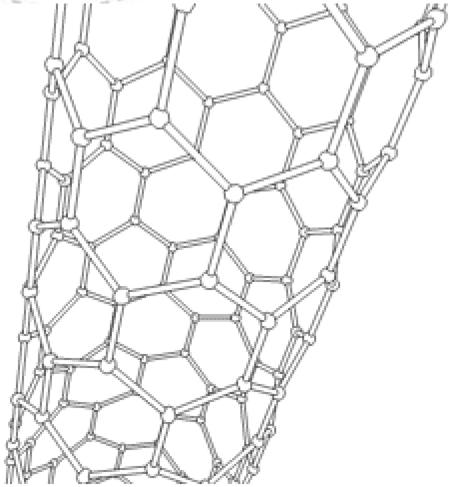
NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
October 18th, 2016

- Nanoscience – Chapter 8
  Fullerenes and carbon nanotubes

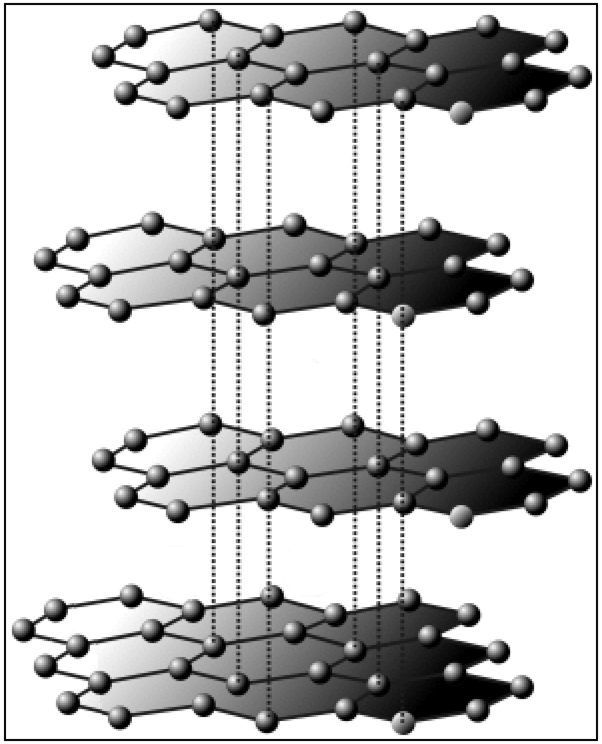


Wikipedia

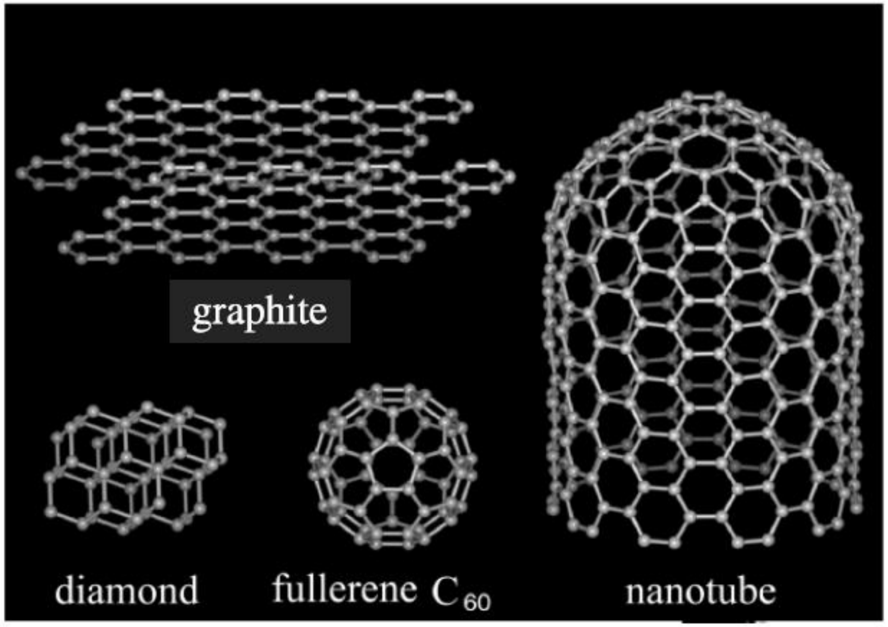
Fullerenes and carbon nanotubes

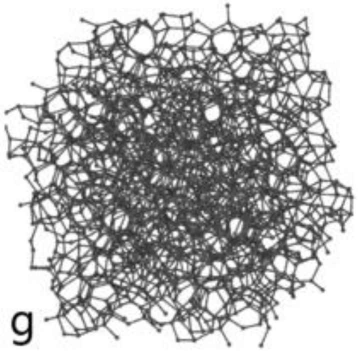
- 8.1 Introduction
- 8.2 Nanotubes and the crystalline forms of carbon
- 8.3 Fullerenes
  - Structure, synthesis, and properties
- 8.4 Carbon nanotubes
  - Structure, synthesis, properties, and applications
- 8.5 Conclusion

