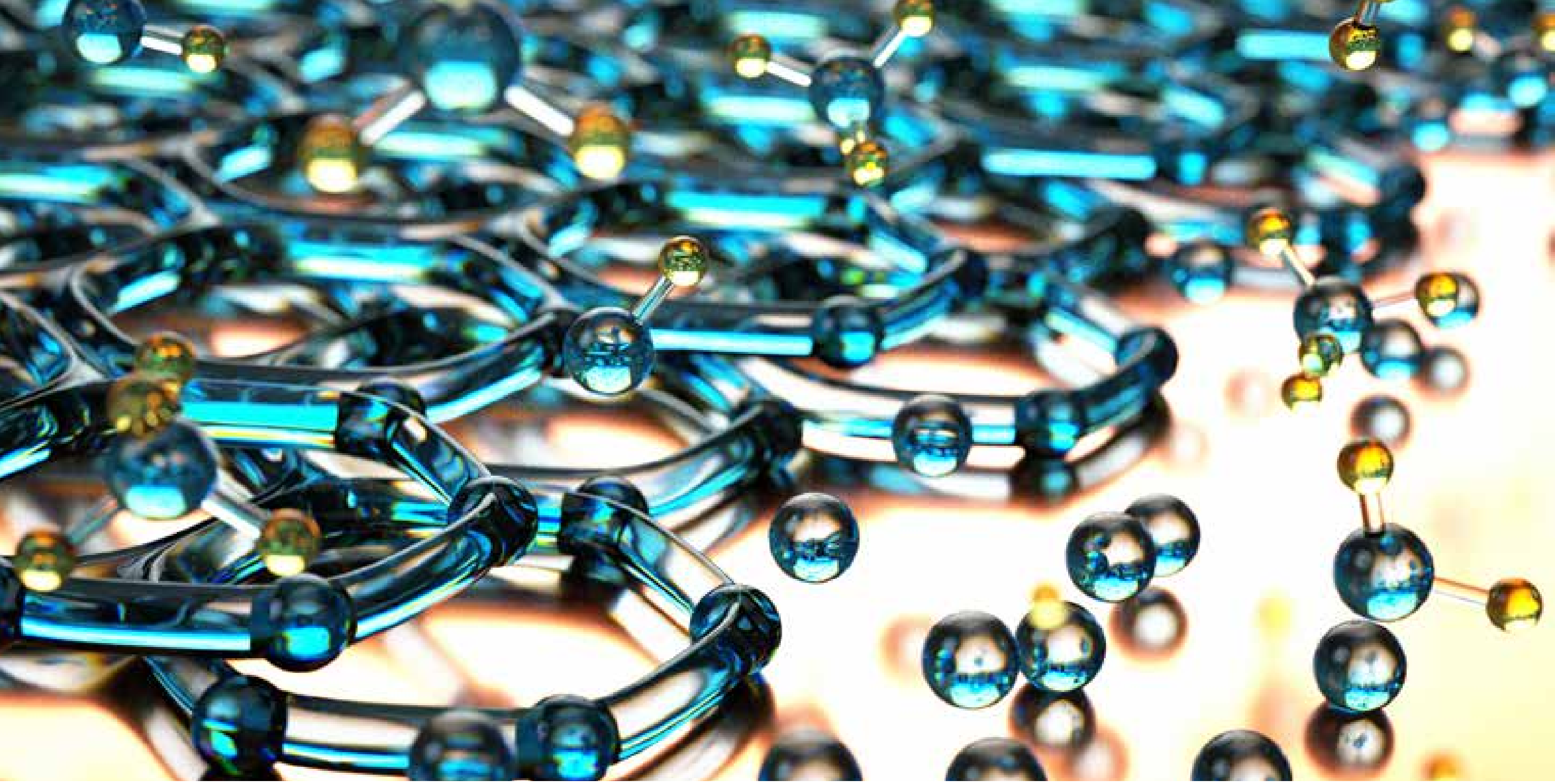

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# 纳米材料：应用预防原则

## 纳米维度– 关于常见材料的新发现

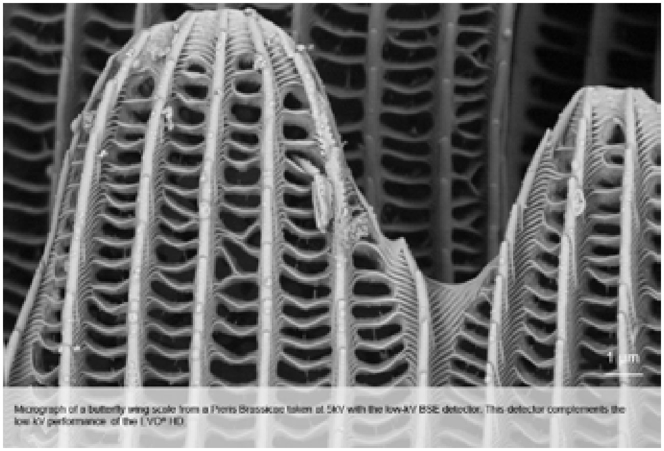
2016年诺贝尔化学奖被授予让皮埃尔·索瓦日、弗雷泽·斯托达特爵士和伯纳德·L·费林加，以表彰他们三十年来对分子机器设计和合成的研究。一辆靠分子发动机驱动的四纳米长的四轮“汽车”展示了他们的成果。[1]科学家们不断挑战极限，探索新技术，在这个案例中，他们的创新超越了物理限制，激发了日常生活中无数应用的潜力。纳米科学领域的最新进展已赋予了其足以改变世界的物理和化学新特性。[2,3,4]

纳米材料由纳米大小的颗粒组成，这些颗粒至少在一个维度上小于100纳米：1纳米等于1米的十亿分之一，大约比人类的头发细八万倍。纳米材料不是新材料，也不完全是合成材料；它们确实在自然中存在，而且无处不在。它的新特性在于我们用普通材料设计并将其用于不同功能的能力。

