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金银纳米粒子的合成、组装及其在表面增强拉曼光谱的应用

Au and Ag Nanoparticles: Synthesis, Assembling and Their SERS Applications

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Au and Ag Nanoparticles: Synthesis, Assembling and Their SERS Applications

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By

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Abstract

Broadly speaking, the term nanoparticle encompasses any and all types of particles (hybrid nanoparticles, core-shell nanoparticles, etc.) with a diameter on the nanoscales. Synthesis noble metal nanoparticles stand apart as the most popular group of probes. The Nobel metals have retained their premince s amongst researchers due to their stability, ease synthesis, and optical properties. Silver and gold are the most popular options, and they can provide a strong optical signal in the visible or near-IR range. During the recent work, three main challenging issues have been widely concerned for the synthesis of nanoparticles: (1) how to get nanoparticles monolayer at large area on the silicon substrate; (2) how to synthesis seed “AuNRs” with high yield; (3) how to generate silver shell on Au nanorods. To conquer this harsh issue, we have paid many efforts on this work and achieved important breakthrough and outstanding results.

In chapter-3, silver nanocubes (AgNCs) were successfully assembled on silicon substrate by a two-phase method. Prepared AgNCs were firstly mixed with milli-Q water, and then cyclohexane was mixed with the solution by means of sonication. Then ethanol was added, leading to the formation of monolayer films at the cyclohexane/water interface. Finally, the monolayer film was take out from the solution and deposited on the silicon substrate. The SEM and SERS results showed that the self-assembled monolayer on silicon substrate were uniform. Taking into consideration SEM, SERS results, we found that silver nanocube monolayer at cyclohexane/water interface prepared via liquid–liquid interface at large area is uniform. Electrostatic interactions with interfacial oppositely charged molecules of hydrophilic nanoparticles assembled on substrates. These nanoparticles can easily aggregate in the mixture solution of cyclohexane and water, and can form self-assembled monolayer.

In chapter-4, we have employed a symmetric silver overgrowth on the gold nanorods. For the convenience of comparison, the molar ratio of Au/Ag and quantity of seed AuNRs were same for the synthesizing of different sized core-shell nanoparticles. The absorption measurements and theoretical calculations confirm the formation core-shell nanoparticles. The thickness of shell on nanorods were tuned by varying amount of silver nitrate. LSPR of core-shell Au@Ag nanorods was tailored from visible to infrad region, which is a great evidence of uniformity and tuning of nanoparticles. Different sized core-shell nanoparticles show good stability of SERS activity by

using same concentration of MBA (10^{-3} M) probe molecule. Au@Ag nanoparticles with the sizes of 110,130,150nm were considered as optimal SERS substrates when excitation wavelength of laser was change from 532,638,785nm respectively. This is totally supported by the three-dimensional finite-difference time-domain (3D-FDTD) calculations. Besides, this kind of well controlled different sized Au@Ag core-shell nanoparticles can be easily reproduced for the purpose of SERS measurement.

Key words: Silver nanocube monolayer; synthesis techniques; Au nanorods; core-shell nanoparticles, Au@Ag cuboids

摘 要

广泛地说，所有直径在纳米级别的粒子（杂化纳米粒子，核壳纳米粒子等）都称之为纳米粒子。由于贵金属粒子稳定性好，易合成以及光学特性等优点，因此合成贵金属纳米粒子仍然是探针研究中最受欢迎的一部分。同时，银和金在可见光和近红外区域能够提供很强的光学信号，使得它们成为最受欢迎的贵金属粒子。在最近的工作中，合成纳米粒子的三个主要挑战分别是：(1) 如何在硅基底上获得大范围的单层纳米粒子；(2) 如何合成高产率的金纳米棒；(3) 如何在金纳米棒外包裹上银壳。为了克服上述难题，我们做出很多的努力，并且取得了重要突破和结果。

在第三章中，我们利用两相法成功地将银立方体单层组装在了硅基底上。首先往银立方体中加入超纯水混匀，然后加入环己烷进行超声分散；接着加入适量的乙醇，从而在环己烷/水界面形成单层膜。最后，从溶液中将单层膜取出并且沉积在硅基底上。SEM 和 SERS 的表征结果显示，在硅基底上自组装得到的单层膜是统一均匀的。并且，根据 SEM 和 SERS 的实验结果，我们发现：银立方体的单层膜在环己烷/水这个液-液界面中，大面积下都是均匀分散的，亲水纳米粒子的界面电荷相反的分子通过静电相互作用从而自组装在基底上。这些纳米粒子可以很容易地聚集在环己烷和水的混合溶液中，同时自组装形成单层膜。

