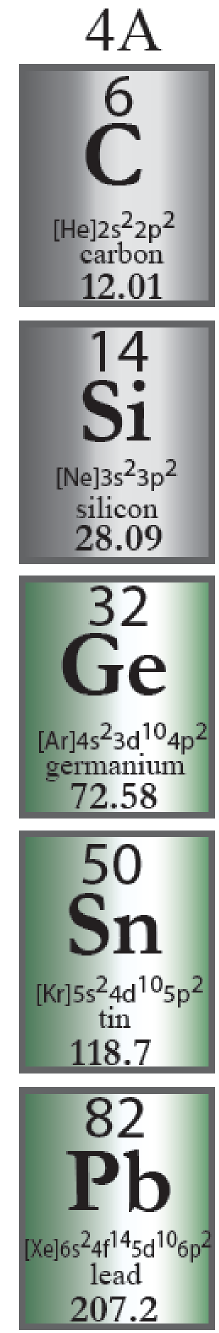
第十五章 碳族元素
Chapter 15 The carbon family elements

Carbon (C)   Silicon (Si)

Germanium (Ge)   Stannum (Sn)
Tin

Plumbum (Pb)
Lead



ns^2np^2

碳族元素结构的相似性及递变性

		carbon	silicon	germanium	tin	lead
Valence electron configuration		**$2s^2 2p^2$**	**$3s^2 3p^2$**	**$4s^2 4p^2$**	**$5s^2 5p^2$**	**$6s^2 6p^2$**
Atomic number		6	14	32	50	82
Covalent radius/pm		77	118	122	141	154
ionic radius /pm	M^{2+}	-	-	73	93	120
	M^{4+}	16	42	53	71	84
I1/kJ • mol^{-1}		1086	787	762	709	716
I2/kJ • mol^{-1}		2353	1577	1537	1412	1450
I3/kJ • mol^{-1}		4621	3232	3302	2943	3081
I4/kJ • mol^{-1}		6223	4356	4410	3930	4083
Electronegativity (pauling)		**2.55**	1.90	2.01	1.96(IV) 1.80(II)	2.33(IV) 1.87(II)
E(x-x) (kJ • mol^{-1})		345.6	222	188	146.4	-

- 易形成共价键，难形成离子键；
- 碳元素形成的化合物种类是最多的。

碳族元素结构的相似性及递变性

元素名称	元素符号	原子半径（nm）	主要化合价	状态(标况)	单质密度（克/立方厘米）	单质熔点（℃）	单质沸点（℃）
碳	C	0.077	0，+2，+4	固体	3.51（金刚石） 2.25（石墨）	3550	4827
硅	Si	0.117	0，+2，+4	固体	2.33	1410	2355
锗	Ge	0.122	0，+2，+4	固体	5.35	937.4	2830
锡	Sn	0.141	0，+2，+4	固体	7.28	231.9	2260
铅	Pb	0.175	0，+2，+4	固体	11.34	327.5	1740

clear (diamond) & black (graphite)

C

crystalline, reflective with bluish-tinged faces

Si

Grayish-white

Ge

A 12 gram (2x3 cm) polycrystalline block of Ge with uneven cleaved surfaces

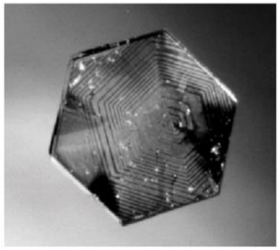
Sn silvery (left, beta) or gray (right, alpha)

Metallic gray

Pb

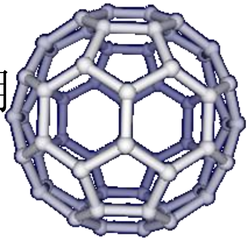
§ 15-1 Carbon and its compounds

- **存在：**以多种形式广泛存在于大气和地壳之中（在地壳中的含量约0.027% ）。碳单质很早就被人认识和利用，碳的一系列化合物——有机物更是生命的根本。生物体内大多数分子都含有碳元素。
- **同位素：**在地球的自然界里，碳12在所有碳的含量占98.93%，碳13则有1.07%。C的原子量取碳12、13两种同位素丰度加权的平均值，一般计算时取12.01。**碳12是国际单位制中定义摩尔的尺度，以12克碳12中含有的原子数为1摩尔**。
- **用途：**



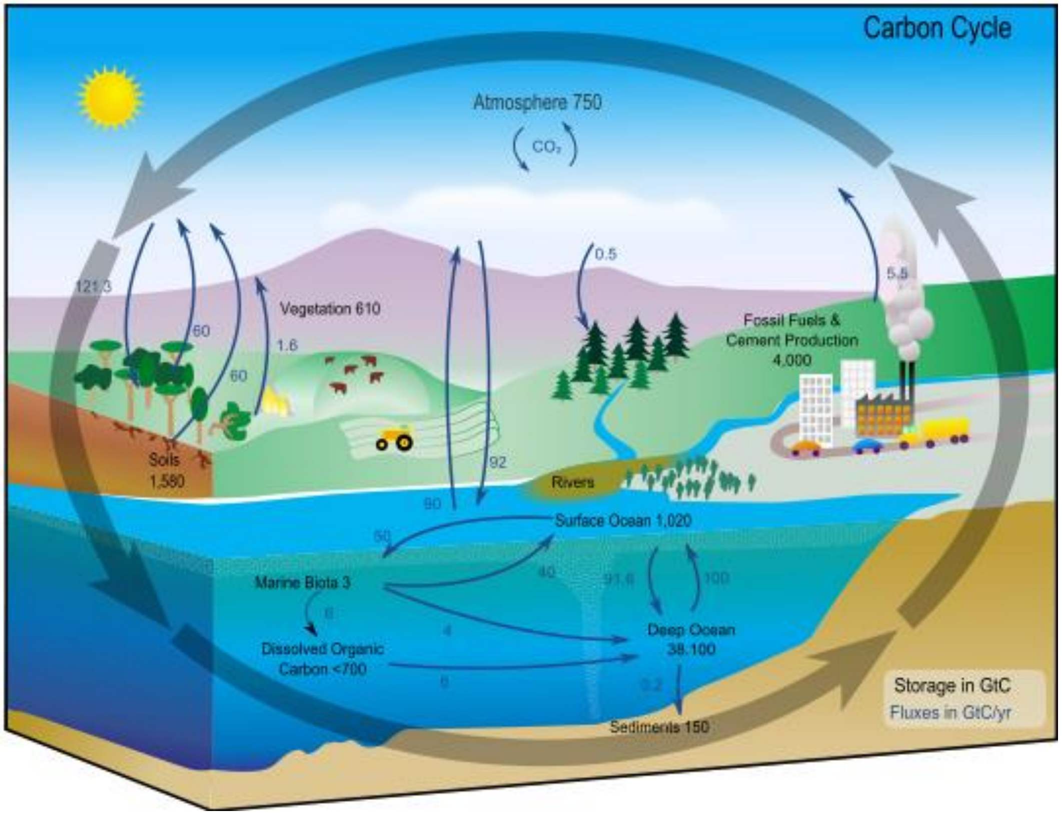
- 在工业上和医药上，碳和它的化合物用途极为广泛。
- 测量古物中碳14的含量，可以得知其年代，这叫做碳14断代法（由于碳14具有较长的半衰期）。
- 石墨可以直接用作炭笔，也可以与粘土按一定比例混合做成不同硬度的铅芯。

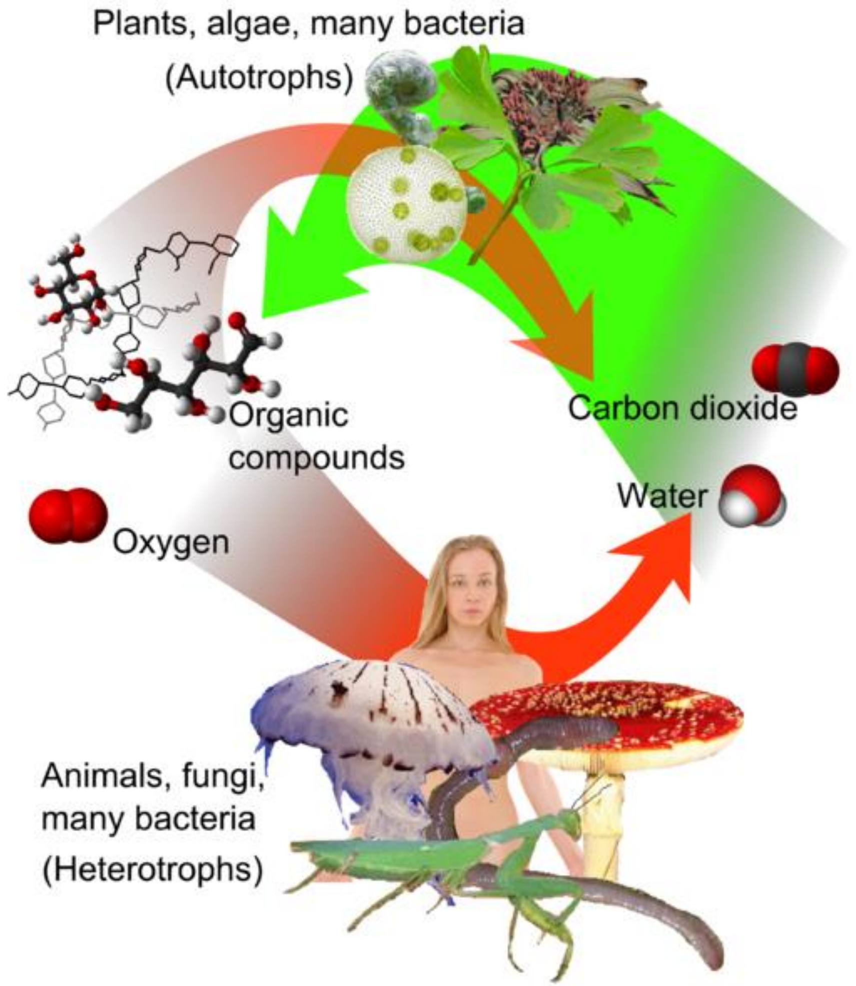
- 金刚石除了装饰之外，还可使切削用具更锋利。
- 无定形碳由于具有极大的表面积，被用来吸收毒气、废气。
- **富勒烯、碳纳米管**和**石墨烯**则对纳米技术极为有用。
- 由于石墨的分子间只有微弱的范德华作用力，所以它们容易滑动，适合用来作润滑剂，而石墨处於高温时不容易挥发，所以适合在掘隧道时使用。



- 碳是钢的成分之一。
- 碳能形成大量化合物，在生物上和商业上是重要的分子。

Carbon cycle





Correlation between the carbon cycle and formation of organic compounds

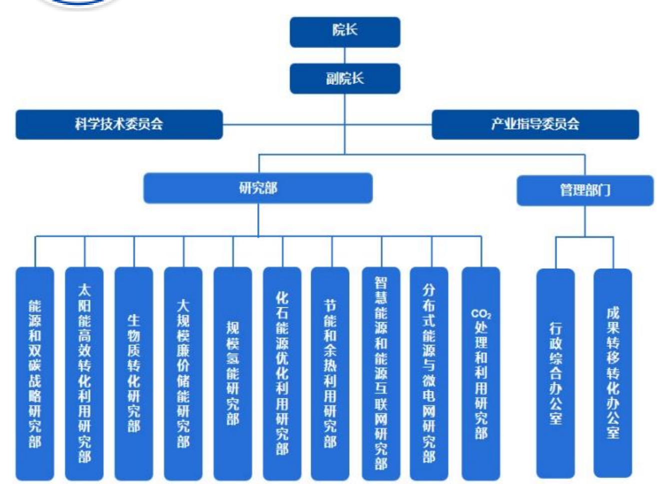
“双碳”战略目标

2020年9月22日，习近平主席在第75届联合国大会上发表重要讲话，提出我国将提高国家自主贡献力度，采取更加有力的政策和措施，二氧化碳排放力争于2030年前达到峰值，努力争取2060年前实现碳中和。这为我国应对气候变化、推动绿色发展提供了方向指引、擘画了宏伟蓝图，得到国际社会高度赞誉和广泛响应。

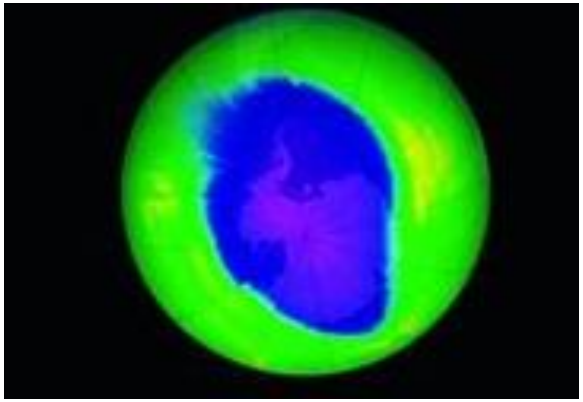
碳达峰和碳中和目标的提出，是党中央、国务院统筹国际国内两个大局作出的重大战略决策，彰显了我国走绿色低碳发展道路的坚定决心，为世界各国携手应对全球性挑战、共同保护好地球家园贡献了中国智慧和中国方案，体现了我国主动承担应对气候变化国际责任、推动构建人类命运共同体的大国担当。

碳中和（Carbon neutrality）是指企业、团体或个人测算在一定时间内，直接或间接产生的温室气体排放总量，通过植树造林、节能减排等形式，抵消自身产生的二氧化碳排放量，实现二氧化碳“零排放”。

中国科学技术大学碳中和研究院
USTC Institute for Carbon Neutrality

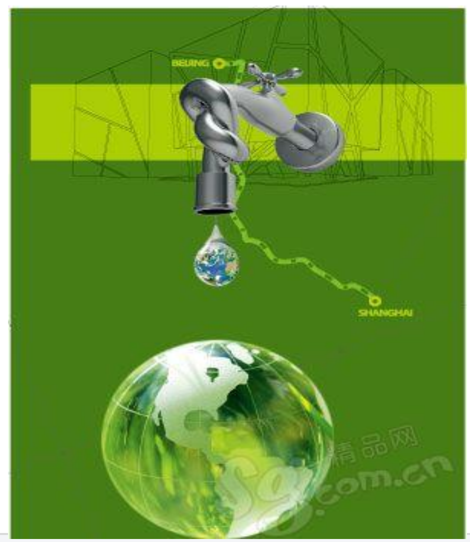


“低碳生活”(low-carbon life)



生活作息时所耗用的能量要尽量减少，从而减低碳，特别是二氧化碳的排放量，从而减少对大气的污染，减缓生态恶化，主要是从节电、节气和回收三个环节来改变生活细节。

低碳生活
从我做起!



low-carbon-life 专业低碳生活网站

检索

http://www.low-carbon-life.cn/

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一、General properties

- 根据σ键的数目，碳可采取sp、sp^2、sp^3杂化，其最大配位数为4
- 由于碳碳单键的键能特别大，所以C—C键非常稳定，具有形成均键(homochains)的倾向

	C—C	N—N	O—O	F—F
E (kJ·mol^{-1})	374	250	210	159
实　例	$H_3C—CH_3$	$H_2N—NH_2$	HO—OH	

※从碳到氮的单键键能的突减，是由于氮原子非键电子对排斥的缘故。

碳的成键形式

成键形式	价键结构		化合物举例
sp^3杂化 4个单键	$-\overset{\vert}{\underset{\vert}{C}}-$	正四面体	
sp^2杂化，2个单键，1个双键	$>C=$	平面三角形	
sp杂化，1个单键，1个叁键	$-C\equiv$	直线形	
sp杂化, 1个叁键, 1个孤电子对	$:C\equiv$	直线形	

二、Simple substance

1. 在第二周期中，**F**、**O**、**N**都以双原子分子存在

— F_2、O_2和N_2；而碳则存在多聚物?

∵ O_2和N_2的多重键要比**σ**单键(均键)强得多，而C_2分子中的多重键比均链中的两个**σ**单键之和小

如：	$\mathrm{O}\stackrel{\cdots}{\underset{\cdots}{-}}\mathrm{O}$		—O—O—O—	，	N≡N		—N—N—N—
E (kJ·mol^{-1})	494	>	210 + 210	，	946	>	250 + 250
而：	C═C		—C—C—C—				
E (kJ·mol^{-1})	627	<	374 + 374				

∴ 碳往往形成多原子均键，虽然在星际空间存在有C_2(g)分子

2. Allotropes（同素异形体）：

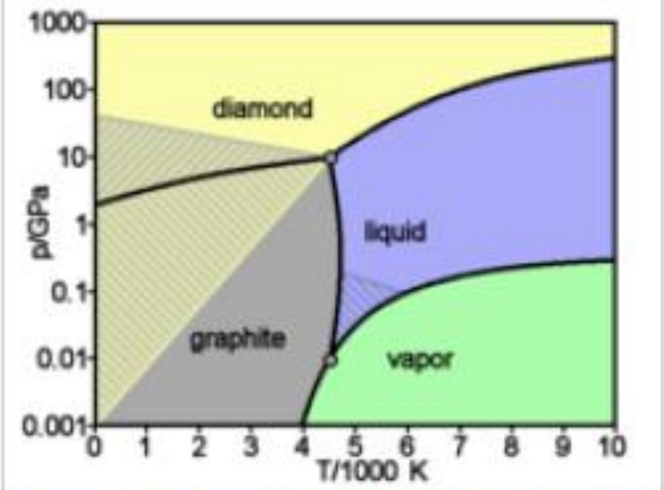
diamond, graphite, fullerene, carbon nanotube, graphene, graphdiyne, carbin (carbon fibers)

(1) 熵: $S_{carbin} > S_{graphite} > S_{diamond}$

(2) $d_{C\text{-}C}$ (nm): diamond > graphite > carbin

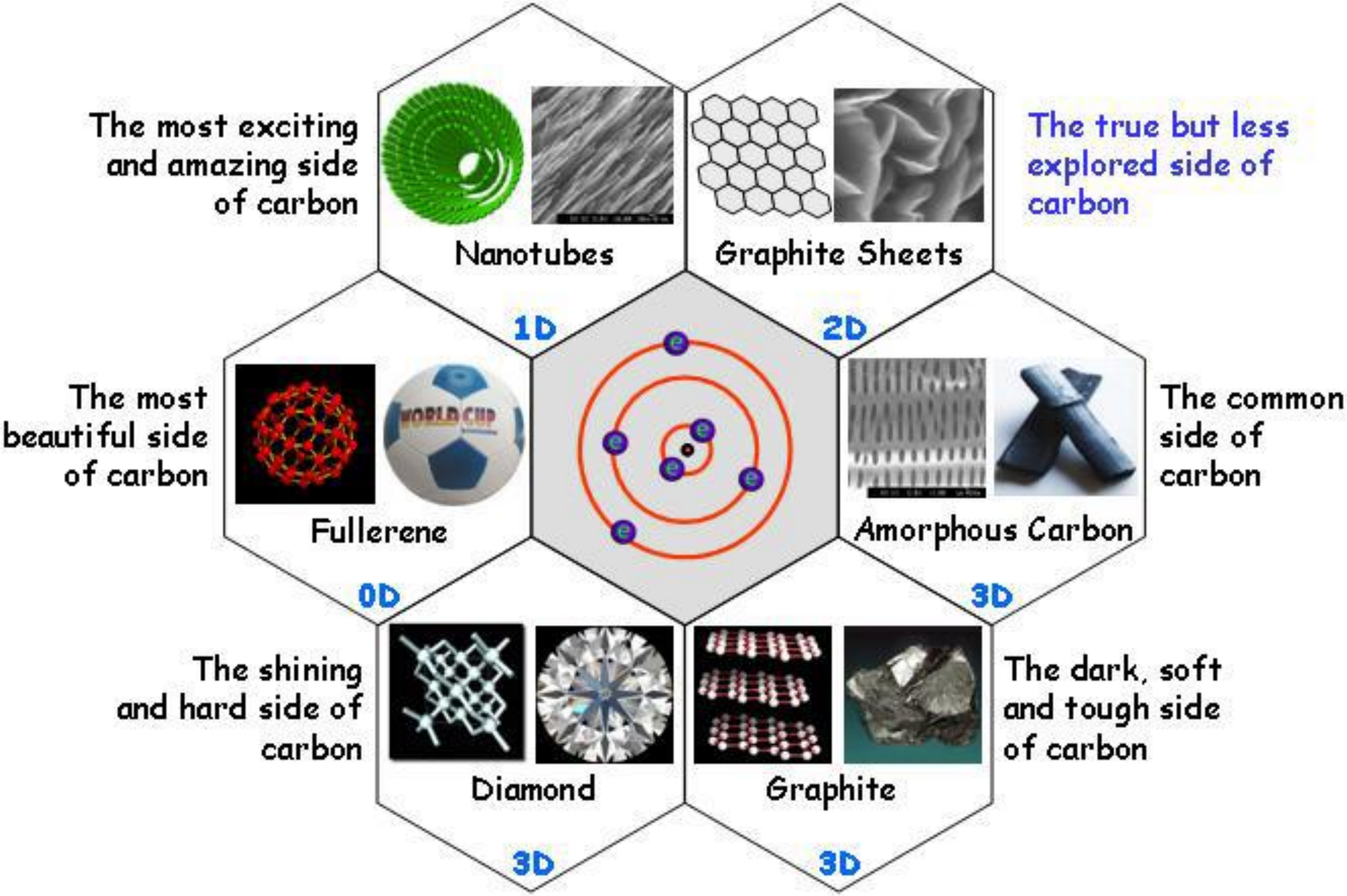
(3) $C_{graphite} \longrightarrow C_{diamond}$ $\Delta H > 0$ $\Delta S < 0$

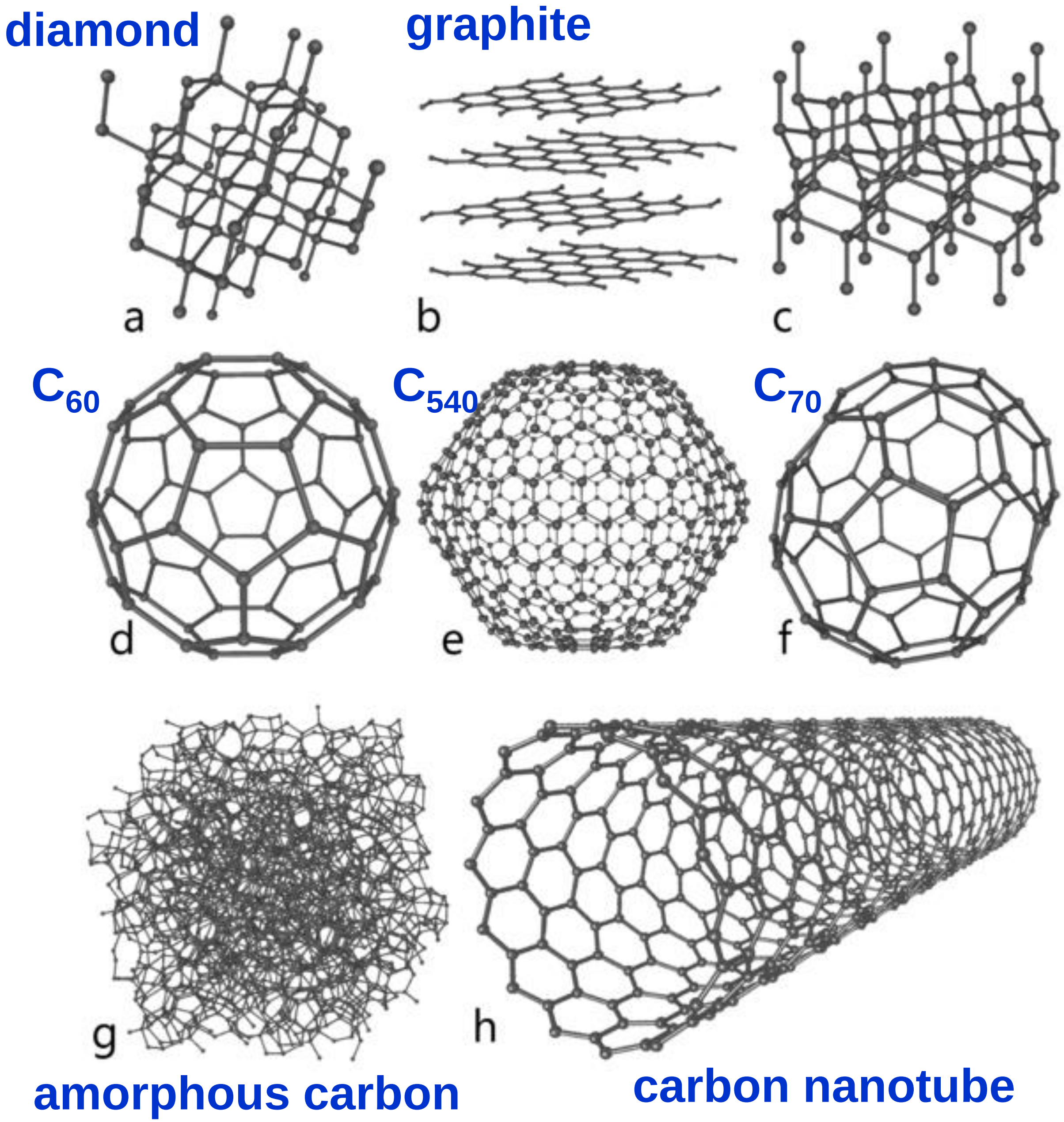
根据平衡，需要高压6×10^{9}—1×10^{10}Pa，升高温度不利于平衡的移动，但为了达到该过程可以接受的速率，反应温度大约在2000℃。近来已发明一种低压生产金刚石的方法：把金刚石晶种(seed)放在气态碳氢化合物（甲烷methane, 乙烷ethane）中，温度升高到1000℃,可以得到金刚石粉末或者crystal whiskers。



Theoretically predicted phase diagram of carbon

The carbon family




diamond
graphite
a
b
c
C_{60}
C_{540}
C_{70}
d
e
f
g
h
amorphous carbon
carbon nanotube

The system of carbon allotropes spans a range of extremes

Synthetic nanocrystalline diamond is the hardest material known.[19]	Graphite is one of the softest materials known.
Diamond is the ultimate abrasive.	Graphite is a very good lubricant, displaying superlubricity.[20]
Diamond is an excellent electrical insulator.[21]	Graphite is a conductor of electricity.[22]
Diamond is the best known naturally occurring thermal conductor	Some forms of graphite are used for thermal insulation (i.e. firebreaks and heat shields)
Diamond is highly transparent.	Graphite is opaque.
Diamond crystallizes in the cubic system.	Graphite crystallizes in the hexagonal system.[23]
Amorphous carbon is completely isotropic.	Carbon nanotubes are among the most anisotropic materials ever produced.

※ 两个Nobel Prizes!

从“卖炭翁”到“卖纳米碳商”

卖炭翁

朝代：唐代
作者：白居易
原文：

卖炭翁,伐薪烧炭南山中。

满面尘灰烟火色，两鬓苍苍十指黑。

卖炭得钱何所营？身上衣裳口中食。

可怜身上衣正单，心忧炭贱愿天寒。

夜来城外一尺雪，晓驾炭车辗冰辙。

牛困人饥日已高，市南门外泥中歇。

翩翩两骑来是谁？黄衣使者白衫儿。

手把文书口称敕，回车叱牛牵向北。

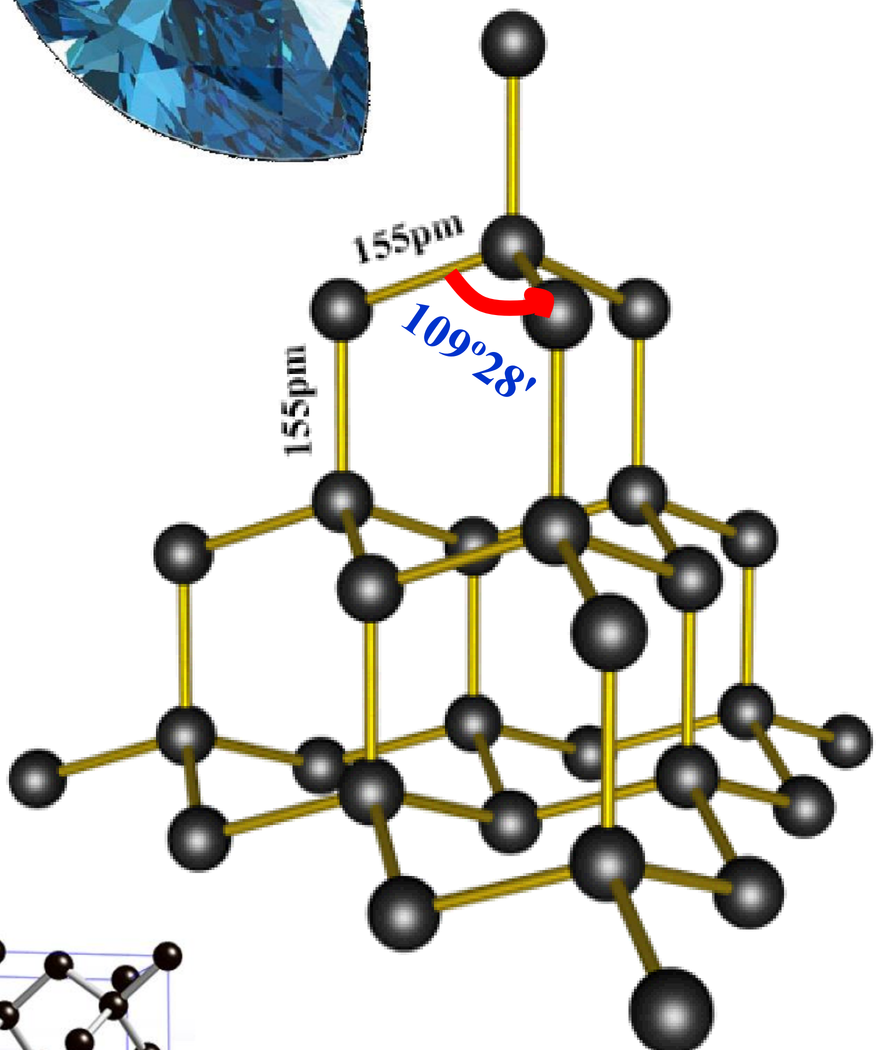
一车炭，千余斤，宫使驱将惜不得。

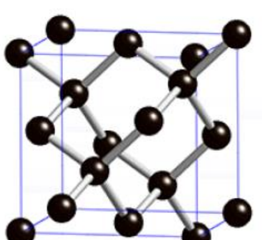
半匹红绡一丈绫，系向牛头充炭直。

http://www.nano-c.com/

http://www.dadec60.com/

金刚石





- 原子晶体，C：sp^3等性杂化，所有价电子都参与了共价键的形成。⇒硬度大、熔点高；

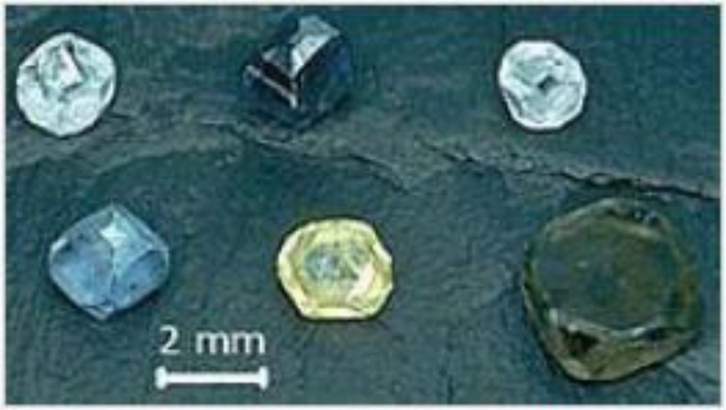
- 晶体中没有自由电子，因此不导电。

- 室温下对所有化学试剂显惰性。但在空气中加热到1100K左右燃烧生成CO_2。

用途：钻石、装饰品，钻头，磨削工具。

Synthetic diamonds: HPHT

The majority of commercially available synthetic diamonds are yellow and are produced by so called High Pressure High Temperature (HPHT) processes. The yellow color is caused by nitrogen impurities. Other colors may also be reproduced such as blue, green or pink

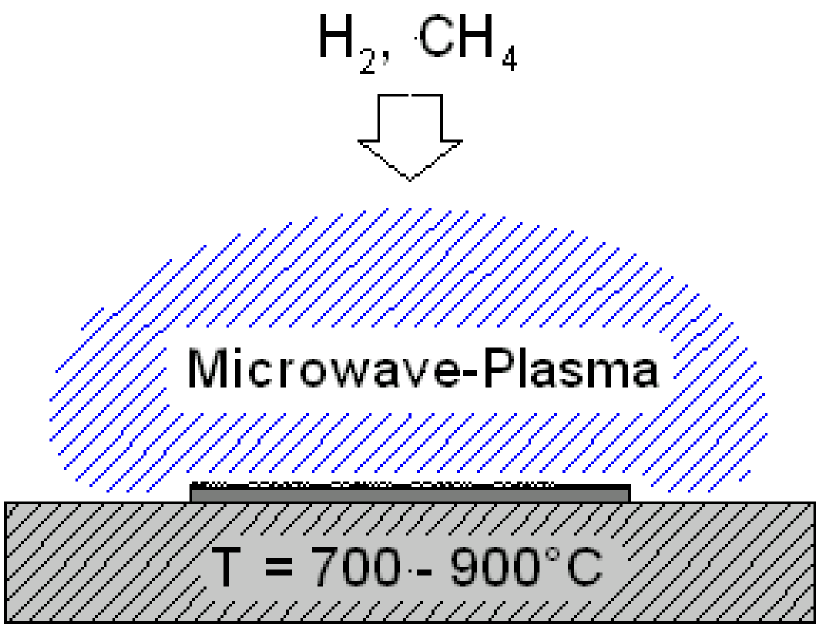


Synthetic diamonds of various colors grown by the high-pressure high-temperature technique

CVD technique for diamond growth

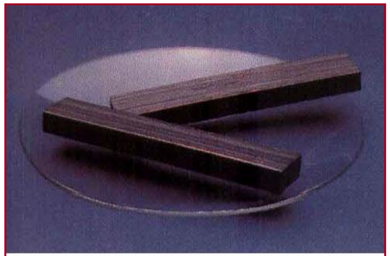
➢ The excellent mechanical, thermal, optical and insulating properties of diamond became accessible through the advent of **low pressure Chemical Vapour Deposition (CVD)** techniques which allow diamond in the form of extended films and free-standing wafers to be fabricated.

➢ The fundamental problem of diamond synthesis is the allotropic nature of carbon. Under ordinary conditions graphite, not diamond, is the thermodynamically stable crystalline phase of carbon. Hence, **the main requirement of diamond CVD is to deposit carbon and simultaneously suppress the formation of graphitic sp²-bonds**. This can be realized by establishing high concentrations of non-diamond carbon etchants such as atomic hydrogen. Usually, those conditions are achieved by admixing large amounts of hydrogen to the process gas and by activating the gas either thermally or by a plasma.

