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博 士 学 位 论 文

纳米粒子生长机理研究及生物纳米复合材料的制备及应用研究

Investigation of Growth Mechanism of Nanocrystals and Fabrication and Application of Bionanocomposite Materials

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摘　要

当材料的尺寸减小到100 nm时，量子化学和经典物理理论不再适用，导致材料出现了一些重要的效应和新的性质。因此纳米科学在最近20年间一直是多学科交叉的前沿研究领域，无论是在应用还是基础研究方面都吸引了大量的关注和兴趣。尤其是不同的纳米材料组成纳米复合材料后巨大应用前景，纳米科学和生物科学的结合更是在今年成为研究的热点。本论文工作主要分为两部分，其一是生物纳米复合材料的制备及其在催化、生物传感器方面的应用；其二是特殊形貌和表面结构的贵金属纳米粒子与合金纳米粒子的合成，及运用透射电子显微镜原位研究纳米粒子的生长过程、并指导其形貌控制合成。主要内容和结果如下：

1、制备了氧化石墨烯/十六烷基三甲基溴化铵/室温离子液体纳米复合薄膜（FGS / CTAB / RTIL），并以其为载体组装肌红蛋白。由于FGS / CTAB / RTIL良好的生物兼容性，亲水性质及大的表面积，使得其保持了极好的蛋白生物活性，同时离子液体的存在加强了肌红蛋白与电极间的导电性。石墨烯表面的功能基团有利于蛋白的组装，加入室温离子液体后，更促进了蛋白与石墨烯，电极间的电子传输，以复合物膜制备的电极对双氧水具有极好的催化活性，作为双氧水传感器具有极低的检测限和较高的浓度检测范围。研究结果表面石墨烯是一种良好的第三代生物传感器蛋白的修饰载体，在新型生物传感器的应用中具有重要作用。

2、用氯金酸为前躯体，采用化学还原的方法在低温共融物中合成了金纳米珊瑚，并将细胞色素C组装到其表面。以组装细胞色素C的金纳米珊瑚所制备的电极具有极好的电化学响应，远超目前文献所报道，结果证明纳米珊瑚的笼状结构，对促进蛋白与金基底间的电子传输有极大的作用，并且能很好的长时间保持蛋白的活性，是理想的生物传感器蛋白载体。进一步地以铁蛋白为模板采用化学还原法合成了壳厚度可控铁蛋白@金纳米壳结构，具有可调的近红外吸收性质，将可应用到细胞成像和癌症的光热疗法中。以去铁铁蛋白为模板合成了金纳米团簇，具有近红外荧光发光性质，可应用到不需要无标记物的高灵敏度、高选择性的生物传感器中。

3、发展了一种以导电聚合物（PDDA）作为还原剂和稳定剂的简便绿色的方法制备出了水溶性的石墨烯。透射电镜、X-射线衍射和原子力显微镜证明所合成的石墨烯

是单层的，同时导电聚合物还有使纳米粒子单分散的作用，因此我们实现了在石墨烯上原位生长高分散的铂纳米粒子，形成石墨烯/铂纳米复合材料，该材料对甲酸氧化表现出极好的催化性能。同时通过还原法在石墨烯表面制备了单分散的钯，金钯合金粒子，相比与同样方法制备的粒子负载在碳黑载体上所得的纳米复合材料具有较好的甲酸氧化催化性能和更高的稳定性。研究表明石墨烯是一种非常有潜力的催化剂载体。

4、金和金@钯纳米晶体在低温共融物（DES）中的形貌控制合成。以低温共融物为溶剂采用抗坏血酸为还原剂通过控制合成的温度，低温共融物中水含量，还原剂浓度等条件，合成得到了具有高指数晶面和非常规形状的金纳米粒子和金铂核壳结构的纳米粒子，极大的丰富了形貌控制合成并且有益于深入研究表面结构与性能间的联系规律。

5、运用原位透射电镜实时观察了金纳米粒子在溶液中的生长过程，并研究其生长机理。原位透射电镜研究获得了非原位实验不可能获得的纳米粒子生长过程的重要信息，对深入理解纳米晶体的合成有重要的作用。包括以下几方面

a. 首次通过原位透射电镜观察了五重孪晶的形成过程和方式。五重孪晶星形金纳米粒子的生长过程中，在开始生长和中后期生长中，每一个孪晶块因为尺寸和表面结构的不同可以采用连续生长或层生长模式。同时对于整个孪晶粒子，可以由孪晶晶种逐渐生长也可一块一块孪晶块生长，或者是由粒子聚合直接重构成五重孪晶。

b. 纳米粒子生长过程中在溶液中的聚合。通过观察发现聚合时首先在两个粒子间生成一个连接的颈部，两个粒子以不同取向连接到一起，然后粒子通过结构重构和弛豫，或者重结晶来完成结构调整，最后生成一个单晶粒子，而不是通过同晶向的附着连接，直接聚合为单晶。对纳米粒子的结构和形貌演化的直接观察，极大的促进了对纳米粒子生长和结构控制的机理研究。

c. 首次原位观察到了纳米粒子的奥氏熟化过程。通过观察纳米粒子的在溶液中的奥氏熟化过程，发现小粒子的溶解速度是一个加速过程，尺寸越小，溶解越快，大粒子的生长则基本是匀速，且小粒子的溶解速度受到环境的影响会有所波动。这项研究将对催化剂合成的粒径控制和抗老化研究有重要的指导作用。

