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还原型氧化石墨烯负载铂、钯纳米材料的清洁合成及其电分析应用

Nanocomposites of Pt, Pd supported on reduced graphene oxide: its clean synthesis and applications in electroanalysis

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摘要

石墨烯是继碳纳米管被发现后碳家族中又一纳米级功能性材料。目前，石墨烯最理想的二维纳米材料之一。石墨烯具有优异的力学性能、导电性能、高的比表面积等性能。还原型氧化石墨烯（RGO）为石墨烯的重要衍生物，由于表面缺陷，其理化性能较石墨烯有所欠缺，但表面上富含的含氧官能团使 RGO 具有亲水性及易衍生化等特点，使之成为一种负载贵金属纳米的理想二维材料。Pt、Pd 等贵金属纳米材料具有优异的光、电、磁和催化性能，在工业、科研界扮演者极其重要的作用。本论文工作通过调控 RGO 的合成，探究简易、清洁的合成方法，将 Pt、Pd 纳米材料负载于 RGO 片层，考察合成的纳米复合材料的性能并研究其在电分析领域的应用。

本论文共分为五章，研究内容主要包括：

第一章，文献综述，主要介绍了石墨烯、GO、贵金属纳米材料的基本概念；GO 的合成与还原方法、RGO 贵金属复合纳米材料的合成与应用并介绍了化学修饰电极的概念及其制备方法。

第二章，结合实验室前期工作，采用自氧化还原方法合成了高分散性、高表面洁净度的 PdNPs/GO 复合材料。利用所合成的具有优异电催化性能的 PdNPs/GO 复合材料，构建一种新型的抗坏血酸（AA）电化学传感器。循环伏安（CV）结果证实了 PdNPs/GO 对 AA 有显著的电催化活性，时间电流（i-t）结果表明，PdNPs/GO 对 AA 有较高的响应灵敏度、选择性和良好的稳定响应，有望发展成为一种应用于实际样品中 AA 浓度测定的新型电化学传感器。

第三章，结合实验室前期工作，以乙醇为还原剂合成了铂纳米花载 GO（PtNFs/GO）复合材料，构建一种新型的非酶葡萄糖电化学传感器。CV 结果证实了 PtNFs/GO 对葡萄糖有优异的电催化性能。在 0.1 M Cl⁻存在下，PtNFs/GO 依然保存着较高的催化活性。I-t 曲线说明了所合成的复合材料对不同浓度的葡萄糖传感灵敏度高、响应时间短（5 s）、线性范围宽（2 μM ~ 20.3 mM）且响应稳定。所构筑的葡萄糖传感器选择性好，主要干扰物尿酸和抗坏血酸的响应信号小。通过实际样品的测定，验证了 PtNFs/GO 有望发展成为一种新型的非酶葡萄

糖电化学传感器。

第四章，发展了一种在 KOH 介质中合成 RGO 的简易方法，首次发现利用 RGO 的还原性，无需添加乙醇，RGO 与 PtCl_4^{2-} 之间就能够发生自发氧化还原反应，通过一锅法合成 PtNPs/RGO 复合材料。实验结果证实所获得的 RGO 具有比 GO 更强的还原能力。通过 TEM、XPS 等手段进行复合材料的形貌表征。结果表明，合成的 PtNPs 高密度、均匀地分布在 RGO 片层上，粒径在 3 nm 左右。通过改变合成介质的 pH，探究了反应机理，并进行了对不同条件下合成的 PtNPs/RGO 的电催化性能的调控。所合成的 PtNPs/RGO 复合材料具有比商品化 Pt/C 更为优异的电催化氧化甲醇性能，催化氧化电流密度约是商品化 Pt/C 的 2.2 倍，且 i-t 实验证实了所制备的催化剂具有较好的持久催化特性。