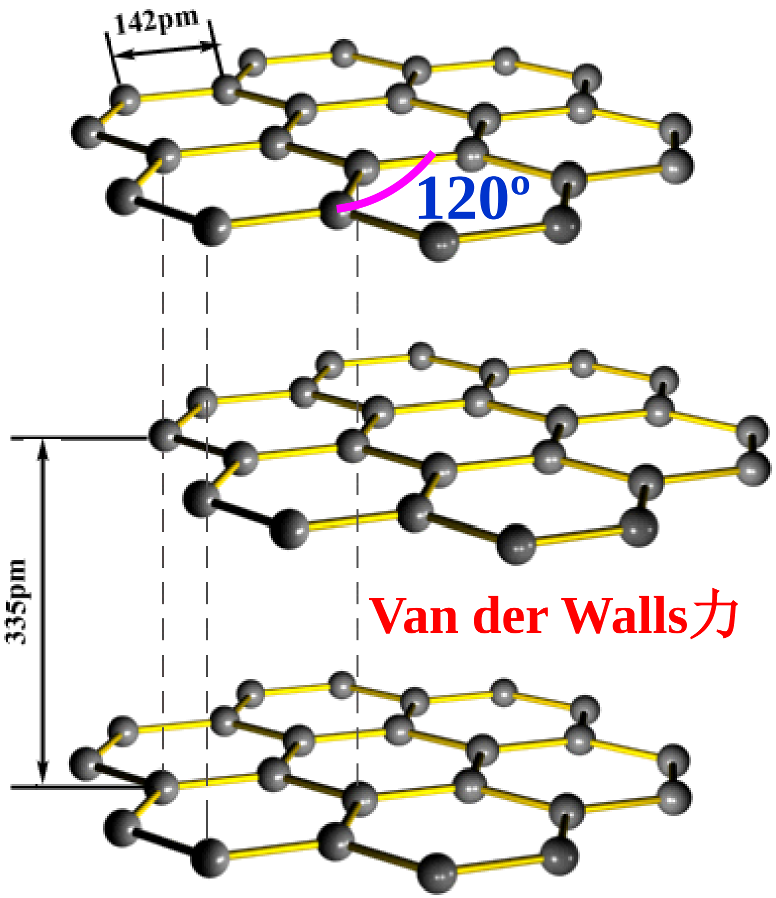


Colorless gem cut from diamond grown by chemical vapor deposition

石墨

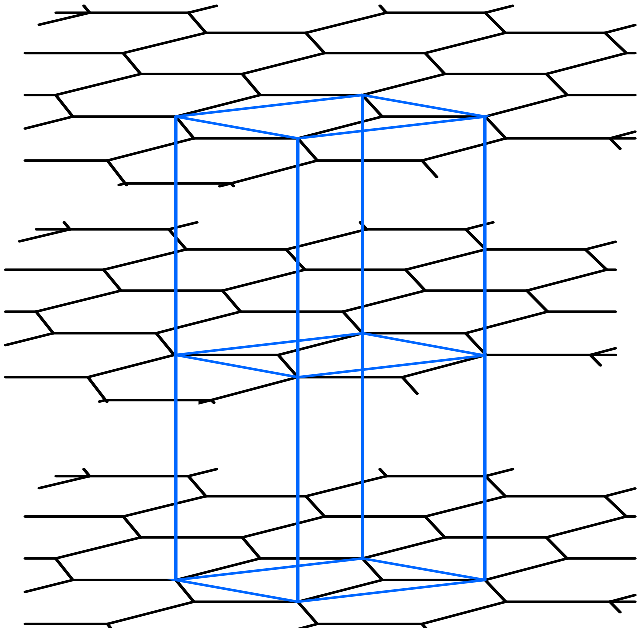


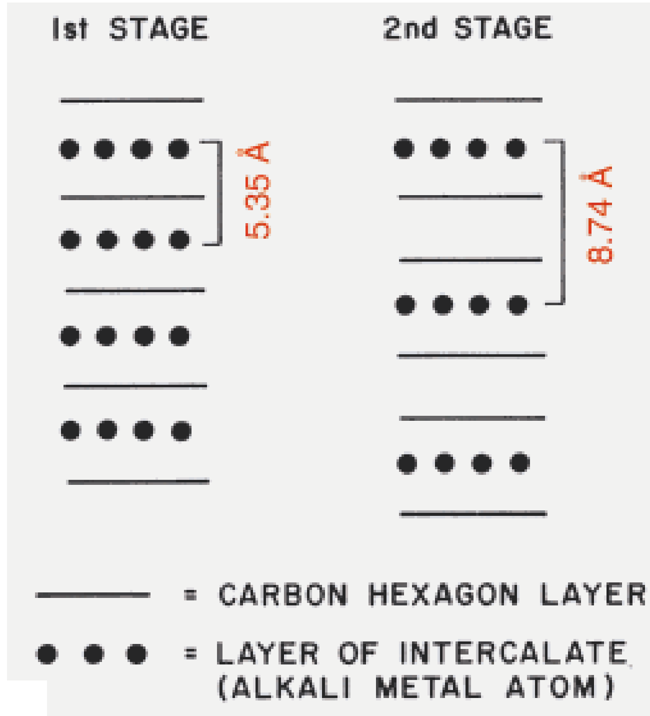
石墨

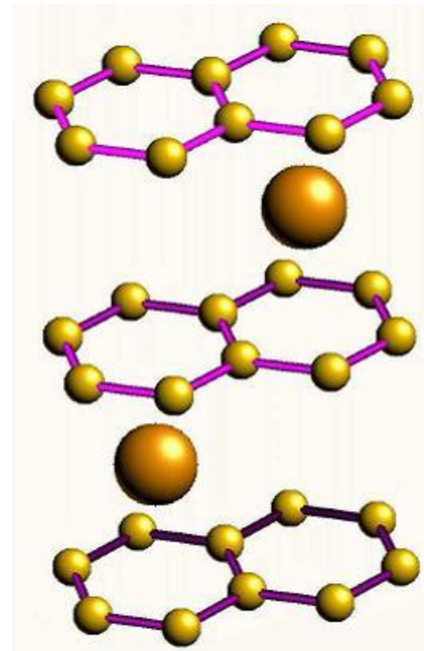


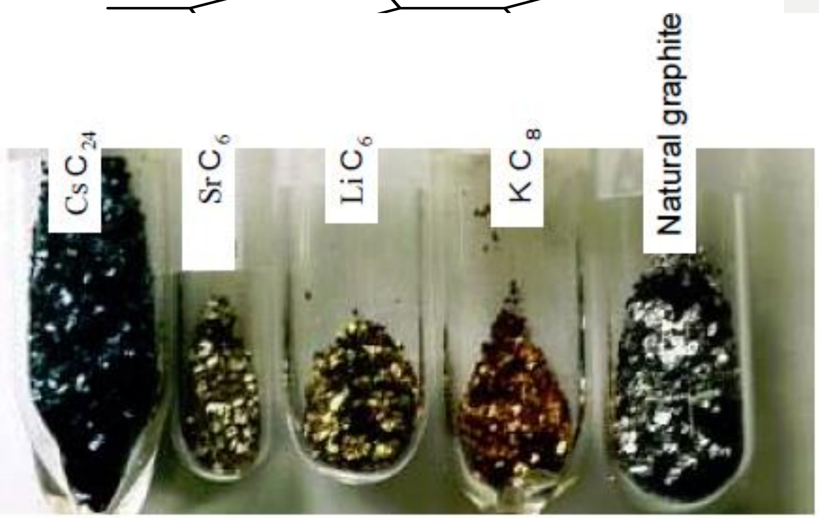
- 碳原子以 sp^2 杂化，形成片层结构 。
- 硬度较小，熔点较高，表现出一定程度的化学活性。
- 每个碳原子的未参与杂化的 *p* 电子，形成大 Π_m^m 键。这些离域电子使得**石墨具有良好导电性**。层间的分子间作用力很弱，所以层间易于滑动，故石墨质软具有润滑性。
- 可制作电极、热电偶、坩锅、铅笔芯等。

Graphite Intercalation Compounds (GICs)

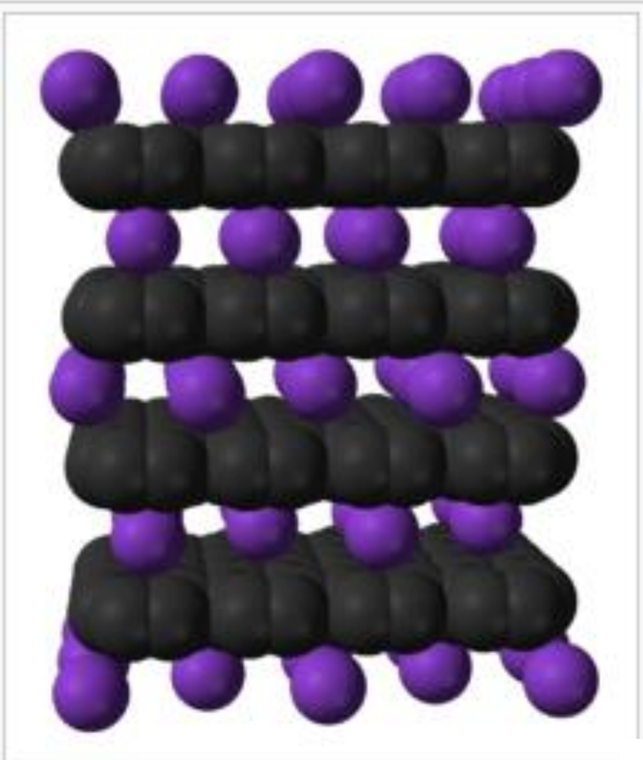




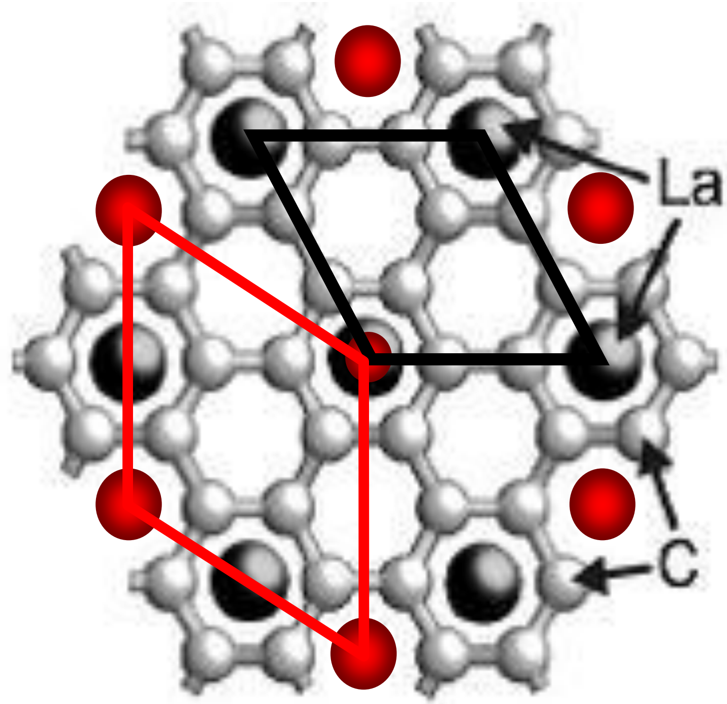


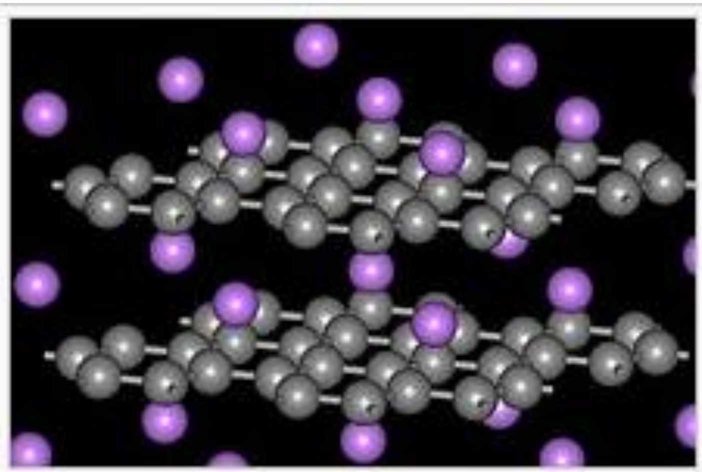


Graphite Intercalation Compounds (GICs)



Space-filling model of potassium graphite KC_8 (side view)





Structure of CaC_6

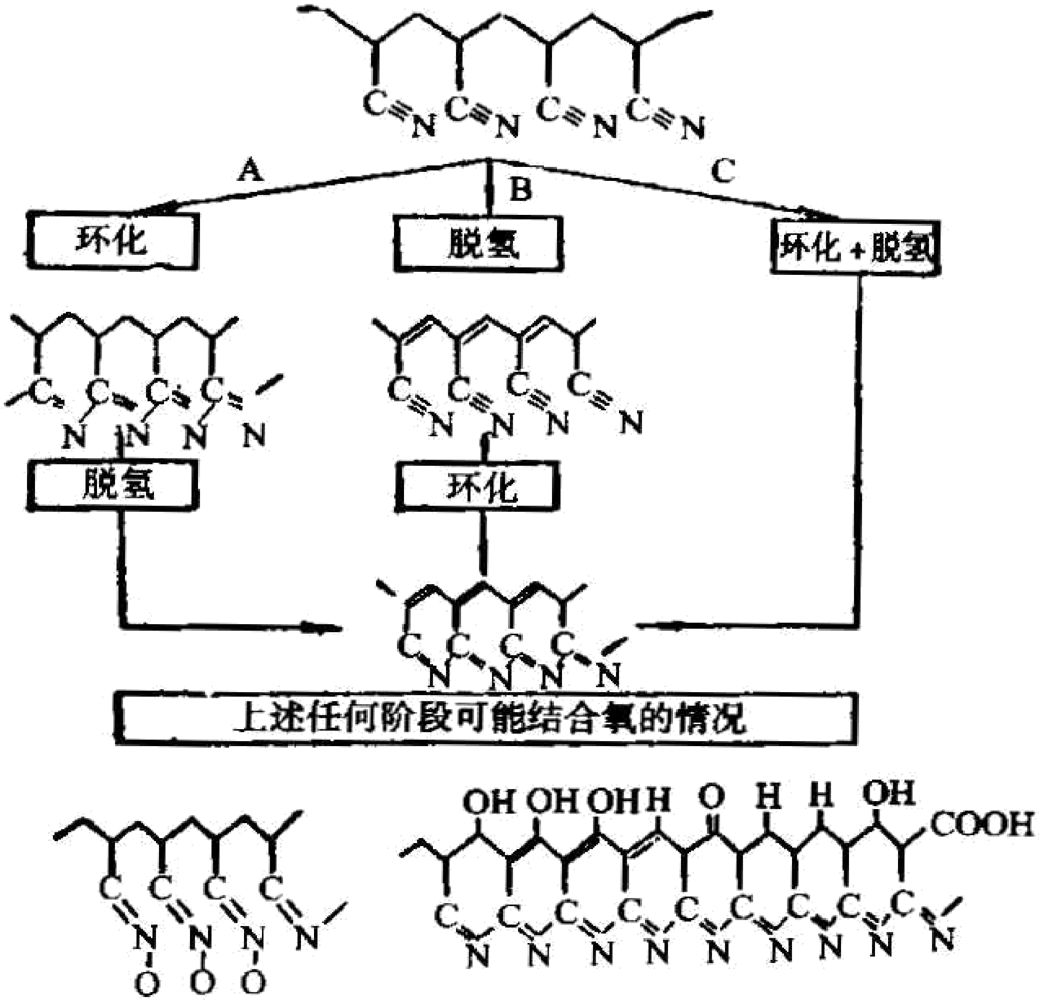
碳纤维 (carbin, carbon fibers)

由有机纤维经炭化及石墨化处理而得到的微晶石墨材料。碳纤维的微观结构类似人造石墨。**不仅具有碳材料的固有本征特性，又兼具纺织纤维的柔软可加工性**，是新一代增强纤维.

- **制备**

目前应用较普遍的碳纤维主要是**聚丙烯腈碳纤维和沥青碳纤维**。

碳纤维的制造包括纤维纺丝、热稳定化(预氧化)、炭化及石墨化等4个过程。其间伴随的化学变化，包括脱氢、环化、氧化及脱氧等。



➢ 性质及其应用

◆ 碳纤维具有模量高、强度大、密度小、耐高温、抗疲劳、抗腐蚀、自润滑等优异性能。从航天、航空、航海等高技术产业到汽车、建筑、轻工等民用工业的各个领域正逐渐得到越来越广泛的应用。主要用于导电、隔热、过滤等方面。

◆ 碳纤维增强复合材料作结构材料, 可作飞机的尾翼或副翼, 通信卫星的天线系统和导波管、航天飞机的货舱门、燃料箱、助推火箭的外壳。在建筑方面，可作碳纤维增强水泥地板，并有取代钢筋的可能性。

◆ 作为非结构材料, 碳纤维复合材料可作密封材料、耐磨材料、隔热材料、电极材料。

◆ 在原子能工程上用碳纤维－石墨复合材料作铀棒的幕墙材料, 不仅可以防止铀棒的辐射变形, 使其对中子的吸收截面变小, 反射中子能力增强, 而且在光氧条件下能耐3000 ℃以上的高温。

◆ 碳纤维复合材料可作优质的化工容器、设备或零部件。

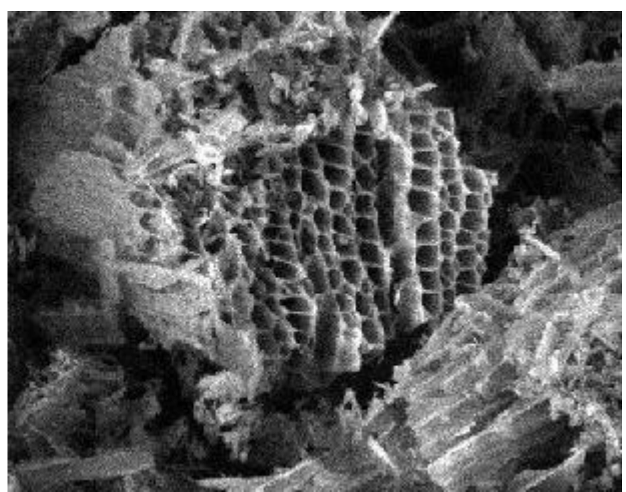
◆ 将碳纤维进行活化处理，得到活性碳纤维，是已知的比表面积最大的物质之一(2500 $m^2 \cdot g^{-1}$)，被称为第3代活性炭，作为新型吸附剂具有重要的应用前景。

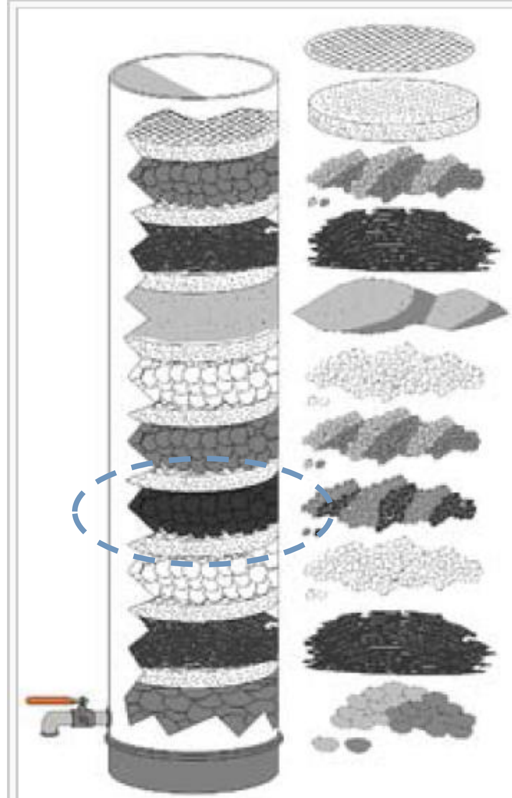
◆ 在医学上，碳纤维增强型塑料是一种理想的人工心肺管道材料，也可作人工关节、假肢、假牙等。

活性炭 (Activated carbon, activated charcoal, activated coal)

黑色粉末状或颗粒状的无定形碳。活性炭主成分除了碳以外还有氧、氢等元素。活性炭在结构上由于微晶碳是不规则排列，在交叉连接之间有细孔，在活化时会产生碳组织缺陷，因此它是一种多孔炭，堆积密度低，比表面积大。

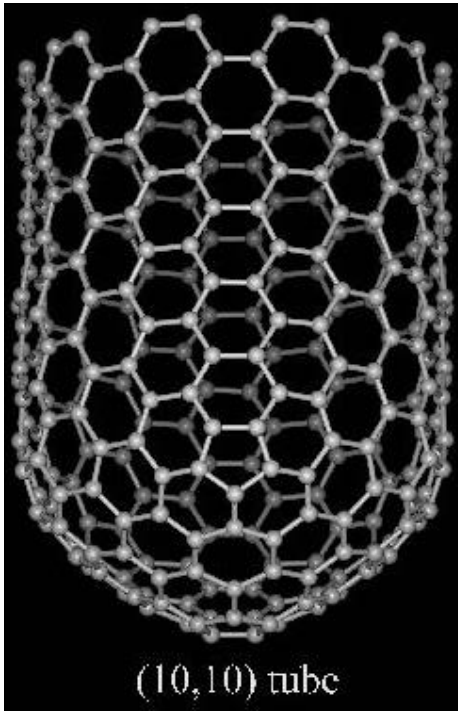
- 粉末炭可用于液相脱色，脱臭精制，上下水净化。
- 粒状炭应用于气相吸附，溶剂回收，空气净化，香烟滤嘴，此外还可用于氯乙烯、醋酸乙烯合成催化剂，贵金属催化剂的载体





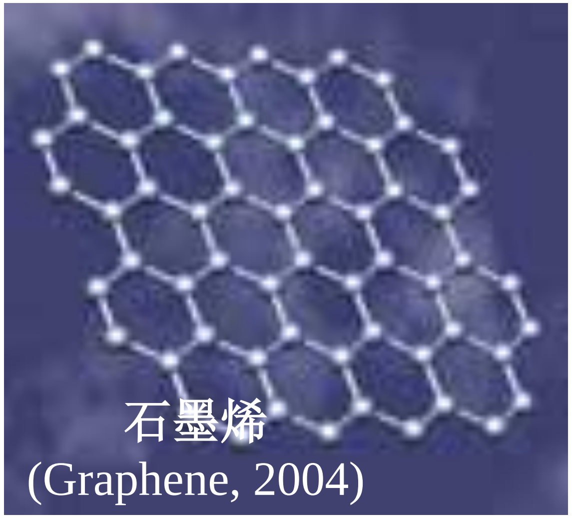
Activated carbon is usually used in water filtration systems. In this illustration, the activated carbon is in the fourth level (counted from bottom).

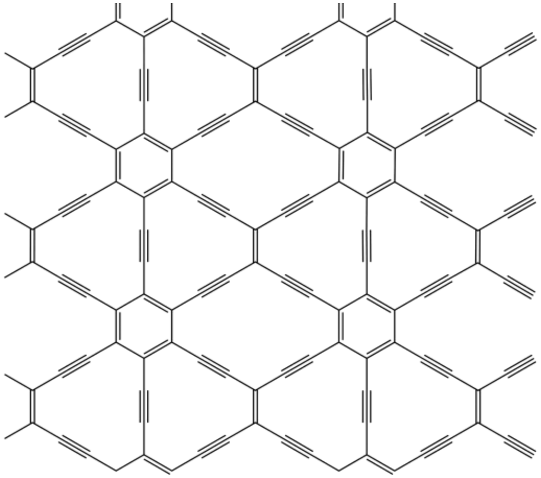
Nanocarbons



碳纳米管
(Carbon Nanotube, 1991)

Source:
Smalley group, Rice Univ.



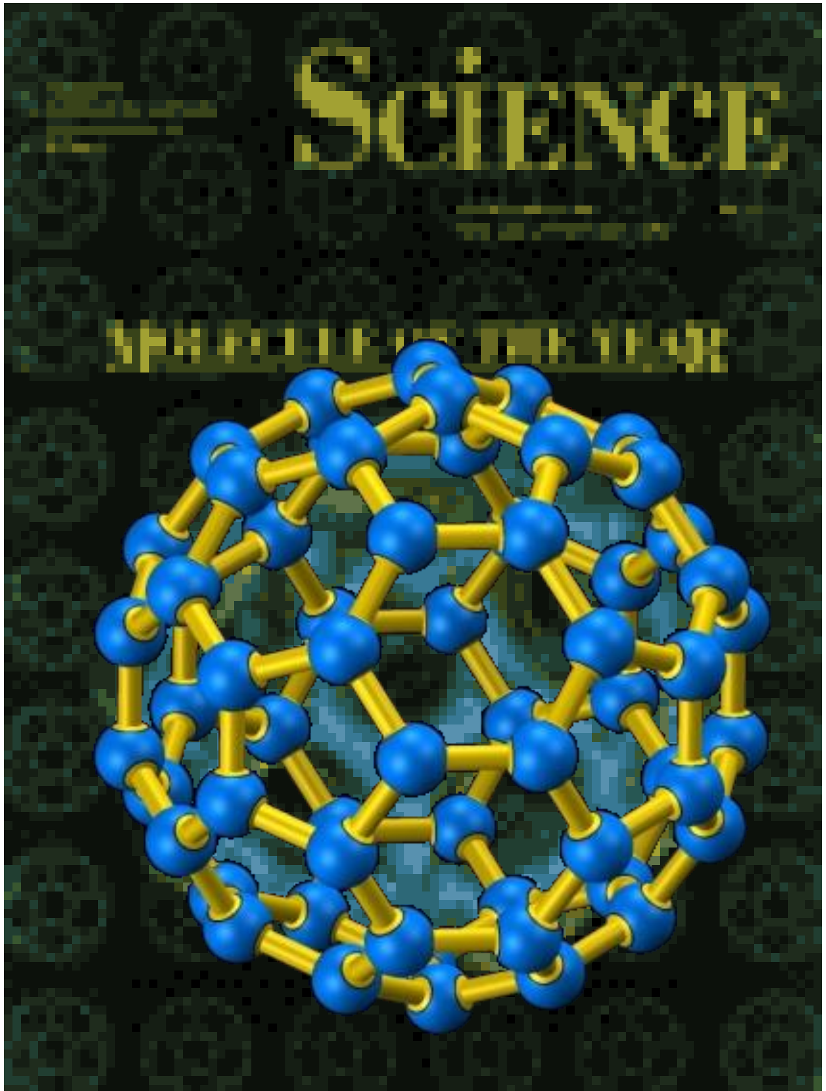


石墨炔
(Graphdiyne/Graphyne, 2010)

D. Malko, et al. *PRL* 108, 086804 (2012)

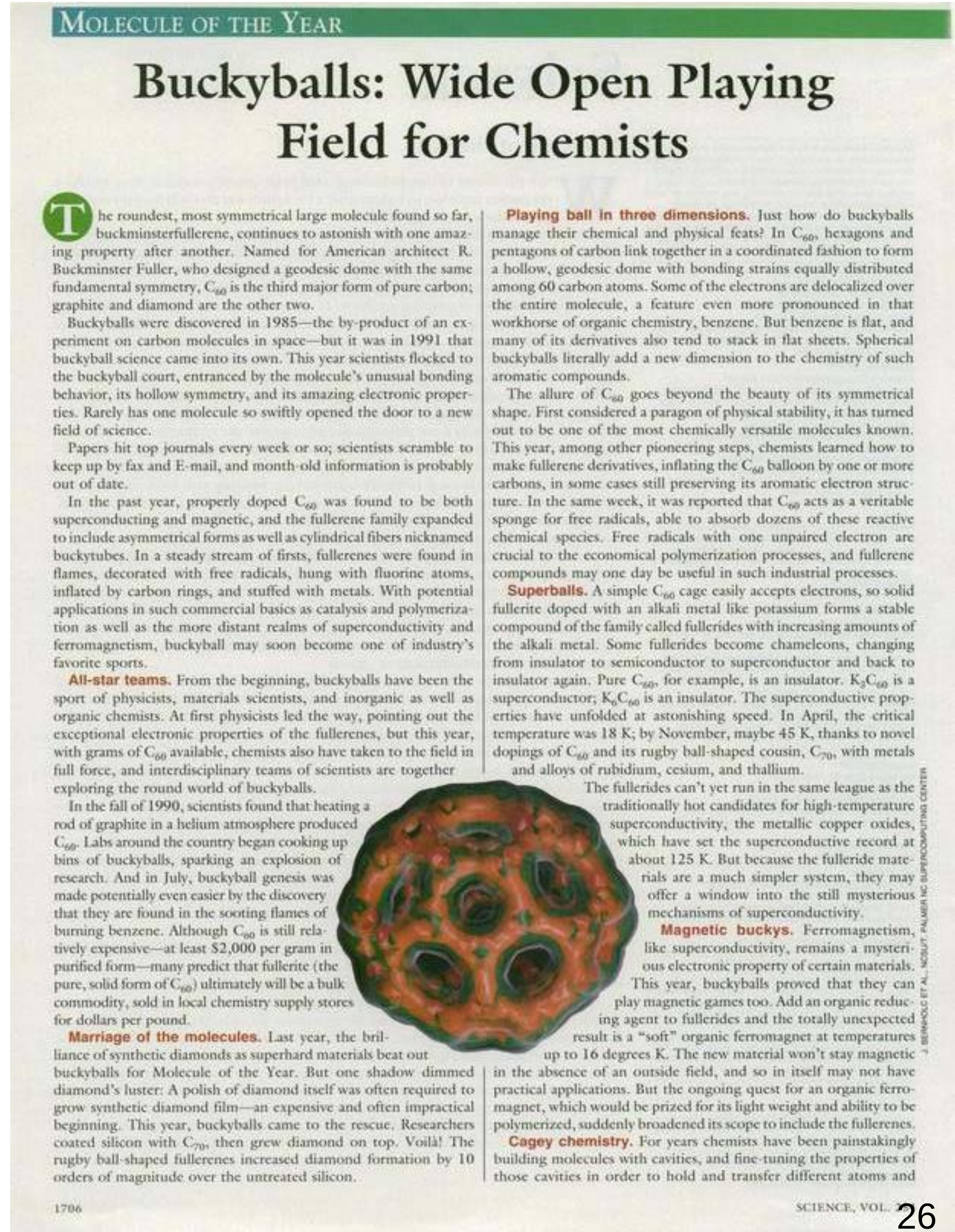
(*http://www.ewels.info/img/science/graphite/index.html*)

Fullerenes (富勒烯)



1991年被Science评为‘年度明星分子’

Science **1991,** ***254*****, 1706.**



MOLECULE OF THE YEAR

Buckyballs: Wide Open Playing Field for Chemists

The roundest, most symmetrical large molecule found so far, buckminsterfullerene, continues to astonish with one amazing property after another. Named for American architect R. Buckminster Fuller, who designed a geodesic dome with the same fundamental symmetry, C_{60} is the third major form of pure carbon; graphite and diamond are the other two.

Buckyballs were discovered in 1985—the by-product of an experiment on carbon molecules in space—but it was in 1991 that buckyball science came into its own. This year scientists flocked to the buckyball court, entranced by the molecule's unusual bonding behavior, its hollow symmetry, and its amazing electronic properties. Rarely has one molecule so swiftly opened the door to a new field of science.

Papers hit top journals every week or so; scientists scramble to keep up by fax and E-mail, and month-old information is probably out of date.

In the past year, properly doped C_{60} was found to be both superconducting and magnetic, and the fullerene family expanded to include asymmetrical forms as well as cylindrical fibers nicknamed buckytubes. In a steady stream of firsts, fullerenes were found in flames, decorated with free radicals, hung with fluorine atoms, inflated by carbon rings, and stuffed with metals. With potential applications in such commercial basics as catalysis and polymerization as well as the more distant realms of superconductivity and ferromagnetism, buckyball may soon become one of industry's favorite sports.

All-star teams. From the beginning, buckyballs have been the sport of physicists, materials scientists, and inorganic as well as organic chemists. At first physicists led the way, pointing out the exceptional electronic properties of the fullerenes, but this year, with grams of C_{60} available, chemists also have taken to the field in full force, and interdisciplinary teams of scientists are together exploring the round world of buckyballs.

In the fall of 1990, scientists found that heating a rod of graphite in a helium atmosphere produced C_{60}. Labs around the country began cooking up bins of buckyballs, sparking an explosion of research. And in July, buckyball genesis was made potentially even easier by the discovery that they are found in the sooting flames of burning benzene. Although C_{60} is still relatively expensive—at least $2,000 per gram in purified form—many predict that fullerite (the pure, solid form of C_{60}) ultimately will be a bulk commodity, sold in local chemistry supply stores for dollars per pound.

Marriage of the molecules. Last year, the brilliance of synthetic diamonds as superhard materials beat out buckyballs for Molecule of the Year. But one shadow dimmed diamond's luster: A polish of diamond itself was often required to grow synthetic diamond film—an expensive and often impractical beginning. This year, buckyballs came to the rescue. Researchers coated silicon with C_{70}, then grew diamond on top. Voilà! The rugby ball-shaped fullerenes increased diamond formation by 10 orders of magnitude over the untreated silicon.

Playing ball in three dimensions. Just how do buckyballs manage their chemical and physical feats? In C_{60}, hexagons and pentagons of carbon link together in a coordinated fashion to form a hollow, geodesic dome with bonding strains equally distributed among 60 carbon atoms. Some of the electrons are delocalized over the entire molecule, a feature even more pronounced in that workhorse of organic chemistry, benzene. But benzene is flat, and many of its derivatives also tend to stack in flat sheets. Spherical buckyballs literally add a new dimension to the chemistry of such aromatic compounds.

The allure of C_{60} goes beyond the beauty of its symmetrical shape. First considered a paragon of physical stability, it has turned out to be one of the most chemically versatile molecules known. This year, among other pioneering steps, chemists learned how to make fullerene derivatives, inflating the C_{60} balloon by one or more carbons, in some cases still preserving its aromatic electron structure. In the same week, it was reported that C_{60} acts as a veritable sponge for free radicals, able to absorb dozens of these reactive chemical species. Free radicals with one unpaired electron are crucial to the economical polymerization processes, and fullerene compounds may one day be useful in such industrial processes.

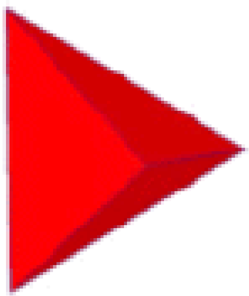
Superballs. A simple C_{60} cage easily accepts electrons, so solid fullerite doped with an alkali metal like potassium forms a stable compound of the family called fullerides with increasing amounts of the alkali metal. Some fullerides become chameleons, changing from insulator to semiconductor to superconductor and back to insulator again. Pure C_{60}, for example, is an insulator. K_3C_{60} is a superconductor; K_6C_{60} is an insulator. The superconductive properties have unfolded at astonishing speed. In April, the critical temperature was 18 K; by November, maybe 45 K, thanks to novel dopings of C_{60} and its rugby ball-shaped cousin, C_{70}, with metals and alloys of rubidium, cesium, and thallium.

The fullerides can't yet run in the same league as the traditionally hot candidates for high-temperature superconductivity, the metallic copper oxides, which have set the superconductive record at about 125 K. But because the fulleride materials are a much simpler system, they may offer a window into the still mysterious mechanisms of superconductivity.

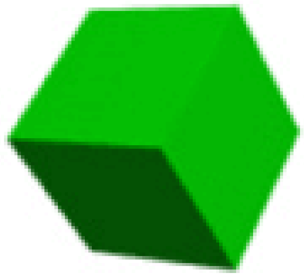
Magnetic buckys. Ferromagnetism, like superconductivity, remains a mysterious electronic property of certain materials. This year, buckyballs proved that they can play magnetic games too. Add an organic reducing agent to fullerides and the totally unexpected result is a "soft" organic ferromagnet at temperatures up to 16 degrees K. The new material won't stay magnetic in the absence of an outside field, and so in itself may not have practical applications. But the ongoing quest for an organic ferromagnet, which would be prized for its light weight and ability to be polymerized, suddenly broadened its scope to include the fullerenes.

Cagey chemistry. For years chemists have been painstakingly building molecules with cavities, and fine-tuning the properties of those cavities in order to hold and transfer different atoms and

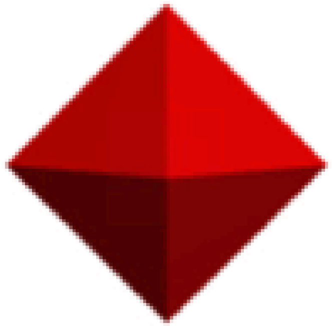
The Platonic Polydedra: f=2+e-v



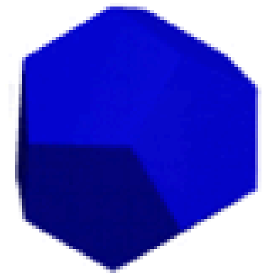
Tetrahedron



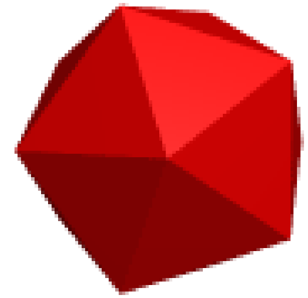
Cube



Octahedron



Dodecahedron



Icosahedron

- **Triangles.** The interior angle of an equilateral triangle is 60 degrees. Thus on a regular polyhedron, only 3, 4, or 5 triangles can meet a vertex. If there were more than 6 their angles would add up to at least 360 degrees which they can't. Consider the possibilities:
- **3 triangles** meet at each vertex. This gives rise to a **Tetrahedron.**
- **4 triangles** meet at each vertex. This gives rise to an **Octahedron.**
- **5 triangles** meet at each vertex. This gives rise to an **Icosahedron**
- **Squares.** Since the interior angle of a square is 90 degrees, at most three squares can meet at a vertex. This is indeed possible and it gives rise to a **hexahedron** or **cube**.
- **Pentagons.** As in the case of cubes, the only possibility is that three pentagons meet at a vertex. This gives rise to a **Dodecahedron.**
- **Hexagons** or regular polygons with more than six sides cannot form the faces of a regular polyhedron since their interior angles are at least 120 degrees.

重要知识点：

■ **Euler's theorem for fullerenes: F – E + V = 2**

F - faces, E - edges, V –vertices

(1) $E = 3V/2 \Rightarrow F+V-2=3V/2 \Rightarrow F=V/2+2$

(2) $F = p + h = V/2+2$

(3) $3V = 5p + 6h$ (where p and h are number of pentagonal and hexagonal faces, respectively)

(4) Let (2)x6-(3) $\Rightarrow$ $p=12$

$\Rightarrow h=V/2+2-p = V/2 - 10$

$V = 2(10 + h)$

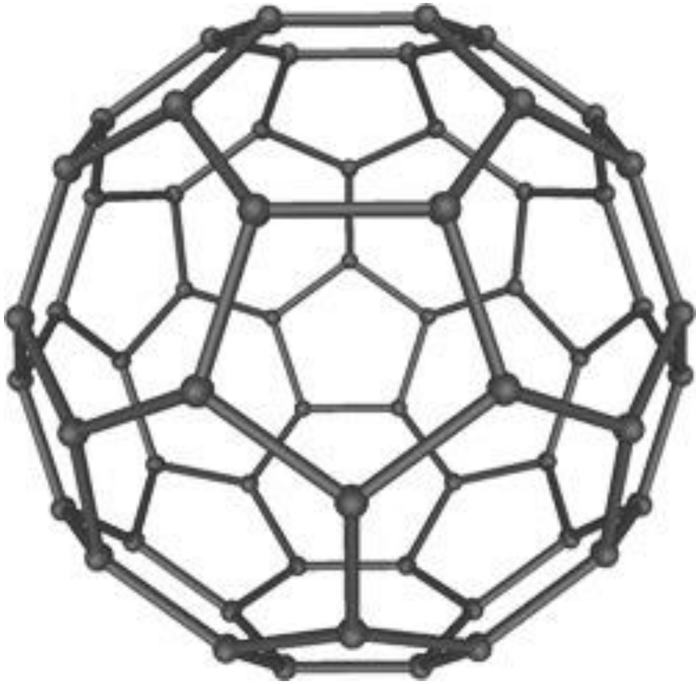
C20, C24, C28, …, C60, C70, C2(10+h) ...

C_{60}

12个正五边形 +

20个正六边形

- 每个碳原子以sp^2杂化轨道与相邻的三个碳原子相连，剩余的p轨道在C_{60}球壳的外围和内腔形成球面π键；
- 根据欧拉定理，通过12个五边形和数个六边形的连接可以形成封闭的多面体结构。



32个面，

60个顶点，

90条棱

F + V = E + 2

- C_{60}为第一个12个五边形互不相邻的封闭碳笼；
- 只有五边形没有六边形的最小碳笼为C_{20}。

Fullerene Discoverers Win Chemistry Nobel

by Science News Staff on 9 October 1996, 8:00 PM

The Nobel Prize in chemistry was awarded today to two Americans and one British researcher for their discovery of fullerenes, a new class of all-carbon molecules shaped like hollow balls.

The researchers, Richard E. Smalley and Robert F. Curl Jr. of Rice University in Houston, and Harold W. Kroto of the University of Sussex in Brighton, United Kingdom, made their discovery in 1985 in Smalley's lab at Rice while working together to study how carbon atoms cluster.

"**The award is richly deserved**," says Robert Haddon, a fullerene chemist at Lucent Technologies' Bell Labs in Murray Hill, New Jersey. "It led to a totally new field of chemistry." Today, fullerenes--which are popularly known as buckyballs--are being investigated for everything from new superconductors and three-dimensional polymers, to catalysts and optical materials, although they have yet to spawn any commercial applications.

Before the group's discovery, crystalline carbon was thought to adopt only a handful of different molecular architectures, including those found in diamond and graphite. But the researchers discovered that sheets of carbon atoms arranged in a pattern of hexagons and pentagons can curl up and ultimately close to form hollow cages. And because the number of atoms in the cage can vary, an almost infinite number of fullerene shapes may exist.

Nobelprize.org

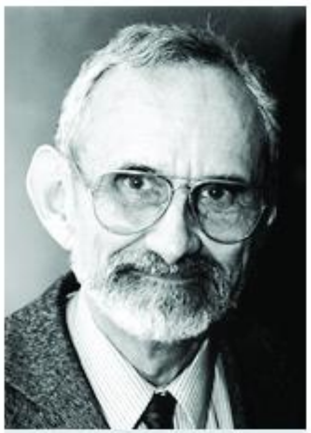
NOBEL PRIZES | ALFRED NOBEL | PRIZE AWARDERS | NOMINATION | PRIZE ANNOUNCEMENT

By Year | Nobel Prize in Physics | **Nobel Prize in Chemistry** | Nobel Prize in Medicine | Nobe

Chemistry

The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"



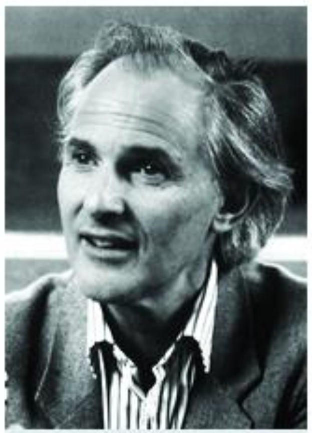
Robert F. Curl Jr.

