

The Evolution of Carbon in the Chemical Industry

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Carbon in the Elemental State





Early Industrial Use of Carbon





- Graphite was used to line the moulds before iron was poured in
- Graphite used as an additive on the outside of cannon balls
- High heat stability ensured higher accuracy when fired



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Coal is an Important Energy Source









- □ Fischer-Tropsch process (1925)
 - $H_2 + CO \rightarrow C_n H_{(2n+2)} + H_2O$
- Coal to Liquid: Creating Synthetic Fuel

Coal is still an important player in the energy landscape

Carbon... the origin of chemistry



The range of products created by chemical reactions are all derived from carbon feedstock





New Carbon Materials: Carbon Fibers



- Thomas Edison used carbon fibers made from cotton or bamboo in early light bulbs
- Low tensile strength but high heat tolerance

Market share of industry leaders





Production methods improved with polyacrylonitrile as a starting material (AIST Japan)



- First attempt at integrating carbon fiber into an engine by Rolls Royce in the 1960s
- Increased use of carbon fiber reinforced polymers / composites (CFRPs)

2010: 36.000 t/a

1,3 bn USD

2015: fcst 60,000 t/a



Carbon fibers



Description

- Organic materials pretreated at a high temperature
- Thin strand of material (5-10 μm) which contains 92% to > 99% Carbon
- Feedstocks:
- Polyacrylonitrile (PAN)
- Pitch (coal or petroleum tar)
- Use as reinforcement in Plastics (CFRP)

Properties

- Light weight
- Good fatigue resistance
- High strength and stiffness
- Good conductivity (thermal and electric)
- Chemical inertness (e.g. towards corrosion)
- Low thermal expansion



Applications



Aerospace & Aeronautic wings, flaps, stabilizers

Sport goods golf shafts, bicylcles, fishing rods, rackets





Automotive body panels, hoods (premium sport cars)

Wind energy turbine blades



Carbon fibers Manufacturing of Carbon fibers



Processes from Pitch and PAN



source: K. Lafdi, M. Wright, Handbook of composites (1998)

Carbon fibers Value chain



We Create Chemistry for Sustainable Mobility





Growing Demand for Carbon Fiber Composite Technology





CARBON FIBRE DEMAND BY REGION BY WEIGHT (2006, 2011 & 2016)

				CAGR %	
Units: '000 tonnes	2006	2011	2016	2006-11	2011-2016
Europe	1.9	4.5	9.9	18%	17%
North America	0.0	1.8	5.7	-	27%
Asia	0.0	1.1	5.7	133%	39%
ROW	0.0	0.4	1.3	-	28%
Total	1.9	7.7	22.6	32%	24%

Cost of Composite Automotive Parts Need to Be Reduced Along the Value Chain

800 Relative comparison UD 800 -30% for parts with same function CFRP process costs 560 (labor + tools) 600 quasi-isotropic -40% matrix relative aluminum material costs high strength part cost (raw materials steel 200 -20% fiber + auxiliaries) 100 steel 135 100 CFRP CFRP steel 25 2020 today relative 55 weight 85 100

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Source: RolandBerger, VDMA, 2012, "Serienproduktion von hochfesten Faserverbundteilen"

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Diverse Markets for Carbon in Energy Storage

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The commodity carbon market is dominated by purification/filtration applications which require high surface area The carbon market for energy storage is a specialty market, requiring high surface area and/or electrical conductivity



Source: Freedonia

Activated Carbon World Market



AC Consumption	2011	2016	Growth p. a.
	[kt/a]	[kt/a]	2011-2016
Global	1.180	1.930	10.3 %



Markets

- 40% water treatment,
- 40% air & gas purification
- 10% food processing
- 10% chemical, pharma & others

Relevant Markets for BASF

- Supercapacitors
- Catalyst Supports
- Batteries & Electrodes
- Solvent Vapor Recovery
- CH₄ Storage
- Protective

Structure of Activated Carbon





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Requirements for Supercapacitors

Major Requirements on AC

- High surface area (BET > 2000 m²/g)
- Defined pore size distribution
- Micropore volume (d_{pore} < 2 nm)
- Mesopore volume (d_{pore} > 2 nm)
- Low impurity content (< 1000 ppm)
- No chemical and electrical activity
- Good wettability for electrolyte
- Uniform particle size distribution (~ 5 μm)
- High packing density
- Low electrical resistance





The Emergence of Nano Carbons



The Nobel Prize in Chemistry 1996

Robert F. Curl Jr., Sir Harold Kroto, Richard E. Smalley







The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley *"for their discovery of fullerenes"*.

