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硕　士　学　位　论　文

微生物还原法制备水溶性纳米银粉及其催化和抗菌应用

Preparation of Watersoluble Nanosilver Powder by Microorganism Reduction and Its Application in Catalysis and Antibiosis

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摘　要

纳米材料由于其维度降低而产生许多特殊的物理和化学性质，成为当今材料科学研究的一个热点。金属离子的生物吸附与生物还原由于其在环境保护、纳米材料制备等方面的潜在应用前景也成为近年来各国学者广泛开展的科研领域。本论文以筛选自金银矿区的气单胞菌(*Aeromonas sp.*)SH10、棒状杆菌(*Corynebacterium sp.*)SH09、地衣芽孢杆菌(*Bacillus licheniformis*)R08等为主要实验菌株，利用微生物细胞丰富的有机官能团，研究在一定条件下快速还原银盐或银氧化物，并利用生物质对还原出来的银单质颗粒可提供修饰、包裹保护作用，制备得到稳定的生物质银溶胶，并尝试揭示还原的可能机理，研究收集生物质银溶胶并制成纳米银粉的方法，尝试开发其在催化和抗菌方面的应用。该研究有助于丰富和完善生物吸附还原过程的机理，也为微生物细胞的资源化提供了一条新途径，同时在银纳米颗粒制备技术上提供了一条新颖的、相对绿色的途径。

微生物细胞60 ℃下可缓慢还原银氨溶液得到稳定的生物质银溶胶。向该还原体系中引入NaOH可大大加快还原，还原周期从一个月甚至更长缩短为几个小时，且随体系碱性增强，还原速率增加。升温也能促进还原，但通过提高[OH^-]来加快还原更为合理，[OH^-]的选择与菌体浓度密切相关。菌体起还原剂及保护剂等多重作用，其浓度的选择主要取决于体系中的银浓度。较为适宜的菌体浓度与银浓度的比例Ra是1~ 2 (w/w)，此时还需保证一定量的[OH^-]。例如，当Ra= 1时，[OH^-]取银浓度的2倍以上为宜(mol/mol)。菌种种类对还原的影响不大，实验所用到的菌种均能有效还原银氨，且还原能力差别并不太大。改用$AgNO_3$及Ag_2O作为银源，仍能实现还原并得到稳定的生物质银溶胶。还原过程具有自催化特征，推测强碱性条件下，还原经历$Ag_2O \rightarrow Ag_2O\text{-}Ag^0 \rightarrow Ag_2O\text{-}Ag_n^0 \rightarrow Ag_n^0$的过程，而生物质上的酰胺结构、氨基酸残基、多羟基结构等在过程中起重要作用。

还原产物生物质银溶胶具有高分子溶液的性质，采用与水互溶的有机溶剂可沉淀银溶胶，真空干燥后可得到含有生物质的水溶性纳米银粉。银晶粒可保持沉淀前的纳米尺度，水溶性、分散性好，银的质量分数在50%以上。将此纳米银粉重新分散于水中制得的生物质银溶胶热稳定性、化学稳定性良好，优于柠檬酸三钠法制得的银溶胶。酸和具有高价阳离子的电解质对生物质银溶胶稳定性的影响

比较明显。

环氧乙烷用银催化剂载体为低比表面积的α -Al_2O_3，表面比较平坦光滑，而银负载量较高，将生物质银溶胶直接浸渍载体，再通过简单的空气焙烧活化难以获得高分散度的性能优良的纳米尺度催化剂，而需研究新的催化剂活化方法。当银催化剂体系为大比表面的载体且银负载量低时，采用浸渍生物质银溶胶并焙烧活化的方法比较可行。无论是生物质银溶胶或是固定于载体上的银晶粒，对大肠杆菌（革兰氏阴性）和金黄色葡萄球菌（革兰氏阳性）均有良好的杀菌性能，杀菌率高，且作用迅速，对大肠杆菌的杀菌性能优于对金黄色葡萄球菌的。将干燥后的生物质纳米银粉末分别在空气气氛和氮气气氛下高温焙烧，可分别获得多孔结构的银以及银纳米粒子/碳复合材料，可能具有良好的应用前景。

关键词：微生物还原；纳米银粉；应用

Abstract

Nanostructured materials are capable of giving unique physicochemical properties and therefore they have been attracting increasing attention. Biosorption and bioreduction of metal ions have been receiving growing attention due to its potential applications in the fields of environment protection, nanomaterial synthesis, etc. Several strains were used to investigate the silver bioreduction in this study, including *Aeromonas sp.* SH10、*Corynebacterium sp.* SH09、*Bacillus licheniformis* R08, which were mainly isolated from the soil or sewage outfall of the metal mine. It had been proven by our group that the abundant organic groups on the cells could slowly reduce $[Ag(NH_3)_2]^+$ and formed stable biomass-silver sol at 60 ℃. This study aims at a rapid silver bioreduction, a probable reduction mechanism, a method of nanosilver powder collection and its applications. The research is expected to be helpful to the better understanding of biosorption and bioreduction processes, and could provide with a novel and relatively green approach to the preparation of silver nanoparticles. In addition, it may offer a new way to take use of the industrial waste biomass.

