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聚吡咯纳米管对抗坏血酸的电化学检测

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摘要: 为了改善导电聚吡咯对于抗坏血酸的电化学检测性能, 采用以甲基橙为软模板, 制备了聚吡咯纳米管。利用扫描电子显微、红外光谱、X射线衍射、X射线光电子能谱对产物的结构与微观形貌进行了表征。分别将聚吡咯纳米管与聚吡咯纳米颗粒对抗坏血酸进行电化学检测。循环伏安测试结果表明, 聚吡咯纳米管和聚吡咯纳米颗粒对于抗坏血酸都有明显的电化学响应, 同时聚吡咯纳米管的比聚吡咯纳米颗粒的响应电流更大, 表明聚吡咯纳米管具有更好的电化学检测能力。差分脉冲伏安法研究发现抗坏血酸浓度在 0.5 mmol/L~20 mmol/L 和 20 mmol/L~45 mmol/L 范围内, 与峰值电流呈良好的线性关系。这表明聚吡咯纳米管作为电化学传感器材料有很好的应用前景。

关键词: 聚吡咯纳米管; 甲基橙; 软模板; 抗坏血酸; 电化学传感器

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Electrochemical Detection of Ascorbic Acid by Polypyrrole Nanotubes

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Abstract: To improve the electrochemical performance of conducting polypyrrole for sensing ascorbic acid, the polypyrrole nanotubes were prepared using methyl orange as a soft template. The microstructure and morphology of the products were characterized by scanning electron microscopy, Fourier transform infrared spectrometry, X-ray diffraction and X-ray photoelectron spectrometry, respectively. The electrochemical detection of polypyrrole nanotubes and polypyrrole nanoparticles for ascorbic acid were conducted. The result of cyclic voltammetry indicated that polypyrrole nanotubes and polypyrrolenanoparticles both had electrochemical response for ascorbic acid. But the response current of polypyrrole nanotubes was higher than that of polypyrrole nanoparticles, suggesting that the polypyrrole nanotubes had better electrochemical performance. The electrochemical response of polypyrrole nanotubes for sensing ascorbic acid were further investigated by differential pulse voltammetry. The responses of this sensor were linear over the ranges of 0.5 mmol/L to 20 mmol/L and 20 mmol/L to 45 mmol/L, respectively. It indicates that the polypyrrole nanotubes can be used as promising materials in the field of electrochemical sensors.

Keywords: polypyrrole nanotubes; methyl orange; soft template; ascorbic acid; electrochemical sensors

抗坏血酸(Ascorbic acid, AA)在维持人体正常生理机能中扮演着重要的角色^[1-2]。抗坏血酸作为一种抗氧化剂被广泛用于医疗制药、食品加工和

化妆产品等领域。因此,检测抗坏血酸,建立能够方便准确的检测方法对患者具有很大的重要性^[3]。国内外研究人员对抗坏血酸检测做出大量的研

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究,常用的方法有化学光学法、电化学法、色谱法和毛细管电泳法,其中电化学检测法因其便捷和灵敏度高为特点而具有明显优势,从而成为各国研究人员研究的热点^[4-14]。

以甲基橙(methyl orange, MO)为软模板合成了聚吡咯纳米管(Polypyrrole nanotubes, PPyNt),利用扫描电子显微镜与红外光谱研究了聚吡咯纳米管的形貌与结构。利用电化学检测方法分别将PPyNt、聚吡咯纳米颗粒(Polypyrrole nanoparticle, PPyNp)对抗坏血酸进行检测,研究了不同形貌结构的聚吡咯电化学检测抗坏血酸的区别。结果表明PPyNt作为电化学传感器材料有很好的应用前景。

1 实验部分

1.1 PPyNt的制备

称取一定量MO溶于去离子水中,配制成5 mmol/L的MO水溶液,用1 mol/L的HCl溶液调节MO水溶液pH=2,然后向上述溶液中加入1 g的吡咯,再加氧化剂12.907 g硝酸铁,在室温搅拌24 h。反应结束后先用乙醇洗涤3遍,去除未反应单体,再用去离子水洗涤过滤,直至滤液变澄清,得到黑色将产物真空冻干,即得到。作为对比,在不加入甲基橙软模板剂的相同条件下,合成PPyNp。