在自然界，纳米材料出现在：海洋浮游生物和珊瑚的骨骼、鸟喙和羽毛、动物的毛发和骨骼基质，包括人类组织的变种、蜘蛛网、鳞片和翅膀，甚至在纸张、丝绸和棉花中。还有天然存在的无机纳米材料，如某些粘土、火山灰、烟灰、星际尘埃和某些矿物质。天然纳米材料从根本上说是化学、光化学、机械、热能和生物过程的结果。[5,6]

研究表明，传统医学中使用的某些制备方法，如煅烧，无意中产生了纳米材料及其特殊性质。[7,8]同样，研究人员正在检查中世纪的武器，如大马士革钢刀片，以检验这一理论：即特定的、程式化的锻造和退火技术利用生成纳米材料来增强钢的强度和柔韧度。[9,10]

在工程界，使用一系列微制造技术专门为光学、电子、机械、医学和酶的应用而设计并合成了纳米材料。如今，纳米材料广泛应用于食品、化妆品、个人护理用品、抗菌剂、消毒剂、服装、电子设备等各种产品中。尽管工程纳米材料的前景令人振奋，关于纳米材料本身的及其生产和应用过程中的环境安全问题也随之浮现。对于纳米材料能做什么以及它们可能产生什么样的影响，我们的了解还远远不够。尽管科研人员正在研发更多的纳米材料，但也存在一个严重的风险，即在没有更好的保护措施的情况下使用这些材料时，我们对其在人类健康或环境的长期影响方面还没有足够的了解。