Carbon crystal structures

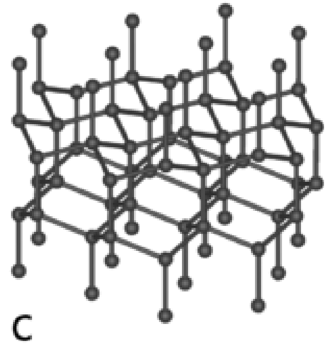


The relation of graphene to graphite.





Amorphous carbon



Lonsdaleite

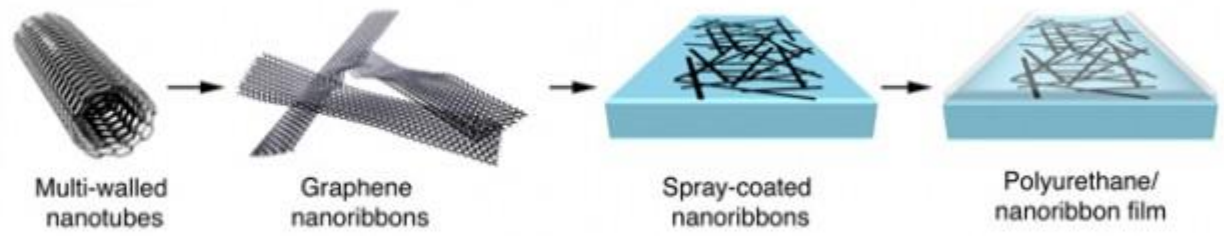
Wikipedia

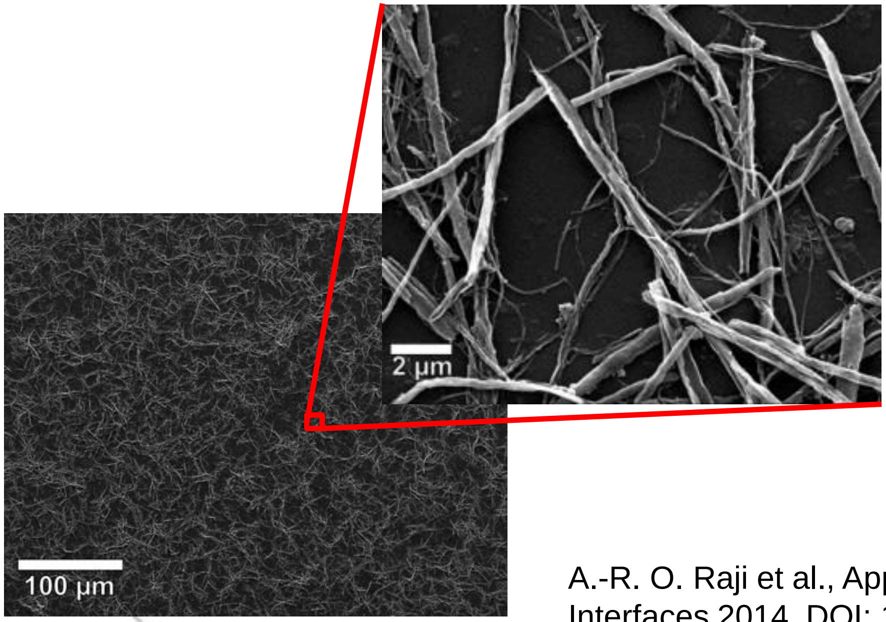
Carbon

- Natural state
  - Graphite
    - Crumbly black mineral
    - Pencil lead
    - Greek: “graphein” = to write
    - Layered structure of parallel graphene sheets
    - sp^2
    - Atoms are only weakly connected to atoms in neighbouring planes
  - Diamond
    - Transparent mineral
    - Extremely hard
    - Tetrahedral symmetry
    - sp^3

