



NEW CARBON MATERIALS

METHODS OF SYNTHESIS

Boyko Tsyntsarski, Assoc. Prof. PhD

Lab. Chemistry of Solid Fuels
Institute of Organic Chemistry with Centre of Phytochemistry
Bulgarian Academy of Sciences

Marie Skłodowska-Curie Actions-Innovative Training Networks

H2020-MSCA-ITN-2018: BIKE 813748

TRAINING EVENT 2

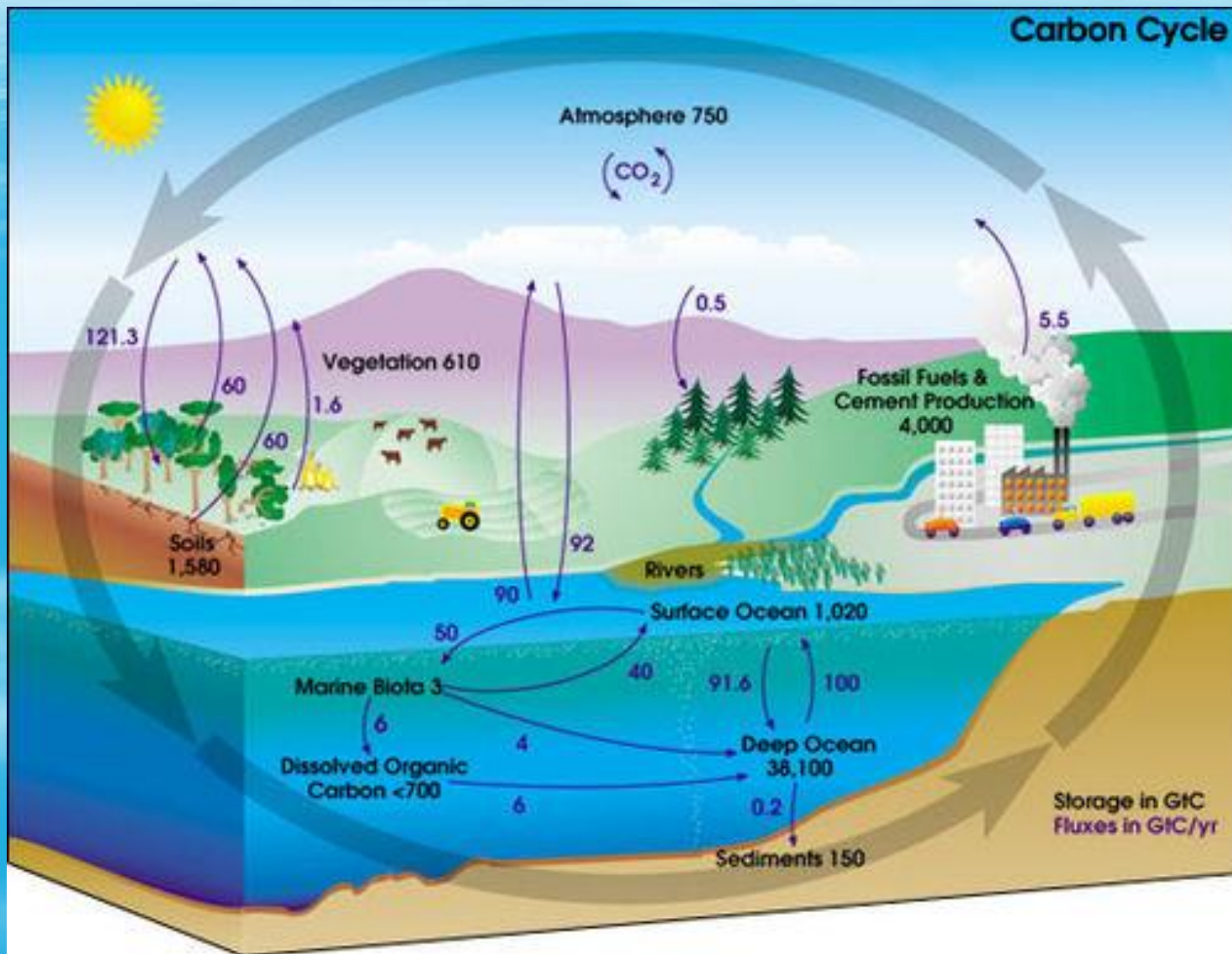
Preparation and characterization of catalysts for hydrogen production

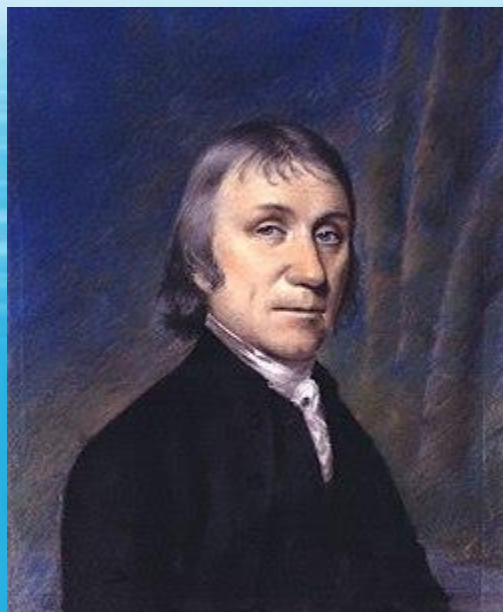


24-26 June 2020

**Institute of Organic Chemistry with Centre of Phytochemistry
Bulgarian Academy of Sciences, Sofia, Bulgaria**

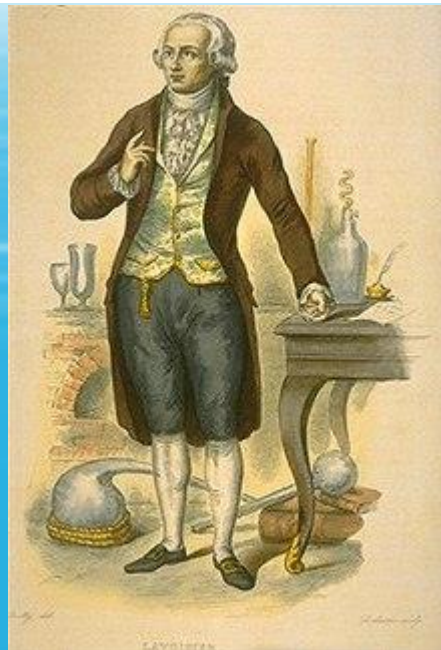
**This project has received funding from the European Union's Horizon 2020
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Innovative Training Networks (MSCA-ITN), grant agreement 813748**





1733-1804

Joseph Priestly,
English scientist



1743-1794

Antoine-Laurent de Lavoisier,
French scientist

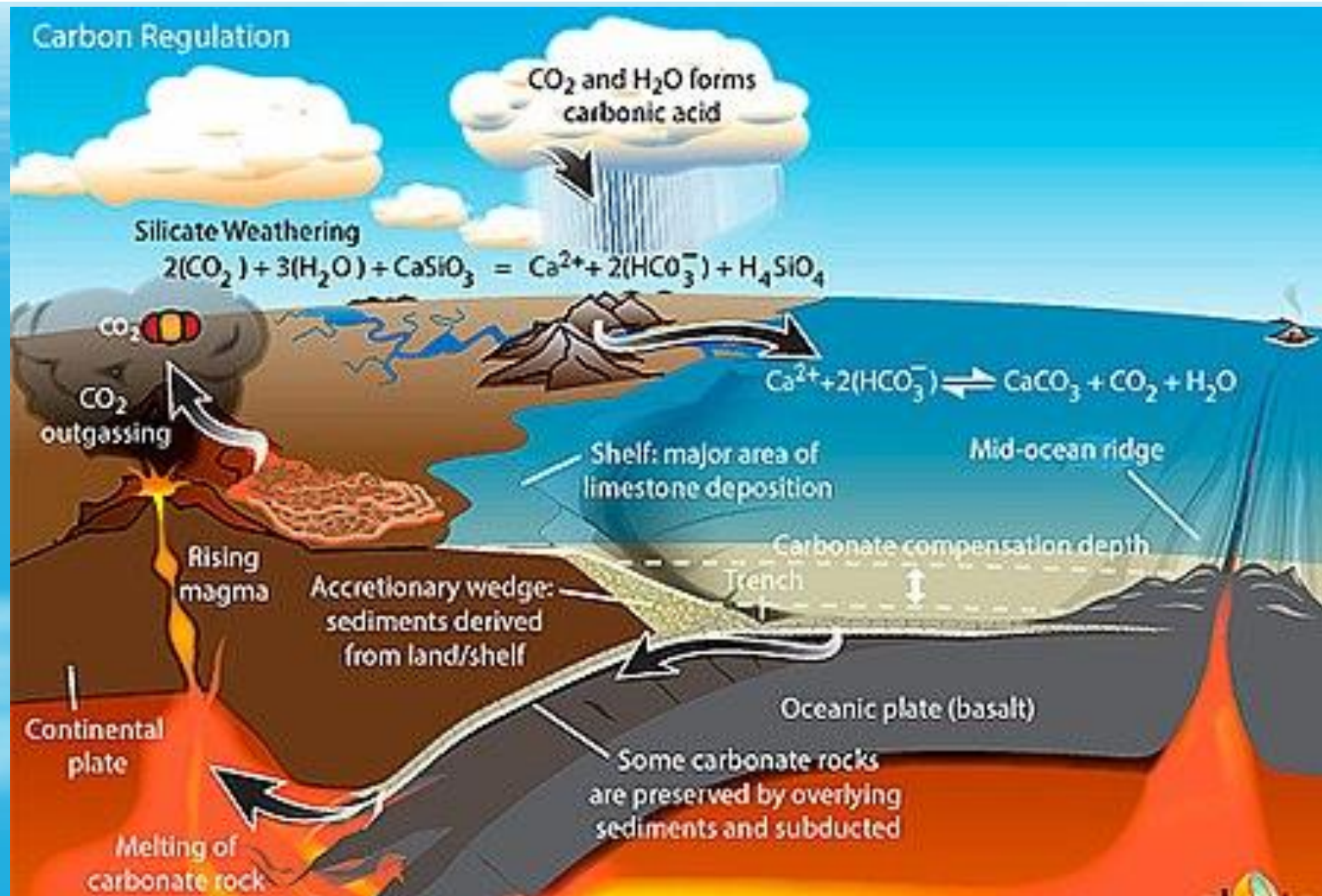


1778-1829

Sir Humphry Davy,
English scientist

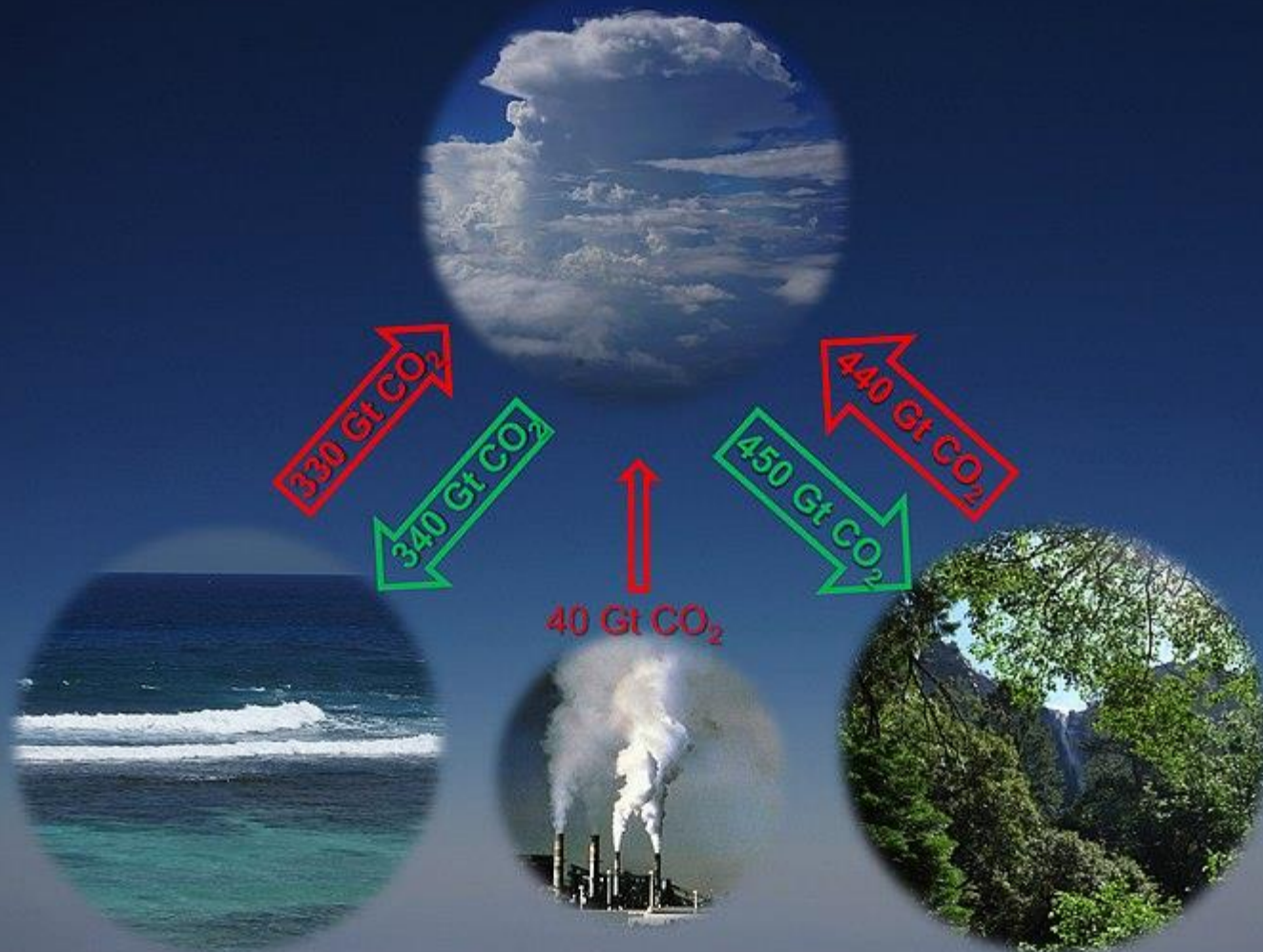
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Geological aspects and processes of the carbonate silicate cycle within the long-term carbon cycle

The Global Carbon Cycle

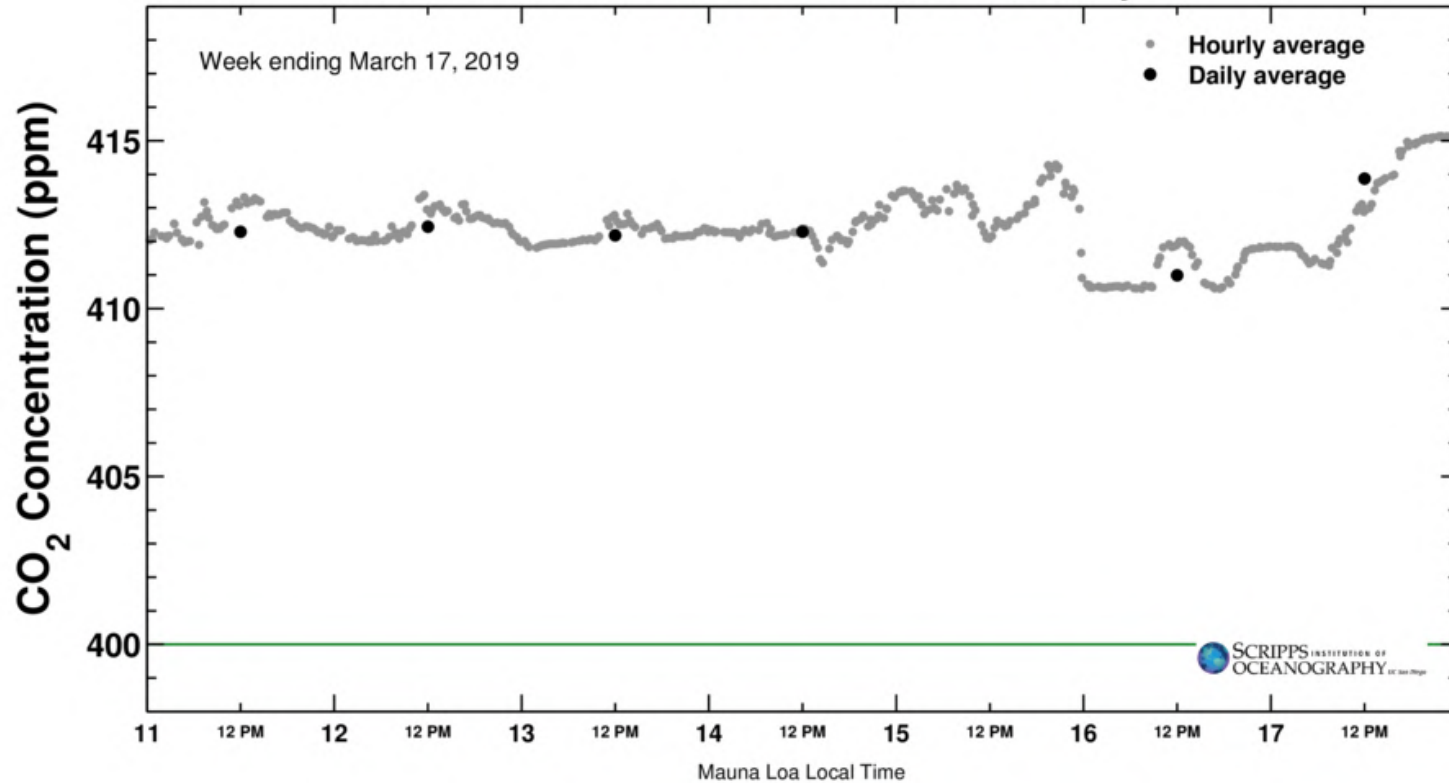


The ocean and land have continued to absorb about half of all carbon dioxide emissions into the atmosphere, even as anthropogenic emissions have risen dramatically in recent decades. It remains unclear if carbon absorption will continue at this rate.

