BASF Research Press Conference
on May 27, 2014

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Out of the Black: Will graphene materials have a bright future?

Dr. Matthias Schwab
Head of Graphene Research, BASF SE, Ludwigshafen

Outline

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1. An industrial view on graphene materials
2. Graphene research at BASF
3. The Carbon Materials Innovation Center
4. Insight into MPI-P research (Prof. Dr. Klaus Müllen)

Outline

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1 An industrial view on graphene materials

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Carbon-based innovations

Adding value to BASF's growth fields

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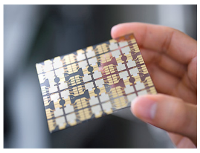
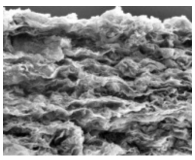
Motivation

- Current & future growth fields benefit from strong know-how on carbon materials:
  - ▶ Batteries for mobility
  - ▶ Lightweight composites
  - ▶ Heat management
  - ▶ Organic electronics





- Graphene is the youngest member of the "carbon family":
  - ▶ Early market examples
  - ▶ Number of patents still climbing
  - ▶ Global research initiatives



- Joint research on carbon materials with the MPI for Polymer Research, Mainz at the Carbon Materials Innovation Center since 2012

Graphene is a fascinating nanomaterial

… in one dimension

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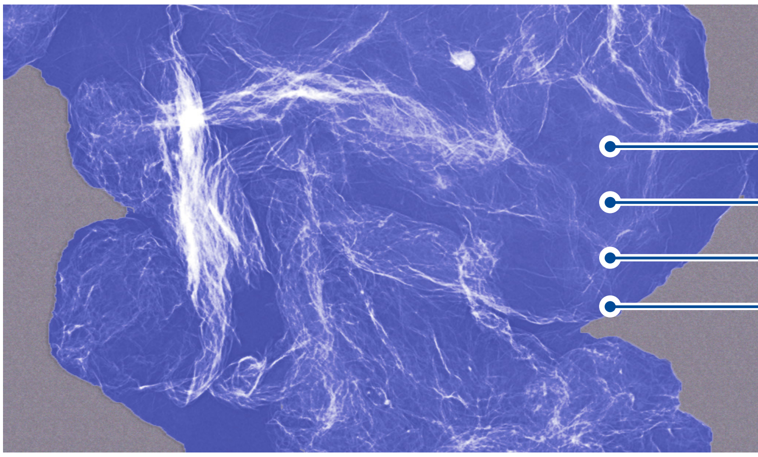
Lateral dimensions = Micrometer

Thickness = Nanometer



- High electron mobility
- High thermal conductivity
- High transparency
- High mechanical strength

"Graphene is not graphene"

The importance of defining the material

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TOP-DOWN

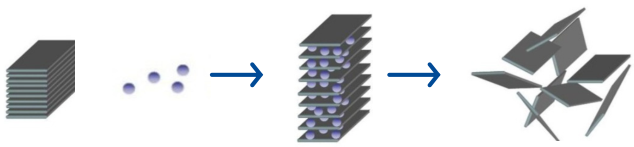
Graphite

GRAPHENE MATERIALS

Chemical Precursors

BOTTOM-UP

Graphene via exfoliation of graphite



Oxidation or intercalation

Graphite oxide or intercalated graphite

Reduced graphene oxide, exfoliated graphite

Schniepp, H. C. et al.; *J. Phys. Chem. B* **2006**, *110*, 8535 - 8539
Source: Ahmed Abdala

Graphene's competitors

- Carbon black, graphite, activated carbon
- Large-volume commodities
- Typical price range 1 – 10 US$/kg
- Higher margins for specialty applications

Graphene materials

A full range of different grades

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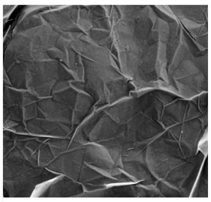
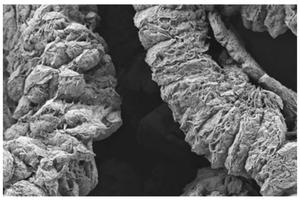
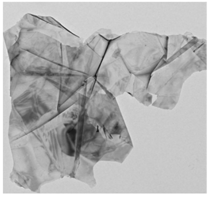