1/3 of the prize

USA

Rice University
Houston, TX, USA

b. 1933
d. 2022



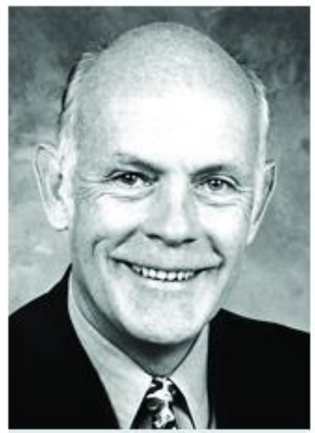
Sir Harold W. Kroto

1/3 of the prize

United Kingdom

University of Sussex
Brighton, United Kingdom

b. 1939
d. 2016



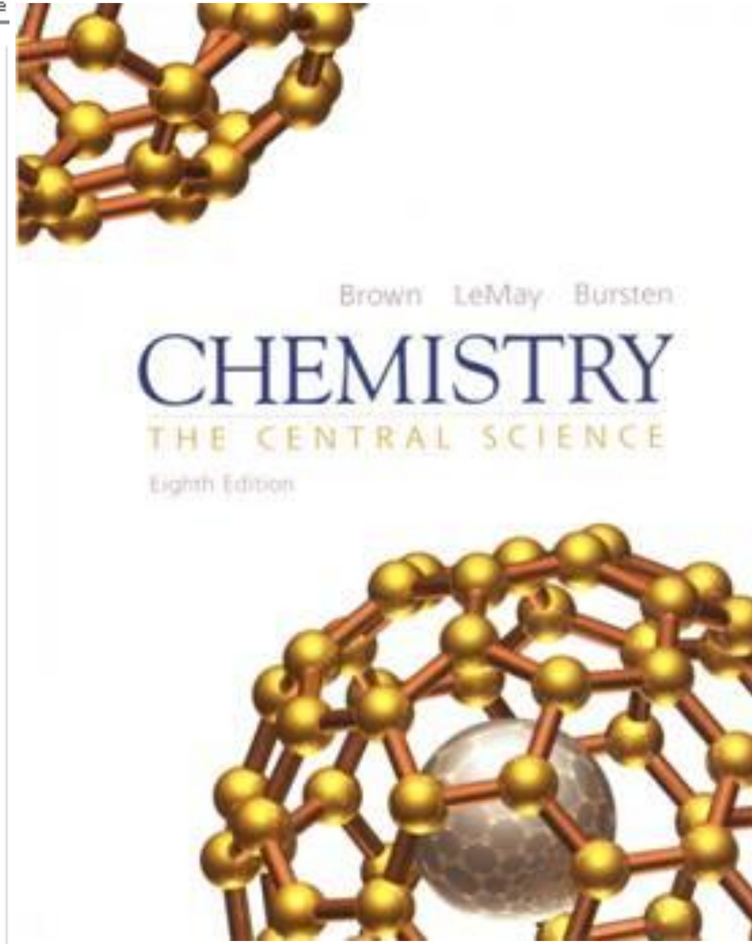
Richard E. Smalley

1/3 of the prize

USA

Rice University
Houston, TX, USA

b. 1943
d. 2005

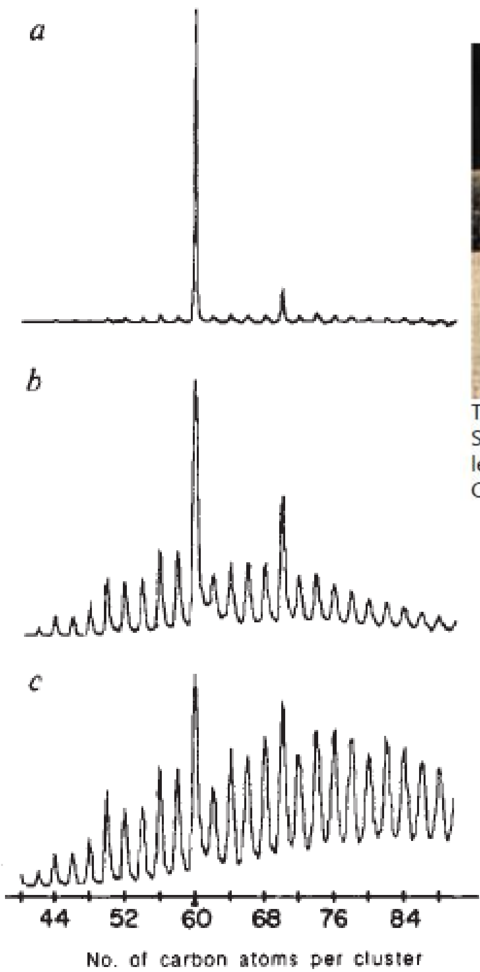


Discovery of C_{60} (Smalley group, Rice Univ.)

162 LETTERS TO NATURE NATURE VOL. 318 14 NOVEMBER 1985

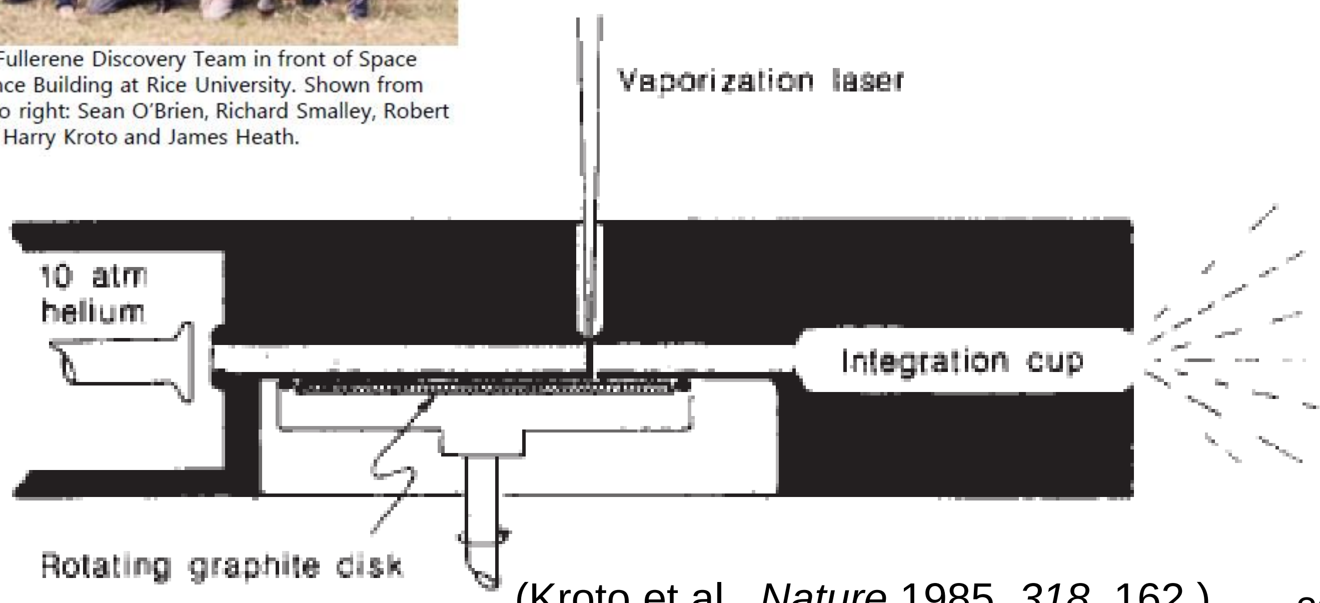
C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley



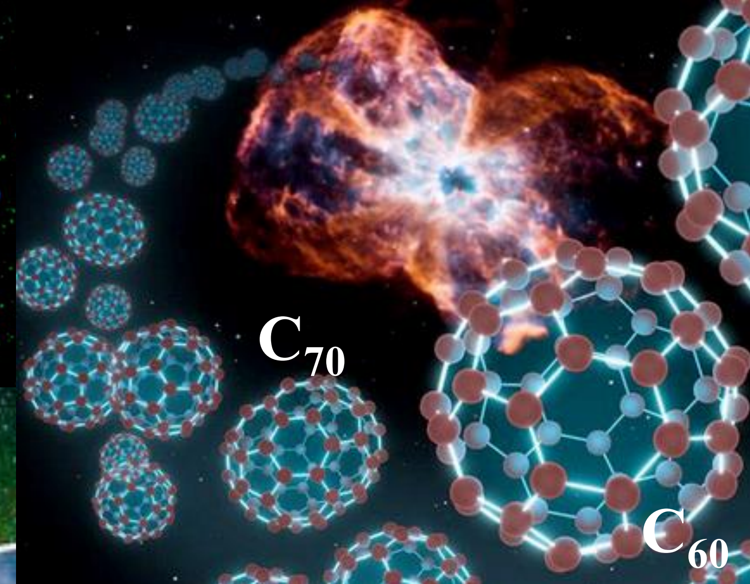
The Fullerene Discovery Team in front of Space Science Building at Rice University. Shown from left to right: Sean O'Brien, Richard Smalley, Robert Curl, Harry Kroto and James Heath.

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



(Kroto et al., *Nature* 1985, *318*, 162.)

富勒烯：人间奇迹，
还是 天外来客？



REPORTS

Detection of C_{60} and C_{70} in a Young Planetary Nebula

Jan Cami,[1,2]* Jeronimo Bernard-Salas,[3,4] Els Peeters,[1,2] Sarah Elizabeth Malek[1]

J. Cami *et al Science*, **2010**, *329*, 1180.

Symmetry and stability

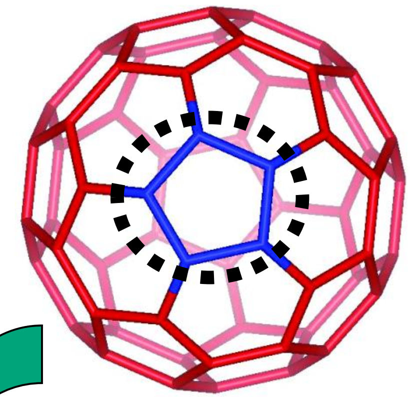
- EULER'S polyhedron theorem (ca. 1750):

  vertices + faces – edges = 2

⇒ For a closed cage, always 12 pentagons needed

- Pentagons determines the curvature of the surface (*adjacent pentagons are not stable, too much bending !*)

→ C_{60}: the smallest stable fullerene

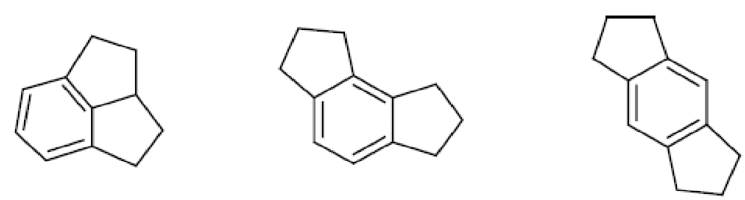


Isolated-**P**entagon-**R**ule

(“独立五元环” 规则)

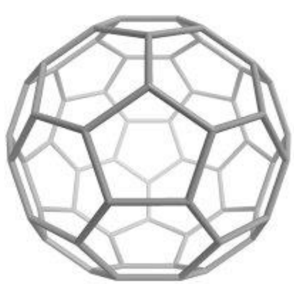
Stable fullerene !

“**isolated pentagon rule (IPR)**”

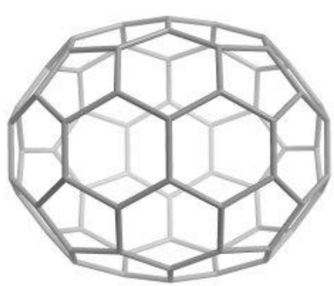


IPR forbidden IPR favored

(Kroto, H., Nature **1987**, *329*, 529.)



C_{60}



C_{70} ……

Isolated-**P**entagon-**R**ule
(“独立五元环” 规则)

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
J. Am. Chem. Soc. 2017, 139, 4651−4654
pubs.acs.org/JACS

Skeletal Transformation of a Classical Fullerene C_{88} into a Nonclassical Fullerene Chloride $C_{84}Cl_{30}$ Bearing Quaternary Sequentially Fused Pentagons

Fei Jin,[†] Shangfeng Yang,*[,†] Erhard Kemnitz,*[,‡] and Sergey I. Troyanov*[,§]

[†]Hefei National Laboratory for Physical Sciences at Microscale, Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences, Department of Materials Science and Engineering, Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China (USTC), Hefei 230026, China
[‡]Institute of Chemistry, Humboldt University Berlin Brook-Taylor-Straße 2, 12489 Berlin, Germany
[§]Department of Chemistry, Moscow State University, 119991 Moscow, Leninskie gory, Russia

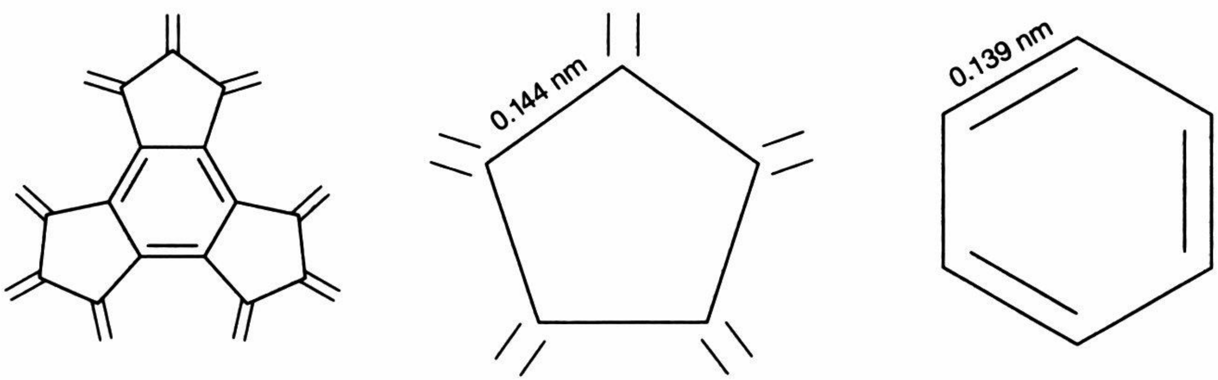
GDCh
Reviews
Angewandte Chemie International Edition
Check for updates
Non-IPR Fullerenes
Angew. Chem. Int. Ed. 2020, 59, 1048–1073

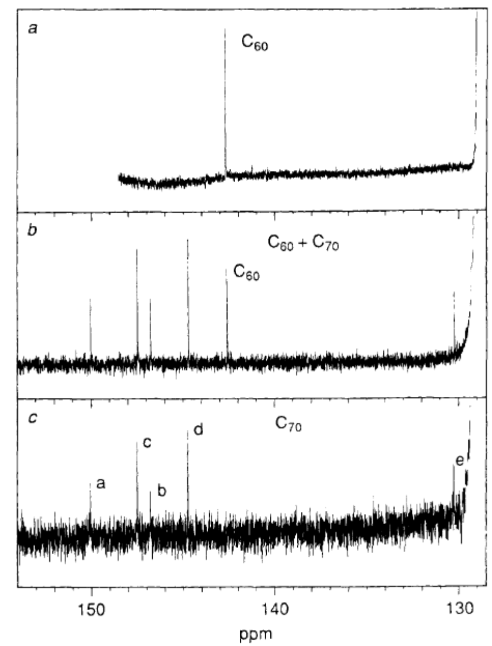
Strain Release of Fused Pentagons in Fullerene Cages by Chemical Functionalization

*Runnan Guan, Muqing Chen, Fei Jin, and Shangfeng Yang**

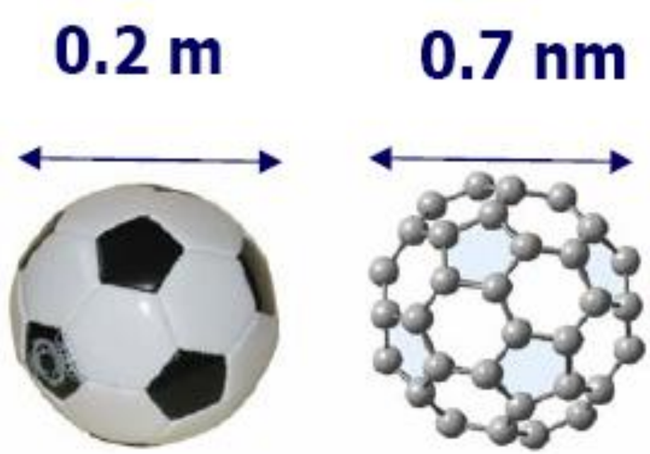
Bonding nature in C_{60} (I_h)

- Bond length between two hexagons: 0.139 nm
  → double bond
  (Benzene 0.139 nm; graphite 0.141 nm)
- Bond length at the pentagonal edge: 0.144 nm (- 0.146 nm)
  → single bond





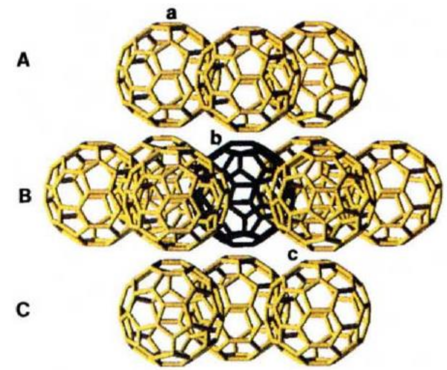
R Taylor et al. *J. Chem. Soc. Chem. Commun* 1990, 1423



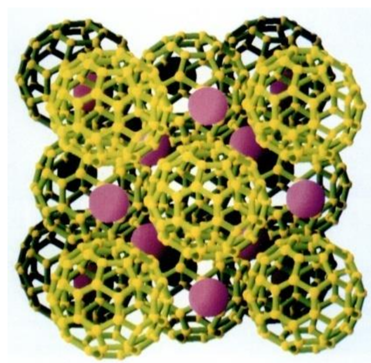
全碳纳米材料！

Physical Properties of C_{60} (Solid)

- Density: 1.650±0.05 g/cm^3
- Melting point: >700 ^oC
- Sublimation temperature: 500 ^oC in inert gas atmosphere (ca. 350 ^oC in vacuum)
- Degradation: >1000 ^oC
- At room temperature (f.c.c., a = 1.416 nm)
- Semi-conducting (*n*-type)



Face-centred cubic (f.c.c.)
Guo, Y. et al., *Nature* 351, 1991, 464.
David, W. et al., *Nature* 353, 1991, 147.



Superconductivity

- in Alkali fullerides, e.g.

  K_3C_{60} (T_C 18 K)

  (Hebard et al., *Nature* 350, 1991, 600.);

  Rb_3C_{60} (T_C ~ 28 K)

  (Zhang et al., *Nature* 353, 1991, 333.);

  Cs_3C_{60} (T_C ~ 30 K)

  (Kelty et al., *Nature* 352, 1991, 223.);

- highest T_C at atmospheric pressure: $Cs_xRb_yC_{60}$ (33 K)

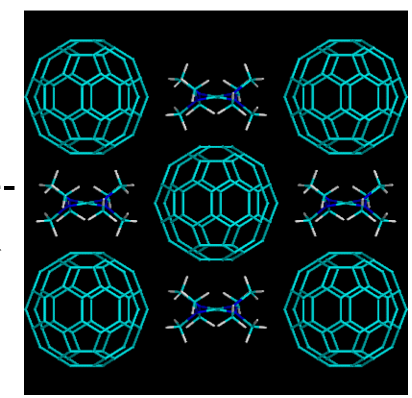
  (Tanigaki et al., *Nature* 352, 1991, 252.)

Ferromagnetism

- in TDAE-C_{60} (TDAE: Tetrakis-(dimethylamin)ethylene) Currie T_C 16.1 K

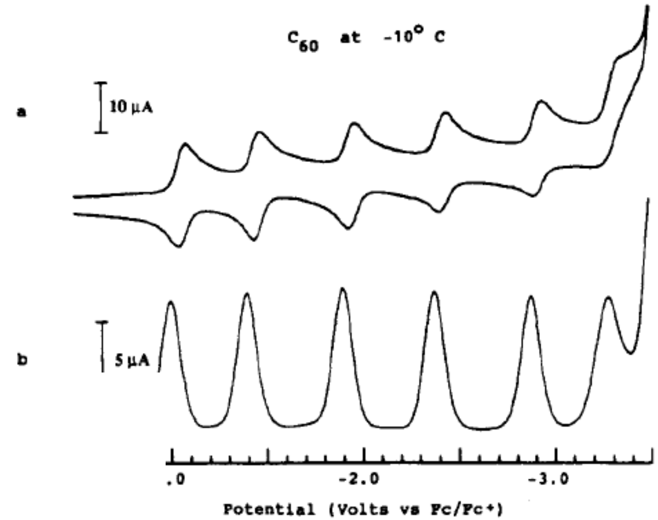
  (Allemand et al., *Science* 253, 1991, 301.)
- only s and p orbitals
- 2D polymer of C_{60}: CurrieT$_C$ ≈ 500 K

  (Makarova et al., *Nature* 413, 2001, 716.)



Chemical Properties of fullerenes

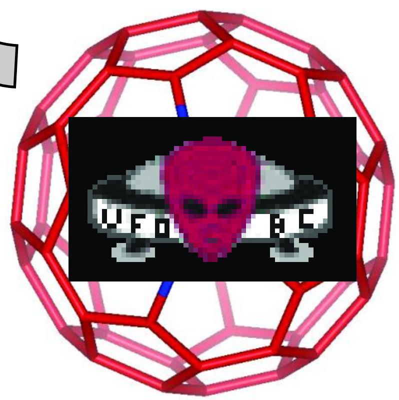
- High symmetry (C_{60} - I_h)
- Solubility: CS_2, benzene, toluene, chlorobenzene
- High stability in air and in solution
- **Strong electron-accepting ability**
- **High chemical reactivity**



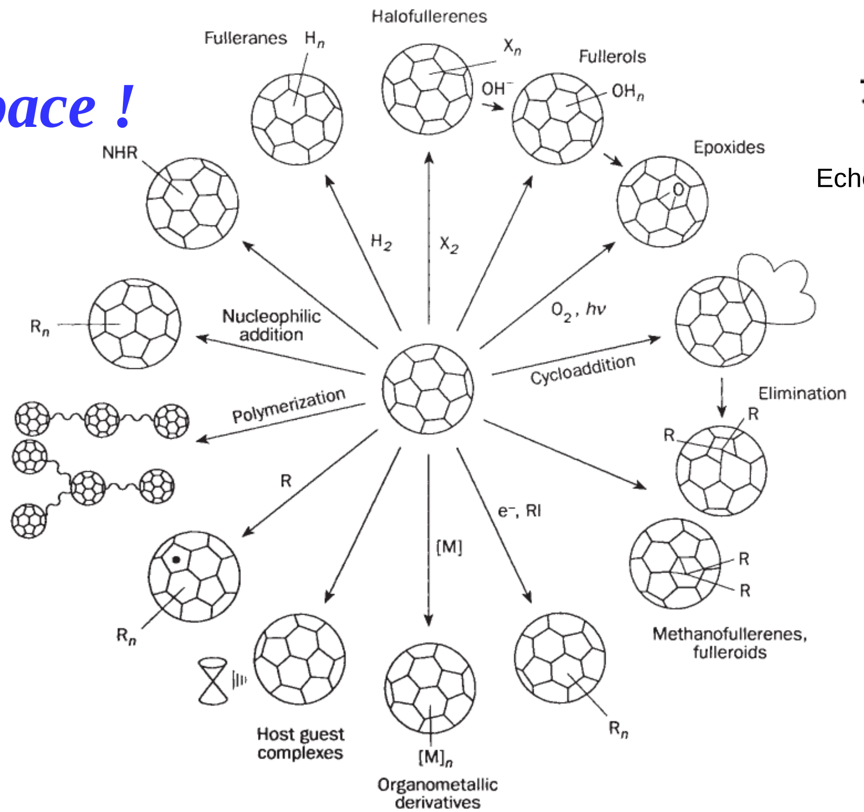
Echegoyen, et al *JACS* 114, 1992, 3978.

- ***Hollow inner space !***

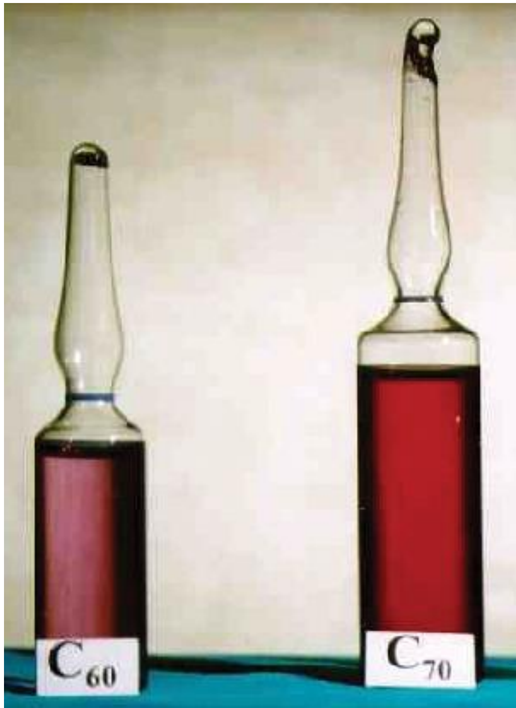
Endohedral fullerenes



内嵌富勒烯



Taylor, Walton *Nature* 363, 1993, 685.
Hirsch et al. *Fullerenes: Chemistry and Reactions*, Wiley-VCH, 2005.



Endohedral fullerene

http://en.wikipedia.org/wiki/Endohedral_fullerene

From Wikipedia, the free encyclopedia

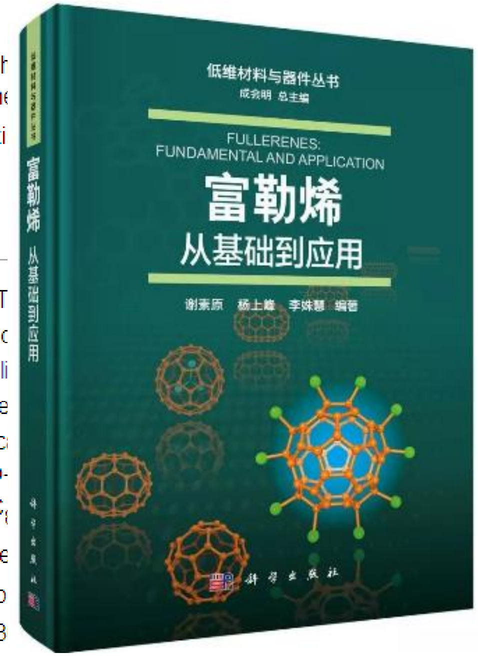
Endohedral fullerenes are fullerenes that have additional atoms, ions, or clusters enclosed within th spheres. The first lanthanum C_{60} complex was synthesized in 1985 called La@C_{60}. The @ sign in the reflects the notion of a small molecule trapped inside a shell. Two types of endohedral complexes exi **endohedral metallofullerenes** and **non-metal doped fullerenes** [1].

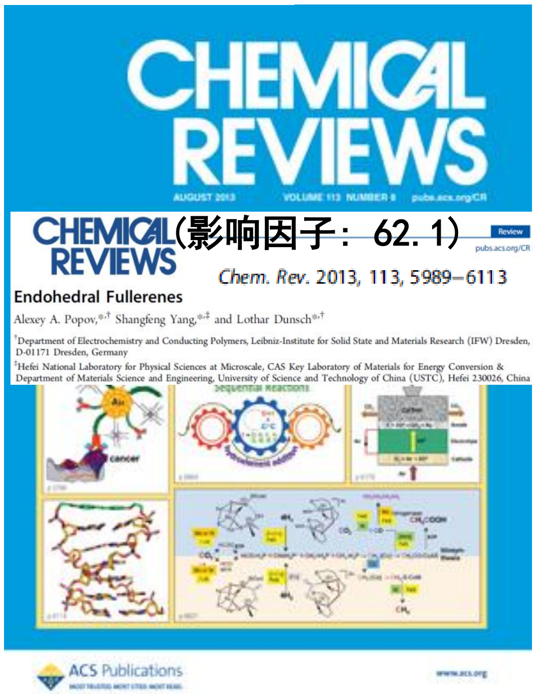
Endohedral metallofullerenes

Doping fullerenes with electropositive metals takes place in an arc reactor or via laser evaporation. T can be transition metals like scandium, yttrium as well as lanthanides like lanthanum and cerium. Alsc are endohedral complexes with elements of the alkaline earth metals like barium and strontium, alkali like potassium and tetravalent metals like uranium, zirconium and hafnium. The synthesis in the arc re however unspecific. Besides unfilled fullerenes, endohedral metallofullerenes develop with different c like La@C_{60} or La@C_{82} and as different isomer cages. Aside from the dominant presence of mono- cages, numerous di-metal endohedral complexes and the tri-metal carbide fullerenes like Sc_3C_2@C

In 1998 a discovery drew large attention. With the synthesis of the Sc_3N@C_{80}, the inclusion of a mole succeeded for the first time. This compound can be prepared by arc-vaporization at temperatures up scandium(III) oxide iron nitride and graphite powder in a K-H generator in a nitrogen atmosphere at 3

WIKIPEDIA
The Free Encyclopedia





Chem Soc Rev (影响因子：46.2)

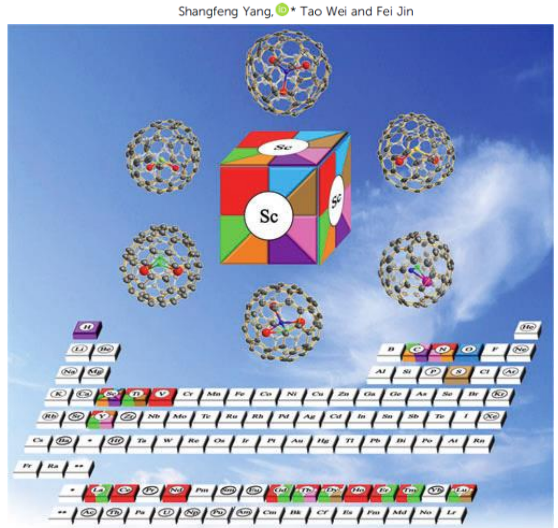
REVIEW ARTICLE *Chem. Soc. Rev.*, 2017, **46**, 5005–5058

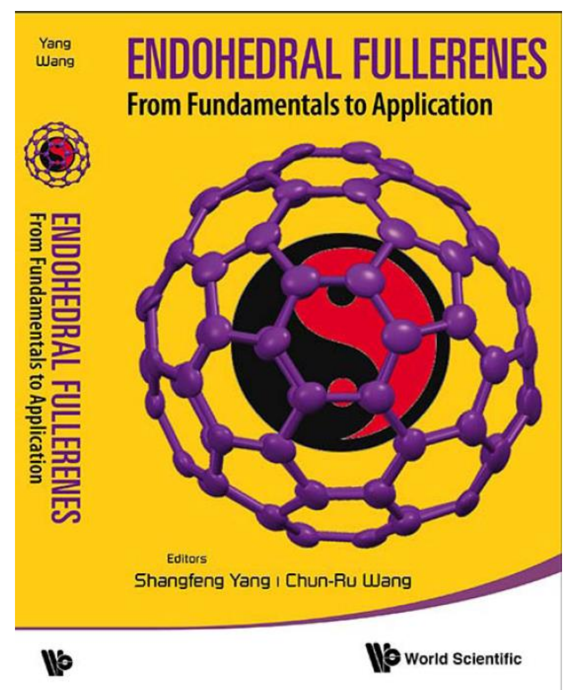
Check for updates

Cite this: DOI: 10.1039/c6cs00498a

When metal clusters meet carbon cages: endohedral clusterfullerenes

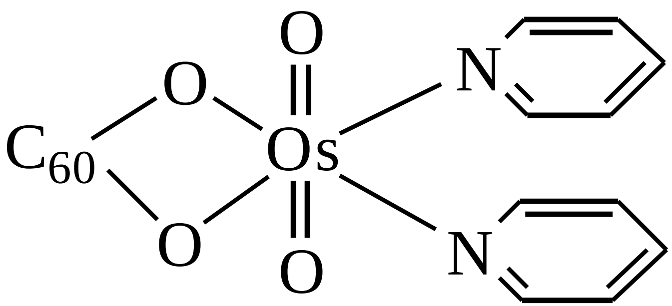
Shangfeng Yang,* Tao Wei and Fei Jin

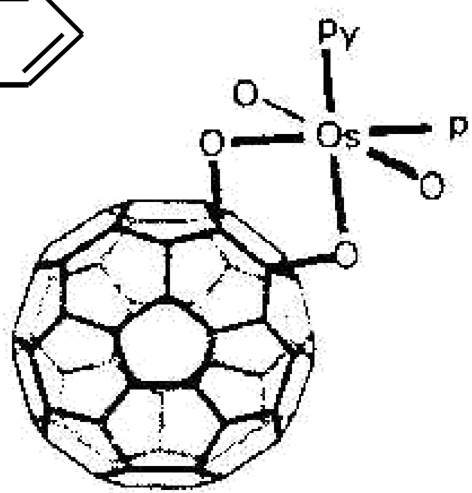


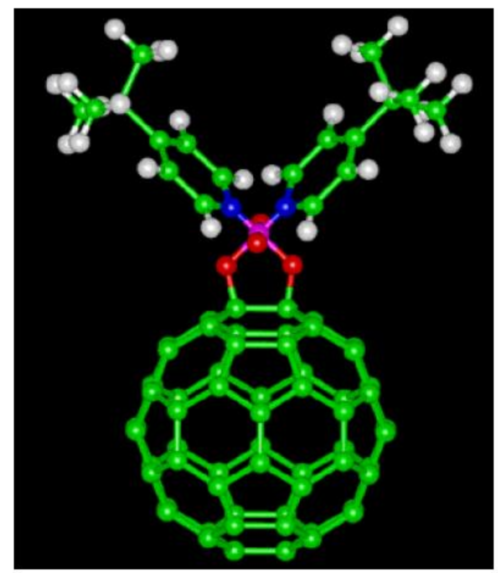


C_{60}可以像烯烃一样用OsO_4氧化，生成C_{60}的锇酸酯。该反应是由吡啶加成物或在吡啶存在的条件下与化学计量的OsO_4反应来完成:

$$C_{60} + OsO_4 + 2C_5H_5N \xrightarrow{C_6H_5CH_3,\ 0\sim25℃} [Os(O)_2(py)_2(OC_{60}O)]$$



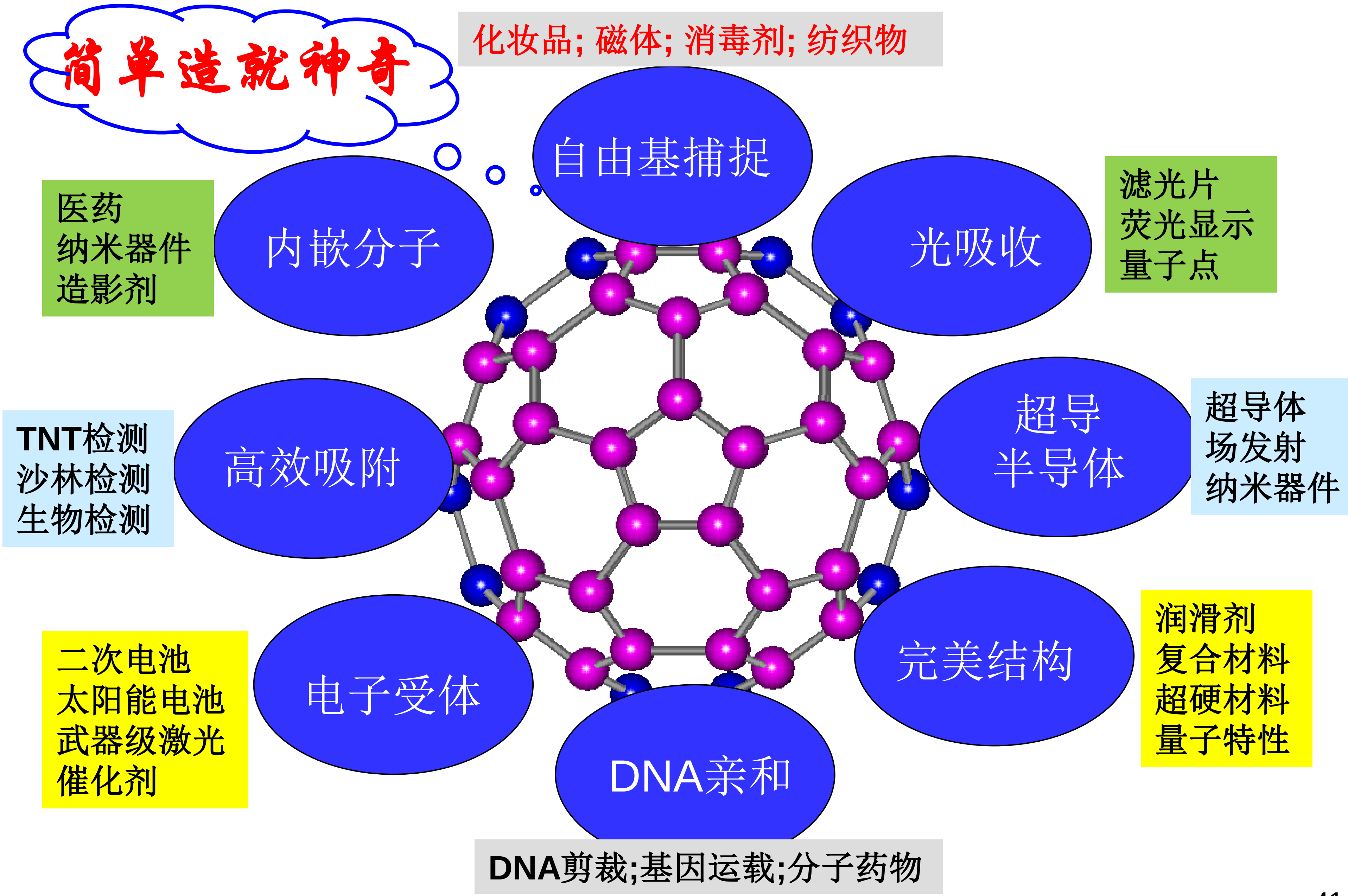




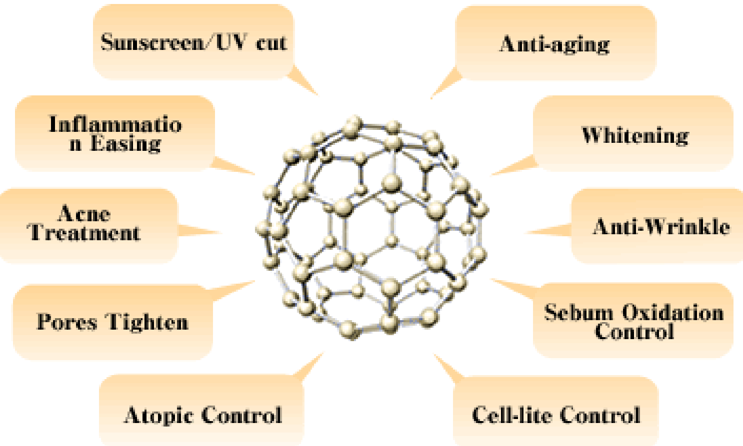
$C_{60}(OsO_4L_2)$

JM Hawkins *et al Science* 1991, *252*, 312

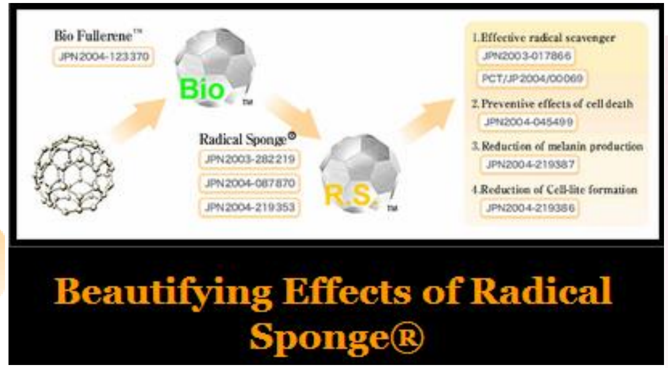
Applications of Fullerenes



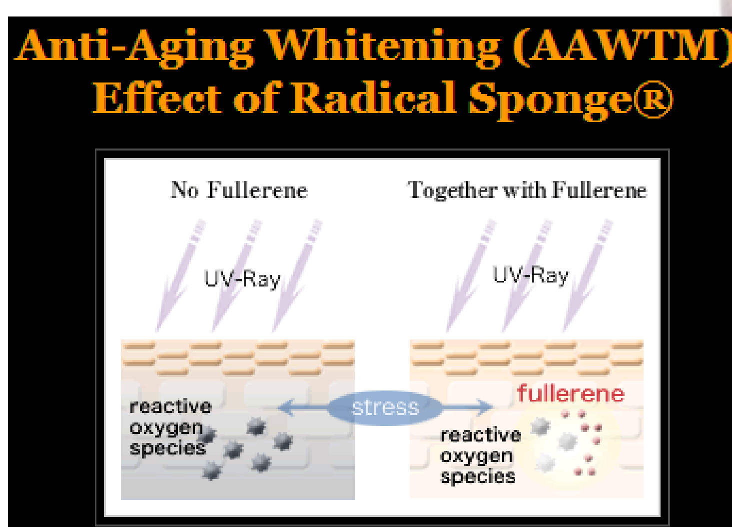
Fullerene antioxidants – application in cosmetics



