学校编码：10384　　　　　　　　　　　　分类号_____密级______
学　　号：20620131151492　　　　　　　　　　UDC_______

厦门大学

硕　士　学　位　论　文

# 基于植物还原的银纳米颗粒在织物及聚醚砜超滤膜中的抗菌应用

# Plant-mediated synthesis of silver nanoparticles and its antibacterial applications in textile and polyether sulfone ultrafiltration membranes

厦门市科技计划项目（3502Z20133006）资助

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专 业 名 称：化　学　工 程

论文提交日期：2016　年　　月

论文答辩时间：2016　年　　月

学位授予日期：2016　年　　月

答辩委员会主席：_____________

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# 摘要

目前市场上存在的各种抗菌材料中，银系抗菌剂因其安全、高效、不易产生耐药性以及良好的耐久性，已占据主导地位。纳米银是以纳米技术为基础研制而成的新型抗菌产品，由于量子效应和尺寸效应，具有普通银系抗菌剂无法比拟的抗菌效果。生物还原法是一种近年来发展起来的一种制备金属纳米颗粒的绿色合成方法，该法具有绿色、环保、生物兼容性好等诸多优点。本研究以植物提取液还原制备银纳米颗粒（AgNPs），探讨其粒径的调控规律，并着重研究将其作为抗菌剂应用于织物整理以及聚醚砜（PES）超滤膜改性中的性能。

首先，以黄芩提取液在 90 ℃条件下快速还原硝酸银得到纳米银溶胶，并借助紫外可见吸收光谱（UV-Vis）、X 射线衍射（XRD）、透射电镜（TEM）等技术对其进行表征，研究其制备银纳米颗粒的粒径调控规律。结果表明提高植物提取液浓度、增加氢氧化钠的加入量均有利于制得粒径较小的银纳米颗粒。该粒径调控规律对芳樟、洋浦桃、丁香等植物提取液同样适用，实验条件下四种植物质对银离子的还原率均在 99%以上。将黄芩提取液所制得的 AgNPs 以浸渍法负载到纯棉织物上，通过 AAS 测定织物上银的负载量，从而得到较优的浸渍工艺条件为：时间 30 h，温度 55 ℃，浴比 1：25。分别研究了植物质种类、AgNPs 粒径对织物载银量及抗菌效果的影响，发现在所用的四种植物质提取液中抗菌织物的载银量与 AgNPs 的粒径大小无关，而与植物质的种类有关；抑菌效果则与粒径密切相关，AgNPs 的粒径越小，所得载银织物的抑菌效果越好；利用本身具有抑菌效果的黄芩、丁香植物质来制备 AgNPs，有利于增强所得载银织物的整体抗菌性能。

进一步，以四种植物提取液中筛选出的抑菌效果最优的黄芩为目标生物质，在上述确定的较优浸渍工艺条件下制得载银抗菌织物，对其抗菌广谱性、耐洗性、以及拉伸性能等进行了测试。抗菌广谱性测试结果表明，该载银织物对大肠杆菌、金黄色葡萄球菌、枯草芽孢杆菌、地衣芽孢杆菌的抑菌率均高达 99%，且对霉菌也具有抑制作用。耐洗性检测表明，织物经过水洗或皂洗之后，载银量明显降低，抑菌效果也显著下降；适量丙烯酸乳液的引入成功地改善了织物的耐洗性能，且抑菌效果不受影响。织物的拉伸性能测试结果表明添加 AgNPs 以及粘合剂所得的抗菌织物的断裂强力保持率均在 80%以上，达到实际应用要求。

最后，选用黄芩提取液制备的粒径约为 6 nm 的 AgNPs 通过湿法相转化法改性 PES 超滤膜。利用扫描电镜观察膜表面及断面结构，发现改性前后超滤膜的孔径并没有明显的改变，通过能谱（EDS）在改性膜表面确认了银元素的存在。膜的水接触角测试结果表明，改性膜的亲水性能优于未改性膜，且载银量越高，亲水性越强。分别测定改性前后 PES 超滤膜的通量、截留率，发现膜通量随着亲水性能的改善而呈增大的趋势，且 AgNPs 的引入对 PES 膜的截留率几乎没有影响。PES 膜上银纳米颗粒的稳定性测试显示，在银损失最严重的第 1 次过滤过程中银的流失率都低于 1%，所以，AgNPs 在膜上具有非常理想的稳定性。以大肠杆菌为测试菌种，对 PES 超滤膜进行抑菌性能测试及抗生物污染性能测试。抑菌测试结果表明改性膜的抑菌率接近 100%，说明改性膜具有极强的抑菌能力。通过 SEM 观察细菌在膜表面培养 24 h 之后的生长情况，发现未改性膜的表面粘附了大量的细菌，形成了生物膜；而改性膜的表面则只有少量的细菌附着，阻止了生物膜的形成，有效降低了膜的生物污染。

**关键词**：植物还原法；银纳米颗粒；抗菌织物；聚醚砜超滤膜；生物污染

# Abstract

Silver-based antimicrobial agents are dominant among various antimicrobial materials on the market due to its safety, highly efficient and less likely to produce drug resistance. Nanosilver, based on nanotechnology, exhibits excellent antibacterial ability on account of the quantum and size effect. Plant-mediated synthesis is a novel green method for preparing metal nanoparticles developed in recent years. Hence in this study, silver nanoparticles (AgNPs) were prepared by plant-mediated bio-reduction and the laws of regulation on particle size were explored, also, their performances as an antibacterial agent applied in textile finishing and modification of polyether sulfone ultrafiltration membrane were mainly studied.

