

纳米银的制备及其生物活性研究进展

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摘 要:综述了不同形貌、大小纳米银的可控合成,并介绍了纳米银对大肠杆菌、金黄色葡萄球菌等细菌的抗菌活性,以及对艾滋病、乙型肝炎等病毒和乳腺癌细胞等的抑制作用;同时,对有关纳米银的产品作了简单的介绍,并对其未来发展方向进行了展望。

关键词:纳米银;制备;抗菌;抗病毒;抗肿瘤;研究进展

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0 引 言

随着纳米技术的迅猛发展,纳米材料因其独特的量子效应、小尺寸效应以及大的比表面积而显现出特有的性质,引起人们广泛的研究兴趣。二十世纪九十年代以来,研究人员在纳米材料的制备、表征上做了大量工作,取得了丰硕的研究成果。近年来,人们已越来越多的把目光集中在纳米材料的性质及其应用上^[1-2],而不是仅仅局限在材料的合成与制备。人类很早就认识到了银具有广谱的抗菌作用,银及其化合物,已广泛应用于日常生活和生物医药领域^[3]。而近年来,纳米银的研究更是取得了极为丰富的研究成果。在众多的纳米材料中,无论从制备、性质,还是应用,纳米银无疑是一种研究最为广泛、深入的材料。在已报道的文献中,人们已经通过不同的方法合成出不同粒径和不同形貌的纳米银颗粒以及多种一维纳米结构,如银纳米线、纳米棒和具有一定空间结构的树枝状的纳米银等。在纳米银的活性研究中,人们发现其不但具有显著的抗菌活性^[4-9],还具有抗病毒^[10-11],抗肿瘤^[12-13]等生物活性。正是这些显著的生物活性,使得纳米银在生物医药和纺织上得到广泛的应用^[14],并且已有多种关于纳米银的产品市场化。本文简要综述了不同粒径和形貌的纳米银的各种制备方法,及其抗菌、抗病毒、抗肿瘤等

生物活性和其产业化应用。

1 纳米银的制备

在不同形貌和大小的银纳米结构的制备方法中,根据所用还原剂或还原方法的不同,主要分为三类:化学还原法、物理还原法、生物还原法。

1.1 化学还原法

化学还原法是制备纳米银最简单也最常用的方法。一般指在液相条件下,将 Ag^+ 还原为单质银,所用还原剂常有硼氢化钠、柠檬酸钠、乙二醇、抗坏血酸、葡萄糖等。不同的还原剂和分散剂对纳米银的形貌和大小有很大的影响,在纳米银颗粒的合成中,人们通过控制不同的反应条件,分别得到了不同粒径大小的纳米银颗粒(如图1所示)。例如,Logar等以 NaBH_4 为还原剂,制备得到颗粒大小为 7 nm 左右的纳米银颗粒^[15]。Lee 课题组报道了利用 1,2-二羟基十六烷还原 Ag^+ 得到晶种并通过银纳米粒子的自组装,得到粒径为 10 nm 左右的单分散纳米银颗粒^[16]。殷亚东课题组还报道了使用多羟基还原的方法,以乙二醇为溶剂和还原剂,并且使用聚丙烯酸(PAA)为表面活性剂,得到了粒径为 20 nm 的银纳米颗粒^[17]。夏幼南课题组在引入少量 NaCl 的条件下,以乙二醇为溶剂和还原剂,可得到粒径为 30 nm 左右的银纳米颗粒及其二聚体^[18]。还有报道直接用柠檬酸钠还原硝

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酸银,可制备出了 30 ~ 50 nm 的银纳米颗粒^[19]。陈代荣课题组使用抗坏血酸还原氯化银可得到 50 nm 的银纳米颗粒^[20]。Pyatenko 等采用晶种技术,首先生成纳米银种子颗粒,然后合成纳米银溶

胶,再经多步合成过程,便可得到 80 nm 左右的纳米银颗粒^[21]。Quaroni 等使用乳液聚合作用,制备了尺寸均一、稳定、粒径为 100 nm 的纳米银颗粒^[22]。