1.2 PPyNt与PPyNp的表征

用JSM-5510LV(JEOL Co)型扫描电子显微镜(scanning electron microscopy, SEM)、傅里叶变换红外光谱仪、X射线衍射仪、X射线光电子能谱表征PPyNt、PPyNp的微观形貌与化学结构;利用电化学工作站(CHI 660C)进行电化学检测抗坏血酸。

1.3 修饰电极的制备

先将1.0 mg样品分散在1.0 mL水中,取10 μ L分散液滴在玻碳电极上制备得到工作电极。以铂丝为对电极,Ag/AgCl电极为参比电极,与样品修饰的电极作为工作电极,利用电化学工作站(CHI 660C)进行电化学测试检测抗坏血酸。

2 结果与讨论

2.1 微观形貌表征

为了研究模板法制备聚PPyNt和不加入模板剂制备PPyNp的微观形貌,图1为两种产物的扫描电镜图,在酸性条件下以MO为软模板,通过静电吸附作用,吡咯单体吸附在软模板上,以氧化剂硝酸铁引发PPyNt,最后用乙醇和水去除未反应单体和MO软模板得到产物。从图1可以看出聚吡咯

明显的棒状结构,PPyNt的管径为400 nm左右,管长为5 μ m~10 μ m。在不加入MO软模板剂的情况下,吡咯单体在氧化剂硝酸铁引发聚合时,分子链向随机方向生长,最终得到PPyNp,从图1可以看出PPyNp粒径约为200 nm。这是因为Fe³⁺离子与MO分子复合成为具有一维纳米结构的模板,吡咯单体在这个模板表面发生聚合。反应结束后,MO分子会溶解于水中而被除去,最终形成聚吡咯的管状结构^[15-17]。

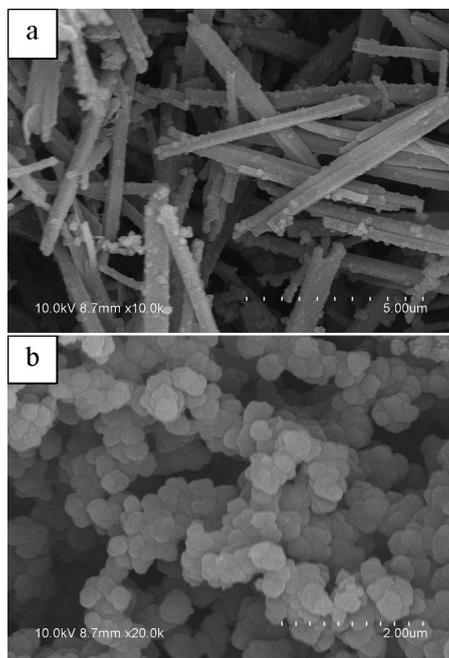


图1 (a) PPyNt与(b)PPyNp的扫描电镜图
Fig. 1 SEM images of (a) PPy nanotubes and (b) PPy nanoparticles

2.2 化学结构分析

图2(a)为PPyNt、PPyNp红外吸收光谱图。图2(a)中均出现聚吡咯结构的特征吸收峰,其中在1 655 cm^{-1} 和1 434 cm^{-1} 附近为聚吡咯基本单元结构五元杂环的对称伸缩振动和非对称伸缩振动特征吸收峰,1 126 cm^{-1} 附近为吡咯五元杂环上的N—H键的面内伸缩振动峰,3 437 cm^{-1} 的宽峰为典型的N—H与C—H伸缩振动混合吸收峰。另外在图2(a) PPyNt红外吸收光谱中,在2 900 cm^{-1} 和2 833 cm^{-1} 处有两个非常弱的MO分子—CH₃、—CH₂—的伸缩振动吸收峰,1 178 cm^{-1} 处为甲基橙分子的磺酸基伸缩振动吸收峰。这表明甲基橙不仅作为软模板合成PPyNt,同时由于电荷效应、使其掺杂进入到聚吡咯分子链中。