At first, nano silver sol was obtained by reduction of silver nitrate with *Scutellaria baicalensis* (SB) extract under 90 ℃. The as-synthesized AgNPs were characterized by UV-Vis, TEM and XRD techniques. The results indicated that the obtained AgNPs tended to be smaller with the increase of biomass concentration or adding amounts of NaOH, also applicable for *Syzygium aromaticum*, *Syzygium samarangense* and *Cinnamomum camphora* extracts. Then AgNPs produced by SB was loaded onto cotton fabric through impregnation, and the optimal conditions were: impregnation time of 30 h, temperature of 55 ℃ and liquor ratio of 1:25. Furthermore, the effects of plant species and AgNPs size on the silver content loaded on fabrics and antibacterial ability were investigated. The Ag content loaded on antibacterial fabric was related with plant species rather than AgNPs size based on the four extracts studied. However, the antibacterial effect was closely relevent to AgNPs size, the Ag-coated fabrics with smaller size of AgNPs loaded displayed superior antibacterial activity against *Escherichia coli*. Moreover, employing AgNPs prepared by SB and *Syzygium aromaticum* extracts with own antibacterial ability would enhance the overall antibacterial properties of the Ag-coated fabrics.

Further, the broad-spectrum antimicrobial property, washing endurance and tensile property of as-prepared fabric by the extract of SB, which exhibited the best antibacterial ability, were tested. The antibacterial rate of this Ag-coated fabric against

*Escherichia coli, Bacillus subtilis, Bacillus licheniformis* and *Staphylococcus aureus* all reached up to 99%, and it also had inhibition on mold. Washing endurance tests showed that silver content on fabric reduced a lot after washing the antibacterial effect was also significantly decreased. The introduction of an appropriate amount of acrylic emulsion successfully improved the washing endurance of the fabric, and the antibacterial effect was not affected. The results of tensile tests showed that breaking strength retention of antibacterial fabric maintained more than 80% after adding AgNPs and adhesive, meeting the requirements in practical application.

Finally, AgNPs with mean size of 6 nm prepared by SB extract were used to modify polyether sulfone ultrafiltration membrane (PES) by wet phase inversion method. SEM images of membrane surface and sectional structure indicated that the pore size of ultrafiltration membrane did not change significantly after modification, and the existence of silver on the modified membrane was confirmed by EDS analysis. The water contact angle tests showed that the hydrophilicity of modified membrane is better than the unmodified one, and the hydrophilicity enhanced with the amount of loaded silver. The flux and rejection rate of PES ultrafiltration membrane before and after modification were measured, the flux of the membrane would increase as hydrophilicity improved, and the introduction of AgNPs almost had no effect on rejection rate of PES membrane. Stability tests of AgNPs on PES membrane showed that the loss ratio of silver in the first filtration of which silver lost most is less than 1%, indicating satisfied stability for the AgNPs on the membrane. The antibacterial and antibiofouling properties of PES ultrafiltration membranes were evaluated by using *E. coli* as test bacteria. The antibacterial rate of the modified membrane were nearly 100%,. The growth of bacterial after culturing on the membrane surface for 24 h was observed by SEM, it turned out that there were much bacteria adhered on the unmodified membrane surface while little on the modified one.

**Key Words:** Plant-mediated; Silver nanoparticles; Antibacterial fabric; Polyether sulfone ultrafiltration membrane; Biofouling

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# 第一章 文献综述

## 1.1 抗菌剂及其分类

抗菌剂是指能通过物理或化学作用杀死微生物的化学成分。抗菌材料是指经抗菌剂处理，使其具有可以杀死有害微生物能力的一类材料。抗菌技术近年来发展很快，虽然抗菌剂的种类繁多，应用较广，但日常使用的抗菌剂只能产生短期效应，因此新型抗菌材料的开发从未停止。常见的抗菌剂主要可以分为天然生物抗菌剂、有机抗菌剂以及无机抗菌剂 3 种类型[1]。

### 1.1.1 天然生物抗菌剂

人们很早以前就开始使用地球上的本土植物作为草药来处理伤口。据史料记载，6000 多年前生活在今天伊拉克地区的尼安德塔人就使用诸如蜀葵[2, 3]这类的植物，且现在这些植物仍然在世界各地的传统医药中被广泛使用。几十年前，植物提取液已经被证明作为制霉菌素使用是有效果的。1996 年，用公认的对尿路感染具有疗效的红莓汁对一组老年妇女的尿液进行了研究，发现使用红莓汁的一组人尿液中的细菌量明显少于未使用红莓汁的一组人尿液中的细菌量[4]。且植物提取液中的一些成分被证明对病毒同样具有良好的抑制效果。很多研究表明抱茎獐牙菜苷[5]、甘草中的甘草酸[6]、黄芩纯化物[7]中所含的黄酮类物质对 HIV 病毒具有明显的抑制作用。天然抗菌剂不仅有植物源抗菌剂，而且还有微生物源抗菌剂、动物源抗菌剂（半胱氨酸、壳聚糖、溶菌酶等）。K. H. Yu 等 [8]报道来自 3 种昆虫（大蜡螟、蚕、白薯天蛾）幼虫血淋巴的溶菌酶对革兰氏阳性菌有很强的抗性，对革兰氏阴性菌也有一定的抑制作用。

### 1.1.2 有机抗菌剂

有机抗菌剂是引起人们关注最早的一类抗菌材料，常用的有几十种，主要是指香醛、乙基香草醛类化合物、季铵盐和双胍类以及甲苯青霉素等有机物。从杀菌机理的不同可以分成氧化型杀菌剂和非氧化型杀菌剂两类[9]。有机抗菌剂的优点是杀菌能力强、见效快、来源丰富，但是也有耐热性差、易产生细菌耐药性以