Photos: Copyright © The Nobel Foundation

Named after Buckmister Fuller, designer of the geodesic dome





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- The discovery of fullerenes paved the way toward tailored syntheses of complex carbon materials
- With electronic characteristics that expanded the use of organic molecules into electronics
- Very good n-dopant material for organic photovoltaics

Dyes and Organic Electronics

The chemistry and physics of conducting molecules and polymers developed into the field of organic electronics

Ever increasing adoption of organic electronics into systems

From the building blocks:



Synthesis of new dyes for DSSCs, with several contributions from Prof. Müllen







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Organic PV in smart4vision

Carbon Nanotubes



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Enhancement of Mechanical and Electrical Properties

CNT Application Milestones



Carbon Nanotubes

1-Dimensionality

- Production of CNTs undertaken by several companies
- Most notable is the divestiture of CNT business by BayerMaterialScience in 2013
- Key to success is system enhancement and integration rather than large scale production of CNTs

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- BASF product: Ultraform® N2320 C for fuel filter housing
- MWCNT filler
- Launched in 2009, used by Bosch in Audi A4 and A5





Graphene is a fascinating nanomaterial

... in one dimension



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

Nanometer

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Promising Properties of Graphene

Property	Values comparison	Transistors		Longer time
Mobility (cm ² /V•s)	Graphene – 200k Si – 1400 GaAs - 8500			
Transparency (%)	Graphene – 97.7	Photovoltaic		films, higher
Resistivity (μΩcm)	Graphene - 10 Doped graphene – 4.02 Cu – 1.68	Interconnect		application complexity
Surface area (m²/g)	Graphene - 2630 Activated C - 500 Silica - 800	Energy storage	ĺ	Moderate time to market
Thermal conductivity (W/m•K)	Graphene - 5300 Silicon – 149 Diamond - 2320	Heat management	\mathbf{F}	Powder/flakes, lower application complexity
Ultimate strength (GPa)	Graphene – 130 C-fiber – 4 Steel - 1	Composites		

The Carbon Materials Innovation Center at BASF

Joint research laboratory leveraging knowledge of BASF and MPI-P

- □ Facts & Figures:
 - First co-location lab on BASF site
 - 8 Postdocs, 4 BASF employees
 - Total investment over 3 years: €10 million
- Among the Focus Fields:
 - Energy Storage Materials
 - Catalysis
 - Transparent Conductive Layers
 - Carbon Semiconductors

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





"Graphene Is Not Graphene"

The Importance of Defining the Material





Graphene via Exfoliation of Graphite



Oxidation or Intercalation Graphite Oxide

Intercalated Graphite



Reduced Graphene Oxide Exfoliated Graphene

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 \$/kg

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Recent Research Highlights from BASF

www.advenergymat.d

Makrials Views-

Screen-Printable Thin Film Supercapacitor Device Utilizing Graphene/Polyaniline Inks

Yanfei Xu,* Matthias Georg Schwab, Andrew James Strudwick, Ingolf Hennig, Xinliang Feng, Zhongshuai Wu, and Klaus Müllen*

- Printable energy storage devices
- Increased printing speed of 0.1 sec/electrode
- Capacity 269 F g⁻¹, Energy Density 9.3 Wh kg⁻¹ (1M H₂SO₄)





Plastic Sheet



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

Various Approaches of Making Si Anode Materials Employing Carbon & Graphene

Si coating of C Si-Graphene Core / Shell multilayer coating Void C coating of Si Porous Si-C Si LIB 10 µm Graphene encapsulation of Si Anode Si & C or Graphene mixing by milling or pyrolysis e d Silicon Si thin film Si (111) a

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The Future Role of Carbon

Solving New Technical Challenges

Today's Trend: Synergies with combinations of new and established materials

Future Trends: Creating Hybrid Materials (Contribution by Prof. K. Müllen)

Carbon for efficient water and air purification membranes





DOI: 10.1021/nl3012853

Lightweight composites





Energy Storage and Mobile Technologies

New supercapacitor technologies with hybrid structures



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3D Macroporous Graphene Aerogels

DOI:10.1021/ja308676h

DOI: 10.1021/ja204953k



3D Macro-/Meso-porous Graphene Frameworks

Photoluminescent graphene quantum dots (D ≈ 60 nm)

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Prof. Müllen in the Academic Space