纳米级的菜粉蝶的翅鳞，*欧洲粉蝶*

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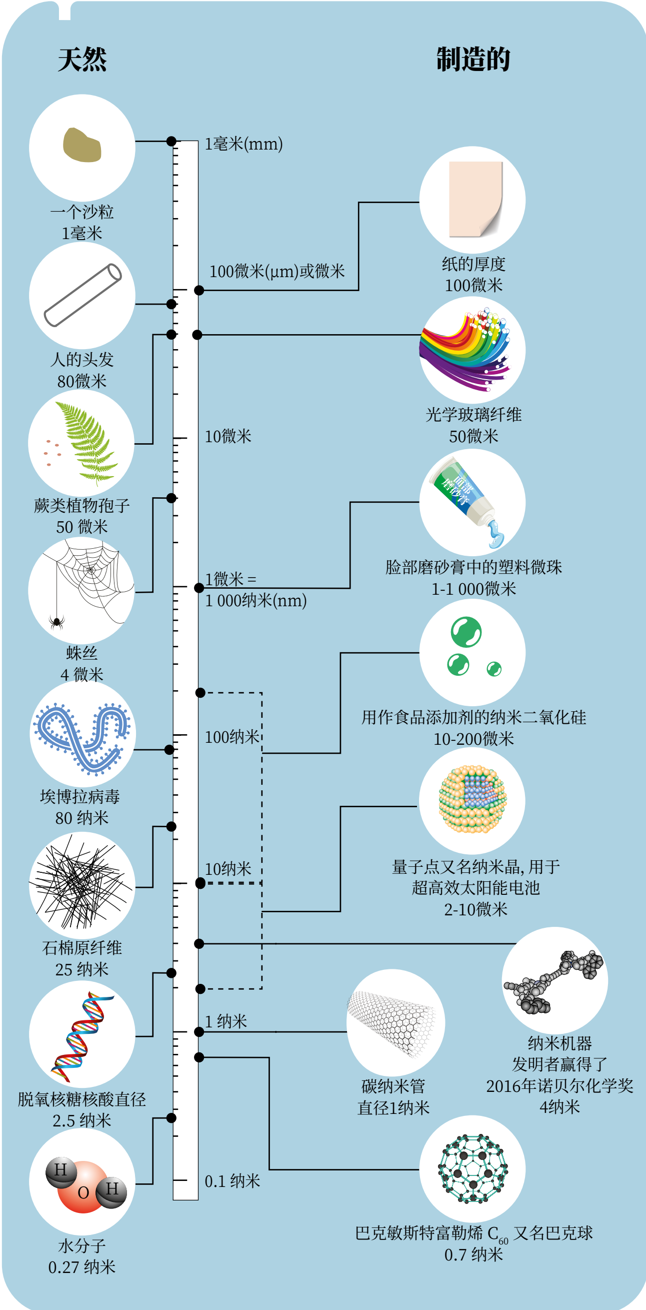
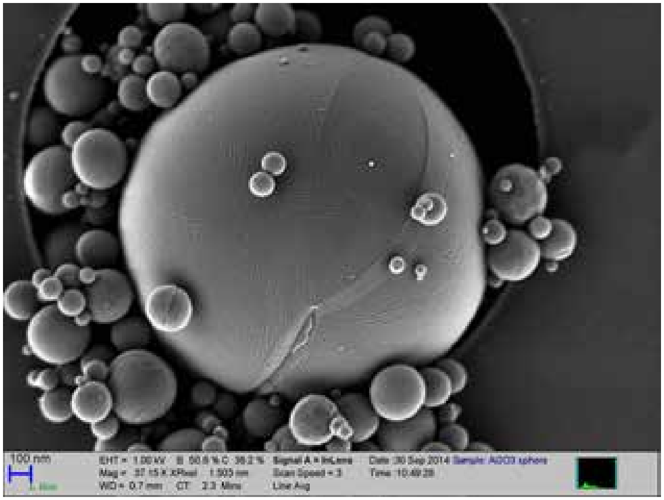


物的行为都非同寻常,完全不像他们在原来世界里的同类。与较大尺寸的相同材料相比,纳米材料的物理、化学、光学、磁性和电学特性和行为发生了显著变化。这是因为,随着材料变小,其表面积与体积比急剧增加,出现了量子效应。制造一种材料的纳米级版本可以使原本的惰性材料产生各种新特性。例如,黄金是具有抗磁性的——它对磁场的反应非常弱,但黄金纳米颗粒却具有不寻常的磁性。[11]

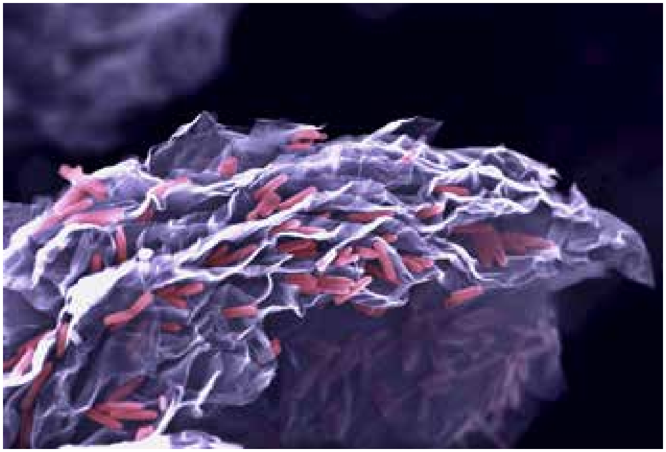
和大块材料一样,纳米金属材料,如银、钛和锌及其氧化物被用于防晒霜、牙膏、化妆品、食品、油漆和衣服中。[12]由于具有抗菌性能,纳米银已被广泛地加入许多消费品,如运动纺织品、鞋子、除臭剂、个人护理用品、洗衣粉和洗衣机。

