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不锈钢电极电化学传感器的研究进展

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摘　要

电化学传感器的应用不仅是一门实用的技术，更是科研领域重要的研究课题。而电极作为电化学传感器中至关重要的一部分，受到了广泛的研究。由于不锈钢具有低成本、环保、易操作、高机械强度和良好的导电性等特点，使其十分适合作为电极与新型材料和电化学传感技术相结合，设计出成本低廉且性能优异的新型电化学传感器。本文简要介绍了不锈钢电极在电化学传感器中的发展和应用。

关键词

不锈钢电极，电化学传感器，生物分子检测，电化学分析

Research Progress of Electrochemical Sensors with Stainless Steel Electrodes

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Abstract

The application of electrochemical sensors is not only a practical technology but also an important research topic in the field of scientific research. As a crucial part of the electrochemical sensor, the research of the electrode has been widely studied. With the advantages of low cost, environmental protection, easy operation, high mechanical strength and good conductivity, stainless steel is well-suited for application of electrodes. Combined with the new materials and electrochemical sensing technology, the stainless steel electrodes are beneficial to design the sensors with merits of low cost and excellent performance. This review briefly introduces the development and application of stainless steel electrode in the electrochemical sensors.

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Keywords

Stainless Steel Electrode, Electrochemical Sensor, Biomolecular Detection, Electrochemical Analysis

1. 引言

本文通过调查研究论证，讲述了基于不锈钢独特的优势特点，目前是如何应用的。而在此基础上继续进行改进创新，以期在电化学传感器方面有更大的潜力，应用到实际。电化学传感器是一种以电化学传感技术为基础，准确识别被测物质信息，进而将其转化为另一种信息并将其传输出来的元件[1]。电化学分析技术以其操作简便、经济廉价、灵敏度高等特点，在环境检测、食品安全检测、生物医学分析等各个领域都具有广阔的应用前景[2] [3] [4]。据调查研究发现，一些电极材料由于成本高、导电性能一般或者稳定性不好的原因，无法制作廉价且性能优异的电极。直到现在，由于成本和性能之间的平衡与否的关系，工作电极的制作仍有很大的发展空间。不锈钢是一种应用广泛的铁合金，它主要含有碳、铜、镍、铬等，以增强钢的性能[5]。并且，不锈钢中的铬暴露在空气中会迅速形成一层薄的氧化膜，正因如此，不锈钢具有高度稳定、抗腐蚀和抗氧化的特性[6] [7]。除了耐腐蚀之外，不锈钢还具有低成本、环保、易操作、高机械强度和良好的导电性等特点，可以用于制作一次性电极[8] [9]。近几年，不锈钢电极在电化学分析领域中得到了越来越多的研究和关注(图 1)。有研究者开发了一种用不锈钢棒制作而成的工作电极，并应用于重金属元素和吲哚乙酸(IAA)的电化学检测[10]。另外，也有研究者利用不锈钢电极检测地下水样品中的重金属离子，所设计的传感器具有检测限低、灵敏度高以及良好的重现性[11]。此外，还有研究者使用经过碳浆改性的不锈钢片对塑料玩具样品是否含有重金属以及大豆幼苗中生物大分子吲哚乙酸进行了分析[5]。还有研究是基于 304 不锈钢经聚多巴胺电沉积后用于分析鱼类样品中的甲醛的检测[12]。除此之外，不锈钢电极还可以应用于与人体疾病相关的分析研究中，比如，有研究者报道了一种基于不锈钢电极的新型电化学葡萄糖传感器，提高了人血清中血糖水平检测的准确性和精密度[13] [14] [15]。还有研究者将改性的不锈钢电极应用到检测癌细胞上，对细胞生物学的研究做出了贡献[16] [17]。不锈钢作为电极在电化学传感器方面具有很大潜力，将为电化学传感器的广泛应用做出贡献。

Figure 1. Applications of stainless steel electrode in electrochemical sensors
图 1. 不锈钢电极在电化学传感器中的应用

