A disposable non-enzymatic histamine sensor based on the nafion-coated copper phosphate electrodes for estimation of fish freshness

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A B S T R A C T

Histamine is an important index for the estimation of allergic reaction and food freshness. This study develops a single-step dipping and coating method to fast produce an electrochemical histamine sensor based on a nafion-coated copper phosphate \(\text{Cu}_3\left(\text{PO}_4\right)_2\)-dominated electrode. The flake-like \(\text{Cu}_3\left(\text{PO}_4\right)_2\) nanostructures can be fast formed on Cu-electrodeposited screen printed carbon electrodes (SPCEs) within 20 min. Moreover, the 1% nafion-coated \(\text{Cu}_3\left(\text{PO}_4\right)_2\)/SPCEs presented good selectivity for the detection of histamine in the pH 8.5 solution. The nafion/\(\text{Cu}_3\left(\text{PO}_4\right)_2\)/SPCEs can be integrated with a flow-injection device for the detection of histamine with a good correlation coefficient \((R = 0.999)\) in the range of 5–500 ppm. The calculated limit of detection was 3.0 ppm. Moreover, the histamine concentration of 45 h-rotten fish samples detected by the nafion/\(\text{Cu}_3\left(\text{PO}_4\right)_2\)/SPCEs had a less than 10% deviation from that measured by the commercialized liquid chromatography-mass spectroscopy. The nafion/\(\text{Cu}_3\left(\text{PO}_4\right)_2\)/SPCEs have great promise for estimating the freshness of fish meat without expensive separation equipment and labor-intensive labeling procedures.

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A novel electroanalytical assay for sulfamethazine determination in food samples based on conducting polymer nanocomposite-modified electrodes

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ABSTRACT

The toxicity of sulfa drugs has attracted great attention, and the reported electrochemical methods for sulfa drugs usually employ a high oxidation potential. In this work, a one-pot synthesized conducting polymer nanocomposite containing poly(3,4-ethylenedioxythiophene) (PEDOT) and MnO₂ was cast on a screen-printed carbon electrode (SPCE), and the modified electrode showed superior electrochemical activity over a bare electrode for sulfamethazine (SMZ) detection. The SMZ detection was based on the electrochemical oxidation product, which showed an adsorptive property and exhibited a redox couple at 0.39 V in pH 3 phosphate buffer solutions (PBS). The electrode surfaces were well characterized by the water contact angle technique, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and cyclic voltammetry. By the use of square wave voltammetry (SWV), a wide linear response to SMZ, from 1.0 μM to 500 μM, was obtained. The sensitivity and detection limits (S/N = 3) were 0.115 μA μM⁻¹ and 0.16 μM, respectively. The proposed method and a reference high-performance liquid chromatographic method (HPLC) were applied for the determination of SMZ in two real samples using the standard addition method, and satisfactory recoveries and good agreement were obtained.

Fig. 7. Electroanalytical performance of the proposed assay. (A) SWV responses for various concentrations of SMZ (0–500 μM) at SPCE/PEDOT/MnO₂ in pH 3 PBS (after CV scanning and SMZ dimers adsorption). Potential increment = 4 mV. Amplitude = 25 mV. Frequency = 15 Hz. (B) Plot of anodic peak current (Ip) vs. SMZ concentrations at SPCE/PEDOT/MnO₂ (○) and bare SPCE (△).
Microwave-assisted synthesis of Bi$_2$WO$_6$ flowers decorated graphene nanoribbon composite for electrocatalytic sensing of hazardous dihydroxybenzene isomers

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ABSTRACT

A microwave-assisted synthesis is described for the preparation of bismuth tungstate/graphene nanoribbons (Bi$_2$WO$_6$@GNRs) nanocomposite as cost-effective alternative to existing hydrothermal method. HR-TEM, XRD, XPS, EDX, BET and Raman characterizations reveal the incorporation of Bi$_2$WO$_6$ flowers on GNRs. The electrochemical and interfacial properties of the composite were probed by voltammetry and impedence studies. The electrocatalytic ability of the composite was assessed by studying the redox reactions of hazardous dihydroxybenzene isomers. Bi$_2$WO$_6$@GNRs modified screen-printed electrode was found to distinguish the voltammetric signals of catechol and hydroquinone (separation gap of 140 mV, vs. Ag/AgCl), minimizes reaction over-potentials, and amplifies the electrochemical current signal. The effects of concentration scan rate and cross-reactivity are studied. Bi$_2$WO$_6$@GNRs incorporated sensor displayed detection limits of 5.31 nM and 7.24 nM for catechol and hydroquinone, respectively. The method was found to be practically applicable in the determination of catechol and hydroquinone in water samples and face cream sample, respectively.