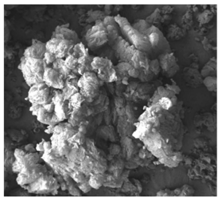
Graphite



Expanded graphite



Graphite nanoflake



Few-layer graphene

Graphene-like

Current Status

- At present g to kg amounts available from startups
- Challenges for commercial success:
  - Availability
  - Cost competitiveness
  - Consistency

Graphene	A	B	C
Bulk density [g/L]	7.6	19.6	5.3
BET [m^2/g]	74	650	476

Creating economic value from graphene

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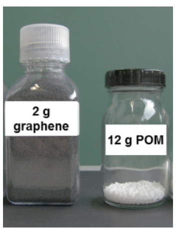
Graphene raw materials → **BASF as enabler** → **Target applications**

Graphene raw materials

- Low bulk density
- Hydrophobicity
- Handling safety



BASF as enabler

- Compounds
- Masterbatches
- Slurries
- Films & foils

Target applications

- Automotive
- Electronics
- Energy
- Consumer goods

BASF has developed strong know-how along the value chain: Chemistry will be required to unlock graphene's potential

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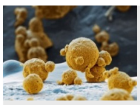
Graphene research & development

BASF roadmap towards graphene applications

Short term → Mid term → Long term

Conductive formulations and inks
- Printable electronics, e-textiles, coatings

Composite materials
- Antistatics, barrier, mechanical reinforcement



Energy storage materials — CMIC
- Batteries, capacitors

Catalysis
- Support materials, electrocatalysis

Transparent conductive layers
- OLED, display, photovoltaics

Carbon semi-conductors
- Transistors, spintronics

Graphene research & development

BASF Roadmap towards graphene applications

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REVIEW

doi:10.1038/nature11458

A roadmap for graphene

K. S. Novoselov[1], V. I. Falko[2], L. Colombo[3], P. R. Gellert[4], M. G. Schwab[5] & K. Kim[6]

Recent years have witnessed many breakthroughs in research on graphene (the first two-dimensional atomic crystal) as well as a significant advance in the mass production of this material. This one-atom-thick fabric of carbon uniquely combines extreme mechanical strength, exceptionally high electronic and thermal conductivities, impermeability to gases, as well as many other supreme properties, all of which make it highly attractive for numerous applications. Here we review recent progress in graphene research and in the development of production methods, and critically analyse the feasibility of various graphene applications.

Could graphene become the next disruptive technology (that is, could it replace the old technology and lead to new markets)? Is it versatile enough to revolutionize many aspects of our life simultaneously? In terms of its properties, graphene certainly has the potential. Graphene is the first two-dimensional (2D) atomic crystal available to us. A large number of its material parameters—such as mechanical stiffness, strength and elasticity, very high electrical and thermal conductivity, and many others[1,2]—are supreme. These properties suggest that graphene could replace other materials in existing applications. However, that all these extreme properties are combined in one material means that graphene could also enable several disruptive technologies. The combination of transparency, conductivity and elasticity will find use in flexible electronics, whereas transparency, impermeability and conductivity will find application in transparent protective coatings and barrier films; and the list of such combinations is continuously growing. However, is graphene special and versatile enough to justify the inconveniences of switching to a new technology, usually a lengthy and expensive process?

Graphene properties

One reason that graphene research has progressed so fast is that the laboratory procedures enabling us to obtain high-quality graphene are relatively simple and cheap. Many graphene characteristics measured in experiments have exceeded those obtained in any other material, with some reaching theoretically predicted limits: room-temperature electron mobility of $2.5 \times 10^5 cm^2 V^{-1} s^{-1}$ (ref. 3) (theoretical limit[4] $\sim 2 \times 10^5 cm^2 V^{-1} s^{-1}$); a Young's modulus of 1 TPa and intrinsic strength of 130 GPa (ref. 5, very close to that predicted by theory[6]); very high thermal conductivity (above 3,000 W mK^{-1}; ref. 7); optical absorption of exactly $\pi\alpha \approx 2.3\%$ (in the infrared limit, where α is the fine structure constant)[8]; complete impermeability to any gases[9], ability to sustain extremely high densities of electric current (a million times higher than copper)[10]. Another property of graphene, already demonstrated[11–13], is that it can be readily chemically functionalized.

