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硕 士 学 位 论 文

两亲性核-壳结构功能性聚合物微球的制备 及其作为贵金属催化载体的应用

Synthesis of Amphiphilic Functional Core-shell Structures
Polymeric Particles and Application as Catalyst Scaffold of
Noble Metal Nanoparticles

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摘要

采用亲水单体与疏水单体直接共聚的方法可以在没有添加任何稳定剂的条件下一步合成两亲性核-壳结构功能性聚合物微球，并且两亲性核-壳结构功能性聚合物微球在作为贵金属纳米粒子载体方面具有显著优势。要使金属纳米粒子固定在微球的壳层并保持复合微球的稳定性，一般要求两亲性核-壳结构聚合物微球的壳层带有可以与金属离子产生静电作用或者具有孤对电子可以与金属离子产生络合作用的功能基团。亲水性单体甲基丙烯酸二甲氨基乙酯 (DMAEMA) 可以在酸性条件下被质子化成带正电的季铵盐与 AuCl_4^- 通过静电作用结合在一起，并且 DMAEMA 上的氮原子带有孤对电子可以与 Ag^+ 络合，因此，本论文采用亲水单体 DMAEMA 与疏水单体 tBA 通过无皂乳液聚合一步合成了壳层同时具备以上两种性能的 P(tBA-co-DMAEMA) 微球，并将该微球作为 Au 纳米粒子与 Ag 纳米粒子的载体制备复合微球。采用扫描电镜 (SEM)、透射电镜 (TEM)、动态光散射 (DLS) 以及紫外-可见分光光谱仪 (UV-Vis) 等对 P(tBA-co-DMAEMA) 微球及复合微球进行表征，取得了以下几方面的成果：

1、本文首次以亲水单体甲基丙烯酸二甲氨基乙酯 (DMAEMA) 与疏水单体丙烯酸叔丁酯 (tBA) 为共聚单体，利用无皂乳液聚合一步法合成了单分散的 P(tBA-co-DMAEMA) 核-壳结构微球。改变 DMAEMA/tBA 投料比或乙醇与去离子水体积比可以制备得到具有不同表面形貌的单分散 P(tBA-co-DMAEMA) 核-壳结构微球。本文还推测了微球的形成机理。

2、采用表面规整的两亲性 P(tBA-co-DMAEMA) 核-壳结构聚合物微球制备 P(tBA-co-DMAEMA)/Au 复合微球。在酸性条件下二甲氨基被质子化形成带正电的季铵盐， AuCl_4^- 作为抗衡离子被吸附到微球壳层上，在还原剂 NaBH_4 作用下，生成的 Au 纳米粒子固定在微球壳层上。实验发现：1 wt% 微球溶液，使微球壳层完全质子化的 HAuCl_4 摩尔浓度在 0.2~0.3 mmol/L 之间，在该摩尔浓度范围内微球壳层完全质子化的时间需要 3 h 以上，过量的 HAuCl_4 及还原剂 NaBH_4 加入速度太快都会导致形成粒径较大，且呈多分散性的 Au 纳米粒子；微球壳层二甲

氨基的弱还原性不会对本实验 Au 纳米粒子形貌及粒径产生影响；P(tBA-co-DMAEMA)/Au 复合微球对亲水的和疏水的物质都具有良好的催化还原作用。

3、我们采用表面规整的两亲性 P(tBA-co-DMAEMA)核-壳结构聚合物微球制备 P(tBA-co-DMAEMA)/Ag 复合微球。微球壳层二甲胺基上的氮原子可以与 Ag^+ 通过络合作用结合在一起，在还原剂 NaBH_4 的作用下，生成的 Ag 纳米粒子固定在 P(tBA-co-DMAEMA)微球壳层上。实验发现：1 wt% 微球溶液， AgNO_3 浸泡时间长一些（24 h）有利于形成粒径较小及相对较均一的 Ag 纳米粒子；随着 AgNO_3 摩尔浓度的增大，形成的 Ag 纳米粒子数目逐渐增多、粒径及粒径分散性也逐渐增大，并且 Ag 纳米粒子并不完全负载在微球壳层，我们对可能原因作出了讨论。P(tBA-co-DMAEMA)/Ag 复合微球对亲水的和疏水的物质都具有良好的催化还原作用。