Latest CO₂ reading
March 17, 2019

413.87 ppm

Carbon dioxide concentration at Mauna Loa Observatory



[One Week](#) | [One Month](#) | [One Year](#) | [Two Years](#) | [Record Since 1958](#) | [Since 1700](#) | [800,000 Years](#)

Source Graphics: [Scripps Keeling Curve Website](#)

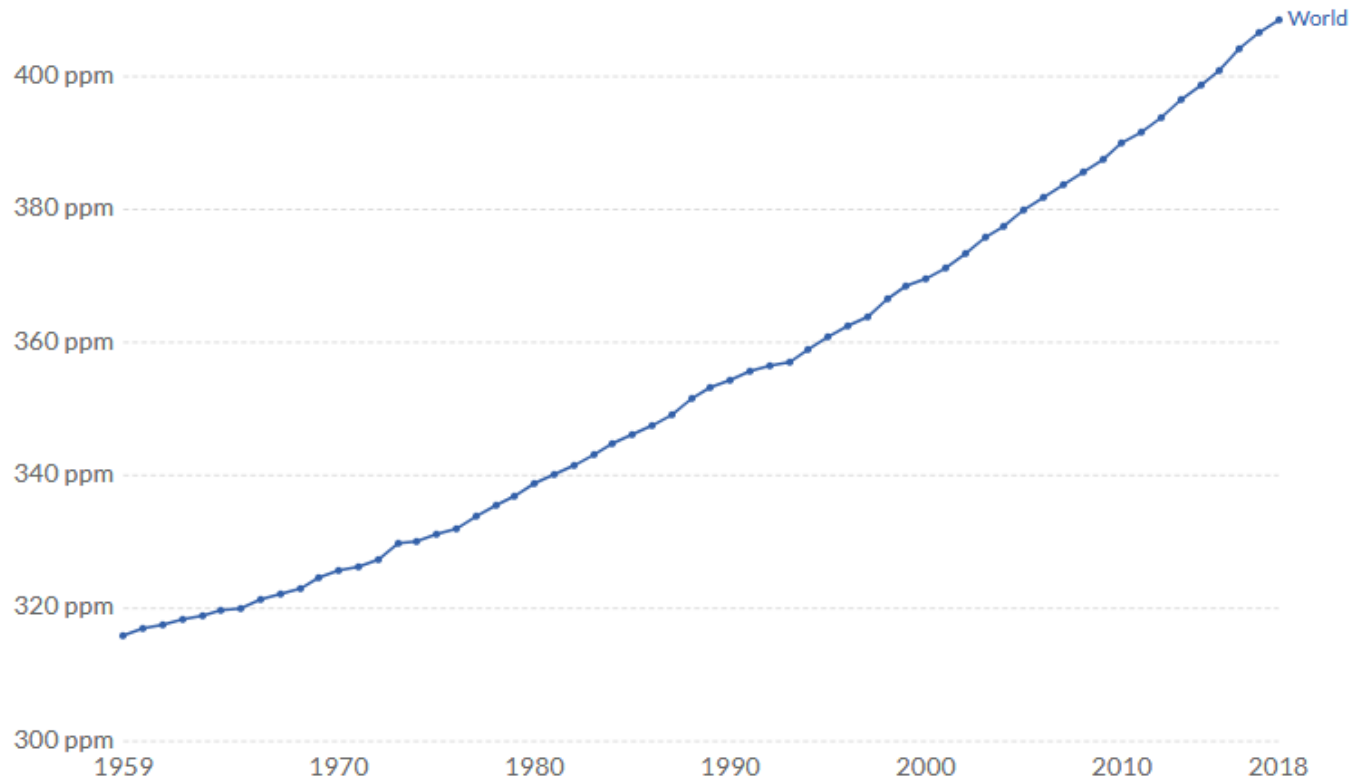
Scripps reports daily averages based on Mauna Loa local time.

<https://www.co2.earth/daily-co2>

Global CO₂ atmospheric concentration


Global mean annual concentration of carbon dioxide (CO₂) measured in parts per million (ppm).

Our World
in Data



Source: NOAA/ESRL (2018)

CC BY

▶ 1959  2018

CHART

DATA

SOURCES

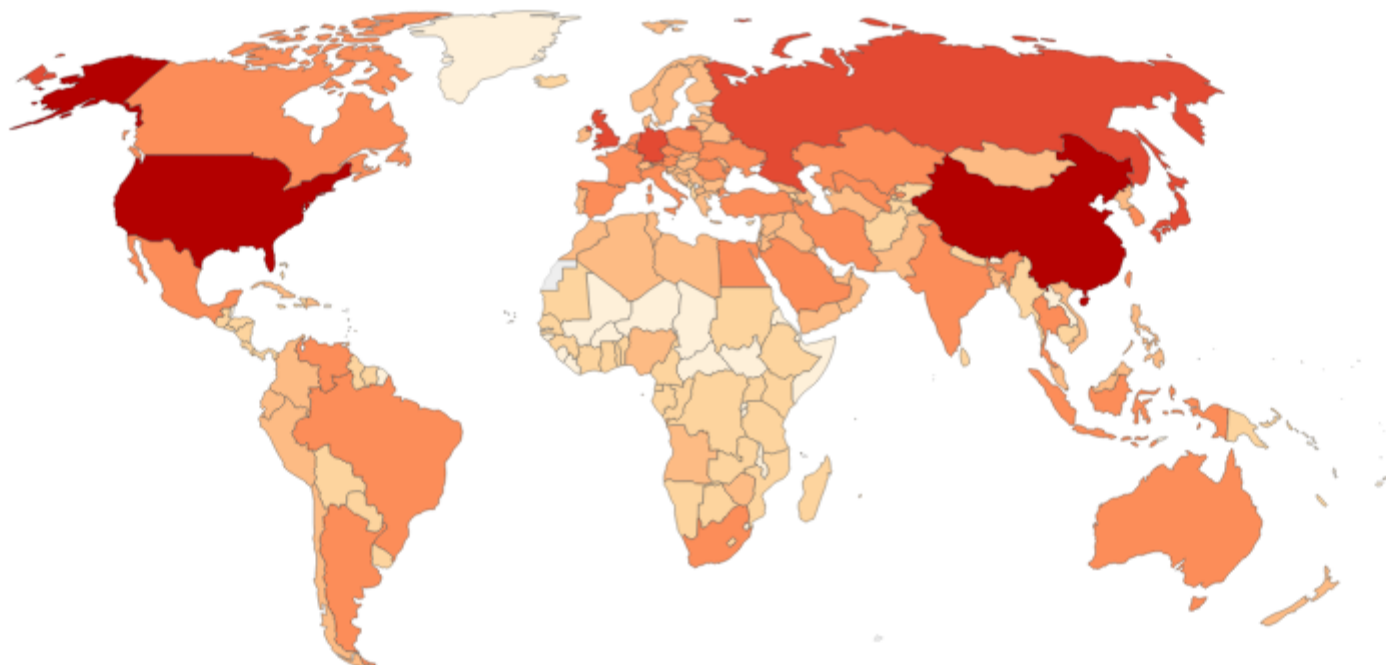


Atmospheric CO₂ concentration (ppm)

Our World
in Data

Cumulative CO₂ emissions, 2016

Cumulative carbon dioxide (CO₂) emissions represents the total sum of CO₂ emissions since 1751, and is measured in tonnes.



Source: Global Carbon Project (GCP); Carbon Dioxide Information Analysis Centre (CDIAC)

CC BY

▶ 1751

■ 2016

CHART

MAP

DATA

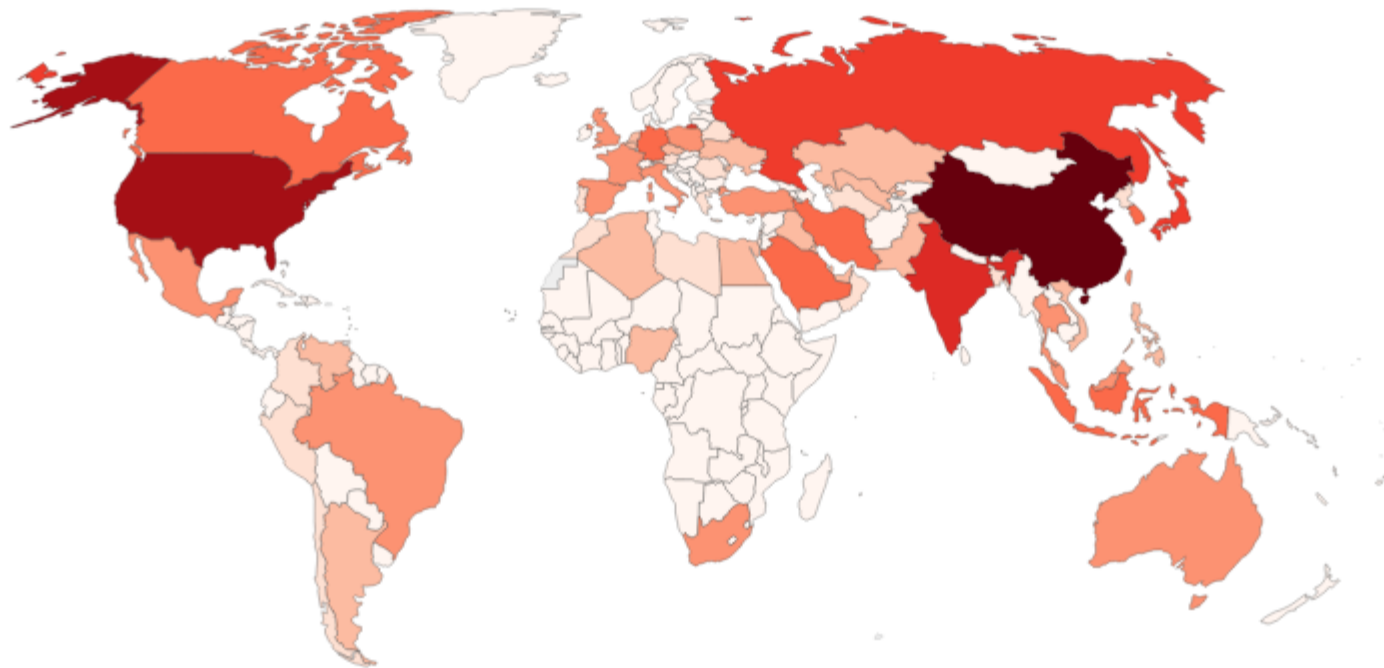
SOURCES



Annual CO₂ emissions, 2016

Annual carbon dioxide (CO₂) emissions, measured in tonnes per year.

Our World
in Data



Source: Global Carbon Project; Carbon Dioxide Information Analysis Centre (CDIAC)

CC BY

▶ 1751

2016

CHART

MAP

DATA

SOURCES



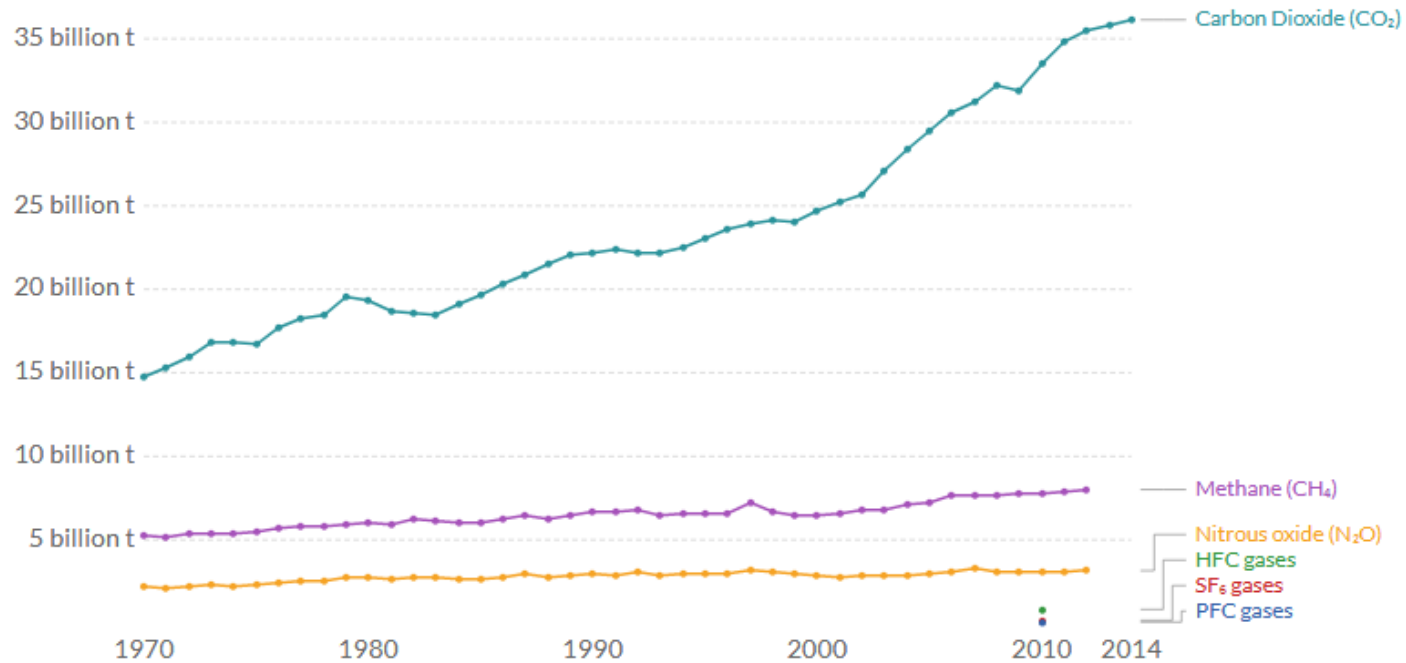
<https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions>

only a small contribution to total warming.

Greenhouse gas emissions (CO₂e) by gas, World

Global greenhouse gas emissions by gas source, measured in tonnes of carbon dioxide equivalents (tCO₂e). Gases are converted to their CO₂e values based on their global warming potential factors. HFC, PFC and SF₆ are collectively known as 'F-gases'.

Our World
in Data



Source: World Bank - World Development Indicators (WDI)

CC BY

1960 2014

Change country

CHART

DATA

SOURCES



Hydro-pyrolysis

Gas products /high-energy fuel/

Agricultural by-products, low-rank coal, polymers

Liquid products

Carbon adsorbents

Carbon adsorbents with low ash content

Synthetic pitch

Synthetic nanoporous carbon – for electrodes and supercapacitors

C-C composites for electrodes, contactors for electromotors, Construction materials

Carbon fibres

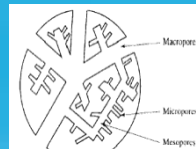
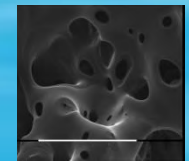
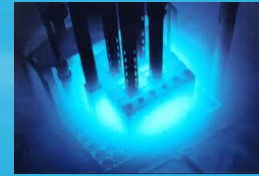
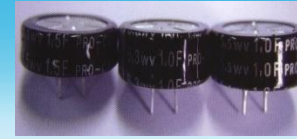
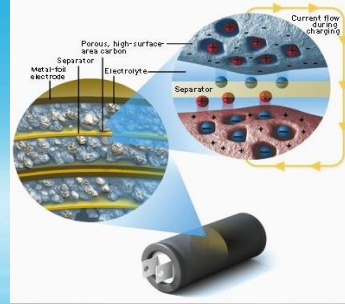
Carbon foam

Medicine

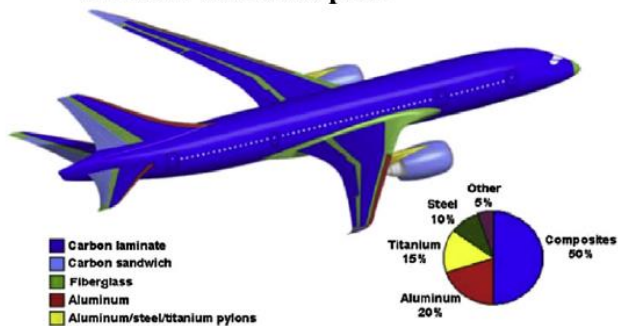
Water purification

Catalysts and catalyst supports

Materials for hydrogen storage



Aircraft and aerospace



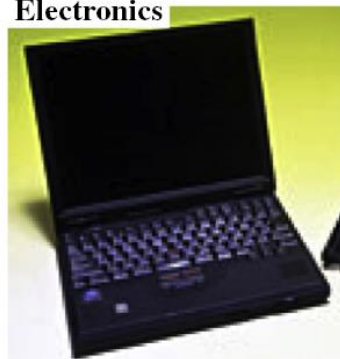
Automobiles



Civil engineering



Electronics



Sustainable energy



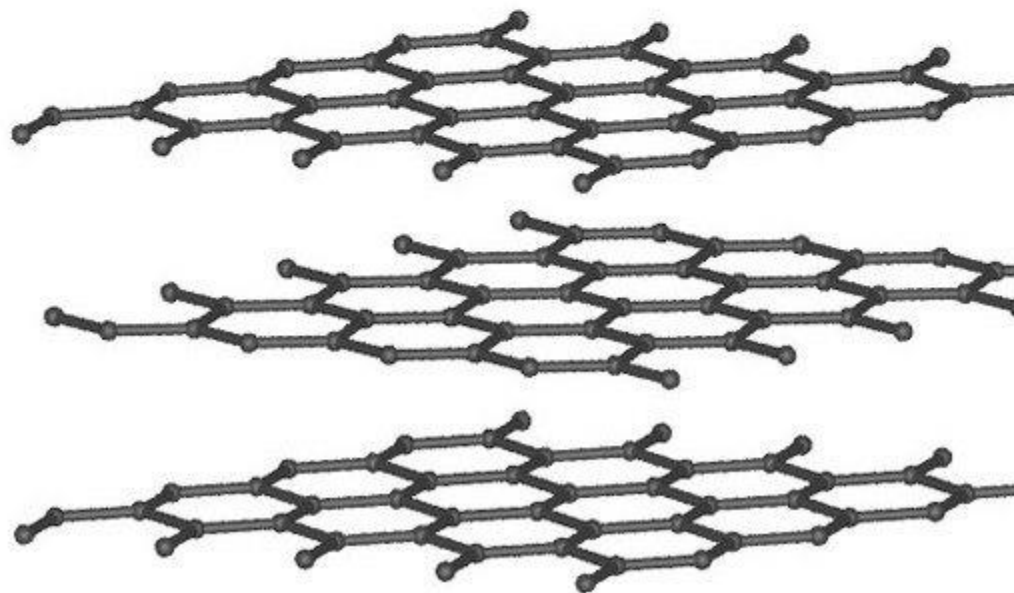
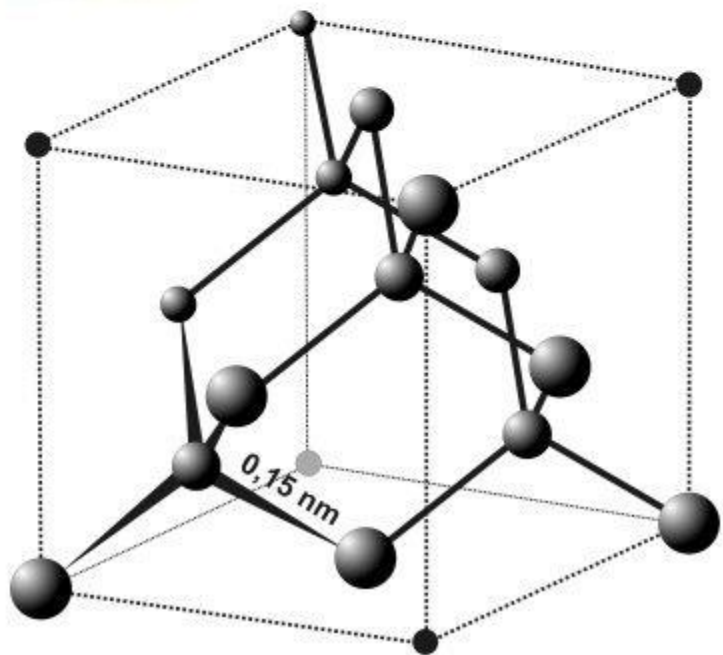
Industrial equipment