Graphenes as potential material for electronics | Atomically precise bottom-up fabrication of graphene nanoribbons | Large single-molecule fluorescence enhancements produced by a bowtle nanoantenna | Nitrogen-Doped Ordered Mesoporous Graphitic Arrays with High Electrocatalytic Activity for Oxygen Reduction | Transparent carbon films as electrodes in organic solar cells | Fabrication of Graphene-Encapsulated Oxide Nanoparticles: Towards High-Performance Anode Materials for Lithlum y ionrage | Two-dimensional graphene nanoribbons | Composites of Graphene with Large Aromatic Molecules | Field-effect transistors based on a benz othin adiazole-cyclopentadithiophene conjumer | Disposites of Graphene Sheets in Organic Solvent Supported by phonic interactions | Uitrahigh Mobility in Polymer Field-Effect Transistors by Design | Polyphenylen-Based Materials for Organic Portovoltaics | Towards high charge-carrier mobilities by rational design of the shape and periphery of discotics | The influence of Morpheles and their polymers. Efficient Metal-Free Electrocatalysts for Oxygen Reduction R eactions | Large Aromatic expections and their polymers. Efficient Metal-Free Electrocatalysts for Oxygen Reductions | Composites of discotics | The influence of Morpheles and their polymers. Efficient Metal-Free Electrocatalysts for Oxygen Reduction R eactions | Large Aromatic expections | Composites of discotics | The influence of Morpheles and their polymers. Efficient Metal-Free Electrocatalysts for Oxygen Reduction R eactions | Large Aromatic expections | Carrier mobilities by rational design of discotics | The influence of Morpheles and their polymers. Efficient Metal-Free Electrocatalysts for Oxygen Reduction R eactions | Large Aromatic expections | Carrier mobilities by rational design of the shape and their polymers. Efficient Metal-Free Electrocatalysts for Oxygen Reduction R eactions | Carrier mobilities by Reduction R eactions | Carrier expections | Carrier expections | Carrier expections | Carrier expections | Carrier expec

