin Graphite
- Oxidation-Reduction
- Plasma
- Liquid-Phase Exfoliation
- CVD
- Epitaxial
- Scotch-Tape

Graphene Quality vs. Cost

* ID TechEx
Mass Production

Graphite

Intercalation

Acid

Oxidant

Oxidation

Graphene powder

Thermal reduction

Chemical reduction

Graphene suspension
Applications

Graphite

Graphite intercalated compound

- Multi layer graphene
  - Polymer composites
    - Graphene/rubber
    - Graphene/resin
  - Graphene/rubber
- Graphene suspension
  - Transparent component
    - Transparent conductive film
- Few layer graphene
  - Electrochemical component
    - Li-ion battery
    - Supercapacitor
  - Printed electronics
    - Coating application
- Graphene ink
  - Flexible component
    - Printed electronics
    - Coating application
Graphene Product

Few layer graphene

Multi layer graphene

Graphene ink

Graphene suspension
Application

Tap density (g/cm³)

- LFP: >1 g/cm³
- graphite: ~0.6 g/cm³
- multi layer graphene: ~0.05 g/cm³
- Few layer graphene: <0.01 g/cm³
Multi layer graphene

P-ML20

O content: < 2.5 wt%
Specific surface area: > 20 m²/g
Thickness: 10 ~ 50 nm
Lateral size: > 10 um
Applications

Graphene Lubricant

Graphene lubricant with graphene reduces friction coefficient by more than 35% compared to 10W40 lubricant.

Temperature vs. Time:
- Black line: 10W40
- Blue line: with graphene

Friction Coefficient vs. Time:
- Black line: 10W40
- Blue line: with graphene
Graphene / Polymer Composite

- Graphene / Epoxy
- Graphene / Nylon
- Graphene / PC
Graphene / Ag Paste

Resistivity (Ω-cm) vs. filler concentration (wt%)

10 wt% ML-10

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<th>Resin (wt%)</th>
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Application

Graphene / Carbon Fiber Composite
P-MF10

O content: 1 ~ 20 wt%
Specific surface area: > 400 m²/g
Thickness: < 3 nm
Lateral size: > 1 um
Graphene supercapacitor

AC Electrode

separator

AC Electrode

- Aqueous-0%
- Aqueous-0.5%
- Aqueous-1%

Specific capacitance (F/g)

Cycle (no.)

Capacitance retention (%)

- Blank
- 0.5wt% graphene
- 0.5wt% graphene

0 10000 20000 30000 40000
60 80 100 120 140 160 180 200
blank 0.5wt% graphene blank

0 10000 20000 30000 40000
60 80 100 120 140 160 180 200
blank 0.5wt% graphene blank

Specific capacitance (F/g)

Cycle (no.)

Capacitance retention (%)

- Blank
- 0.5wt% graphene
- 0.5wt% graphene

0 10000 20000 30000 40000
60 80 100 120 140 160 180 200
blank 0.5wt% graphene blank

Resin / Graphene composites

Resin base: SBS rubber
Graphene content: ~ 1 wt%
Sheet resistance:

$10^{14} \ \Omega/\square \Rightarrow 10^{11} \ \Omega/\square$
Graphene suspension

S-ON20

Solvent: NMP, DMSO, Terpeniol
Concentration: 150 ~ 250 ppm
Thickness: < 10 nm
Application

Graphene based supercapacitor

Graphene

Activated carbon

- Control
- Suspension

Specific capacitance (F/g)

Cycle number

Enerage Inc. - California - Taiwan
**Application**

$\text{Li}_{1.2}\text{Ni}_{0.4}\text{Mn}_{0.6}\text{O}_2$ electrode

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**Graphs:**

- **Upper Graph:**
  - Title: $2^{nd}$ cycle, 20 mA/g
  - Data points for Bare LNMO, LNMO_G100, LNMO_G200, LNMO_G150L

- **Lower Graph:**
  - Title: Charge: 20, 45 mA/g
  - Discharge: 20, 112.5, 225, 450, 675, 1125, 2250 mA/g
  - Potential range: 2-4.6V
  - Data points for Bare LMNO, LMNO_G100, LMNO_G200, LMNO_G150L

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**Notes:**

- Specific Capacity (mAh/g)
- Current density (mA/g)
Graphene based
Transparent Conductive Film

Substrate: glass / PET

Content: graphene / matrix resin

Transparency: > 85%

Sheet resistance: < 200 Ω/□
Graphene Ink

Content: few layer graphene conductive binder
Concentration: 250ppm ~ 10wt%
Solvent: H$_2$O, organic solvent

Graphene / Al foil

Graphene / Cu foil
Graphene Fiber

Diameter: < 10 um
Resistivity: < 10 Ω
Graphene based semiconductor

Resistance Random Access Memory

Cycle: > 100 times

HRS / LRS: > 27
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