图2(b)是PPyNp与PPyNt的X射线衍射图。两者都在25°附近显示一个宽峰,对应于PPy的无定形结构。

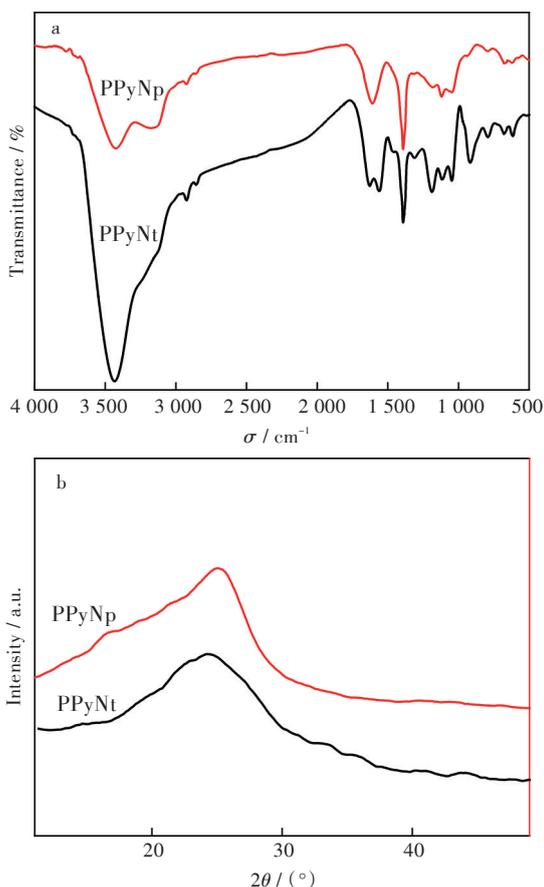


图2 PPyNp与PPyNt的(a)红外吸收光谱图和(b)X射线衍射图
Fig. 2 (a) Infrared absorption spectra (b) X-ray diffraction patterns of PPyNp and PPyNt

进一步用X射线光电子能谱对PPyNt的氮峰进行了分析。如图3所示,通过对氮峰的分峰处理,在399.5 eV对应 -NH- ,在401.5 eV与404 eV对应于 $\text{-N}^+\text{-}$ 。这表明利用MO为模板,成功合成了聚吡咯。

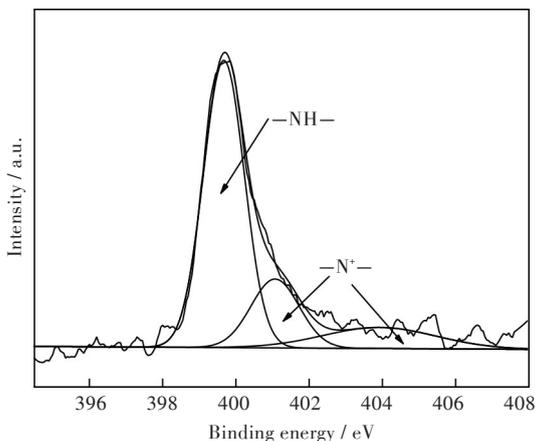


图3 PPyNt的N 1s的X射线光电子能谱图
Fig. 3 N 1s XPS spectra of PPy nanotubes

2.3 电化学检测抗坏血酸

用PPyNt和PPyNp分别做成修饰电极,并用纯铂电极作为空白对比。利用循环伏安法研究其对抗坏血酸的电化学响应。图4中显示出Pt电极、PPyNt修饰电极、PPyNp修饰电极三种不同电极在50 μmol 的AA溶液中的电化学响应,扫描电势为 $-200\text{ mV} \sim 800\text{ mV}$,扫描速率为50 mV/s。从图4中可以看出,Pt电极没有显示出明显的氧化峰,说明Pt电极对抗坏血酸没有催化效应。而PPyNt修饰电极、PPyNp修饰电极在0.37 V附近出现了明显氧化峰,而且PPyNt与PPyNp相比,氧化峰电流明显增加,峰面积大,说明PPyNt具有对AA更好的电催化性能。