via a common Intermediate | Pyrene-Based Materials for Organic Electronics | Graphene-Based Nanosheets with a Sandwich Structure | Patterned Graphene Electrodes from Solution-Processed Graphite Oxide Films for Organic Field-Effect Transistors | 3D Nitrogen-Doped Graphene Aerogel-Supported Fe3O4 Nanoparticles as Efficient Eletrocatalysts for the Oxygen Reduction | Graphene as Transparent Electrode Material for Organic Electronics | Nanographene-Constructed Hollow Carbon Spheres and Their Favorable Electroactivity with Respect to Lithium Storage | intramolecular charge-transfer tuning of perylenes: Spectroscopic features and performance in Dye-sensitized solar cells | Dithieno[2,3-d; 2 ',3 '-d ']benzo[1,2-b; 4,5-b ']dithiophene (DTBDT) as Semiconductor for High-Performance, Solution-Processed Organic Field-Effect Transistors | Sandwich-Like, Graphene-Based Titania Nanosheets with High Surface Area for Fast Lithium Storage | A bottom-up approach from molecular nanographenes to unconventional carbon materials | High thermal stability and rigid rod of novel organosoluble polyimides and polyamides based on bulky and noncoplanar naphthalene-biphenyidiamine | The Rylene Colorant Family-Tailored Nanoemitters for Photonics Research and Applications | Synthesis and self-organization of core-extended perviene tetracarboxdilmides with branched aikyl substituents. | Porous graphenes: two-dimensional polymer synthesis with atomic precision | Liguid Crystalline Ordering and Charge Transport in Semiconducting Materials | An improved Perviene Sensitizer for Solar Cell Applications | Self-assembly of periodic bicomponent a and ribbons | Epitaxial composite layers of electron donors and acceptors from very large polycyclic aromatic hydrocarbons | Nanographenes as active components of single-molecule electronics and how a scanning tunneling microscope, Structure-Property Relationships in Dithienosilole-Benzothiadiazole Donor-Acceptor Copolymers | Blue-green upconversion: Noncoherent excitation by NIR light | A one-step approach towards carbon-encapsulated hollow ti lithium batteries | Polyphenylene-type emissive materials: Poly(para-phenylene)s, polyfluorenes, and ladder polymers | Revealing competitive Forster-type resonance energy-transfer pathways in single bichromophoric on bridged phenylenes as electronic materials | Catalyst-free Preparation of Melamine-Based Microporous mide-based dendrimer by ensemble and single-molecule fluorescence spectroscopy (improving polymer Polymer Networks through Schiff Base Chemistry | Probing intramolecular Forster resonance energy transfe transistor performance via morphology control | Molecular clusters in two-dimensional surface-confined n dyn a mics | A Germanium-Carbon N an ocomposite Material for Lithium Batteries | Probing conformational dynamics in single donor-acceptor synthetic molecules by means of photoinduced reversible electron netal and carbon/metal oxide nanocomposites | Three-Dimensional Nitrogen and Boron Co-doped Graphene for High-Performance All-Solid-State Supercapacitors | Ladder-type pentaphenylene dyes f UV Photoreduction of Graphene-Polyoxometalate Composite Films for Electronics | From Industrial colorants to single photon sources and biolabels. The fascination and function of rylene dyes | Rej of branched alkyl hexa-peri-hexabenzocoronenes | A new photostable terrylene diimide dye for applications in single molecule studies and membrane labeling | Efficient Synthesis of Heteroatom (Silica Sheets for Oxygen Reduction Reactions | Bottom-Up Fabrication of Photoluminescent g properties | Three-Dimensional Graphene-Based Macro- and Mesoporous Frameworks for High-Graphene Quantum Dots with Uniform Morphology | Mesitylboron-substituted ladder-type pentaphi Performance Electrochemical Capacitive Energy Storage | Direct Access to Metal or Metal Oxide | for Electrochemical Energy Storage | Photovoitalc charge generation visualized at the nanoscale: A proof of principle | Synthesis and applications of core-enlarged perviene dyes | A hexa-peri-hexal electronics | Transparient, Thermailly Stable and Mechanically Robust Superhydrophobic Surfaces Made from Porous Silica Capsules | Surface-assisted cyclode hydrogenation provides a synthetic in tes | Tuning the Columnar Organization of Discotic Polycyclic Aromatic Hydrocarbons | Electronic excitation energy transfer between two single molecules embedded in a polymer host | Two-Dime ecursor Mobility and Reactivity | Large polycyclic aromatic hydrocarbons: Synthesis and discotic organization | Graphene Nanoribbons by Chemists: Nanometer-Sized, Soluble, and Defect-Free | fuctor at surfaces: Long-range mass transport forming giant functional fibers | Exciton fission and fusion in bis(tetracene) molecules with different covalent linker structures (Energy and electron trans m armchair to zigzag peripheries in nanographenes | Controlled Self-Assembly of C-3-Symmetric Hexa-peri-hexabenzocoronenes with Alternating Hydrophilic and Hydrophobic Substituents in Solu matic hydrocarbons | Porous Graphene as an Atmospheric Nanofilter | From Nanographene and Graphene Nanoribbons to Graphene Sheets: Chemical Synthesis | Charge-Carrier Transporting Gra h Highly Ordered Single Polymer Fibers | Rational Optimization of Benzo (2, 1-b; 3, 4-b] dthilophene-Containing Polymers for Organic Field-Effect Transistors | Design strategies for organic semico ophene Dendrimers with a Hexa-peri-hexabenzocoronene Core-Synthesis, Characterization and Performance In Bulk Heterolunction Solar Cells | Self-Assembly of a Donor-Acceptor