Scheme 1. Schematic illustration for the preparation of Bi$_2$WO$_6$@GNRs nanocomposite for sensing dihydroxybenzene isomers in water samples and face cream sample. WE= Working electrode, RE = Reference electrode, CE = Counter electrode.
An electrooxidative technique to fast fabricate copper phosphate electrodes capable of integrating high performance liquid chromatography for the label-free detection of fish freshness

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**A B S T R A C T**

A simple and fast one-step electrooxidative method has been developed to monolithically produce a copper phosphate ($\text{Cu}_2(\text{PO}_4)_2$) compound on a disposable copper tape, which can be integrated with high performance liquid chromatography (HPLC) for the estimation of fish freshness. The $\text{Cu}_2(\text{PO}_4)_2$ compound of flake-like nanostructures was formed by applying a first anodic peak potential at the copper tape for 10 min in a 1 M sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4$) (pH 5.0) solution. The $\text{Cu}_2(\text{PO}_4)_2$ electrodes can detect the oxidative reaction of histidine and histamine in 20 mM $\text{NaH}_2\text{PO}_4$ solutions with pH 5.0–8.5. When integrating the electrodes with a flow injection system, the linear range and the calculated detection limit of histamine were respectively 2.5–250 ppm and 0.15 ppm. The electrodes integrated to HPLC can specifically detect the histamine concentrations in fish samples in the pH 7.5 $\text{NaH}_2\text{PO}_4$ solution, achieving an accuracy rate of 95.3% and a recovery rate of 101.1%.

![HPLC chromatograms](image)

Fig. 5. HPLC chromatograms of separate 100 ppm histamine (solid line) and histidine (dashed line) samples prepared and performed in the 20 mM $\text{NaH}_2\text{PO}_4$ solutions of pH 5.0, 7.5 and 8.5 (a), the mixture of 100 ppm histidine and 100 ppm histamine (b) and fresh, 45 h-rotten and 50 ppm histamine-spiked 45 h-rotten mackerel samples performed in the 20 mM $\text{NaH}_2\text{PO}_4$ solutions of pH 7.5 (c). Applied potential: +0.12 V vs. Ag/AgCl; flow rate: 1.0 mL/min; sample loop: 20 μL.

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Selective amperometric and flow injection analysis of 1,2-dihydroxy benzene isomer in presence of 1,3- and 1,4-dihydroxy benzene isomers using palladium nanoparticles-chitosan modified ITO electrode

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ABSTRACT

Amongst various isomers of dihydroxy benzene, 1,2-dihydroxy benzene (Catechol, CA) isomer and its derivative based natural compounds are considered to be the key functional group for various health benefits. In electrochemistry, pulse voltammetric techniques combined with chemically modified electrodes (CMEs) have been often reported for simultaneous detection of 1,2- (CA); 1,3- (Resorcinol, RE) and 1,4-dihydroxy benzene (hydroquinone, HQ) isomers at discreet potentials, ~0.1, ~0.2 and ~0.4 V vs Ag/AgCl, respectively, in a neutral pH condition. Indeed, the above technique and the reported CMEs were not suitable for selective amperometric i-t based detection of CA without interference from HQ and RE. In fact, at CA detection potential, ~0.2 V, HQ also got co-detected. Herein, we report a palladium nanoparticles-Chitosan indium tin oxide modified electrode (ITO/CHIT@Pd (nano)) as a selective amperometric sensor system for CA isomer detection without any interference of HQ and RE. A specific interaction between Pd²⁺ and CA as (Pd²⁺-CA complex) is proposed as a key factor for the selectivity achieved in this work. As a proof of concept, flow injection analysis of CA functional group in wine and tea real samples was demonstrated.