第五章，首次提出利用 $\text{Pt}_3\text{PdNPs/RGO}$ 修饰玻碳电极 (GCE) 作为工作电极，使用阳极溶出伏安法 (ASV) 进行葡萄糖的检测。研究工作在第四章的基础上，利用一锅法获得表面清洁的 $\text{Pt}_3\text{PdNPs/RGO}$ 复合材料，该合成无需加入额外的还原剂与表面活性剂。实验通过 TEM、XPS 等手段对复合材料进行形貌表征。结果表明，合成的复合纳米粒子高密度、均匀分布在 RGO 片层上，粒径在 7 nm 左右。EDX 数据进一步证实了 Pt_3PdNPs 在 RGO 上的负载。通过 CV 实验考察了 $\text{Pt}_3\text{PdNPs/RGO}$ 对葡萄糖的电催化能力，同时根据相关出峰电位选定“电析”电压与溶出电压范围，使用 ASV 方法进行葡萄糖浓度的测定。实验还考察了 Cl^- 的影响，并将 ASV 方法的实验结果与 CV、LSV、i-t 等方法的实验结果进行比较。结果表明，ASV 方法的最低可检测浓度较一般电化学方法更低，达到 nM 级别。

关键词：氧化石墨烯；纳米贵金属；电催化；非酶传感；燃料电池

Abstract

Graphene, consisting of a 2-D atomic layer of sp^2 hybridized carbon arranged in a hexagonal network, is the strongest material ever measured, chemically stable and inert, and conducts electricity better than any other known material at room temperature. One specific branch of graphene, graphene oxide (GO), can be considered as a precursor for graphene synthesis by either chemical or thermal reduction processes. GO is highly hydrophilic and water soluble due to its abundant oxygen-containing functional groups. This is concomitant with some loss in electrical conductivity. In addition, the characteristic makes GO easy for been modified and ideal 2D supporter for nano noble metal such as Pt and Pd. In this dissertation, by tuning the reduction of GO and utilized the reducibility of RGO, we developed a clean and facile method to synthesis nanocomposites of Pt, Pd supported on RGO. The electrocatalysis activity of PdNPs/GO, PtNFs/GO, PtNPs/RGO and Pt₃PdNPs/RGO were investigated. Furthermore, novel electrochemical nonenzymatic glucose sensors were fabricated using PtNFs/GO and Pt₃PdNPs/RGO; an electrochemical ascorbic acid (AA) sensor was fabricated using PdNPs/GO.

This dissertation includes five chapters.

In chapter I, the concept of graphene, GO and noble metal nanoparticles (NMNPs) were introduced. The development of preparation and application of GO, NMNPs and their nanocomposites were summarized. The concept of chemical modified electrode and its preparation were also introduced.

In chapter II, based on our previous research, PdNPs/GO was prepared by the redox reaction between $PdCl_4^{2-}$ and GO. A PdNPs/GO modified glassy carbon electrode (GCE) was developed and applied in the detection of AA. Cyclic voltammetric (CV) results showed that the PdNPs/GO modified GCE presented obvious electrocatalytic activity towards AA, and the amperometric *i-t* curves indicated that the modified electrode was highly sensitive and presented stable sensing

characteristics for AA. These results indicated that the proposed sensor was promising for the development of novel electrochemical sensing for AA determination.

In chapter III, a non-enzymatic electrochemical method was developed for glucose detection using a glassy carbon electrode modified with platinum nanoflowers supported on GO (PtNFs/GO). CV and i-t were used to evaluate the electrocatalytic activity of PtNFs/GO towards glucose in neutral media. The modified electrode exhibited strong and sensitive amperometric responses to glucose even in the presence of 0.1 M Cl⁻. The response time was within 5 s with a linear range from 2 μM to 20.3 mM. The interference effects from ascorbic acid and uric acid were comparatively small when operated at suitable potential. The modified electrode was also applied to the determination of glucose in glucose injection samples, and the results indicated that PtNFs/GO was promising for the development of a novel non-enzymatic electrochemical glucose sensor.

In chapter IV, facile hydrothermal method has been proposed to prepare reduced graphene oxide (RGO) and enhanced its reducibility. For the first time, the spontaneous redox reaction between PtCl₄²⁻ and RGO has been reported. No additional reductant and surfactant were needed. TEM and XPS were employed to characterize PtNPs/RGO. PtNPs with a diameter of 3 nm were well dispersed on RGO sheets. Inspired by the clean, uniform and well dispersed PtNPs, the PtNPs/RGO showed excellent electro-catalytic activity and tolerance for methanol oxidization. Moreover, the mechanism was investigated and electro-catalytic was tuned by adjust the medium pH. The peak current density value (J_f) in a forward (positive) scan for PtNPs/RGO (1.89 mA cm⁻²) were about 2.2 folds higher than that of commercial Pt/C (0.88 mA cm⁻²), which demonstrated the excellent electrochemical catalytic activity of the PtNPs/RGO toward methanol electro-oxidation. I-t experiment also revealed that the PtNPs/RGO is of durable and higher catalytic activity than that of Pt/C systems in the electro-oxidation of methanol.

