Recent developments on electrochemical flow injection in pharmaceuticals and biologically important compounds

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ABSTRACT

The improvement of life quality has stimulated considerable research in drug design bioavailability and safety. Thus, to reach these targets, highly sensitive, specific, and rapid methods of analysis are necessary. Flow injection analyses (FIA) has been used successfully in proof-of-principle research studies to the pharmaceuticals and biologically important compounds via electrochemical methods. Different types of FIA methods such as reverse FIA and stopped FIA have applied over the last few years significantly changing the scope and sensitivity of analytical methods, especially using electrochemical detectors. Electrochemical methods are widely used in flow injection techniques on drug active and biologically important compounds. Hence, drugs can be selectively detected and sensitively determined using electrochemical methods as detector. In recent years, the flow injection methodology of analytical determinations has gained already many technical modifications using electrochemical methods. It is a general solution-handling technique, applicable to a variety of tasks ranging from pH or conductivity measurement, to column measurements and enzymatic assays. Analyses, which used a FIA system, requires less analyte than conventional methods accompanied by a rapid detection as well as shorter reaction time. FIA based on electrochemical methods can be called most environmentally friendly and analyzing method owing to less analyte consumption. In this review, some selected commercially available devices, recent papers and patents will be discussed related with electrochemical FIA methods in the period of 2000 to up-to-date.

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Development toward a novel integrated tear lactate sensor using Schirmer test strip and engineered lactate oxidase

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\section*{A R T I C L E   I N F O}

\begin{table}[h]
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\begin{tabular}{|c|c|c|}
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Keywords: & Tear lactate & Schirmer’s test strip \hline
& Integrated sensor & Lactate oxidase \hline
& Oxygen interference & \hline
\end{tabular}
\end{table}

\section*{A B S T R A C T}

\(\alpha\)-Lactate is an important biomarker for clinical diagnostics and fitness monitoring that shows oxygen deficiency or elevated salt concentrations due to pathophysiological conditions or intensive exercise. To avoid current painful and inconvenient blood testing techniques of measuring lactate levels, tears represent a non-invasive and potential sampling medium. However, lactate oxidase (LOx) is susceptible to the fluctuation and deficiency of oxygen, leading to inaccurate lactate measurements in tears. By utilizing a recently published, protein engineered LOx that eliminates the oxygen interference, a novel tear lactate (TL) sensor was assembled and tested. Screen-printed sensors were prepared with a redox solution containing the engineered LOx, and a novel tear sampling component made of Schirmer’s test strip was attached to absorb the simulated tear fluid samples. The dynamic range of the TL sensor was found to be 0.39–16.60 mM in simulated tear fluid, satisfying the clinically relevant range of TL. In addition, the proposed TL sensor was found to be insensitive to ascorbic acid, acetaminophen, and uric acid, which are common interfering compounds in tears, and showed no sign of degradation after 8 weeks of shelf life study. The proposed sensor exhibited potential usefulness in providing an alternative noninvasive method of measuring lactate and in calibrating the continuous lactate contact lens.
Novel tungsten phosphide embedded nitrogen-doped carbon nanotubes: A portable and renewable monitoring platform for anticancer drug in whole blood

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A B S T R A C T

Biosensors based on converting the concentration of analytes in complex samples into single electrochemical signals are attractive candidates as low cost, high-throughput, portable and renewable sensor platforms. Here, we describe a simple but practical analytical device for sensing an anticancer drug in whole blood, using the detection of methotrexate (MTX) as a model system. In this biosensor, a novel carbon-based composite, tungsten phosphide embedded nitrogen-doped carbon nanotubes (WP-N-CNT), was fixed to the electrode surface that supported redox cycling. The electronic transmission channel in nitrogen doped carbon nanotubes (N-CNT) and the synergistic effect of uniform distribution tungsten phosphide (WP) ensured that the electrode materials have outstanding electrical conductivity and catalytic performance. Meanwhile, the surface electronic structure also endows its surprisingly reproducible performance. To demonstrate portable operation for MTX sensing, screen printing electrodes (SPE) was modified with WP/N-CNT. The sensor exhibited low detection limits (45 nM), wide detection range (0.01–540 μM), good selectivity and long-term stability for the determination of MTX. In addition, the technique was successfully applied for the determination of MTX in whole blood.
Real-time circulating tumor cells detection via highly sensitive needle-like cytosensor—demonstrated by a blood flow simulation

