

学校编码: 10384  
学号: 20520060153261

分类号  
密级  
UDC

廈門大學

博 士 学 位 论 文

纳米结构导电聚合物及其复合材料

Nanostructures of conducting polymers and their composites

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专 业 名 称: 物 理 化 学  
论文提交日期: 2009 年 10 月  
论文答辩时间: 2009 年 11 月  
学位授予日期: 年 月

答辩委员会主席: \_\_\_\_\_  
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2009 年 10 月

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## 摘要

导电聚合物是人工合成的具有类似半导体、金属导电性，同时具有传统聚合物特点的一种新型材料。由于导电聚合物特殊的掺杂机理、较高的环境友好性和稳定性、易加工性以及廉价的优点，在化学、生物传感器，发光二极管，分子、电子、光学器件等领域中的潜在应用前景，引起了广泛的研究热潮。近来，纳米科学技术的发展以及导电聚合物本身的性质和应用前景，纳米导电聚合物的可控合成以及相关的纳米复合材料的制备已经得到了研究人员越来越多的重视。纳米结构导电聚合物的制备途径主要包括“硬模板”法、“软模板”法和“无模板”法。同时，制备导电聚合物的纳米复合材料是改善导电聚合物性能和应用潜力的重要方法。本论文从导电聚合物中常见的聚苯胺着手，利用化学法和电化学方法，结合模板法和无模板法制备纳米结构的聚苯胺和基于聚苯胺的纳米复合材料，并探讨了纳米结构聚苯胺的电子传递性能，光学性能以及聚苯胺纳米复合材料的电化学性能，气敏性能等。取得了以下主要成果：

1：利用阳极氧化铝模板结合恒电位短时间聚合得到聚苯胺纳米点阵列，并且利用导电原子力显微镜测量单个聚苯胺纳米点电荷传递性。研究结果表明聚苯胺纳米点阵列排列有序，每个聚苯胺纳米点直径约为 40 nm，而且处于半氧化还原态的聚苯胺纳米点表现出库仑阻塞效应的电荷传递特点。同时研究表明处于还原态或氧化态的聚苯胺纳米点的电荷传递没有出现库仑台阶的现象。

2：采用恒电位电沉积的方法，在 ITO 导电玻璃电极上直接电沉积制备了樟脑磺酸（HCSA）诱导掺杂的聚苯胺纳米纤维。研究发现，当采用 2 M 樟脑磺酸诱导电沉积制备得到螺旋状的聚苯胺纳米纤维，而采用 1 M 樟脑磺酸诱导电沉积制备得到的聚苯胺纳米纤维不具有螺旋状结构，但是这两种聚苯胺纳米纤维均具有旋光特性。通过采用具有镜像对称的 D-和 L-樟脑磺酸，得到具有镜面对称圆二色光谱的聚苯胺纳米纤维。通过对聚苯胺纳米纤维进行化学掺杂-去掺杂处理发现聚苯胺纳米纤维的旋光性质是由于聚苯胺的链结构引起的。此外，通过进一步电化学控电位改变聚苯胺纳米纤维的氧化态，得到不同氧化态聚苯胺纳米纤维的圆二色信号随着氧化态的变化而发生可逆移动。这个发现可为聚苯胺纳米纤维的光学器件应用提供了一种新思路。首次发现采用恒电位电沉积方法制备了具

有多级树状纳米结构的聚苯胺,为聚苯胺纳米结构多样化的合成提供了一种新的途径。

3: 结合利用自组装和现场聚合的方法,在两相法制备得到的聚苯胺纳米纤维表面聚合吡咯,得到聚吡咯包覆聚苯胺的聚苯胺-聚吡咯同轴纳米纤维(PPCF),其中芯层为聚苯胺纳米纤维,套层为聚吡咯。通过改变吡咯的浓度可以得到不同套层厚度的 PPCF。通过 FTIR 和 Raman 表征证明了 PPCF 中芯层的 PANI 纳米纤维与套层的 PPy 之间界面层存在强的化学相互作用。此外,将 PPCF 应用气敏检测,发现 PPCF 具有在室温下对浓度变化的 TEA 气体具有高灵敏度,快速响应和恢复的特点。进一步扩展应用了自组装和现场聚合的方法,制备了聚苯胺-聚吡咯-Au 三元复合纳米纤维,具有在乙醇中良好的分散性和稳定性。