Graphene's many superior properties justify its nickname of a 'miracle material'. However, some of these characteristics have been achieved only for the highest-quality samples (mechanically exfoliated

Nature provides us with many other 2D crystals, such as boron nitride and molybdenum disulphide[16]. Being structurally related to graphene but having their own distinctive properties, they offer the possibility of fine-tuning material and device characteristics to suit a particular technology better or to be used in combination with graphene (for example, 2D-based heterostructures[17,18]). Being part of such a large and diverse family of 2D crystals and heterostructures will improve graphene's chances of commercial success, although we do not cover these other 2D crystals in this Review (see Box 1).

Challenges in production

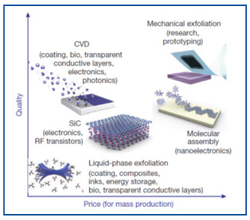
The market of graphene applications is essentially driven by progress in the production of graphene with properties appropriate for the specific application, and this situation is likely to continue for the next decade or at least until each of graphene's many potential applications meets its own requirements. Currently, there are probably a dozen methods being used and developed to prepare graphene of various dimensions, shapes and quality. Here we concentrate only on those that are scalable.

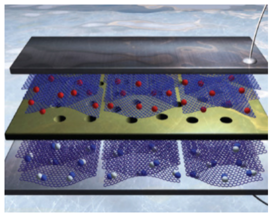
It is logical to categorize these by the quality of the resulting graphene (and thus the possible applications): (1) graphene or reduced graphene oxide flakes for composite materials, conductive paints, and so on; (2) planar graphene for lower-performance active and non-active devices; and (3) planar graphene for high-performance electronic devices. The properties of a particular grade of graphene (and hence the pool of applications that can utilize it) depend very much on the quality of the material, type of defects, substrate, and so forth, which are strongly affected by the production method; see Fig. 1 and Table 1.

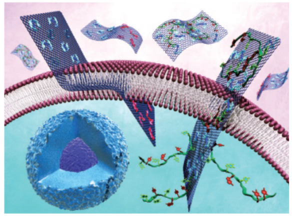
Liquid phase and thermal exfoliation

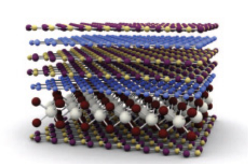
Liquid-phase exfoliation of graphite[19,20] (or any other layered material[21]) is based on exposing the materials to a solvent with a surface tension that favours an increase in the total area of graphite crystallites. The solvent is typically non-aqueous, but aqueous solutions with surfactant can also be used. With the aid of sonication, graphite splits into individual platelets, and prolonged treatment yields a significant fraction of monolayer flakes

nature International weekly journal of science









Example: Graphene-based E-textiles

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smart forvision

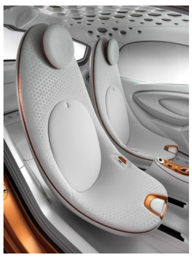
- Joint project of Daimler and BASF
- Graphene e-textiles for seat heating

Technical requirements

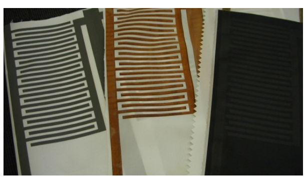
- Homogenous heating
- Mechanical robustness
- Superior energy balance

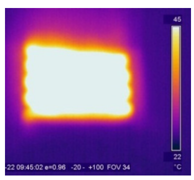
Advantages of graphene

- Sheet-like morphology
- Mechanical strength
- Electrical conductivity



Steron ® Design Coating
Functional Luquafleece® Layer
Graphene-based E-Textile
Elastoflex® Foam
Ultramid® Seat Shell