纳米金刚石具有能穿透血脑屏障,并将药物有针对性地送达多种类型的癌性肿瘤的功能特性。[13,14]由于具有荧光、光学和电化学特性,纳米金刚石被用于先进的生物成像技术,和传输指示脑功能健康信号等具有广阔前景的材料中。[15,16]




氧化铝($Al_2O_3$)纳米球

*图片来源:蔡司显微镜,根据CC BY-NC-ND 2.0授权*



用于超级电容器的生长在还原氧化石墨烯上的三氧化二铁($Fe_2O_3$)纳米棒

*图片来源:Dilek Ozg/剑桥大学工程,根据CC BY-NC-ND 2.0授权*

纳米酶是自身具有酶的特性的纳米材料,用于生物传感、生物成像、肿瘤诊断和治疗。[17] 它们还可被用于预防海洋污染,污染物去除和环境监测。

碳纳米材料能以各种形状和形式出现。石墨烯是单个原子厚度的碳片。碳纳米管实质上是被卷制成直径为一纳米级的无缝中空圆柱体的石墨烯片。[18]在1985年被发现的巴克敏斯特富勒烯又名巴克球,是一个由60个碳原子组成的球形结构,它以巴克敏斯特·富勒(Buckminster Fuller)的名字命名,富勒因设计了网格状圆顶结构而闻名。

碳纳米管具有惊人的特性。它具有比钢更高的强度,比铜更好的传导性,和比钻石更高的热导率。碳纳米管广泛用于笔记本电脑和手机的锂离子电池、轻型

# 纳米材料

## 什么是纳米材料?

**纳米材料**
是任何外部尺寸
**小于100纳米**的材料 ——
一纳米等于十亿分之一米

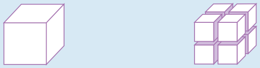
铜
银　铁　金　锌

**纳米材料**既能**天然存在**，也可通过把常用材料(例如碳、金属氧化物和贵金属)**缩小**到纳米尺寸来制造

**全球纳米材料市场**

**20.7%** 年增长
预测到2022年达到
**550亿美元**

与较大尺寸的相同材料相比，纳米材料**特性和行为**发生了显著变化。这是由于其**表面积与体积比**的增加以及**量子效应**



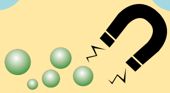

随着材料尺寸减小，表面积与体积比增加，使材料更容易与周边环境发生化学反应。

## 应用

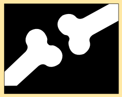
纳米材料独特的**机械**、**磁性**、**电学**和**光学特性**使其在制药、生物医学、电子和材料工程中得到广泛应用

由于具有**抗菌特性**，**纳米银**被广泛用于纺织品、玩具、个人和保健产品、医疗器械和食品等产品中

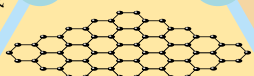
工程纳米材料存在于**各种消费品**中，例如食品、化妆品、消毒剂、厨具、婴儿用品、服装、布料、电子产品和电器等



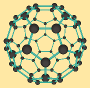
由于具有磁性，**氧化铁纳米粒子**在癌症治疗中的靶向给药、医学成像技术和去除水中的砷等方面有很大潜力



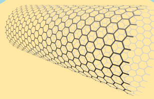
由于具有发光性质、高化学稳定性和生物相容性，**纳米钻石**被用于生物医学成像应用



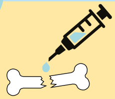
**石墨烯**是一个碳原子厚的碳原子片。其潜在的应用包括药物输送系统、分子转运体、组织工程和植入物