Pressure bombs



FROM GRAPHITE AND COAL
TO
NEW CARBON MATERIALS



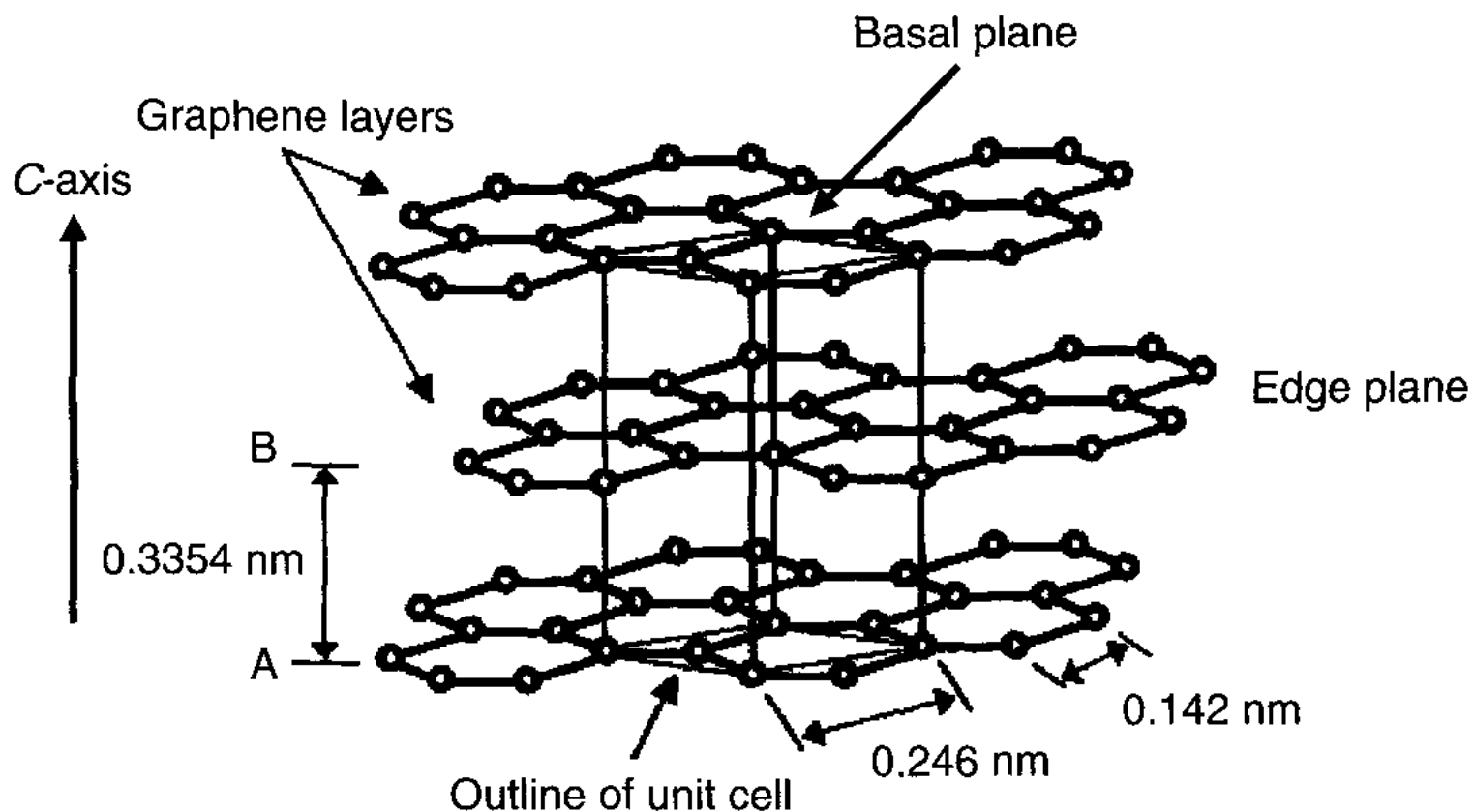


Figure 2.2. The structure of hexagonal graphite, with trigonal planar bonding within the graphene layers.

Apart from diamond, structures in all known carbon forms are considered as a continuous decrease in the degree of order from the single-crystal hexagonal graphite to the most disordered (there is never total disorder) of the porous carbons and the glassy carbons with their closed (inaccessible) porosity (see Pikunic, 2001; Chapter 3). Within hexagonal graphite, the layers of hexagonal arrangements of carbon atoms are described as *graphene layers*. These layers do not lie immediately above and below each other but are displaced to form an ABABAB sequence. The density of hexagonal graphite is 2.25 g cm^{-3} . The distance between the layers is 0.335 nm (335 pm) and the distance between two bonded carbon atoms is 0.142 nm (142 pm). Within the graphitic layers, the bonding is trigonal sp^3 -hybrid σ -bonds with delocalized π -bonds within the layers. The interlayer spacing of 0.335 nm , being larger than the 0.142 nm of the C—C bond, indicates no chemical bonding between the layers, the forces of attraction being limited to van der Waals forces. This distance is between the values of 0.153 and 0.132 nm for $\text{Csp}^3\text{—Csp}^3$ bonding as in ethane, and $\text{Csp}^2=\text{Csp}^2$ bonding as in ethene. Resonance considerations indicate that the C to C bonding within a graphite layer has about one-third double-bond character. Such a graphite structure is referred to as AB graphite.

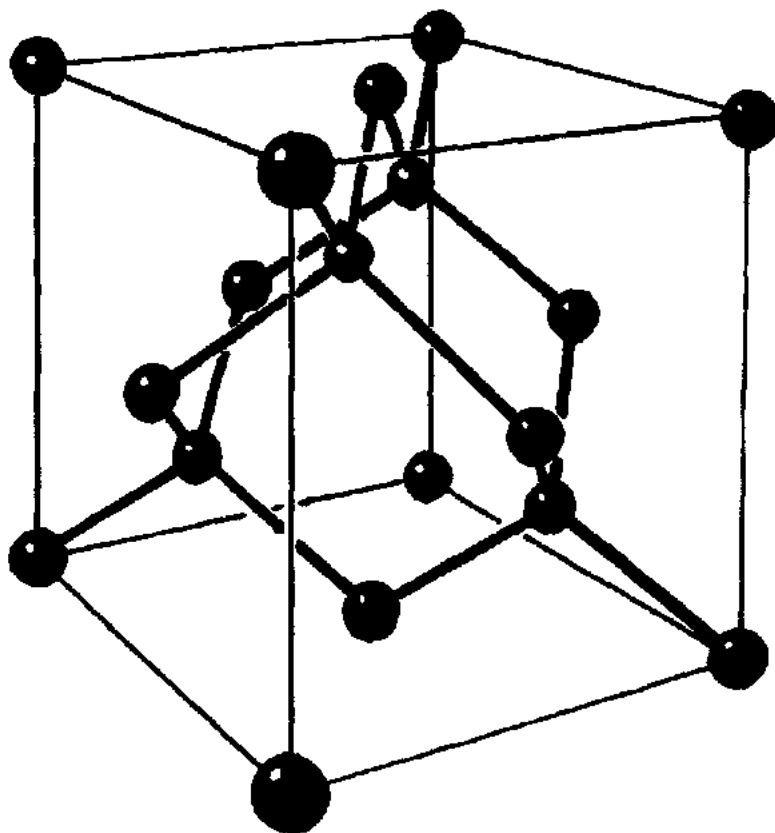


Figure 2.1. A model of the cubic unit cell of diamond. The internal carbon atoms are bonded to three other carbon atoms, with sp^3 -symmetry, as in methane.



Diamond has a more dense structure than graphite with a density of 3.52 g cm^{-3} indicating, overall, a much closer packing of carbon atoms. The bond distances within diamond are 0.154 nm (for zinc blende structure) and 0.152 nm (for the Lonsdaleite structure). The hardness of diamond is associated with the close strong carbon-carbon bonds. The distance of the carbon-carbon within the graphite layer is 0.142 pm indicating a stronger bond than in diamond. The absence of any equivalent of a graphene layer in diamond excludes any possibility of creating a porous diamond. The defective *micro-graphene layer* is totally central to the structure of activated carbon.



Bituminous (black) coal

- as a fuel
- for preparation of metallurgical coke
- valuable substances for organic synthesis



Anthracite coal

- expensive and with high energy value
- for preparation of effective carbon adsorbents



Lignite coal

- low grade fuel



!

First new carbon materials appeared in the middle of 20th century. Carbon fibers (from polyacrylonitrile), pyrolytic carbons and glassy carbons are first synthesized in the period 1950-1960. In 60s high-power graphite electrodes for industry are produced and successfully applied. After 1970 begins industrial production of carbon fibers from coal and petroleum pitches [1].

Carbon fibers are distinguished by high strength and flexibility. Nowadays they are produced in industrial scale, and they have found wide applications – construction materials for instruments, buildings, bicycles, bridges, etc.

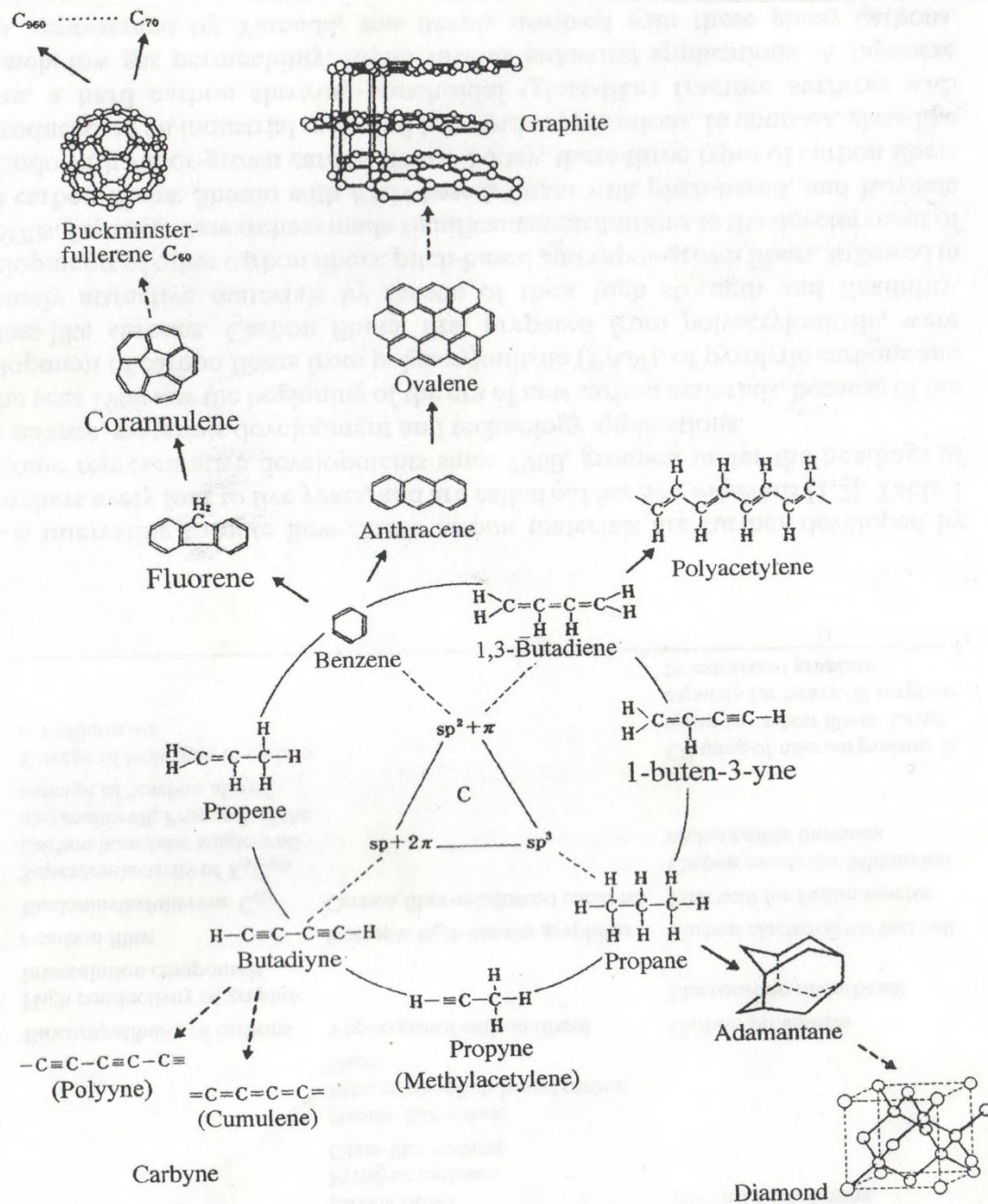
Glassy carbon is extremely hard material with very low fluid permeability. In 70s heart valves, tooth roots, prostheses are being constructed due to biocompatibility of carbon materials.

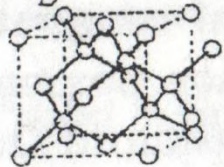
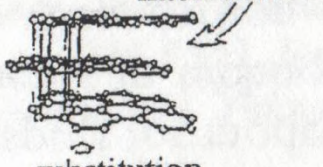
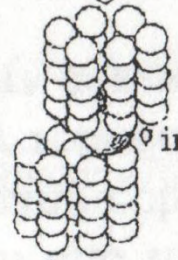

In 1990 lithium-ion rechargeable batteries are developed, using intercalation of Li⁺ cations into graphite anode.

Hans-Peter Boehm first described single-layer carbon foils in 1962 [2]. After discovery of very high electrical conductance of graphite intercalation compounds [3], fullerene C₆₀ (predicted theoretically in 1970) successfully synthesized in 1985 [4]. In the beginning of 90s single-and multi-wall carbon nanotubes were found. In 2004 A. Geim and K. Novoselov [5] successfully extracted single-atom-thick crystallites and obtained graphene layers from graphite on thin SiO₂. For the first time carbon foams were obtained in 1960s by Ford [6] from a phenol–formaldehyde foam, through gradual heating in an inert gas atmosphere. Over the next decades, various precursors (phenolic resins, polyurethanes, coals, coal-tar pitches, petroleum pitches, synthetic pitches, pitch mesophases, and biomass) and different methods for synthesis of carbon foam were used.

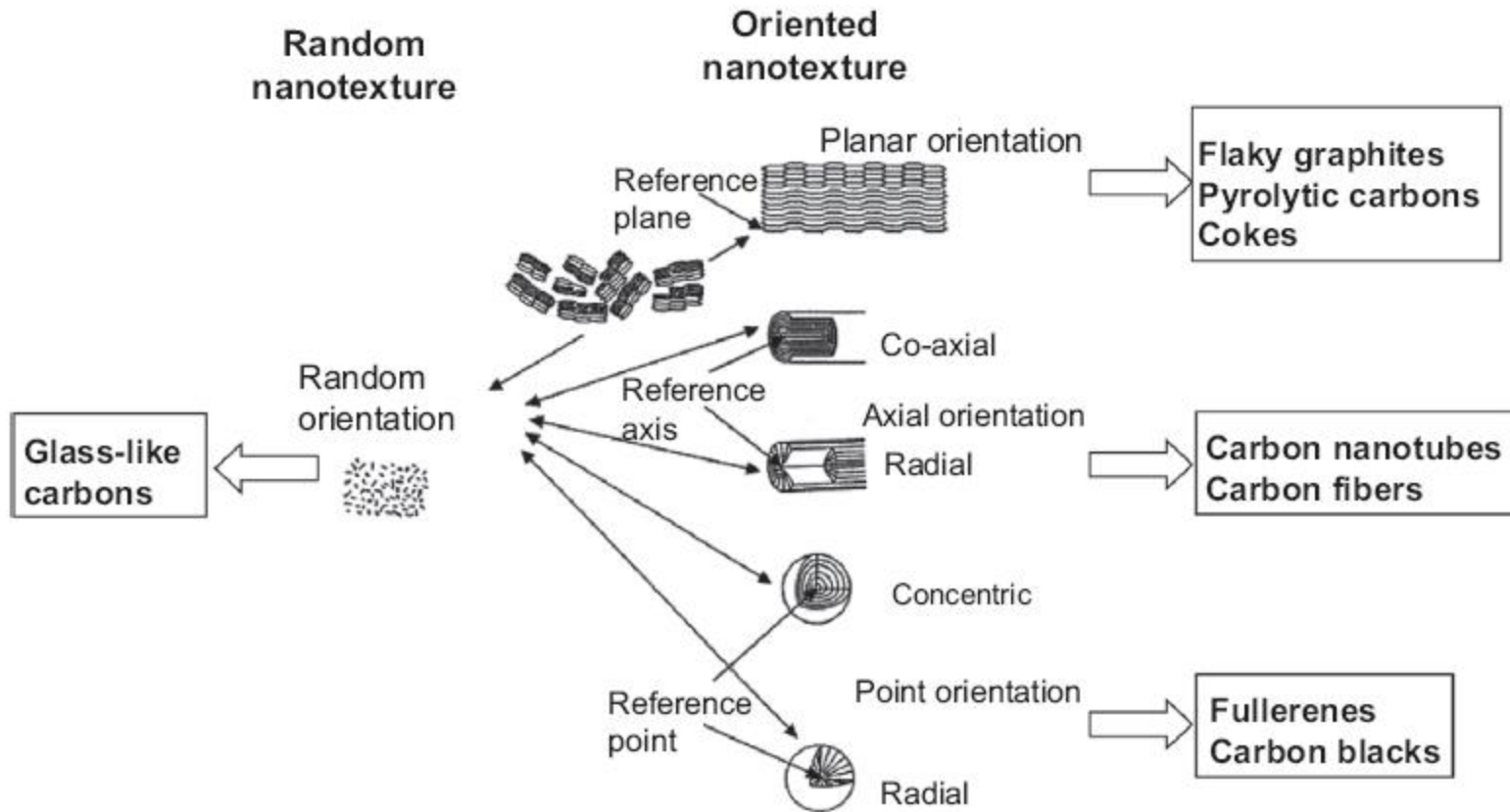
[1] Yasuda E, Inagaki M, Kaneko K, Endo M, Oya A, Tanabe Y. Carbon Alloys, Elsevier; **2003**. [2] Boehm HP, Clauss A, Fischer G, Hofmann U. *Surface properties of extremely thin graphite lamellae*. Proc.5thConference on Carbon. **1962**:73-80. [3] . Lincoln Vogel, J. Mater. Sci. 1977, 12, 982; B. Levi, Phys. Today 1977, 30, 18. [4] H.W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, Nature 1985, 318, 162. [5] Novoselov, KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. *Electric Field Effect in Atomically Thin Carbon Films*. Science. **2004**, 306 (5696): 666–9. [6] Ford WD. Method of making of cellular refractory thermal insulating materials. *US Patent 3121050*. **1964**.

Organic compounds based on carbon-carbon bonds using sp^3 , sp^2 and sp hybrid orbitals and inorganic carbon materials as their extension.



Carbon family:	DIAMOND	GRAPHITE	CARBYNE	FULLERENES
Dimensionality:	three-dimensional	two-dimensional	one-dimensional	zero-dimensional
Structural diversity:	cubic & hexagonal systems	hexagonal & rhombohedral systems	cumulene & polyene types	bucky-balls to nanotubes
	diamond-like carbon	diversity in structure graphitic to turbostratic diversity in texture	diversity in length & density of chains	single-wall & multiwalled
Possibility of accepting foreign species:	substitution 	intercalation  substitution	doping in interstices  intercalation substitution	doping in interstices doping into sphere  substitution addition

Carbon family, their dimensions, structural diversity and possibility to accept foreign species.



