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硕 士 学 位 论 文

硫醇保护的金/银纳米团簇的合成与表征

Synthesis and Characterization of Thiol-protected Gold/Silver Clusters

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摘　要

金属纳米团簇的尺寸介于小分子（例如，有机金属化合物）与纳米颗粒（大于2nm）之间，因此，对其进行可控合成和结构与性能的研究可为纳米功能材料的开发提供分子水平上的指导，亦可成为连接小分子与纳米颗粒研究的桥梁。贵金属纳米团簇因其在催化、电化学、光学、传感、生物医学等领域具有良好应用前景而受到广泛关注，尤其是具有优良催化性能的金（Au）纳米团簇和具有独特发光性质和良好生物应用前景的银（Ag）纳米团簇均备受研究者的青睐。本文在前人研究的基础上展开工作，选取了硫醇保护的币金属（金、银、铜等）纳米团簇体系进行研究，对产物的晶体结构和相关性质进行了表征分析，拓展了贵金属纳米团簇的化学合成。本论文主要研究结果概括如下：

采用两相合成法，以AuPPh3Cl/AuDppyCl（Dppy=二苯基-2-吡啶基膦）代替HAuCl4做为Au源，以醋酸铜为铜（Cu）源，选用双齿配体2-巯基吡啶（C5H4NSH），在NaBH4的还原作用下合成Au-Cu双金属纳米团簇，得到了化合物Au13Cu2(C5H4NS)6(PPh3)6（1）、Au13Cu8(C5H4NS)12●(CH2Cl2)4（2)和Au2Cu6(C4H9S)6(PPh3)2（3）。其中，化合物1和2的结构具有核壳结构特征，其结构中心均为一个由Au13组成的带心二十面体，而壳层分别有2个和8个Cu原子分布在中心二十面体三角面的面心位置，外围则由硫醇和PPh3保护。化合物3的结构是由一个Cu6形成的平面六边形和2个分布在六边形面的上下两侧的Au原子组成。

在上述Au-Cu团簇合成的基础上，采用相似的合成方法，同时引入膦和硫醇两种配体，成功合成出了四个Ag纳米团簇：Ag14(C6H3F2S)12(PPh3)8●(CH2Cl2)6（4)、Ag14(C8H4F3S)12(PPh3)8（5)、[Ag13S(C6H3F2S)12(PPh3)7]-（6)和Ag16(C6H3F2S)14Dppe4（7)（Dppe=双(二苯基膦)乙烷）。化合物4和5的结构均有如下特点：中心是一个Ag6八面体组装在由Ag8立方体和S12二十面体组成的笼状结构内。XPS表征分析发现化合物4、5和7中均含有零价Ag。此外，化合物4和5在365 nm紫外灯的照射下发黄色荧光。

关键词：金属纳米团簇；硫醇保护；晶体结构

Abstract

Metal cluster is a class of special species, whose size is between those of the small molecule (e.g., organometallic compounds) and nanoparticles (>2 nm). Studies on controllable synthesis of metal clusters, and their structures and properties provide guidance in developing functional nanomaterials on molecular level. Metal clusters can be also considered as a bridge between small molecules and nanoparticles. Noble metal clusters have attracted extensive interest for their wide-range applications in fields such as catalysis, electrochemistry, optics, sensing, biomedicine and so on. Especially, Au and Ag nanoclusters have gained much attention because of good catalytic properties, and promising biological applications with excellent luminescent properties, respectively.

Based on previous work, in this thesis, the thiol-protected coinage-metal (Au, Ag, Cu, etc.) cluster systems were chosen as our study subjects. Crystal structures and related properties of the products were fully characterized by single crystal X-ray diffraction, elemental analysis, infrared spectroscopy (IR), fluorescence spectroscopy (FS), mass spectrometry (MS), thermogravimetry (TG), etc. Further understanding would be achieved on the chemical synthesis and further applications of noble metal clusters. Main achievement in this thesis is as followed:

1. In two-phase synthesis of Au-Cu bimetallic clusters, instead of the traditional Au source HAuCl4, AuPPh3Cl and AuDppyCl (Dppy= Diphenyl-2-pyridylphosphine) were chosen as the Au precursors; while Cu(OAc)2 was applied as the copper source and NaBH4 was the reducing agent. Three clusters, Au13Cu2 (C5H4NS) 6(PPh3)6 (1), Au13Cu8 (C5H4NS) 12 (CH2Cl2)4 (2), Au2Cu6 (C4H9S) 6(PPh3)2 (3) were synthesized and their structures were successfully determined by single X-ray diffractometer. By analyzing the structures of 1 and 2, we found that their structures can be described as

Au13@Cun (n=2, 8) core-shell structures. The core is an Au13 icosahedron, and the Cu atoms are located above nearly the centers of the triangular faces of Au13 icosahedron forming a shell. The core-shell Au13@Cun (n=2, 8) is encapsulated by organic shell of PPh3 and S-Ph groups. Compound 3 is composed of a planar hexagon of Cu6, and two Au atoms located on each side of the planar hexagon separately.

2. Based on the successful synthesis of Au-Cu bimetallic clusters, we extended this method to prepare their silver analogues. Four silver clusters were obtained: Ag14(C6H3F2S)12(PPh3)8·(CH2Cl2)6 (4), Ag14(C8H4F3S)12(PPh3)8 (5), [Ag13S(C6H3F2S)12(PPh3)7]- (6), Ag16(C6H3F2S)14Dppe4 (7) (Dppe= 1,2-Bis(diphenylphosphino)ethane). Compound 4 and 5 both have the same structural characteristics: an Ag8 octahedral assembled in a cage which is composed of an Ag8 cube and a S12 icosahedron. There are Ag (0) in cluster 4, 5, and 7, which are determined by the X-ray photoelectron spectroscopy (XPS). Moreover, Compound 4 and 5 show yellow fluorescence under the 365 nm UV light which could be observed with naked eyes.

Keywords: metal nanometer clusters; thiol protected; crystal structure

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