由60个碳原子组成的像足球的盒子，被称为**巴克敏斯特富勒**($C_{60}$)，又名巴克球，有望治疗骨和软骨变性，及肌肉骨骼和骨髓疾病



**碳纳米管**是用一层碳原子卷成的无缝中空圆柱体。其强度是同直径的钢材的117倍，导电性比铜要好



**纳米管**广泛用于锂离子电池、轻量级风力涡轮机叶片和数据电缆。可能的应用包括组织工程和再生，以及癌症生物标志物

## 不利影响

极小的体积和很大的表面积与体积比赋予了工程纳米材料显著的性质，也**改变了与生物系统互动**和在生物系统(从环境、生物体、器官、细胞直到DNA一级)中积累的方式

把材料纳米化能改变材料的性质，这可能会**加剧其对健康和环境的影响**

例如，碳纳米管的外观和行为类似于石棉纤维。它们的长而尖的结构可以穿透组织，并引起炎症和纤维化，这与接触石棉产生的影响非常相似。纳米银会干扰免疫系统并引起基因表达异常

如果我们希望释放纳米工程材料的全部潜力，那么我们还必须**预测其影响**，否则我们就会冒着将来置身于更大影响下的风险

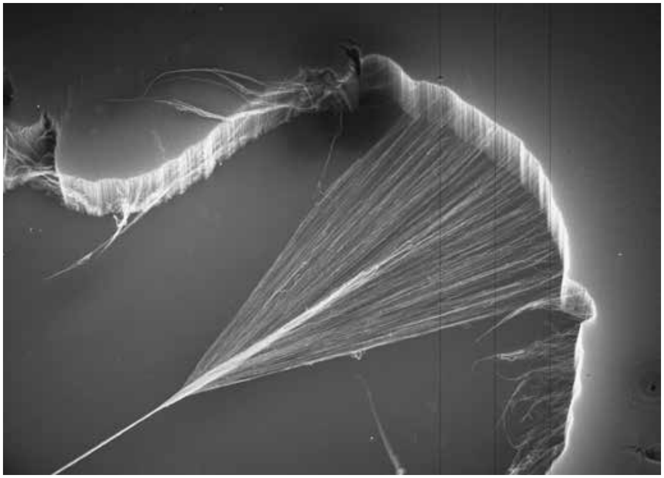
需要**应用预防原则**的反复的和反应灵敏的监管框架，以尽量减少风险，保证人类健康和环境安全

风力发电机叶片、船体、数据电缆、生物传感器和医疗设备中。[19]碳纳米管的全球商业生产能力现已超过每年数千吨。

由于工程设计纳米材料在日常产品中取代了更多的常规材料，了解这些纳米材料的不利影响非常关键。要想充分发挥纳米材料的潜力，我们还必须预测其对环境和人类健康的影响，否则我们将使自己在未来置于更大的风险之中。[20]

通过纳米化改变材料的性质可能会加剧其对环境和健康的影响。纳米银的毒性可能会导致：银中毒，皮肤会永久地变为金属蓝色；肺部炎症；改变器官功能，干扰免疫系统和基因表达。[12,21,22]暴露于银纳米颗粒可会使细菌产生应激反应，引起基因组变化，这可能助长抗菌剂耐药基因的发展。[12,23]硅和二氧化钛可引起肺部炎症。[24]

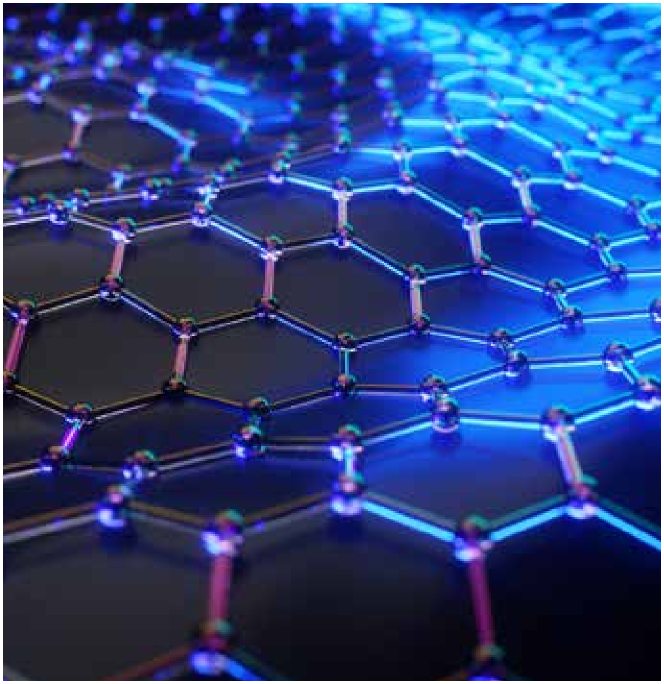
随着富勒烯（包括$C_{60}$巴克球）在新型生物医学应用和治疗应用方面的诸多发现，人们也在研究这些令人难以置信的纳米材料对细胞、基因表达、免疫功能、代谢和生育能力的潜在影响。[25]碳纳米管和碳纳米纤维表现出对皮肤、眼睛、肺和脑组织造成伤害并在体内累积的能力。[26,27]