Nanotexture of different carbon materials

Conventional carbons

Graphite electrodes
Carbon blacks
Activated carbons

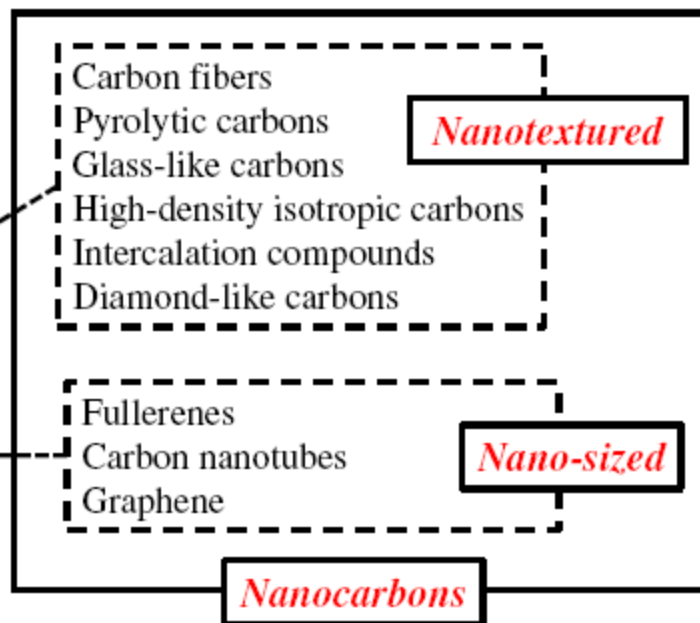
*Classic
carbons*

*New
carbons*

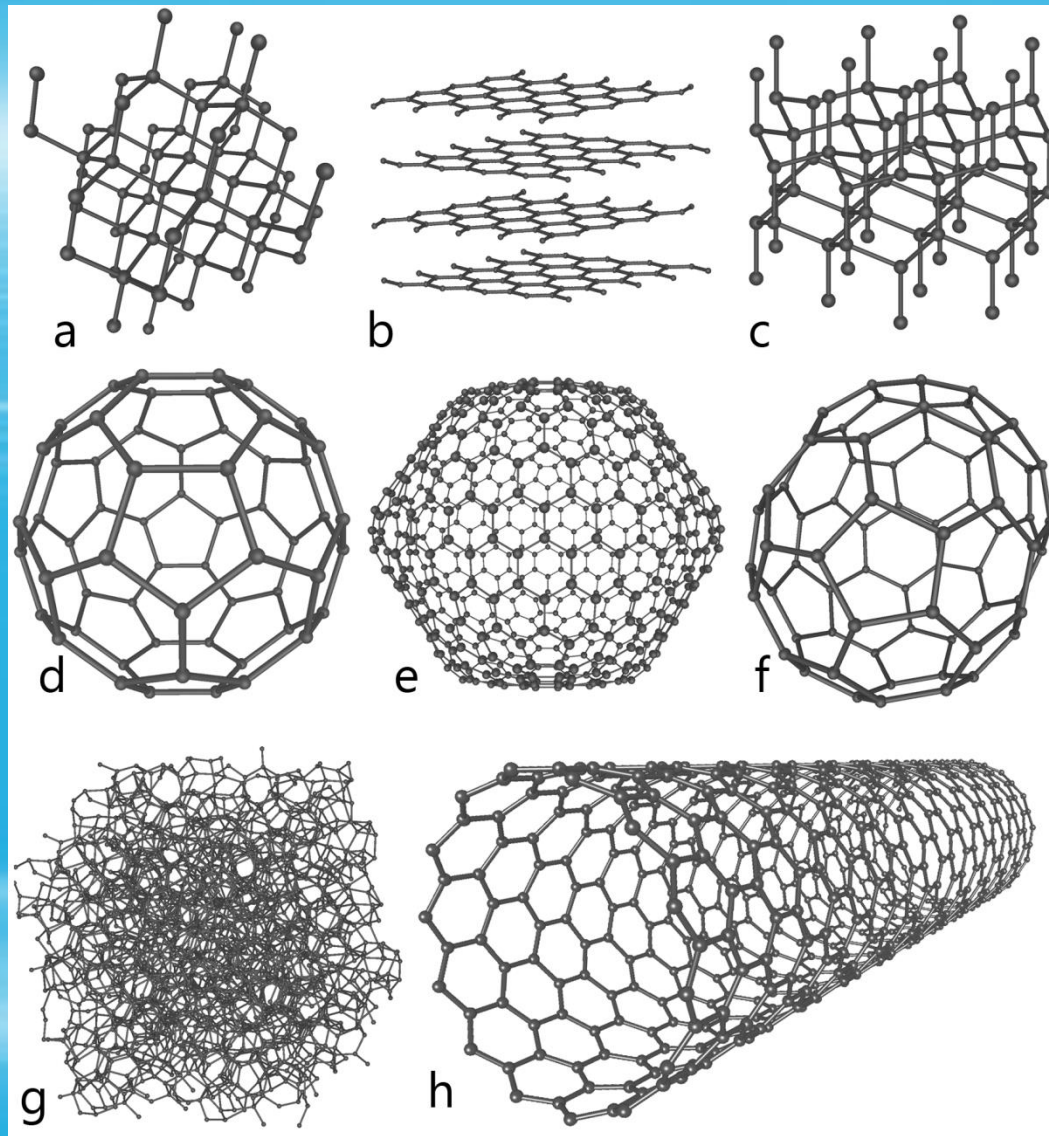
Natural diamond

*Nano-
carbons*

Newly developed carbons



Classification of carbon materials



Eight allotropes of carbon: a) diamond, b) graphite, c) lonsdaleite, d) C₆₀ buckminsterfullerene, e) C₅₄₀, Fullerite f) C₇₀, g) amorphous carbon, and h) single-walled carbon nanotube.

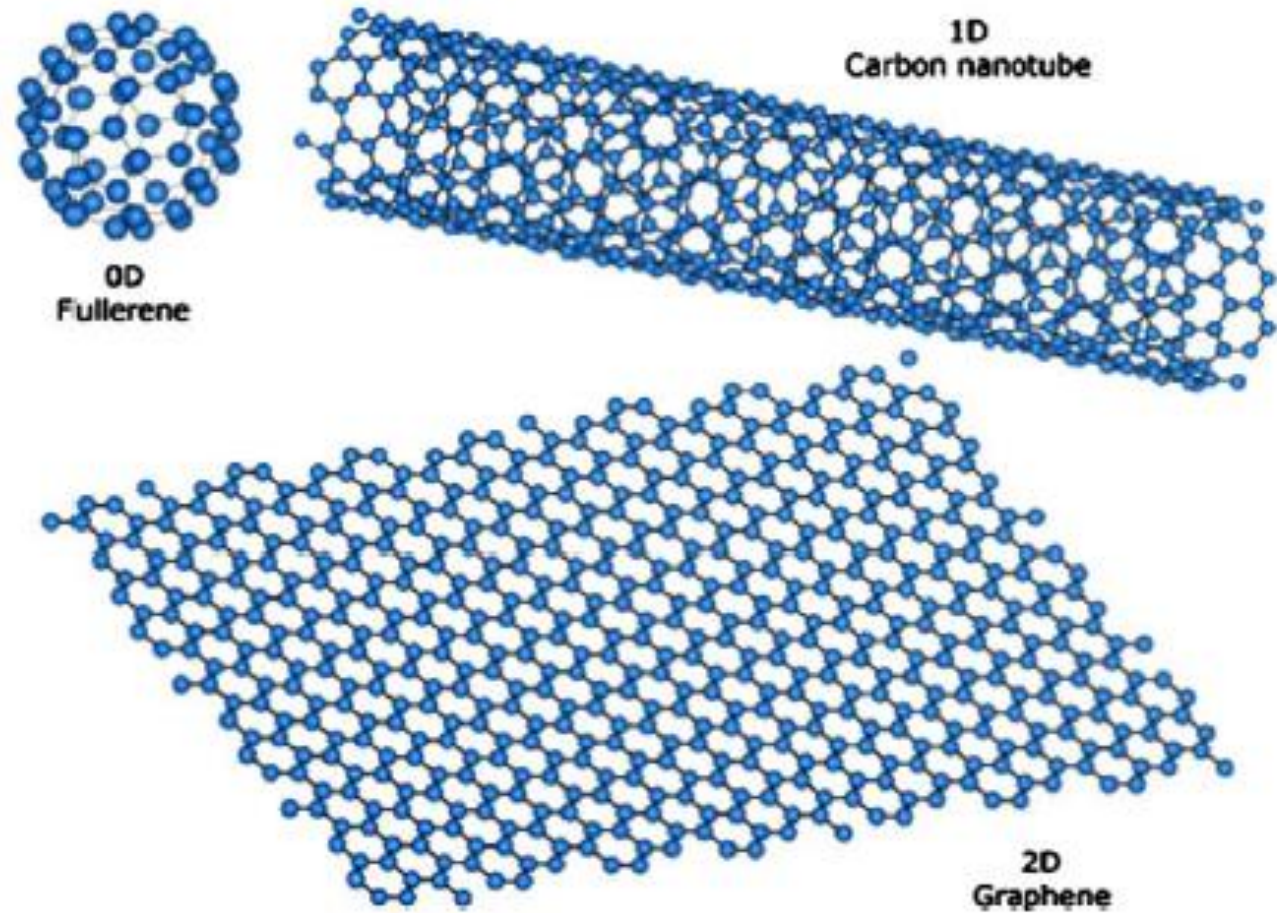
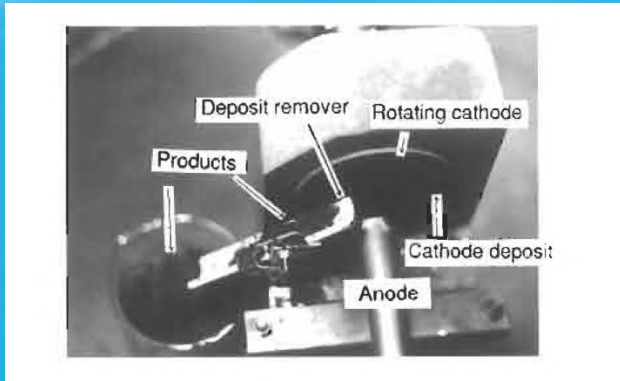
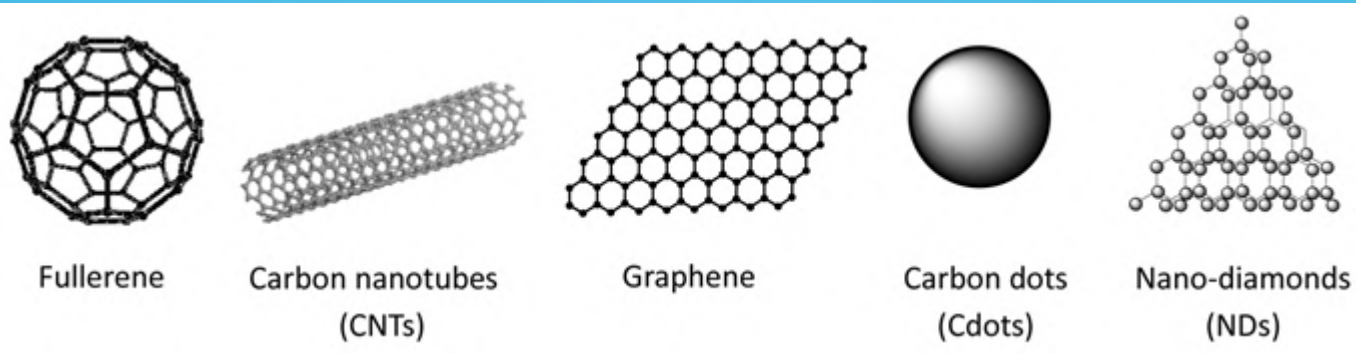


Fig. 1 - Low-dimensional carbon allotropes: fullerene (0D), carbon nanotube (1D) and graphene (2D).



The rotating-cathode DC arc method for production of carbon nanotubes. The cathode deposit is immediately taken out of the discharge by rotation and cropped within one turn. This method offers high stability and reliability of the handling and makes the continuous mass production possible

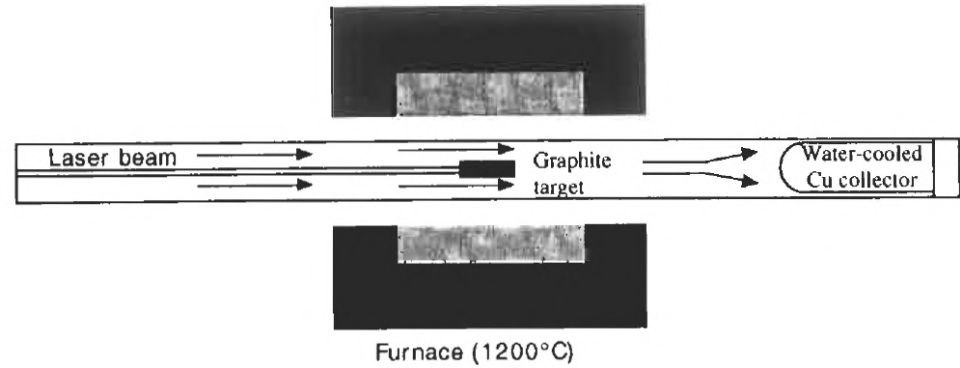


Fig. 3. Schematic drawing of the laser-ablation method.

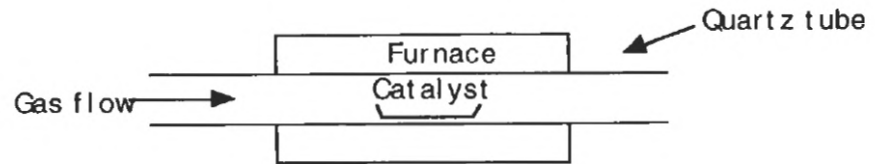


Fig. 4. Schematic drawing of the apparatus used for the catalytic decomposition of hydrocarbon.

production of carbon nanotubes

Graphene – a single-atom-thick sheet of hexagonally arranged, sp^2 -bonded carbon atoms that is not an integral part of a carbon material, but is freely suspended or adhered on a foreign substrate. The lateral dimensions of graphene can vary from several nanometers to the macroscale. Note with this definition, other members of graphene family of 2D materials cannot be simply called “graphene” but must be named using a unique multi-word term that distinguishes them from the isolated monolayer (see below).

Graphene layer – a single-atom-thick sheet of hexagonally arranged, sp^2 -bonded carbon atoms occurring within a carbon material structure, regardless of whether that material structure has 3D order (graphitic) or not (turbostratic or rotationally faulted).

The “graphene layer” is a conceptual structural unit that has been used for many years to describe the structure and texture of 3D carbon materials with primary sp^2 -hybridized bonding.

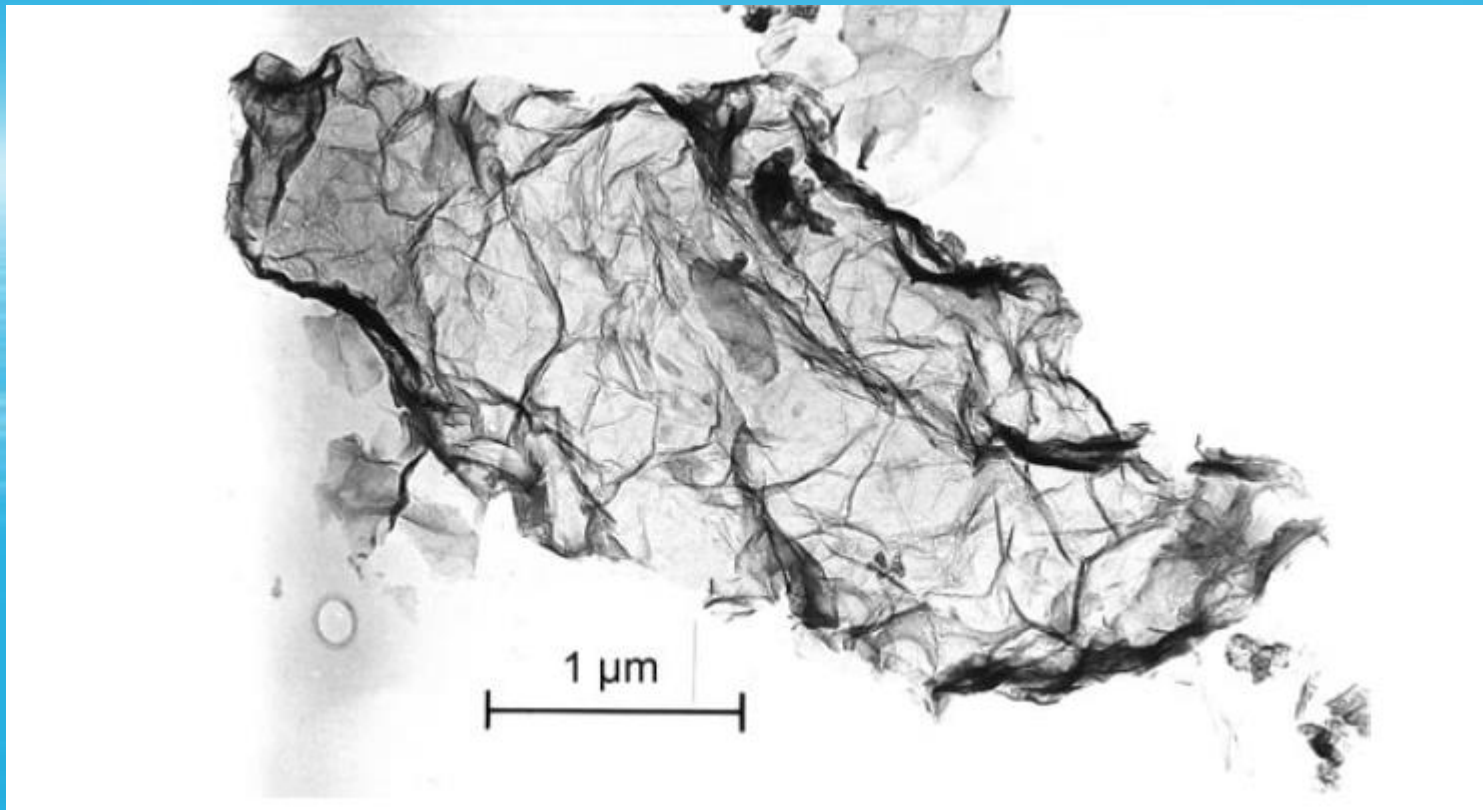
Turbostratic carbon – three-dimensional sp^2 -bonded carbon material in which there is no defined registry of the layers, meaning there is no spatial relationship between the positions of the carbon atoms in one graphene layer with those in adjacent layers. The name derives from “turbo” (rotated) and “strata” (layer) and can also be called rotationally faulted. This is a common structure in carbon materials prepared at lower temperatures or in “hard carbons” that do not pass through a fluid phase during carbonization and resist the development of 3D crystalline order even upon very high temperature heat treatment

Graphene oxide (GO) – chemically modified graphene prepared by oxidation and exfoliation that is accompanied by extensive oxidative modification of the basal plane. Graphene oxide is a monolayer material with a high oxygen content, typically characterized by C/O atomic ratios less than 3.0 and typically closer to 2.0.

Graphite oxide – a bulk solid made by oxidation of graphite through processes that functionalize the basal planes and increase the interlayer spacing. Graphite oxide can be exfoliated in solution to form (monolayer) graphene oxide or partially exfoliated to form few-layer graphene oxide.

Reduced graphene oxide (rGO) – graphene oxide that has been reductively processed by chemical, thermal, microwave, photo-chemical, photo-thermal or microbial/bacterial methods to reduce its oxygen content.

Similar to carbon fibers and carbon nanotubes, graphene has a very high tensile strength in the layer direction, which together with a high flexibility, makes sharp folds in the layer possible. Their radius of curvature corresponds to that of carbon nanotubes. Interest in graphenes increased dramatically after Novoselov, Geim et al. reported on the unusualelectronic properties of single layers of the graphite lattice, in other words graphene: Graphene is a semiconductor with a zero band gap and is characterized by an exceptionally highmobility of the charge carrier, a very high electrical conductance, and an unusual quantum Hall effect. The charge carriers behave like relativistic particles of rest mass zero, to which the Dirac Equation can be applied. This had previously been derived theoretically. Narrow ribbons of graphene with a thickness of 1 to 2 nm are, however, semiconductors with a distinct band gap, and these can be used to produce transistors. Many applications of graphene have been hoped for and promised.