Graphene – the new hype

- Keeping glass free from ice with graphene nanoribbons





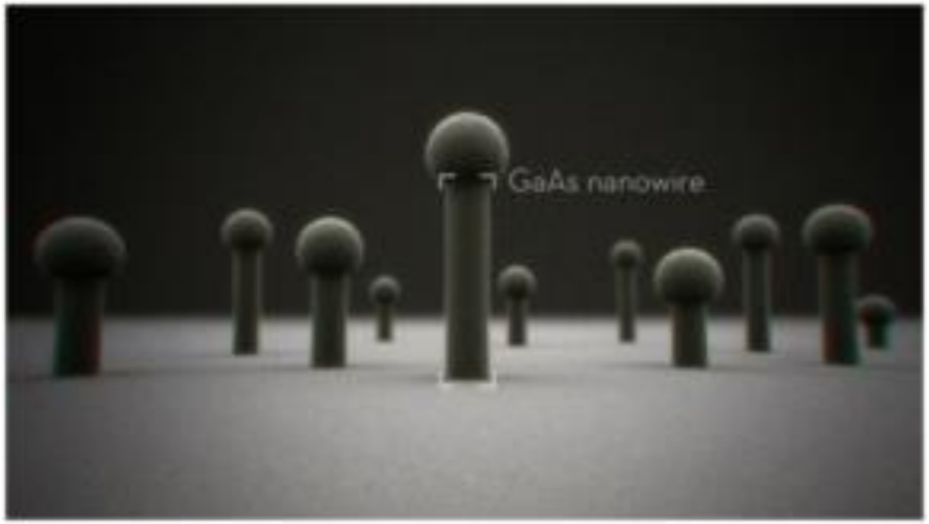
Graphene film:

- 50–200 nm thick
- Conducts electricity and heat across the glass when a voltage is applied
- It melts ice down to –20°C
- Transparent to visible light and radio frequency signals

A.-R. O. Raji et al., Applied Materials and Interfaces 2014, DOI: 10.1021/am503478w

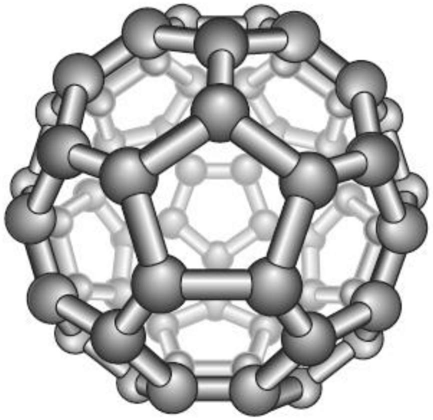
CrayoNano

http://crayonano.com/



Discovery of fullerenes

- 1985: H.W. Kroto, R.F. Curl and R.E. Smalley found carbon molecules with a cage structure using mass spectrometry.
- The hexagons in the C_{60} molecule are the same as those in graphite
- Difficult to synthesize in macroscopic quantities
- Buckminsterfullerene
  - C_{60}
  - The most commonly produced and studied
  - Many other types of fullerenes exist (C_n)



Discovery of carbon nanotubes

- 1991: S. Iijima found carbon nanotubes as a byproduct when trying to synthesize C_{60}
- Tubular objects with nanometric diameter and micrometric length, closed at the ends and made of perfectly graphitic carbon
- Possibly previous discoveries
- Iijima first to realized their importance

LETTERS TO NATURE

Helical microtubules of graphitic carbon

Sumio Iijima

NEC Corporation, Fundamental Research Laboratories,
34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

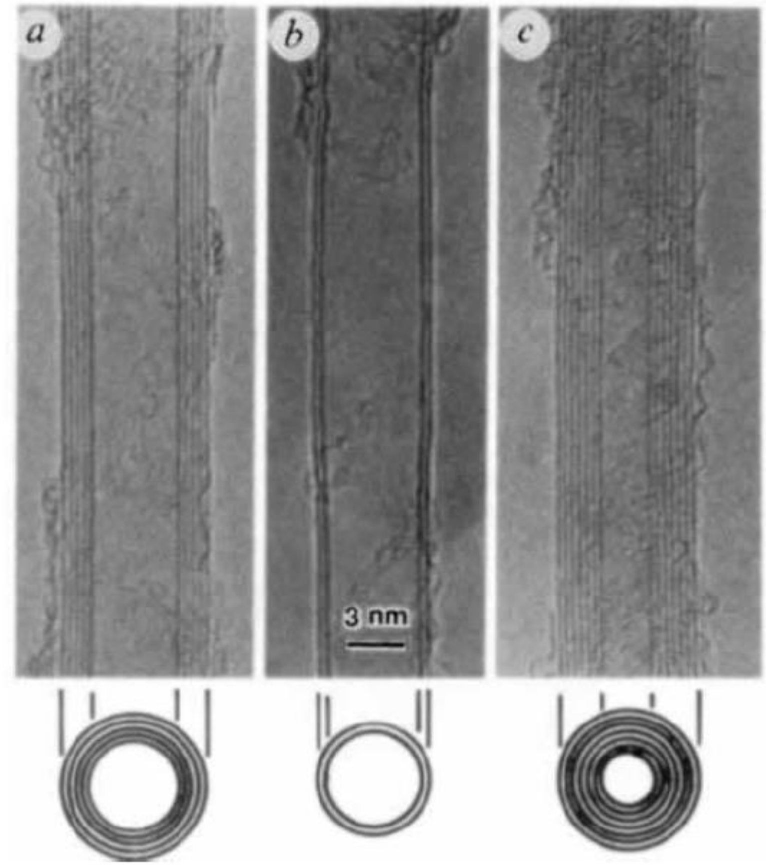
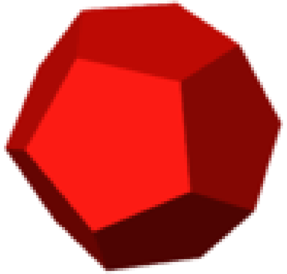