Novel Free-Radical Scavenger for Cosmetics



“自由基海绵”



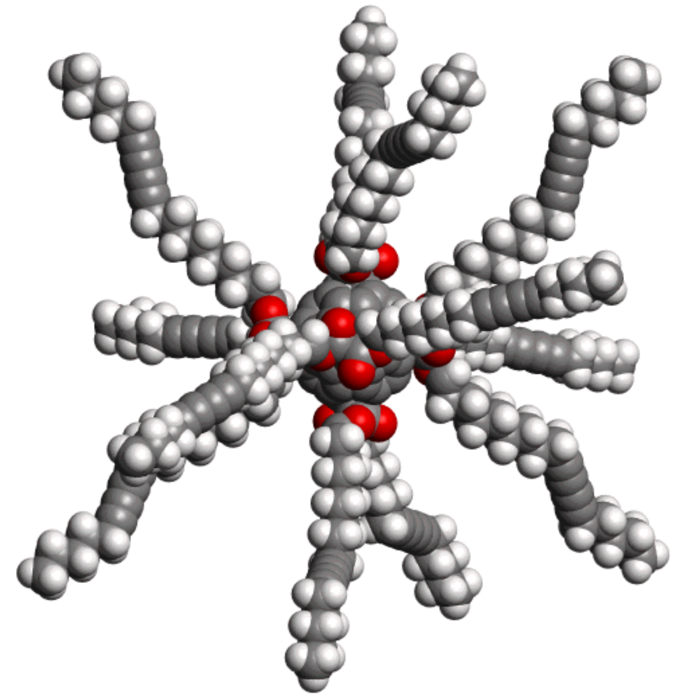

Fullerene Cream


fullerene
essence lotion


Whitening & Repair
Hydrating Jelly Mask
LABORATORY
DoctorBeauty
Fullerence
Nonapeptide
Matrixy
150 ml

C_{60} anti-aging oil

Aerobic- & strength gains, longevity, brain rejuvenation and tumor prevention with lipofullerene C_{60} olive oil

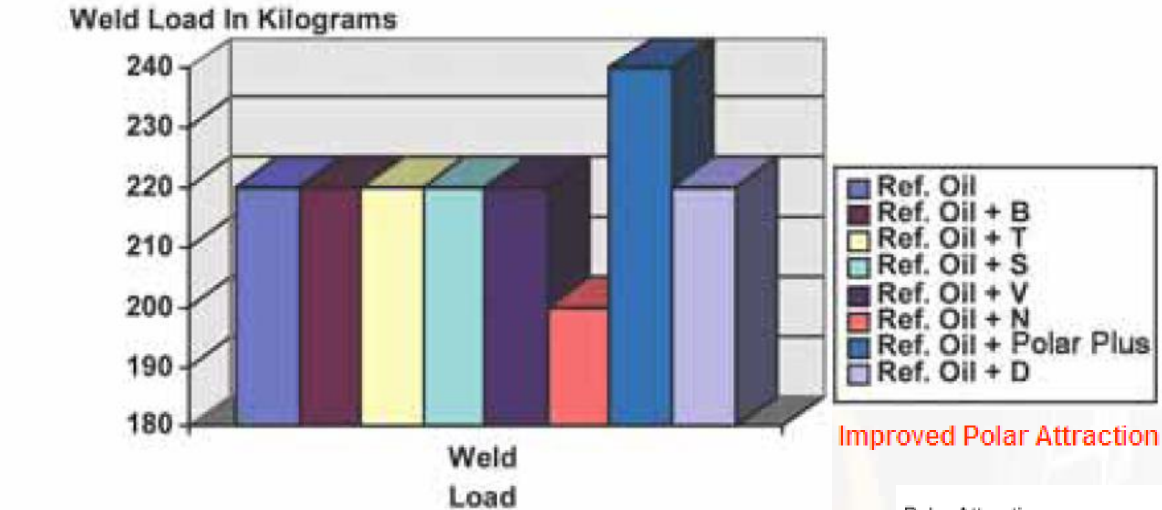


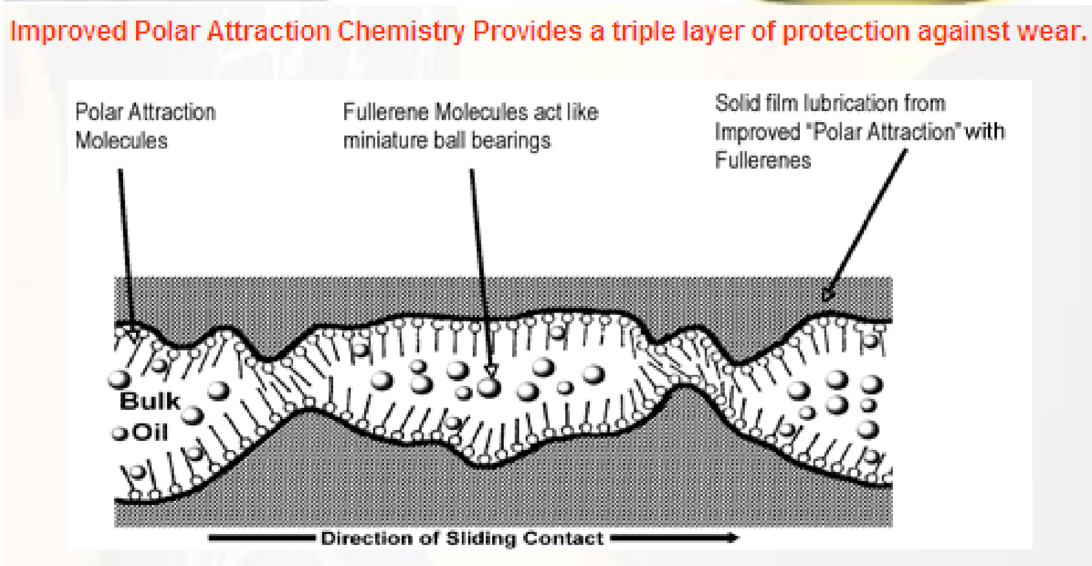
45 mg of 99.95% pure Buckminsterfullerene C_{60} dissolved in 50 ml extra virgin olive oil, stirred for two weeks, centrifuged for one hour at 5000 g and filtered through a 0.22 μm microfilter. This is the exact same preparation as used in the original rat study.

Rats lived 90% longer on C_{60} in olive oil.

Fullerene as lubricant additive

Graph # 1
Bardahl 4-Ball EP Testing "Fullerene - Polar Plus" Formula





- 30% enhancement on the lifetime !

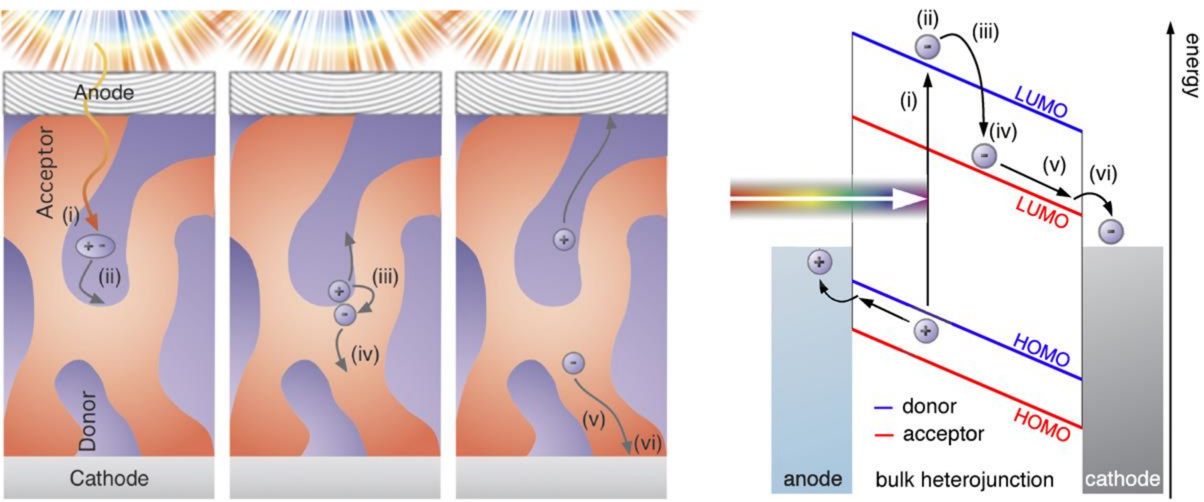
Source: http://www.bardahl-ap.com/polarplus.php

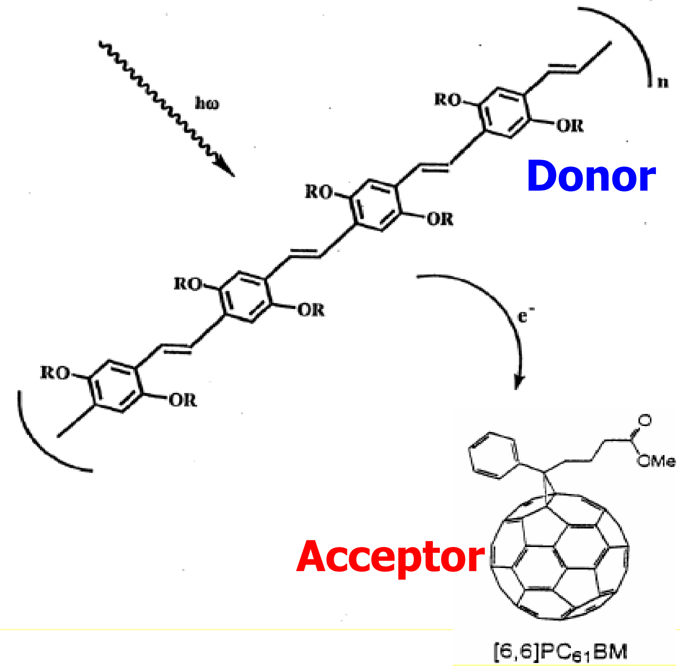
Fullerene-based polymer solar cells (BHJ-PSCs)
基于富勒烯的有机聚合物太阳能电池

Heeger et al., *Science* **1992**, *258*, 1474.
er et al. *Science* **1995**, *270*, 1789.
6 at 20 mW/cm², 430 nm)

(i) 光子的吸收⇒产生激子；
(ii) 激子扩散到给体/受体界面处；
(iii) 激子离解成自由载流子—电子和空穴；
(iv) 电子和空穴的分离；
(v) 电荷输运；
(vi) 电荷收集⇒产生光电流。

优点：
- ✓材料来源广泛；价格低廉；
- ✓重量轻；可制成柔性、特种形状器件；
- ✓可用湿法成膜的廉价大面积制造技术；
- ✓易于加工；

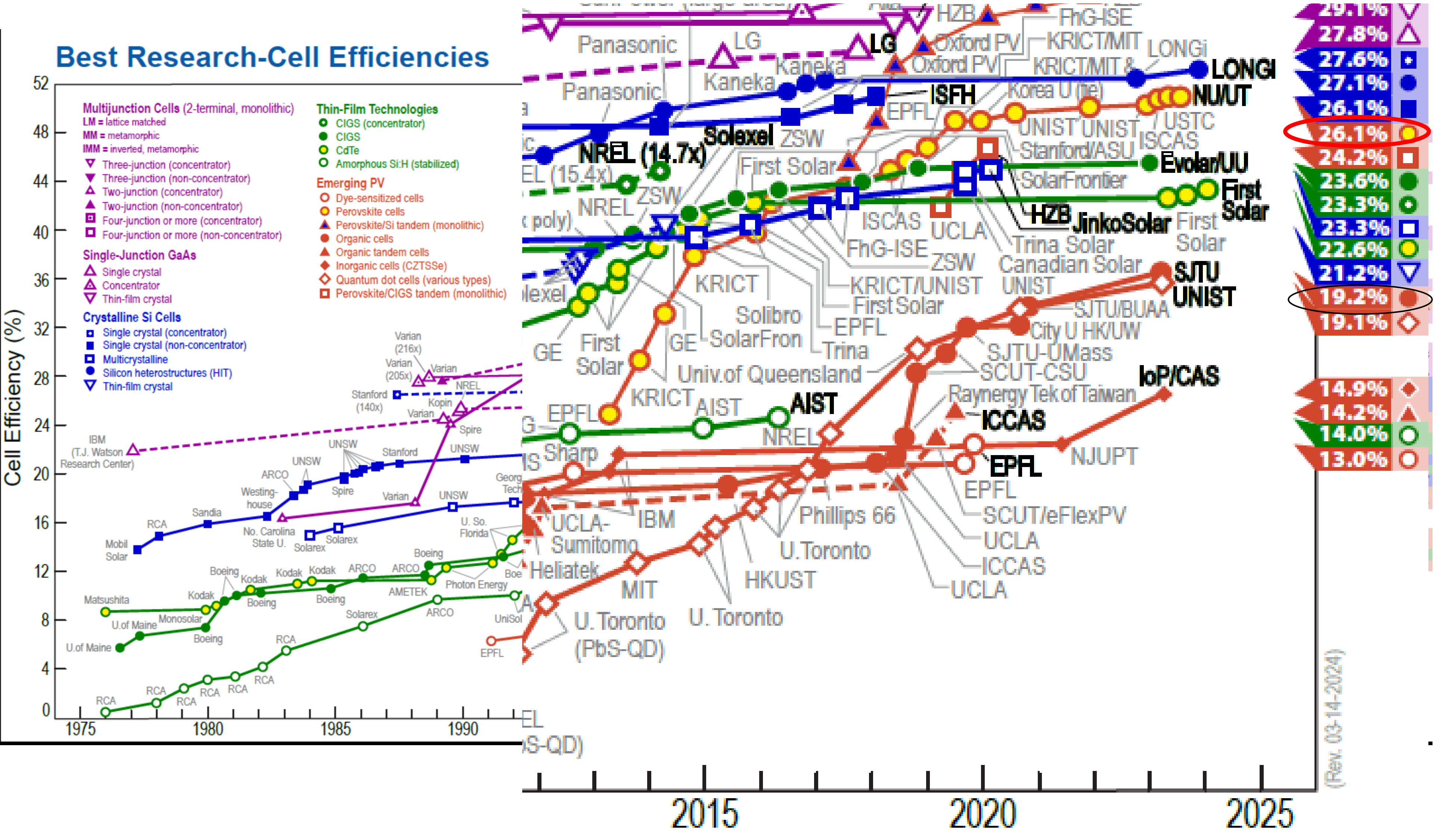




([6,6]-phenyl-C61 butyric acid methyl ester)

• Deibel, Dyakonov, *Rep. Prog. Phys.* **2010**, *73*, 096401.

新型薄膜太阳能电池



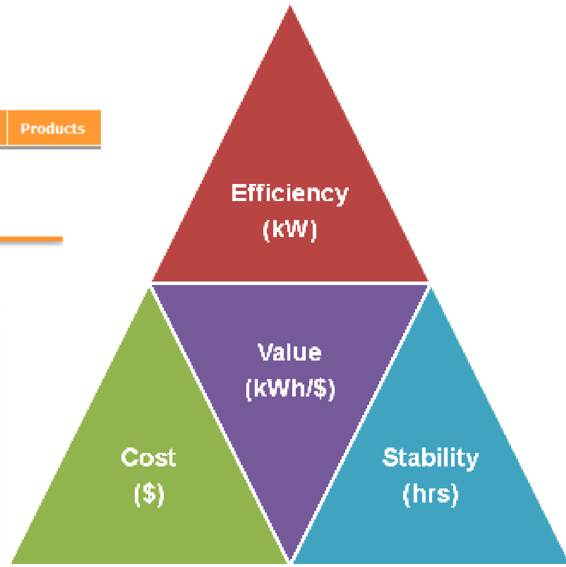
https://www.nrel.gov/pv/cell-efficiency.html

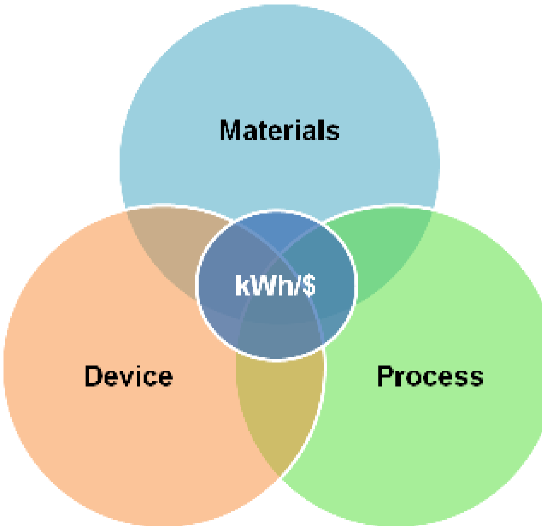
Home | Company | Technology | Products

PRODUCT ROADMAP

SOLARMER PV SPECS

Cost	30 - 50 $/m²
Color	Red, Purple, Blue, Dark Green
Power Output	30 W/m²
Lifetime	1 - 3 years
Weight	~ 100 g/m²
Thickness	< 0.5 mm
Transparency	Up to 45%
Size	Customizable
Environmental Profile	Non-toxic, recyclable.





Source: http://www.solarmer.com

Helios Flying by AeroVironment Inc.

Carbon Nanotubes (CNTs)

LETTERS TO NATURE

Helical microtubules of graphitic carbon

Sumio Iijima

NATURE · VOL 354 · 7 NOVEMBER 1991

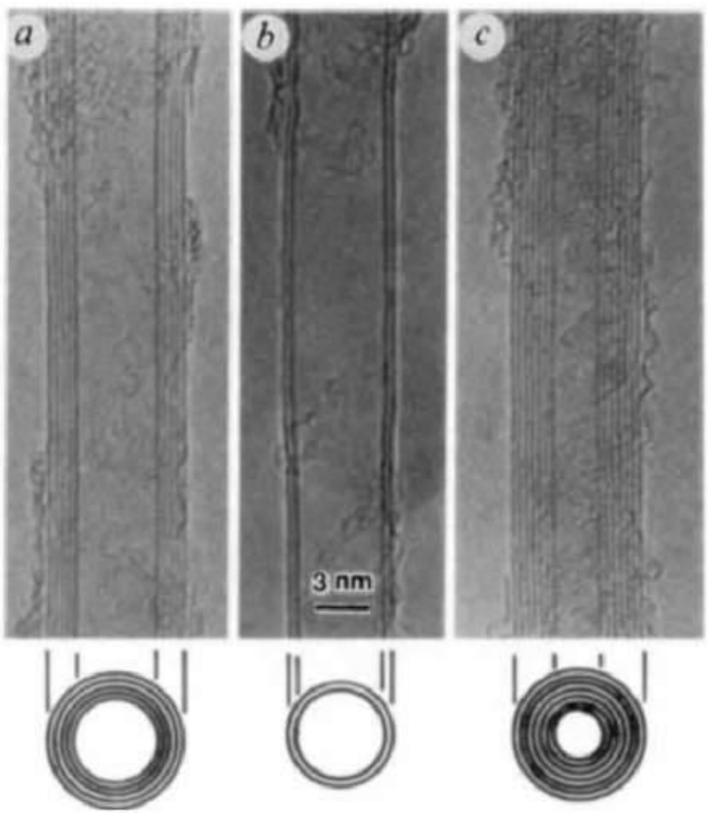


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet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

- Have been working at the development of high resolution electronic microscope.
- Started to work at NEC at the age of 48, developed a high resolution microscope (TEM).
- Discovered CNT at 51.

DOI: 10.1002/cssc.201100330

20 Years of Carbon Nanotubes**

Dang Sheng Su*[a, b]

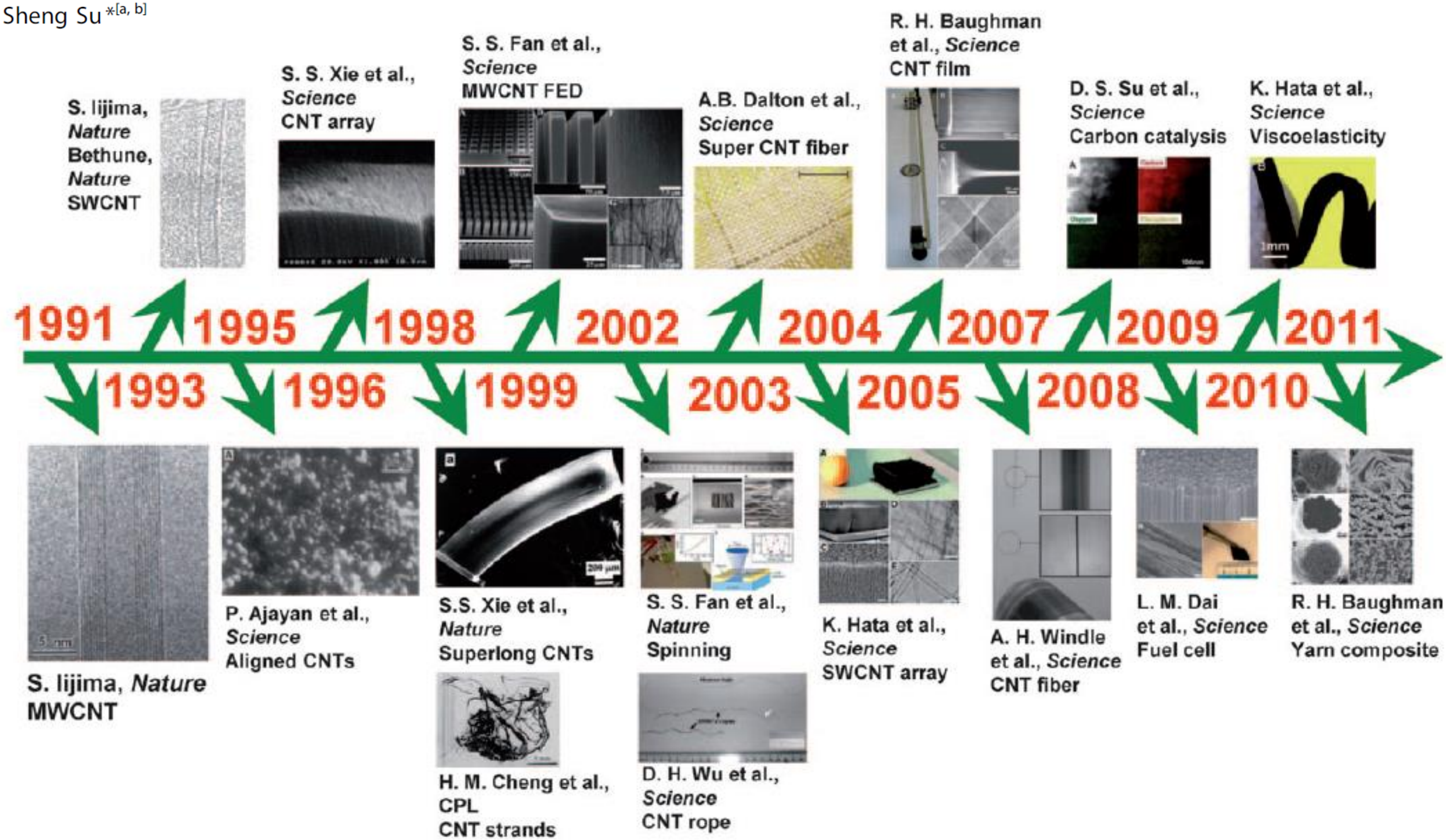
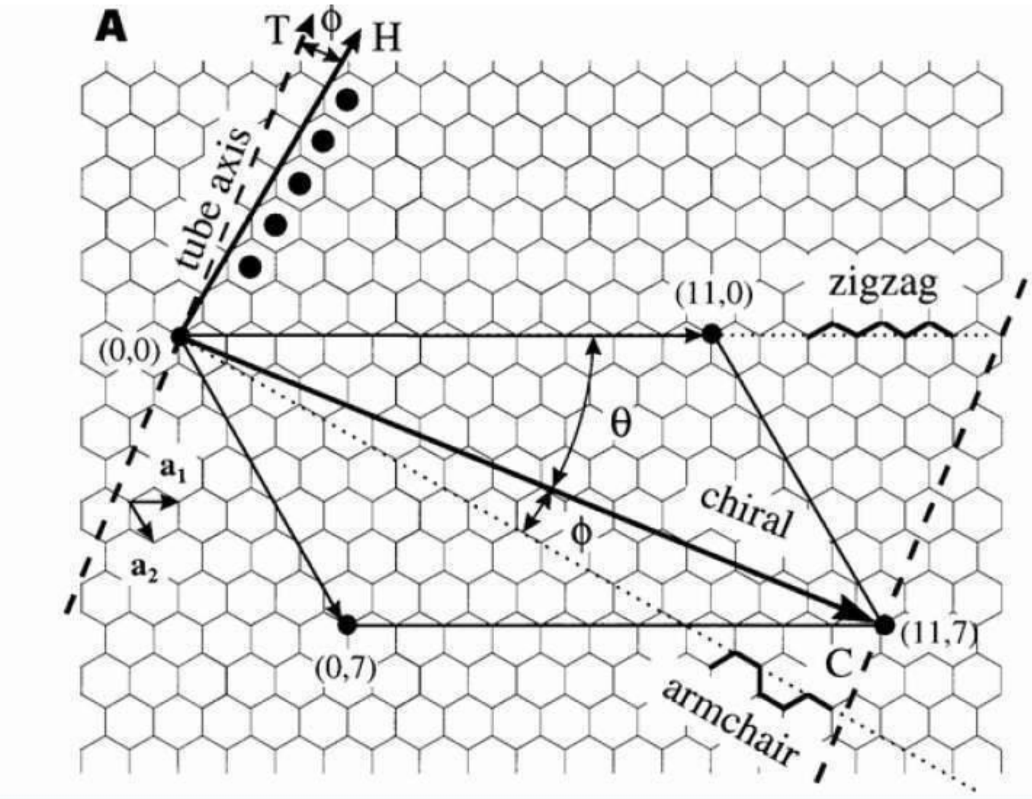
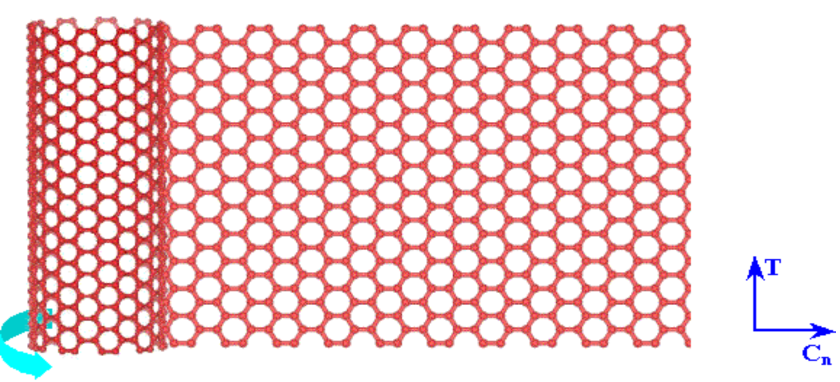


Figure 1. Selected major events and milestones during twenty years of CNTs. The illustration shows that the major advances in the first ten years were made in synthesis, while in the second ten-year period advances were made in their application. Due to the limited space, only one or two papers were selected per year, and only one author for each paper, and only the journal is mentioned, while hundreds of papers are published each year. The illustration starts in 1991, but CNTs were already reported in 1976.

◆ Single-walled carbon nanotubes

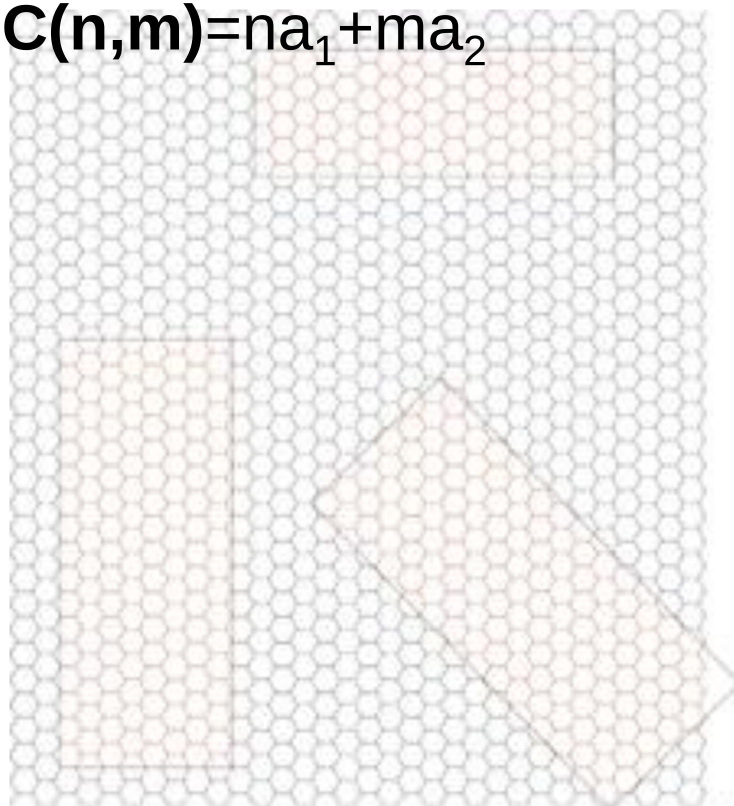


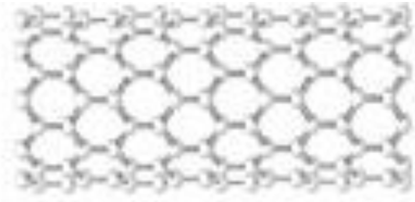


从石墨烯片层构造纳米碳管的示意图

The (*n*,*m*) nanotube naming scheme can be thought of as a vector ($\mathbf{C}=na_1+ma_2$) in an infinite graphene sheet that describes how to "roll up" the graphene sheet to make the nanotube. **T** denotes the tube axis, and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of graphene in real space.

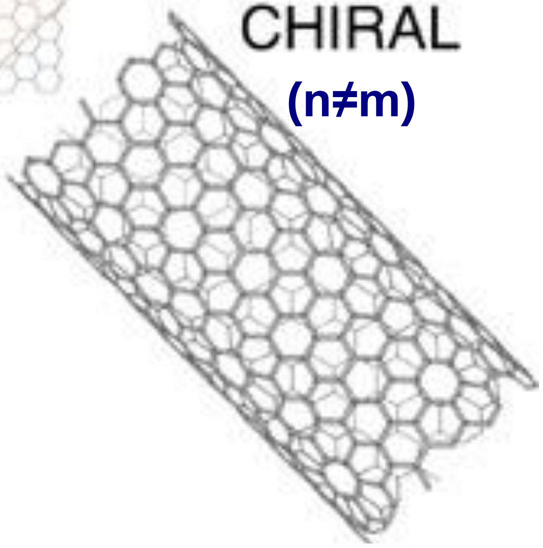
C(n,m)$=na_1+ma_2$





ZIGZAG

(m=0)



CHIRAL

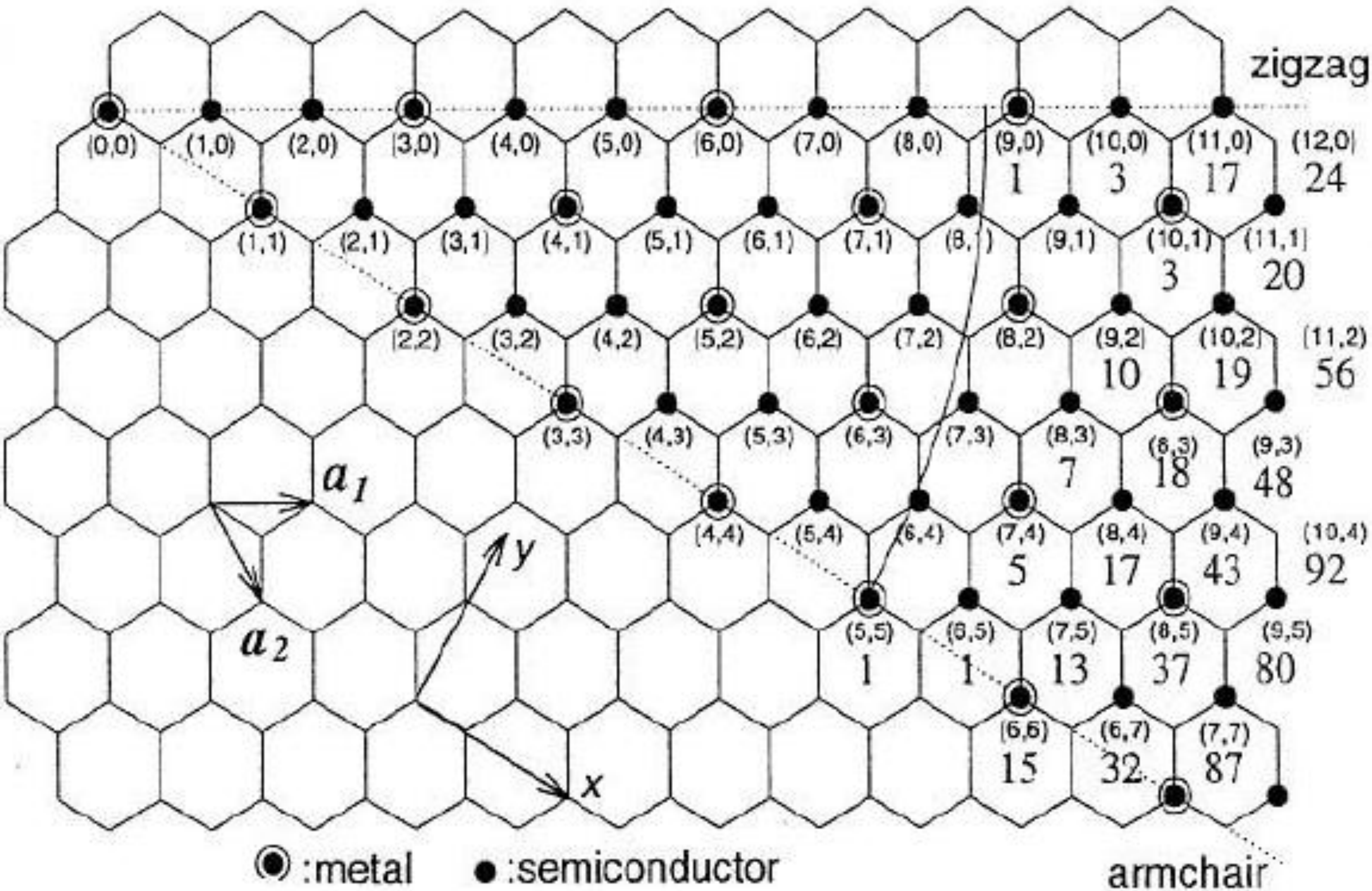
(n≠m)

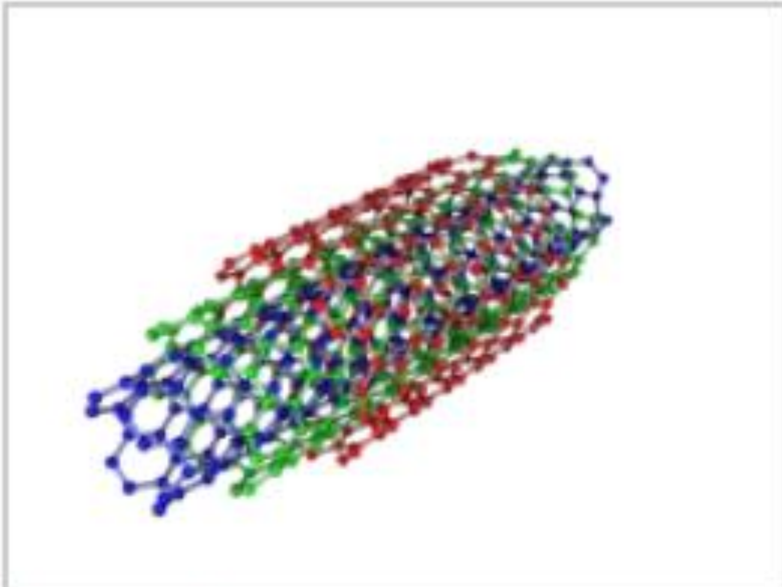
ARMCHAIR

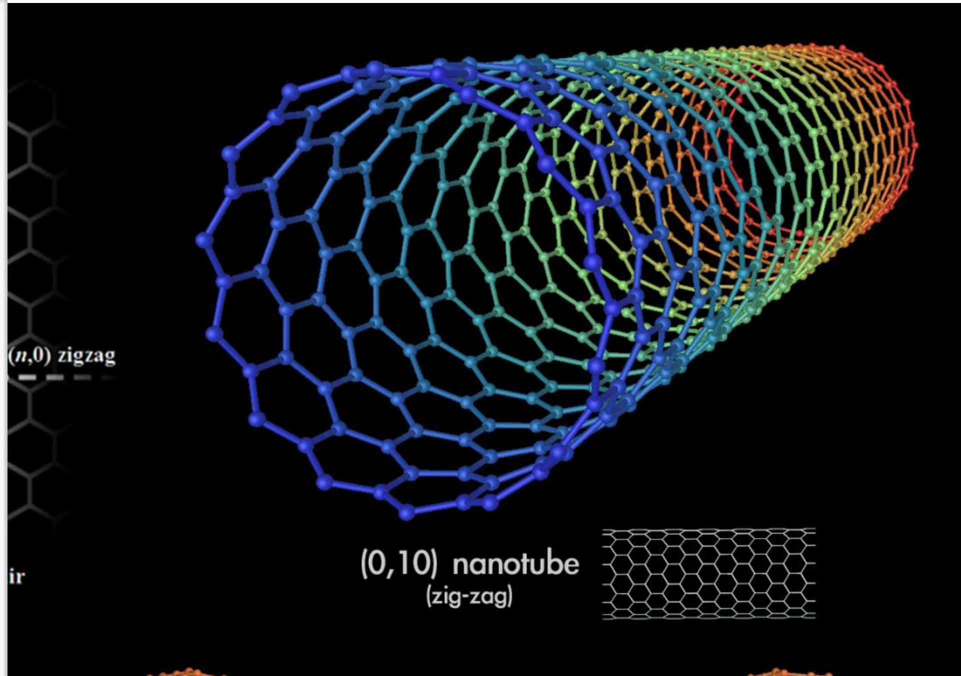
(n=m)