TEM

The thickness of the air-stable graphene layers can be determined by SEM, TEM and atomic force microscopy (AFM). They are also visible under an optical microscope, however, if they are supported on a suitable carrier surface, for example, a 300 nm thick SiO₂ film on silicon. Depending on how many graphene layers are present, other interference colors appear because of the increased optical path length. This greatly simplifies the localization of the graphenes.

Thin graphite layers suitable for investigation by electron microscopy have for a long time been prepared by “stripping off” highly ordered pyrographite (HOPG) or graphite crystals with cellophane-based adhesive tape. Novoselov and Geim found that the skillful and patient use of this method enabled extremely thin films with only one or just a small number of graphene layers to be obtained. If the adhesive tape with a thin graphite layer is pressed onto a thin SiO₂ coating on a silicon wafer, the graphene layers remain attached to the SiO₂ surface after skillfully peeling away the tape. This method produces defect-free and smooth preparations, but has the disadvantage, however, that only small amounts can be produced. Preparative methods are, therefore, being sought that can provide graphene reproducibly in large amounts with little effort.

Graphite crystals or flakes may be dispersed in aqueous solutions of surfactants by ultrasound into graphene mono-layers or layer packets (exfoliation). This is also possible without additives in many organic solvents that have an affinity for graphite.
M.Loty, P.J.King, U.Khan, S.De, J.N.Coleman, ACSNano2010,4,3155.

It has long been known that defect-free graphene layers are formed by the thermal decomposition of SiC crystals at 1300 °C.
A.J.VanBommel, J.E.Crombeen, A.VanTooren, Surf.Sci.1975,48,463.

The formation of monolayers had been observed even before the work of Novoselov, Geim et al. The adjustment of the reaction conditions (primarily temperature and time) for the targeted formation of monolayers is, however, extremely difficult. Well-ordered graphene monolayers are also formed by the pyrolytic deposition of carbon from hydrocarbons (for example, methane) onto the surface of transition metals or transition-metal carbides.
C.Oshima, A.Nagashima, J.Phys.Condens.Matter1997,9,1–20.

This method has also been resurrected recently to obtain large graphene layers on surfaces by deposition onto a thin copper film. The graphenes can be isolated by dissolution of the metal.
X.Li, W.Cai, J.An, S.Kim, J.Nah, D.Yang, R.Piner et. al., Science2009,324,1312.

Larger amounts of extremely thin carbon films may be prepared from graphite oxide (GO) by flash heating or by the reduction of aqueous dispersions. GO was prepared for the first time by Brodie about 150 years ago (!) by the oxidation of graphite with fuming nitric acid and potassium chlorate under cooling.

B.C.Brodie,Philos.Trans.R.Soc.LondonSer.A,1859,149,249.

Graphite is first oxidized with a mixture of concentrated H₂SO₄ and HNO₃ to the blue first stage of graphite hydrogen sulfate, with HSO₄⁻ ions and H₂SO₄ molecules intercalated in the interlayers, and in a second stage finally oxidized to GO with KClO₃ or KMnO₄.

L.Staudenmaier,Ber.Dtsch.Chem.Ges.1898,31,1481

W.S.Hummers,R.E.Offeman,J.Am.Chem.Soc.1958,80,1339;

N.I.Kovtyukhova,P.J.Ollivier,B.R.Martin et al.,Chem.Mater.1999,11,771.

Colorless transparent flakes are formed on complete oxidation. Longer storage of the washed and dried preparations, especially on exposure to light, results in GO taking on a dark brown color via a brownish intermediate. Since the compound has acidic properties, it was at first called graphitic acid. My academic teacher, Ulrich Hofmann, showed by X-ray diffraction in 1932 that it had a turbostratic layer structure, whose layers of 0.6 nm are clearly thicker than those of graphite (0.3354 nm).

[28]U.Hofmann,Kolloid-Z.1932,61,297.

The composition of anhydrous GO is approximately $C_8O_2(OH)_2$. Almost none of the carbon of the graphite used is lost during the formation of GO. The yield of GO in the reaction of relatively coarse graphite flakes is 96%.

U.Hofmann,A.Frenzel,Ber.Dtsch.Chem.Ges.B1930,63,1248.

H.P.Boehm,M.Eckel,W.Scholz,Z.Anorg.Allg.Chem.1967,353,236.

Significant amount of weakly acidic hydroxy groups have been detected in GO which can be neutralized with NaOH and sodium ethanolate. OH groups are part of enol groups, and carboxy groups are formed at the edges of the layers.

A.Clauss,R.Plass,H.P.Boehm,U.Hofmann,Z.Anorg.Allg.Chem.1957,291,205

Epoxide, aliphatic OH groups, and C=C bonds have been detected by solid-state ^{13}C NMR spectroscopy. A structural model for GO has been developed based on these observations.

A.Lerf,H.He,M.Forster,J.Klinowski,J.Phys.Chem.B1998,102,4477.

H.He,J.Klinowski,M.Forster,A.Lerf,Chem.Phys.Lett.1998,287,53.

D.R.Dreyer,S.Park,C.W.Bielawski,R.S.Ruoff,Chem.Soc.Rev.2010,39,228–240.

According to Boehm (2010):

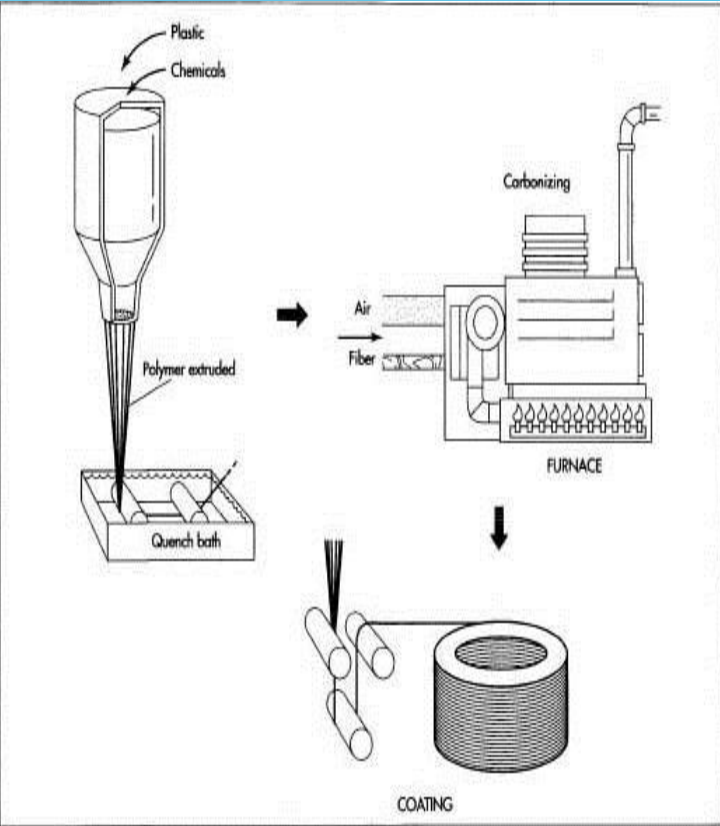
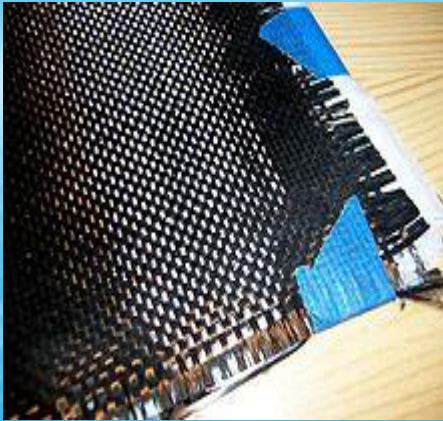
GO is reducible to carbon monolayers.

GO flakes separated into single layers in highly diluted sodium hydroxide solution (ca. 0.01M). The hydroxy groups of GO dissociate in alkaline media. The layers repel each other through the resulting negative charge and a colloidal sol is formed at low ion strengths. Reduction of GO in this state should allow single carbon layers to be obtained—in today's language graphene layers.

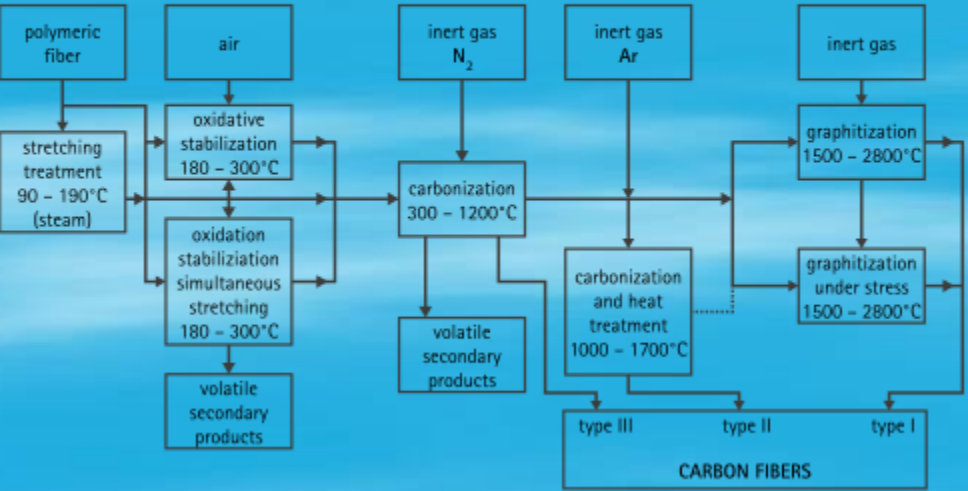
Such solutions could be prepared and reduced with hydrazine or hydroxylamine.

The brownish colloidal solution changes to dark brown and then to black, and after a short time a loose black precipitate separated. The exfoliation into single graphite oxide layers is today usually supported by ultrasound.

Carbon fibres



First stage	Second stage	Third stage
pretreatment stabilization up to 300°C	carbonization up to 1700°C	graphitization up to 2800°C



Glassy carbon



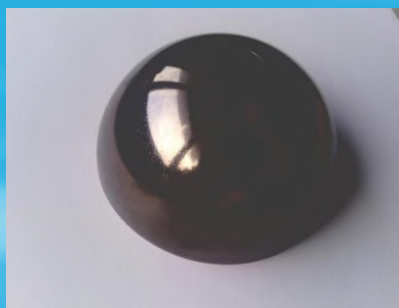
large sample of glassy carbon, with 1 cm³ graphite cube for comparison



A small rod of glassy carbon



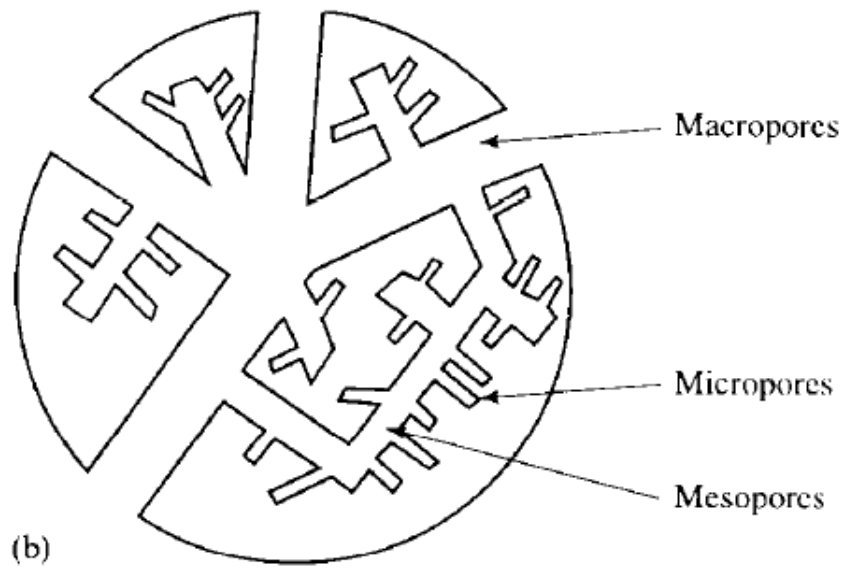
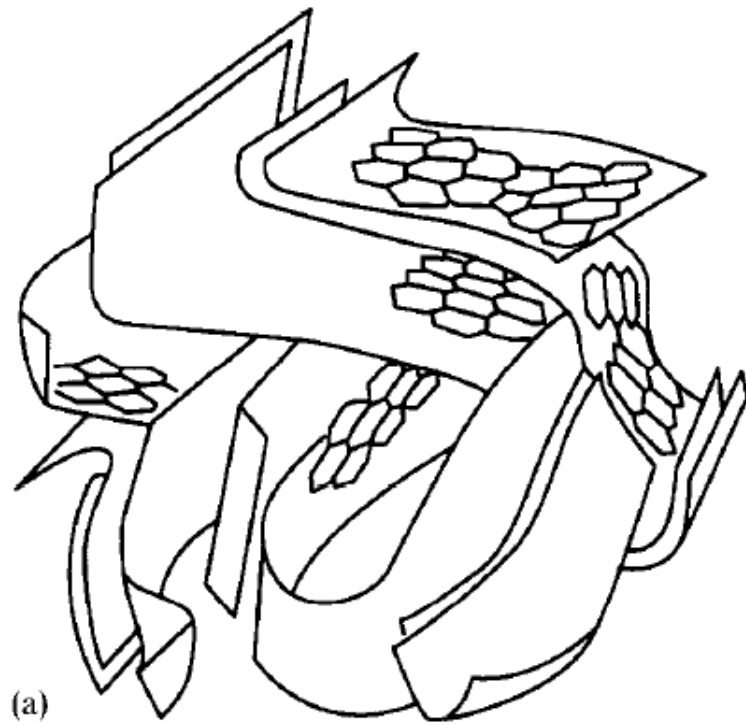
By original technology, developed in our Lab. Chemistry of Solid Fuels, Institute of Organic Chemistry, Bulgarian Academy of Sciences, we obtained non-porous carbon material with spherical form, based on a composite, prepared from coal tar pitch and petroleum coke (after mixing, pressing, and heating up to 1000°C). The obtained semi-spheres are covered with glassy carbon by multiple immersion in liquid PVC and subsequent thermal treatment at 1000°C. The resulting spheres were used for construction of radiation measuring modules in the outer space.



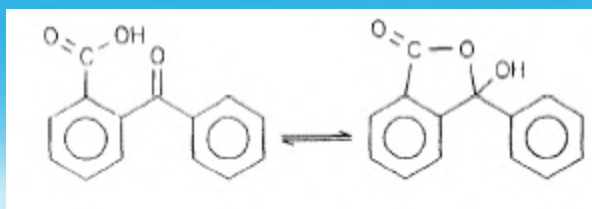
Vitreous-glassy carbon crucibles

Glass-like carbon, often called **glassy carbon** or **vitreous carbon**, is a non-graphitizing, or nongraphitizable, carbon which combines glassy and ceramic properties with those of graphite. The most important properties are high temperature resistance, hardness (7 Mohs), low density, low electrical resistance, low friction, low thermal resistance, extreme resistance to chemical attack and impermeability to gases and liquids. Glassy carbon is widely used as an electrode material in electrochemistry, as well as for high temperature crucibles and as a component of some prosthetic devices, and can be fabricated as different shapes, sizes and sections.

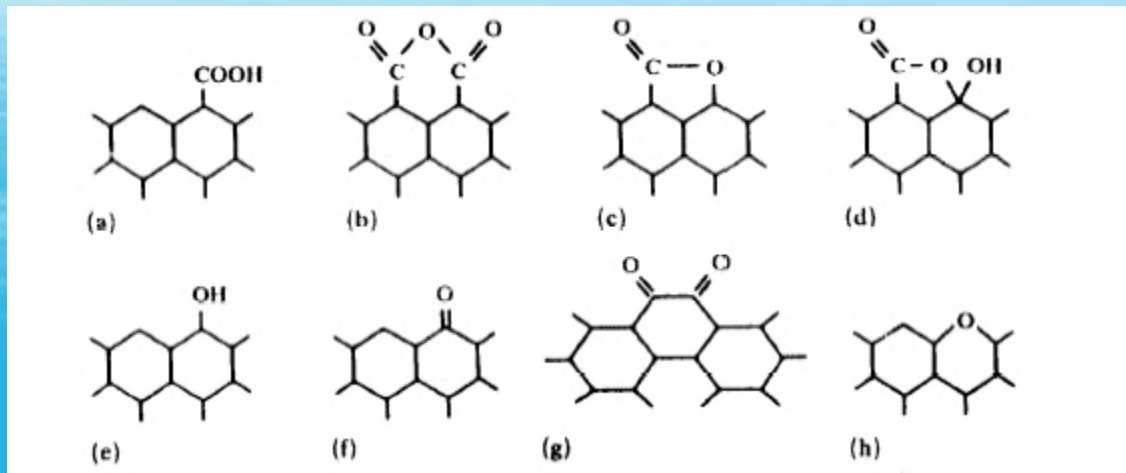
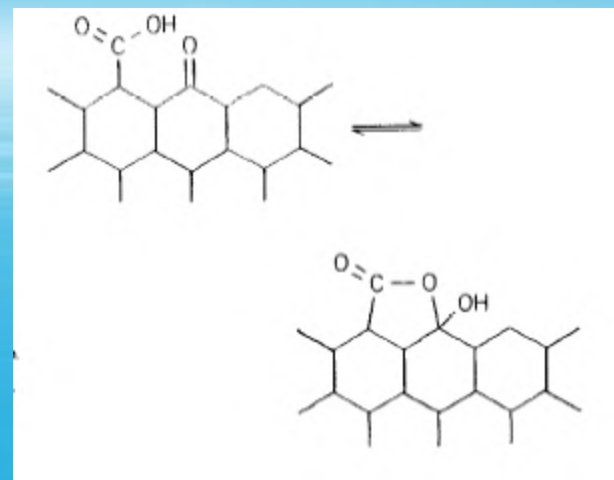
NANOPOROUS CARBONS



- **Activated carbons are efficient adsorbents.**
Their adsorptive properties are due to their high surface area, a microporous structure, and a high degree of surface reactivity.
- **Microporous carbon with a surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ contains about 10^{20} adsorption sites. Assuming an apparent carbon density of $1.0 \text{ cm}^3 \text{ g}^{-1}$ (no penetration of a displacement fluid into the carbon) means that every 1.0 cm^2 of surface of a 1 cm^3 carbon sample has contain 10^{14} pore entrances (a number comparable with the number of stars in the sky).**
- **They are, used, therefore, to purify, decolorize, deodorize, dechlorinate, separate, and concentrate in order to permit recovery and to filter, remove, or modify the harmful constituents from gases and liquid solutions.**
- **Activated carbon adsorption is of interest to many economic sectors and concern areas as diverse as food, pharmaceutical, chemical, petroleum, nuclear, automobile, and vacuum industries as well as for the treatment of drinking water, industrial and urban waste water, and industrial flue gases.**



The formation of lactols from aromatic carboxylic acids with neighboring carbonyl groups is well known, for example, for 2-benzoylbenzoic acid.



Several structures of oxygen functional groups that might be found at the edges of graphene layers. Carboxyl groups (a) might give carboxylic anhydrides (b) if they are close together. In close neighborhood to hydroxyl groups or carboxyl groups, carbonyl groups might condense to lactone groups (c) or form lactols (d). Single hydroxyl groups (e) on the edge of “aromatic” layers would be of phenolic character.

The existence of carbonyl groups is very plausible; they could come either isolated (f) or arranged in quinone-like fashion (g). Obviously, other arrangements could be envisaged for quinone-type functions. Finally, oxygen could simply be substituted for edge carbon atoms (h); such xanthene- or ether-type oxygen is very difficult to detect.