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

S. Iijima, *Nature*, 1991, 354, 56-58.

Fullerenes - structure

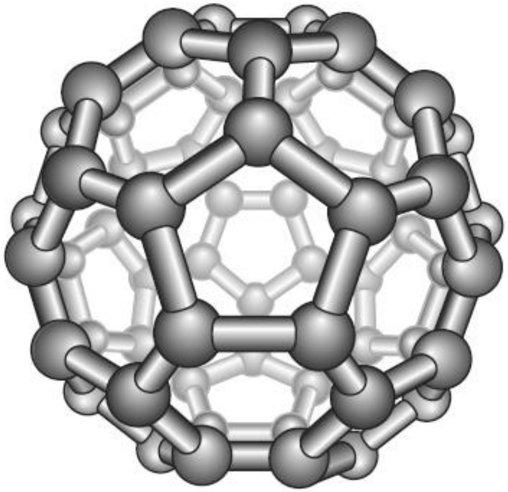
- Fullerenes are molecules with a cage structure containing $2(10 + n)$ carbon atoms which form 12 pentagons and n hexagons
- The smallest fullerene that can be imagined theoretically is C_{20} ($n = 0$)
  - Dodecahedron (12 pentagons)

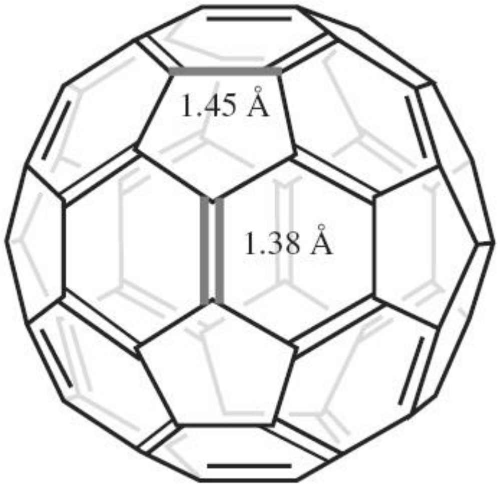


- Above C_{20}, any cluster made up of an even number of carbon atoms can form at least one fullerene-type structure
- The number of isomers increases with increasing n, from one for $n = 0$ to more than 20 000 for $n = 29$

Buckminsterfullerene, C_{60}

- The smallest stable fullerene
- Truncated icosahedron
- The exact replica of a football
- 12 pentagons and 20 hexagons
- Each pentagon is surrounded by 5 hexagons
- C_{60} is a highly symmetrical molecule in which all the carbon atoms are equivalent





Structure of C_{60}.

C_{60}

- Two types of carbon–carbon bonds
  - 6–6 bonds and 5–6 bonds
- Why this unusual localization of the *π* electrons?
  - The spherical structure prevents full orbital overlap, which leads to pyramidalization of the *sp*^{2} carbon atoms

C_{60} is not an aromatic molecule

Isolated pentagon rule

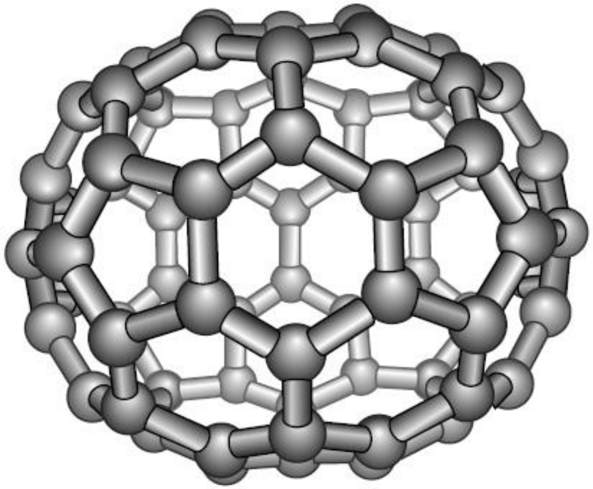
- **The fullerene-type structures in which all pentagons are separated from one another by hexagons are more stable than those in which there are two adjacent pentagons**