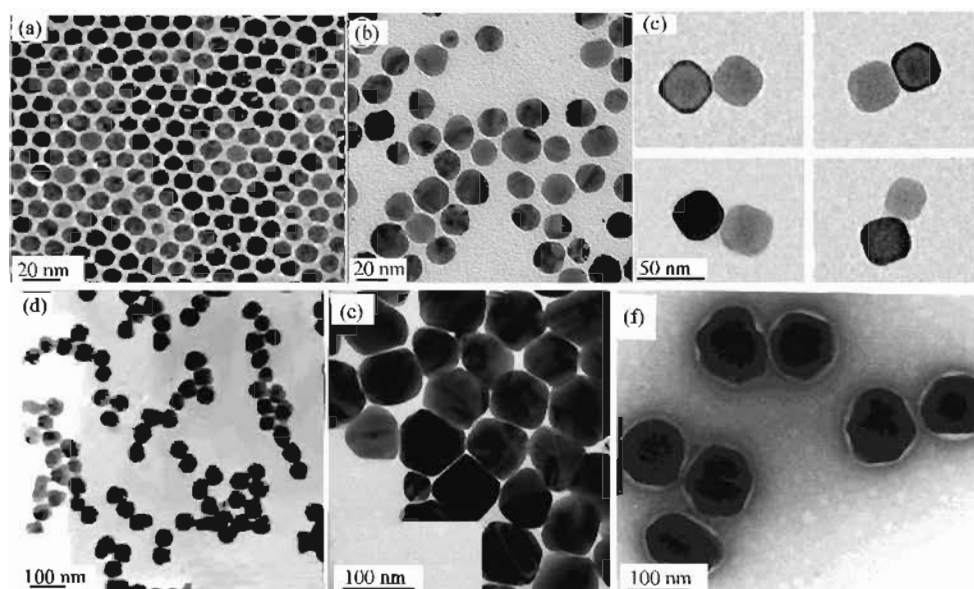


图 1 不同粒径的纳米银颗粒透射电镜图

Fig. 1 TEM images of silver nanoparticles with different sizes

注:(a)10 nm;(b)20 nm;(c)30 nm;(d)50 nm;(e)80 nm 和(f)100 nm。图片经允许分别转载自文献[16]、[17]、[18]、[20]、[21]、[22],美国化学学会,1999,2007,2009,2010;爱思维尔,2008,版权所有。

目前,除了用各种方法制备出不同粒径的银纳米颗粒外,人们也制备出了银纳米线^[23-25]、纳米立

方^[26-27]、纳米棒^[28-29]、纳米球^[30]、纳米三角片^[31]、纳米双锥体^[32]等不同形貌结构(如图 2 所示)。

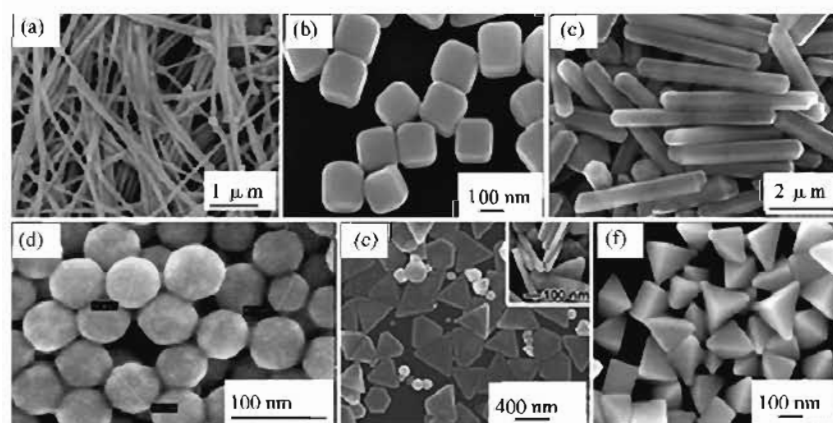


图 2 不同形貌的纳米银扫描电镜图

Fig. 2 SEM images of silver nanoparticles with different shapes

注:其中(a)银纳米线;(b)银纳米立方;(c)银纳米棒;(d)银纳米球;(e)银纳米三角和(f)银纳米双锥体。图片经允许分别转载自文献[25]、[26]、[29]、[30]、[31]、[32],威立,2005,2006;美国科学促进会,2002;美国化学学会,2007,2009,2010,版权所有。