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ABSTRACT

The concept of rapid detection of circulating tumor cells (CTCs) has always been the focal point of modern and future medicine. However, the dispersity and rarity of CTCs in the bloodstream makes it hard to detect metastasis. Herein, our newly designed needle-like cytosensor demonstrates that the capture and analysis of CTCs are a much less laborious process and have more potential than ever. Our aim is to detect and capture CTCs directly in the bloodstream without altering the genetic information; further, benefit of current cytosensor is allows for the whole circulation of blood to run through the cytosensor, giving a much better sensitivity and chance of detecting CTCs. Our functionalized needle-like cytosensor has been modified with 3-aminopropyltriethoxysilane, 1-ethyl-3(3-dimethylaminopropyl) carbodiimide, N-hydroxysuccinimide and conjugated streptavidin to allow the binding of the biotinylated-antibody of epithelial cell adhesion molecules, which captures targeted colon cancer CTC. The capability of our needle-like cytosensor to detect CTCs spanned from 10^2 to 10^6 cells/mL. Beyond this, the needle-like cytosensor avoids the distortion of the cell information. In addition, we constructed a blood flow simulation that mimics human circulating system about 10 mL/min speed; by using cyclic volumetry we could detect significant signals from captured cancer CTCs more than 21 cells/mL without delay; the fluorescence detection was further performed for data confirmation. The future of biosensors begins with this, by providing early monitoring quality care in cancer therapy.

Fig. 1. (A) Needle-like cytosensor surface modification. (B) The scheme for construction of blood circulation model and cells capturing by needle-like cytosensor.
Design of novel 3D flower-like neodymium molybdate: An efficient and challenging catalyst for sensing and destroying pulmonary toxicity antibiotic drug nitrofurantoin

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HIGHLIGHTS

- 3D Flower-like neodymium molybdate (Nd\textsubscript{2}Mo\textsubscript{6}O\textsubscript{17}) was prepared via sol–gel method.
- The as-prepared Nd\textsubscript{2}Mo\textsubscript{6}O\textsubscript{17} is an efficient catalyst for detection and degradation of NFT.
- The NFT was identified and determined through electrochemical reduction.
- The detection range of NFT is 0.1–21 and 28–481 \textmu M with a LOD of 16 nM.
- The NFT drug was effectively degraded (> 99%) by Nd\textsubscript{2}Mo\textsubscript{6}O\textsubscript{17} catalyst within 45 min.

GRAPHICAL ABSTRACT

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ABSTRACT

The extensive use of antibiotic drug (Nitrofurantoin; NFT) in pharmaceuticals and food producing animals may cause severe threats to both human health and animals. Besides, the residues of NFT can be found or discharged into soil, rivers, lakes and local ground water can also cause serious health risks to living things. Therefore, rapid and highly selective detection as well as the removal of NFT from the foodstuff and water samples is very important concern. In the present study, we designed a novel 3D flower-like neodymium molybdate (Nd\textsubscript{2}Mo\textsubscript{6}O\textsubscript{17}; NdM) catalyst by simple sol–gel route and evaluated for its bifunctional catalytic activity for the electrochemical detection andphotodegradation of NFT for the first time. Moreover, the physicochemical properties of NdM were scrutinized by various analytical and spectrocopic techniques. The NdM modified screen printed carbon electrode (SPCE) showed an excellent electrocatalytic activity towards NFT with wide linear ranges (0.1–21 \textmu M; 28–481 \textmu M), lower detection limit (16 nM) and excellent selectivity in the existence of potentially co-interfering compounds (nitro group containing drugs; other nitro aromatic and biological compounds). Besides, the NdM modified SPCE was successfully applied to the real sample analysis in NFT oral suspension, water and urine samples, and the obtained recovery are well-satisfactory. Interestingly, the UV–visible spectroscopy results envisage that NdM could act as a superior photocatalyst which degrades above 99% of NFT solution under visible light irradiation. The trapping experiments revealed that hydroxyl radicals (-OH) played the major role in the
Trimetallic Hybrid Nanoflower-Decorated MoS$_2$ Nanosheet Sensor for Direct in Situ Monitoring of H$_2$O$_2$ Secreted from Live Cancer Cells