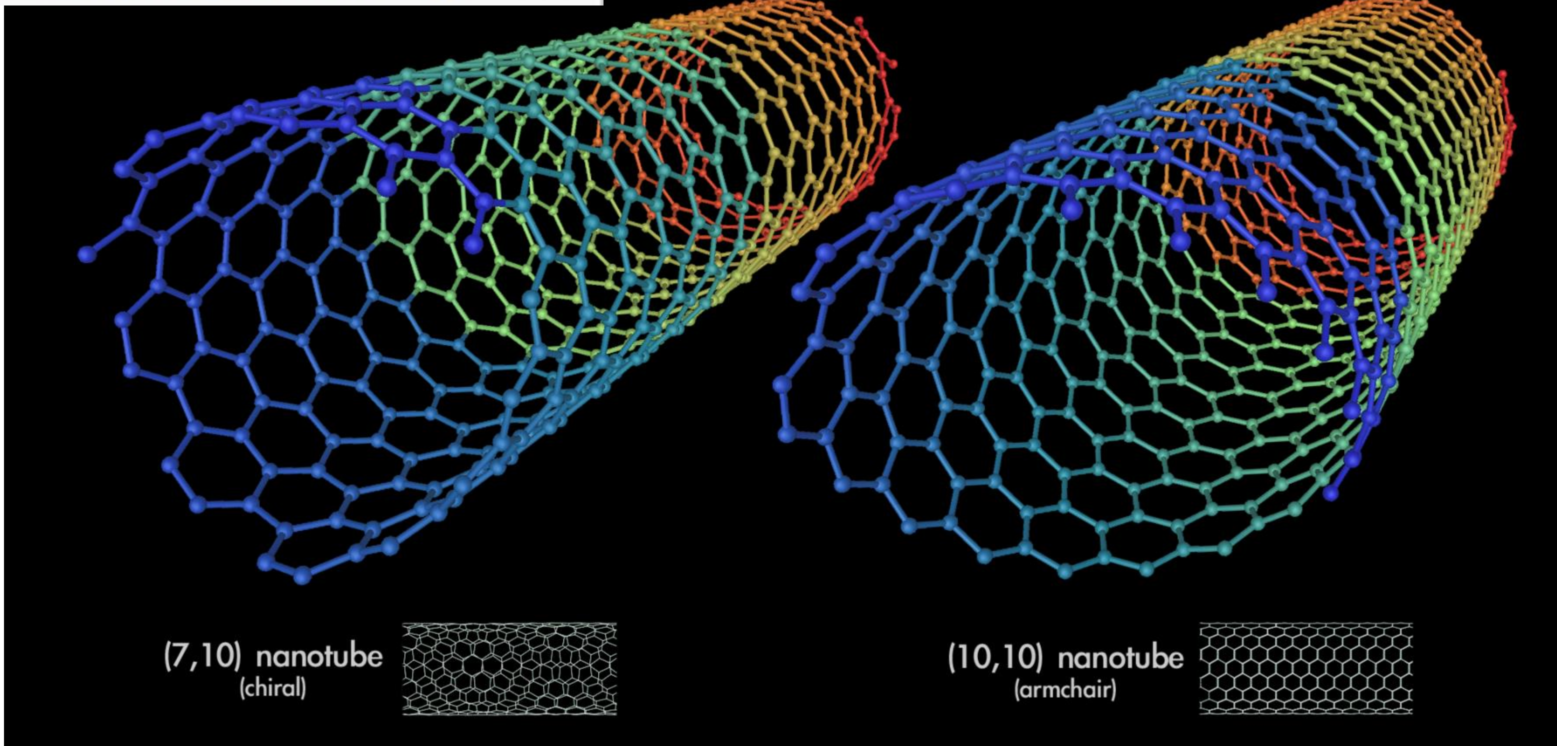
- **For a given (n,m) nanotube, if n – m = 3q (where q is an integer), then the nanotube is metallic, otherwise the nanotube is a semiconductor.**
- **Thus all armchair (n=m) nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting.**
- **In theory, metallic nanotubes can have an electrical current density more than 1,000 times greater than metals such as silver and copper.**

$$d = \frac{a}{\pi}\sqrt{(n^2+nm+m^2)}$$ where $a = 0.246$ nm


zigzag
(0,0) (1,0) (2,0) (3,0) (4,0) (5,0) (6,0) (7,0) (8,0) (9,0) (10,0) (11,0) (12,0)
1 3 17 24
(1,1) (2,1) (3,1) (4,1) (5,1) (6,1) (7,1) (8,1) (9,1) (10,1) (11,1)
3 20
(2,2) (3,2) (4,2) (5,2) (6,2) (7,2) (8,2) (9,2) (10,2) (11,2)
10 19 56
(3,3) (4,3) (5,3) (6,3) (7,3) (8,3) (6,3) (9,3)
7 18 48
(4,4) (5,4) (6,4) (7,4) (8,4) (9,4) (10,4)
5 17 43 92
(5,5) (6,5) (7,5) (8,5) (9,5)
1 1 13 37 80
(6,6) (6,7) (7,7)
15 32 87
armchair
a1
a2
y
x
:metal
:semiconductor

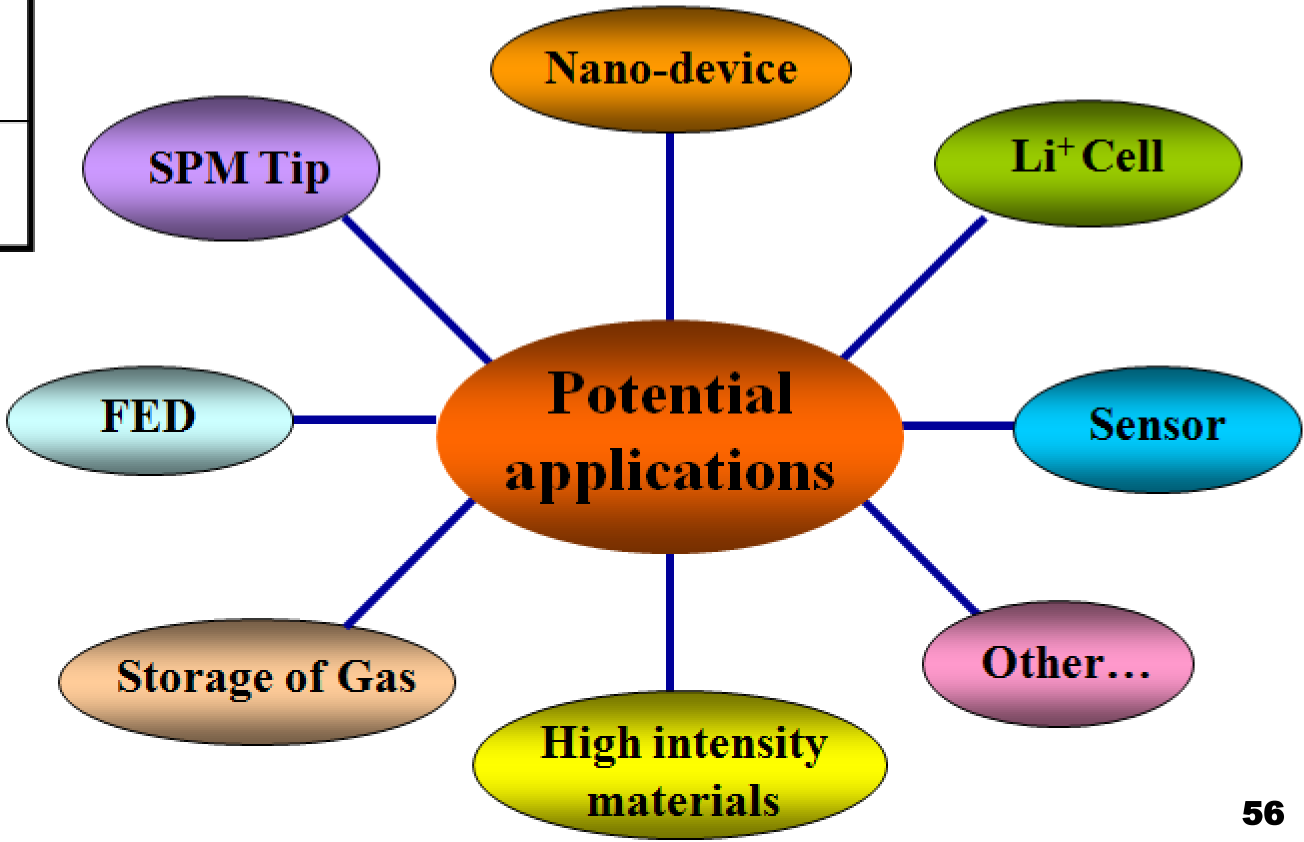

Triple-walled armchair carbon nanotube





Applications of CNTs

Young's modulus	SWCNT	1054 GPa
	MWCNT	1200 GPa
Tensile strength	SWCNT	~60 GPa
	MWCNT	~150 GPa
Current density	10^9 A/cm^2	
Electric conductivity	1.5 kW-cm	
Thermal conductivity	2000 W/m.K	



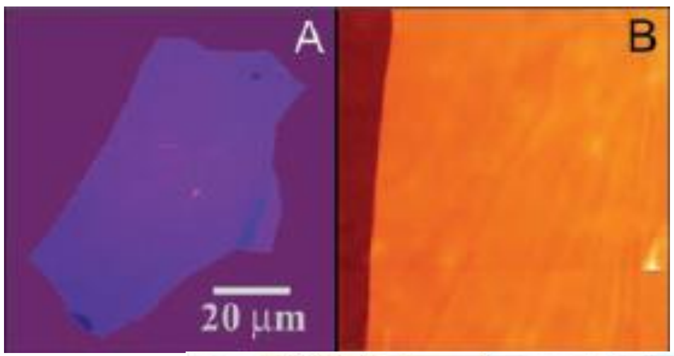
Graphene （石墨烯）

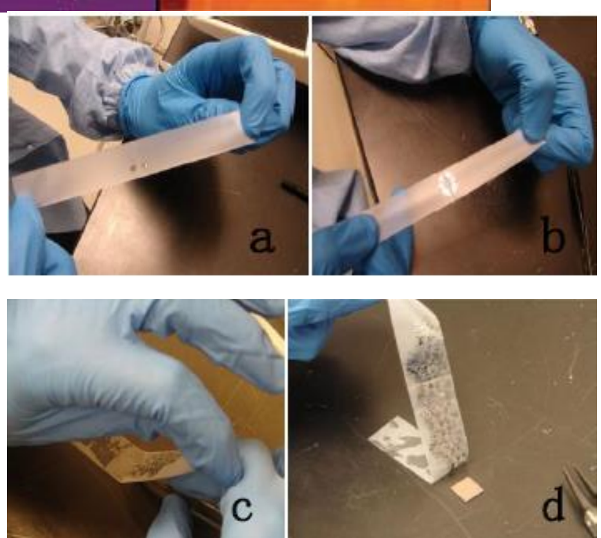
discovered (2004)

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

22 OCTOBER 2004 VOL 306 SCIENCE www.sciencemag.org





Nobelprize.org

The Official Web Site of the Nobel Prize

The Nobel Prize in Physics 2010

Andre Geim, Konstantin Novoselov

- The Nobel Prize in Physics 2010
- Nobel Prize Award Ceremony
- Andre Geim
- Konstantin Novoselov

Photo: U. Montan

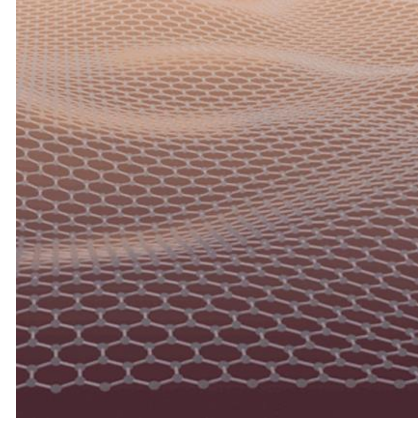
Andre Geim

Photo: U. Montan

Konstantin Novoselov

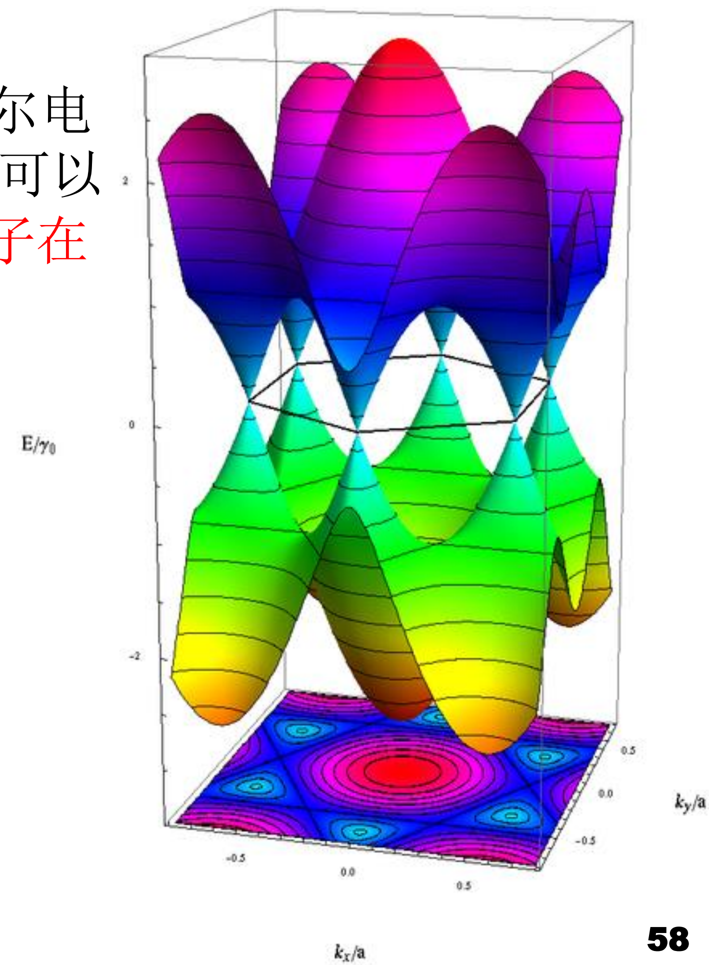
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

Graphene: Properties



- 在发现石墨烯以前，大多数（如果不是所有的话）物理学家认为，热力学涨落不允许任何二维晶体在有限温度下存在。所以，它的发现立即震撼了凝聚态物理界。虽然理论和实验界都认为完美的二维结构无法在非绝对零度稳定存在,但是单层石墨烯在实验中被制备出来。这些可能归结于石墨烯在纳米级别上的微观皱纹；

- 石墨烯表现出了异常的整数量子霍尔行为。其霍尔电导=$2e^2/h$, $6e^2/h$,$10e^2/h$.... 为量子电导的奇数倍，且可以在室温下观测到。这个行为已被科学家解释为“电子在石墨烯里遵守相对论量子力学，没有静质量”。



Graphene: Properties

- **电学性质——电子运输：**碳原子有四个价电子，这样每个碳原子都贡献一个未成键的π电子，这些π电子与平面成垂直的方向可形成轨道，π电子可在晶体中自由移动，赋予**石墨烯良好的导电性**。此外，石墨烯是具有零带隙的能带结构。
- **导电性：**石墨烯结构非常稳定，迄今为止，研究者仍未发现石墨烯中有碳原子缺失的情况。石墨烯中各碳原子之间的连接非常柔韧，当施加外部机械力时，碳原子面就弯曲变形，从而使碳原子不必重新排列来适应外力，也就保持了结构稳定。这种稳定的晶格结构使碳原子具有优良的导电性。石墨烯中的电子在轨道中移动时，不会因晶格缺陷或引入外来原子而发生散射。由于原子间作用力十分强，在常温下，即使周围碳原子发生挤撞，石墨烯中电子受到的干扰也非常小。石墨烯最大的特性是其中电子的运动速度达到了光速的1/300，远远超过了电子在一般导体中的运动速度。这使得石墨烯中的电子，或更准确地，应称为“载子”(electric charge carrier)，的性质和相对论性的中微子非常相似。
- **透光性：**石墨烯可以吸收大约2.3%的可见光。而这也是石墨烯中载荷子相对论性的体现；
- **机械特性：****石墨烯是人类已知强度最高的物质，比钻石还坚硬，强度比世界上最好的钢铁还要高上100倍**。哥伦比亚大学的物理学家对石墨烯的机械特性进行了全面的研究。在试验过程中，他们选取了一些在10—20微米之间的石墨烯微粒作为研究对象。研究人员先是将这些石墨烯样品放在了一个表面被钻有小孔的晶体薄板上，这些孔的直径在1—1.5微米之间。之后，他们用金刚石制成的探针对这些放置在小孔上的石墨烯施加压力，以测试它们的承受能力。

Graphene: Applications

石墨烯

复合材料

- 高力学性能
- 高电学性能

电子器件

- 室温霍尔效应
- 无损迪拉克费米子
- 极高电子迁移率
- 高透光率

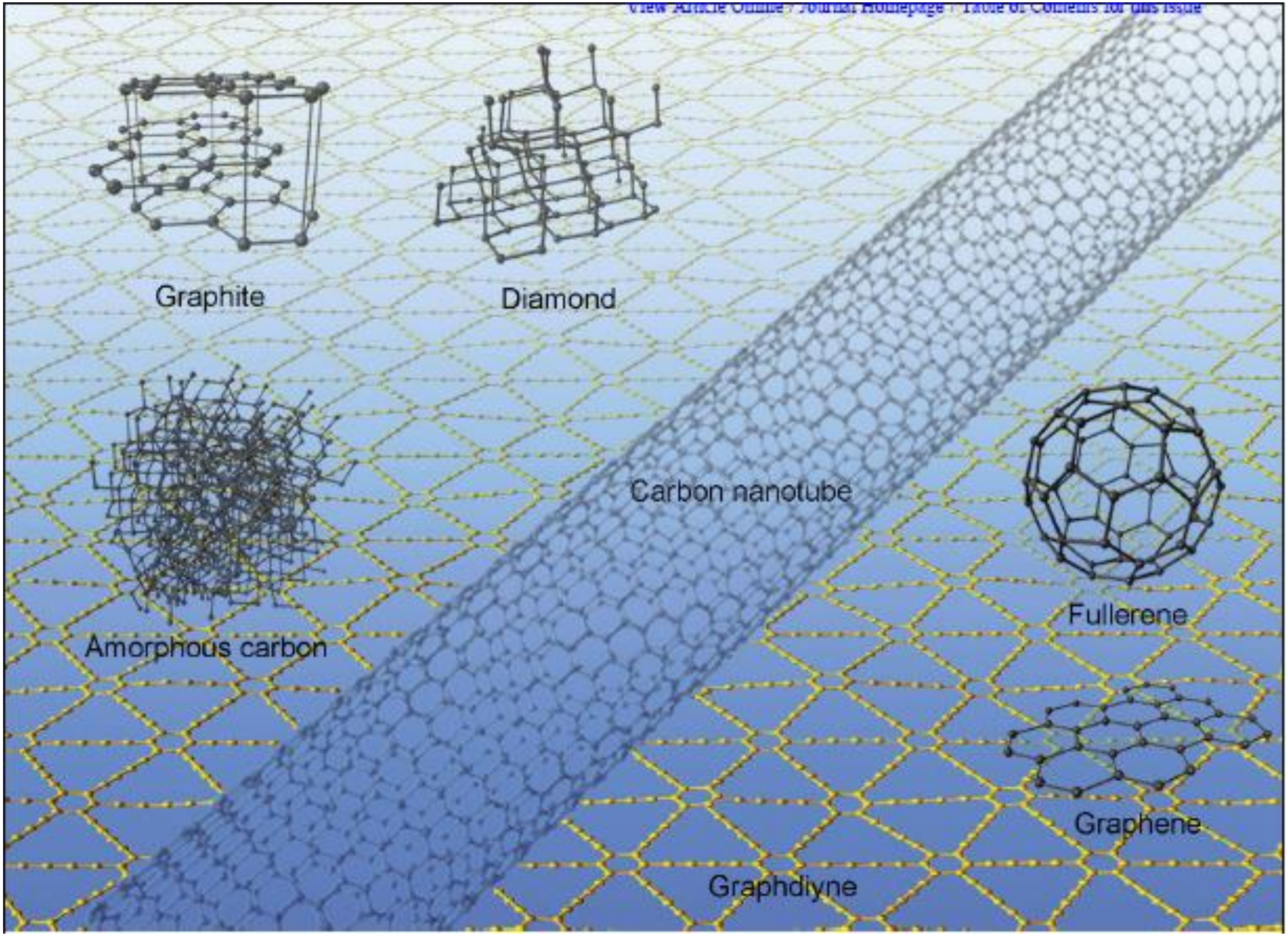
储能材料

- 高表面积
- 高电导率

石墨烯的出现可能会将摩尔定律延续下去⇒

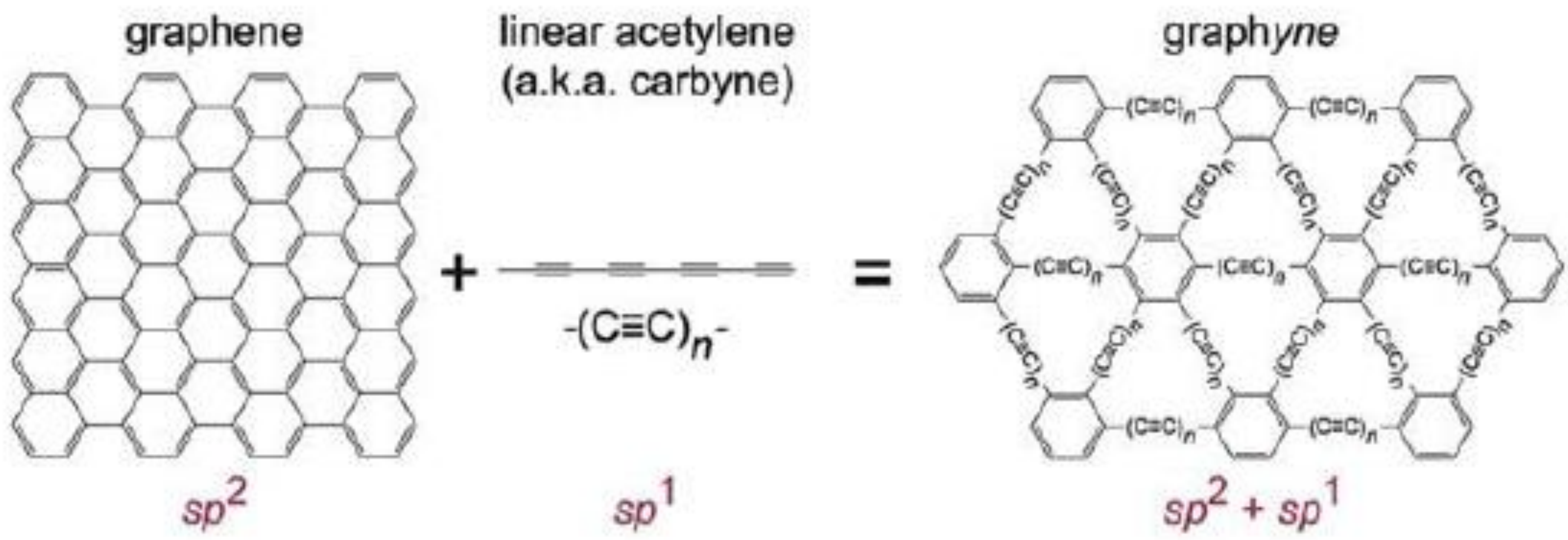
2025年以后可能是从“硅”时代跨越到“石墨烯”时代

Graphyne/Graphdiyne (石墨炔)



Graphyne: Structure

- 石墨炔是第一个以sp和sp^2两种杂化态形成的碳同素异形体。
- sp杂化态的碳碳三键具有线性结构、无顺反异构体和高共轭等优点。



M. J. Buehler, et al. *Nanoscale*, **2012**, *4*, 7797–7809.

三、Compounds of carbon

1. Carbide

Compound composed of **carbon and a <u>less electronegative</u> element**.

(i) salt-like (ionic carbides):

水解性(或与水反应)

$$\mathbf{Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4\uparrow}$$

$$\mathbf{CaC_2 + 2H_2O = Ca(OH)_2 + HCCH}$$

(ii) covalent carbides:

$$\mathbf{SiO_2 + 3C = SiC + 2CO\uparrow}$$

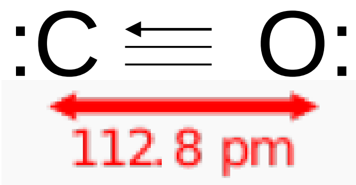
$$\mathbf{2B_2O_3 + 7C = B_4C + 6CO\uparrow}$$

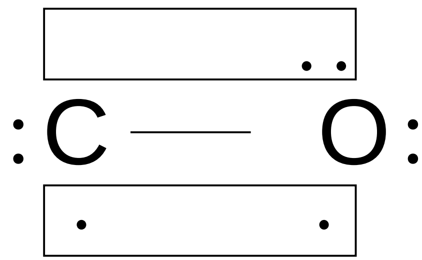
(iii) metallic carbides (TiC, VC):

- **碳原子的价电子进入过渡金属原子的空d轨道而形成。**
- **碳原子充填在密堆积金属晶格的四面体空隙中,不影响金属的导电性**

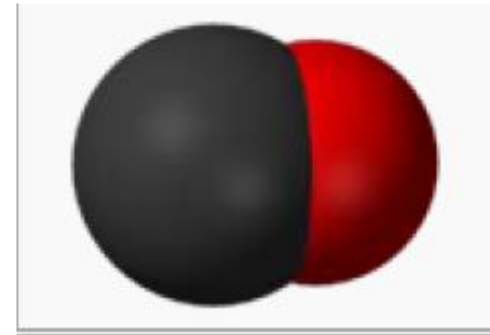
2. [+ 2] O.S CO：无色、无臭、有毒

$(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2$





一个 σ 键
两个π键



CO (6+8=14e$^-$)与 N_2 (2×7=14e$^-$)是等电子体，结构相似；但具有偶极矩（μ = 0.112 D）

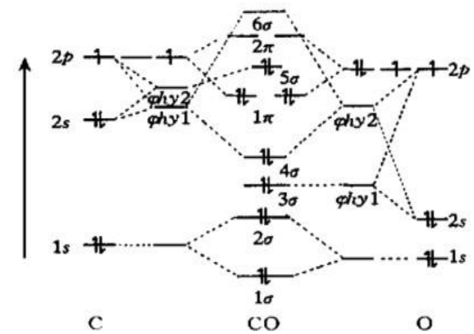


图1 CO分子轨道的能级图

	A—B	A=B	A ≡ B
CO 键能(kJ/mol)	357.7	798.9	1071.9
键能差值(kJ/mol)	441.2	273	
N_2 键能(kJ/mol)	154.8	418.4	941.7
键能差值(kJ/mol)	263.6	523.3	

??? CO的总键能大于N_2的总键能， 但CO比N_2活泼，为什么？

- 制备：

$$C + O_2(\text{不足}) \rightarrow CO$$

实验室：$HCOOH \xrightarrow[\Delta]{\text{浓}H_2SO_4} CO\uparrow + H_2O$

$$H_2C_2O_4 \xrightarrow{\text{浓}H_2SO_4} CO_2\uparrow + CO\uparrow + H_2O$$

工业制水煤气（CO和H_2）：由空气和水蒸气交替通入赤热碳层

$$C(s) + H_2O(g) \rightarrow H_2(g) + CO(g) \quad \Delta H^{\theta} = 131.30\,KJ \cdot mol^{-1}$$

➢ 性质

- 还原剂:

$$CO(g)+\frac{1}{2}O_2(g)\longrightarrow CO_2(g)$$

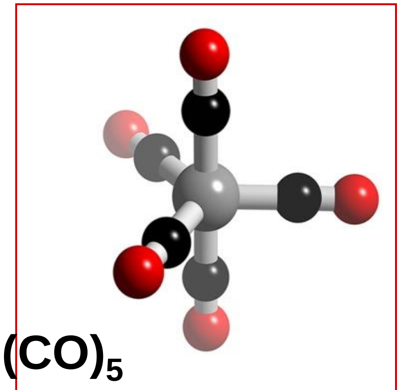
$$Fe_2O_3(s)+3CO(g)\longrightarrow 2Fe(s)+3CO_2(g)$$

$$CO+PdCl_2+H_2O\rightarrow CO_2+2HCl+Pd\downarrow$$ **检 CO**

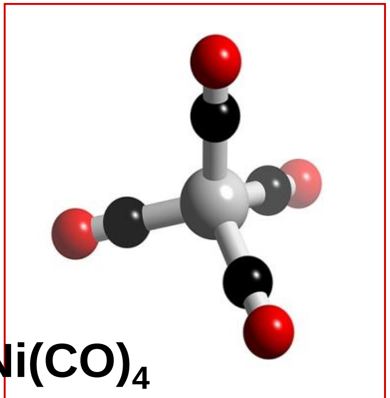
$$CO+2[Ag(NH_3)_2]OH\rightarrow CO_2+4NH_3+2Ag\downarrow+H_2O$$

- 作配体，形成羰基配合物 $Fe(CO)_5$, $Ni(CO)_4$, $Co_2(CO)_8$

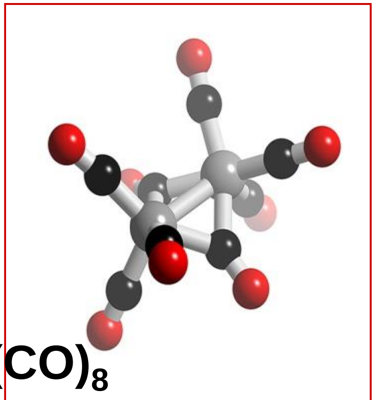
※ 其中C是配位原子。



$Fe(CO)_5$



$Ni(CO)_4$



$Co_2(CO)_8$

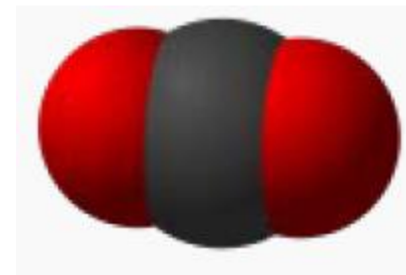
3. [+ 4] O.S CO_2

经典的分子结构：O=C=O

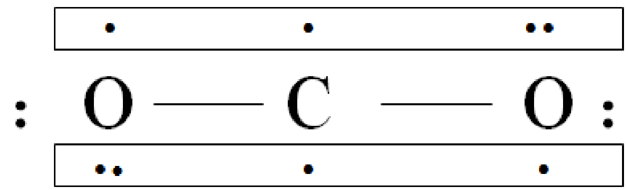
C=O双键键长124pm（在CH_3--C(=O)--CH_3中）

C$\leftarrow\!\!\!\equiv$O叁键键长113 pm

O=C=O中，C=O双键键长116 pm



C：sp杂化



Π_3^4

※ 非极性分子，无色、无味（酸性）、不燃、不助燃，可灭火，但不能灭Mg、Al、P等引起的火灾。

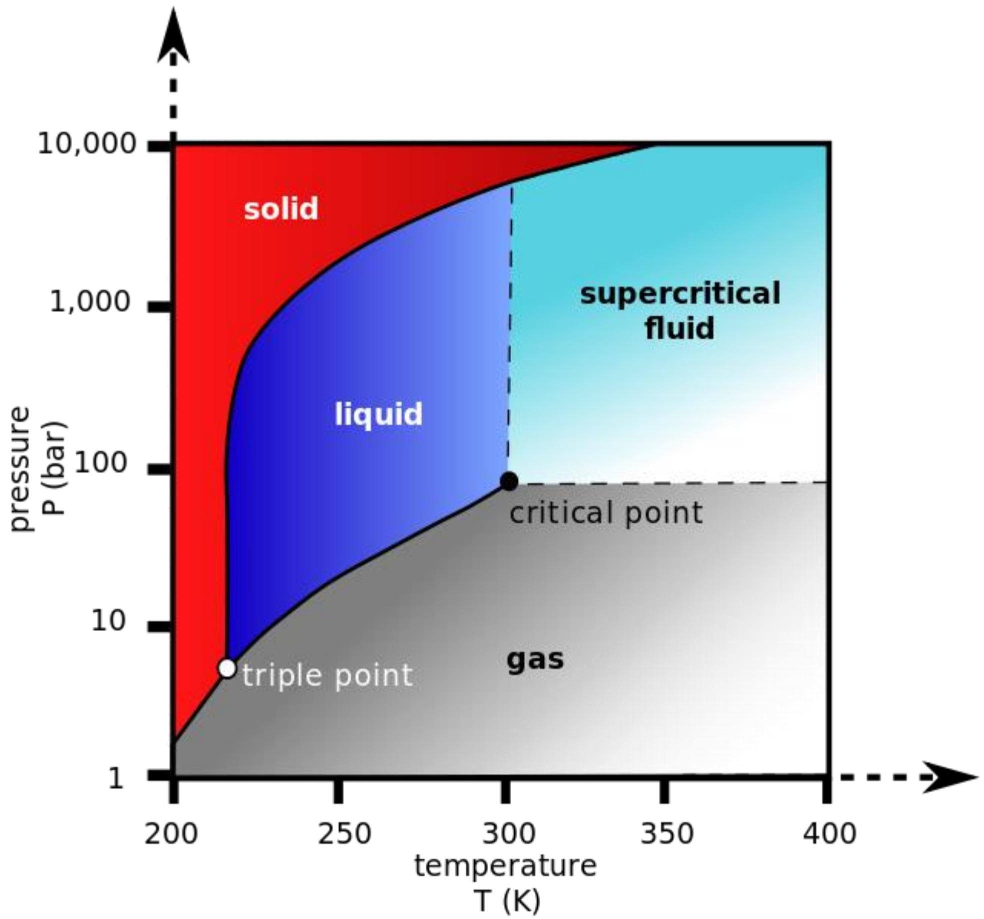
CO_2 + Mg = 2MgO + C

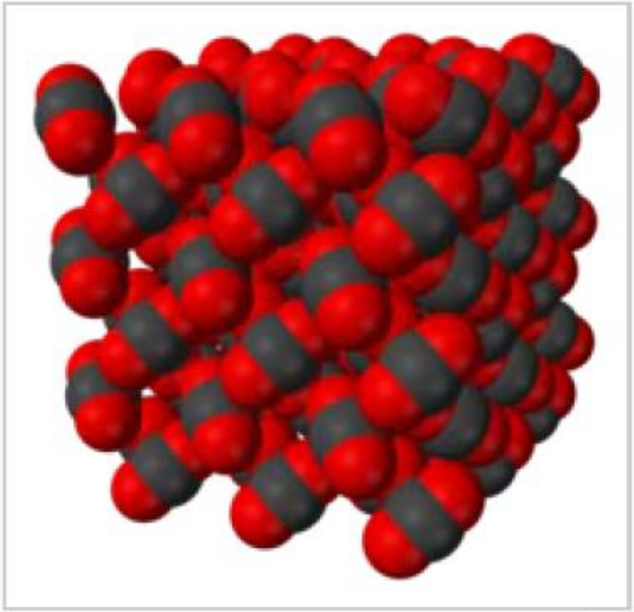
4P + $10CO_2$ = P_4O_{10} + 10CO

Dry ice (干冰)

CO_2加压液化得固体二氧化碳
— 干冰

- $CO_{2(l)}$ 蒸发 $CO_{2(g)}$ + $CO_{2(s)}$ 干冰(制冷剂)





Crystal structure of dry ice

碳酸和碳酸盐：CO_3^{2-}

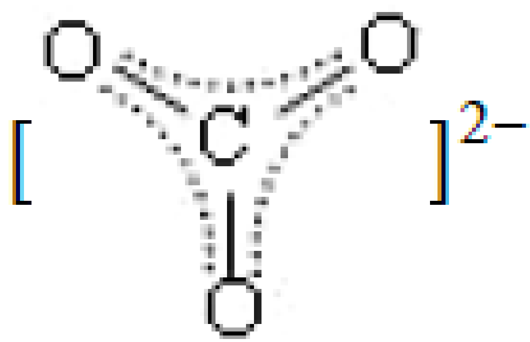
a. structure

CO_2溶于水，大部分形成$CO_2 \cdot H_2O$，极小部分形成

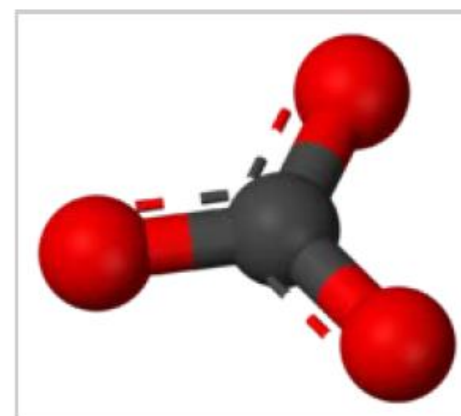
H_2CO_3（**二元弱酸**）

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_1^\ominus = 4.4\times10^{-7}$$

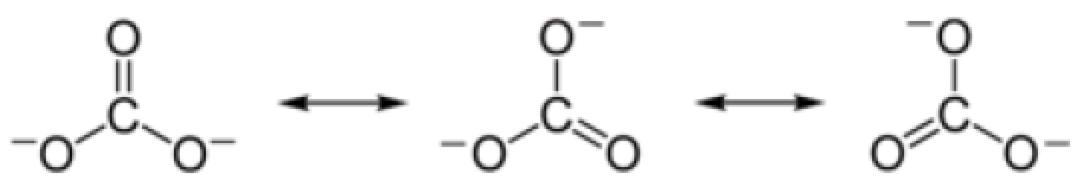
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2^\ominus = 4.7\times10^{-11}$$



Π_4^6



sp^2杂化



碳酸盐

H_2CO_3																	He
Li_2CO_3	$BeCO_3$											B	C	N	O	F	Ne
Na_2CO_3	$MgCO_3$											$Al_2(CO_3)_3$	Si	P	S	Cl	Ar
K_2CO_3	$CaCO_3$	Sc	Ti	V	Cr	$MnCO_3$	$FeCO_3$	$CoCO_3$	$NiCO_3$	$CuCO_3$	$ZnCO_3$	Ga	Ge	As	Se	Br	Kr
Rb_2CO_3	$SrCO_3$	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag_2CO_3	$CdCO_3$	In	Sn	Sb	Te	I	Xe
Cs_2CO_3	$BaCO_3$		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl_2CO_3	$PbCO_3$	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

↓

$La_2(CO_3)_3$	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

http://en.wikipedia.org/wiki/Carbonate

工业上生产碳铵肥料：

$$2NH_4^+ + CO_3^{2-} + CO_2 + H_2O = 2NH_4HCO_3$$

b. 水溶性

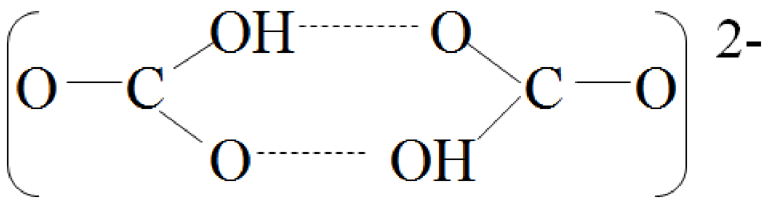
(i) 碳酸盐: 正盐中除碱金属(不包括Li^+)，铵及Tl^+盐外，都难溶于水；