夏幼南课题组报道在 PVP 存在下,用乙二醇还原 AgNO_3 ,以 Pt 或 Ag 的小粒径的纳米颗粒作为晶种,合成出长度 50 μm ,直径 30 ~ 40 nm 的银纳米线^[23-24]。夏幼南课题组还报道了使用多羟基还原的方法,在 PVP 存在条件下,通过改变 PVP 与 AgNO_3 的摩尔比,可控合成了平均粒径为 80 ± 7

nm 的银纳米立方结构^[26]。该课题组还使用多羟基还原的方法,通过控制纳米银种子晶型来控制最终产物的形貌,选择性的合成出不同形状的银纳米结构,如纳米三角、纳米双锥体、纳米棒、纳米线、纳米束、纳米立方体、纳米球等结构,并通过调节 AgNO_3 浓度,PVP 与 AgNO_3 的比例等因素也可

来改变纳米银的粒径和形貌^[31,33]。在此基础上, Yam 课题组使用水热法,以葡萄糖为还原剂还原 $[\text{Ag}(\text{NH}_3)_2]^+$ 得到边长为 $55 \pm 5 \text{ nm}$ 的银纳米立方结构^[27]。钱逸泰课题组使用水热法,并以氯化银作为前驱体反应生成银的纳米线,其长度可达 $500 \mu\text{m}$,平均直径约为 100 nm ^[25]。Maiyalagan 利用多元醇方法通过改变 AgNO_3 与 PVP 的比例,得到不同长径比的银纳米棒^[28]。Pictrobon 等采用水热法,并以柠檬酸为还原剂,将单分散的纳米银颗粒,自组装成银的纳米棒结构^[29]。Liang 等采用水热法,使用聚乙二醇(PEG)作为还原剂和溶剂,通过控制 PVP 与 AgNO_3 的摩尔比,制备出了单分散的银纳米球结构^[30]。李亚栋课题组通过溶剂热法,合成三角片、球型、立方体形状的纳米银^[34]。化学还原法操作简单,容易控制,常使用表面活性剂(如 PVP、CTAB、PEG、SDS 等)防止纳米银颗粒聚集,并诱导其晶体生长。

1.2 物理还原法

物理还原法主要是指借助于物理手段或方法等辅助条件将 Ag^+ 还原为单质银的方法,主要有:紫外光照射法、电子束辐照法、微波还原法等。Giovanna 等使用紫外光照射的方法制备出 $2 \sim 4 \text{ nm}$ 的纳米银颗粒^[35]。在聚乙烯醇(PVA)存在下,通过电子束辐照,可将 AgNO_3 还原制得稳定的银纳米粒子^[36-37]。而微波法由于具有加热速度快、加热均匀、无温度梯度、无滞后效应等特点,近年来也被广泛应用于纳米银颗粒的制备。在乙二醇溶剂里,通过微波加热可制备得到粒径为 10 nm 左右的纳米银颗粒^[38]。俞书宏课题组发现在 AgNO_3 中加入一定比例的氨基酸、淀粉,通过微波加热也可合成出平均粒径约为 26 nm 的纳米银颗粒^[39]。Baruwati 等人还报道了在谷胱甘肽促进下,水溶液中微波合成粒径为 $5 \sim 10 \text{ nm}$ 的纳米银颗粒^[40]。

1.3 生物还原法

随着人们对环境友好型技术的逐渐重视,研究人员发现利用微生物体系也可来制备纳米银颗粒。生物还原法主要有:细菌还原法、真菌还原法、植物还原法等^[3]。1999 年, Klaus 等首次报道了利用施氏假单胞菌合成银的纳米颗粒,高浓度 AgNO_3 在施氏假单胞菌中被还原成颗粒大小为 200 nm 左右的银纳米晶体^[41](如图 3 所示)。随后不同研究小组分别报道了用肺炎克雷伯杆菌^[42]、地衣芽孢杆菌^[43-44]、烟曲霉^[45]、黄曲霉^[46]、黑曲霉^[47]、木霉菌^[48]、白腐真菌^[49]、尖孢镰刀菌^[50]等