2. 不锈钢电极电化学传感器的应用

2.1. 重金属检测

目前，环境重金属污染的研究是一大热点。重金属污染与其他有机化合物的污染不同，在自然界中，大多数有机化合物可以通过物理、化学或生物等方式进行降解，使有害性降低或消除。而重金属包括金、银、铜、铁、铅等，具有富集性，很难在环境中降解。即使是有益的金属元素，含量超过某一数值也会产生剧烈的毒性，使动植物中毒死亡。另外，重金属在人体内能和蛋白质及各种酶发生作用，使它们失去活性，也可以在人体的某些器官中富集，若超过人体所能耐受的限度，就会造成人体急性中毒、亚急性中毒、慢性中毒等，从而给人体带来很大的危害。随着现在经济的发展，伴随而来的是河流重金属的污染。而重金属由于其在水中不可溶解且不可生物降解的特性，导致重金属成为主要污染物之一。有专家指出，重金属对土壤的污染有不可逆性，且我们日常饮用水中存在重金属将是一个世界性的难题。所以其对人类，动物以及生活在水中的生物的不利影响引起了广泛关注。例如，日本发生的水俣病(汞污染)、骨痛病(镉污染)等公害病，都是由重金属污染引起的。另一方面，铅、镉等痕量重金属经常被添加到各种塑料中，以提高塑料的稳定性、柔韧性和光泽度。而许多玩具又是由塑料制成的，所以它们可能成为儿童接触重金属的潜在来源[18]。因此，对重金属进行灵敏选择性地检测至关重要。

一般来说，重金属的检测是通过原子吸收光谱法或电感耦合等离子体质谱法等方式进行测定的，然而由于仪器的昂贵以及操作人员操作技术的要求，使得这些仪器的广泛使用受到了很大的限制[19] [20] [21]。除此之外，如何使用低成本、简单快速且易于操作的设备，检测极低浓度的痕量金属离子是一大热点话题。目前，可代替这些仪器检测重金属的重要方法之一就是电化学传感器。电化学传感器不仅可以减少检测时间，降低检测成本，还具有多元素分析的能力[22] [23] [24]。目前已知溶出分析对重金属离子检测有着显著的灵敏性，阳极溶出伏安法(ASV)是最有效、也是最广泛使用的技术[25] [26]。ASV 具体是将金属离子预先沉积在电极表面，然后根据溶出的步骤进行检测分析。汞基电极因其显著的灵敏度和良好的重现性而被广泛应用于溶出伏安分析[27] [28] [29]。但由于汞具有毒性，因此要进行改进，比如用更环保的电极代替汞电极，同时还可以很好地测定极低浓度的痕量重金属，比如碳材料、金、铋基、锑基、纳米复合材料、钽电极等。

不锈钢由于具有优异的导电性，低成本的特点可用于制造一次性工作电极。电极经碳浆改性修饰，然后装配到制作的分析装置中，可用于分析玩具中含有的重金属如铅、镉[5] [10] [22]。实验结果表明，碳浆的稀释比例对电化学传感器至关重要，而修饰后的电极在分析性能上的变化，很大程度归因于不锈钢优异的导电性能。对于镉和铅的溶出分析，对碳水泥的稀释比、缓冲溶液的 pH 值、预沉积电位和时间、铋浓度进行了优化，检测限达到 1 mg/L。且所修饰的不锈钢电极在阴极和阳极区均展现出了显著且尖锐的剥离峰、高灵敏度、低背景、良好的重现性和较宽的电化学窗口[30]。与汞基或铋基电极相比，不锈钢电极显示出与其相当的结果，还具有低毒性，操作更简单的特点，可成功应用于各种水样品的测定。因此，不锈钢可代替汞电极用于制作一次性电极并用于重金属的电化学检测。

2.2. 植物激素检测

吲哚-3-乙酸(IAA)在植物生长发育的每个阶段都发挥着关键作用。其在植物的生理过程中可调控顶端优势、细胞延伸、维管束分化、脱落抑制和气孔发育等过程，生长素的含量及在器官中的分布决定了植物器官的形态建成、株型以及向重性反应等生物学进程[31] [32]。因此，对其含量的跟踪对植物学研究具有重要意义。IAA 是一种小而非常不稳定的生物分子，在光照和加热等条件下很容易分解[10]。随着对植物研究的各项要求越来越复杂，对植物中 IAA 的实时检测分析就有了很大的挑战性。有研究者用拟南芥作为检测 IAA 的样品，为植物的生长研究提供了基础[5]。然而，拟南芥不同部位原位定量检测 IAA 仍具有挑战性。

检测 IAA 一般最常用的方法有质谱分析法(MS) [33]、液相色谱法(LC) [34]、荧光分光光度法[35]、毛细管电泳(CE) [36]、化学发光法[37]和放射免疫测定法[38]等，但是这些方法都是体外测定。且要对植物进行预处理，在这个过程中复杂又耗时，所以会导致一些重要生物信息丢失。因此，现在都致力于开发一种可以在植物体内检测植物信号分子的方法，从而获得植物在不同环境条件下，经植物体内反应调节机制作用而产生更准确、更及时的信息来进行实时监测。