- Two adjacent pentagons have bond angles far from 120° → large tension in the carbon ring

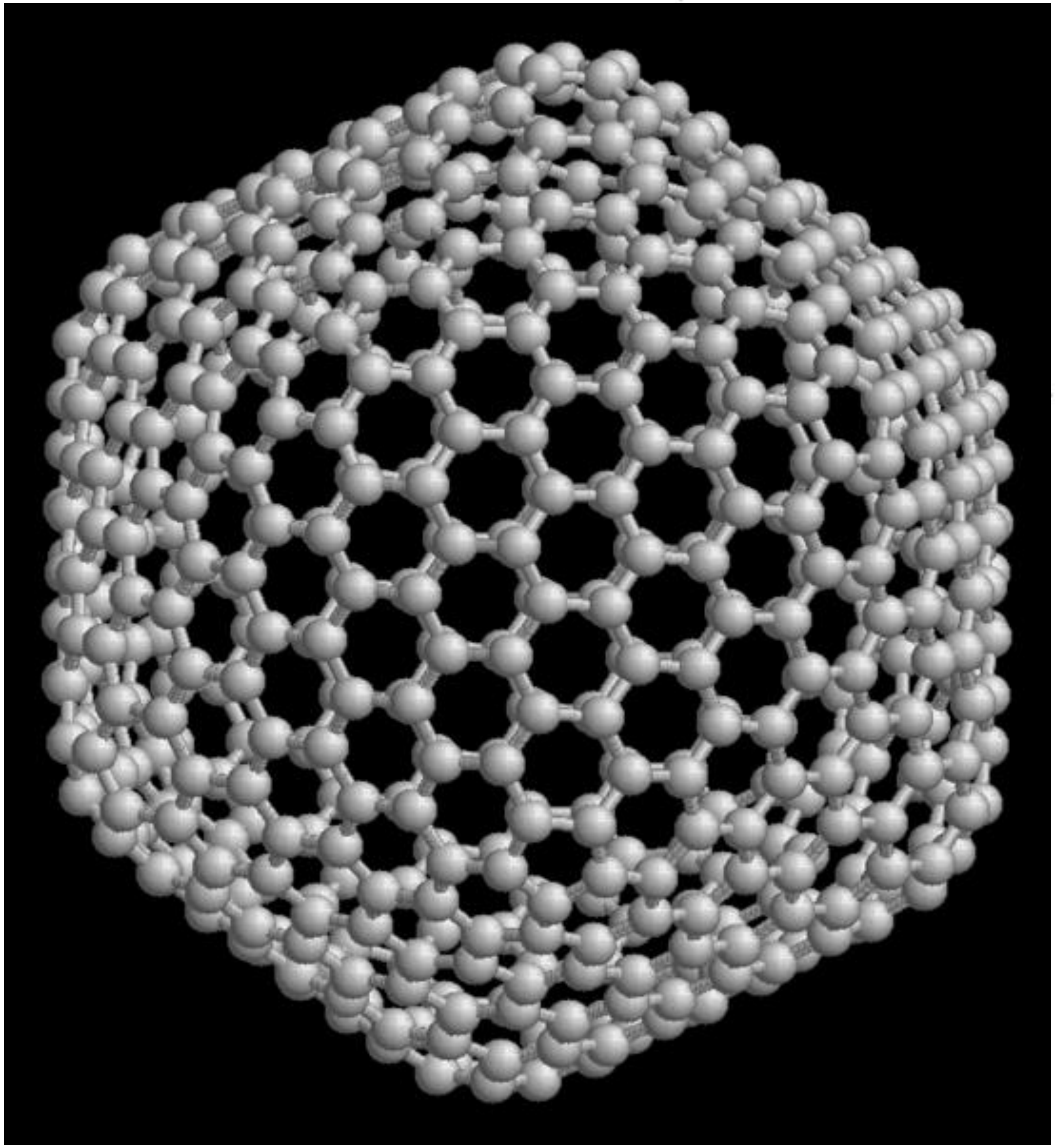
- Only the fullerenes C_x respecting the isolated pentagon rule are stable → magic numbers
  - x = 60, 70, 72, 76, 78, 84, etc

C_{70}

- Respects the isolated pentagon rule and has an oval profile (like a rugby ball)
- Ends (or poles) have a structure similar to C_{60}.
- Main difference from C_{60} is an equatorial belt made up of a chain of hexagons



Structure of C_{70}.

