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金属纳米粒子 的尺寸和形状可控合成及其表征

Synthesis and Characterization of Metal Nanoparticles with Controllable Size and Shape

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谨以此文献给我亲 爱的母亲、兄弟姐妹及我 的爱青!



目 录

摘要	
I	······································
Abstract	
»»»»»	······
第一章 绪论	
××××××××××××××××××××××××××××××××××××××	·····
××1	
§1.1纳米材料的基本概念	
*************************************	1
1.1.2 纳米结构单元	2
§ 1.2纳米材料的特性	
»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»»	
××××××××××××××××××××××××××××××××××××××	5
1.3.1 物理性能	5
1.3.2 化学性能	9
§1.4 纳米结构和纳米材料的应用	

×××××××××××10	
1.4.1 纳米材料的应用10	
1.4.2 纳米结构的应用12	
§1.5 纳米材料的制备	
×××××××××15	•
1.5.1 制备尺寸可控的球形纳米粒子的方法	
1.5.2制备长径比可控的一维纳米粒子的方法19	
1.5.3制备新颖的、尺寸和形状可控的纳米粒子的方法	3
§1.6 纳米材料的表征	
××××××××××25	
1.6.1 TEM、HRTEM和SEM表征26	
1.6.2 AFM和STM表征27	
1.6.3 UV-visible 吸收光谱表征27	
1.6.4 SERS 表征28	
1.6.5 XRD、HRTEM、EDAX和SAED晶体结构表征2	8
§ 1.7 本论文的目的和设想	
29	
参考文献	
31	
第二章 实验	
*************************************	~
20	~
39	
§ 2.1 试剂39	
§ 2.2 仪器39	
§ 2.3 溶胶纳米粒子的制备 ····································	

§2.4 溶胶纳米粒子的分离及其表征	54
§ 2.5 溶胶纳米粒子性质的表征 ····································	·····56
第三章 银纳米粒子的尺寸和形状可控合成及其表	
另一早 银物不位了的人的相似似的迂口从及兵心	(TILL)
××××××××58	
§ 3.1 前 言 ··································	···58
§ 3.2 结果及其讨论	
60	
3.2.1 透射电子显微镜和扫描电子显微镜表征	60
	66
	······68
3.2.4 银纳米棒或纳米线的晶体结构表征	
3.2.5 银纳米棒或纳米线的晶体生长机理	74
§ 3.3 结 论	
× × × × × × × × × × × × × × × × × × ×	78
参考文献	
xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx	·····79
第四章 金纳米粒子的尺寸和形状可控合成及其表	紅
	K III
***************************************	***************************************
××××××××82	
	82
§ 4.2 结果与讨论	J -

4.2.1 透射电子显微镜表征	·····83

4.2.2 原子力显微镜表征	90
4.2.3 紫外可见吸收表征	92
4.2.4 表面增强拉曼光谱表征	97
4.2.5 金蝌蚪纳米粒子电学性质表征	99
4.2.6 金纳米粒子的晶体结构表征	103
4.2.7 金纳米粒子的晶体生长机理	107
4.2.8 银纳米粒子和金纳米粒子的晶体生长机理的比较	交和探讨
109	~
§ 4.3 结 论	
××××××××××××××××××××××××××××××××××××××	11
参考文献	
×*************************************	2
第五章 金和铂包金纳米粒子的尺寸可控合成及其	表征
xxxxxxxx115	
§ 5.1 前 言 ·······	115
§ 5.2 结果与讨论	
××××××××××××117	
5.2.1 透射电子显微镜和原子力显微镜表征	117
5.2.2 紫外可见吸收表征	125
5.2.3 表面增强拉曼光谱表征	127
5.2.4 球形金和铂包金纳米粒子的晶体结构表征	130
5.2.5 球形金纳米粒子的晶体生长机理的探讨	133
§ 5.3 结 论	
xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx	34
参考文献	

××××××××××××××××××××××××××××××××××××××
第六章 尺寸和形状可控的金属纳米粒子的SERS研究
xxxxxxxx140
§ 6.1 前 言 ······140
§ 6.2 结果与讨论