由于不锈钢具有高灵敏度、良好导电性、高稳定性、低成本且操作简单易于小型化和集成的特点，有研究者基于此特点开发了一种不锈钢一次性电极电化学传感器，用于植物体内部 IAA 的检测。在此研究中，研究者用电化学方法在不锈钢微电极上修饰高度有序的纳米孔、Pt 纳米颗粒、爆米花状 Au 纳米结构和壳聚糖(CS)等，以提高检测效果[5] [39] [40] [41] [42]。将制备好的电极作为工作电极，银丝和铂丝分别作为参比电极和对电极，研制出一种可供一次性使用的植物体内 IAA 检测电化学微传感器。使用这种微传感器，在盐胁迫下检测了大豆幼苗茎叶的 IAA 的演化情况。该微传感器表现出优异的选择性和高灵敏度，检测限(LOD)低至 43 pg/mL。而最终的实验结果也得到了超高效液相色谱−质谱(UPLC-MS)的证实。因此，制作的传感器为植物体内 IAA 的检测提供了一个出色的检测平台[10]。不锈钢一次性电极电化学传感器为我们提供了新的思路，有望成为高效检测植物体内生物信号分子较好的解决方案之一。

2.3. 甲醛检测

甲醛是一种普遍存在于化工产品中的一种化学物质，无色有刺激性气味。在诸多的装修材料中，比如涂料、油漆、胶水中都要加入甲醛。如果居住在甲醛超标的房间太长时间的话，就会引起各种各样中毒症状，比如食欲减退、失眠多梦、记忆力减退等症状。甲醛尤其对孕妇、幼儿和老人这几类人群会造成更大危害，会导致小孩生长发育畸形或致癌情况的发生，这些都是不可逆的伤害[43] [44]。所以在日常生活中一定要重视甲醛对人类的危害，以免造成不可挽回的后果。因此，对甲醛的监测非常重要。

一般情况下，监测甲醛的方法有分光光度法、毛细管电泳法、GC、HPLC 和荧光法等[45] [46]。文献调查表明，可实时监测且灵敏度高的电化学分析法对甲醛的检测优于光谱法和色谱法的检测，且检测结果与之前检测方法得到的结果相比，更直接可靠、省时省力且结果之间具有一致性[12]。例如用多壁碳修饰有氨基的纳米管薄膜电极，以及贵金属纳米材料制作的电极，都可用于甲醛的检测[47]。这是因为金属纳米粒子具有较之前增大的表面积和出色的电子传输特性。有文献报道了一种基于无孔钯修饰的 TiO_2 电极，在碱性溶液中检测甲醛的新型电极[48]。实验结果表明，该电极具有高灵敏度和宽线性范围 65.0 μM 至 7.80 mM，其对甲醛的氧化，表现出优异的电催化活性和可持续性。有研究表示在不锈钢上电沉积聚多巴胺(PDA)被开发用于鱼类样品中甲醛的检测，最优条件下甲醛检测的线性动态范围为 0.43~1.60 μm。检测限和定量限分别为 0.14 和 0.43 μm [49] [50]。该电化学传感器具有低检测限、稳定性和宽线性范围的优势，因此使其成为甲醛检测的电化学传感平台。

2.4. 血糖检测

目前，美国高油、高糖、肥胖现象比较严重，中国也一样，且不说美国糖尿病发病率如何，就中国糖尿病发病率已经达到 11.6%，糖尿病前期入群的比例高达 50.1%，即：每 2 个人中就有一个人可能患糖尿病。糖尿病的发病与多种因素有关，如遗传、病毒感染、不健康饮食、高油高糖高热量、肥胖不爱运动，吸烟酗酒、经常加班熬夜等。这些因素导致了糖尿病的频发[51] [52] [53]。因此，对糖尿病血糖水平以及胰岛素给药持续、准确的监测至关重要。而每天将近有数百万人使用可测量血糖水平的便携式血糖监测系统，来进行糖尿病健康与否的自我管理。

目前，光谱法和电化学技术是检测葡萄糖的主要测量方法。前者主要是利用酶促氧化的过程再通过吸光度法或荧光信号的变化来测定葡萄糖水平的高低[54] [55]。后者是利用固体基质表面上血糖的氧化还