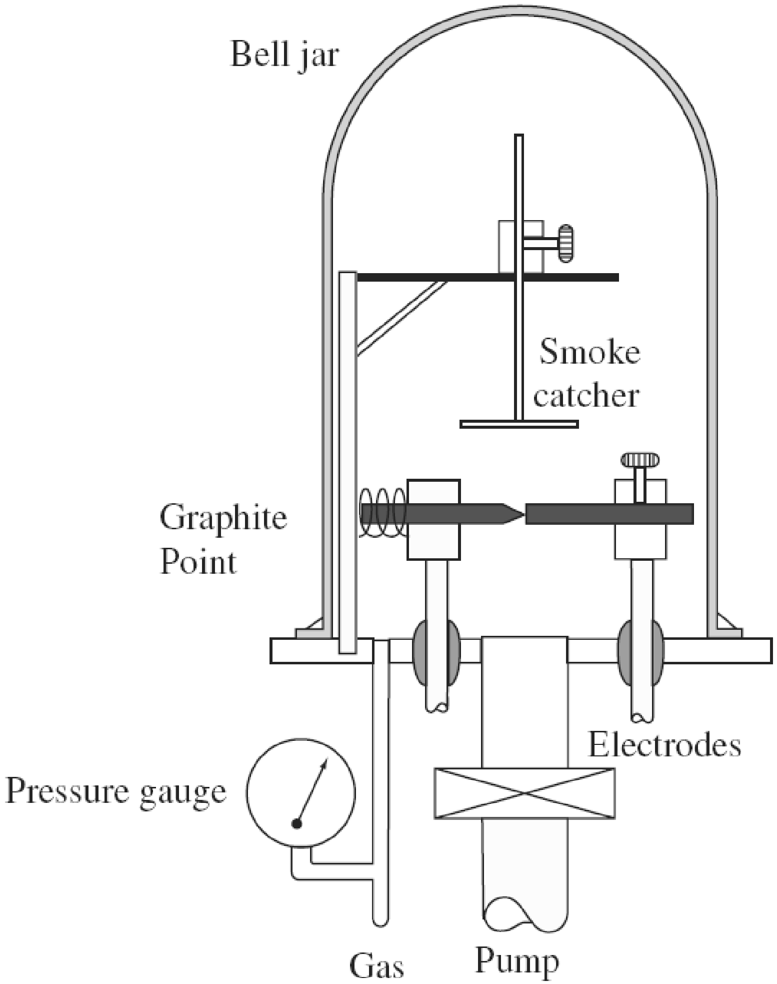


Structure of the icosahedral fullerene C_{540}.

Wikipedia

Production of fullerenes

- Vaporization of carbon in a helium atmosphere
- Two graphite rods connected to copper electrodes
- Ohmic heating due to electric current
- 2 500–3 000 °C
- Graphite is vaporized as a plasma and cools on contact with helium



Experimental setup for fullerene production.