Precursors for synthesis of carbon materials

Carbon foam



- **Coal tar pitch**
- **Petroleum pitch**
- **Liquid products from biomass treatment**
- **Polymers**

Activated carbon



- **Agricultural by-products**
- **Low rank coal**

Synthetic activated carbon



- **Liquid products from biomass treatment**
- **Polymers**
- **Furfural**
- **Coal tar pitch**

✓UTILIZATION OF BIOMASS, POLYMERS AND COAL WASTES!



Why polymer waste?

- Many materials in everyday life are produced from plastics and other petroleum derivatives
- Plastics have unique properties and strong chemical bonds, which are not biodegradable, thus contributing to environmental pollution after use.

Utilization of plastic waste can be performed by using of various methods.

Pyrolysis is often used as effective method to convert waste plastic into useful products

- fuels, lubricant oils, different chemicals, etc.

Carbon materials from different polymers, polymer resins and polymer waste:

- Thermoplastic polymers (polyethylene, polypropylene, polyvinyl chloride, polyamide, polystyrene, polyacrylic, etc.)
- Thermo-setting resins/epoxy resins, formaldehyde resins, melamine resin, etc./ also are suitable precursors.

Utilization of polyethylene is major environmental challenge.

Polyolefin wax $/(CH_2)_nH_2$, $n=50$ and $1000/$ is a by-product from polyethylene production, and it is formed as a result of side reactions, i.e. polyethylene cracking at high temperatures ($>400^\circ C$).



SYNTHESIS OF NANOPOROUS ACTIVATED CARBON

- Two stage procedure, including preliminary thermo-oxidation treatment with mineral acids at 200 °C and subsequent carbonization at 600 °C, was applied to produce porous carbon materials.
- Hydrolysis at 800 °C was used as additional procedure to obtain activated carbon.



The object of this investigation is synthesis of new carbon materials from different polymers and biomass.

Carbon samples were synthesized by thermo-oxidation treatment of polymers with mineral acids at 220°C and subsequent carbonization at 650°C. Some samples were subjected to graphitization at 1800°C. For other samples hydrolysis at 800°C was used as additional procedure to increase the porosity. The structure and properties of obtained carbon materials were studied by SEM, TEM, XRD, Raman spectroscopy, BET, etc.

Obtained carbons are distinguished by significant BET surface area and high mechanical strength. Results from TEM and Raman spectroscopy imply presence of small amount of single graphene layers.

Preparation of samples

The polyolefin wax sample is a waste product from polyethylene production at low pressure, from Burgas petroleum plant, Bulgaria. Polyolefin wax has melting point of 115 °C, average molecular mass of 1100, and decomposes when heating in air at 360 °C. Sample of polyolefin wax (POW) was heated up to 115 °C until melting. Conc. sulfuric acid was added by drops during continuous stirring until solidification. The obtained solid product was washed with distilled water, then dried at 150 °C, and carbonized at 600 °C under nitrogen atmosphere. POW carbonizate was subjected to subsequent water vapor activation at 800 °C for 1 h in a stainless steel vertical reactor.

A mixture of POW and phenol-formaldehyde resin (50:50 %) is heated to the melting temperature (150 °C), and then, conc. sulfuric acid is added to obtain solid product. The sample was carbonized at 600 °C and subjected to water vapor activation at 800 °C for 1 h

A mixture of coal tar pitch and furfural (50:50 wt%) was treated with conc. H_2SO_4 at 150 °C until solidification. The obtained solid product was heated at 600 °C under nitrogen atmosphere. The carbonized solid was further submitted to steam activation at 800 °C for 1 h

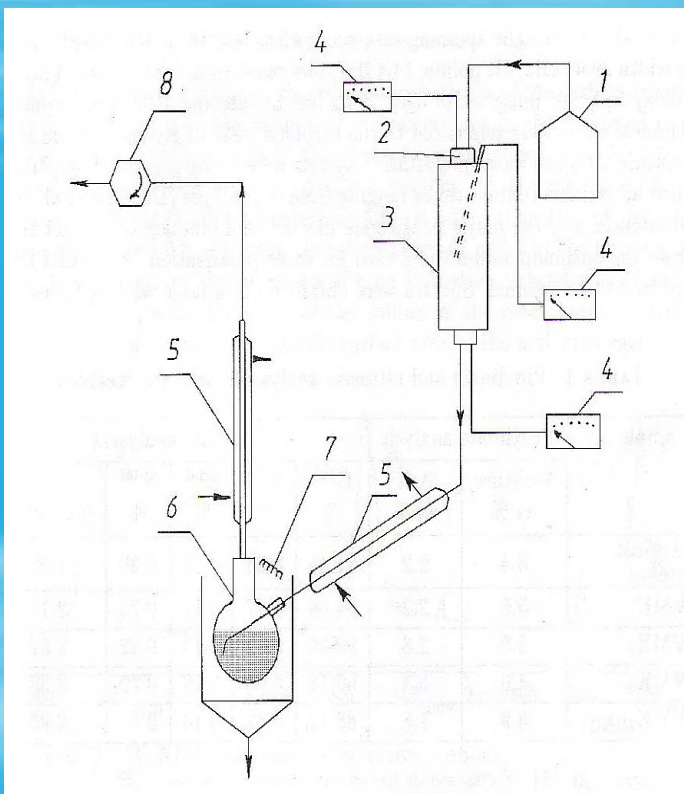


Advantages of the selected method for thermo-oxidation treatment

- | | |
|--|--|
| 1. Low operation temperature | 120-160 °C vs 320 °C for oxidation with O ₂ and air |
| 2. Fast process | 10 min. vs 3-5 h for oxidation with O ₂ and air |
| 3. Significant yield of the final product | 98 % vs 60-70 % for oxidation with O ₂ and air |
| 4. H ₂ SO ₄ is a catalyst of polycondensation reactions, which additionally accelerates the process. | |
| 5. The process can be easily controlled by the temperature and the amount of acid added. | |

Disadvantages

1. H₂SO₄ (oxidizing agent used) and SO₂ (evolved during synthesis) are hazardous substances, regardless that the method needs small acid amount (3 wt.%).
Good ventilation, gloves, glasses and safe suit are required.
2. Sulfur content in the final product is increased, which in many cases have negative effect on other characteristics of the sample.



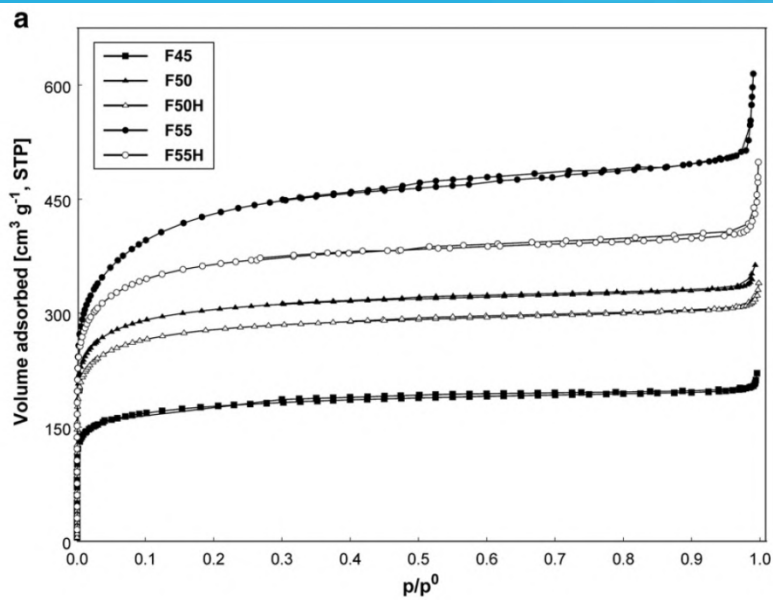
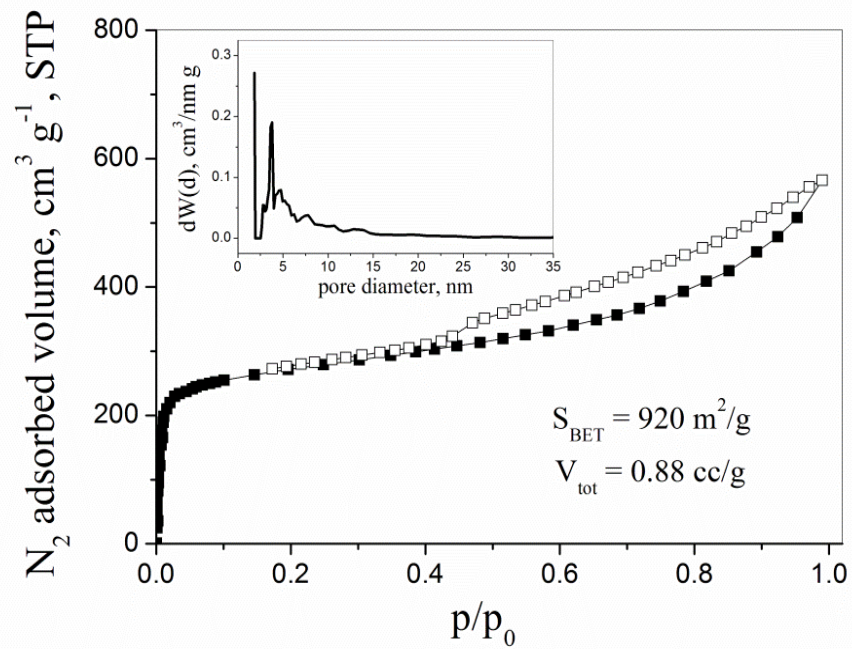
Apparatus for the pyrolysis under steam and inert gas atmosphere

1- steam generator; 2- reactor;

3- oven; 4-thermocouple;

5- cooler; 5- receiver;

7- water cooling; 8- gas counter.



Main textural parameters of the catalysts obtained from N₂ adsorption isotherms at 77 K.

	S_{BET} [m ² g ⁻¹]	$V_{\text{TOTAL}}^{\text{a}}$ [cm ³ g ⁻¹]	$V_{\text{MICRO}}^{\text{b}}$ [cm ³ g ⁻¹]	$V_{\text{MESO}}^{\text{b}}$ [cm ³ g ⁻¹]	Wo N ₂ ^c [cm ³ g ⁻¹]
F45	678	0.316	0.213	0.030	0.255
F50	1173	0.551	0.374	0.033	0.533
F50H	1071	0.486	0.338	0.033	0.473
F55	1613	0.761	0.492	0.177	0.604
F55H	1397	0.620	0.440	0.074	0.509

^a Evaluated at relative pressures of 0.99.

^b Evaluated by DFT method applied to N₂ adsorption data using slit-shaped pore model.

^c Evaluated by DR approach.

Nature of the oxygen groups on surface of the prepared carbons, obtained by Boehm titration.

	Acidic groups (meq g ⁻¹)				Total acidic	Total basic groups (meq g ⁻¹)
	Carboxylic	Lactone	Phenolic, hydroxyl	Carbonyl		
F45	0.012	0.011	0.026	0.550	0.599	0.592
F50	0.019	0.015	0.047	0.658	0.739	0.585
F55	0.024	0.029	0.085	0.839	0.977	0.575
F60	0.043	0.049	0.201	1.093	1.386	0.555
F50H	BDL ^a	BDL ^a	0.072	0.120	0.192	0.192
F55H	BDL ^a	BDL ^a	0.005	0.057	0.062	0.064

^a BDL – below detection limit.



CO₂ adsorption by carbon materials !

Balsamo, M., **Budinova, T.**, Erto, A., Lancia, A., **Petrov, N.**, **Tsyntsarski, B.** CO₂ adsorption onto synthetic activated carbon: Kinetic, thermodynamic and regeneration studies. Separation and Purification Technology, 116, Elsevier, 2013, ISSN:1383-5866, DOI:10.1016/j.seppur.2013.05.041, 214-221. SJR:1.171, ISI IF:3.494
ISI IF - Q1

Balsamo, M., **Tsyntsarski, B.**, Erto, A., **Budinova, T.**, **Petrova, B.**, **Petrov, N.**, Lancia, A.. Dynamic studies on carbon dioxide capture using lignocellulosic based activated carbons. Adsorption, 21, 8, Springer, 2015, ISSN:0929-5607 (Print); 1572-8757 (Online), DOI:10.1007/s10450-015-9711-7, 633-643. SJR:0.6, ISI IF:1.771. **ISI IF - Q1**

Erto, A., **Tsyntsarski, B.**, Balsamo, M., **Budinova, T.**, Lancia, A., **Petrova, B.**, **Petrov, N.** Synthesis of Activated Carbons by Thermal Treatments of Agricultural Wastes for CO₂ Capture from Flue Gas. Combustion Science and Technology, 188, 4-5, Taylor & Francis, 2016, ISSN:Print ISSN: 0010-2202. Online ISSN: 1563-521X, DOI:10.1080/00102202.2016.1138809, 581-593. SJR:0.93, ISI IF:1.38 **C ISI IF - Q2**

Hydrogen Storage

Grigorova, E., Nihtianova, D., Tsyntsarski, B., Stoycheva, I.
Investigation of hydrogen storage characteristics of MgH_2 based materials
with addition of Ni and activated carbon
(2020) *Inorganics*, 8 (2), art. no. 12, .
DOI: 10.3390/inorganics8020012

Grigorova, E., Khristov, M., Stoycheva, I., Tsyntsarski, B.
Effect of activated carbon from polyolefin wax on the hydrogen sorption
properties of magnesium
(2017) *International Journal of Hydrogen Energy*, 42 (43), pp. 26872-26876.
DOI: 10.1016/j.ijhydene.2017.06.155

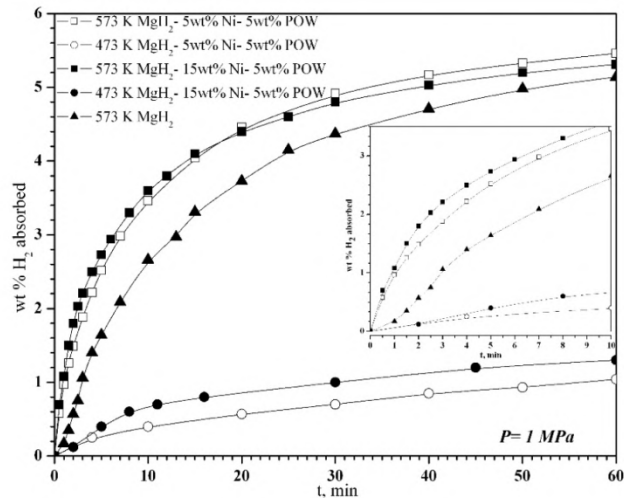
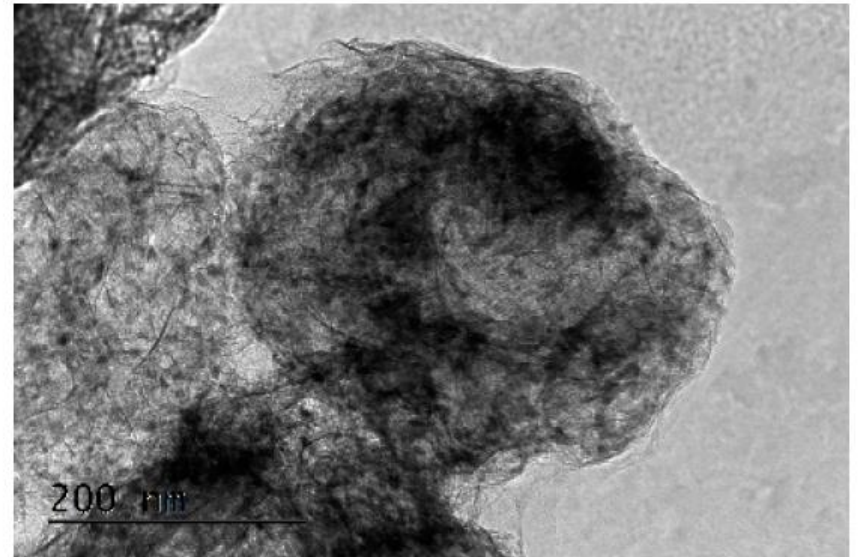


Figure 2. Kinetic curves of hydrogen absorption by the composites 80 wt % MgH_2 -15 wt % Ni-5 wt % POW (polyolefin wax), 90 wt % MgH_2 -5 wt % Ni-5 wt % POW and MgH_2 at different temperatures.



Hydrogen production

Tsoncheva, T., Spassova, I., Issa, G., Ivanova, R., Kovacheva, D., Paneva, D., Karashanova, D., Velinov, N., Tsyntsarski, B., Georgieva, B., Dimitrov, M., Petrov, N.

Ni_{0.5}M_{0.5}Fe₂O₄ (M = Cu, Zn) Ferrites Hosted in Nanoporous Carbon from Waste Materials as Catalysts for Hydrogen Production

(2020) Waste and Biomass Valorization, 1-14, Published online 23 May 2020

DOI: 10.1007/s12649-020-01094-2

Tsoncheva, T., Tsyntsarski, B., Ivanova, R., Spassova, I., Kovacheva, D., Issa, G., Paneva, D., Karashanova, D., Dimitrov, M., Georgieva, B., Velinov, N., Mitov, I., Petrov, N.

Ni_xZn_{1-x}Fe₂O₄ modified activated carbons from industrial waste as catalysts for hydrogen production

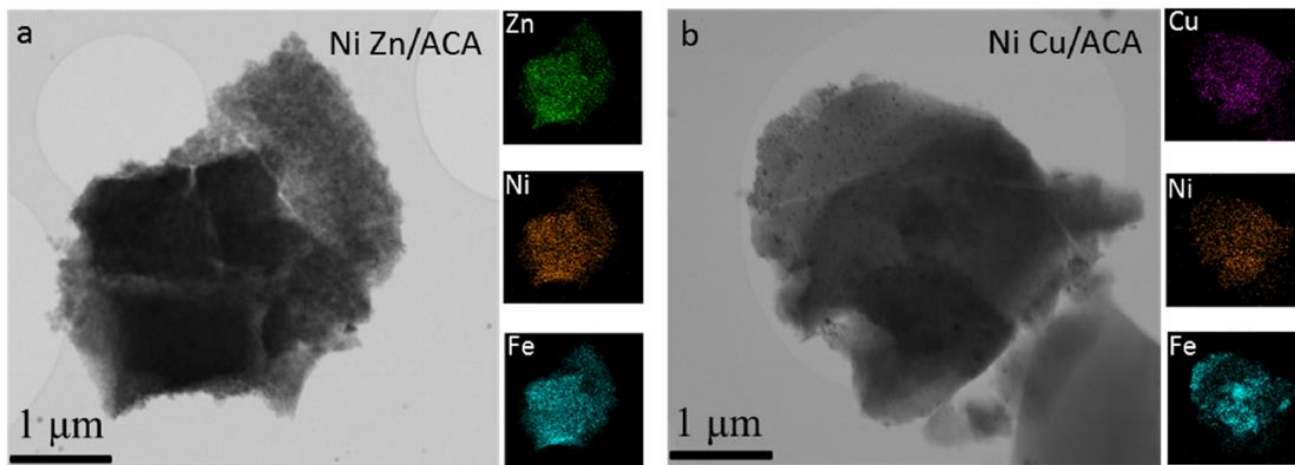
(2019) Microporous and Mesoporous Materials, 285, pp. 96-104.

Tsoncheva, T., Spassova, I., Ivanova, R., Kovacheva, D., Paneva, D., Velinov, N., Tsyntsarski, B., Petrov, N.

Valorization of coal treatment residues as a host matrix of nanosized nickel, copper and zinc ferrites

(2019) Reaction Kinetics, Mechanisms and Catalysis, 127 (2), pp. 691-703.