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**ABSTRACT:** In situ monitoring of hydrogen peroxide (H$_2$O$_2$) secreted from live cells plays a critical role in elucidating many cellular signaling pathways, and it is a significant challenge to selectively detect these low levels of endogenous H$_2$O$_2$. To address this challenge, we report the establishment of a trimetallic hybrid nanoflower-decorated MoS$_2$ nanosheet-modified sensor for in situ monitoring of H$_2$O$_2$ secreted from live MCF-7 cancer cells. The Au–Pd–Pt nanoflower-dispersed MoS$_2$ nanosheets are synthesized by a simple wet-chemistry method, and the resulting nanosheet composites exhibit significantly enhanced catalytic activity toward electrochemical reduction of H$_2$O$_2$, due to the synergistic effect of the highly dispersed trimetallic hybrid nanoflowers and the MoS$_2$ nanosheets, thereby resulting in ultrasensitive detection of H$_2$O$_2$ with a subnanomolar level detection limit in vitro. Also the immobilization of the laminin glycoproteins on the surface of the nanocomposites increases its biocompatibility for cell adhesion and growth, which enables in situ electrochemical monitoring of H$_2$O$_2$ directly secreted from live cells for potential application of such sensor in cellular biology, clinical diagnosis, and pathophysiology.
Innovative Strategy Based on a Novel Carbon-Black–β-Cyclodextrin Nanocomposite for the Simultaneous Determination of the Anticancer Drug Flutamide and the Environmental Pollutant 4-Nitrophenol

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Supporting Information

**ABSTRACT:** In the present work, a noncovalent and eco-friendly approach was proposed to prepare a carbon-black/β-cyclodextrin (CB/β-CD) nanocomposite. CB/β-CD-nanocomposite-modified screen-printed carbon electrodes were applied for the simultaneous determination of the anticancer drug flutamide (Flut) and the environmental pollutant 4-nitrophenol (4-NP). The electrochemical performance of the proposed sensor relied on the conductivity of CB, the different binding strengths of the guests (Flut and 4-NP) to the host (β-CD), and the different reduction potentials of the nitroaromatic compounds. Fascinatingly, the proposed sensor exhibited an excellent electrochemical performance with high sensitivity, selectivity, and reproducibility. The obtained wide linear ranges were 0.05–158.3 and 0.125–225.8 μM for Flut and 4-NP. The low detection limits of 0.016 and 0.040 μM with the higher sensitivities of 5.476 and 9.168 μA μM⁻¹ cm⁻² were achieved for the determination of Flut and 4-NP, respectively. The practical feasibility of the proposed sensor was studied in tap-water and human-serum samples.

Scheme 1. Preparation and Application of the CB/β-CD Nanocomposite
Highly selective electrochemical detection of antipsychotic drug chlorpromazine in drug and human urine samples based on peas-like strontium molybdate as an electrocatalyst†

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The countless use of antibiotics in veterinary and human medicine causes severe health risks to both humans and animals. In this context, monitoring of the antibiotic drug in the veterinary and human pathological system is important and provokes a universal challenge. Therefore, development of simple and sensitive inorganic materials with unique morphology is of great importance for the trace level monitoring of pharmaceutical content in the environment. Herein, we developed a novel peas-like strontium molybdate catalyst (SrMoO₄, SrM) synthesized by a simple sonochemical approach and utilized as an electrochemical sensor for the detection of antipsychotic drug chlorpromazine (CPZ). The crystalline structure, surface morphology, elemental compositions and textural properties were systematically investigated by various analytical and spectroscopic techniques. As an electrochemical sensor, inorganic binary SrM modified screen printed carbon electrode (SrM/SPCE) exhibited an enhanced electrocatalytic activity towards CPZ sensing with excellent analytical performance such as wide linear response ranges and lowest detection limit of 0.1–143 and 153–1683 μM and 0.028 μM respectively. Moreover, the as-prepared SrM/SPCE showed an excellent selectivity even in the presence of co-interfering drugs, biological compounds and common metal ions. In addition, the SrM/SPCE applied to the real samples analysis in commercially available CPZ drug and human urine samples and the observed recoveries are quite satisfactory.