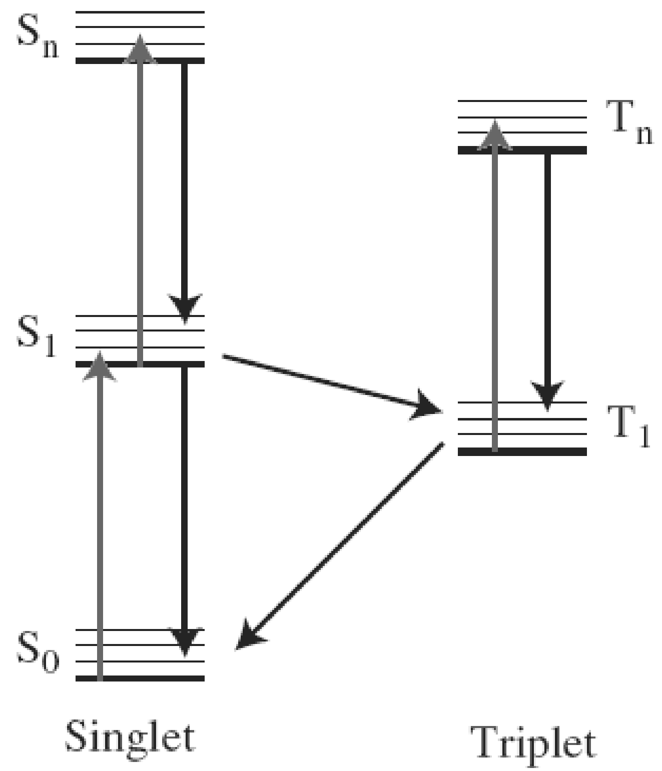
Properties of C_{60}

- Solubility in organic solvents
  - Insoluble in polar solvents (i.e. acetone, alcohols, tetrahydrofuran, etc)
  - Weakly soluble in hydrocarbons (i.e. pentane, hexane or cyclohexane)
  - The best solvents for C_{60} are the aromatic solvents
    - Benzene (1.7 mg/mL)
    - Toluene (2.8 mg/mL)
    - 1-chloronaphthalene (51 mg/mL)

From left to right: **C60, C70, C76/C78, C84** in solution.

Photophysical properties of C_{60}

- Nonlinear absorption effect
  - Weak absorption of low intensity light
  - The transition $S_0 \rightarrow S_1$ is forbidden for symmetry reasons and the associated absorption is therefore low
  - Certain transitions from the state S_1 to the states S_n are allowed in the visible range of the spectrum



Five-level model explaining the photophysical properties of C_{60}.

Electrochemical properties of C_{60}

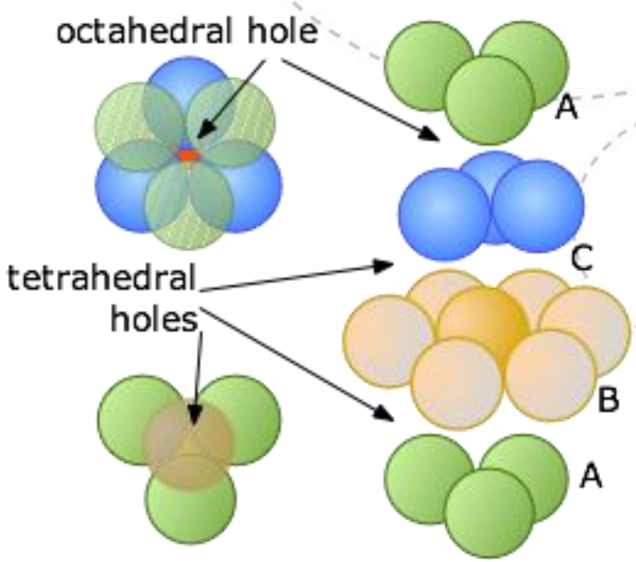
- Electron acceptor
- Can accept up to 6 electrons to form a hexa-anion C_{60}^{6-}
- Easy to reduce, difficult to oxidize

Table 8.1. Reduction potentials obtained at −10 °C in a CH_3/toluene mixture. Values are obtained in volts (vs. Fc^+/Fc) for a scan rate of 100 mV s^{-1}.

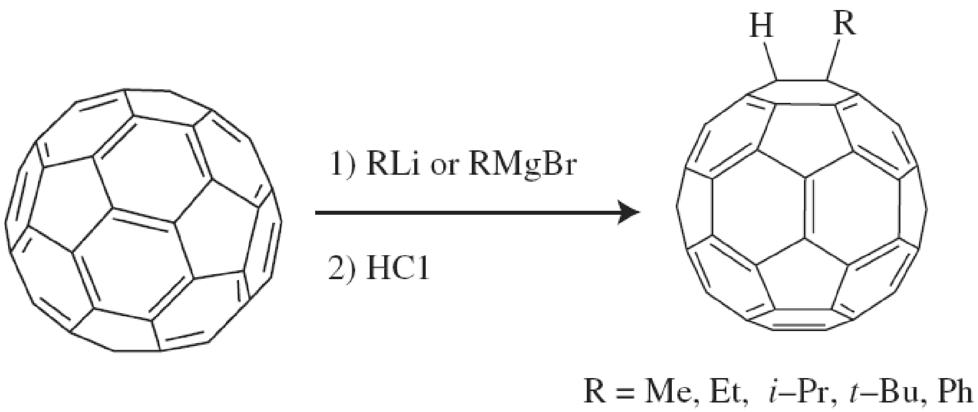
Single-electron pair	Reduction potential [V]
C_{60}/C_{60}^{-}	−0.98
C_{60}^{-}/C_{60}^{2-}	−1.37
C_{60}^{2-}/C_{60}^{3-}	−1.87
C_{60}^{3-}/C_{60}^{4-}	−2.35
C_{60}^{4-}/C_{60}^{5-}	−2.85
C_{60}^{5-}/C_{60}^{6-}	−3.26