与 Ag^+ 作用得到不同粒径的纳米银颗粒。除细菌、真菌外,印度学者还报道了用植物还原法合成纳米银。研究发现天竺葵叶提取物在较短时间内,可将银离子还原成粒径为 $16 \sim 40 \text{ nm}$ 的银纳米颗粒^[51]。李清彪课题组也报道了利用香樟叶合成粒径约为 $55 \sim 80 \text{ nm}$ 的银纳米颗粒^[52]。生物还原法具有原料来源广、价廉易得、绿色环保、反应条件温和等优点,可能引领一种简易的生物合成纳米银方法的新发展,但其还原能力较弱,寻找新的具有较强还原能力的生物源是此法的主要突破口。

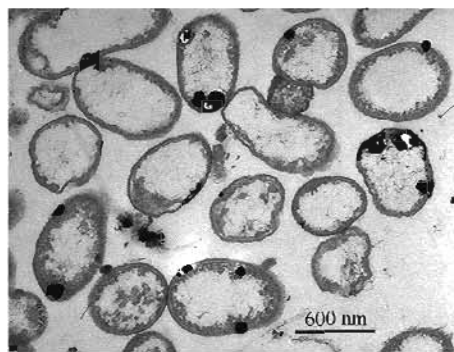


图 3 施氏假单胞菌细胞的超薄切片的高分辨透射电子显微镜照片

Fig. 3 TEM of a thin section of *P. stutzeri* AC259 cells. Large crystalline Ag_0 and Ag_2S particles are deposited between the cell wall and the plasma membrane.

注:银单质晶体和硫化银颗粒存在于细胞壁与原生质膜之间。图片经允许转载自文献[41],美国国家科学院,1999,版权所有。

2 纳米银的生物活性

2.1 纳米银的抗菌活性

人类很早就认识到银具有广谱杀菌作用,并用银来杀菌消毒。近年来,随着纳米技术的发展,纳米级无机抗菌剂的应用日益广泛。其中纳米银系列抗菌剂是研究最为广泛和深入的纳米抗菌材料,有关纳米银的抗菌活性的报道层出不穷,研究发现,纳米银对大肠杆菌、金黄色葡萄球菌有较好的抑制作用^[6-7,53-60],不同研究小组还分别报道了纳米银对枯草芽孢杆菌^[8,61]、铜绿假单胞菌^[62-63]、鼠伤寒沙门氏杆菌^[64]、真菌^[65]等的抗菌作用。随后 Hernández-Sierra 等报道了其对口腔细菌:致龋菌变形链球菌的抑制作用^[9,66]。Arora 等研究了纳米银颗粒经细胞毒性实验、动物实验,证明纳米银基本属无生物毒性的纳米材料,其具有高效抗菌活性并且使用安全^[67-68]。支志明课题组系统研究了纳米银对大肠杆菌的抑制作用,并探讨了其抗菌机制,说明纳米银可能是通过破坏细菌细胞膜,

从而消耗其质子驱动力,这样来达到其抗菌效果^[69-71].Sondi等在前人研究的基础上总结了银系抗菌剂的抗菌机理,他们指出纳米银颗粒可以直接进入微生物体内,中断DNA的复制,通过阻断细菌的呼吸酶系统,杀灭细菌,从而阻止微生物繁殖,杀灭各种致病细菌^[7,72].

2.2 纳米银的抗病毒活性

人们对银的抗病毒活性研究起步较晚,随着纳米科技的快速发展,近年,人们对纳米银的抗病毒活性研究越来越多.2005年,Yacaman课题组和支志明课题组相继报道了纳米银对HIV病毒的抑制作用,研究表明粒径在1~30 nm的纳米银颗粒均能起到杀灭HIV病毒的作用,阻止其HIV病毒的繁殖^[10,73].2008年,支志明课题组和Rogers课题组又相继报道了纳米银对乙型肝炎病毒^[11]和腮腺红热病毒^[74]的抑制作用.张若愚等人还报道了纳米银颗粒对禽流感病毒也有较好的抑制作用^[75].