Dyad Across c Electronics | Self-assembly of positively charged discotic PAHs: From nanofibers to nanotubes | Polyoxometal ate assisted photoreduction of graphene oxide and its nanocomposite formation | Rein hydrogen bonds: From microscopic aggregates to macroscopic fluorescent organogels | Pyrene as chromophore and electrophore: Encapsulation in a rigid polyphenylene shell | Blue-emitting carbon- and Visualizing and controlling vibrational wave packets of single molecules | Water-soluble monofunctional perviene and terrylene dyes: Powerful labels for single-enzyme tracking | A conjugated polycarbazole ring opping in Single Molecular Junctions by Measuring Length and Temperature Dependence | Controllable Growth and Field-Effect Property of Monolayer to Multilayer Microstripes of an Organic Semiconductor | Expl g with ultrastable perviene dyes i Diffusion of oriented single molecules with switchable mobility in networks of long unidimensional nanochannels | Vapor sorption and electrical response of Au-nanoparticle-dendrimer of cale Architecture and Function in Photovoitalc Multichromophoric Arrays as Visualized by Kelvin Probe Force Microscopy | Benzo[1,2-b : 4,5-b ']bis[b]benzothiophene as solution processible organic semiconductor for field nction photovoltaics based on alkyl substituted discotics | The Effect of Solvent Additives on Morphology and Excited-State Dynamics in PCPDTBT: PCBM Photovoltaic Blends | Solution Processable Fluorenvil Hexa-peri-hexaber Effect Transistors and Solar Cells | Synthesis of Microporous Carbon Nanofibers and Nanotubes from Conjugated Polymer Network and Evaluation in Electrochemical Capacitor | Polypyrene Dendrimers | Arylamine-substituted oligo(ladde lene)s: Electronic communication between bridged redox centers | Novel core-expanded rylenebis(dicarboximide) dyes bearing pentacene units: Facile synthesis and photophysical properties | From ambi- to unipolar behavior in discotic dive field-effect transistors | Polytriphenylene Dendrimens: A Unique Design for Blue-Light-Emitting Materials | One-dimensional porous carbon/platinum composites for nanoscale electrodes | Synthesis of conjugated polymer nanoparticles in non-aqueous emulsions | Virus-like Particles Templated by DNA Micelles: A General Method for Loading Virus Nanocarriers | Poly(phenylene-pyridyli) dendrimens: Synthesis and templating of metal nanoparticles | Helical packing of discotic hexaphenyl hexa-peri-hexabenzocoronenes: Theory and experiment | A Divergent Synthesis of Very Large Polyphenylene Dendrimens with Iridium(III) Cores: Molecular Size Effect on the Performance of Phosphorescent Organic Light-Emitting Diodes | Self-assembly, molecular dynamics, and kinetics of structure formation in dipole-functionalized discotic liquid crystals | Forever young: polycyclic aromatic hydrocarbons as model cases for structural and optical studies | Self-assembly of chiral molecular honeycomb networks on Au(111) | Electron-deficient N-heteroaromatic linkers for the elaboration of large, soluble polycyclic aromatic hydrocarbons and their use in the synthesis of some very large transition metal complexes | Helter-Skelter-Like Perylene Polylsocyanopeptides | Temperature-Enhanced Solvent Vapor Annealing of a C-3 Symmetric Hexa-peri-Hexabenzocoronene: Controlling the Self-Assembly from Nano- to Macroscale | Nitrogen-Doped Graphene and its iron-Based Composite As Efficient Electrocatalysts for Oxygen Reduction Reaction | Detection of TNT explosives with a new fluorescent conjugated polycarbazole polymer | Transparent, highly conductive graphene electrodes from acetyleneassisted thermolysis of graphite oxide sheets and nanographene molecules | Cooperative Molecular Motion within a Self-Assembled Liquid-Crystalline Molecular Wire: The Case of a TEG-Substituted Perylenediimide Disc | Rainbow Perylene Monoimides: Easy Control of Optical Properties | 8-Quinolinolates as ligands for luminescent cyclometalated iridium complexes | Poly(2,7-phenanthrylene)s and poly(3,6-phenanthrylene)s as polyphenylene and poly(phenylenevinylene) analogues | Backbone Curvature in Polythlophenes | Synthesis, helical organization, and fibrous formation of C-3 symmetric methoxy-substituted discotic hexa-peri-hexabenizocoronene | Photophysical study of bay substituted perylene dilmides | Polythlophene: Perylene Dilmide Solar Cells - the impact of Alkyl-Substitution on the Photovoitaic Performance | Core, Shell, and Surface-Optimized Dendrimers for Blue Light-Emitting Diodes | Electronic Transport Properties or Ensembles of Perylene-Substituted Poly-Isocyanopeptide Arrays | A polyphenylene dendrimerdetergent complex as a highly fluorescent probe for bloassays | Controlling single-molecule conductance through lateral coupling of pl orbitals | Diffusion in Polymer Solutions Studied by Fluorescence Correlation Spectroscopy | A simple approach towards onedimensional mesoporous carbon with superior electrochemical capacitive activity | Self-assembly of perviene monoimide substituted hexa-peri-bexabenzoeoronenes: Dyads and triads at surfaces | Triangular Trinuclear Metal-N-4 Complexes with High Electrocatalvtic Activity for Oxygen Reduction | Controllable Columnar Organization of Positively Charged Polycyclic Aromatic Hydrocarbons by Choice of Counterions | Defocused Wide-field Imaging Unravels Structural and Temporal Heterogeneity in Complex Systems | Blue-Emitting Poly(2,7-pyrenylene)s: Synthesis and Optical Properties

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CMIC is in the center of BASF Ludwigshafen