将碳纳米管纺成纱线

*图片来源：英联邦科学和工业研究组织(CSIRO)*

**视频：**石墨烯 - 未来的材料



*视频链接：https://www.youtube.com/watch?v=TFo2xShvtj0* *© DW Tomorrow Today*

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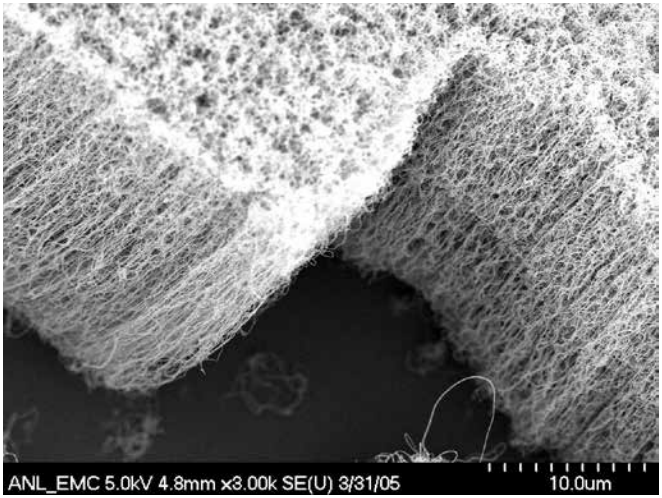
## 工程纳米材料的环境和健康风险

据估计，全球纳米技术市场每年将增长约18%，至2025年，其价值将达到近1740亿美元。[28]工程纳米材料在不同行业的生产和使用可能会导致其在产品生命周期的任一时刻被无意释放到环境中。[29]例如，来自衣服和织物的纳米银在洗涤过程中被释放；涂料和建筑材料中的二氧化钛纳米颗粒由于风化而排放到空气和水中；碳纳米管在生产过程中随空气传播，或者从废弃的锂离子电池进入土壤和地下水中。[19,30,31]

要评估工程纳米材料对人类健康和环境的潜在风险，首先要需要了解它的的暴露程度和不利影响。[32]然而目前我们只有有限的研究能解释释放到大气、土壤、沉积物、水和生物群中的工程纳米材料的命运，包括其行为、浓度、运输、分布、转化、生物利用率、食物链中的生物累积和与生态社区的生物化学相互作用。[29,33-36]相比之下，关于纳米材料的毒性作用的知识和证据正在增加。研究结果表明，纳米材料可能导致广泛的健康风险。对形状和化学特性相似的材料，例如石棉、超细颗粒和柴油废气等进行的毒性比较研究提供了关于暴露于纳米材料中的潜在健康威胁的见解。[37]此外，我们从管理这些常见的有害物质中学到的知识也可以帮助我们更好地为不为人知的纳米材料做好预防准备。

碳纳米管被发现具有与石棉纤维相似的特性。[38]它们的形状像针，并且都具有生物持续性。它们能穿透肺组织并引发炎症。[39]暴露在石棉环境中带来的健康危害的证据最早来自1898年的露西·迪恩（Lucy Deane），她是英国工厂的首批妇女检查员。[40]她指出，石棉“对于工人健康是一个明显的危险因素……因为已有证据表明受害者的支气管和肺部损伤在医学上可归因于他们的工作环境。”

1982年，一部名为《爱丽丝：为生命而战》的电视纪录片讲述了爱丽丝·杰斐逊（Alice Jefferson）的故事。爱丽丝是一位47岁的女性，她因为在英国当地一家石棉厂工作了几个月而感染了间皮瘤这种致命的癌