本论文发展了纳米粒子结构控制合成及纳米复合材料的合成方法，成功地制备出多

种高指数晶面的纳米晶体，并制备多种纳米复合材料，并将其应用到催化和生物传感器领域。并通过新颖原位TEM方法实时观察了纳米材料的生长过程，对纳米材料生长的许多重要问题提供了新的认识和解决的途径。本研究所发展的合成方法，为实现在原子或分子水平层次设计结构规整、高活性的催化剂和传感器打下了基础，具有重要的理论意义和应用价值。

关键词：石墨烯 ；肌红蛋白； 纳米晶体； 形状控制合成； 原位透射电镜；

Abstract

When the size of materials reduced to below 100 nm, both quantum chemistry and classical laws of physics are not suitable, which lead to novel and important properties, are unavailable in conventional materials and devices. Nowadays, the studies of nanomaterials have become an active foreland field of multidisciplinary and arisen scientists' swinging interests and extensive attentions on both fundamental research and applications. Furthermore, when different nanomaterials assembled to nanocomposite materials or when biomaterials incorporate on to nanomaterials have wide applications and attract huge interests. The synthesis and control of materials in nanometer dimensions can access new material properties and device characteristics in unprecedented ways. Thus, this thesis focuses primarily on two parts: 1) nanocomposite materials preparation and application in catalysis and biosensor. 2) Shape and surfaces structure control of nanomaterials, and use in-situ TEM to investigate the growth kinetics of noble metal nanoparticles.

The main results are as follows.

1. We have explored FGS/CTAB/RTIL nanocomposite film as a support matrix for immobilizing Mb. The prepared nanocomposite film can effectively retain the activity of entrapped Mb because of its biocompatibility, hydrophilic environment, and large specific surface area. Surface functional groups of the graphene also play an important role in bonding Mb. The electrochemical behaviors of the modified electrode suggest that graphene can provide a favorable microenvironment for MB, and RTIL can improve the direct electron transfer at the electrode surface. In addition, the MB/nanocomposite films perform good catalytic reactivity to H2O2. The Mb/graphene-based H2O2 sensor has a low detection limit and a satisfactory linear range. The present study suggests that graphene is an excellent transducing material for immobilizing proteins to fabricate third-

generation biosensors. It shows potential for immobilizing other biologically active materials on these kinds of nanosheets for constructing novel biosensors.

2. A novel gold nanocorals was synthesized by reducing HAuCl4 in deep eutectic solvent(DES); the unique cage structures of nanocorals greatly promote the electron transfer between cyt c and gold and could keep the activity of cyt c forlong time. The electrodes modified by the mixed nanocomposite materials were shown to have fine-tuned reproducible quasi-reversible electrochemistry of cyt c. The modified electrodes showed the high stability and reproducibility as well as an excellent electron transfer promotion characteristics for cyt c, providing high and reproducible current responses as evidenced by better defined CV shapes than any other reported to our knowledge. We have synthesized gold nanoshells and with adjustable thickness and NIR absorption properties by using ferritin as template, which may have wide application in cell image or caner thermal therapy. With this method to could also synthesize highly fluorescent gold clusters by using apoferritin as template, which can be used for highly sensitive and selective label free sensor.

3. We have developed a green and facile approach to prepare soluble graphene nanosheets. The key is the introduction of a positively charged polyelectrolyte, PDDA, which acts as both a reducing agent and a good stabilizer during the formation of graphene nanosheets. Another important role of PDDA is to facilitate the uniform deposition of metal nanoparticles on graphene nanosheets. Pt, Pd, PtAu alloy NPs on graphene were prepared with a uniform dispersion via a polyelectrolyte-assisted process. They exhibited highly electrocatalytic activity and stability for formic acid oxidation. The finding is of significance for the application of graphene because polyelectrolytes can faciliate the uniform disperson of metal NPs on graphene, which has been demonstrated as a promising anode electrocatalyst of direct formic acid fuel cells. Moreover, this facile preparation method can be readily extended to the synthesis of other noble

metal NPs. We therefore expect that our findings will lead to the further development in preparation of high-quality graphene nanosheets and graphene-based nanocomposite, which may significantly facilitate the application of graphene in fuel cells and other fields.