2.3 纳米银的抗肿瘤活性

尽管纳米银在抗肿瘤活性方面的研究不及抗菌活性方面的研究广泛,但也有不少研究小组对其抗肿瘤活性做了相关报道.Gopinath等报道了纳米银可以使细胞内线粒体膜通透性发生改变,从而促进肿瘤细胞凋亡^[76].Verma等也研究了纳米银具有较好的抗癌活性^[77].Oltrock等报道了纳米银的靶向治疗,在杀死癌细胞时,对正常细胞没有损伤^[78].Youngs等报道了纳米银对乳腺癌细胞的抑杀作用^[12].在预防和治疗与细胞凋亡缺陷有关的疾病方面(如恶性肿瘤等),纳米银的作用值得进一步深入研究.

3 纳米银产品

由于纳米银具有广谱抗菌性,且其有抗菌活性高、毒性低等特点,载银纳米无机抗菌材已成为目前应用最广泛的无机抗菌材料.国内外研究人员研制出的相应的纳米银产品已应用于各领域.例如:香港安信纳米科技公司率先研发的纳米银速效抗菌颗粒,已通过香港大学、中国科学院、中国医学院等权威机构的认证并投产.除此以外,安信公司还研制开发了纳米抗菌袜、纳米银创可贴等纳米产品.江苏瑞德纳米材料技术有限公司推出的宣氏纳米银抗菌凝胶(烧伤用),其产品具有超强的抗菌活性,能促进组织修复与再生,加快创面愈合,减少疤痕组织的形成.中山市国宇医疗器械有限公司开发研制的纳米银痔疮净、沈阳高名医药科技有限公司的纳米银前列腺宝、济南龙邦生物科技有限公司的纳米银脚癣净、西安华康生物

科技有限公司妇科千金(纳米银)凝胶、上海沪正纳米科技有限公司的纳米银牙膏以及深圳清华源兴纳米医药科技有限公司研制开发的纳米银制剂阿希米都已经产业化.

4 总结与展望

随着纳米科技的发展,纳米银在人类生活中有着举足轻重的作用.近年来通过化学还原法和物理还原法可以合成出不同大小、不同形貌的纳米银.以细菌、真菌以及植物为原料的生物还原法也是具有很大的潜力的绿色合成方法.未来的纳米银制备方法将向低成本、低能耗、环境友好的方向发展.纳米银对常见革兰氏阴性菌和革兰氏阳性菌都有较好的抗菌作用,其抗菌活性高、抗菌谱广且毒性较低等,其且对HIV病毒、腮腺红热病毒及禽流感病毒均有较好的抑制作用.纳米银还可通过靶向治疗促使肿瘤细胞凋亡.随着人们对其抗菌、抗病毒、抗肿瘤原理及其活性与生物稳定性研究的进一步深入,将开发出更多安全、有效的纳米银制剂.由于纳米银在生物医学等方面有着广泛的应用,其产业化引起了人们的高度重视,并且许多成果已经开始产业化.真正全面实现纳米银的产业化,造福人类,也是当前科技工作者努力的方向.

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水剂产品具有一定的优势,但不便于长途运输,它适宜于公司自产自销为主,惠顾其它公司的发展模式,也适宜于其公司比较集中的地方投资建厂。

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Application research in concrete about sodium gluconate aqua instead of sodium gluconate powder

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Abstract: To manufacture sodium gluconate aqua by using the multi-metal as catalyst and the catalytic oxidation technology, this paper discuss application effect in concrete about sodium gluconate aqua instead of sodium gluconate powder.

Key words: glucose; catalytic oxidation; sodium gluconate aqua; concrete; apply

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Research progress on the synthesis and biological activities of silver nanoparticles

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Abstract: This article reviewed the controllable synthesis of silver nanoparticles with different morphologies and sizes. The antibacterial activities against *Escherichia coli*, *Staphylococcus aureus*, etc were summarized. The inhibition towards human immunodeficiency virus (HIV), hepatitis B virus and breast adenocarcinoma cancer cell were presented. At the same time, the products with relevance to silver nanoparticles and the prospect on the development of silver nanoparticles were also introduced.

Key words: silver nanoparticles; preparation; antibacterial; anti-viral; anti-tumor; research progress