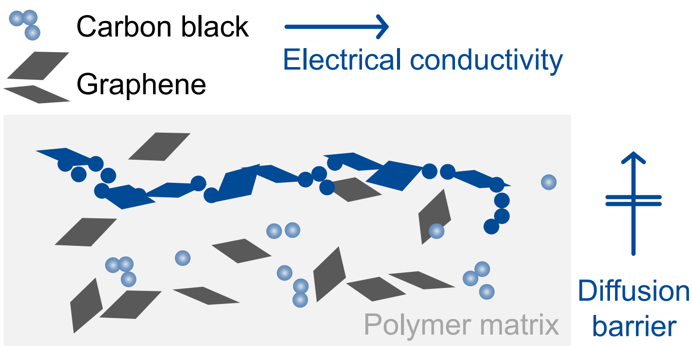


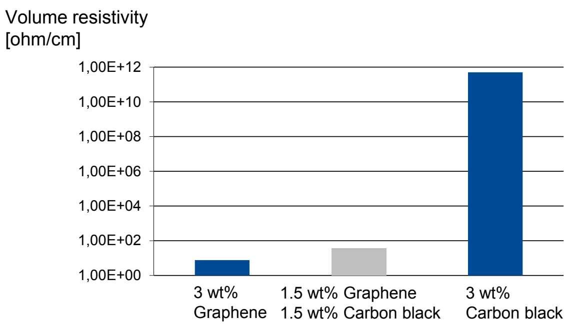
Example: Engineering plastics

Desired functionalities

- Electrical conductivity
- Thermal conductivity
- Gas and fuel barrier
- Mechanical performance

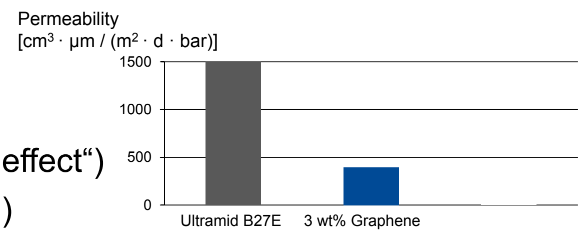
Example: Engineering plastics





Advantages of graphene

- Strong effects at low additive content
- Combinded properties in one additive ("plus effect")
- Synergism with other carbons ("boost effect")



Example: Printable supercapacitors

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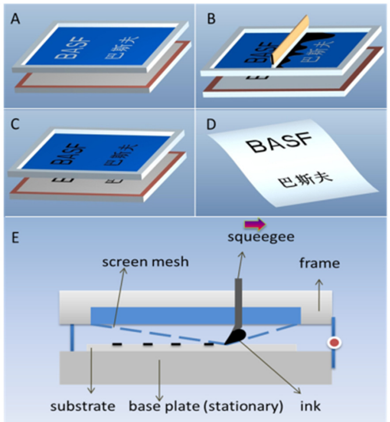
Goal: Increased storage capacity for supercapacitors from abundant feedstocks
Advantage of graphene: Electrical conductivity, enhanced porosity

Hybrid electrodes for supercapacitors

- Formulation of graphene/polyaniline inks
- Fast electrode production via printing
- Speed: 0.1 seconds/electrode
- Specific capacity: 269 F g^{-1}



Y. Xu, M. G. Schwab, A. J. Strudwick, I. Hennig, X. Feng, Z. Wu, K. Müllen *Adv. Energy Mater.* **2013**, *3*, 1035 - 1040.
Xu, Y.; Hennig, I.; Freyberg, D.; Strudwick, A. J.; Schwab, M. G.; Weitz, T.; Cha, K. C. *J. Power Sources* **2014**, *248*, 483 - 488

Example: Line filtering with graphene

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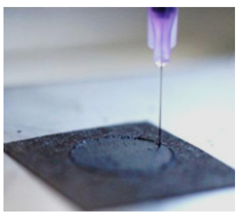
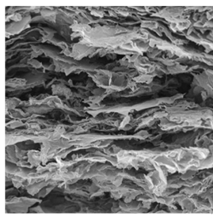
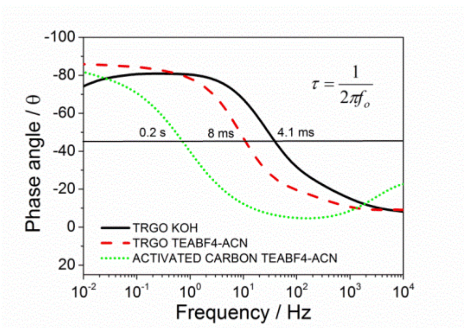
Goal: Development of new approach to state of the art electrolytic capacitors
Advantages of graphene: Electrical conductivity, film-forming character