6.2.1 不同形状的银纳米粒子的SERS研究142
6.2.2 不同形状的金纳米粒子的SERS研究145
6.2.3不同尺寸的球形和蝌蚪形金纳米粒子的SERS研究 ······151
6.2.4不同尺寸的铂包金纳米粒子的SERS研究154
§ 6.3 结 论
参考文献
××××××××××××××××××××××××××××××××××××××
-7/1/
作者攻读博士学位期间发表与交流论文
xxxxxxxxxxxxxxxx160
자는 Yel
致谢

××××××163

Table of Contents

Abstract in Chinese
I
Abstract in English
xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxXII
I Introduction
xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
∞1

 $\S 1.1$ Basic concenption of nanomaterials

······································
1. 1. 1 Basic concenption of nanomaterials1
1. 1. 2 Structure units of nanoparticles2
§ 1. 2 Characteristics of nanomaterials
»»»»3
§ 1.3 Properties of nanomaterials
××××××××××××××××××××××××××××××××××××××
1. 3. 1 Physical characteristic of nanomaterials5
1. 3. 2 Chemical characteristic of nanomaterials9
§ 1.4 Applications of nanostructures and nanomaterials
10
1. 4. 1 Applications of nanostructures10
1. 4. 2 Applications of nanomaterials12
§ 1.5 Synthesis of nanomaterials
××××××××××15
1. 5. 1 Synthetic methods of spherical nanoparticles with controllable size16
1. 5. 2 Synthetic methods of one-dimensional nanoparticles with controllable
aspect ratio19
1. 5. 3 Synthetic methods of novel nanoparticles with controllable size and shape
23
§ 1.6 Characterization of nanomaterials
<u>~~~~25</u>
1. 6. 1 TEM, HRTEM, and SEM characterizations26
1. 6. 2 AFM and STM characterizations27
1. 6. 2 AFM and STM characterizations ————————————————————————————————————

1. 6. 4 XRD, HRTEM, EDAX, and SAED crystal structure characterization -28
§ 1.7 Objectives and conceivability of this dissertation
29
References
II Experimental
§ 2.1 Reagents
§ 2. 2 Instruments
§ 2. 3 Synthesis of colloidal nanoparticles
§ 2.4 Separation and characterization of colloidal nanoparticles54
§ 2. 5 Property characterization of colloidal nanoparticles ************************************
III Size and shape-controlled synthesis and characterization of
silver nanoparticles
§ 3.1 Introduction
§ 3. 2 Results and discussions
×····································

	3. 2. 1 TEM and SEM characterizations60
	3. 2. 2 UV-visible absorption characterization66
	3. 2. 3 SERS characterization ———68
	3. 2. 4 Crystal structure characterization of silver nanorods or nanowires71
	3. 2. 5 Crystal growth mechanism of silver nanorods or nanowires74
	§ 3.3 Conclusions
>	······································
	References
	······79
IV	Size and shape-controlled synthesis and characterization of
	gold nanoparticles

	82
	§ 4.1 Introduction
****	***************************************
	§ 4. 2 Results and discussions
>	***************************************
	4. 2. 1 TEM characterization ——83
	4. 2. 2 AFM characterization90
1	4. 2. 3 UV-visible absorption characterization92
	4. 2. 4 SERS characterization97
	4. 2. 5 Electrics property characterization of gold tadpoles99
	4. 2. 6 Crystal structure characterization of gold nanoparticles103
	4. 2. 7 Crystal growth mechanism of gold nanoparticles107
	4. 2. 8 Comparison and discussion of crystal growth mechanism between silver

and gold nanoparticles109
§ 4.3 Conclusions
×××××××111
References

V Size-controlled synthesis and characterization of spherical Au
and Au _{core} Pt _{shell} nanoparticles
×××××××××××××××××××××××××××××××××115
§ 5.1 Introduction
× 3. 1 Introduction
§ 5. 2 Results and discussions
× 3. 2 Results and discussions
5. 2. 1 TEM and AFM characterizations117
5. 2. 2 UV-visible absorption characterization125
5. 2. 3 SERS characterization127
5. 2. 4 Crystal structure characterization of spherical Au and Au _{core} Pt _{shell}
nanoparticles
5. 2. 5 Crystal growth mechanism discussion of spherical gold nanoparticles
§ 5. 3 Conclusions
×*************************************
References