关键词：两亲性；核-壳结构；功能性聚合物微球；甲基丙烯酸二甲氨基乙酯（DMAEMA）；丙烯酸叔丁酯（tBA）；Au 纳米粒子；Ag 纳米粒子；催化性能

Abstract

Amphiphilic functional polymeric particles with core-shell structures can be synthesized directly by copolymerization of hydrophilic monomers and hydrophobic monomers without addition of any stabilizers. They have significant advantages as the carriers of noble metal nanoparticles. In order to immobilize and stabilize metal nanoparticles on the surface of the core-shell particles, the surface functional groups of the particles should meet the following requirements: they can immobilize metal ions onto the particle shell via electrostatic interactions or complexation. Since the hydrophilic monomer dimethyl amino ethyl methacrylate (DMAEMA) meets the requirements, narrowly dispersed amphiphilic P(tBA-co-DMAEMA) core-shell polymeric nanoparticles were synthesized via one-stage soap-free emulsion polymerization of hydrophilic monomer DMAEMA and hydrophobic monomer tBA. The resultant P(tBA-co-DMAEMA) core-shell particles were used as scaffold to prepare shell-embedded Au nanoparticles (Au NPs) and Ag nanoparticles (Ag NPs). The P(tBA-co-DMAEMA) particles and composite particles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS) and UV-Visible Spectrophotometer (UV/Vis) etc. The main results have been obtained as follows.

1. Monodispersed amphiphilic P(tBA-co-DMAEMA) core-shell polymeric particles were synthesized first time via one-stage soap-free emulsion polymerization of hydrophilic monomer DMAEMA and hydrophobic monomer tBA. P(tBA-co-DMAEMA) particles with different surface morphology were synthesized by changing the feed ratio of the monomer or the volume ratio of ethanol to distilled water. The formation mechanism of the P(tBA-co-DMAEMA) particles were also studied.

2. P(tBA-co-DMAEMA) core-shell particles were used as scaffold to prepare

P(tBA-co-DMAEMA)/Au composite particles. Because the dimethylamino groups on the shell layer of the P(tBA-co-DMAEMA) core-shell particles would be protonated to form positively charged quaternary ammonium salt under acidic conditions, AuCl_4^- ions would be absorbed within the shell as the counter-ions at the same time. Reduction of these immobilized AuCl_4^- ions with NaBH_4 led to well-defined AuNPs. Experiments demonstrated that the dimethylamino groups would be protonated completely with 0.2~0.3 mmol/L HAuCl_4 with the time consuming more than 3 h for 1 wt% P(tBA-co-DMAEMA) particles solution. An excess of AuCl_4^- ions and much quicker reduction rate may lead to the formation of large and more polydisperse AuNPs. Additional experiments demonstrated that the weak reduction of dimethylamino groups would not have bad effect on the Au NPs. P(tBA-co-DMAEMA)/Au composite particles also exhibited high catalytic activity for both hydrophilic and hydrophobic reactants.

3. P(tBA-co-DMAEMA) core-shell particles were used as scaffold to prepare P(tBA-co-DMAEMA)/Ag composite particles. Ag^+ ions would locate within the shell by a complexation of Ag^+ ions and the nitrogen atoms of PDMAEMA. Reduction of these immobilized Ag^+ ions with NaBH_4 led to the formation of P(tBA-co-DMAEMA)/Ag composite particles. Experiments demonstrated that more soak time of AgNO_3 resulted in much smaller size of AgNPs. An excess of Ag^+ ions would lead to the formation of large and more polydisperse Ag NPs. P(tBA-co-DMAEMA)/Ag composite particles also exhibited high catalytic activity for both hydrophilic and hydrophobic reactants.

Keywords: Amphiphilic; core-shell; functional polymeric particles; DMAEMA; tBA ; Au NPs; Ag NPs; catalytic property

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