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Fig. 1. Cyclic voltammetric responses of ITO/CHIT@Pd (nano) (A), GCE/CHIT@Pd (nano) (B) and SPE/CHIT@Pd (nano) (C) modified and bare ITO (D), GCE (E) and SPE (F)-unmodified electrodes in presence of 1 mM (each) 1,2-dihydroxy benzene (CA), 1,3-dihydroxy benzene (RE) and 1,4-dihydroxy benzene (HQ) isomers at v = 10 mV s⁻¹ in pH 7 PBS.
Multiplexed aptasensor based on metal ions labels for simultaneous detection of multiple antibiotic residues in milk

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**ABSTRACT**

A dual-target electrochemical aptasensor was developed for the simultaneous detection of multiple antibiotics based on metal ions as signal tracers and nanocomposites as signal amplification strategy. Metal ions such as Cd\textsuperscript{2+} and Pb\textsuperscript{2+} could generate distinct differential pulse voltammetry (DPV) peaks. When targets were present, kanamycin (KAN) and streptomycin (STR) as models, the KAN aptamer (KAP) and STR aptamer (STP) were released from their complementary strands, with more change of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} corresponding to peak currents. At the same time, complementary strand of KAP (cKAP) and STP (cSTP) were linked with the poly (A) structure (cSTP-PolyA-cKAP) to increase their conformational freedom. Graphitized multi-walled carbon nanotubes (MWCNT\textsubscript{G}) and carbon nanofibers-gold nanoparticles (CNF-AuNPs) as a biosensor platform enhanced the surface area to capture a large amount of cSTP-PolyA-cKAP, thus amplifying the detection response. Under the optimal conditions, the aptasensor could detect KAN and STR as low as 74.50 pM and 36.45 pM respectively with the range from 0.1 to 100 nM and exhibited excellent selectivity. Moreover, this aptasensor showed promising applications for the detection of other analytes by changing corresponding aptamers.

![Schematic illustration of the preparation process for the aptasensor.](image-url)
Reduced graphene oxide supported raspberry-like SrWO₄ for sensitive detection of catechol in green tea and drinking water samples


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Abstract

The raspberry-like strontium tungstate microspheres supported on reduced graphene oxide nanosheets (rGOSs@SrWO₄) were prepared by a hydrothermal method and it was applied to the electrocatalytic sensing of catechol. The as-prepared rGOSs@SrWO₄ composite was characterized by XRD, Raman, FESEM, EDX, EIS, and voltammetric techniques. Morphology studies reveal the uniform wrapping of raspberry-like SrWO₄ microstructure by thin sheets of rGOSs and the composite possesses large surface area and abundant catalytic active sites. The rGOSs@SrWO₄ composite modified screen-printed multi-conventional electrode (SPME) was fabricated which was found to exhibit extraordinary electrocatalytic activity and excellent selectivity towards the detection of catechol. The rGOSs@SrWO₄/SPME displayed a linear range of 0.034–672.64 µM and detection limit of 7.34 nM using differential pulse voltammetry as signal read-out. Furthermore, the electrode was durable, reproducible and repeatable. The practical utility of the method was demonstrated in green tea and drinking water samples.

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Homogeneous electrochemical aptasensor based on a dual amplification strategy for sensitive detection of profenofos residues

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A homogeneous type of electrochemical aptasensor was designed based upon the principle of target-induced and tool enzyme-assisted signal amplification, which was employed for the detection of profenofos residues. In this experiment, profenofos, a type of organophosphorus pesticide, was used as a model target. The electrochemical signals of the aptasensor were acquired via electrostatic adsorption of negatively charged screen-printed electrodes (SPEs) and positively charged ferrocene (Fc). The ingeniously designed hairpin structure of the probe was unfolded with profenofos bound to the aptamer sequences, and after this, the target profenofos and the complementary DNA sequences with hairpin probes (HP) were separately recycled with the help of Vent polymerase and T7 exonuclease (T7 Exo). At the same time, due to the employment of T7 Exo, the Fc labeled DNA duplex could be digested into mononucleotides, making the end-labeled Fc approach the electrode surface and generate an enhanced electrochemical response. Based on this strategy, an ultrasensitive electrochemical aptasensor was fabricated with a low detection limit (LOD) of 0.01 ng mL⁻¹. The developed method can be applied for the determination of profenofos residues in vegetables, and it produced satisfactory results.

Fig. 2 Principle of the target-induced and T7 Exo-assisted recycling amplification strategy for profenofos detection.