4: 利用在溶液 pH 值为 3 的情况下,介孔材料 SBA-15 表面荷负电,而苯胺单体发生质子化的特点,采用静电吸附制备了 SBA-15/PANI 纳米复合材料。通过调节制备过程中加入苯胺的量,可以调节 SBA-15 的孔径、比表面积和孔容等参数,从而得到结构差异的 SBA-15/PANI 纳米复合材料。此外,SBA-15/PANI 纳米复合材料具有较好的导电性和良好的电化学活性,而且具有在中性溶液中的电化学活性,并将其应用于电分析检测抗坏血酸共存下的尿酸,发现能够有效的区分开抗坏血酸和尿酸的氧化峰,而且通过 DPV 定量分析抗坏血酸浓度固定情况下的尿酸浓度。

关键词: 纳米结构; 纳米复合材料; 聚苯胺; 电聚合;

## Abstract

Conducting polymers, which possess semiconducting or metallic conductivities and traditional characteristics of polymer, are synthesized as novel materials. Owing to the special doping mechanism, well environment-friendly and environmental stability, facile preparation and cheap, also the potential applications in chemical and biological sensors, light-emitting diodes, molecular electronic optics machine areas, the researches of conducting polymers have attracted extensive interests. Recently, as for the development of nanotechnology and the intrinsic properties and application prospects of conducting polymers, the controllable synthesis of nanostructure of conducting polymers and the corresponding nanocomposites have gained more and more recognition of researchers. The synthetic approaches of nanostructure of conducting polymers contain “hard-template” method, “soft-template” method and “template-less” method. Simultaneously, the preparation of nanocomposites based on conducting polymers will be the important route to improve the performance and applications of conducting polymers. In this dissertation, we focus on polyaniline (PANI), one of the most popular conducting polymers. We utilize chemical and electrochemical method, combing the template and template-less techniques to prepare nanostructure of PANI and nanocomposites based on PANI. And probe into the electron transport properties and optical properties of nanostructure of PANI and the electrochemical properties and gas sensor properties of nanocomposites based on PANI. The following text is the details:

1: PANI nanodots array was fabricated in AAO template with potentiostatic method in a short time, and the charge transfer property of a single PANI nanodot was

measured using atomic force microscopy (AFM). The results showed that PANI nanodots were orderly arrangement, the diameter of single nanodot was about 40 nm and the charge transfer characteristic of mid-oxidized state of PANI nanodot performed like coulomb blockade. Furthermore, the results exhibited that the charge transfer characteristic of reduced or oxidized state of PANI nanodot did not display the coulomb staircase behavior.

2: PANI nanofibers induced by HCSA and PANI hierarchical nanostructures induced by p-TSA were direct electrodeposited on indium tin oxide (ITO) coated electrode with potentiostatic method. It is found that the PANI nanofibers electrodeposited from 2 M HCSA show helical structure while the PANI nanofibers electrodeposited from 1 M HCSA did not show helical structure, but both of the PANI nanofibers prepared from different concentrations of HCSA exhibit optical properties. Moreover, when using mirror-symmetrical D-CSA and L-CSA, the induced PANI nanofibers show mirror-imaged CD spectra. The retention of optical activity of PANI nanofibers with dedoping-redoping treatment demonstrates that the observed optical property for the PANI nanofibers arises from the macroasymmetry of polymer backbone. Furthermore, when the PANI nanofibers were changed the oxidized forms with electrochemical approach, the CD spectra of different oxidized states of PANI nanofibers shows the reversible movements with the change of oxidized forms. This discovery may provide a new idea for the possible applications of optical devices based on PANI nanofibers. PANI hierarchical tree-like nanostructures induced by p-TSA were electrodeposited on indium tin oxide (ITO) coated electrode with potentiostatic method first time. The result offers a new approach to the synthesis of variable nanostructures of PANI.

3: Combining self-assemble and in-situ polymerization methods, pyrrole was polymerized on the surface of PANI nanofibers which were prepared by interfacial polymerization to prepare Polyaniline-Polypyrrole coaxial nanofibers (PPCF). The core layer is PANI nanofibers, the sheath layer is PPy. PPCF with Different thickness of sheath layer can be synthesized through changing the concentrations of pyrrole in the experiment. The FTIR and Raman characteristics proved that the presence of



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