In chapter V, based on the research of chapter IV, Pt₃PdNPs/RGO was prepared using the spontaneous redox reaction between PtCl₄²⁻, PdCl₄²⁻ and RGO. TEM and EDX demonstrated that Pt₃PdNPs were successfully supported on the RGO sheet. The

NPs were uniform with a diameter about 7 nm. Considering the mechanism of the electrocatalytic oxidation of glucose on Pt based electrode, we proposed a platform for the sensitive non-enzymatic glucose sensing base on Pt₃PdNPs/RGO combining anodic stripping voltammetry (ASV). The electrocatalytic oxidation of glucose on Pt₃PdNPs/RGO was investigated using CV, and the proper parameters were obtained for ASV. CV, LSV and i-t results were compared and confirmed that ASV was more sensitive among them. The lowest detection concentration of glucose reached to nM level. For the first time, Pt based material has been used in ASV.

Key words: Graphene oxide; Nano noble metal; Electrocatalysis; Non-enzymatic sensor; Fuel cells

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第一章 前言

1.1 氧化石墨烯

1.1.1 石墨烯的概述

碳是一种非金属元素,广泛存在于地球上,是人类最早认识的化学元素之一。同时碳元素是地球上一切生物有机体的骨架元素,是生命的基本单元。早在18世纪时,金刚石和石墨就已经被确定为由碳元素所组成的同素异形体,但是直到1924年研究人员才准确地确定了金刚石和石墨的三维结构。20世纪80年代兴起的纳米材料科学为碳材料打开一个全新的研究领域。1985年研究人员又发现了球形的富勒烯^[1]。这标志着人类对碳元素的研究进入了一个新的阶段。1991年,日本NEC公司的电子显微镜专家Iijima在高分辨透射电子显微镜(TEM)下观察真空电弧蒸发石墨电极时发现了由管状同轴纳米管组成的新的碳材料——碳纳米管(CNTs)^[2]。2004年,英国曼彻斯特大学的Geim等人发现了由碳原子以 sp^2 杂化连接形成的单原子层二维原子晶体——石墨烯^[3]。石墨烯是继碳纳米管被发现后碳家族中又一纳米级功能材料。目前,石墨烯是最理想的二维纳米材料之一。石墨烯的发现使人们对碳元素的多样性有了更深刻的认识,形成了从零维的富勒烯、一维的碳纳米管、二维的石墨烯到三维的金刚石与石墨的完整碳家族体系(图1.1)。

石墨烯是一种严格二维晶体材料,其中碳原子以六元环形式周期性排列于石墨烯平面内。每个碳原子通过 σ 键与临近的三个碳原子相连, s , p_x 和 p_y 三个杂化轨道形成强的共价键合,组成 sp^2 杂化结构,具有 120° 的键角,赋予石墨烯极高的力学性能。剩余的 p_z 轨道的 π 电子在与平面垂直的方向形成 π 轨道,此 π 电子可以在石墨烯晶体平面内自由移动,从而使得石墨烯具有良好的导电性,室温下载流子迁移速率可达 $10000\text{ cm}^2\text{ V}^{-1}\text{ S}^{-1}$ ^[3,4]。此外石墨烯还具有其他诸多显著的理化特性,如理论比表面积可达 $2630\text{ m}^2\text{ g}^{-1}$,优良的光透射率(97.7%)^[5],优异的导热性能($3000\sim 5000\text{ W m}^{-1}\text{ K}^{-1}$)^[6],高的拉伸模量或者杨氏模量(1000 GPa)和极限强度(116 GPa)^[7]。这些优越的性质及其特殊的二维结构使得石墨烯拥有良好的发展前景,目前已迅速成为国际新材料领域研究的热点。Geim教

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