4. We achieved shape-control synthesis of gold NPs without using any surfactants and seeds but employing DES as solvent. Star-shape gold NPs that are bounded with high-index (331) were successfully synthesized for the first time. It has also illustrated that Au and Au/Pd NPs of various shape and surface structure can be obtained just by adjusting the content of water, reaction temperature, or precursor concentrations in the DES. The variety in shape offers opportunity to change the surface structure of nanoparticles and examine the structure-functionality in electrocatalysis. The work of minimizing Au NPs' size has been also conducted, and our preliminary results demonstrated that smaller star-shape gold NPs could be synthesized by adding Au seeds. The present method may be also applied to carry out shape-control synthesis of other metal NPs.

5. We have observed the dynamic growth of single colloidal gold nanocrystals in DES solution with an in situ TEM. This observation reveals much important information about colloidal nanocrystal growth and is very beneficial in developing a detailed understanding of growth mechanisms and the precise control of nanoparticle's growth with desired shape and properties. Moreover, this in situ TEM observation based on DES is a convenient and low-cost method which could have great potentials for addressing many fundamental issues in materials science, chemistry, and other fields of science.

a) We directly observed the growth of individual five-fold nanocrystal in a eutectic-based ionic liquid solution with in situ transmission electron microscopy (TEM). The observation depicts much important information regarding five-fold twinned nanocrystal growth. In single fivefold star-shaped nanocrystal, the five branches

can adopt different growth mechanisms at different growth stage, due to the size and structure difference. The coalescence-based growth is also an important mechanism for multi-twinned nanocrystal's formation in solution. This is of great significance for fully understanding the growth mechanism and controlling of the growth of colloidal nanocrystal.

b)The particle's coalescence in solution is not through an oriented attachment-based growth, but rather, generates necks first and then through a grain rotation and a recrystallization process to form a single crystal. During the growth and shape evolution process many dislocations and stacking faults were generated. This may be of great help for us to fully understand the colloidal nanocrystal shape and structure evolution mechanism.

c) The nanoparticle's Ostwald ripening was observed by in situ TEM for the first time, and the quantitive data get form the observation will help to understand many fundamental issues of colloidal chemistry and materials science.

In this thesis we developed a novel method to synthesize nanocrystal and nanocomposite materials. Break through the limit of conventional chemical method, NPs bounded with high-index facets were successfully synthesized; nanocomposite materials was prepared, and applied in catalysis and biosensor. We observed the real time growth process of nanocrystal in liquid by using in-situ TEM and get important information about nanocrystal growth that cannot get from ex-situ experiment. The method developed in this thesis will support the design of catalyst and biosensor at atom scale, and it is also an important progress from the fundamental research to application, which will have great influence in research and economy.

Keywords: Nanocomposite materials; Nanocrystals; Shape-controlled synthesis; Biosensor; In-situ TEM

参考资料

1 Ding, R. G., Lu, G. Q., Yan, Z. F. & Wilson, M. A. Recent advances in the preparation and utilization of carbon nanotubes for hydrogen storage. Journal of Nanoscience and Nanotechnology 1, 7-29, doi:10.1166/jnn.2001.012 (2001).
2 Pang, L. S. K. et al. Competitive reactions during plasma arcing of carbonaceous materials. Energy & Fuels 9, 38-44, doi:10.1021/ef00049a006 (1995).
3 Pang, L. S. K., Wilson, M. A., Pallasser, R. & Prochazka, L. Isotope effects in plasma arcing experiments with various carbon anodes. Energy & Fuels 9, 704-706, doi:10.1021/ef00052a019 (1995).
4 Wilson, M. A. et al. Fullerene production in alternative atmospheres. Carbon 31, 393-396, doi:10.1016/0008-6223(93)90045-c (1993).
5 Weigle, J. C. et al. Generation of aluminum nanoparticles using an atmospheric pressure plasma torch. Journal of Physical Chemistry B 108, 18601-18607, doi:10.1021/jp049410q (2004).
6 Fievet, F., Lagier, J. P., Blin, B., Beaudoin, B. & Figlarz, M. Homogeneous and heterogeneous nucleations in the polyol process for the preparation of micron and sub-micron size metal particles. Solid State Ionics 32-3, 198-205, doi:10.1016/0167-2738(89)90222-1 (1989).
7 Stephan, O. et al. Doping graphitic and carbon nanotube structures with boron and nitrogen. Science 266, 1683-1685, doi:10.1126/science.266.5191.1683 (1994).
8 Pang, G. S. et al. Preparation of La(1-x)SrxMnO(3) nanoparticles by sonication-assisted coprecipitation. Materials Research Bulletin 38, 11-16, doi:Pii s0025-5408(02)01002-410.1016/s0025-5408(02)01002-4 (2003).
9 Roucoux, A., Schulz, J. & Patin, H. Reduced transition metal colloids: A novel family of reusable catalysts? Chemical Reviews 102, 3757-3778, doi:10.1021/cr010350j (2002).
10 Gui, Z. et al. Synthesis and characterization of reduced transition metal oxides and nanophase metals with hydrazine in aqueous solution. Materials Research Bulletin 38, 169-176, doi:Pii s0025-5408(02)00983-210.1016/s0025-5408(02)00983-2 (2003).