The $[Ag(NH_3)_2]^+$ bioreduction was well promoted by the introduction of more OH^- to the system, by which the reduction time was shortened from more than one month to a couple of hours. Increasing $[OH^-]$ was more effective on the acceleration of the reaction than raising the temperature and $[OH^-]$ was much dependent on the biomass content. The biomass played multiple roles such as reductant and protectant, thus its content was related to the initial silver content. A reasonable biomass-to-metal ratio, Ra, was in the range of $1\sim2$ (w/w) while $[OH^-]$ should be controlled to achieve a rapid reduction, for instance, hydroxyl-to-silver ratio at 2 (mol/mol) when Ra is 1. All the strains investigated could well reduce $[Ag(NH_3)_2]^+$ and their reductive capacity deviated little. Serving $AgNO_3$ or Ag_2O as the silver source, a similar reduction took place. As the silver bioreduction presented the characteristic of autocatalysis, the reduction mechanism probably followed the course of $Ag_2O \rightarrow Ag_2O\text{-}Ag^0 \rightarrow Ag_2O\text{-}Ag_n^0 \rightarrow Ag_n^0$. The amide, amino

acid residues, hydroxyl groups, etc. might play important roles during the reduction process.

The bio-silver sol prepared by the bioreduction had the property of macromolecular solution. Therefore, a kind of watersoluble bio-nanosilver powder could be prepared by precipitating the bio-silver sol with water soluble organic solvent as precipitator, such as ethanol and acetone, followed by a simple treatment of vacuum drying at room temperature. The silver particles in the bio-silver powder could keep their original size before precipitation, and the silver mass content of the bio-silver powder was higher than 50%. The water solubility and dispersibility of the bio-silver powder were extremely good. The thermal and chemical stabilities of the bio-silver sol which was prepared by dissolving the bio-silver powder into the deionized water were superior to that of the silver sol prepared by the method of sodium citrate reduction. The effects of the acids and the electrolytes with cations of high valence on the stability were relatively significant.

Since the silver catalyst for the ethylene oxide production requires high silver loading and low specific surface area carrier, it is difficult to prepare the catalyst with good performance on the ethylene epoxidation by the impregnation method with bio-silver sol as impregnation liquid and followed by simple calcinations. A novel treatment after impregnation should be invented. Silver catalyst with low silver loading and high specific surface area carrier requirements might be successfully prepared by this bio-silver sol impregnation method. Both the free bio-silver sol and immobilized silver particles presented good antibacterial performance on *staphylococcus aureus* and *E. coli*, especially on the latter. A kind of polyporous silver and silver nanoparticle/amorphous carbon composite could be prepared by a heat treatment of the bio-silver powder at high temperature under the atmosphere of air and nitrogen, respectively, which may potentially have broad applications in future.

Key Words: Microorganism Bioreduction; Nanosilver Powder; Application.

主要符号一览表

abs	吸光度
abs_f	生物还原反应稳定后的吸光度
B	XRD 样品衍射峰半高峰宽，rad
B_e	XRD 样品显微畸变引起的衍射峰宽化，rad
B_{hkl}	XRD 样品亚晶块细化引起的衍射峰宽化，rad
B_{obs}	实验获得的 XRD 衍射峰半高峰宽，°(2θ)
B_{std}	XRD 仪器引起的衍射峰宽化，°(2θ)
B_{struct}	B_{obs}-B_{std}，°(2θ)
C_{Ag}	单质银浓度，$g\cdot L^{-1}$
C_b	菌体浓度，$g\cdot L^{-1}$
C_e	电解质浓度，$mol\cdot L^{-1}$
C_f	生物还原后产物聚沉后残余的银浓度，$g\cdot L^{-1}$
C_f'	AAS 直接测得的银浓度，$mg\cdot L^{-1}$
C_i	生物还原体系中起始银浓度，$g\cdot L^{-1}$
D	XRD 样品通过谢乐公式计算得到的平均晶粒大小，nm
d	晶粒的晶面间距，Å
D_{hkl}	XRD 样品垂直于(hkl)晶面方向上的平均晶粒大小, nm
E	生物还原中银的还原率
e	(=δd / d)XRD 样品垂直于(hkl)晶面方向上的平均晶粒畸变大小
K	反应的平衡常数，或 XRD 谢乐公式中的颗粒形状因子，球形时为 0.89
$K_{\alpha1}$	XRD 衍射仪发出的 Cu $K_{\alpha1}$ 衍射线
$K_{\alpha2}$	XRD 衍射仪发出的 Cu $K_{\alpha2}$ 衍射线
m	测量银粉质量分数时银粉的取样量，mg
N	AAS 分析银浓度时样品的稀释倍数
n	HRTEM 照片中颗粒粒径统计时被统计的颗粒数目
R	相关系数
Ra	生物还原体系中菌体浓度与初始银浓度之比（质量浓度比）
t_f	生物还原反应时吸光度达到稳定时所用的反应时间，h
V_1	AAS 分析 C_f 时产物首次离心后银溶胶上清液的取样量，ml
V_2	AAS 分析 C_f 时聚沉采用的 $MgSO_4$ 或 H_2SO_4 的量，ml

希腊字母

δ	FTIR 中的变形振动
θ	XRD 衍射峰布拉格(Bragg)角，°
λ	XRD 中 X 射线波长，=0.1542 nm
λ_{max}	UV-Vis 谱中单质银表面等离子体共振吸收最大吸收峰位，nm
ν	FTIR 中的伸缩振动
ω	银粉的质量分数

下标

as	非对称
ads	吸附
m	构成晶粒的原子数目
max	最大值
n	构成晶粒的原子数目
s	对称

目 录

CONTENTS