(ii) 许多金属的酸式盐的溶解度大于正盐， S(难溶正盐)<S(相应酸式盐) ,但

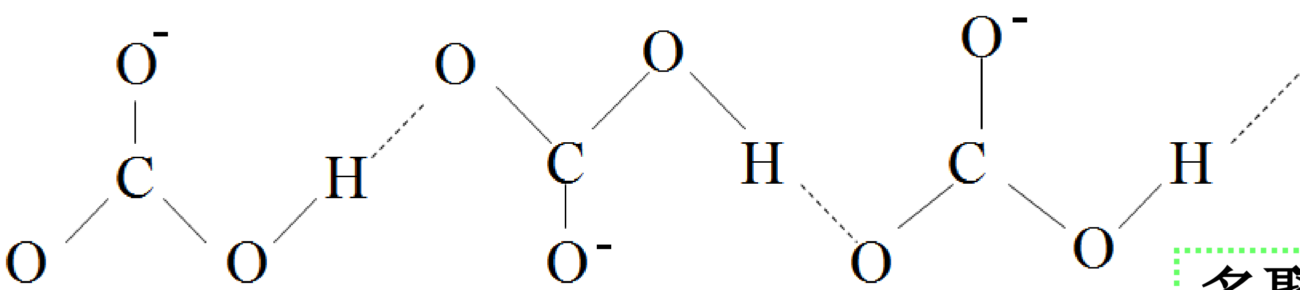
$$S_{NaHCO_3} < S_{Na_2CO_3}$$

易溶盐：	Na_2CO_3	$NaHCO_3$	K_2CO_3	$KHCO_3$
100℃溶解度 (g/100g H_2O)	45	16	156	60

解释：这是由于在$NaHCO_3$溶液中HCO_3^-以氢键相连成二聚或多聚链状离子，降低了它们的溶解度：



双聚$(HCO_3)_2^{2-}$



多聚$(HCO_3)_n^{n-}$

c. 热稳定性：

- 酸<酸式盐<正盐（$H_2CO_3 < MHCO_3 < M_2CO_3$）

$$H_2CO_3 \longrightarrow H_2O + CO_2(g)$$

$$2M^{I}HCO_3 \longrightarrow M^{I}_2CO_3 + H_2O + CO_2$$

$$M^{II}CO_3 \longrightarrow M^{II}O + CO_2(g)$$

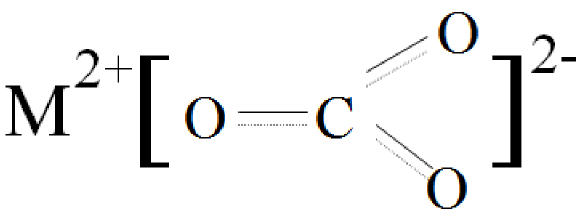
- 同一族金属的碳酸盐稳定性从上到下增加

	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
分解T/℃	100	540	900	1290	1360

➢ 碱金属碳酸盐 > 碱土金属碳酸盐 > 过渡金属碳酸盐（过渡金属碳酸盐稳定性差）

	$CaCO_3$	$PbCO_3$	$ZnCO_3$	$FeCO_3$
分解T/℃	900	315	350	282
价电子构型	8 e⁻	(18+2) e⁻	18 e⁻	(9-17) e⁻

离子反极化：



$$MCO_3 \longrightarrow MO + CO_2$$

$r(M^{2+})$ 愈小，M^{2+} 反极化力愈大，MCO_3 愈不稳定； M^{2+} 为18e⁻，(18+2)e⁻，(9-17)e⁻ 构型相对于 8e⁻构型的极化力大， 其 MCO_3 相对不稳定。

d. 水解性

$$CO_3^{2-} + H_2O = HCO_3^- + OH^- \quad（强碱）$$

$$K^{\theta}_{h_1}(CO_3^{2-}) = \frac{K^{\theta}_W}{K^{\theta}_2(H_2CO_3)} = 1.78 \times 10^{-4}$$

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \quad (弱碱）$$

$$K^{\theta}_{h_2}(CO_3^{2-}) = \frac{K^{\theta}_W}{K^{\theta}_1(H_2CO_3)} = 2.32 \times 10^{-8}$$

金属离子（碱金属除外）$\xrightarrow{Na_2CO_3}$

碳酸盐↓（或氢氧化物↓或碱式碳酸盐）

① 氢氧化物沉淀：$S_{氢氧化物} < S_{碳酸盐}$

Al^{3+}、Fe^{3+}、Cr^{3+}、Sn^{2+}、Sn^{4+}、Sb^{3+}等(水解性强)

$2Fe^{3+}+3CO_3^{2-}+3H_2O=2Fe(OH)_3\downarrow+3CO_2\uparrow$

② 碱式碳酸盐：$S_{氢氧化物} \approx S_{碳酸盐}$

Mg^{2+}、Pb^{2+}、Cu^{2+}、Bi^{3+}、Zn^{2+}、Hg^{2+}、Cd^{2+}等

$2Cu^{2+}+2CO_3^{2-}+H_2O=Cu_2(OH)_2CO_3\downarrow+CO_2\uparrow$

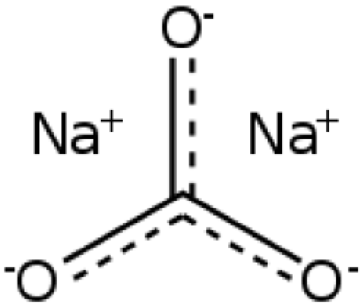
③ 碳酸盐沉淀：$S_{氢氧化物} > S_{碳酸盐}$

Ca^{2+}、Sr^{2+}、Ba^{2+}、Ni^{2+}、Ag^{+}、Mn^{2+}等(难水解)

$Ba^{2+}+CO_3^{2-}=BaCO_3\downarrow$

- 鉴定：
  - 加入稀盐酸，将产生的气体通入澄清的石灰水中，如果澄清的石灰水变浑浊，说明含有CO_3^{2-}

碳酸钠(Sodium carbonate) 纯碱，苏打



➢ 氨碱法（亦称为索尔维制碱法）：比利时人Ernest Solvay于1862年发明（在巴黎世界博览会上获得铜制奖章），应用最为广泛。

反应分三个步骤进行：

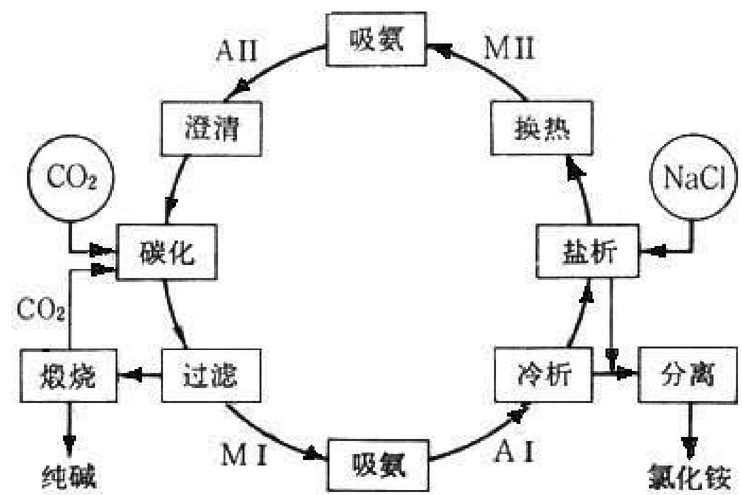
1. $NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$
2. $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$
3. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

NH_3的循环使用：$2NH_4Cl + CaO \rightarrow 2NH_3 + CaCl_2 + H_2O$

➢ **侯氏制碱法（联合制碱法）**：中国化学家侯德榜1943年在氨碱法的基础上改进而成，该法在世界博览会上获得金制奖章。

$NH_3 + CO_2 + H_2O + NaCl = NH_4Cl\downarrow + NaHCO_3$

$2NaHCO_3$（加热）$= Na_2CO_3 + H_2O + CO_2\uparrow$

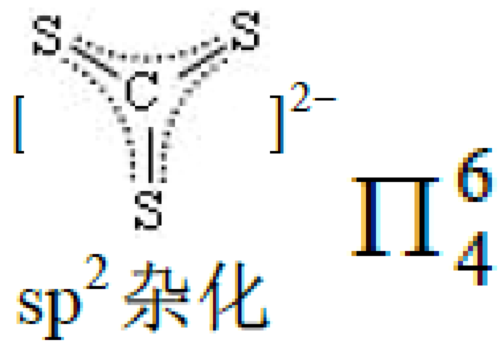


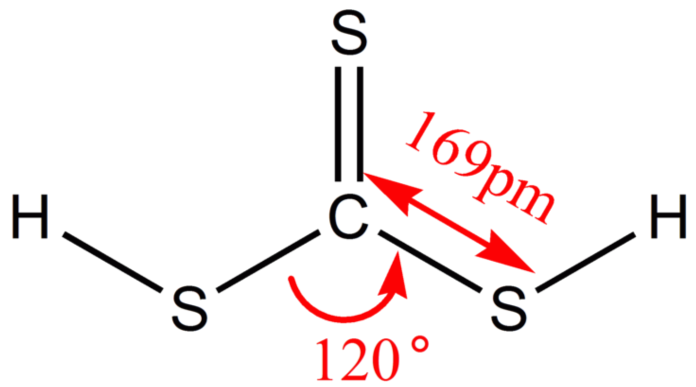
侯氏制碱法过程

本次作业
(张祖德编著<无机化学习题>
2011.6版)

Chapter 14. 碳族元素
(P65)
1、【<u>2、25</u>】、7、23、26

硫代碳酸盐（thiocarbonic acid, CS_3^{2-}）





$$K_2S + CS_2 = K_2CS_3 \overset{H^+}{=} H_2CS_3$$

$$CS_2 + SH^- \rightarrow S_2CSH^-$$

$$S_2CSH^- + OH^- \rightarrow CS_3^{2-} + H_2O$$

- H_2CS_3是高折射率油状物，易分解成H_2S和CS_2
- H_2CS_3的水溶液为弱酸，在水中缓慢分解

$$H_2CS_3 + 3H_2O = H_2CO_3 + 3H_2S$$

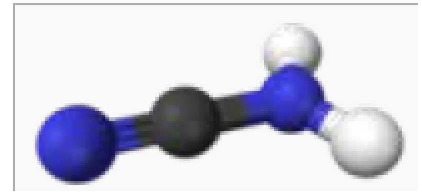
- K_2CS_3 酸化制备H_2CS_3:

$$K_2CS_3 + 2H^+ = H_2CS_3 + 2K^+$$

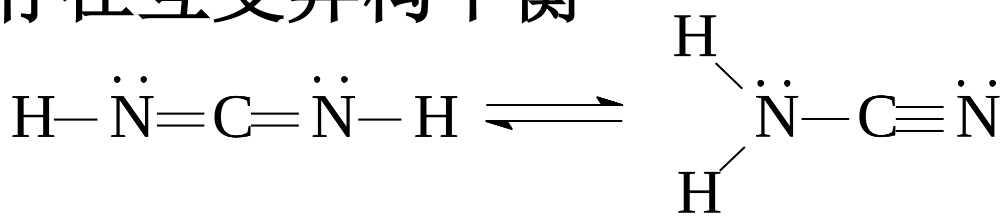
氨基腈化物 (Cyanamide) (CN_2^{2-})（氮代碳酸盐）

$[N{=}C{=}N]^{2-}$　　2 个 Π_3^4

sp 杂化



H_2CN_2 (Hydrogen dinitride carbonate)是无色晶体，易溶于水，alcohol和ether，显示弱酸性，在有机溶剂中可能存在互变异构平衡

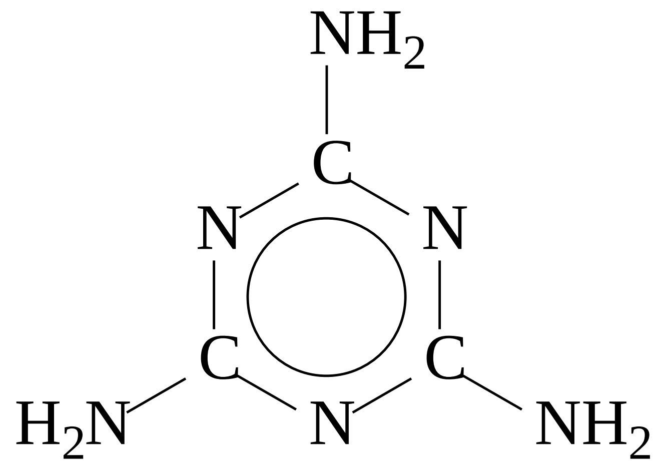


H_2CN_2在水中缓慢分解:

$H_2CN_2 + 3H_2O = H_2CO_3 + 2NH_3$

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

$$3H_2CN_2(l) \xrightarrow{\text{聚合}} (H_2CN_2)_3$$



三聚氰胺

3. [+ 4] O.S

(1) $CHal_4$ (halides of carbon)

a. 制备 $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$

CCl_4: 无色液体, 有机溶剂(不燃), 常用的灭火剂

b. 水解性

$$CHal_4 + 2H_2O = CO_2 + 4HHal$$

CF_4（$\Delta_r G_m^\ominus$ $= -150 kJ \cdot mol^{-1}$），CCl_4（$\Delta_r G_m^\ominus$ $= -250 kJ \cdot mol^{-1}$）

从热力学上看是可行的，它们之所以不能水解是由于在通常条件下缺乏动力学因素：碳的配位数已饱和，不能与水分子结合；

从$CF_4 \rightarrow CI_4$随着键长的增大，键的强度减弱，稳定性减弱，活泼性增强。

(2) $COHal_2$（卤氧化碳或碳酰卤）

所有的$COHal_2$比$CHal_4$的化学性质活泼,特别是它们易水解:

$$COCl_2 + H_2O = CO_2 + 2HCl$$

它们都有极性,都是平面三角形。

※ $COCl_2$ (光气) 是剧毒的！

光气的制备:

$$CO + Cl_2 = COCl_2$$

(3) CS_2

a. Preparation

(i) $C + 2S = CS_2$ (900°C)

(ii) $4S + CH_4 = CS_2 + 2H_2S$ (600°C, Al_2O_3或硅胶)

b. Properties

CS_2易挥发，易燃，无色的有机溶剂

明显水解 $CS_2 + 2H_2O = CO_2 + 2H_2S$

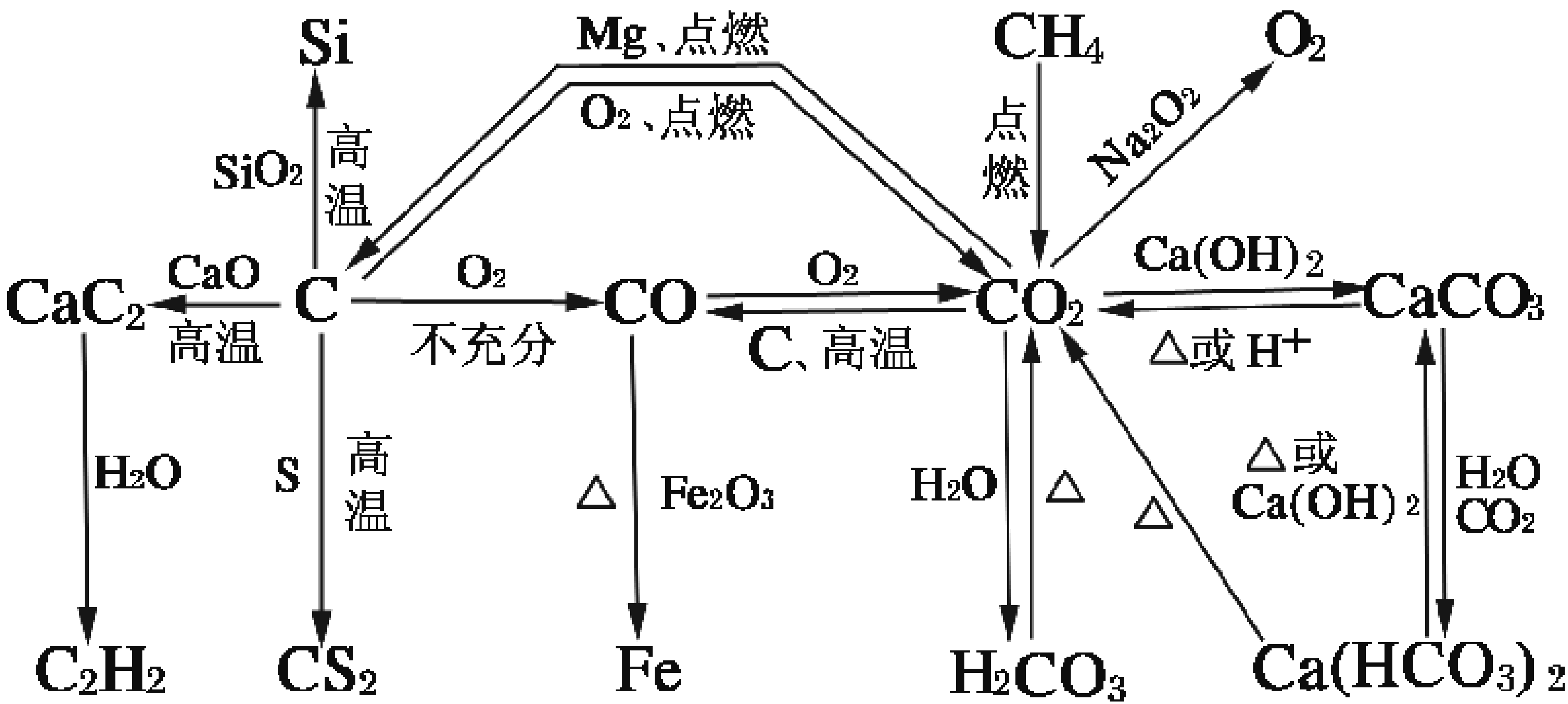
与碱性硫化物反应 $Na_2S + CS_2 = Na_2CS_3$

CS_2在空气中极易着火，反应为:

CS_2 (l) + $3O_2$ $\underline{点火}$ $CO_2\uparrow + SO_2\uparrow$

$$CS_2 + 3Cl_2 \xrightarrow{MnCl_2} CCl_4 + S_2Cl_2$$

碳及其化合物的相互转化



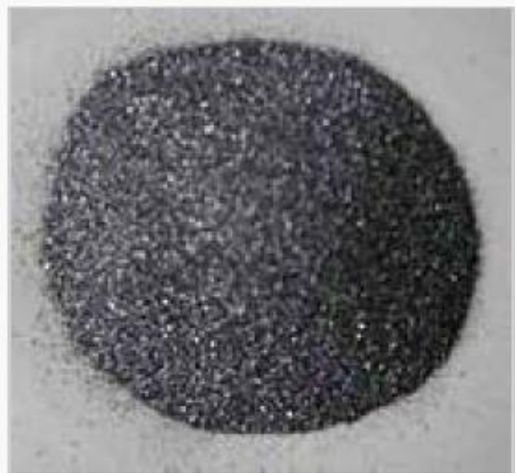
§ 15-2 Silicon and its compounds

一、General properties:

1. 由于Si的原子半径大，电离能低，电子亲合能和极化率高，因此**Si在化学性质上与碳有许多不同之处**，例如Si和Si之间基本上不形成pπ－pπ键，换言之，Si的sp或sp^2杂化不稳定。

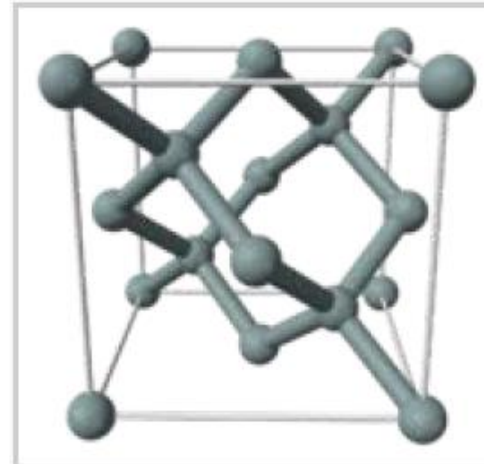
2. 由于Si原子的价轨道存在3d空轨道，所以Si的最大配位数可以达到6，可以形成d—pπ键，例如$N(SiH_3)_3$中N原子采取sp^2杂化，分子为平面三角形。这是由于N原子上的孤对电子对占有Si原子的3d空轨道，形成d－pπ键所致。显然$N(CH_3)_3$与$N(SiH_3)_3$的碱性也不同，前者的Lewis碱性大于后者。

3. **Si在自然界中占第二位，仅次于氧。在地壳中的丰度为0.277**，以石英矿(silica)、硅酸盐(silicate)和硅铝酸盐(aluminosilicate)存在。

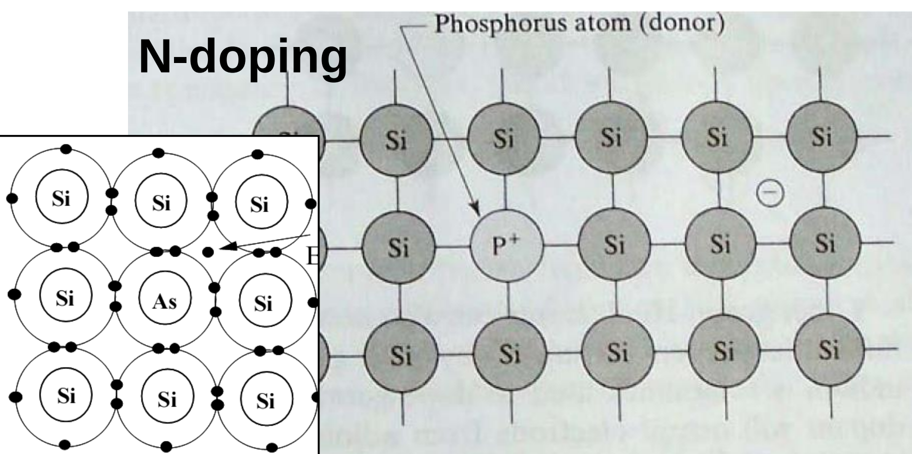


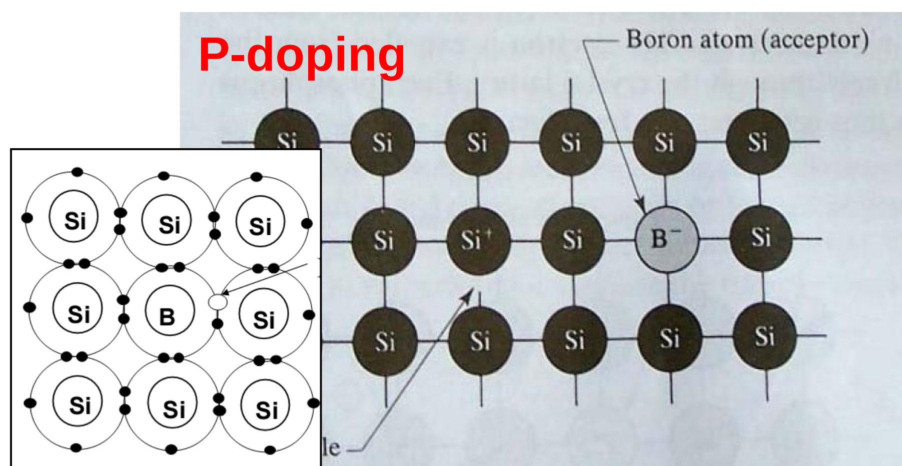
二、The simple substance

- 有晶态（银灰色）和无定形态（非晶深灰黑色粉末）两种，其晶体类似金刚石。熔点高、硬度大，具金属光泽。在常温下化学性质不活泼。
- 硅的所有价电子参与σ键的形成，在平常状态下导电性很差。当高纯硅中掺杂少于百万分之一的磷原子时，成键后就有了多余的电子；若杂质是硼原子，成键后就有了空轨道。能导电（但导电率不及金属），随T↑导电性↑，用作半导体材料。

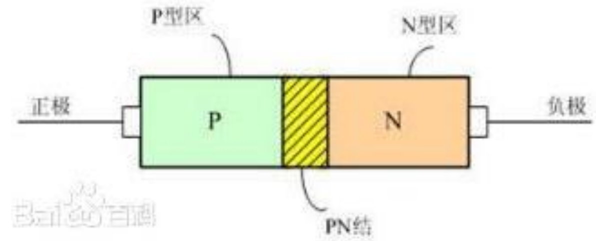


Silicon crystallizes in a diamond cubic crystal structure

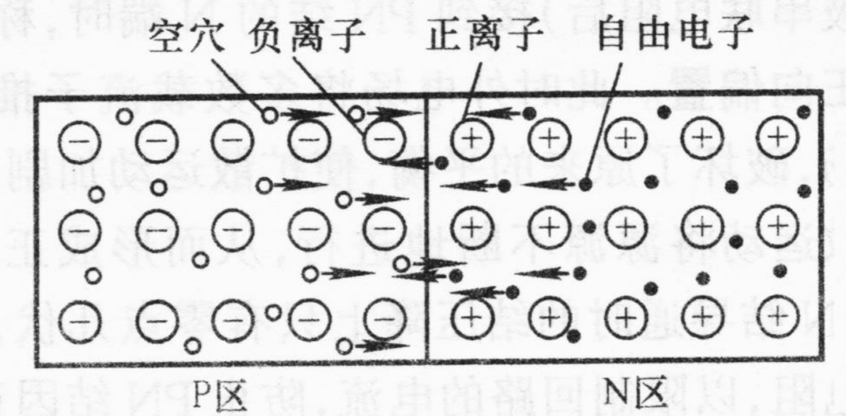




PN结



- **PN结的形成：**将一块半导体的一侧掺杂成P型半导体，另一侧掺杂成N型半导体，在两种半导体的交界面处将形成一个特殊的薄层 ⇒ PN结

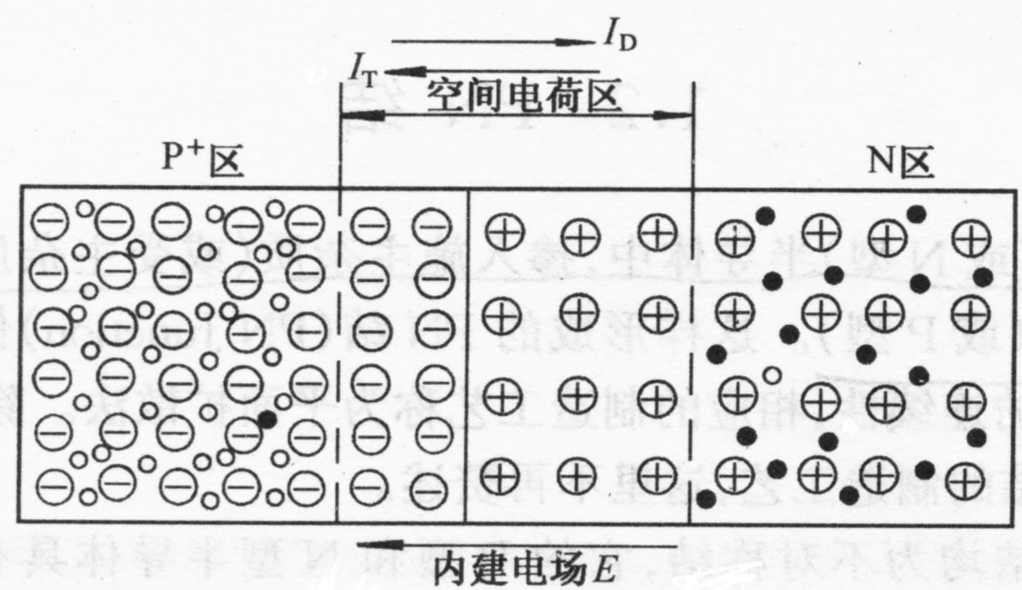


(a)

P区与N区中载流子的扩散

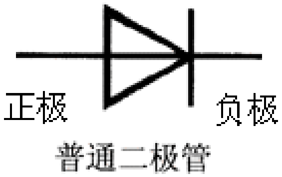
+

少子的漂移



平衡状态下的PN结

➢ PN结的单向导电性



正向偏置：外加电场与内建电场方向相反，扩散运动加强，形成较大的正向电流，这时称PN结处于导通状态。

“正偏导通，呈小电阻，电流较大”

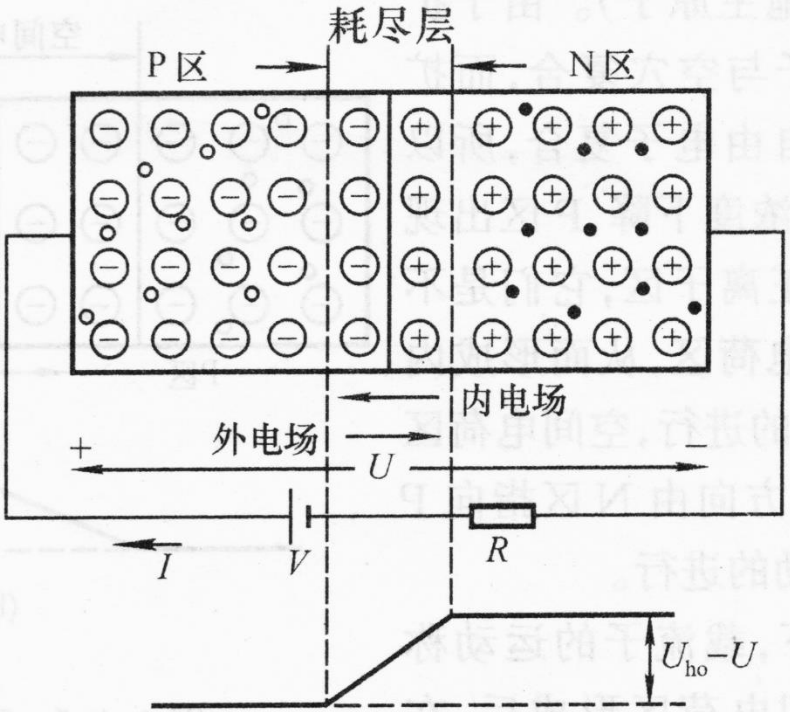


图 1.1.6　PN 结加正向电压时导通

反向偏置：外加电场与内建电场方向相同，漂移运动产生很小反向电流，这时称PN结处于截止状态。

“反偏截止，电阻很大，电流近似为零”

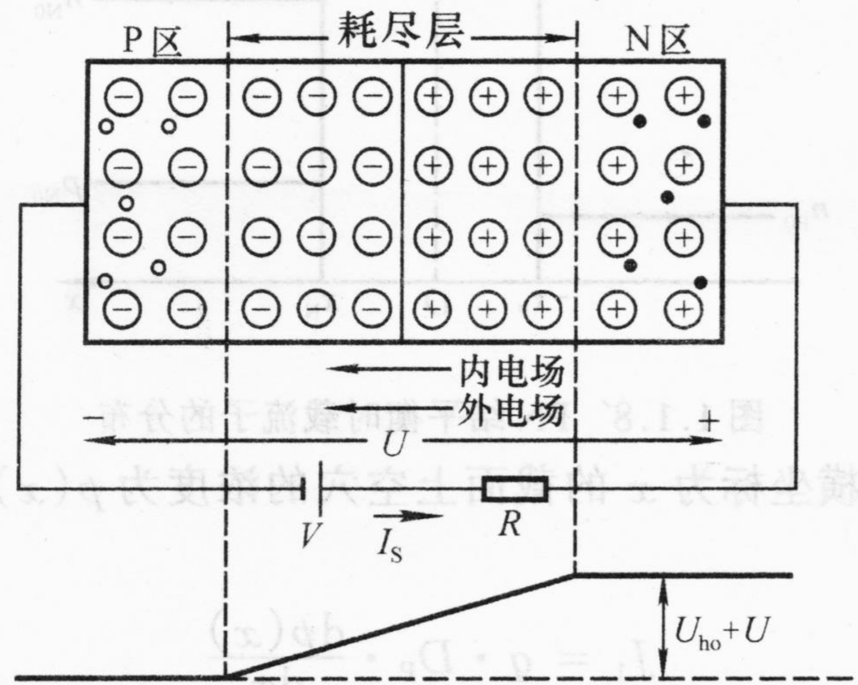


图 1.1.7　PN 结加反向电压时截止

1. preparation:

(1) $SiCl_4 + 2Zn \overset{\triangle}{=} Si + 2ZnCl_2$

(2) SiO_2和C混合，在电炉中加热:

$SiO_2 + 2C = Si + 2CO\uparrow$

(3) $SiO_2 + CaC_2 = Si + Ca + 2CO$

(4) 硅烷的分解:　$SiH_4 \overset{\triangle}{=} Si + 2H_2$

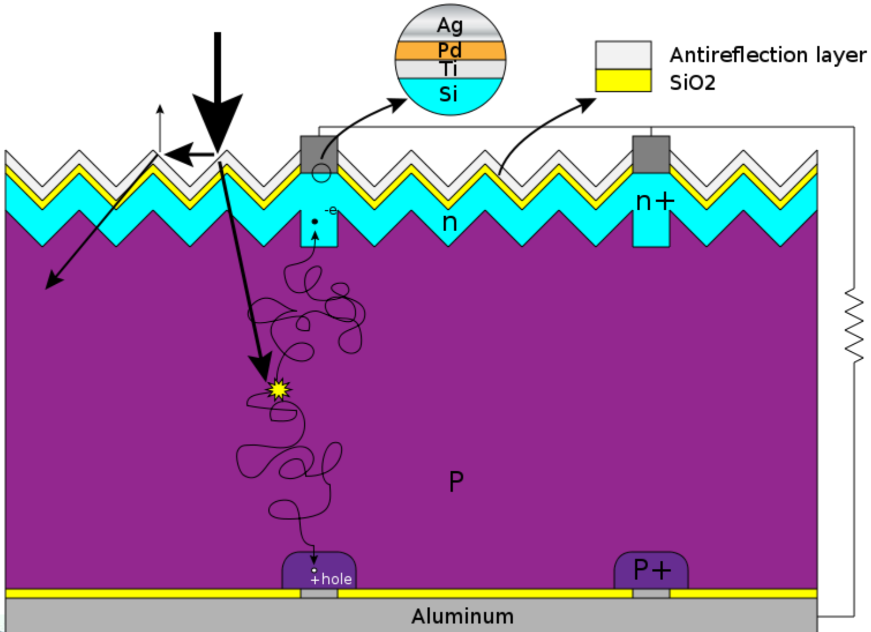
◆用作半导体的超纯硅，需用区域熔融的方法提纯

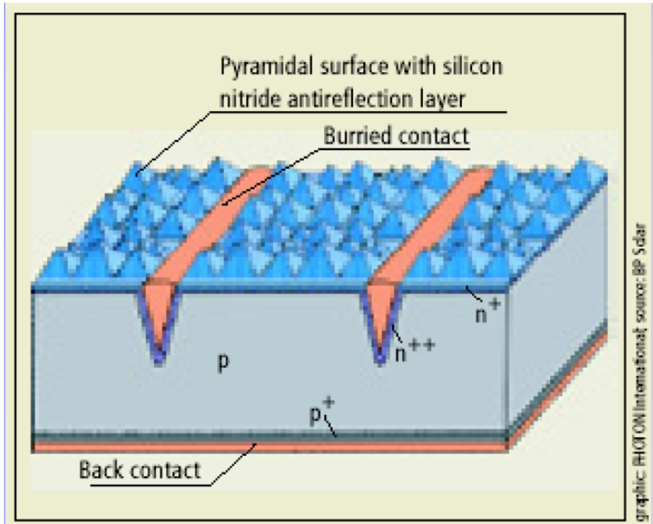
纯度 > 99.9999999%

用　途

- **高纯的单晶硅是重要的半导体材料**。在单晶硅中掺入微量的第IIIA族元素，形成p型硅半导体；掺入微量的第VA族元素，形成n型；和p型半导体结合在一起，就可做成太阳能电池，将辐射能转变为电能。在开发能源方面是一种很有前途的材料。
- **金属陶瓷、宇宙航行的重要材料**。将陶瓷和金属混合烧结，制成金属陶瓷复合材料，它耐高温，富韧性，可以切割，既继承了金属和陶瓷的各自的优点，又弥补了两者的先天缺陷。 可应用于军事武器的第一架航天飞机“哥伦比亚号”能抵挡住高速穿行稠密大气时磨擦产生的高温，全靠它那三万一千块硅瓦拼砌成的外壳。
- **光导纤维通信，最新的现代通信手段**。用纯二氧化硅拉制出高透明度的玻璃纤维，激光在玻璃纤维的通路里，无数次的全反射向前传输，代替了笨重的电缆。光纤通信容量高，一根头发丝那么细的玻璃纤维，可以同时传输256路电话，它还不受电、磁干扰，不怕窃听，具有高度的保密性。光纤通信将会使21世纪人类的生活发生革命性巨变。
- **性能优异的硅有机化合物**。例如有机硅塑料是极好的防水涂布材料。在地下铁道四壁喷涂有机硅，可以一劳永逸地解决渗水问题。在古文物、雕塑的外表，涂一层薄薄的有机硅塑料，可以防止青苔滋生，抵挡风吹雨淋和风化。天安门广场上的人民英雄纪念碑，便是经过有机硅塑料处理表面的，因此永远洁白、清新。

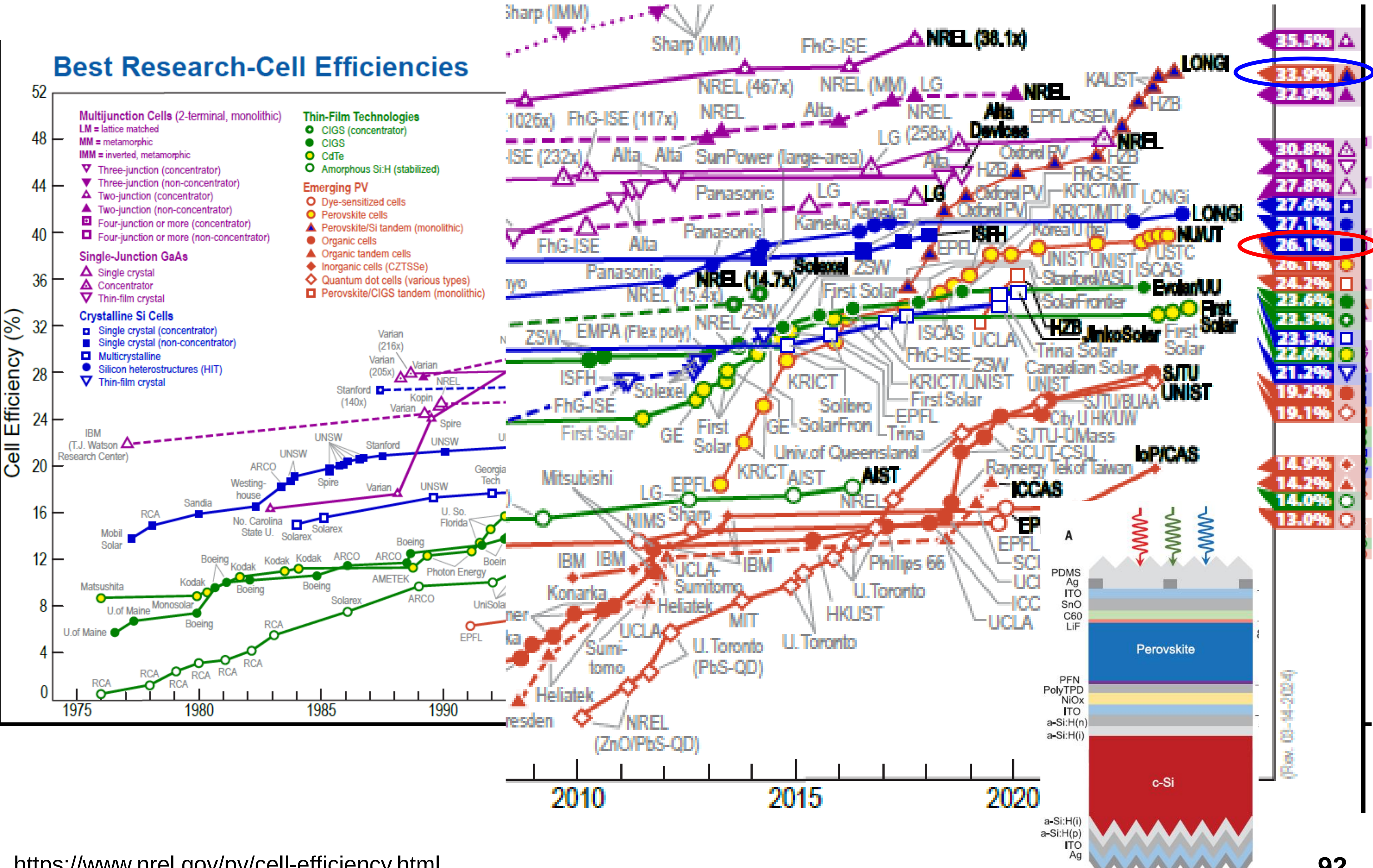
晶体硅太阳能电池





Buried-contact cell/UNSW
BP Solar – 18.3%

新型薄膜太阳能电池



https://www.nrel.gov/pv/cell-efficiency.html

2. Properties

(1) 在通常情况下，硅非常惰性，但加热时与许多非金属单质化合，还能与某些金属反应：

$$SiC \xleftarrow[2000°C]{C} Si \xrightarrow[400°C]{Cl_2} SiCl_4$$

$$Si_3N_4 \xleftarrow[1000°C]{N_2} Si \xrightarrow[600°C]{O_2} SiO_2$$

$$2Mg + Si = Mg_2Si$$

(2) 硅遇到氧化性的酸发生钝化(passivation)，它可溶于 **HF—HNO$_3$**的混合酸中

$$3Si + 4HNO_3 + 18HF = 3H_2SiF_6 + 4NO + 8H_2O$$

(3) 硅溶于碱并放出H_2： $Si + 2KOH + H_2O = K_2SiO_3 + 2H_2\uparrow$

(4) 硅在高温下与水蒸气反应： $Si + 3H_2O = H_2SiO_3 + 2H_2\uparrow$

SiC

俗称金刚砂（碳硅石），为硅与碳相键结而成的陶瓷状化合物。由于天然含量甚少，碳化硅主要为人造。用石英砂、石油焦(或煤焦)、木屑为原料通过电阻炉高温冶炼而成。碳化硅在大自然也存在罕见的矿物：莫桑石。在当代C、N、B等非氧化物高技术耐火原料中，碳化硅为应用最广泛、最经济的一种。

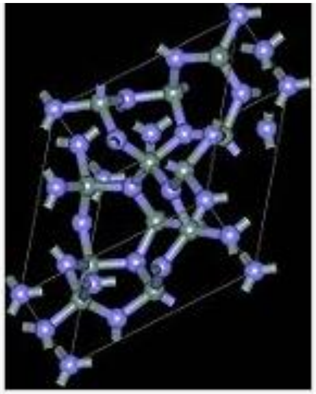
- **作为磨料，可用来做磨具，**如砂轮、油石、磨头、砂瓦类等。
- **作为冶金脱氧剂和耐高温材料；**
- **功能陶瓷；**
- **高级耐火材料；**
- **冶金原料；**
- **高纯度的单晶，可用于制造半导体、制造碳化硅纤维。**
- **用于3—12英寸单晶硅、多晶硅、砷化镓、石英晶体等线切割。太阳能光伏产业、半导体产业、压电晶体产业工程性加工材料。**

β-碳化硅

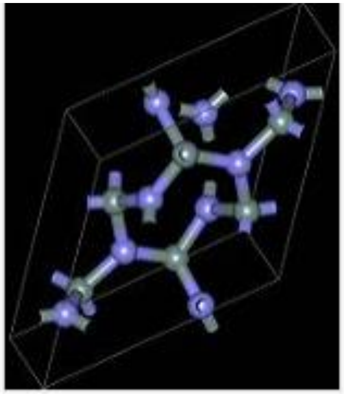
避雷器

Si_3N_4

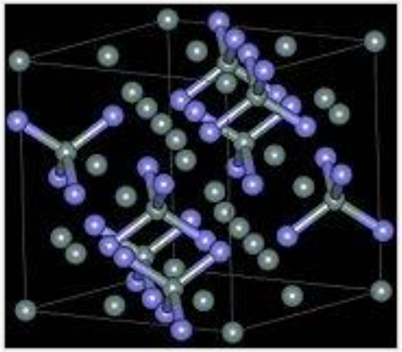
- Silicon nitride (Si_3N_4) is a hard, solid substance, that can be obtained by direct reaction between silicon and nitrogen at high temperatures. **Silicon nitride is the main component in silicon nitride ceramics**, which have relatively good shock resistance compared to other ceramics.



trigonal α-Si_3N_4.