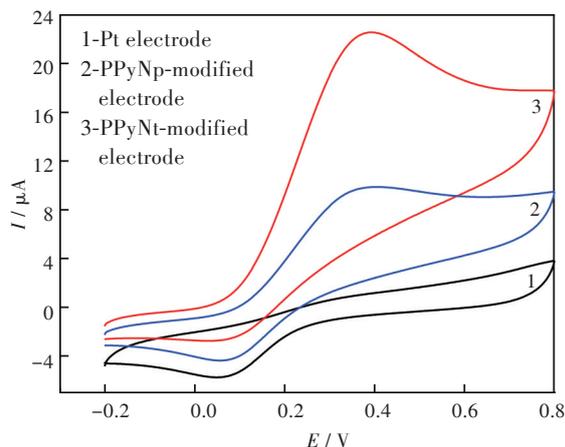


图4 在含有50 mmol/L AA溶液中电极的电化学响应
Fig. 4 Electrochemical responses of working electrodes in the solution containing 50 mmol/L of AA

图5分别为PPyNt修饰电极、PPyNp修饰电极在50 mmol/L的AA溶液中对AA进行电化学检测的循环伏安曲线,并给出了对应的扫描速率与峰值电流的线性关系图。由图4(a)、(c)可以看出PPyNt修饰电极和PPyNp修饰电极的氧化峰电流随着扫描速率的逐步增大而增大,而且PPyNt比PPyNp对AA的响应电流更大。另外,PPyNt与PPyNp对AA的电催化过程中,对应的峰值电流与所采用的扫描速率有着良好的线性关系,这表明电化学氧化过程是受吸附控制的。