对齐的碳纳米管

*图片来源：Junbing Yang/阿贡国家实验室，根据CC BY-NC-SA 2.0授权*

在扫描电子显微镜下放大1500倍的石棉纤维

*图片来源：美国疾病控制与预防中心/John Wheeler/Janice Haney Carr*

1918年9月，英国兰开夏郡一家工厂的女工躺在她们生产的石棉床垫上

*图片来源：©帝国战争博物馆(Q 28250)*

症。[20]爱丽丝的故事立刻在英国舆论中激起千层浪。作为回应，政府推出了降低石棉暴露限值的石棉许可法规。很快，自愿性标签计划也随之出现。舆论压力持续发酵，因过去暴露于石棉而引起的间皮瘤疾病的科学证据也在增加。[41]

直到1999年，所有类型的石棉才在英国被禁止：此时距离相关积累伤害且数千人死于石棉肺或相关癌症的证据已过去了101年。今天，我们仍然需要努力减少从事改造和维护含石棉建筑物的工人的暴露风险。[42]

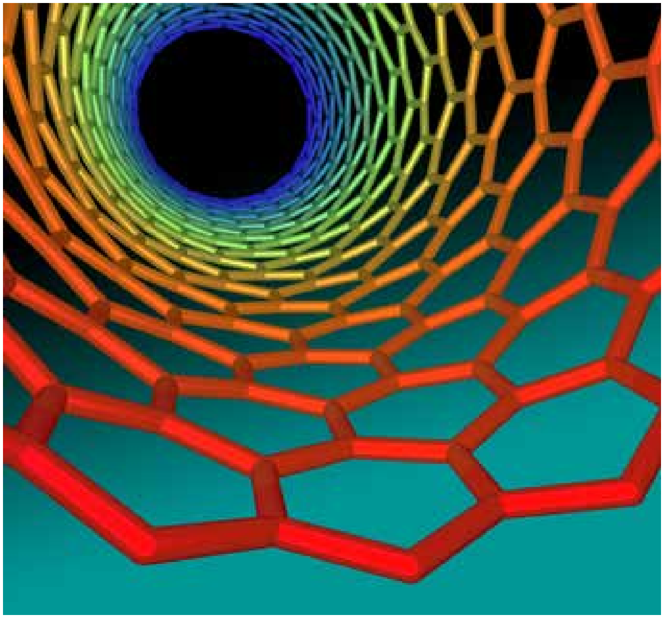
问题是，“在未来管理和确保纳米材料安全的过程中，我们能从已经过去了的长达一个世纪石棉斗争中吸取什么教训？”

## 应用卫生与环境安全条例

根据我们对石棉和其他危险材料的经验，我们知道具有潜在威胁的列表很长。工程纳米材料的环境风险是不可避免的。它们的不利影响和持续性可能对生物、生态系统和食物链产生重大影响。[32,35,43,44]口服、皮肤和肺部暴露可导致炎症和纤维化，破坏代谢和器官功能，并引起DNA损伤和遗传不稳定。[22,26,45,46]

工业发展的速度远远超过了监管的发展速度。在没有对纳米材料毒性和毒理学的许多方面进行长期监测，而且缺乏相关科学信息的情况下，尽管越来越多的迹象显示出潜在接触和风险，但具体法规的制定却进展缓慢。[47]

**视频：**碳纳米管是下一个石棉吗？



*视频链接：https://www.youtube.com/watch?v=6L7xXgWcbrQ*



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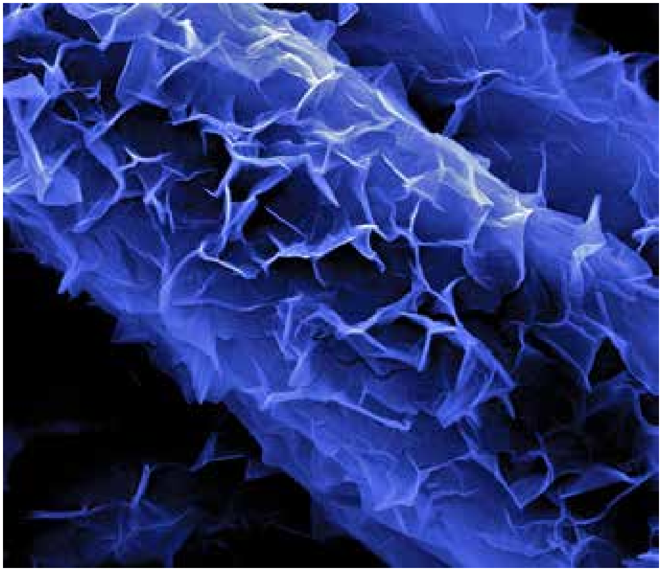
和石棉的情况一样，接触纳米材料的第一批人也是工人。20世纪90年代末和21世纪初开展的前几项评估碳纳米管职业暴露的研究为下一步的工作场所调查、以及随后于2007年制定的首个界定职业纳米悬浮微粒暴露的国际标准化组织指南奠定了基础。[48,49]