Chemical properties of C_{60}

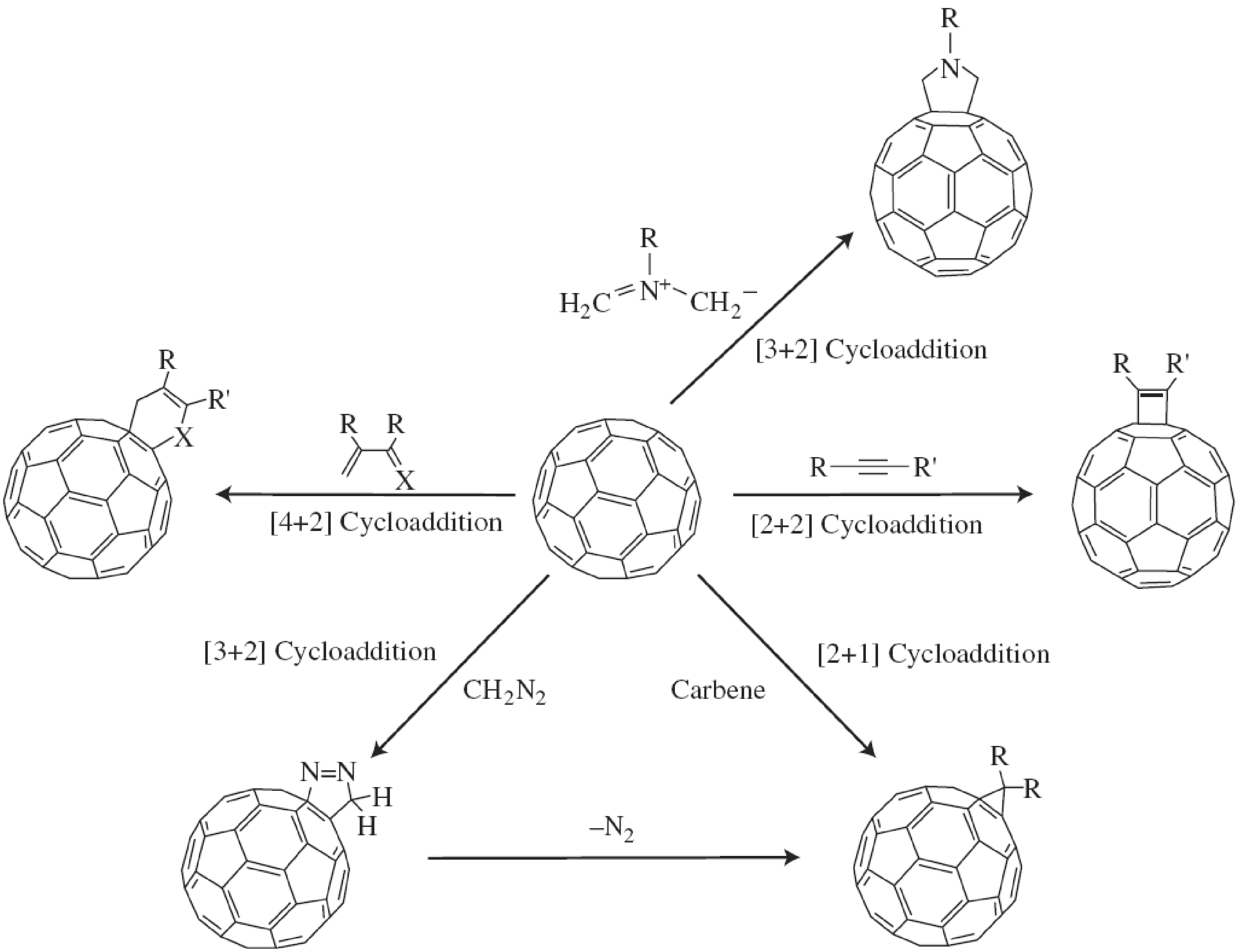
- Grafting of groups of molecules onto the surface of C_{60} → molecules with novel properties
- A large number of derivatives of C_{60} have been produced
- Chemical modification of C_{60} is done mainly to increase its solubility → corresponding derivatives become much easier to manipulate



- C_{60} is a good electrophilic reagent and can host nucleophilic addition reactions



Nucleophilic addition of an organolithic or organomagnesium compound to C_{60} followed by acid hydrolysis.



Different cycloaddition reactions involving C_{60}.

Next time

- 8.4 Carbon nanotubes
- CNT-related research at NTNU and SINTEF