Graphene electrodes for line-filtering

- 3D micro-extrusion technique for viscous pastes
- Thin and flexible electrodes on carbon cloth
- "Conversion of AC wall power to DC power"
- Time constant (120 Hz): 2.3 ms







Nathan-Walleser, T.; Lazar, I.-M.; Fabritius, M.; Tölle, F. J.; Xia, Q.; Bruchmann, B.; Venkataraman, S. S.; Schwab, M. G
Mülhaupt, R. *Adv. Funct. Mater.* **2014**, DOI: 10.1002/adfm.201304151

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BASF is part of global academic network on graphene

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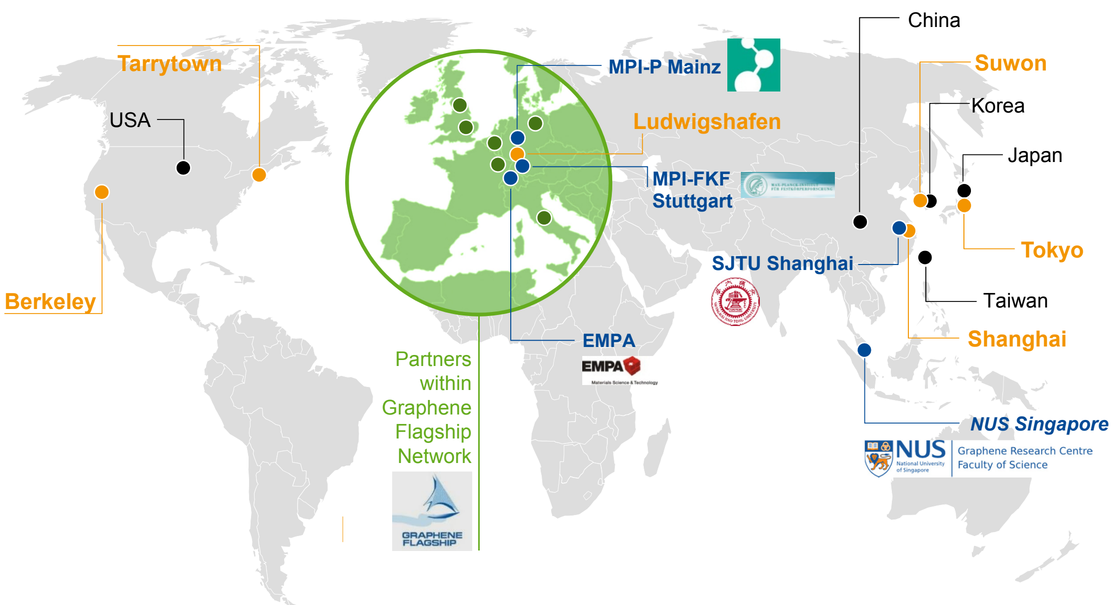

● BASF sites & innovation teams ● R&D cooperations ● Scouting activities

The Carbon Materials Innovation Center

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Role of CMIC

- Jointly leverage knowledge of BASF and MPI-P
- Unlock opportunities for advanced carbon materials
- Generate early and strong IP

Max-Planck-Institut für Polymerforschung
Max Planck Institute for Polymer Research

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Facts & figures

- First co-location lab on BASF site
- Two BASF research divisions involved
- 8 Postdocs, 4 BASF employees
- 200 m^2 state-of-the-art lab space
- Total investment over 3 years: €10 million

CMIC launch September 24th, 2012

CMIC setup

From research to market applications: 4 focus fields

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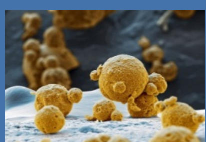
CMIC

Fundamental research

- New materials
- Synthetic protocols
- Characterization

Focus fields

- Energy storage materials
- Catalysis
- Carbon thin films
- Carbon semi-conductors

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Application check
Market know-how

- Feasibility
- Device integration
- Securing joint IP

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Nanotechnology

Small dimensions – great opportunities