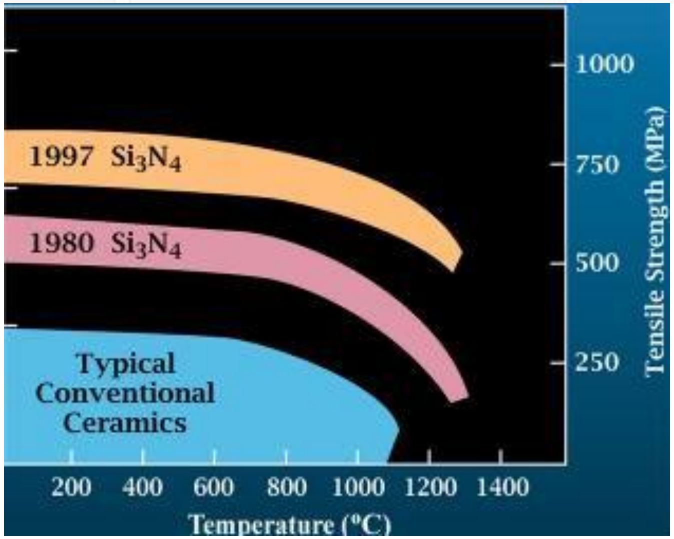


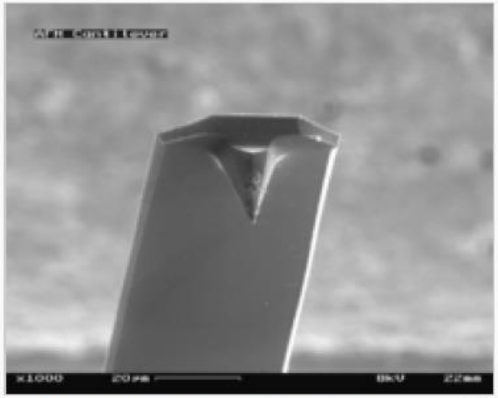
hexagonal β-Si_3N_4



cubic γ-Si_3N_4

Si_3N_4 axial rotor for a gas turbine engine.





Si_3N_4 cantilever used in atomic force microscopes

三、Compounds

C—H/C—O 键构成了动物, 植物及有机界;

C—C 键能 374kJ/mol ⇒ C—C 可以形成长链

Si—Si 键能为222kJ/mol ⇒ Si—Si 不可能形成长链

Si—O 键能为452kJ/mol ⇒ Si—O 可以形成长链

Si—O—Si 链构成了岩石, 土壤和泥沙 — 矿物界;

e.g. 二氧化硅(砂子), 硅酸盐(石头), 泥土

1. [- 4] O.S. 硅化物 (silicides)

(1) IA、 IIA族硅化物:

Ca_2Si , $CaSi$, $CaSi_2$

不稳定，与水反应，还可与H_2, N_2反应;

$$CaSi + 3H_2O = CaSiO_3 + 3H_2\uparrow$$

$$Ca_2Si + H_2 = CaSi + CaH_2$$

$$CaSi + N_2 = CaSiN_2$$

(2) 副族(d区)元素硅化物:

Mo_3Si , Mo_5Si_3 , $MoSi$, $MoSi_2$（2050℃）

高熔沸点，不溶于HF和王水，仅溶于HF-HNO_3混合液或者在碱液中，如

WSi_2（2165℃），Ti_5Si_3（2120℃），V_5Si_3（2150℃）

(3) f区元素的硅化物在反应堆中吸收中子。

2. [+4] O.S.

$SiHal_4$, SiO_2, Si_3N_4, SiC和SiH_4

	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
聚集态	g	l	l	s
分子量	小	→	→	大
熔沸点	低	→	→	高

- **制备:**

a. $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$

$SiO_2 + 4HF = SiF_4 + 2H_2O$ 刻蚀玻璃

b. $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$

- **水解:**

$$SiCl_4 + 4H_2O \rightarrow H_4SiO_4 + 4HCl$$

$$SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 4HF$$

$$SiF_4 + 2HF \rightarrow H_2[SiF_6]$$ （氟硅酸）

SiF_4

- **制备:**

$SiO_2+2CaF_2+2H_2SO_4 \xrightarrow{\text{加热}} SiF_4\uparrow+2CaSO_4+ 2H_2O$

$SiO_2 + 4HF = SiF_4$(不纯) $+ 2H_2O$

$BaSiF_6 \xrightarrow{\text{真空, 加热}} BaF_2 + SiF_4\uparrow$(纯)

- **水解:**

$\mathbf{SiF_4 + 3H_2O = H_2SiO_3 + 4HF}$

$\mathbf{4HF + 2SiF_4 = 2H_2SiF_6}$

即：$\mathbf{3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6}$

※目前只制得60%的H_2SiF_6溶液, 其为强酸，强度相当于硫酸

$3SiF_4 + 2Na_2CO_3 + 2H_2O =$

$2Na_2SiF_6$(白色晶体)$\downarrow + H_4SiO_4 + 2CO_2$

$SiCl_4$ (液态)

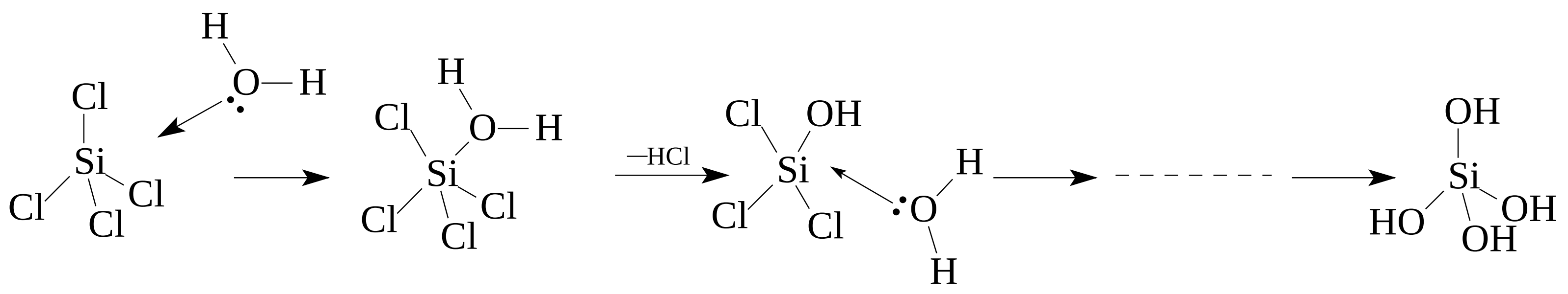
- **制备:**

$SiO_2 + 2C + 2Cl_2 \xrightarrow{\text{加热}} SiCl_4(l) + 2CO\uparrow$

- **水解:**

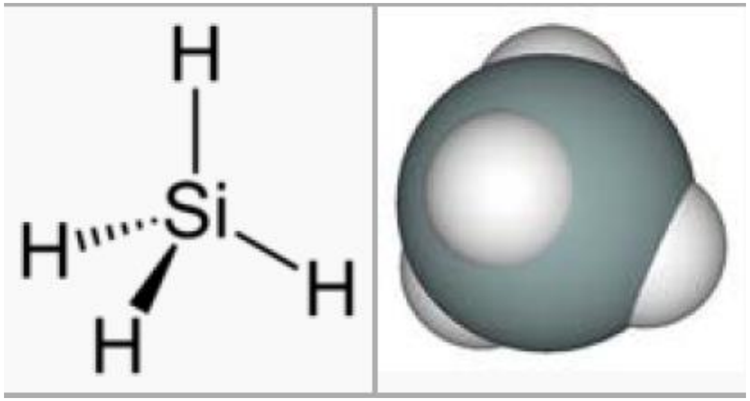
$SiCl_4(l) + 4H_2O(l) = H_4SiO_4(s) + 4HCl(aq)$

(烟雾剂)



(2) 硅烷(silane) $Si_nH_{(2n+2)}$ n可高达15

最简单的硅烷：SiH_4 (甲硅烷) $Si + H_2 \not\longrightarrow$



a. preparation:

$$Mg_2Si + 2H_2SO_4 \overset{H_2O}{=} SiH_4 + 2MgSO_4$$

$$Mg_2Si + 4NH_4Br \overset{NH_3}{=} SiH_4 + 2MgBr_2 + 4NH_3$$

$$SiCl_4 + LiAlH_4 = SiH_4 + LiCl + AlCl_3$$

b. properties

(i) reduction:

$$SiH_4 + 2KMnO_4 = 2MnO_2\downarrow + K_2SiO_3 + H_2O + H_2\uparrow$$

可以用$KMnO_4$来鉴别在纯水中硅烷（还原性比 CH_4 强）

$$SiH_4 + 8AgNO_3 + 2H_2O \longrightarrow 8Ag\downarrow + SiO_2\downarrow + 8HNO_3$$

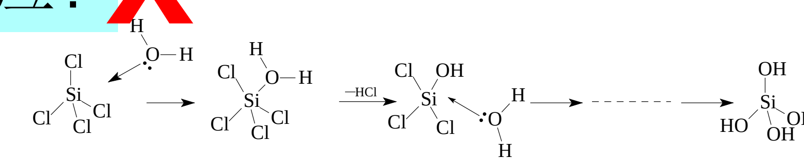
$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

自燃

(ii) hydrolysis: SiH_4在纯水和微酸性溶液中不水解，但在微量碱作催化剂时，迅速水解生成硅酸与氢气

$$SiH_4 + (n+2)H_2O \longrightarrow SiO_2 \cdot nH_2O + 4H_2$$

Note: CH_4 能否发生水解反应? X

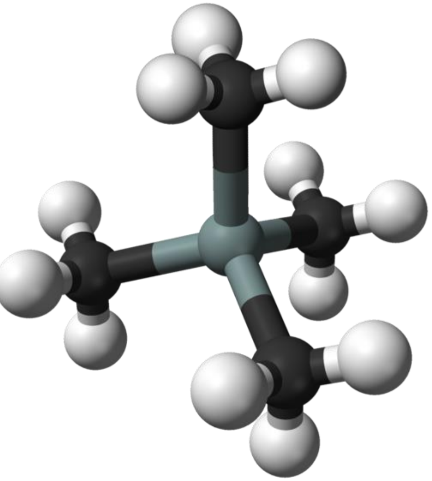


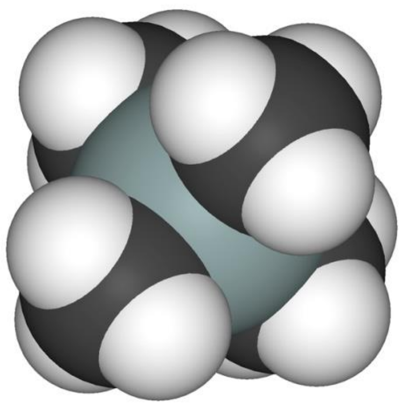
(iii) 热稳定性差:

$$SiH_4 \xrightarrow{500°C} Si + 2H_2$$

$$2\,CH_4 \xrightarrow{1773K} C_2H_2 + 3\,H_2$$

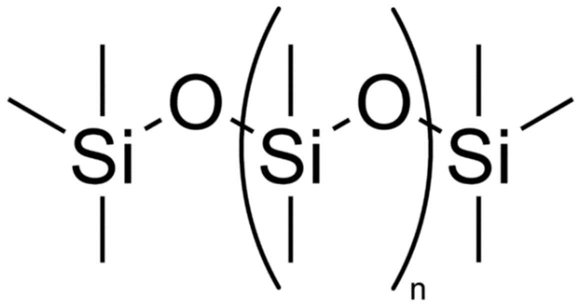
Tetramethylsilane

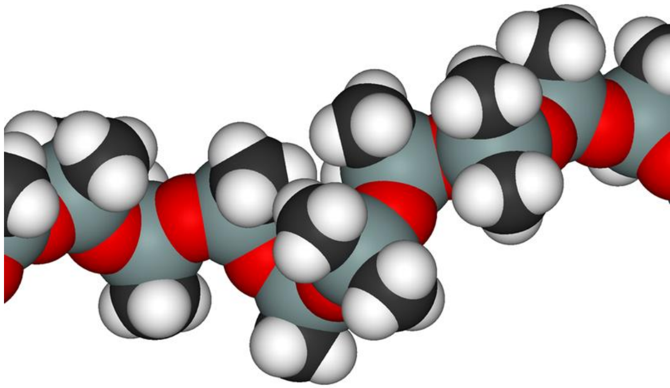




- Tetramethylsilane (TMS) is the accepted internal standard for calibrating chemical shift for ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy in organic solvents (where TMS is soluble). In water, where it is not soluble, sodium salts of DSS, 2,2-dimethyl-2-silapentane-5-sulfonate, are used instead. Because of its high volatility, TMS can easily be evaporated, which is convenient for recovery of samples analyzed by NMR spectroscopy.
- **Because all twelve hydrogen atoms in a tetramethylsilane molecule are equivalent, its ^{1}H NMR spectrum consists of a singlet**. The chemical shift of this singlet is assigned as δ=0, and all other chemical shifts are determined relative to it. The majority of compounds studied by ^{1}H NMR spectroscopy absorb downfield of the TMS signal, thus there is usually no interference between the standard and the sample. Similarly, **all four carbon atoms in a tetramethylsilane molecule are equivalent**. In a fully decoupled ^{13}C NMR spectrum, the carbon in the tetramethylsilane appears as a singlet, allowing for easy identification. The chemical shift of this singlet is also set to be δ 0 in the ^{13}C spectrum, and all other chemical shifts are determined relative to it.

Silicone rubber





- A polymer contains silicon together with carbon, hydrogen, and oxygen. There are multiple formulations.
- Silicone rubber is generally non-reactive, stable, and resistant to extreme environments and temperatures from −55 ^{o}C to +300 ^{o}C while still maintaining its useful properties.
- Silicone rubbers are widely used in industry, and may contain fillers to improve properties or reduce cost. Due to these properties and its ease of manufacturing and shaping, **silicone rubber can be found in a wide variety of products**, including: automotive applications; cooking, baking, and food storage products; apparel such as undergarments, sportswear, and footwear; electronics; medical devices and implants; and in home repair and hardware with products such as silicone sealants.

(3) 硅的含氧化合物

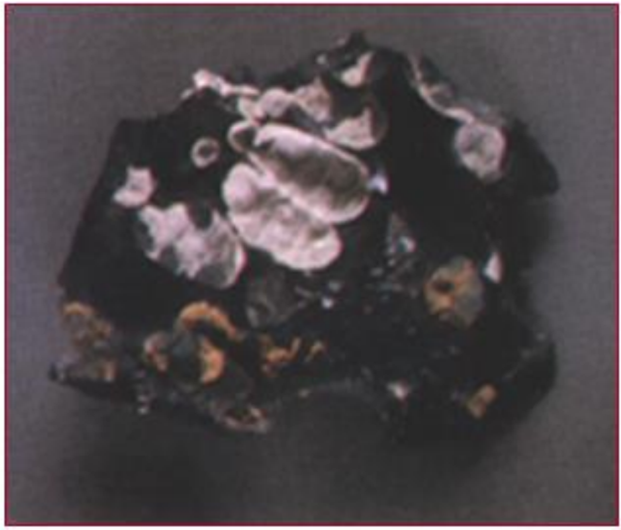
- 无定型体：石英玻璃、硅藻土、燧石
- 晶体：天然晶体为石英，属于原子晶体
- 纯石英：水晶
- 含有杂质的石英：玛瑙，紫晶，碧玉
- 混有杂质的石英细粒：砂粒

石英 —(～1600℃)→ 粘稠液体 —(急剧冷却)→ 石英玻璃（过冷液体）

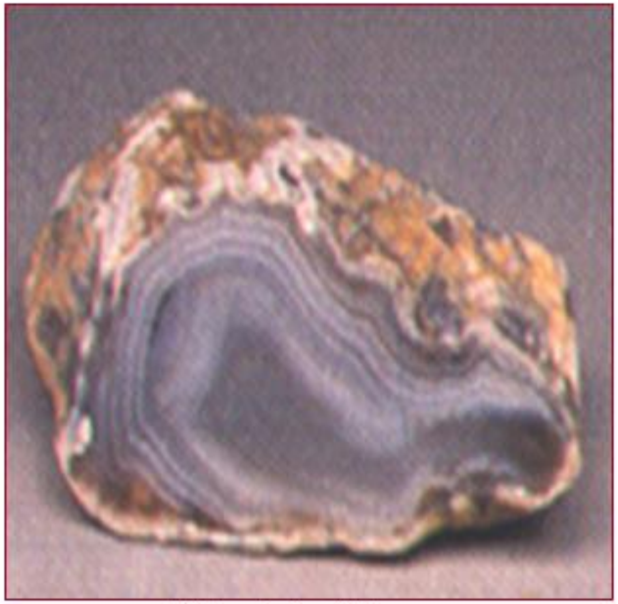
- 具有特殊性能


水晶


石英盐


黑曜(yao)石

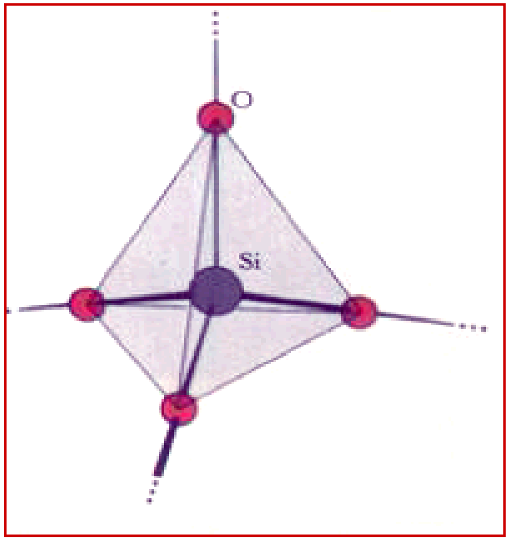

紫晶


缟玛瑙

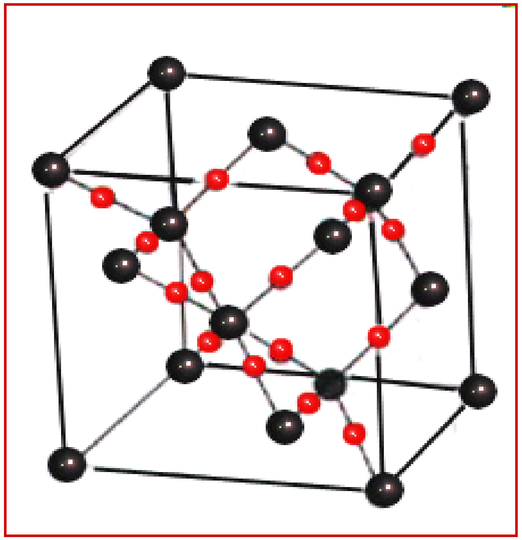

玛瑙

Silicone dioxide

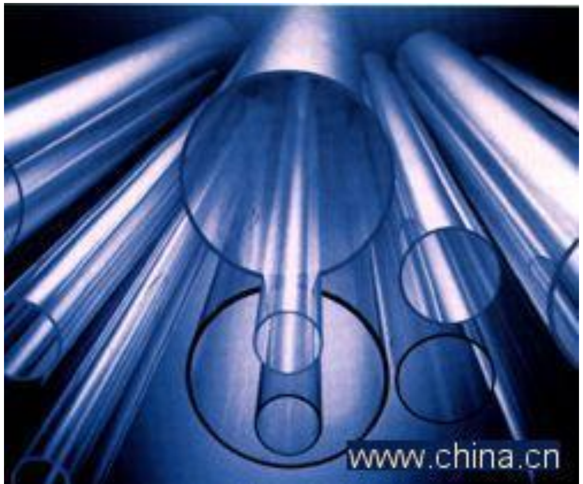
Si采用sp^3杂化轨道与氧形成硅氧四面体

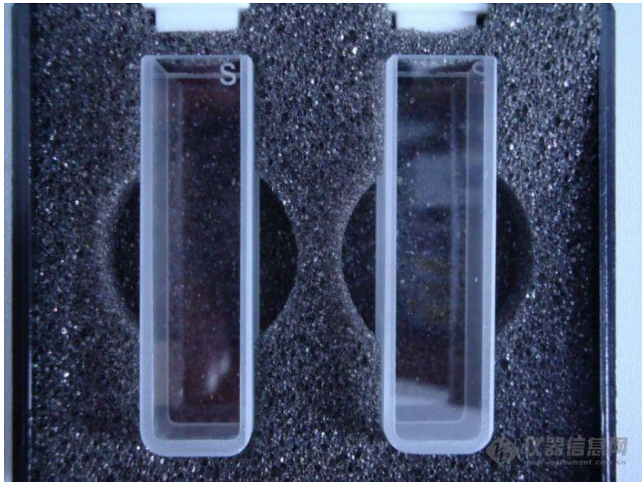


硅氧四面体

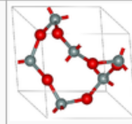
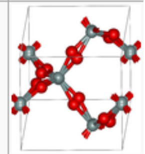
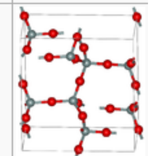
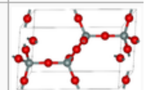
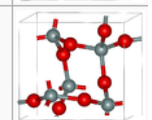
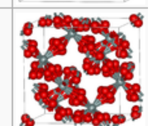
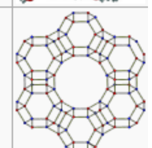
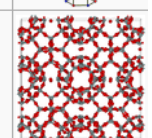
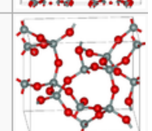


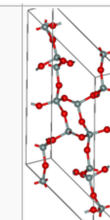
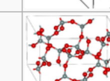
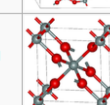
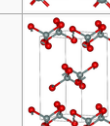
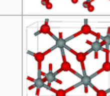
二氧化硅





Crystalline forms of SiO_2

Form	Crystal symmetry Pearson symbol, group No.	Notes	Structure
α-quartz	rhombohedral (trigonal) hP9, $P3_121$ No.152[13]	Helical chains making individual single crystals optically active; α-quartz converts to β-quartz at 846 K	
β-quartz	hexagonal hP18, $P6_222$, No.180[14]	closely related to α-quartz (with an Si-O-Si angle of 155°) and optically active; β-quartz converts to β-tridymite at 1140 K	
α-tridymite	orthorhombic oS24, $C222_1$, No.20[15]	metastable form under normal pressure	
β-tridymite	hexagonal hP12, $P6_3/mmc$, No. 194[15]	closely related to α-tridymite; β-tridymite converts to β-cristobalite at 2010 K	
α-cristobalite	tetragonal tP12, $P4_12_12$, No. 92[16]	metastable form under normal pressure	
β-cristobalite	cubic cF104, $Fd\bar{3}m$, No.227[17]	closely related to α-cristobalite; melts at 1978 K	
faujasite	cubic cF576, $Fd\bar{3}m$, No.227[18]	sodalite cages connected by hexagonal prisms; 12-membered ring pore opening; faujasite structure.[10]	
melanophlogite	cubic (cP*, $P4_232$, No.208)[5] or tetragonal ($P4_2/nbc$)[19]	Si_5O_{10}, Si_6O_{12} rings; mineral always found with hydrocarbons in interstitial spaces-a clathrasil[20]	
keatite	tetragonal tP36, $P4_12_12$, No. 92[21]	Si_5O_{10}, Si_4O_{14}, Si_8O_{16} rings; synthesised from glassy silica and alkali at 600–900K and 40–400 MPa	

moganite	Si_4O_8 and Si_6O_{12} rings	
coesite	Si_4O_8 and Si_8O_{16} rings; 900 K and 3–3.5 GPa	
stishovite	One of the densest (together with seifertite) polymorphs of silica; rutile-like with 6-fold coordinated Si; 7.5–8.5 GPa	
fibrous	like SiS_2 consisting of edge sharing chains	
seifertite	One of the densest (together with stishovite) polymorphs of silica; is produced at pressures above 40 GPa.[27]	

http://en.wikipedia.org/wiki/Silicon_dioxide

- property：
  - 与**HF**反应

    $SiO_2 + HF = SiF_4 + 2H_2O$

  - 与含氧酸盐反应

    $SiO_2 + Na_2CO_3 \xrightarrow{加热} Na_2SiO_3 + CO_2\uparrow$

    $SiO_2 + Na_2SO_4 \xrightarrow{加热} Na_2SiO_3 + SO_3\uparrow$

    $SiO_2 + KNO_3 \xrightarrow{加热} Na_2SiO_3 + NO_2\uparrow + NO\uparrow + O_2\uparrow$

  - 与碱反应

    $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$

  - 与碱性氧化物反应

    $NiO + SiO_2 \xrightarrow{873\sim1174K} NiSiO_3$

    $CaO + SiO_2 = CaSiO_3$

  - 与金属反应

    $SiO_2 + 2Mg \xrightarrow{高温} 2MgO + Si$

(4) 硅酸(silicic acid)及硅酸盐(silicate)

硅酸通式：$x\,SiO_2 \cdot y\,H_2O$

$x = 1$， $y = 1$， H_2SiO_3 偏硅酸

$x = 1$， $y = 2$， H_4SiO_4 正硅酸

$x = 2$， $y = 1$， $H_2Si_2O_5$ 二偏硅酸

$x = 2$， $y = 3$， $H_6Si_2O_7$ 焦硅酸

硅酸易于缩聚成大分子

(弱含氧酸均如此)

例如:

$HClO_4$, 强酸, 极难缩合, 脱水 Cl_2O_7

H_2SO_4, 强酸, 难缩合, 脱水 $M_2S_2O_7$

H_3PO_4, 中强酸, 脱水, 偏, 焦, 多聚磷酸盐

H_4SiO_4, 弱酸, 易缩合

H_2SiO_3溶解度小，是二元弱酸：

$K_1^\theta = 3.0 \times 10^{-10}$， $K_2^\theta = 2.0 \times 10^{-12}$

制备：可溶性硅酸盐与H^+, CO_2, NH_4^+反应得到H_2SiO_3

$$SiO_3^{2-} + 2H^+ = H_2SiO_3$$

$$SiO_3^{2-} + 2CO_2 + 2H_2O = H_2SiO_3 + 2HCO_3^-$$

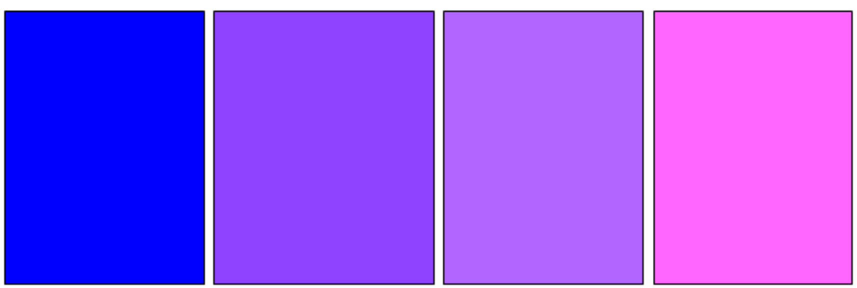
$$SiO_3^{2-} + 2NH_4^+ = H_2SiO_3 + 2NH_3$$

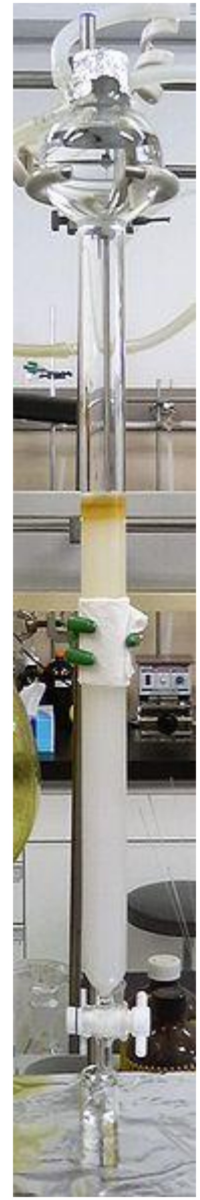
Silica gel

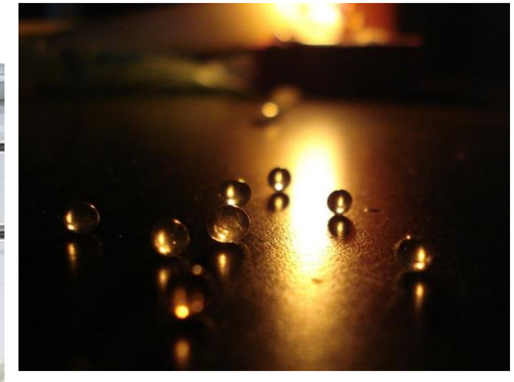
胶冻状硅酸 $\xrightarrow{-H_2O}$ 硅胶

硅胶的成分为SiO_2，但体系内部的硅氧四面体杂乱无序。300 ℃ 活化后，可作为吸附剂。

Na_2SiO_3溶液中加酸 → 硅酸胶体溶液和盐 —静置老化 24 *h*→ 凝胶 —热水洗涤 ＜100°C烘干→ 多孔性硅胶







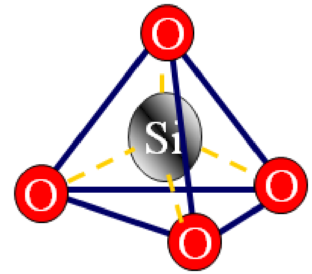
无水$CoCl_2$ → $CoCl_2 \cdot 6\,H_2O$

【**重要**】浸透过$CoCl_2$的硅胶为变色硅胶,作干燥剂。

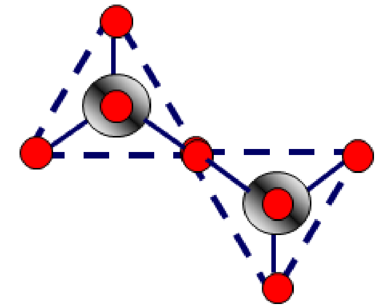
硅酸盐【重要知识点】

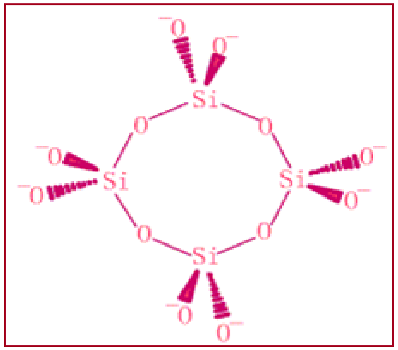
a. 结构（复杂！）：一般写成氧化物形式，它的基本结构单位为硅氧四面体$[SiO_4]^{4-}$。

- (1) 每个$[SiO_4]$四面体Si:O=1:4⇒SiO_4^{4-}
- (2) 两个$[SiO_4]$以角氧相连，Si和O的原子数之比是1:3.5 ⇒$Si_2O_7^{6-}$
- (3) $[SiO_4]$以两个角氧分别和其它$[SiO_4]$两个角氧相连成环状或长链状结构，Si:O=1:3 ⇒ $[SiO_3]_n^{2n-}$
- (4) $[SiO_4]$以角氧构造成双链，Si : O = 4 : 11 ⇒ $[Si_4O_{11}]_n^{6n-}$
- (5) $[SiO_4]$分别以三个角氧和其它三个$[SiO_4]$相连成层状结构，Si:O = 2:5 ⇒ $[Si_2O_5]_n^{2n-}$
- (6) $[SiO_4]$分别以四个氧和其他四个$[SiO_4]$相连成骨架状结构，Si:O = 1:2 ⇒ $(SiO_2)_n$

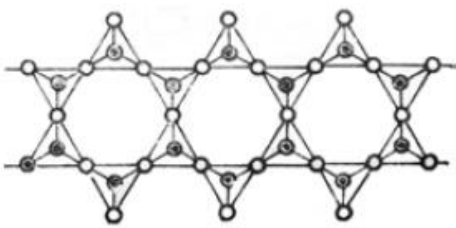


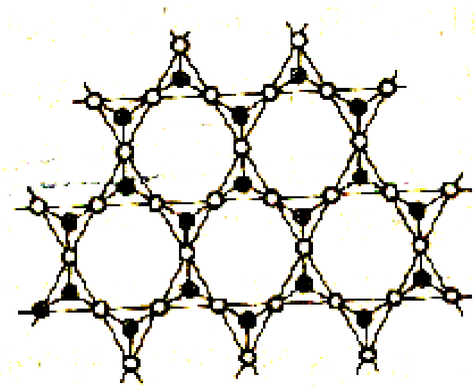
正硅酸根 SiO_4^{4-}


焦硅酸根 $Si_2O_7^{6-}$



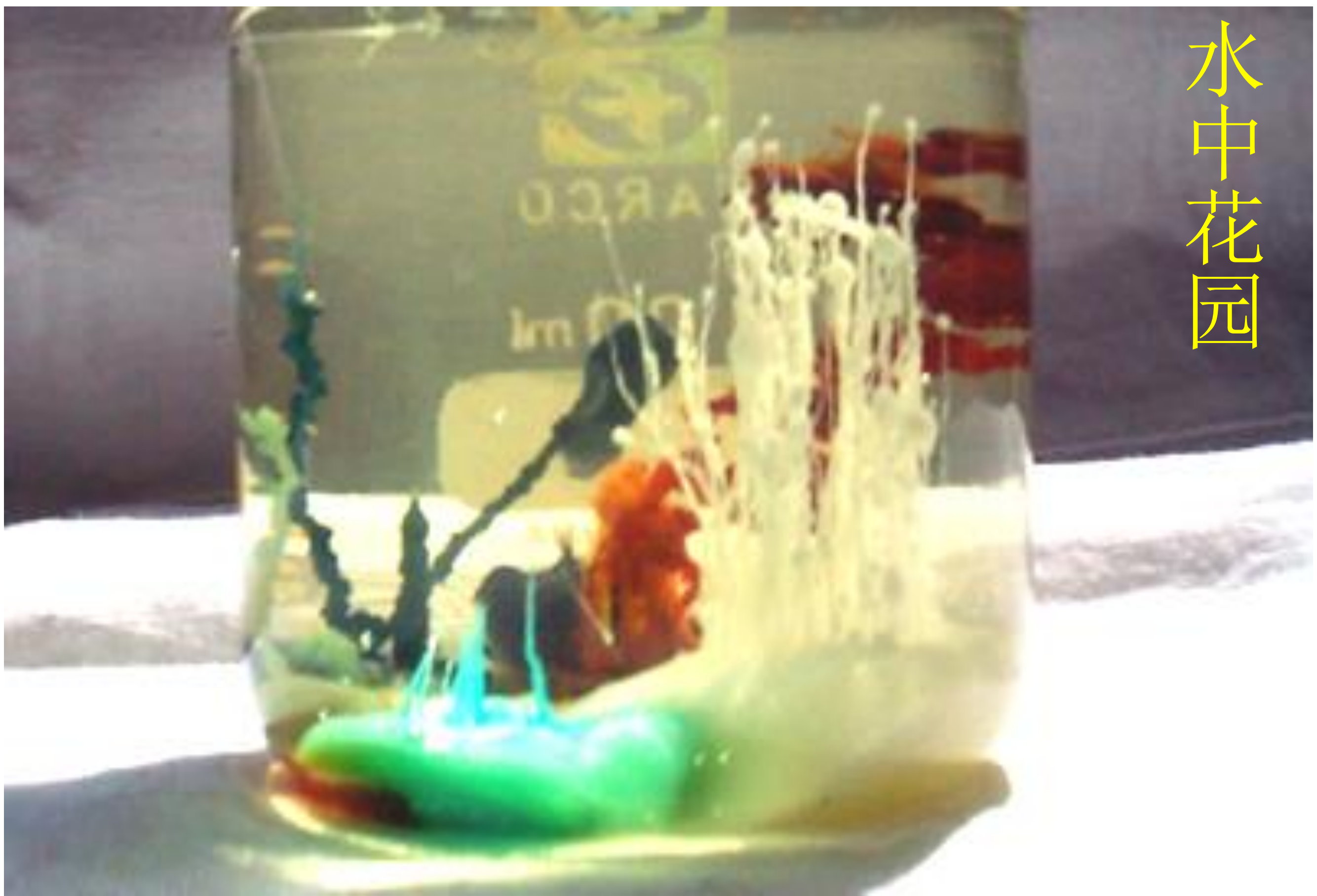
$Si_4O_{12}^{8-}$


$[Si_4O_{11}]_n^{6n-}$


$[Si_2O_5]_n^{2n-}$

硅酸盐
- 可溶性：Na_2SiO_3 (水玻璃)、K_2SiO_3
- 不溶性：大部分难溶于水且有特征颜色。

$ZnSiO_3$	$CuSiO_3$	$CoSiO_3$	$Fe_2(SiO_3)_3$	$MnSiO_3$	$NiSiO_3$
白	蓝	紫	红棕	肉	翠绿



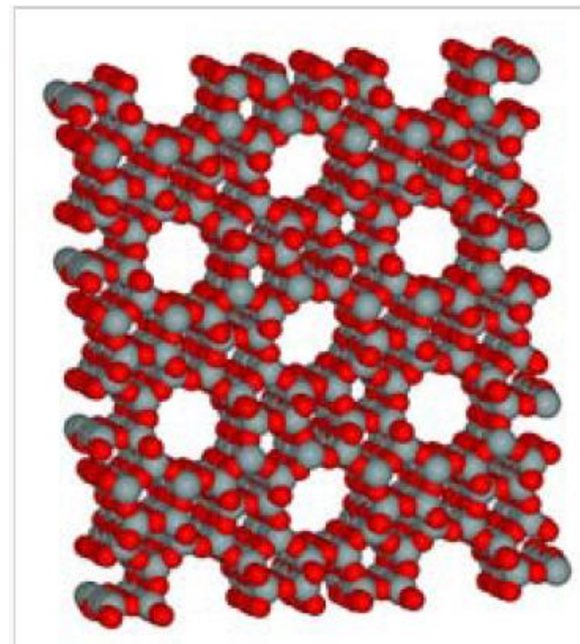
铝硅酸盐——沸石(zeolite)