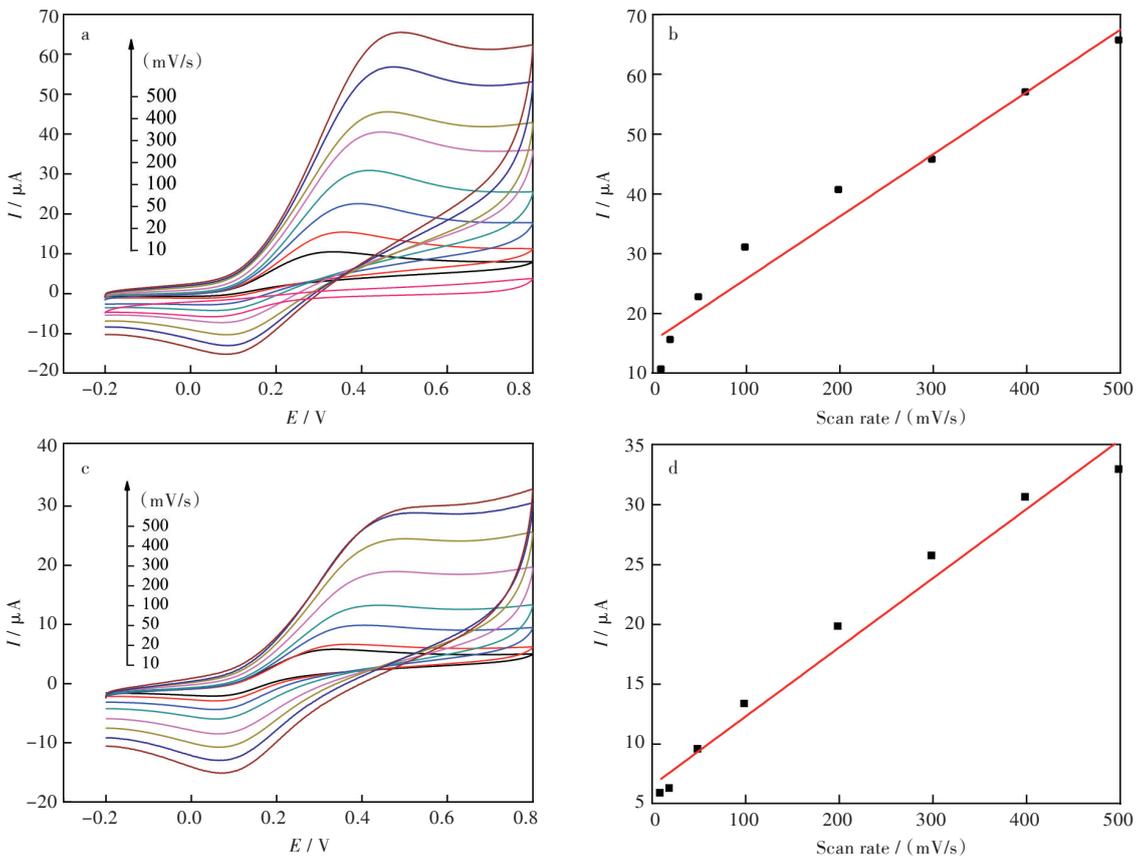


图5 在50 mmol/L的AA溶液中,(a)PPyNt修饰电极对AA电化学检测的循环伏安曲线;(b)扫描速率与峰值电流的线性关系;
(c)PPyNp修饰电极对AA电化学检测的循环伏安曲线;(d)扫描速率与峰值电流的线性关系

Fig. 5 In 50 mmol/L of AA, (a)Cyclic voltammetry of PPyNt-modified electrode of AA ;

(b)Linear relationship between the scanning rate and the peak current; (c)Cyclic voltammetry of PPyNp-modified electrode of AA;
(d)Linear relationship between the scanning rate and the peak current

如图6所示,进一步用差分脉冲伏安法研究了PPyNt修饰电极对于AA的电化学响应。差分脉冲伏安法的参数设置如下:初始电位-200 mV;终止电位800 mV;电位增量5 mV;振幅0.06 V;脉冲宽度0.05 s;脉冲周期0.2 s;采样宽度0.01 s。在电解液中依次加入一定量的AA溶液,每次加样后,混合均匀,静置30 s后立即用差分脉冲伏安法对溶液进行检测。随着AA溶液的加入量不断增加,峰值电流逐渐增大。如图6(b)所示,在AA在浓度范围为0.5 mmol/L~20 mmol/L和20 mmol/L~45 mmol/L时,峰值电流(peak current, PC)与AA浓度分别呈现出良好的线性关系,线性相关系数 R^2 分别为0.989和0.970。

体系中共存的生物分子有可能对于抗坏血酸的电化学检测产生影响。多巴胺(dopamine)对于抗坏血酸的影响如图7所示。在不同浓度的抗坏血酸溶液中加入8 mmol/L的多巴胺。多巴胺的存在对于抗坏血酸的电化学峰电流影响不大。PPyNt修饰电极的稳定性与重复性也被研究。制备了5个PPyNt修饰电极,分别置于抗坏血酸溶液中,这五个PPyNt修饰电极表现出相似的电化学响应行为,相对标准偏差为3.24%。PPyNt修饰电极的长期稳定性每2 d测试1次。经过10 d后,PPyNt修饰电极对于AA的电化学峰电流仍然能保持约93%。这表明PPyNt修饰电极对于抗坏血酸的电化学检测具有良好的重复性与稳定性。