VI SERS studies of Size and shape-controlled metal

nanoparticles

×××××××××140
§ 6.1 Introduction
······140
§ 6. 2 Results and discussions
»142
6. 2. 1 SERS studies of different shape silver nanoparticles142
6. 2. 2 SERS studies of different shape gold nanoparticles145
6. 2. 3 SERS studies of spherical and tadpole-shaped gold nanoparticles with
size-controlled151
6. 2. 4 SERS studies of Au _{core} Pt _{shell} nanoparticles with size-controlled ······154
§ 6.3 Conclusions
»156
References
157
Publications list during Ph. D.
Study \$\text{Study}\$ 11. \text{D.}
Acknowledgements
>>>>>>>>>163

摘要

金属纳米粒子的特殊性质和潜在应用与它的尺寸和形状密切相关, 迄今人们已发展了许多金属纳米粒子的制备方法,但绝大多数方法的产物皆是球形纳米粒子,如何建立可对目标材料进行人为的尺寸和形状调控的简易方法是一个极具挑战的课题。

本论文工作的目标是设计一种简单有效的水相合成方法,制备出尺寸和形状可控的金和银纳米粒子。在作为包裹剂的十二烷基磺酸钠(SDSN)存在下,用柠檬酸钠(Na₃C₆H₅O₇)分别还原硝酸银(AgNO₃)或氯金酸(HAuCl₄)。它最鲜明的特点在于不需要任何模板和种子诱导,仅通过控制还原剂的浓度就可以实现对纳米粒子的尺寸和形状控制,而包裹剂的主要作用是防止粒子聚集和得到更好晶型结构。使用TEM、HRTEM、SEM、AFM、XRD、SAED、ED、UV-Visible和SERS等手段较系统地表征了这些纳米粒子的结构、尺寸、形状及其光学和电学性质。本论文工作获得的主要成果如下:

- 1. 制备了尺寸和长径比可控的银纳米棒和纳米线。还原剂的浓度与纳米棒或纳米线的直径(10-24 nm)成线性关系,与纳米棒和纳米线的长径比(8-150)成对数关系。
 - 2. 合成出具有蝌蚪和项链形的新颖形状的金纳米粒子。蝌蚪纳米粒子

具有新颖的三维结构 蝌蚪纳米粒子的尺寸可控范围为12-31 nm(头部宽度), 项链形纳米粒子的尺寸可控范围在20-35 nm。它们皆具有特殊的光学和电学性质。

- 3.提出有关纳米粒子的生长模型,分别解释金和银两种金属由还原剂浓度控制粒子生长的生长机理。而两种金属纳米粒子的形状完全不同的主要原因则主要来源于其离子被还原能力的差异和与包裹剂作用能力的不同。
- 4. 合成出尺寸较均一且可控的球形金纳米粒子(10-40 nm)。另用种子法合成出单分散性好且尺寸可控的铂包金纳米粒子(8-150 nm),并得到了铂纳米粒子的SERS谱图。

总之,该创新的合成方法可望用于上述纳米粒子的批量生产,并可能发展成为合成其它金属的尺寸和形状可控纳米粒子的通用方法。

关键词:纳米粒子;水相合成;形状可控

Abstract

The unique properties and potential applications of metal nanoparticles are mainly determined by the size and shape. So far there have been many methods to prepare metal nanostructures, but spherical nanoparticles are usually the major products. It is therefore a great challenge to develop some simple and effect methods of synthesizing nanoparticles whose size and shape can be controlled at will.

The main goal of the present work is to develop a simple and effective aqueous-phase method to synthesize gold and silver nanparticles with controllable size and shape. The synthesis was realized by the reduction of AgNO₃ or HAuCl₄ with Na₃C₆H₅O₇ respectively in the presence of SDSN as a capping agent. This non-template and non-seed method has its unique advantage that control the particle's shape and size by changing the reductant concentration. The role played by the capping agent is to assist the growth of good crystalline of nanoparticles. Their structure, size, shape, and optical and electronic properties were characterized systemically using TEM, HRTEM, SEM, AFM, XRD, SAED, ED, UV-Visible, and SERS. The major results of the thesis are outlined as follows:

1. Silver nanoparticles with controllable diameter and aspect ratio were

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