- 硅氧四面体中，如有部分硅被铝取代而形成铝硅酸盐：

  钠长石：$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$

  粘土：$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

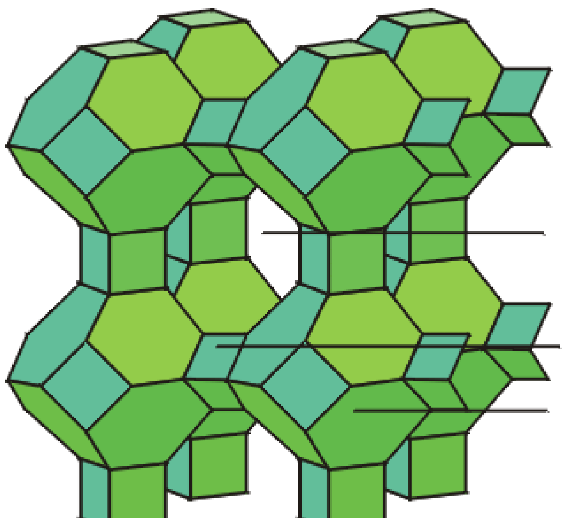
  钠沸石：$Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$



The microporous molecular structure of a zeolite, ZSM-5

- 自然界中存在的某些硅酸盐和铝硅酸盐具有笼形三维结构，可以有选择地吸附一定大小的分子，称为分子筛(Molecular sieve)。<u>优点</u>：分子筛的选择性远远高于活性炭等吸附剂。

http://news.ustc.edu.cn/info/1055/82467.htm



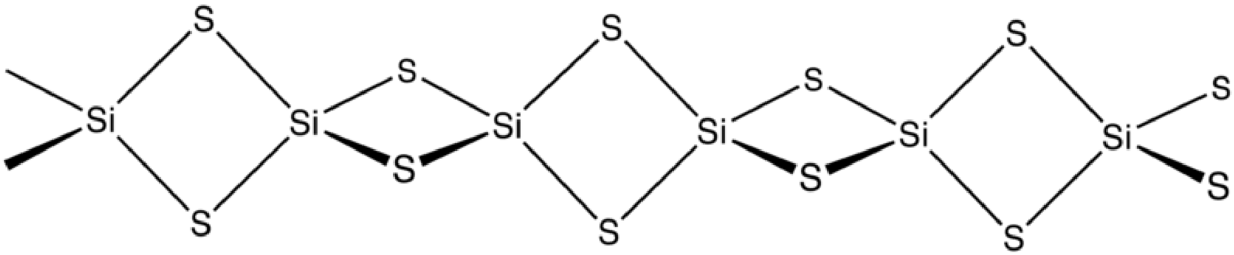
硅酸盐工业

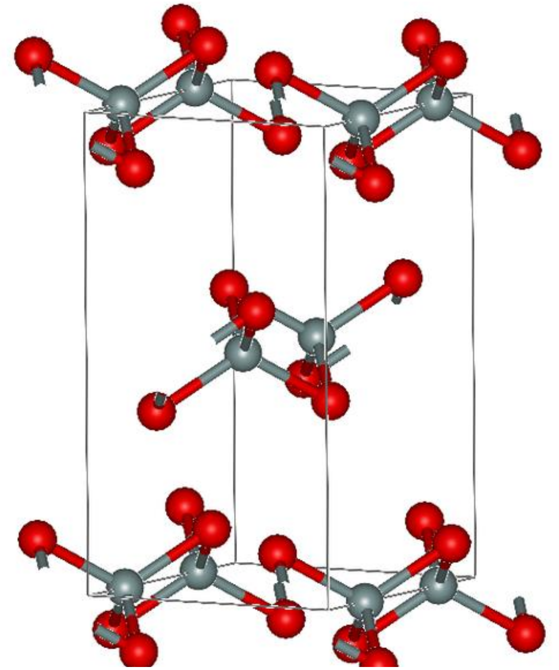
硅酸盐工业	水　泥	玻璃（普通玻璃）
原料	黏土、石灰石	纯碱、石灰石、石英
条件	高温	高温
发生变化	复杂的物理化学变化	同左
产品主要成分	$3CaO \cdot SiO_2$、$2CaO \cdot SiO_2$、$3CaO \cdot Al_2O_3$	$Na_2O \cdot CaO \cdot 6SiO_2$
产品特性	水硬性	无固定熔点

$$粘土+石灰石 \xrightarrow{1723K} 烧结块 \xrightarrow{磨碎} 水泥$$

$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

(5) SiS_2





Research Article

Silicon Disulfide and Silicon Diselenide

Henry Gabriel, C. Alvarez-Tostado

J. Am. Chem. Soc., 1952, *74* (1), pp 262-264

$$Si + 2S \longrightarrow SiS_2 + 59.9 \pm 0.5 \text{ kca}$$

Science 30 July 1965:
Vol. 149 no. 3683 pp. 535-537
DOI: 10.1126/science.149.3683.535

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Germanium and Silicon Disulfides: Structure and Synthesis

C. T. Prewitt and H. S. Young

± Author Affiliations

ABSTRACT

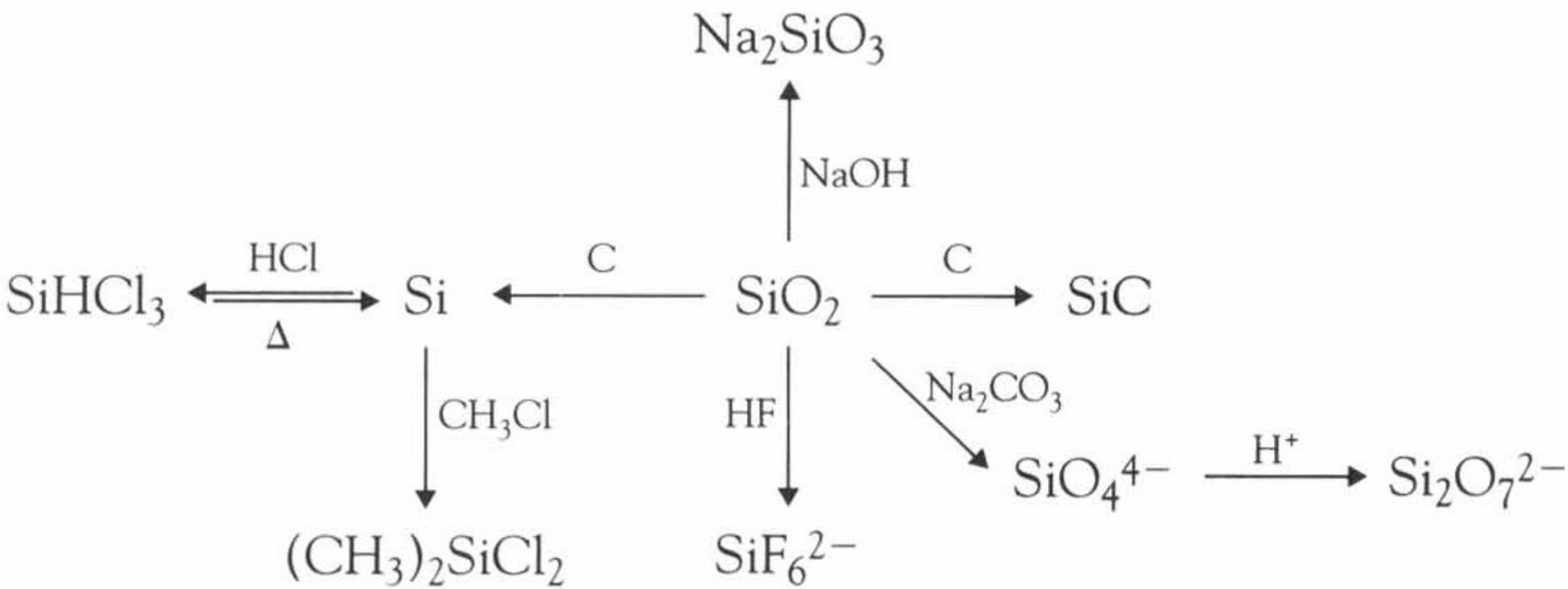
Crystal structures of the tetragonal forms of germanium and silicon disulfide are similar and consist of $(SiS_4)^{4-}$ and $(GeS_4)^{4-}$ tetrahedra which share vertices to form three-dimensional networks. These tetragonal materials, synthesized at high pressure and temperature, are different from the previously known germanium and silicon disulfides.

$$SiO_2 + Al_2S_3 = SiS_2 + Al_2O_3$$

Property:

$$CaS + SiS_2 = CaSiS_3$$

$$SiS_2 + 4H_2O = H_4SiO_4 + 2H_2S \quad \text{(Hydrolysis)}$$


Na2SiO3
NaOH
SiHCl3
HCl
Δ
Si
C
SiO2
C
SiC
CH3Cl
HF
Na2CO3
SiO4 4−
H+
Si2O7 2−
(CH3)2SiCl2
SiF6 2−

§ 15-3 Germanium Subgroup

一、General properties

$6s^2$惰性电子对效应

+4氧化态　Ge　Sn　Pb　+2氧化态

稳定性增大 ⟵　⟶ 稳定性增大

$Ge(s) + GeO_2(s) = 2GeO(s)$　　$\Delta_r G_m^\ominus = 47 kJ \cdot mol^{-1}$

$Sn(s) + SnO_2(s) = 2SnO(s)$　　$\Delta_r G_m^\ominus = -67 kJ \cdot mol^{-1}$

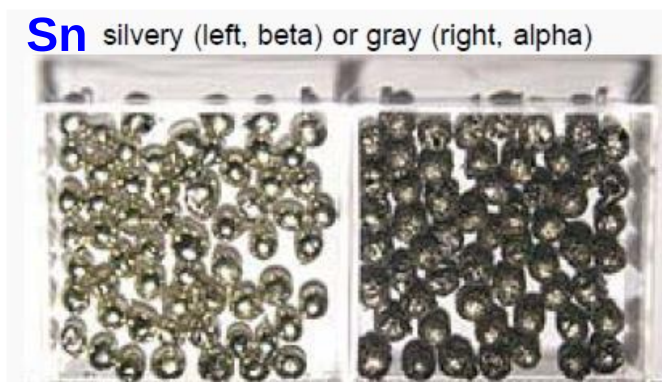
$PbO_2 + 4H^+ + 2e \longrightarrow Pb^{2+} + 2H_2O$　　$\varphi^\ominus = +1.45V$

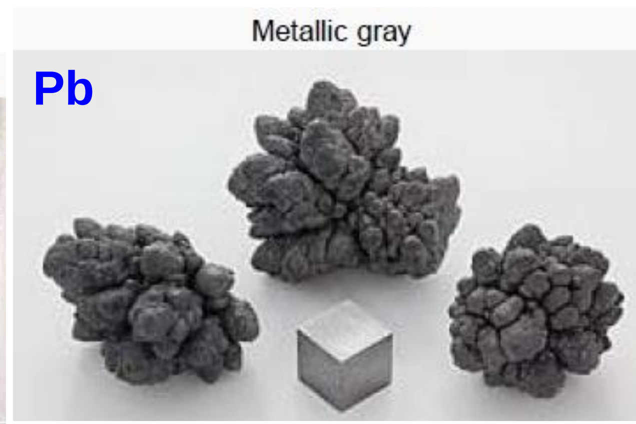
$GeO_2 + 4H^+ + 2e \longrightarrow Ge^{2+} + 2H_2O$　　$\varphi^\ominus = -0.15V$

- **Ge, Sn, Pb在地壳中的含量分别为7e-7, 4e-5, 1.6e-5。自然界中存在argyrodite 硫银锗矿($4AgS \cdot GeS_2$)， germanite锗矿石 ($CuS \cdot FeS \cdot GeS_2$)， tinstone 锡石($SnO_2$)， galena (方铅矿) (PbS)， cerusite (白铅矿) ($PbCO_3$);**
- **Pb存在于Uranium 和Thorium矿中，这是由于Pb是U和Th放射性衰变的产物。**
- **Pb可防alpha, gamma和X-ray，但对beta和neutron效果差。**

二、The simple substances

	Ge	Sn	Pb
外观	银白色金属	银白色金属	暗灰色
硬度	硬金属	硬度居中	软金属
	原子晶体，金刚石型晶体结构 为良好半导体材料	白锡是银白略带蓝色的金属，有延展性	密度大，熔点低 能阻挡X射线





$$\text{灰锡}(\alpha\text{锡}) \underset{}{\overset{13.6^\circ C}{\rightleftharpoons}} \text{白锡}(\beta\text{锡}) \overset{161^\circ C}{\rightleftharpoons} \text{脆锡}$$

锡瘟(Tin disease)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拿破仑兵败俄国竟是纽扣惹的祸

编辑

1812年，充满传奇色彩的拿破仑兵败俄罗斯，自此他苦心经营的法兰西大帝国分崩离析，最后自己也在圣赫勒拿岛的流放生活中抑郁而亡。世人往往将其失败归结为战线拖得太长、后勤供应不上。但加拿大一位化学家近日在著作中提出新解，小小的纽扣是导致拿破仑60万大军覆没的罪魁祸首。

Chemical properties

	Ge	Sn	Pb
O_2	—	—	PbO, $Pb_2(OH)_2CO_3$(表面)
H_2O	—	—	$Pb(OH)_2$ (有O_2存在时)
HCl	—	$SnCl_2$(浓HCl) $SnCl_2$(慢,稀HCl)	$PbCl_2$(微溶, 表面覆盖而阻止反应进行)

$$Sn + 2\,HCl\,(conc.) = SnCl_2 + H_2$$

Sn 与冷的稀盐酸反应慢

$$Pb + 2\,HCl\,(dilu.) = PbCl_2\downarrow + H_2$$

生成 $PbCl_2$ 覆盖反应物，反应会停止。

$$Pb + 3\,HCl\,(conc.) = H[PbCl_3] + H_2$$

	Ge	Sn	Pb
HNO_3(稀)	—	$Sn(NO_3)_2$(冷)	$Pb(NO_3)_2$
HNO_3(浓)	$xGeO_2 \cdot yH_2O$	H_2SnO_3	—

(钝化！因$Pb(NO_3)_2$不溶于浓HNO_3)

$$Ge + 4\,HNO_3\,(conc.) = GeO_2 \cdot H_2O\downarrow + 4\,NO_2 + H_2O$$

$$Sn + 4\,HNO_3\,(conc.) = H_2SnO_3(\beta)\downarrow + 4\,NO_2 + H_2O$$

$$3\,Sn + 8\,HNO_3(dilu.) = 3\,Sn(NO_3)_2 + 2\,NO + 4\,H_2O$$

$$Pb + 4\,HNO_3\,(conc.) = Pb(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$

$$3\,Pb + 8\,HNO_3(dilu.) = 3\,Pb(NO_3)_2 + 2\,NO + 4\,H_2O$$

⇒ 硝酸不能将 Pb 氧化到 +4 氧化态！

- Pb有氧时溶于HAc:

$$2Pb + O_2 \longrightarrow 2PbO$$

$$PbO + 2CH_3COOH \longrightarrow Pb(CH_3COO)_2 + H_2O$$

	Ge	Sn	Pb
H_2SO_4(稀)	—	—	$PbSO_4$(难溶, 反应终止)
H_2SO_4(浓)	$Ge(SO_4)_2$	$Sn(SO_4)_2$ (热的浓H2SO4)	$Pb(HSO_4)_2$ (热的浓H2SO4)

$$Ge + 4\,H_2SO_4\,(conc.) = Ge(SO_4)_2 + 2\,SO_2 + 4\,H_2O$$

$$Sn + 4\,H_2SO_4\,(conc.) = Sn(SO_4)_2 + 2\,SO_2 + 4\,H_2O$$

$$Pb + 3\,H_2SO_4\,(conc.) = Pb(HSO_4)_2 + SO_2 + 2\,H_2O$$

$$Pb + H_2SO_4\,(dilu.) = PbSO_4\downarrow + H_2$$

	Ge	Sn	Pb
NaOH	$Ge(OH)_6^{2-}$	$Sn(OH)_4^{2-}$	$Pb(OH)_4^{2-}$

$$Ge + 2\,OH^- + 2\,H_2O_2 = Ge(OH)_6^{2-}$$

Ge (II) 不稳定，生成 Ge (IV)!

$$Sn + 2\,OH^- + 2\,H_2O = Sn(OH)_4^{2-} + H_2$$

$$Pb + 2\,OH^- + 2\,H_2O = Pb(OH)_4^{2-} + H_2$$

➢ 制备

含锗矿石 $\xrightarrow{\text{煅烧}}$ GeO_2 $\xrightarrow{HCl}$ $GeCl_4$(挥发性) $\xrightarrow{\text{水解}}$ GeO_2 $\xrightarrow{H_2\text{(还原)}}$ **Ge**

锡石 $\xrightarrow{\text{焙烧}/O_2}$ (S, As挥发) $\xrightarrow{\text{酸溶}}$ SnO_2(其他金属氧化物溶于酸) $\xrightarrow{\text{碳}}$ Sn(粗) $\xrightarrow{\text{电解}}$ **Sn**(精)

PbS_2 $\xrightarrow{\text{焙烧}/O_2}$ PbO_2 $\xrightarrow{\text{还原}/C,\ CO}$ Pb(粗) $\xrightarrow{\text{电解}}$ **Pb**(精)

三、Compounds

1. 卤化物(halides)　　$EHal_4$　　$EHal_2$

(1) $SnCl_2$

a. 水解性:

$$SnCl_2 + H_2O = Sn(OH)Cl\downarrow + H^+ + Cl^-$$

在配制$SnCl_2$时必须防止氧化和水解:

$SnCl_2 \xrightarrow{O_2} SnCl_4$　■ $2Sn^{2+} + O_2 + 4H^+ = 2Sn^{4+} + 2H_2O$

※ 用盐酸酸化蒸馏水，并在$SnCl_2$中加入Sn粒:

$$SnCl_4 + Sn = 2SnCl_2$$

b. 还原性:

$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$ (白色)

$Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg\downarrow$ (黑色)

(※ 常用此反应检测Hg^{2+}, Sn^{2+}离子的存在)

(2) $GeCl_4$, $SnCl_4$也强烈水解

$$GeCl_4 + 2H_2O = GeO_2\downarrow + 4HCl$$

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl$$

※ 在盐酸中：$SnCl_4 + 2HCl = H_2SnCl_6$ (配合物)

(3) $PbCl_2$在冷水中溶解度小，但在热水中溶解度大，在盐酸中溶解度增大

∵ $PbCl_2 + 2Cl^- = PbCl_4^{2-}$

(4) $PbCl_4$在低温下稳定，在常温下即分解

$$PbCl_4 = PbCl_2 + Cl_2$$

(5) PbI_2：黄色丝状有亮光沉淀，溶于热水→冷却生成亮晶晶的金属小片

$$PbI_2 + 2KI = K_2[PbI_4]$$

2. 硫化物(sulfides)   ES ES_2

(1) SnS:

$$H_2S + Sn^{2+} = SnS\downarrow(\text{暗棕色}) + 2H^+$$

SnS不溶于Na_2S溶液中，但可溶于中等浓度的HCl和碱金属的多硫化物溶液中

$$SnS + 4Cl^- + 2H = SnCl_4^{2-} + H_2S\uparrow$$

$$SnS + S_2^{2-} = SnS_3^{2-} \xrightarrow{H^+} SnS\downarrow + H_2S\uparrow$$

(2) SnS_2：可溶于Na_2S溶液中

$$Sn^{4+} + 2H_2S = SnS_2\downarrow(\text{黄色}) + 4H^+$$

$$SnS_2 + S^{2-} = SnS_3^{2-}$$

$$SnS_2 + 6HCl \rightarrow H_2SnCl_6 + 2H_2S$$

$$3\,SnS_2 + 6\,NaOH = 2\,Na_2SnO_3 + Na_2SnS_3 + 3\,H_2O$$

(3) PbS:

$$Pb^{2+} + S^{2-} = PbS\downarrow(\text{黑色})$$

PbS可溶于浓HCl和稀HNO_3、H_2O_2，不溶于Na_2S和无氧化性的稀酸

$$PbS + 4HCl(\text{浓}) = H_2S\uparrow + H_2PbCl_4$$

$$3PbS + 2NO_3^- + 8H^+ =$$
$$3Pb^{2+} + 3S\downarrow + 2NO\uparrow + 4H_2O$$

※ 由于Pb(Ⅳ)有极强的氧化性，所以PbS_2不存在！

(4) GeS 和 GeS_2 在水中有一定的溶解度

$$GeS_2(\text{白}) + Na_2S = Na_2GeS_3 \quad (\text{硫代锗酸钠})$$

3. 氧化物(oxides)　　MO　　MO_2

MO 两性偏碱，MO_2 两性偏酸，均不溶于水。

GeO(黑色)；

GeO_2(白色);

SnO(蓝色)；

SnO_2(灰色);

PbO(黄色，又名密陀僧，massicot)；

PbO_2(黑色)；

Pb_2O_3(黄色)，可看作：$PbO \cdot PbO_2$;

Pb_3O_4(红色)，又名铅丹，可看作：$2PbO \cdot PbO_2$

(1) SnO_2

- 制备：$Sn + O_{2(空气)} \xrightarrow{焙烧} SnO_2$

- 性质：不溶于水, 难溶于酸碱, 但可与NaOH, Na_2CO_3和S共熔, 得到可溶性盐：

$$SnO_2 + 2NaOH = Na_2SnO_3 + H_2O$$

$$SnO_2+2Na_2CO_3+4S=Na_2SnS_3+Na_2SO_4 +2CO_2\uparrow$$

$$E_A^{\ominus}/V \quad Sn^{4+} \xrightarrow{0.154} Sn^{2+} \xrightarrow{-0.136} Sn$$

$$E_B^{\ominus}/V \quad [Sn(OH)_6]^{2-} \xrightarrow{-0.96} [Sn(OH)_4]^{2-} \xrightarrow{-0.79} Sn$$

(2) 铅的氧化物

PbO(黄色，又名密陀僧，massicot)；

PbO_2(黑色)：

Pb_2O_3(黄色)，可看作：$PbO \cdot PbO_2$； $Pb^{II}(Pb^{IV}O_3)$

Pb_3O_4(红色)，又名铅丹，可看作：$2PbO \cdot PbO_2$ $Pb_2^{II}Pb^{IV}O_4$

- **制备:**

$$2Pb(熔融) + O_2 = 2PbO$$

$$Pb(OH)_3^- + ClO^- = PbO_2 + Cl^- + OH^- + H_2O$$

$$Pb + O_{2(纯氧)} \xrightarrow{加热} Pb_3O_4$$

- **转化**

$$PbO_2 \xrightarrow{563\text{-}593K} Pb_2O_3 \xrightarrow{663\text{-}693K} Pb_3O_4 \xrightarrow{803\text{-}823K} PbO$$

$$Pb_2PbO_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2(黑色) + 2H_2O$$

- **性质**：

- 两性偏酸性:

$$PbO_2 + 2NaOH + 2H_2O \xrightarrow{加热} Na_2Pb(OH)_{6(铅酸盐)}$$

- Pb_2O_3 , Pb_3O_4 , PbO_2都具有强氧化性(在酸性介质中)

$$5PbO_2 + 2Mn^{2+} + 4H^+ = 5Pb^{2+} + 2MnO_4^- + 2H_2O$$

$$PbO_2 + 4HCl = PbCl_2 + Cl_2\uparrow + 2H_2O$$

- PbO_2：Pb（$6s^26p^2$）的惰性电子对效应⇒ $6s^2$电子不易失去，一旦失去，夺回的倾向很强

$$E_A^\ominus/V \quad PbO_2 \xrightarrow{1.45} Pb^{2+} \xrightarrow{-0.126} Pb$$

$$E_B^\ominus/V \quad PbO_2 \xrightarrow{0.25} PbO \xrightarrow{-0.58} Pb$$

$$2PbO_2 + 4H_2SO_4 \longrightarrow 2Pb(HSO_4)_2 + O_2 + 2H_2O$$

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + O_2 + 2H_2O$$

4. 氢氧化物(hydroxides)

$$Sn^{2+} \underset{H^+}{\overset{适量OH^-}{\rightleftharpoons}} Sn(OH)_2(s,白) \xrightarrow{过量OH^-} [Sn(OH)_4]^{2-}$$

$$Pb^{2+} \underset{HNO_3或HAc}{\overset{适量OH^-}{\rightleftharpoons}} Pb(OH)_2(s,白) \xrightarrow{过量OH^-} [Pb(OH)_3]^-$$

$$Sn^{4+} \underset{H^+}{\overset{适量OH^-}{\rightleftharpoons}} \alpha\text{-}H_2SnO_3(s,白) \xrightarrow{过量OH^-} [Sn(OH)_6]^{2-}$$

$$\alpha\text{-}H_2SnO_3 \xrightarrow{放置} \beta\text{-}H_2SnO_3$$

$$Sn \xrightarrow{浓HNO_3} \beta\text{-}H_2SnO_3(s,白)$$ 不溶于酸或碱

$$Sn + 4HNO_3(浓) \longrightarrow \beta\text{-}H_2SnO_3 + 4NO_2 + H_2O$$

- **$Sn(OH)_2$：两性；还原性**

$$Sn^{2+} + 2OH^- = Sn(OH)_2\downarrow$$

$$Sn(OH)_2 + HCl = SnCl_2 + 2H_2O$$

$$Sn(OH)_2 + 2NaOH = Na_2[Sn(OH)_4]$$

$$3Na_2Sn(OH)_4 + 2BiCl_3 + 6NaOH = 2Bi\downarrow + 3Na_2Sn(OH)_6 + 6NaCl$$

- **$Sn(OH)_4$：两性**

$$SnCl_4 + 4NH_3\cdot H_2O = Sn(OH)_4\downarrow + 4NH_4Cl$$

$$Sn(OH)_4 + 2NaOH = Na_2Sn(OH)_6$$

$$Sn(OH)_4 + 4HCl = SnCl_4 + 4H_2O$$

- **$Pb(OH)_2$：两性**

$$Pb^{2+} + OH^- = Pb(OH)_2\downarrow$$

$$Pb(OH)_2 + OH^- = Pb(OH)_3^-$$

$$Pb(OH)_2 + 2HCl \xrightarrow{\text{加热}} PbCl_2 + 2H_2O$$

$$Pb(OH)_2 \xrightarrow{\text{加热}} PbO$$

➢ 酸碱性

酸性增强

酸性增强

$Ge(OH)_4$	$Sn(OH)_4$	$Pb(OH)_4$
棕	白	棕
$Ge(OH)_2$	$Sn(OH)_2$	$Pb(OH)_2$
白	白	白

碱性增强

碱性增强

3. 铅的化合物

(1) $Pb(NO_3)_2$

易水解：$Pb^{2+} + NO_3^- + H_2O \rightleftharpoons Pb(OH)NO_3\downarrow + H^+$

易分解：$2Pb(NO_3)_2 \xlongequal{\triangle} 2PbO + 4NO_2 + 2H_2O$

(2) $Pb(CH_3COO)_2$ (弱电解质，有甜味，俗称铅糖)

共价化合物，易溶于水，难离解，毒性大

$$Pb(Ac)_2 + Cl_2 + 4KOH = PbO_2 + 2KCl + 2KAc + 2H_2O$$

(3) $PbSO_4$

可溶于浓H_2SO_4中,也可溶于NH_4Ac或NaAc溶液中

$$PbSO_4 + H_2SO_{4(浓)} = Pb(HSO_4)_2 \xrightarrow{H_2O} PbSO_4 + H_2SO_4$$

$$PbSO_4(白色) \xrightarrow{Ac^-} PbAc_2(可溶) + SO_4^{2-}$$

(4) $PbCrO_4$

难溶于水的黄色晶体，有毒，加热分解可放出氧气，是氧化剂。

$$Pb^{2+} + CrO_4^{2-} = PbCrO_4 \downarrow (黄)$$

※ 用于Pb^{2+}的鉴定（$PbCrO_4$溶于过量的碱，这与黄色$BaCrO_4$有别；$SrCrO_4$溶于HAc，不溶于碱。）

$$PbCrO_4 + 2\ NaOH \rightarrow Pb(OH)_2 + Na_2CrO_4$$

$$Pb(OH)_2 + NaOH \rightarrow Na[Pb(OH)_3]$$

$$PbCrO_4 + H^+ \rightarrow Pb^{2+} + HCrO_4^-$$

$$2PbCrO_4 + 2H^+\ (过量) \rightarrow 2Pb^{2+} + Cr_2O_7^- + H_2O$$

$$PbCrO_4(黄色) \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} PbCr_2O_7(可溶)$$

➢ 铅的盐类的转化、溶解性：

$PbCl_2$(白) $\xrightarrow{\triangle}$ Pb^{2+}

$PbCl_2$(白) $\xrightarrow{浓HCl}$ $PbCl_4^{2-}$

$PbSO_4$(白) $\xrightarrow{浓H_2SO_4}$ $Pb(HSO_4)_2$

PbI_2(黄) $\xrightarrow{I^-}$ PbI_4^{2-}

$PbCrO_4$(黄) $\xrightarrow{OH^-}$ $Pb(OH)_3^-$

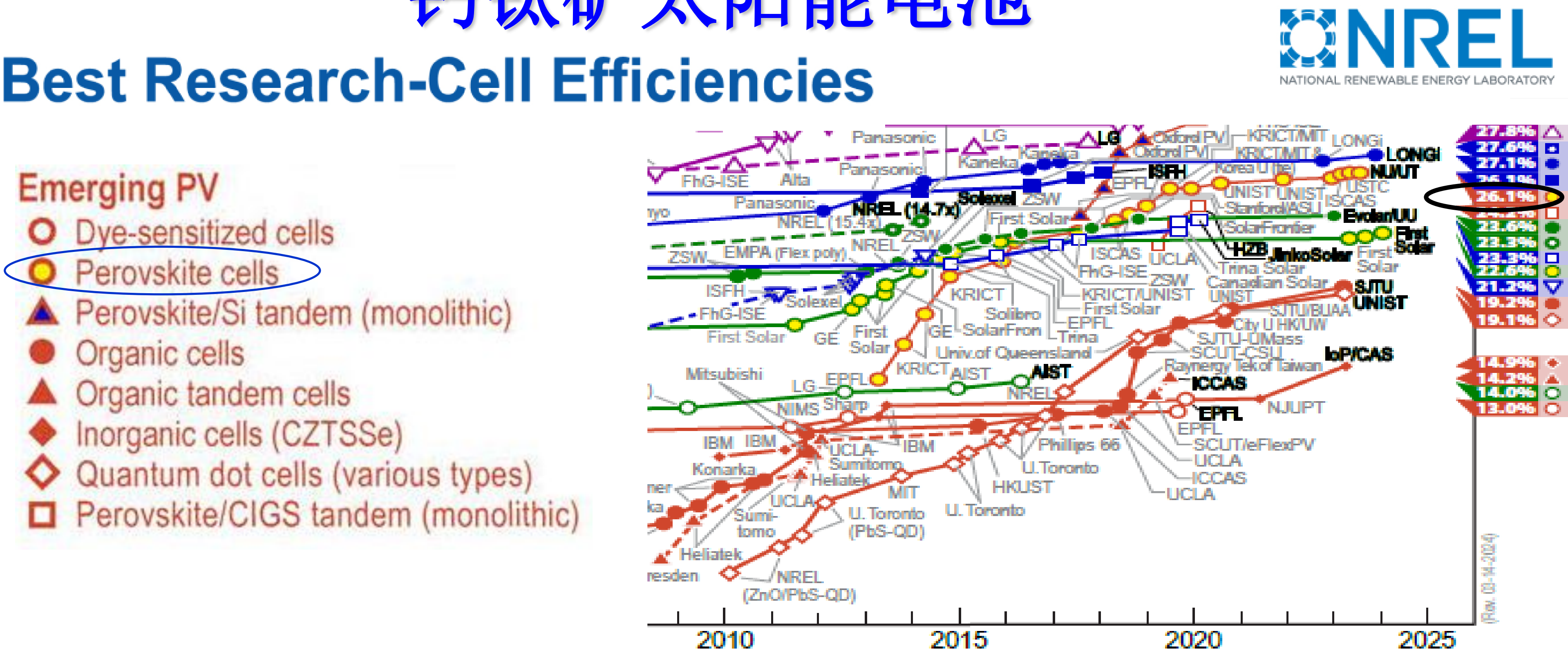
$PbCrO_4$(黄) $\xrightarrow{HNO_3}$ $Pb^{2+}+Cr_2O_7^{2-}$

少数可溶：$Pb(NO_3)_2$, $Pb(Ac)_2$，铅的可溶性化合物都有毒。

多数难溶：$PbCl_2$，PbI_2，$PbSO_4$，$PbCO_3$, $PbCrO_4$等。

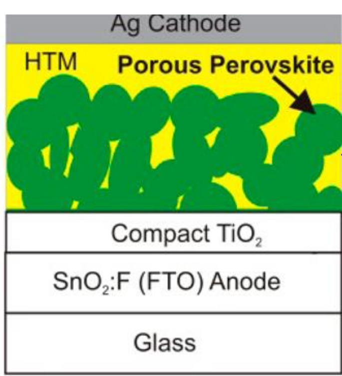
钙钛矿太阳能电池

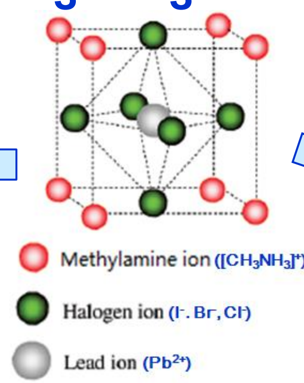
Best Research-Cell Efficiencies

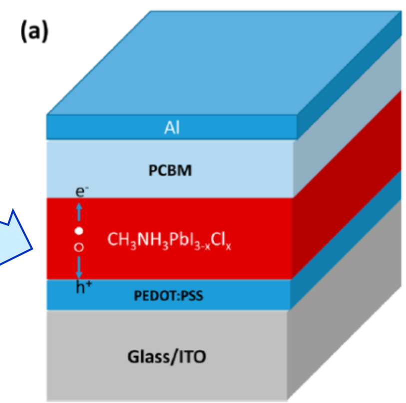


※ 《Science》期刊评为2013 年
十大科技突破。

$CH_3NH_3PbX_3$





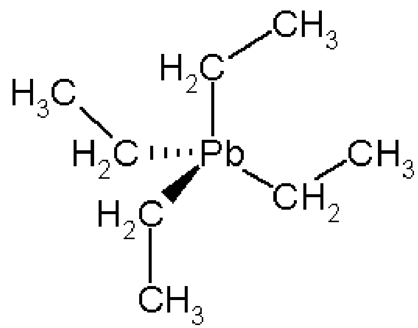


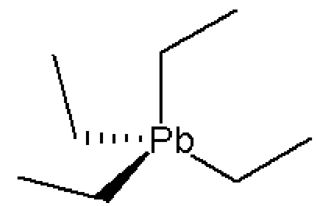
(5) 铅的有机化合物

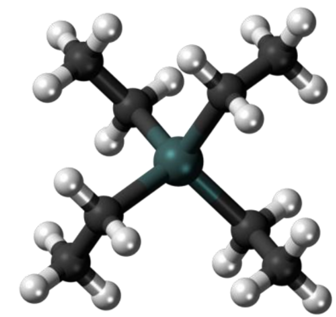
4NaPb (铅钠合金) + $4C_2H_5Cl = Pb(C_2H_5)_4 + 4NaCl + 3Pb$

四乙基铅（tetraethyl lead）是汽油抗震剂，其 $\Delta H_f^{\Theta}=217.6 KJ\cdot mol^{-1}$，但在常温下尚能稳定存在。

- 作为添加剂在汽油，以提高燃料的辛烷值，以防止发动机内发生震爆，从而能够使用更高的压缩比率，藉以提高汽车发动机效率和功率。







- 四乙基铅结构中的四个C-Pb键的引力相当弱，内燃机燃烧的温度可使其分解。分解时，会先转变为三乙基铅$(CH_3CH_2)_3Pb$和乙基自由基，这些自由基会清除其他自由基。通过自由基反应，从而不致过早开始燃烧，使**点燃适当地延迟，预防震爆（爆震）**。

Note: 由于用$Pb(C_2H_5)_4$作为汽油抗震剂，汽油燃烧后的废气中含有铅的化合物，污染环境。现已开发出不含铅的抗震剂，称为无铅汽油。

$$(CH_3CH_2)_4Pb + 13O_2 \rightarrow 8CO_2 + 10H_2O + Pb$$

$$2Pb + O_2 \rightarrow 2PbO$$

本次作业
（张祖德编著<无机化学习题>2011.6版）

Chapter 14. 碳族元素
(P65)

3、5、16、19、24