通过对暴露于碳纳米管和碳纳米纤维的动物的研究，美国国家职业安全卫生研究所认为，在受试动物中发现的肺部炎症、肉芽肿和纤维化等结果，有足够理由采取行动来设置建议的暴露限值。[22]经济合作与发展组织（OECD）开展了一些长期项目，旨在生成关于各种纳米材料的毒理学数据，以修订现有的制造商测试指南。[50]

由于纳米材料应用广泛，监管机构需要依靠化学品、药品、化妆品、食品、污染、废物和标签等领域的现行法规来寻求制定有关纳米材料的规定。[51]然而，把现行法规框架应用于纳米材料也面临着挑战。[47]例如，如果纳米级材料和散装材料属于同种化学物质，那么材料尺寸的缩小可能很难促成对现行法规的修改或制定新的法规。此外，某些消费品不受安全要求制约，可以不经测试就进入市场。

在欧盟，《化学品注册、评估、许可和限制法规》（REACH）用于确保在欧盟制造和销售的任何化学物质对人类健康和环境都是安全的。各公司需要对有意制造和交易的化学物质进行注册，并根据REACH的具体指导方针说明与这些化学物质有关的风险是如何管理的，以确保人类健康和环境安全。[52,53]

在全球层面，在联合国环境署管理的国际化学品管理战略方针（SAICM）的政策框架下，纳米材料是新



碳石墨烯多级核壳纳米纤维

*图片来源：Ranjith Shanmugam/蔡司显微镜，根据CC BY-NC-ND 2.0授权*

出现的政策问题之一。SAICM与各国政府和国际利益攸关方合作，促进关于纳米技术和工程纳米材料的信息交流，并制定国际通用的技术和法律指导，以实现对纳米材料的良好管理。[54]

在新技术面前，监管机构面临着前景、风险和不确定性混杂的局面。[55]加强全球对工程纳米材料的研究、生产和使用将需要变革性的政策，鼓励创新和绿色化学的工业应用。更为关键的是，鼓励建立基于预防原则的迭代式的、能够积极响应的监管框架，以确保安全和无污染。面对新材料创造的充满前景的机会，我们同样不能忘记人类健康和环境曾经的教训。

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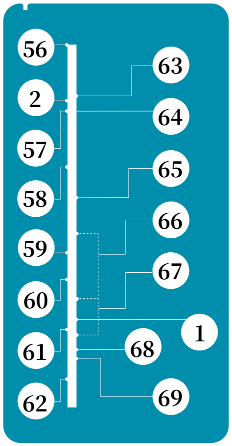



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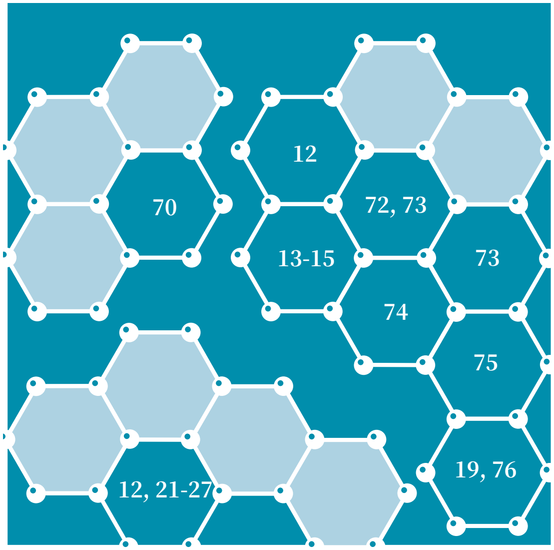



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