在第四章中，我们系统地研究了在金纳米棒的外面生长上一层银壳的方法。为了便于比较，在合成不同尺寸的纳米粒子时，Au/Ag 的摩尔比和 Au 纳米棒种子的量是一样的。同时，吸收实验和理论计算结果都证实了该方法的可行性。在实验中，通过加入不同量的硝酸银来进行调控纳米棒的壳层厚度。并且，核壳 Au@Ag 纳米棒的 LSPR 从可见光到近红外区域都是可调的，证明了该纳米粒子的均匀性和可调性。同时，不同尺寸的核壳纳米粒子在使用相同浓度的 MBA (10^{-3} M)探针分子的 SERS 实验中表现出良好的 SERS 活性和稳定性。而且，尺寸为 110 nm，130 nm，和 150 nm 的 Au@Ag 纳米粒子基底分别在 532 nm，638 nm，和 785 nm 激光下显示出最好的 SERS 性能。另外，该结果和 3D-FDTD 的

理论计算相吻合。此外，这种控制不同尺寸大小的 Au@Ag 核壳纳米粒子可以很好地进行重复。

关键词： 银立方体单层膜；合成技术；金纳米棒；核-壳纳米粒子；Au@Ag 长方体

Chapter -1 Introduction

1.1 Gold Nanoparticles

1.1.1 Introduction to the nanoparticles

Nanoparticles are the particles having size 1 to 100 nm, from the field of nanotechnology, a particle can be defined as a small object that behave as complete unit with respect to its properties. The word nanoparticles came among us during the 1970s[1].This term began appears quit frequently in the pages of literature in 1990s. However, these kind of nano-sized particles has been utilized for almost 65 years in weather modifications[2] and also for millennia in the glass making[3]. The newly explosive growth in the nanosized particles has been added by improvements on many directions. Advances in the instrumentation and imaging have made it possible to study the nanosized particles in the contest of real time and bellow the diffraction limits. The improvement in the computers and processing speeds have create a situation where quit hard simulations in past was taking days and even months but now these kind of simulation can take minutes and hours. In this modern technology world, research is also at point where big spacing data can be controlled and stored quit easily, especially when we will compare it to the 20 years ago when nanoparticles research began to start.

Synthesis, characterization, and the applications of nanoparticles are considered as most important properties of nanoparticles and they have various applications are among much important part of the nanotechnology areas which are falling under the umbrella of nanotechnology. In recent years, research on the nanoparticles have been become the center of attraction of researchers in the different fields of the science, as they observe the transition from the microparticles to the nanoparticles would various changes in physical and chemical properties of materials.

There are many characteristics of nanoparticles, but here we want to mention some most important characteristics of NPs on the basis of nanoscale. First, the nano size of the particles, which leads to increase the surface to volume ratio and as result of the domain where quantum effects predominate, is entered. Second, characteristic of the nanoparticles is that, increasing the surface area to the volume ratio always leads to the dominance of surface atoms of the nanoparticles over those which are in its interior. It is quite interesting that, as the size of particles decreases, a greater proportion of the atoms can be found at the particles surface as compared to the inside of the particles. For example, If the size of particles is 20nm, it would have 5% of surface of its atom. But if the sizes of atom decrease to 2 nm, then there will be 50 – 60 % of the atom on the surface[4]. It is true that synthesizing of atom is somehow complex, but there are many methods that are available to produce different kind of nanoparticles.

Finally, it is impossible to generalize all the available synthesizing methods for nanoparticles. However, broadly these all methods essentially fall into the main two types. (1)Synthesizing by chemical reactions and (2) solid state process such as milling. By using these above methods, researchers synthesized pure nanoparticles but they also synthesized hybrid or coated nanoparticles

1.1.2 Gold nanoparticles literature review and background

Gold nanoparticles are well known as “colloidal gold”, which were used as a colorant to manufacture the ruby glass and ceramics in the 5th century in Egypt and China[5] . The most famous example of these colloidal is Lycurgus Cup, which was made in 4th to 5th century B.C. It appears green which viewed in the reflected light, but it appears red on transmitted light because of the presence of gold colloids. Nanoparticles of gold were also used a pigment of the ruby-colored stained glass in rose window of the Cathedral of Notre dame that was manufactured in the middle ages. Fine control over the wavelength was big issue, but over past few decades this problem has been solved. Many groups of researchers have reported the fine control over the wavelength at which nanoparticles interacts with the incident light. This is accomplished by the well-controlled dimensions of metallic nanostructures of the selected shapes [6-9].The optical resonance frequency of metal is a function of not only metal types but it is also a function of shape of particle especially in the nanoscale level. For example, colloidal dispersion of the gold nanoparticles with the diameter of approximately 30nm absorbs green light at the 530nm and appears deep red in color.