原反应，其中产生的电流的变化反应了葡萄糖水平的高低[56] [57]。目前，电化学技术监测血糖的方式已被更为广泛地应用。电化学技术检测对血清样本产生的干扰相对较小，不会污染到血清样本从而使得结果更真实准确，其次缩短了血糖测量所需时间，降低了制造成本。在过去的几十年中，基于电化学的血糖监测技术，其中包括即时医疗设备、连续的无创的血糖监测已经得到了发展。目前，304 不锈钢是医疗器械中使用最广泛的金属器材，主要用作一次性针头或血糖仪的刺血针。304 不锈钢同样也可以作为工作电极应用于血糖仪中。例如，有相关文献报道了一种基于不锈钢电极地新型电化学葡萄糖传感器，线性范围为 1 至 1000 nM，检测限为 0.456 Nm [信噪比(S/N) = 3] [13] [15]。例如，有研究者通过将壳聚糖(CS)-葡萄糖氧化酶(GOD)生物复合材料电沉积到由 Pt-Pb 纳米粒子(Pt-Pb/SSN 电极)修饰的不锈钢针电极上，制备了葡萄糖生物传感器[58]。电化学检测结果表明检测限为 0.03 至 9 mM，对血糖检测具有很好的效果，且细胞测试结果表明电极具有低细胞毒性。这项工作为针型葡萄糖生物传感器的制造提供了合适的技术。因此，不锈钢电极在检测人血清血糖水平高低上，具有很大地潜在应用价值。

2.5. 细胞检测

活性氧(ROS)是细胞内重要的一种信号分子，在调节蛋白质合成、细胞凋亡、信号转换和免疫活性中发挥了重要作用。若 ROS 在细胞中过量积累可导致神经退行性病变、阿尔兹海默症、自身免疫性疾病、心血管疾病和癌症[59] [60] [61]。过氧化氢(H_2O_2)是 ROS 的常见代表，由于其具有稳定性且具有通透性可通过细胞膜而受到广泛关注。因此，有必要开发一种快速、灵敏、可实时监测细胞中 H_2O_2 动态释放过程的设备，对信号转导通路调控的研究以及疾病如何进行诊断的方案提供了新思路[62] [63] [64]。

迄今为止，测定 H_2O_2 的技术有荧光法[65]、比色法[66]、化学发光法[67]、色谱法[68]和电化学法[69]等。其中，电化学测定法由于其响应快、灵敏度高、选择性好、操作简单和重现性好等特点，在实时监测 H_2O_2 方面引起了广泛关注。304 不锈钢还对 H_2O_2 表现出优于其他传统电极的高度精确且灵敏的电流响应检测限(LOD)估计为 1.4 μM (S/N = 3)。而经文献调查发现，304 不锈钢电极不仅在各种干扰物质存在的情况下表现出较宽的线性范围，而且还对 H_2O_2 还原有出色的选择性[13]。还有文献描述了如何使用不锈钢针作为电极基板，通过二硫化钼(MoS_2)和铂纳米粒子(PtNPs)层修饰，构建了一种微针传感器，用于实时监测活细胞中 H_2O_2 的释放[70]。电化学研究表明，MoS_2/PtNPs 纳米复合改性不锈钢电极表现出优异的电催化性能和较低的 H_2O_2 还原电位。该微针传感器不仅实现了从 1 到 100 μmol/L 的宽线性范围，检测限低至 0.686 μmol/L，而且还实现了对 H_2O_2 的高特异性检测。由于这些显着的分析优势，制备的微针用于测定活细胞中的 H_2O_2 释放，结果令人满意。由于这些显着的分析优势，制备的微针传感器用于测定活细胞中 H_2O_2 释放，结果令人满意。此外，这种超细不锈钢针头传感器在实时监测体内活性氧物质方面显示出巨大的潜力，而且损伤最小。综上，基于不锈钢此特性，可用于检测细胞产生的 H_2O_2 以及可转化为 H_2O_2 的物质或者参与 H_2O_2 反应的物质，这对实际应用具有重要意义。

3. 结论

基于不锈钢电极的电化学传感器由于取材便利、稳定性好、灵敏度高、成本廉价的特性，成为样品检测过程中良好的电催化材料，在环境检测、食品安全检测、生物医学分析等领域具有广阔的应用前景。在实际应用过程中，根据实际需求采用合适的电极材料进行修饰，就可以有效的解决电化学检测样品准确性和灵敏度低等研究难题。除此之外，制作可大规模高效率使用且成本低廉的不锈钢电极电化学传感器仍然是亟待解决的问题。研究表明，不锈钢电极电化学传感器在检测细胞产生 H_2O_2 方面具有独特的优势。进一步考虑到测定过程中细胞的多样化，不锈钢电极电化学传感器有望可以成为实时监测这些化学信号的理想工具，并且可能对相关的生理学和病理学研究有潜在的广泛应用。

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