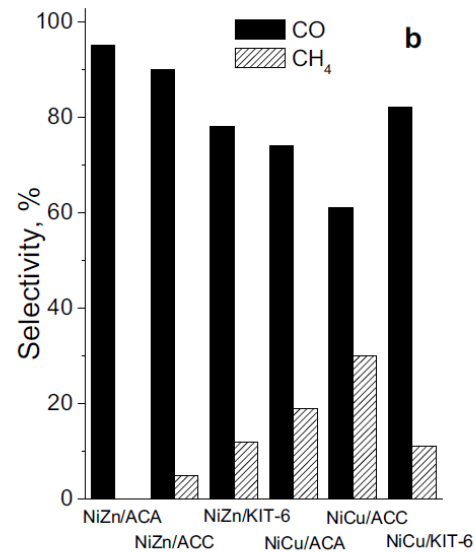
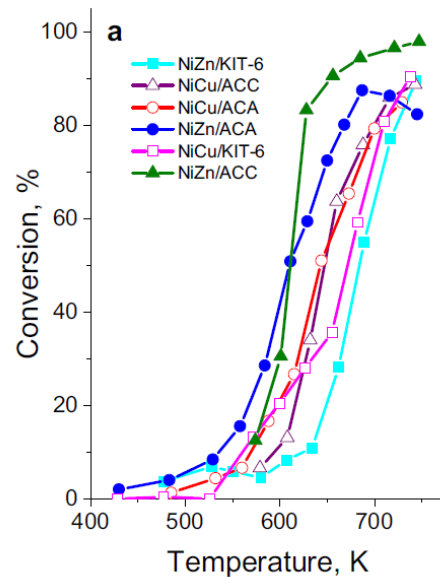
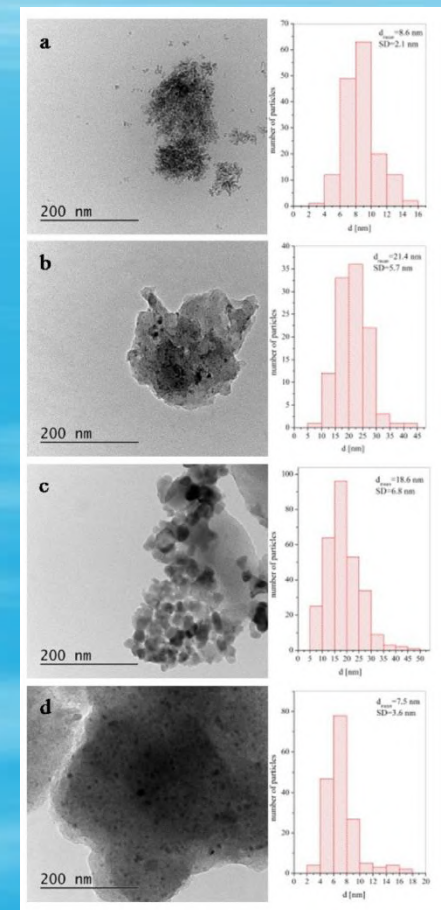
DOI: 10.1007/s11144-019-01596-8



Element	O	Fe	Ni	Zn
Weight %	25.39	43.31	13.95	17.35

Element	O	Fe	Ni	Cu
Weight %	39.3	39	10.59	11.1

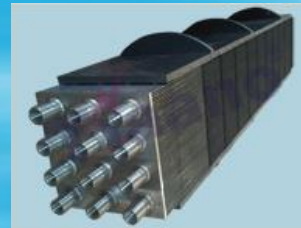
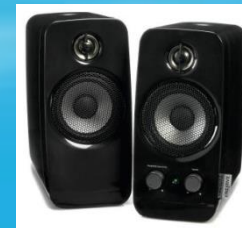
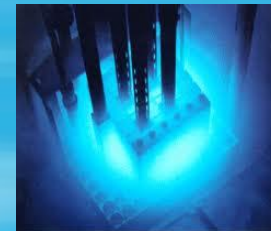
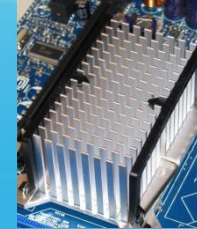
Fig. 4 STEM image, corresponding elemental mapping of **a** Ni Zn/ACA and **b** Ni Cu/ACA and elemental composition of the samples in wt% in the tables below the images



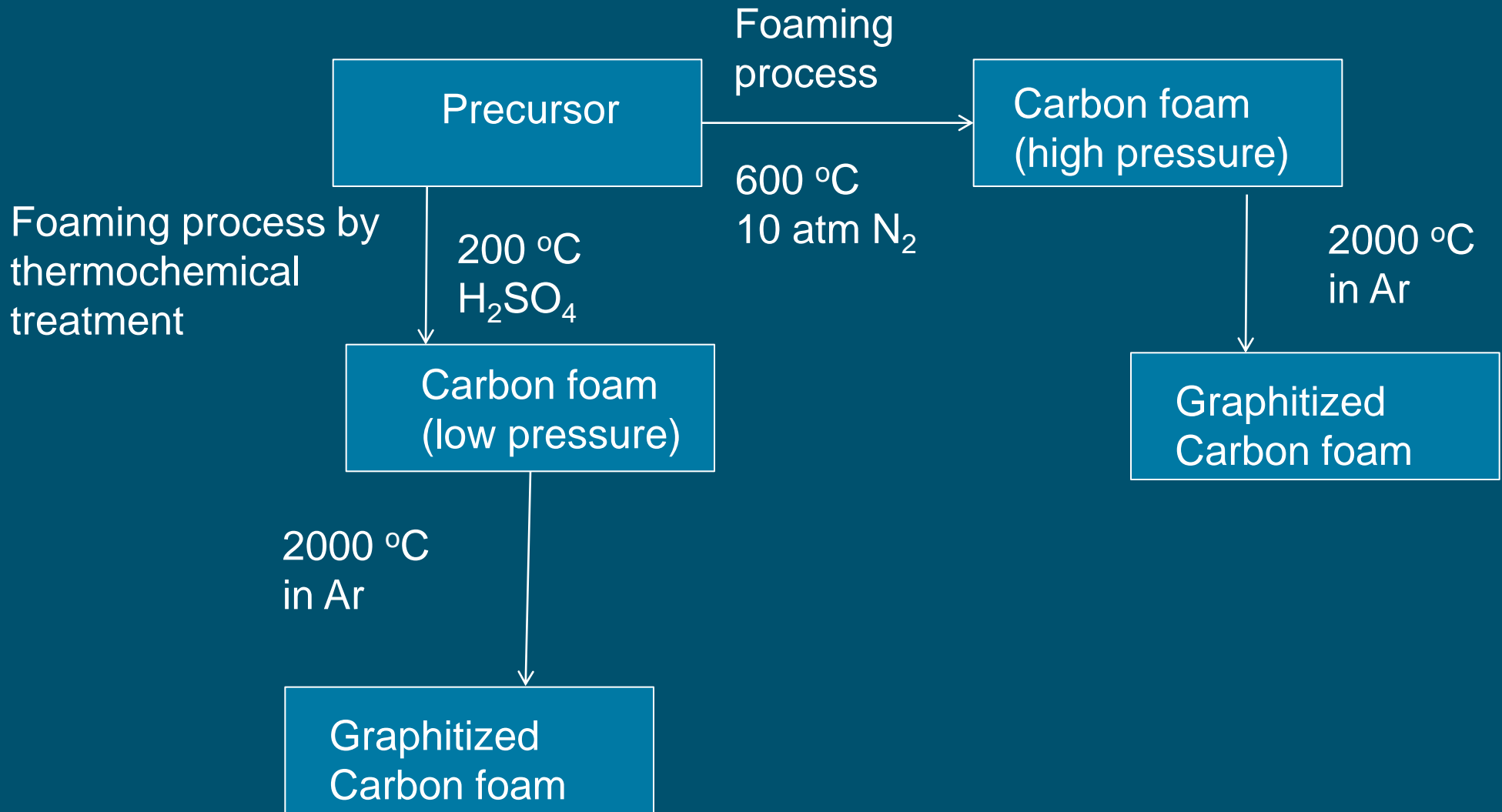
Carbon foam - application

Carbon foam is high-tech material with excellent mechanical, thermal, electrical, acoustic characteristics, and have different applications:

- in **electronics** - e.g. **processor radiators**, which attain 10 times greater cooling in comparison with conventional aluminium radiators
- as **construction material** in aviation, space and defence engineering – **anti-radars, satellites** ; **rocket nozzles; safe jackets** in medicine – **artificial prosteses and joints.** in power engineering – for **rods in nuclear reactors; electrodes** for power stations
- **termal engineering**
- **acoustic engineering**
- **catalysts and catalyst supports**



Carbon foam synthesis

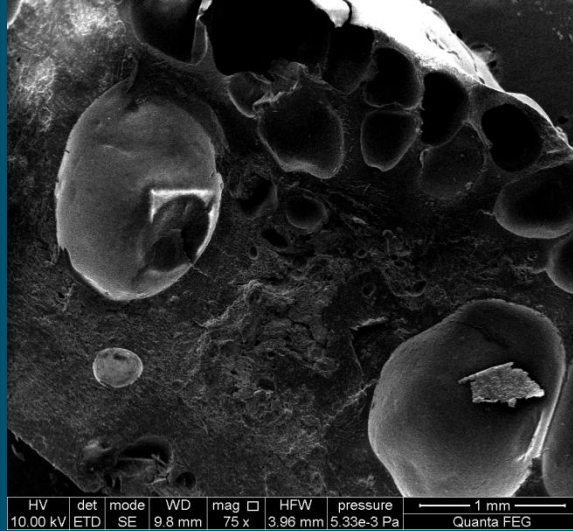




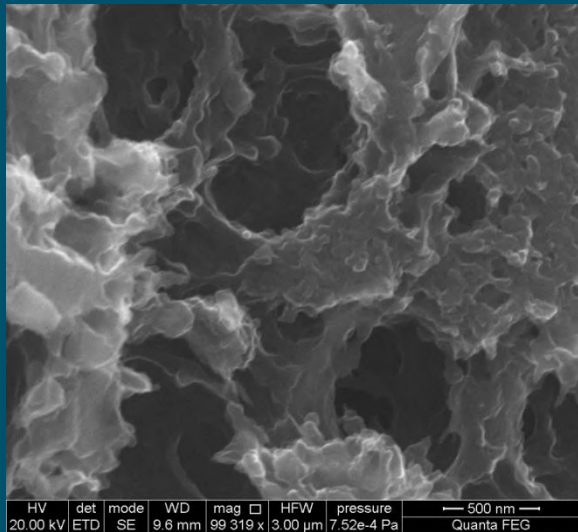
Thermo-chemical modification of coal tar pitch with mineral acids changes the chemical composition and viscosity, thus allowing synthesis of carbon foam at low pressure and without stabilization procedure.

Carbon foam, obtained by this method, is distinguished by irregular porous structure and high mechanical strength.

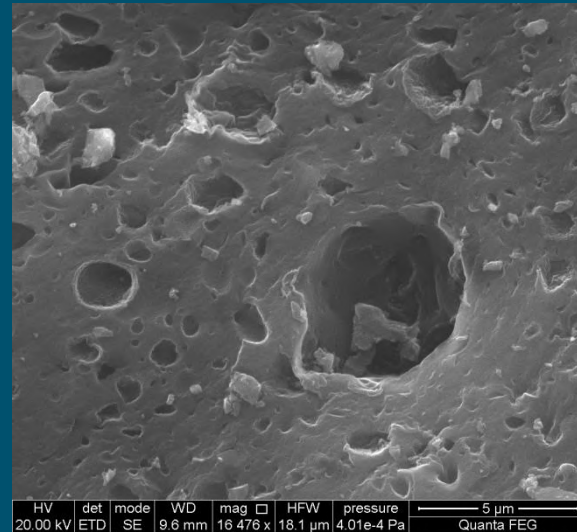
SEM



CF



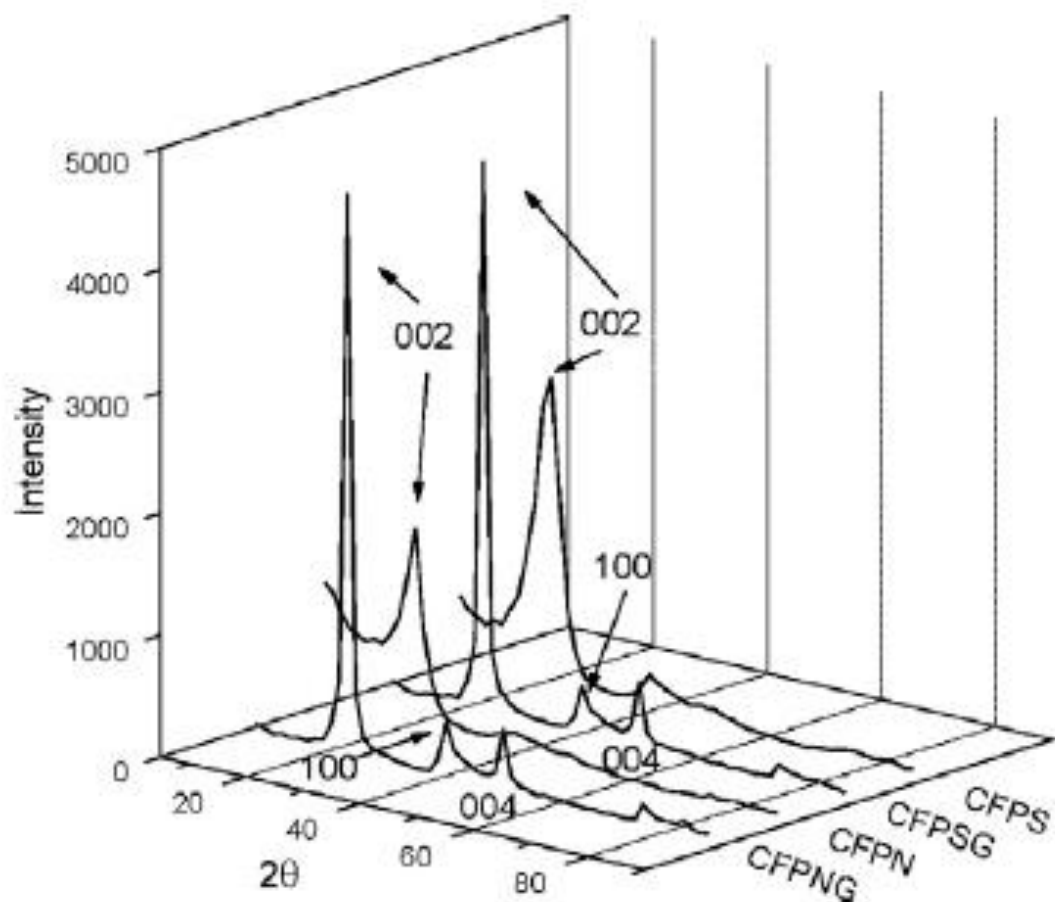
CFR



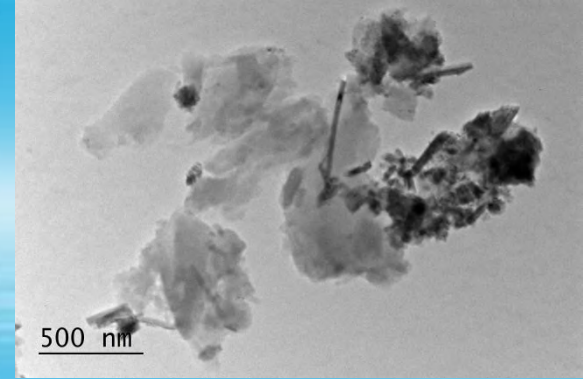
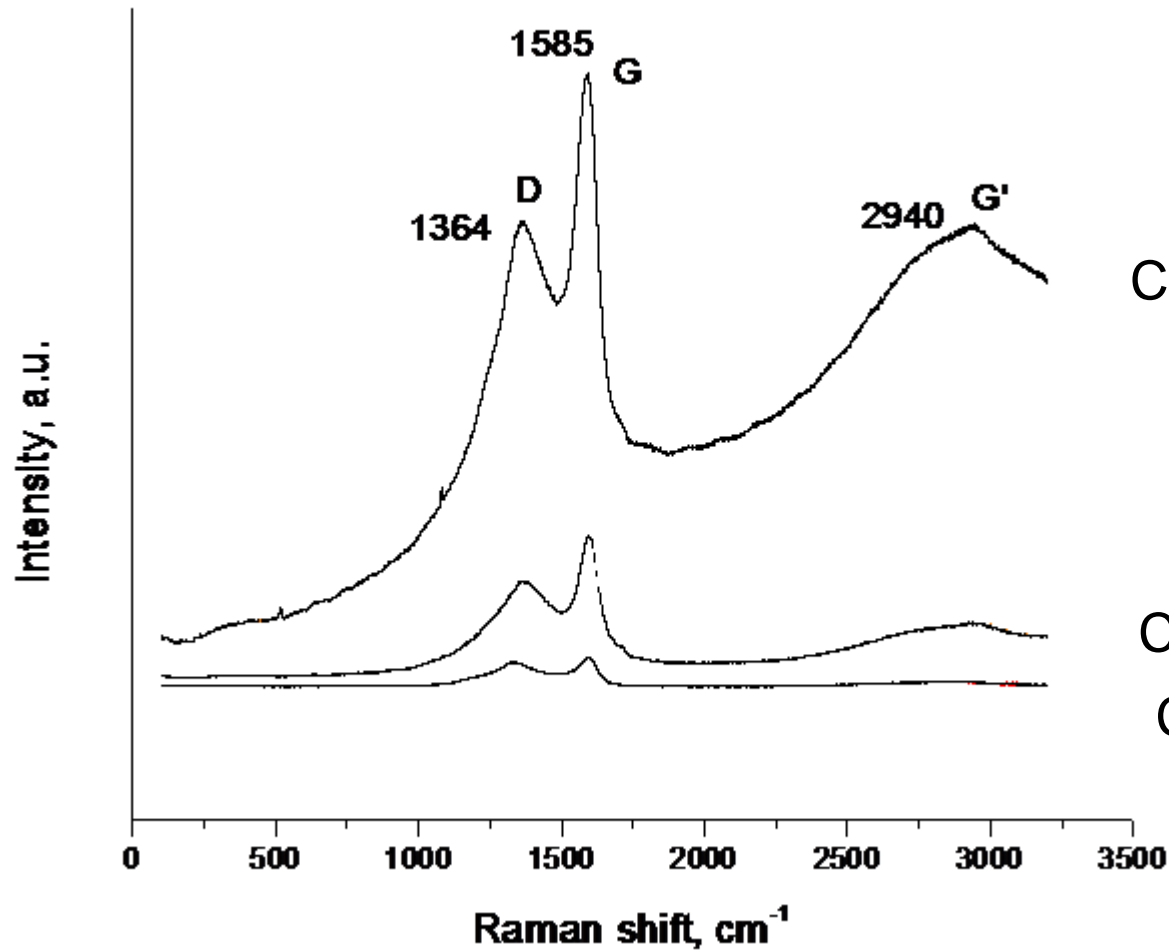
CFP



The synthesized carbon foam is characterized **By well-developed porous structure, high degree of graphitization and high mechanical strength (13 MPa vs 18 Mpa, obtained by USA researchers, but they used higher T and p and longer process)**



Foam	Apparent density (g/cm ³)	Porosity (%)	Open-cell (%)	Compressive strength(MPa)
CFPS	0.52	73.4	92.1	11.9
CFPN	0.57	69.8	90.3	13.5
CFPSG	0.55	71.2	91.5	15.9
CFPNG	0.59	68.1	89.2	17.4



CFR

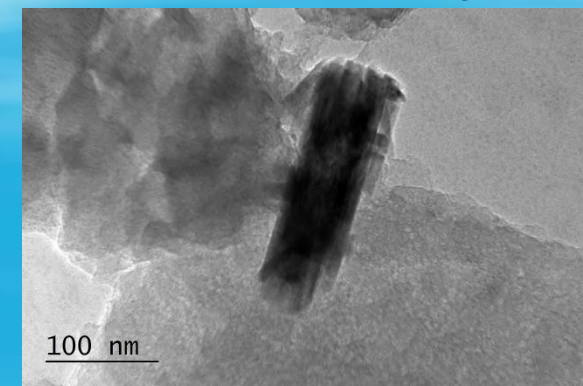
- Probably nanotubes or graphene (in synthesized in our lab AC from biomass) detected by TEM and Raman spectroscopy.