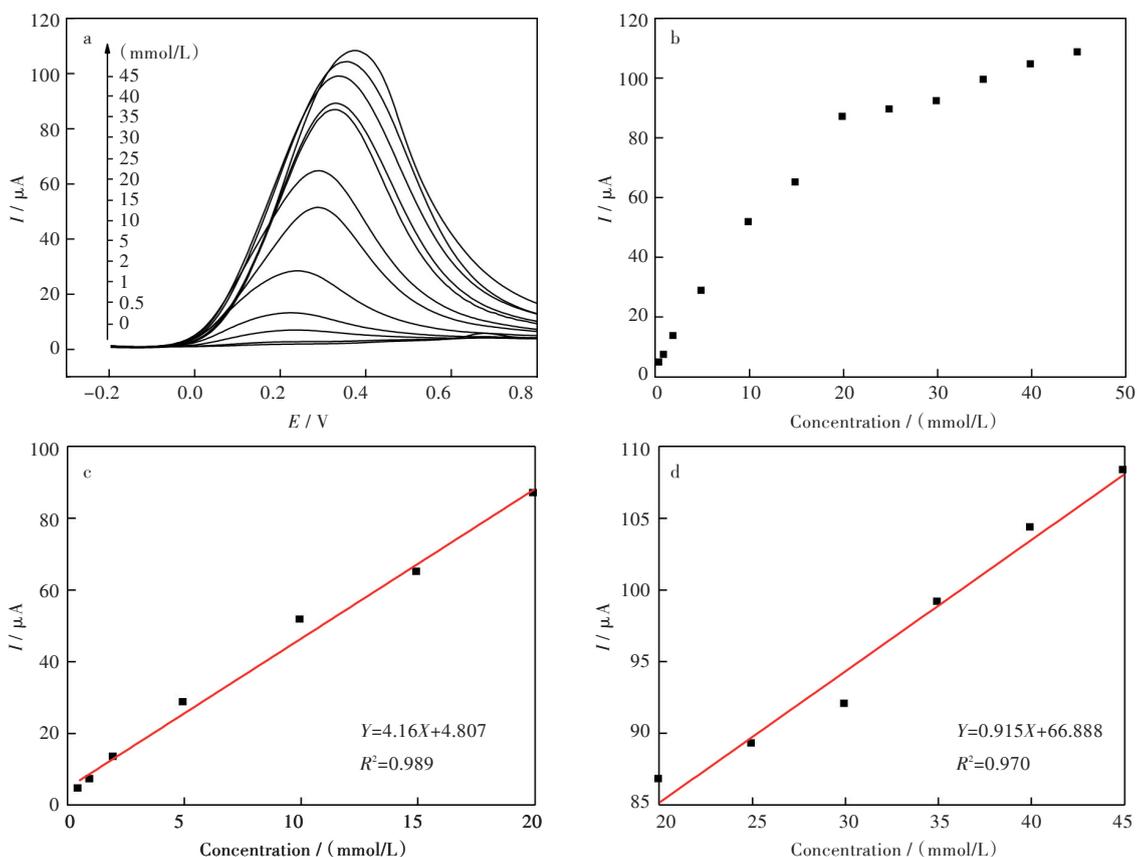


图6 (a)差分脉冲伏安法测量PPyNt修饰电极对不同浓度的AA的电化学曲线;
(b、c、d)对应的峰值电流与AA浓度的线性关系

Fig. 6 (a) Electrochemical responses of PPyNt-modified electrode to different concentrations of AA measured by differential pulse voltammetry; (b, c and d) Linear relationship between peak current and AA concentration

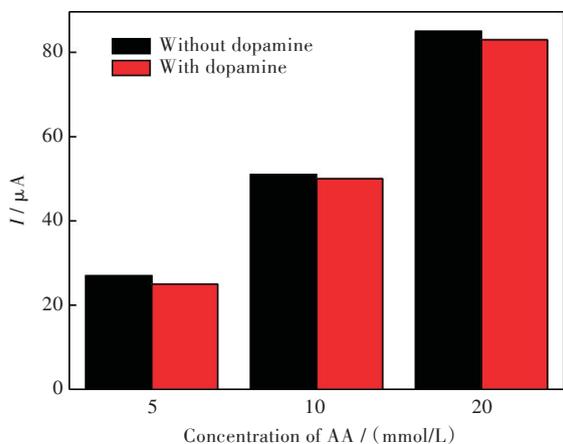


图7 有或没有8 mmol/L多巴胺时,PPyNt修饰电极的峰电流与AA浓度的关系图

Fig. 7 The relationship diagram between current of PPyNt-modified electrode and concentration of AA with and without 8 mmol/L dopamine

3 结 语

本文以偶氮染料甲基橙为软模板剂,以氧化剂硝酸铁引发吡咯聚合,制备了PPyNt,并通过多种方法对其结构和微观形貌等进行表征。研究结果表明PPyNt可以作为一种新型的电化学传感器材料用于AA的电化学检测。在含一定浓度的抗坏血酸溶液中,氧化峰的峰值电流与所采用的扫描速率呈线性关系,说明PPyNt对AA的电催化受吸附效应控制。而且由于PPyNt独特的一维纳米管状结构,使得PPyNt比PPyNp对AA有更好的电化学检测能力。

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