CFP

- Obtained nanomaterials are in a very small amount.

CF

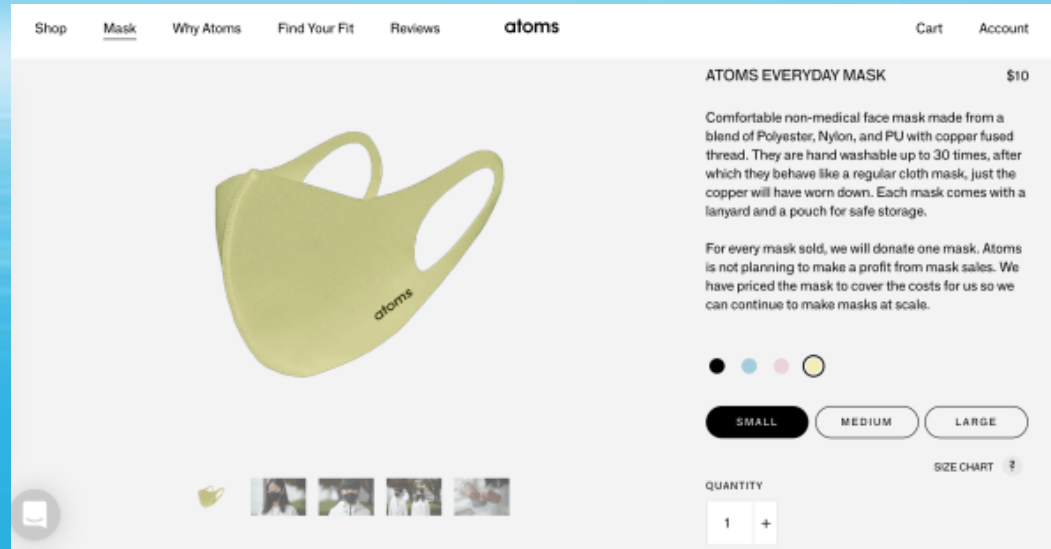
- In our further investigations we intend to isolate these nanomaterials, and stable fraction in higher



- Synthesis of carbon foam, carbon nanotubes, graphene, etc.

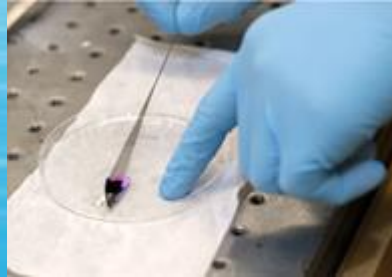
- Extending precursor base by utilization of waste by-products in order to produce carbon materials

CARBON AGAINST COVID-19



You can also find copper-infused cotton masks at some furniture and apparel outlets—like [The Futon Shop](#), [CustomInk](#), and [Atoms](#) shoes—that hopped on the copper bandwagon by leveraging existing production pipelines.

Nobly, some of these companies have done their part to address the mask shortage. Copper Compression donated 18,000 masks to New York and New Jersey-area hospitals, while Atoms is donating one mask for every mask sold to the New York City Housing Authority.



Researchers working with nanotubes. [Photo: courtesy of University of Cincinnati] In battling COVID-19, even the most effective masks need to work in conjunction with other protective measures, like social distancing and hand-washing. And it may be too early to know if high-tech masks work better than their simpler cousins.

“The bottom line, of course, is that you have to have this tested in a real-life environment to see whether what you say it does, it actually does,” says Fichtenbaum. “There’s been testing on a variety of masks, with different results from different viruses. Not every virus is the same.”



Researchers say they have developed a reusable face mask that can kill the novel coronavirus with heat drawn from a cell phone charger.

The disinfection process, which involves a specially designed mask with a USB port, takes about 30 minutes, Yair Ein-Eli, the professor who led the research team at Israel's Technion University in Haifa, told Reuters.

The mask connects to a power source, such as a standard cell phone charger, heating an inner layer of carbon fibers to 70 degrees Celsius – high enough to kill viruses.

Ein-Eli said that because disposable masks were in high demand globally, they were not economically or environmentally friendly.

Video Editor: Natalia Luz

Source(s): Reuters

<https://newseu.cgtn.com/news/2020-06-19/The-face-masks-that-can-kill-COVID-19-with-a-phone-charger--RqJrT1MBEc/index.html>



Factor influencing AC virus uptake

- Presence of pores with suitable pore diameter 100-150 nm
- Hydrophobic or hydrophilic surface of AC are both favorable

Microbial tests

- Face mask – 55 % virus permeability
- Face mask with AC filter – 0 % virus permeability for 50 h



Conclusions

Carbon foams with an anisotropic texture and high mechanical strength were synthesized by thermo-oxidation treatment of commercial coal–tar pitch with mineral acids. The composition and softening point of the pitch precursor significantly affect the foaming process, foam structure and foam mechanical strength. The composition and properties of the modified pitches allow foam formation without pressure and stabilization treatment.

The results show that obtained porous carbons are characterized by microporous structure and high surface area, as well as presence of surface oxygen containing groups, which imply their possible application as adsorbents (metal ions, organic pollutants, bacteria, viruses), electrodes, catalysts, medicine etc.

Marie Skłodowska-Curie Actions-Innovative Training Networks

H2020-MSCA-ITN-2018: BIKE 813748

Contributors:

Tanya Tsoncheva, IOCCP-BAS
Nartzislav Petrov, IOCCP-BAS
Temenuzhka Budinova, IOCCP-BAS
Ivanka Stoycheva, IOCCP-BAS
Bilyana Petrova, IOCCP-BAS
Angelina Kosateva, IOCCP-BAS
Georgi Georgiev, IOCCP-BAS
Pavlina Dolashka, IOCCP-BAS

Eli Grigorova, IGIC-BAS
Daniela Kovacheva, IGIC-BAS
Daniela Karashanova, IOMT-BAS

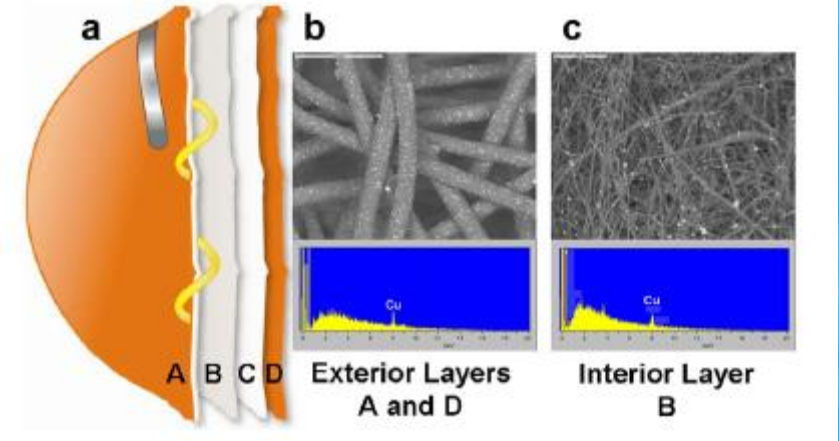
Basia Trzebicka, Polish Academy of Sciences
Slawomira Pusz, Polish Academy of Sciences
Ursula Szeluga, Polish Academy of Sciences



Thank you for your attention!

Marie Skłodowska-Curie Actions-Innovative Training Networks

H2020-MSCA-ITN-2018: BIKE 813748



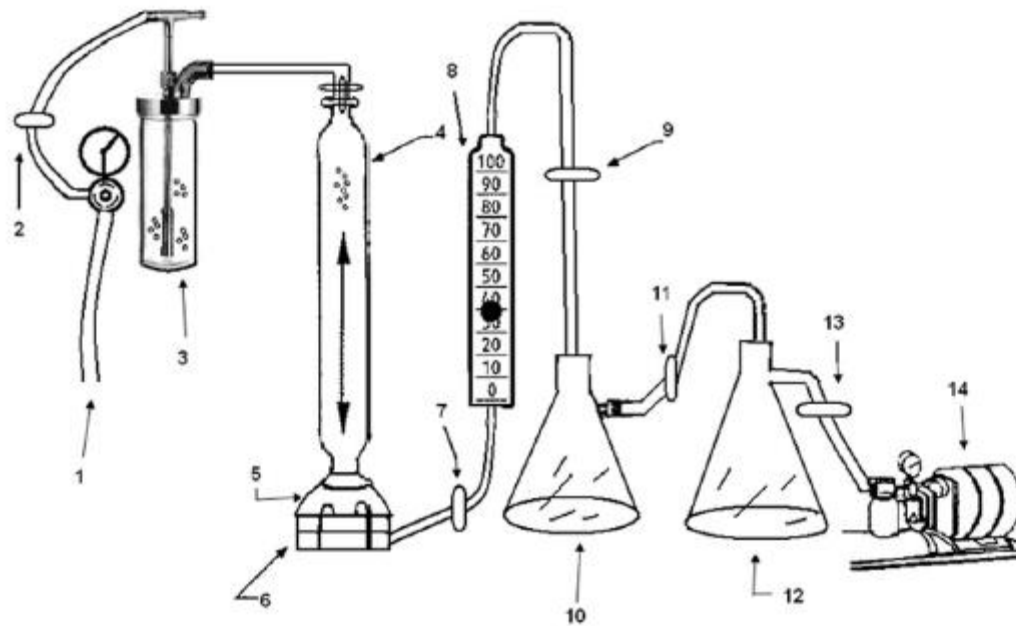


Figure 2. Viral aerosol challenge test apparatus scheme. Key: 1. High pressure air source; 2. Filter; 3. Nebulizer; 4. Aerosol chamber; 5. Test material chamber; 6. Anderson impactor; 7. Filter; 8. Calibrated flow meter; 9. Filter; 10. 4L vacuum flask; 11. Filter; 12. 4L vacuum flask; 13. Filter; 14. Vacuum pump.

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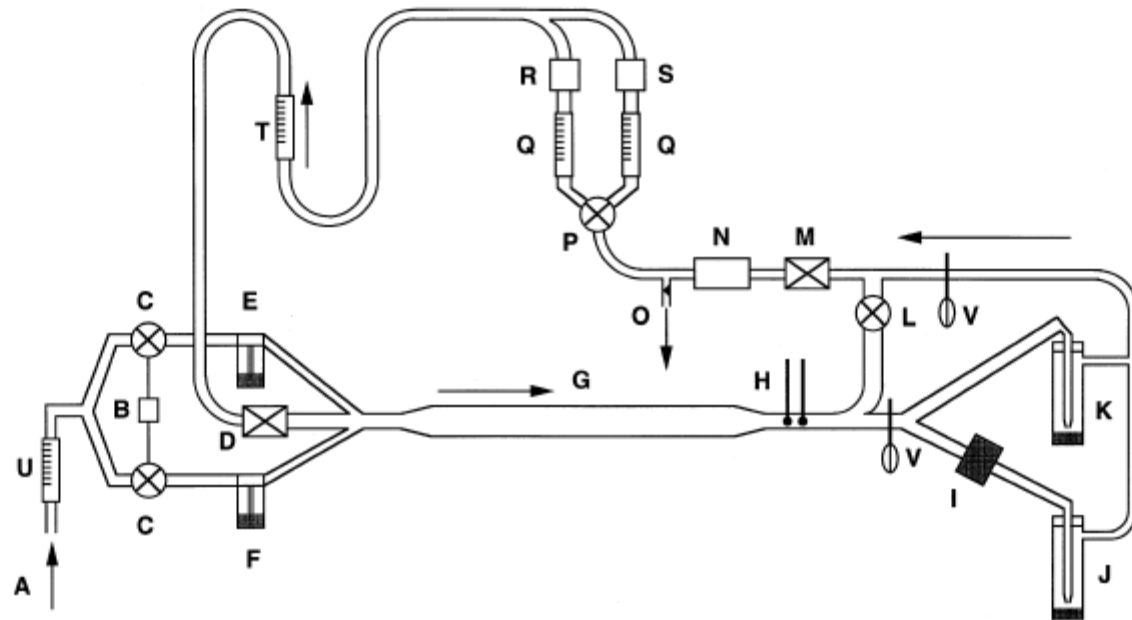


Figure 1 Test arrangement: Henderson apparatus [16, 17]. A, compressed air; B, two-way switch; C, solenoid-operated valve; D, filter; E, Collision spray containing distilled water; F, Collision spray containing challenge micro-organisms; G, spray tube; H, wet and dry thermometers; I, breathing system filter to be tested; J, downstream impinger; K, upstream impinger; L, valve; M, filter; N, compressor-vacuum pump; O, controlled gas leak; P, proportioning valve; Q, flowmeters; R, humidifier; S, drier; T and U, flowmeters; V, clips. Arrows show the direction of flow.

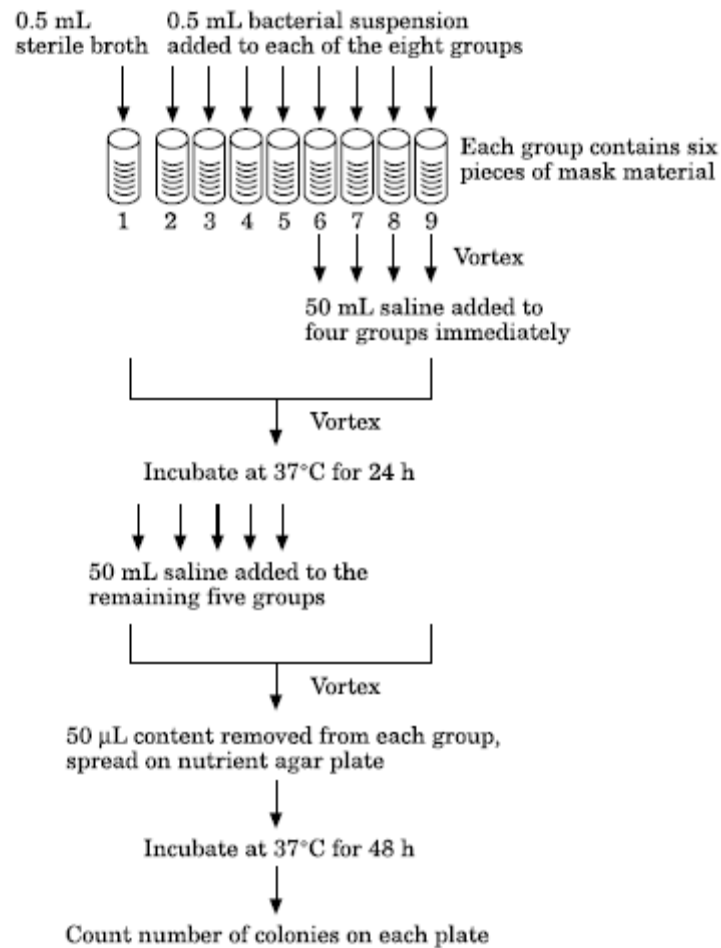


Figure 1 Flow chart showing the experimental procedures for study of antibacterial activity of nanoparticle-coated masks.

Participation in projects supported by BNSF in the last five years

Competition (type and year): „Funding fundamental scientific investigations” – 2014

Number and date of the contract:

DFNI E02-2/12.12.2014

Title: “Biomass based integrated system for clean energy”, 2014-2017

Competition (type and year): „Funding fundamental scientific investigations” – 2014

Number and date of the contract: DFNI E02-64/12.12.2014

Title: “Energy storage systems on the base of asymmetric and hybrid capacitors with nanocomposite electrodes”, 2014-2017

**Competition (type and year): „Funding fundamental scientific investigations” – 2018,
Technical Sciences**

Number and date of the contract: KP-06-N27/9 - 8.12.2018

Title: “Advanced metal-carbon nanocomposites for hydrogen storage”

**Competition (type and year): „Funding fundamental scientific investigations” – 2018,
Chemical Sciences**

Number and date of the contract: KP-06-N29/2 - 6.12.2018

Title: „Renewable integrated system for elimination of organic pollutants from water

Financing organization: ITU NOVA, Istanbul, Turkey

Type of the competition and year: Turkish-Bulgarian Joint Project , 2018

Number or acronym of the project: ITU NOVA – IOCCP Joint Project

Title: “Conversion of biochar to activated carbon” 2018 – 2019

Financing organization: Bulgarian Academy of Sciences

Funding projects in the frame of collaboration between Bulgarian Academy of Sciences and

Polish Academy of Sciences, 2017

Number or acronym of the project:

Title: “Polymer-based carbon materials and their application for synthesis of composites”, 2018-2020

Financing organization: Bulgarian Academy of Sciences

Type of the competition and year: Funding projects in the frame of collaboration between Bulgarian Academy of Sciences and Romanian Academy of Sciences, 2018

Number or acronym of the project: POMCAME

Title: “Polymer membranes and carbon materials on the base of polymers with environmental application”, 2019-2021

Participation in projects supported by other sources in the last five years

Financing organization: Horizon 2020 (European Funding Programs for Research and Innovation)

Type of the competition and year: Horizon 2020 (2016)

Number or acronym of the project: EIT-RIS Project, Horizon 2020, ID 160320, Blow uP

Title: “Waste to Products: Transfer of No1 model to Balkan Area: Desiloing new waste-derived raw materials and developing new applications” (Blow uP), 2017 - 2020

Financing organization: Horizon 2020 (European Funding Programs for Research and Innovation)

Type of the competition and year: Horizon 2020 (2017)

Number or acronym of the project: EIT-RIS Project, Horizon 2020, ID 17167, RAISESEE

Title: “Raw Materials Students Internships in East South East Europe” (RAISESEE), 2018 - 2021

Financing organization: EC

Type of the competition and year: 7 FP, IMAWATCO BS-ERA-NET-226160

Number or acronym of the project: IMAWATCO BS-ERA-NET-226160

Title: “Innovative materials for waste water purification systems to be installed in tourist and other small polluting objectives on the Black Sea coast (IMAWATCO) ”, 2011-2014

Financing organization: Horizon 2020 (European Funding Programs for Research and Innovation), Programme “Science and Education for Smart Growth”

Type of the competition and year: Horizon 2020 (European Funding Programs for Research and Innovation), Programme “Science and Education for Smart Growth”, 2017

Number or acronym of the project: BG05M2OP001-1.001-0008, National Centre of Excellence “Mechatronics and Clean Technologies”, Energy for Circular Economy“, Programme “Science and Education for Smart Growth”, Horizon 2020 (2018-2023)

Financing organization: Horizon 2020 (European Funding Programs for Research and Innovation), Programme “Science and Education for Smart Growth”

Type of the competition and year: Horizon 2020 (European Funding Programs for Research and Innovation), Programme “Science and Education for Smart Growth”, 2017

Number or acronym of the project: BG05M2OP001-1.002-0019, National Competence Centre of Competence “Clean Technologies for Sustainable Development – Waters, By-Products, Energy for Circular Economy“, Programme “Science and Education for Smart Growth”, Horizon 2020 (2018-2023)